

PROTON CONDUCTING MEMBRANE FUEL CELLS I

Edited by

Shimshon Gottesfeld Gerald Halpert and Albert Landgrebe





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PROCEEDINGS OF THE FIRST INTERNATIONAL SYMPOSIUM ON

PROTON CONDUCTING MEMBRANE FUEL CELLS I

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PREFACE

This volume includes papers presented at the first International Symposium on Proton Conducting Membrane Fuel Cells organized by the Electrochemical Society. The decision of the Electrochemical Society to start a series of symposia on this technical subject reflects the significant recent growth in interest in this field of electrochemical science and technology.

The polymer electrolyte fuel cell is a relatively new fuel cell technology. It was introduced in the 1960s as a development for space applications. After further R&D efforts in the 1980s and 1990s, it has recently attracted significant attention as a potential source of primary power for terrestrial transportation applications. The combination of low emissions, high energy conversion efficiency and high power density, expected from a polymer electrolyte fuel cell in transportation applications, explains this recent attention. Application of such fuel cells for stationary power generation has also been considered, and could, in fact, precede transportation applications because of less stringent cost requirements.

The large number of electrochemical science and technology issues associated with this power source present a significant challenge to workers in several fields of electrochemistry and electrochemical engineering. This wide spectrum of technical issues include: electrocatalysis at a unique (catalyst/ionomer) interface, electrocatalysis at partly poisoned catalysts and the treatment/prevention of catalyst poisoning, a wide range of polymeric membrane issues including thermodynamic and dynamic (transport) aspects in membrane/water/proton systems, membrane life and prospects of improved and/or less costly membranes, and, last but not least, a large number of stack related performance and engineering issues including stack materials, stack design and stack life testing.

Consideration of all of these issues requires the participation of several groups within the community of electrochemists. Organization of this Symposium by representatives of the Physical Electrochemistry, Energy Technology and Battery Divisions of the Society reflects this wide interest. This is also reflected by the range of papers included in this Volume which cover (in this order) the subjects of: Catalysis, Components Design and Modeling, Proton Conducting Membranes and Direct Methanol Fuel Cells.

We hope this volume will serve as an important source of updated information on the general subject of polymer electrolyte fuel cells, and will increase the interest in the scientific and technical subjects and challenges described here within the communities of electrochemists and electrochemical engineers.



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FACTS ABOUT THE ELECTROCHEMICAL SOCIETY, INC.

The Electrochemical Society, Inc., is an international, nonprofit, scientific, educational organization founded for the advancement of the theory and practice of electrochemistry, electrothermics, electronics, and allied subjects. The Society was founded in Philadelphia in 1902 and incorporated in 1930. There are currently over 6000 scientists and engineers from more than 60 countries who hold individual membership; the Society is also supported by more than 100 corporations through Patron and Sustaining Memberships.

The Technical activities of the Society are carried on by Divisions and Groups. Local Sections of the Society have been organized in a number of cities and regions.

Major international meetings of the Society are held in the Spring and Fall of each year. At these meetings, the Divisions and Groups hold general sessions and sponsor symposia on specialized subjects.

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OXIDATION OF H₂/CO IN A PROTON EXCHANGE MEMBRANE FUEL CELL

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The objective of the present study is to optimize the catalyst composition on the anode for the oxidation of CO containing fuel gases in a Proton Exchange Membrane Fuel Cell (PEMFC). In a first step, the oxidation of adsorbed CO was studied on porous PtRu electrodes by means of cyclic voltammetry combined with on-line mass spectrometry. It was found that $Pt_{0.5}Ru_{0.5}$ exhibits the highest negative shift for CO oxidation in comparison to pure Pt. Then, membrane electrode assemblies were fabricated using dispersed Pt, $Pt_{0.7}Ru_{0.3}$ and $Pt_{0.5}Ru_{0.5}$ as anode catalyst and pure Pt as cathode catalyst. The catalyst loading was 1 mg/cm². The CO tolerance of the anode catalyst in such single cells was evaluated at 80 °C using H₂ containing defined amounts of CO (25-250 ppmv). $Pt_{0.5}Ru_{0.5}$ showed the best performance compared with pure Pt similar to the results obtained with on-line mass spectrometry. For a $Pt_{0.5}Ru_{0.5}$ anode catalyst no difference in power density was found between pure H₂ and H₂ with 100 ppmv CO up to current densities of 0.4 A/cm² and cell voltages of 0.75 V.

INTRODUCTION

The Proton Exchange Membrane Fuel Cell (PEMFC) is regarded as highly attractive for mobile application due to its high power density at temperatures of 60-100 $^{\circ}$ C. The storage of methanol on board shows advantages compared to liquid hydrogen in terms of weight and volume (1,2). A reformer converts methanol to a hydrogen rich fuel gas containing about 75 % H₂, 24 % CO₂ and 1% CO. Although Pt has proven to be the most effective catalyst for hydrogen oxidation in a PEMFC, this catalyst creates problems when the fuel gas contains CO. This is associated with CO adsorption on active Pt sites inhibiting hydrogen oxidation. So far, PtRu alloys seem to be the most promising electrocatalyst to improve the CO tolerance of the anode in a PEMFC (3,4).

One criterion to assess the better electrocatalytic activity of such alloy electrodes in comparison to pure Pt is the adsorption and oxidation of monolayers of CO. Since the electrocatalysts applied in a PEMFC are highly dispersed noble metals on a carbon support, model systems used for catalyst evaluation should consist of porous diffusion electrodes having a high electrochemical active surface area. Cyclic Voltammetry (CV)

combined with Differential Electrochemical Mass Spectrometry (DEMS) is a powerful method for the identification of volatile and gaseous products formed during electrochemical reactions on porous electrodes (5). As recently described, PtRu alloys with defined compositions can be produced by electrochemical codeposition on porous gold substrates suitable for DEMS measurements (6). The roughness factor of such electrodes is about 100 as determined by the charge required to oxidize a monolayer of adsorbed hydrogen on polycrystalline Pt. The onset potential for CO adsorbate oxidation to CO₂ on Pt_xRu_y can be determined by the mass spectrometer and can be compared with pure Pt. This way the question arises whether results obtained on alloy electrodes in aqueous electrolytes such as HClO₄ or H₂SO₄ can be transferred to carbon supported PtRu alloy catalyst under fuel cell conditions. Thus, the CO tolerance of PEM single cells was studied with Pt and Pt_xRu_y catalysts on the anode and using H₂ containing variable amounts of CO as fuel gas.

EXPERIMENTAL

The experimental-setup for DEMS measurements together with the appropiate electrochemical cell is described elsewhere (6). The substrate for codeposition of various Pt_xRu_y electrodes was a porous Au electrode that was sputtered onto a hydrophobic PTFE membrane. Different compositions of Pt_xRu_y were produced potentiostatically from solutions of 20 mM H₂PtCl₆ and 50 mM RuCl₃ with various volume ratios. The deposition was carried out at U = 0.05 V versus the Reversible Hydrogen Electrode (RHE) for 30 min. The bulk compositions of the alloys were determined by EDAX and the surfaces were characterized by XPS as described in (7). Always freshly prepared electrodes were used.

Adsorption experiments were performed in 1 M HClO₄ saturated with CO at U_{ad} = 0.15 V vs. RHE for 5 min. The electrolyte was then purged with Ar and was continuously replaced by CO free electrolyte for about 6 min. while the electrode potential was kept at U_{ad} . Thus, dissolved CO is removed completely from the electrolyte solution. The remaining CO adsorbate was then oxidized in the first positive going potential scan at a scan rate of 0.01 Vs⁻¹. Simultaneously to the CV the Mass Spectrometric Cyclic Voltammogramm (MSCV) for m/z = 44 was recorded. This mass signal is assigned to the formation of CO₂.

For PEM single cell measurements, gas diffusion electrodes with a catalyst loading of 1 mg/cm² supported on Vulcan XC 72 were used (ETEK, Natick, MA). For the cathode pure Pt and for anodes pure Pt as well as $Pt_{0.7}Ru_{0.3}$ and $Pt_{0.5}Ru_{0.5}$ were used as catalysts. Membrane Electrode Assemblies (MEAs) were fabricated by hot-pressing of gas diffusion electrodes on NAFION 117TM at 130 °C and 10 kN. The electrodes were previously impregnated with NAFION solution (Aldrich) having a final loading of 1 mg/cm². The MEAs were mounted in a laboratory single cell containing stainless steel end plates and Ti current collector plates with parallel ribbed channels for gas manifolding.

Teflon gaskets between MEA and collector plates prevented gas leakage. The active electrode area is 4 cm^2 .

The performance of PEM single cells was evaluated in a test station described elsewhere (8). The cell temperature was 80 $^{\circ}$ C, the pressures in the anode and cathode compartment were 2.2 and 2.4 bar (abs), respectively. The reaction gases were humidified separately by two humidification cells.

RESULTS AND DISCUSSION

Figs. 1 and 2 show the potentiodynamic profiles for CO adsorbate oxidation on porous Pto ₅Ru_{0.5}, and pure Pt, respectively, with the simultaneously recorded ion currents for m/z = 44. The CV of the Pt electrode is characterized by a broad prewave oxidation peak at 0.4 V vs. RHE and a strong oxidation peak centred at about 0.73 V. The onset potential of CO adsorbate oxidation at 0.35 V is parallel to the beginning of CO₂ formation as can be seen in the MSCV. In contrast to pure Pt only one broad oxidation peak is observed at the Pt_0 , Ru_0 , electrode. The potential for adsorbate oxidation on this electrode is shifted to negative potentials by 0.3 V compared with the main CO₂ production onset occurring at approx. 0.6 V on pure Pt. In a similar way, the oxidation peak potentials in the CV and the onset potentials of the ion current in the MSCV were determined for various PtRu alloys and for pure Ru. For characterizing the various alloys the onset of the ion current in the MSCV was chosen. The plot of the onset of CO₂ formation versus the Pt content (Fig. 3) clearly displays that Pt0.5Ru0.5 exhibits the highest negative shift as compared with pure Pt. PtRu alloys prepared by potentiostatic codeposition in the same way as those in the present study, but on smooth Au foil substrates, exhibit also the lowest oxidation peak potential for compositions between 40 and 50 atomic % Pt in the alloy. A negative shift of about 250 mV compared with pure Pt was observed (7). Regarding our results summarized in Fig. 3, it should be mentioned, however, that Pt_{0.93}Ru_{0.03} reveals a comparable negative shift of the CO onset potential as Pto Ruos. The experimental findings on codeposited Pt, Ru, electrodes agree with results obtained by Gasteiger et al. (3) on smooth Pt_xRu_y in 0.5 M H₂SO₄ using cyclic voltammetry. These authors studied four well-defined PtRu alloys with Ru contents of 0.07, 0.33, 0.46 and 0.55 atomic % and found the lowest oxidation peak potential at Pt_{0.54}Ru_{0.46}.

The enhanced reactivity on Pt_xRu_y is explained in terms of the lower oxidation potential for H_2O adsorption ($U_{water,sd}$) on Ru compared to Pt according to

 $Pt + H_2O ----> Pt-OH + H^+ + e^-$ [1]

 $Ru + H_2O - Ru - OH + H^+ + e^-$ [2]

and $U_{water-ad}$ (Ru) < $U_{water-ad}$ (Pt).

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In our experiments the $Pt_{0.5}Ru_{0.5}$ electrode showed the most negative oxidation potential thus supporting the bifunctional mechanism proposed by Watanabe and Motoo (9) according to

$$Pt-CO + Ru-OH ----> Pt + Ru + CO_2 - H^+ + e^-$$
 [3]

where Ru is covered by oxygen containing species and CO binds preferentially to Pt sites. Under these conditions a maximum oxidation rate should be expected when the surface concentrations of both metals atoms are equal. However, the fact that Pt_{0.93}Ru_{0.07} exhibits a rather negative CO oxidation onset potential cannot be explained by this bi-functional mechanism assuming a homogeneous surface composition.

With respect to the application of Pt_xRu_y as anode catalyst in a PEMFC, the oxidation of CO should be investigated with the oxidation of hydrogen under real fuel cell conditions. The performance data of PEM single cells having Pt_xRu_y anodes should be compared using various H_2/CO mixtures in relation to pure H_2 . The highest curve in Fig. 4 shows a current density-cell voltage plot of a PEM single cell with a Pt anode catalyst using H_2/O_2 . The MEA was previously activated at a current density of 0.25 A/cm² until reproducible current-voltage curves were obtained. Pure hydrogen was then replaced by $H_2 + 100$ ppmv CO and the first current-voltage curve was measured after 5 min. Repeated current-voltage measurements showed a continuous decrease of the cell performance until a steady-state curve was obtained after about 210 min. (see Fig. 4). The performance loss with time is explained by increasing adsorption of CO on active sites of the dispersed Pt catalyst at the anode leading to the inhibition of hydrogen oxidation.

Fig. 5 comprises the transients of the cell voltage at 0.5 A/cm^2 for a $Pt_{0.7}Ru_{0.3}$, $Pt_{0.5}Ru_{0.5}$ and Pt as anode catalyst when hydrogen contains 100 ppmv CO. For the same current density the performance loss is significantly lower at PtRu relative to pure Pt. Figs. 4 and 5 illustrate that steady-state current-voltage curves can be obtained after about 2 h. This suggests that the poisoning of the anode in the PEM single cell at low CO concentrations is a rather slow process.

The influence of the CO content on the cell performance is demonstrated in Fig. 6 for a pure Pt anode catalyst and in Fig. 7 for $Pt_{o.5}Ru_{0.5}$. The CO concentration in the fuel gas was varied between 25 and 250 ppmv. Each current-voltage curve represents a steady-state that was achieved after about 2 hours. It should be mentioned that for all measurements an open circuit voltage of about 1.05 V was observed showing no influence of the CO concentration and indicating that the potential of the anode is determined by the $H_2/2$ H⁺ equilibrium.

Regarding the steady-state current-potential curves in Fig. 6 and 7 it can be assumed that the voltage losses at constant current densities of the cell are caused by higher overpotentials at the anode due to CO adsorption. As illustrated in Fig. 5, steady-state conditions were attained after a poisoning period. Fig. 6 shows that the steady-state

for a single cell with a Pt anode catalyst depends on the CO concentration in hydrogen. Thus, the performance of a PEM single cell in the presence of hydrogen with small amounts of CO can be explained by two competing reactions taking place at the anode. These are the CO adsorption on Pt and the adsorption of hydrogen molecules on remaining active sites according to

 $Pt + H_2 / CO = ---> Pt-CO + Pt-H$ [4] followed by the oxidation reactions

Pt-H ----> Pt + $H^+ + e^-$ [5]

 $Pt + H_2O$ ----> $Pt-OH + H^+ + e^-$ [1]

$$Pt-CO + Pt-OH ----> Pt + CO_2 + H^+ + e^-$$
 [6]

The comparison of pure Pt and $Pt_{0.5}Ru_{0.5}$ as anode catalysts in Figs. 6 and 7 demonstrates that the steady-state conditions of a single cell can be influenced by modification of the anode electrocatalyst. The current-voltage curves using a $Pt_{0.5}Ru_{0.5}$ catalyst are shifted to higher cell voltages for the same CO concentration as compared to a pure Pt anode catalyst (see Figs. 5 and 6). According to the bifunctional mechanism the reaction rate for CO oxidation is enhanced by the presence of Ru promoting the oxidation of CO according to reactions [2] and [3].

It should be mentioned that the poisoning of CO on both, Pt and $Pt_{0.5}Ru_{0.5}$ was found to be reversible. When H_2 containing CO as fuel was replaced by pure hydrogen the corresponding performance data of the H_2/O_2 system were achieved. It is interesting that no performance difference of PEM single cells was found for pure H_2/O_2 with Pt or $Pt_{0.5}Ru_{0.5}$ at the anode as to be seen in Figs. 6 and 7 (highest curves). Both anodes had catalyst loadings of 1 mg/cm² and therefore the number of surface Pt atoms in $Pt_{0.5}Ru_{0.5}$ should be lower than in pure Pt. This suggests that under the present experimental condition the macroscopic kinetic for hydrogen oxidation on PtRu is not affected by the presence of Ru.

The improvement of the CO tolerance of a PEMFC can also be illustrated by plotting the power density versus the current density. In Fig. 8 performance data of single cells are given with $Pt_{0.7}Ru_{0.3}$, $Pt_{0.5}Ru_{0.5}$ and Pt anode catalysts using $H_2 + 100$ ppmv CO as fuel. $Pt_{0.5}Ru_{0.5}$ exhibits a better performance than $Pt_{0.7}Ru_{0.3}$ which agrees with results on porous alloys electrodes obtained by means of DEMS (see Fig. 3). The power density of a PEMFC at 0.5 A/cm² for a $Pt_{0.5}Ru_{0.5}$ anode is higher by a factor of 3 relative to pure Pt. Nearly no performance difference is found between pure H_2 and $H_2 + 100$ ppmv CO up to 0.4 A/cm². For application aspects this is an interesting result, because a technical PEMFC should work at current densities up to 0.5 A/cm² with a power density of about

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0.3 - 0.4 W/cm². Under these conditions a reasonable efficiency can be achieved for a complete fuel cell system.

CONCLUSIONS

The potentiostatic co-deposition of Pt_xRu_y on porous substrates is a useful in-situ preparation method. The electrocatalytic activity of such samples towards the oxidation of CO can be studied by a combination of cyclic voltammetry and on-line mass spectrometry. It was found that CO oxidation on $Pt_{0.5}Ru_{0.5}$ shows the lowest onsetpotential for CO₂ production compared to pure Pt that agrees with a bifunctional mechanism.

Performance evaluation of PEM single cells at 80 $^{\circ}$ C exhibit a significant improvement of the CO tolerance when hydrogen with CO concentration between 25 and 250 ppmv was used. Pt_{0.5}Ru_{0.5} as anode catalyst shows the best performance in comparison to pure Pt according to on-line mass spectrometric data.

Dispersed PtRu electrocatalysts as anode material show promising behaviour for the utilization of hydrogen-rich reformer gas in a PEMFC. The power density up to technically interesting current densities exhibits nearly no difference between hydrogen containing 100 ppmv CO and pure hydrogen. However, the long-term stability of such PtRu electrocatalysts are still to be tested in terms of Ru corrosion and possible surface segregation effects.

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FIGURES



Figure 1:

Oxidation of adsorbed CO on a porous $Pt_{0.5}Ru_{0.5}$ electrode in 1 M HClO₄, dU/dt = 0.01 V/s; CV (top); MSCV for m/z = 44; dashed line: second potential scan. Figure 2: Oxidation of adsorbed CO on a porous Pt electrode; same conditions as in Fig. 1.



Figure 3:

Onset potentials of the ion current for m/z = 44 associated to CO_2 formation versus the Pt content in porous Pt_xRu_y alloy electrodes.



Figure 4:

Current-voltage plots of a PEM single cell using $H_2 + 100$ ppmv CO as fuel and pure O_2 ; anode and cathode: dispersed Pt on Vulcan XC 72 (catalyst loading on both gas diffusion electrodes: 1 mg/cm²).



Figure 5:

Cell voltage transients of PEM single cells using $H_2 + 100$ ppmv CO during poisoning of the anode at j = 0.5 A/cm² using dispersed Pt, Pt_{0.7}Ru_{0.3} and Pt_{0.5}Ru_{0.5} as catalyst for the anode.

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Steady-state current-voltage plots of a PEM single cell using $H_2 + CO$ (25 - 250 ppmv) and a pure Pt anode catalyst (cathode: Pt; catalyst loading on both gas diffusion electrodes: 1 mg/cm^2).



Figure 7:

Steady-state current-voltage plots of a PEM single cell using $H_2 + CO$ (25 - 250 ppmv) and a $Pt_{o.5}Ru_{0.5}$ anode catalyst (cathode: Pt; catalyst loading on both gas diffusion electrodes: 1 mg/cm²).

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Performance plots of different PEM single cells with Pt, $Pt_{0.7}Ru_{0.3}$ and $Pt_{0.5}Ru_{0.5}$ anode catalysts using pure H_2 and $H_2 + 100$ ppmv CO.

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OPTIMIZED CO TOLERANT ELECTROCATALYSTS FOR POLYMER ELECTROLYTE FUEL CELLS

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ABSTRACT

Ten different kinds of Pt-based alloy electrocatalysts (Pt-Ru, Pt-Ir, Pt-V, Pt-Rh, Pt-Cr, Pt-Co, Pt-Ni, Pt-Fe, Pt-Mn and Pt-Pd) were studied as potential CO tolerant electrocatalysts for anodes in Polymer Electrolyte Fuel Cells (PEFCs). Of the above, the electrocatalyst made of Pt-Ru showed the highest tolerance to CO. The alloy ratio and the thickness of the active layer have been optimized for the Pt-Ru electrocatalyst. As a result, fuel cell performance equivalent to that of pure hydrogen fuel has been attained, even with a CO concentration of 100 ppm.

INTRODUCTION

Fuel cells have received increasing attention as an energy power source gentle to the earth's environment. Polymer electrolyte fuel cells (PEFCs) in particular are seen as a potential energy source for electric vehicles, because of their high energy conversion efficiency and high power density. In the application of PEFCs to automobiles, hydrogen (H_2) generated from methanol by steam reforming process is a viable fuel source, as it is known that methanol can be stored more easily on vehicles than hydrogen. However, in addition to H_2 , methanol reformate gas can contains as much as 25 % carbon dioxide (CO₂), along with a small amount of carbon monoxide (CO). It has been proven that PEFC performance drops with a CO concentration of only several ppm (1-5). This is due to the strong chemisorption force of CO onto the Pt generally used as the anode electrocatalyst in PEFCs. CO concentration can be reduced by installing a CO selective oxidization unit to the reformer. It is, however, extremely difficult to suppress the CO concentration below 10

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ppm continuously and stably. Moreover, it has been determined that a PEFC must be capable of tolerating a CO concentration of at least 100 ppm in order reduce the size of the reformer unit.

There are two methods to avoid the effect of CO on PEFC performance. The first method is to reduce CO poisoning the electrocatalyst by blowing 2 % of air (O_2) into the anode, as reported by M. S. Wilson et al. (2). This method, however, makes the structure and control of the PEFC system complex. The second method is to enhance the CO tolerance of the electrocatalyst by alloying the Pt with a second element. This method has been studied recently at a number of research institutes (4-6) since it was discovered that it could be used to operate a PEFC system with reformate gas containing CO. No report has been published to indicate that adequate CO tolerance can be obtained with this method.

This paper reports an alloy electrocatalyst with high CO tolerance for anodes of PEFCs, developed by conducting studies on Pt-based alloy electrocatalysts.

EXPERIMENTAL

Pt-based alloy electrocatalysts made of Pt-Ru, Pt-Ir, Pt-V, Pt-Rh, Pt-Cr, Pt-Co, Pt-Ni, Pt-Fe, Pt-Mn and Pt-Pd respectively were studied as anode electrocatalysts. All of them were made of 20wt % alloy on carbon (Vulcan XC72R) with the Pt loading rate of 0.4 mg Pt/cm². Cathode electrocatalysts were made of 20wt % Pt/C (Vulcan XC72R) with 0.4 mg Pt/cm². After mixing the Pt/C or the alloy electrocatalyst on carbon with 5wt % Nafion solution (Aldrich), the mixture was applied onto the uncatalyzed carbon backing (geometric area of electrode: 10 cm²). Such an anode and cathode were hot-pressed into a membrane of Nafion^R 115 to form a membrane and electrode assembly (MEA).

The cell performance was evaluated with single cell testing. The MEA was set into a holder, while pure H_2 or 100 ppm CO/ H_2 was supplied to the anode using a gas cylinder. Air was also supplied to the cathode using a gas cylinder. Pressure was set at 0.15 MPa for both of the gases, while the cell temperature was set at 80°C. The MEA was humidified by bubbling. The cell performance was measured using an electronic load application device (EUL300 *a* B made by FUJITSU DENSO LTD.) and a power supply (PK46 made by KIKUSUI ELECTRONICS CORP.).

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RESULTS AND DISCUSSION

Alloy Electrocatalysts

Pt-based alloy electrocatalysts - Pt-Ru, Pt-Ir, Pt-V, Pt-Rh, Pt-Cr, Pt-Co, Pt-Ni, Pt-Fe, Pt-Mn and Pt-Pd - were compared as anode electrocatalysts in terms of CO tolerance. It was verified with X-ray diffraction (XRD) that all of those electrocatalysts were properly alloyed. Figure 1 shows the CO tolerance where Pt-Ru, Pt-Ir, Pt-V, Pt-Rh, Pt-Cr, Pt-Co and Pt-Ni were used respectively as anode electrocatalysts. Their cell voltages at 0.4 A/cm² are shown in the figure, where the CO concentration was set at 100 ppm. The Pt-Ru electrocatalyst was found to be the only alloy having a higher CO tolerance than the Pt electrocatalyst. The CO tolerances of Pt-Fe, Pt-Mn and Pt-Pd were also evaluated, but none of them showed higher CO tolerance than Pt-Ru.

The mechanism that enhances CO tolerance was studied using the Pt-Ru electrocatalyst. Table 1 shows the analytical results of gases at the anode inlet and the outlet, where the 500 ppm CO/H₂ gas was supplied at the rate of 100 ml/min. The anode electrocatalyst used for the analysis was 20wt % Pt/C (0.4 mg Pt/cm²) with the current density of 0.3 A/cm². At the anode gas outlet, CO₂ was detected together with CO. The sum of the molar quantity of CO and CO₂ at the anode gas outlet agrees roughly with the molar quantity at the gas inlet. It was deduced from the results that part of the CO absorbed onto the Pt was oxidized and became CO₂, then desorbed from the Pt and exhausted out of the cell. It was also deduced that the oxidizing reagent for the CO was the steam supplied for the humidification of electrolytic membrane. Therefore, it is presumed that the oxidization from CO to CO₂ takes place by the reactions that would occur in the following two stages.

$$CO + Pt \rightarrow CO-Pt$$
 [1]

$$CO-Pt + H_{2}O \rightarrow CO_{2} + Pt + 2H^{+} + 2e^{-1}$$
[2]

where reaction [1] is the process of absorbing CO onto Pt, while reaction [2] is the process of the absorbed CO oxidizing into CO, with H_2O .

Figure 2 shows the measured results of CO oxidization potentials of a Pt electrocatalyst and a Pt-Ru electrocatalyst. Cyclic voltammograms measured with the bipolar method using the anode as the working electrode, while using the cathode as the counter/reference electrode, are shown here. 1000 ppm CO/N, gas was fed into the anode, while H, gas was

fed into the cathode. The cell temperature was 40° C and the gas pressure was 0.10 MPa. Voltage was applied to the cell at the scanning speed of 20 mV/sec. In the case of Pt-Ru, the CO oxidization peak shifted toward the lower potential side by 200 mV, compared to that of Pt. The affinity of Ru for H₂O is stronger than that of Pt (that is, water absorption occurs at a lower potential for Ru). Hence the CO absorbed onto Pt should be oxidized into CO, with a lower potential.

Figure 3 shows the CO tolerances of an electrocatalyst in which Pt and Ru are alloyed, and another electrocatalyst in which Pt and Ru are not alloyed but mixed. The latter is a Pt-Ru without heat treatment for alloying. The figure indicates that alloying is necessary in order to obtain high CO tolerance. The oxidization of CO occurs by the interaction between Pt and Ru as expressed in Equation [3]. Therefore, it is confirmed that the Pt atom and Ru atom must be adjacent to each other.

$$Pt-CO + Ru-OH \rightarrow Pt + Ru + CO_{2} + H^{+} + e^{-1}$$
[3]

Pt/Ru Alloy Ratio

It was necessary to optimize the Pt/Ru ratio for the enhancement of the Pt-Ru electrocatalyst's CO tolerance. The atomic ratio of Pt/Ru was hence varied in the range of 100:0 to 0:100. All of those electrocatalysts were made of 20wt % alloy on carbon with the Pt loading rate of 0.4 mg Pt/cm² (except for an electrocatalyst made of 100 % Ru with the loading rate of 0.4 mg Ru/cm²). It was verified by means of XRD that these electrocatalysts, thus prepared, had the crystal structures expected for their alloy compositions (7). Figure 4 shows the cell voltages at a CO concentration of 100 ppm (0.3 A/cm²). The figure indicates that high cell voltages can be obtained only where the Pt:Ru ratio is 50:50, for both pure hydrogen and 100 ppm CO/H₂. In the case of pure hydrogen, practically the same performance was obtained when the Ru rate was 0 to 50 %, while the Pt loading rate was kept constant at 0.4 mg/cm². Performance dropped when the Ru rate was 50 to 100 %, as the active layer became thicker. CO tolerance increased as the Ru rate became higher, up to 50 %. However, when the Ru rate was over 50%, the power was reduced as the electrode performance (in pure hydrogen) was reduced.

It can be seen in the phase diagram shown in Figure 5 that CO tolerance is ensured over a wide range of Pt/Ru ratios (85:15 to 15:85). This is true regardless of the crystal structure of the electrocatalyst, though the crystal structure changes around the Pt/Ru ratio of 30:70. This indicates that proper CO tolerance can be obtained as long as an Ru atom exists in either one of adjacent atoms to a given Pt atom.

Active Layer Thickness

The active layer thickness can be reduced by increasing the weight percentage of electrocatalyst supported in the carbon powder, without changing the amount of electrocatalyst per unit area of electrode. The CO tolerance was measured using three kinds of electrocatalysts of 20, 30 and 40wt % Pt-Ru supported on carbon, where the Pt rate in each electrocatalyst was kept constant at 0.4 mg/cm². Figure 6 shows their cell voltages (0.6 A/cm²) in the CO concentration of 100 ppm. It is seen that the electrocatalyst of 40wt % Pt-Ru on carbon has the highest CO tolerance. Table 2 shows the active layer thickness of each electrocatalyst determined by SEM, and the Pt surface area that can contribute to the electrode reaction determined by the cyclic voltammogram. It was confirmed that the higher the weight percentage of Pt-Ru on carbon, the thinner the active layer becomes and the greater the Pt surface area that can contribute to the reaction.

It was reported in a study conducted by S. Srinivasan et al. (8) that the fuel cell electrode reaction actually occurred in a small area of less than 10 μ m from the surface of the active layer. Where the active layer was thicker than the above, the presence of Pt was limited to the region of shallow depth from the surface of the active layer. An electrocatalyst located at a deeper region (on the membrane side) did not contribute to the reaction of the active layer. By increasing the weight percentage of Pt-Ru on carbon, it was possible to concentrate electrocatalysts in the active region without changing the amount of electrocatalysts per unit geometric area of electrode. As a result, the cell performance was enhanced by increasing the number of Pt particles that could contribute to the reaction.

CO Tolerance of Pt-Ru Electrocatalyst

A membrane and electrode assembly (MEA) was prepared according to the results/ findings described above, using a Pt-Ru electrocatalyst (0.4 mgPt/cm²) with the Pt/Ru ratio of 50:50 and the weight percentage of 40 % on carbon as the anode electrocatalyst. The cell performance using this MEA operated in 100 ppm CO/H₂ is shown in Figure 7. Operated with pure hydrogen, better cell performance was recorded using the optimized Pt-Ru electrocatalyst than that obtained using Pt as the anode electrocatalyst. Moreover, performance equivalent to the Pt electrocatalyst operated with pure hydrogen was attained with the Pt-Ru operated with in a CO concentration of 100 ppm.

SUMMARY

Results of the study done on Pt-based alloy electrocatalyst, identified the Pt-Ru electrocatalyst as having excellent CO tolerance.

It was deduced that the Ru in the Pt-Ru electrocatalyst absorbs H_2O and facilitates the oxidization of CO.

Although, adequate CO tolerance can be obtained over a wide Ru range of 15 to 85 %, the optimum ratio of Pt/Ru was determined to be around 50:50.

By using an electrocatalyst having a high weight percentage of Pt-Ru on carbon, the number of Pt particles that can contribute to the reaction is increased and CO tolerance is also increased without changing the amount of electrocatalyst per unit area.

By optimizing the Pt-Ru electrocatalyst, cell performance equivalent to that of pure hydrogen can be attained with a CO concentration as high as 100 ppm.

It is expected that the improvement in CO tolerance indicated by the above described electrocatalyst will allow PEFCs to be operated stably, even under the condition where the CO concentration in the reformer generated gas is high, such as at the time of system start up.

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Table 1. Molar quantity CO and CO_2 at anode inlet and outlet. Anode electrocatalyst : 20wt %Pt/C, 0.4 mg Pt/cm². Current density : 0.3 A/cm². Anode gas : 500 ppmCO/H₂(100 ml/min). Pressure : 0.10MPa.

	Molar quantity in CO	Molar quantity in CO ₂	Molar quantity in CO+CO ₂
Anode inlet	1.73×10 ⁻⁶ mol	Omol	
Anode outlet	1.26×10 ⁻⁶ mol	0.42×10 ⁻⁶ mol	1.68×10 ⁻⁶ mol

Table 2. The active layer thickness of 20, 30, 40wt % Pt-Ru/C with the Pt loading rate of 0.4 mg Pt/cm^2 determined by SEM and the Pt surface area that can contribute to the electrode reaction determined by the cyclic voltammogram.

Pt-Ru wt % on carbon	20%	30%	40%
Active layer thickness (μ m)	41	24	8
Pt surface area contributable to electrode reaction (m ²)	0.10	0.12	0.14



Figure 1. Cell voltages of alloy electrocatalysts in hydrogen or 100 ppm CO/H₂. All alloy electrocatalysts for anodes are made of 20wt % alloy/C (Vulcan XC72R) with Pt loading rate of 0.4 mg Pt/cm². All alloy electrocatalysts for cathodes are made of 20wt % Pt/C (Vulcan XC72R) with Pt loading rate of 0.4 mg Pt/cm². Cell temperature: 80° C, pressure: 0.15 MPa.



Figure 2. Bipolar cyclic voltammograms using each anode as the working electrode and cathode as the counter/reference electrode. Pt: 20wt % Pt/C, 0.4 mg Pt/cm². Pt-Ru: 20wt % Pt-Ru/C, 0.4 mg Pt/cm². Anode gas: 1000 ppm CO/N₂. Cathode gas: H₂. Scanning speed: 20 mV/sec. Cell temperature: 40°C. Pressure: 0.10 MPa.



Figure 3. CO tolerances of Pt-Ru alloy and mixed Pt-Ru. Pt-Ru alloy: 20wt % Pt-Ru/C (Pt/ Ru = 50:50), 0.4 mg Pt/cm². Mixed Pt-Ru: 13.2wt % Pt/6.8wt % Ru/C, 0.4 mg Pt/cm² (without heat treatment for alloying). CO concentration : 100 ppm. Cell temperature : 80° C. Pressure: 0.15 MPa.



Figure 4. Cell voltage plotted against Ru atomic ratio in Pt-Ru alloy in hydrogen or 100 ppm CO/H₂ (0.3 A/cm²). All anode Pt-Ru electrocatalysts were made of 20wt % Pt-Ru/C (Vulcan XC72R) with Pt loading rate of 0.4 mg Pt/cm². Cell temperature: 80° C. Pressure: 0.15 MPa.



Figure 5. Phase diagram of Pt-Ru alloy (7)



Figure 6. Relationship between Pt-Ru alloy/carbon ratio and cell voltage. Anode Pt loading rate: 0.4 mg Pt/cm². Cathode electrocatalyst : 20wt % Pt/C (Vulcan XC72R) with Pt loading rate of 0.4 mg Pt/cm². Cell temperature: 80 $^{\circ}$ C. Pressure: 0.15 MPa.



Figure 7. Cell voltage plotted against current density in hydrogen or 100 ppm CO/H₂. Anode Pt electrocatalyst: 20wt % Pt/C with 0.4 mg Pt/cm². Pt-Ru electrocatalyst: 40wt % Pt-Ru/C (Pt/Ru ratio = 50:50) with 0.4 mg Pt/cm². Cathode: 20wt % Pt/C with 0.4 mg Pt/cm². Cell temperature: 80 °C. Pressure: 0.15 MPa.

Preparation of Gas Diffusion Electrode with Highly-active Catalyst for PEFCs

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ABSTRACT

The highly-active catalyst for polymer electrolyte fuel cells was prepared by two methods. Trinitro-diammine Pt complex solution was used and directly impregnated onto CB/PTFE electrode sheet. Pt catalyst was loaded by H, reduction. Average particle size was ca. 2 nm. The maximum power density was 6.7W/mg-Pt, at 0.06 mg/cm² of Pt loading amount. In the other method, an ionexchange method was applied on the carbon support. Carbon surface were oxidized by ozone gas. Consequently functional groups such as carboxylic group were generated. The acidic species on the functional groups were exchanged by platinum cationic complex such as [Pt(NH₂)_sCl₄]⁴⁺. The particle size was ave. 2 nm. The cell voltage was 0.5V at 0.4A at 1 atm. These methods were available to prepare the fine active catalyst and avoid a coagulation of platinum particles, comparing with conventional method which is impregnating Pt complex into carbon support, such as H₂PtCl₆ without any pretreatment.

1. Introduction

Recently, there have been various reports on the development of polymer electrolyte fuel cells (PEFCs) and new materials for the PEFCs have been actively developed. Platinum has been regarded as catalytically the most active metal. Recent development of the solid polymer electrolyte fuel cells has lead to intensive studies on platinum supported on gas diffusion electrode. An increase of catalytic activity requires manufacturing an highly-

dispersed Pt loaded carbon electrode(1, 2). The target of lowering Pt amount is assumed at 0.1-0.2g/kW-Pt, i.e., 5-10 W/mg-Pt, because these amounts are comparable with current consumptions in internal combustion engines. However, there are many problems in order to lower loading amount of catalyst. We have been studying a Pt loading technique on carbon powder for PEFC. In previous study, we obtained the cell performance more than $2W/cm^2(3)$. However, we used anionic platinum complex, H_2PtCl_6 , as a precursor. Pt loading amount was still high and reducing catalyst amount has been strongly needed.

In this viewpoint, we have been studying on the preparation method of Pt/C electrode using the pretreated carbon having functional groups on its surface (4). According to the study, the carbon support having functional group is available for ion-exchange method between acidic group and platinum complex.

In this study, we present some results concerning new loading methods of Pt catalyst. One of them is the method using platinum complex containing the legand which does not include chlorine species. Another method is using the pretreated carbon with highly active functional group on its surface by means of oxidation by ozone gas flow. The evaluation tests for these electrodes were carried out.

2. Experimental

One of methods for increasing the activity of catalyst is reducing catalyst particle size at the range at a few nanometers. We prepared two types of gas diffusion electrode supporting an highly active catalyst.

Type-I electrode- Using Trinitro-diammine Pt complexes:

We used platinum complex reacting with hydrogen for reducing rapidly. Using platinum complex containing chlorine species, such as H_2PtCl_6 , coagulation of the reduced platinum particle occurred. In order to avoid the coagulation, platinum complex which does not include chlorine species, trinitro-diammine platinum complex, was used (5). As an electrode substance, we prepared handmade carbon black(CB)/polytetrafluoro-ethylene (PTFE) composite sheet. CB content was 70 w/o. The thickness was 0.1 mm, which were reduced by hot-pressing to 0.06 mm. The obtained CB/PTFE sheet was cut to the electrode size which was 36.5 mm ϕ (10 cm²). Trinitro-diammine platinum complex solution was used as precursor of platinum catalyst. The Pt solution was dipped and penetrated into CB/PTFE sheet, dried, and reduced in H_2 gas flow. H_2 gas was diluted with N_2 gas less than 50 v/o in order to avoid intensive reaction. Pt loading amount was 0.06-4.0 mg/cm² for each

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electrode. For measurement of mass activity, the electrodes with lower platinum loading amount were also used (6). Loading amount is 0.01-0.4 mg/cm². Preparation method is similar as the one for cell performance measurement.

Type-II electrode: Using pretreated carbon:

In this case, pretreated carbon sheet by ozone gas was used, because oxidation process can be carried out in room temperature and without strong oxidant solutions. The surface of CB/PTFE sheet was oxidized by ozone gas flow and acidic functional group was formed, such as carboxyl group. The acidic species on the functional group was ion-exchanged with Pt complex ion such as [Pt $(NH_3)_4$]²⁺. Pt complex was reduced by H₂ gas flow and loaded on carbon surface. Pt loading amount was ca. 0.09 mg/cm².

Characterization and measurement of cell performance:

The loaded Pt catalyst was observed by TEM. Distribution of the particle size of the Pt catalyst was calculated by image analysis (4). For both electrodes, a cell assembly was prepared by hot-pressing with perfluorosulfonic acid membrane. Membrane used was such as Nafion[®] (Du Pont) 112, mainly. We measured a cell performance using these cell assemblies. Feed gases were H₂ and O₂. Operating pressure ranged from 1.00 to 5.84 atm, temperature ranged from 80 to 100°C. In order to classify resistance and overpotential, IR drop was measured with current interrupter.

For calculating platinum mass activity, the platinum surface area is calculated from the distribution of the platinum particle size and measured by BET method using carbon monooxide adsorption. The mass activity was calculated from current values at 0.9V of cathode potential. The cathode potential which was measured by a single cell with a reference electrode using hydrogen standard electrode. Each value of the cathode potential was determined after subtracting overpotentials assigned to the resistance of membrane, electrode, and so on.

3. Results and discussion

Type-I electrode

cell performance and catalytic activity — Typical cell performance of PEFC using Type-I gas diffusion electrode is shown in Fig.1. Platinum loading amount is 0.1 mg/cm². Operating feed gases were hydrogen and oxygen.

In this case, operating under the pressure at 1 atm, as feed gas is mostly water vapor, cell



Fig.1 Cell performance of PEFC using Type-I electrode. Membrane: Nafion®112. Temperature: 100°C. Pt loading amount:0.1mg/cm². Feed gas:H₂/O₂



Fig. 2. Cell performance of PEFC using electrode prepared from trinitro-diammine Pt complex. Feed gas: H_2 and O_2 , 5.84 atm. Temperature: 100°C.
performance was not so high. In the case of 5.84 atm, the power density was reaching to 0.85 W/cm². Although this values are still smaller than that of conventional method using platinum catalyst of 4mg/cm², it is necessary to consider the platinum amount. In order to show activity of catalyst, the specific power density is calculated as ; $iV/2w_{p_i}$; where i, V, and w_{p_i} are current density, cell voltage, and platinum loading amount for cach electrode, respectively. This value represents the output power per a unit weight of platinum loaded on the electrode. This shows the one of performances of catalyst (7). The specific power density increases as the platinum loading amount decreases as shown in Fig.2.

Power density decreased as the platinum loading amount reduced. In this case, however, the performance did not decrease so much at the platinum amount range below 1.0 mg/cm². Therefore, In the case of 0.06 mg/cm², the power density reached up to 6.7 W/mg-Pt, (0.15g-Pt/kW). In the case of > 0.1 mg/cm², the cell performance increases as the Pt loading amount increases. However, the specific power density decreases. It is shown that the effective amount increases.

Then, we calculated the surface area of platinum surface from the distribution of catalyst particle size with assumption that the platinum particles have spherical form. A typical





Pt loading amount	Average particle size	Pt specific surface area	Pt surface area in 1cm ² of the electorde
[mg/cm ²]	[nm]	[m²/g]	[cm ² /cm ² -electrode]
0.06	1.8	64.9	0.389
0.10	2.1	53.4	0.534
0.40	2.3	48.7	1.948
1.00	3.4	40.1	4.01
4.00	4.8	35.0	14.0

Table I. Variations of average particle size, specific surface area, and surface area in 1 cm² of platinum electrode with platinum loading amount using Type-I electrodes.

example of which loading amount is 0.06mg/cm² is shown in Fig.3. This has very narrow distribution of the particle size.

According to studies concerning a relationship between particle size of catalyst and the catalytic activity, it has been suggested that the loss activity exists in the case of using fine particle below ca. 3 nm (8). However, in this case, the activity of the catalyst is obviously increased. The distribution of catalyst depends on the platinum loading amounts. The value of average particle size increases as the loading amount. Table I shows the calculated surface areas. Surface area does not increase so much, except the case of 4.0 mg/cm² of the loading amount, even the loading amount increases. This is because the coagulation effect appeared with increase of an average particle size and particle size increased, when much platinum was loaded. Therefore the activity loss by the particle size effect was not observed in this range of the platinum particle size.

Mass activity of platinum catalyst —— Platinum mass activity has been used as the index showing the activity loss (6, 8). Results of measurement of the surface area by BET method is not so different as that from TEM measurement in Table I (within 5%). In Fig.4, mass activity of the platinum catalyst at 0.9V of the cathode potential. The pressure dependence is also shown. The linear relationships are observed between mass activity and platinum surface area at each pressure. The mass activity did not decrease at the lower range of platinum loading amount, although, in the lower pressure, mass activity decreases at more



Fig.4. Mass activity of the platinum catalyst at 0.9V of the cathode potential. Broken line is a result in various sulfufic acid electrolytes solution from Ref.(6, 9).

than 80 m²/g of platinum surface area because of decrease of fraction of oxygen in cathode inlet gases by humidification.

However, in this case, comparing with the result in various sulfuric acid electrolytes solution, these values are much lower than the results for the liquid solutions (9). It is suggested that the reaction area consisting of three phase; gas, electrolyte, and platinum active surface was not completely constructed. This time, we have not finished optimizing the loading method yet. Then further studies are going to be continued for this optimization of loading method.

Type-II electrode(10)

According to our previous work (4), the deposition of platinum on various carbon blacks was carried out by forming active functional groups on the surface of carbon support, and exchanging these active groups with ammonium platinum chloride. An exchange between cationic platinum complexes and surface functional groups takes place. Platinum particles



Fig.5. Distribution of platinum particle size on Type-II electrode. Loading amount: 0.09 mg/cm².



Fig. 6. Cell performance of PEFC using electrode prepared by ion-exchange method. Feed gas: H_2 and O_2 , 1.00 atm. Temperature: 80°C. a;ion-exchange method (Pt: 0.09 mg/cm²), b; H_2 PtCl_s impregnation (Pt: 0.1mg/cm²).

are extremely small (0.75-1.7 nm) and highly dispersed on the surface of carbon black. The catalytic activity mainly depends on the particle size rather than the loading amount of catalyst. In this case, also, highly-dispersed Pt catalyst was obtained. An average Pt particle size was ca. 2 nm and a S.D. of the distribution is 0.487nm as shown in Fig.5. These results show that the Pt catalyst prepared from ion-exchange method is highly-dispersed and has narrow distribution. The cell performance of the cell assembly is shown in Fig.6. The performance of cell prepared by ion-exchange method is superior to that prepared by conventional method.

4. Conclusion

The highly-active catalyst for polymer electrolyte fuel cells were prepared. One method was that newly Pt complex was used and directly impregnated onto a CB/PTFE electrode sheet. Catalyst was reduced by H_2 and highly-dispersed Pt catalyst was loaded on untreated carbon surface. The power density reached up to 6.7W/mg-Pt, which was obtained in the case that 0.06 mg/cm² of Pt was loaded on each electrode. For another case, an ion-exchange method was applied to preparing the electrode. The particle size was av. 2 nm, and had a narrow distribution. The cell voltage was 0.5V at 0.4A/cm² at 1 atm. Although the cell performance was improved from conventional method, it is necessary to increase the activity more than the present state. However, a possibility of lowering Pt loading amount was shown for various application of PEFCs.

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STUDY OF MASS TRANSFER WITHIN THE ACTIVE LAYER OF P.E.M.F.C. ELECTRODES AT THE PARTICLE LEVEL.

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ABSTRACT

The present tendency is to increase the Pt/C ratio from 20% to 40% within the PEMFC layers and so new limitations on mass transfer could appear at the particle level. Four models presenting an increasing complexity are proposed in order to point out the geometrical effects on mass transfer. They show that the geometrical effect is masked at the cathode where oxygen reduction is limited by kinetics while hydrogen oxidation under diffusion control depends on the geometric characteristics of the active layer.

INTRODUCTION

Many projects in course are devoted to proton exchange membrane fuel cells (P.E.M.F.C.) which could be extremely attractive as a power source for space and terrestrial using. However the potential development of such a solution is strongly dependent on money savings to be performed for these systems. Among several keypoints, the technical ability of reducing the catalyst amount appears to be one of the main priorities. Therefore this work offers several complementary models at the particle level allowing to predict the behavior of the active layer. The goal to be reached should be a more efficient distribution of catalyst particles within the active layer from the basic knowledge of the local catalyst requirements.

CLASSICAL ACTIVE LAYER MODELS

The aim of this first part is to recall some classical models and experimental results presented in literature.

For a P.E.M.F.C. electrode, the kinetic current density related to the geometrical area is related to the specific activity i* by :

$$i_k = \gamma \ i^*(\eta) = W \ S \ i^*(\eta)$$
 [1]

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W being the catalyst loading, γ the ratio of the real surface area to the geometrical one and S the specific area which varies as d⁻¹ for spherical or hemi-spherical particles. Then the mass activity (MA) is defined as :

$$MA = S i^*(\eta)$$
[2]

Numerous authors reported that the specific activity decreases for small Pt particles and thus obtained an experimental evidence of the particle size effect. The mass activity reach a peak value when the catalyst particle size is about 3 nm for O.R.R (1). Consequently, the kinetic current density i_k is optimal when the mass activity is maximal, i. e. when the mean particle diameter d is about 3 nm.

The "experimental" current density $i_{exp} = \varepsilon i_k$ can be optimized taking in mind the calculation of the effectiveness factor ε (2) by the previous flooded model with the parameters relative to P.E.M. (3).

In this relation, the effectiveness factor ε is considered to be defined as following :

$$\varepsilon = \frac{\text{actual rate (current density)}}{\text{rate (current density) without mass and ohmic limitations}}$$
[3]

So, if the ohmic and diffusion limitations are negligible, ε is close to unity and all the catalyst uniformly works in the porous electrode.

At the membrane-particle interface, the charge transfer flux density is expressed by :

$$\varphi = \frac{i(\eta)}{nF} = k(\eta) C$$
 [4]

as a function of the kinetic constant k :

$$k(\eta) = \frac{1}{nF} \frac{di}{dC}$$
 [5]

The continuous flooded model takes into account that the reactant diffuses into the Nafion[®] phase and simultaneously reacts at the catalyst interface. It was both admitted that the system is isothermal and under steady state conditions and that governing equations are reduced to a one-dimension form. At the electrode, a Tafel kinetics is assumed and all the coefficients are supposed to be constant in the active layer. Ionic conduction and diffusion are modelled using the Ohm's and Fick's laws. For the totally flooded model, two characteristic dimensionless parameters can be defined

$$U^{-1} = \frac{\gamma \ k \ L}{D}$$
 [6]

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$$Wa^{-1} = \frac{\gamma \left(\frac{di}{d\eta}\right)}{\sigma}$$
 [7]

For very high values of the ratio U^{-1}/Wa^{-1} such as in the usual case of P.E.M. (Nafion[®]), the active layer behavior is controlled by a strong diffusion limitation (much more important than the ohmic drop one). Then solving equations in respect of the boundary conditions leads to:

$$\varepsilon = \frac{\operatorname{Tanh}\left(\sqrt{U^{-1}}\right)}{\sqrt{U^{-1}}}$$
[8]

Applying the flooded model leads to a theoretical increasing of the effectiveness factor when the active layer thickness L decreases. This implies an advantage when using a thin P.E.M.F.C. layer (4)), but also when the catalyst active surface area per geometrical area decreases and therefore when the interparticle distance increases. For other models with rather close gas pores, as the thin film model (5), the diffusion britten is particular for the form the

limitation is negligible in front of ohmic drops (very low U-1/Wa-1 values), but nevertheless the effectiveness factor ϵ decreases when γ increases.

Whereas numerous works have indicated an effect due to the particle size, Stonehart (6) suggested that an other interparticle effect occurs at the local level. They evoke a mutual influence of particles on diffusion when they are close together. Then it is very important to check if the tendency of present researches consisting in increasing the Pt/C ratio from 10 to 40% (and consequently to decrease L) does not induce new limitations at the particle level.

MODELLING AT THE PARTICLE LEVEL

Definition of the physical problem

Several mathematical models have been developed for describing the behavior of the P.E.M.F.C. electrodes. All these models are classically based on the same description of the active layer structure : catalyst particles form porous aggregates which are flooded with electrolyte in the cell. In this way, a three-dimensional network of catalyst and electrolyte is present throughout the active layer. Moreover the carbon particles form a gas-filled network intermingled with the previous one and supplying gas throughout the active catalyst layer. The two major kinds of models proposed by literature are respectively the thin film model and the flooded model.

On one hand, the statement of the thin film model assumes that all the catalyst particles are located on the pore wall and that the thickness of the electrolyte film covering the whole pore is constant and very small compared to the pore size.

On the other hand the flooded model considers that the catalyst particles are uniformly dispersed within the electrolyte phase, so forming a continuous phase with the electrolyte phase. Obviously such models are not able to satisfactorily describe the spherical diffusion behavior in the neighboring of the carbon substrate nor to point out the interparticle distance effects. These lacks lead us to propose here a modelling at the particle level for predicting the behavior of the active layer.

In order to analyze the geometrical effects, four models concerning systems presenting an increasing geometrical complexity have been elaborated. The two first models are focused on isolated particles and the two other ones allow to consider the whole network of particles. In a more accurate way, the first model is devoted to two isolated particles while the second one concerns a fraction of an isolated particle disposed on a carbon plane. The third model is a thin film model developed from the particle level by considering a two-dimensional hexagonal network of hemispherical particles under a thin film layer of electrolyte. Finally the last model is a flooded model based on a description at the particle level for a three dimensional network (Figure 1).

In spite of the geometrical differences, the same following hypotheses were assumed for the four systems under study :

- the catalyst particles are spheres having the same mean diameter and moreover for models 3 and 4, they are steadily distributed within the electrolyte phase according to an hexagonal network ,

- ohmic drops limitation are negligible in front of the mass transfer limitation and all the transfer coefficients are looked as constant in the neighboring of the substrate,

- The kinetic rate equation for the electrochemical reaction on the particle active surface is described by a Tafel law and it is a first order vs the activity of the gaseous reactant. Thus the transfer current density is given by:

$$i = i_{o} \exp\left(2.3\frac{\eta}{b}\right) \frac{C}{C_{o}}$$
[9]

while the reaction rate for the gas reactant is expressed as : $\varphi = i/n_{\rm F}$.

- At the particle level, overpotentials are assumed to be constant because the characteristic dimensions are small compared to the electrode size and consequently the mass transfer coefficient is also constant.

Formulation of the problem

The modelling depends on a lot of variables such as geometrical parameters (interparticle distance, particle diameter), transfer characteristics (diffusion coefficient, mass transfer coefficient, ionic conductivity), reactant concentration and flux density. A dimensionless formulation is suitable for describing in the most general way the problem under study.

This is done by defining the following variables :

- the dimensionless flux density (mean calculated flux density referred to the particle active surface area in reference to the flux density for an isolated spherical particle) :

$$\frac{\varphi}{DC_{o}(d/2)}$$
[10]

- the dimensionless ratio between charge transfer and ohmic resistances (Wagner number):

$$w_a = \frac{\sigma}{(di/d\eta) d/2}$$
[11]

- the dimensionless ratio of spherical diffusion and charge transfer flux densities (inverse of a modified Damköhler number) :

$$u = \frac{D}{k(d/2)}$$
 [12]

- the dimensionless geometric ratio between the interparticle distance and the particle diameter : a/d

At the particle level, the active layer behavior can be summarized as following. The electroactive species diffuses throughout the thin film of Nafion[®] electrolyte from the gas-membrane interface where gas dissolution occurs to the membrane-particle interface where gas reacts. Diffusion within the electrolyte thin layer is controlled by the Laplace equation [13] and the concentration at the gas-membrane interface is imposed at a constant value while the reactant is consumed at the membrane-particule interface.

The resolution of the dimensionless equation is performed for spherical particles with the commercial software FLUX-EXPERT[®] by using the finite elements method. Subsequently the mass transfer flux density can be deduced by solving the Laplace equation in respect to the following boundary conditions.

All the geometrical systems under study present an axial symmetry. For the two last systems, symmetry is not so obvious as for the two first ones. In fact six symmetry planes are to be considered between a given particle and its neighboring, so implying an hexagonal symmetry which can be approximated by a cylindrical symmetry. As a result, the dimensionless equation can be rewritten in terms of cylindrical coordinates by using axisymmetric conditions for any variable $X (\partial X / \partial \theta=0)$.

Then the Laplace equation :

$$\nabla^2 C = 0$$
 [13]

is reduced to :

$$\frac{1}{r}\left(r\frac{\partial^2 C}{\partial^2 r}\right) + \frac{\partial^2 C}{\partial^2 z} = 0$$
[14]

and has to be solved with the following boundary conditions :

- Dirichlet condition at the gas-membrane interface

- non homogeneous Neumann condition at the membrane-particule interface

$$\varphi = k C_i$$
 [16]

The mean flux density computed at the membrane-particle interface is calculated with:

$$\overline{\phi} = \iint_{S} \phi \, dS/S$$
[17]

where S is the usable particle active surface area.

RESULTS AND COMMENTS

As a preliminary study, the numerical approach using finite element method was validated by comparing the obtained solutions to the well-known ones established in some classical limiting cases for heat transfer. The analogy between heat and mass transfers is obvious owing to the similarity of both Laplace equations and boundary conditions leading to formally equal heat flow and mass transfer densities in a same geometrical system. In order to compare and to validate the numerical solution, two limiting cases leading to the analytical solutions (see appendix) were considered here.

The dimensionless flux density calculated by the software for highest values of the ratio a/d under diffusion control tends to unity, value forecasted by the analytical solution in the case of two isolated particles located in an infinite medium (Figure 2) and characteristic of a spherical diffusion. Moreover, for well dispersed catalyst particles (a/d>10) under a thin film of electrolyte $(e/d\cong10-20)$, the computed flux density tends to the values predicted from the analytical solution (case of an isothermal sphere located in a semi-infinite medium limited by an isothermal surface) (figure 4). As shown by figures 2 and 4, the results obtained from the numerical method proposed here with axisymmetric conditions are in a good agreement with the analytical solutions. Thus the selected computing method appears to be suitable for determining the flux density in the systems under study.

Case 1

For two isolated particles flooded in the Nafion[®] electrolyte under a mixed diffusion and kinetic control, solving the dimensionless equation allows to deduce the mean flux density as a function of the dimensionless a/d and u parameters. Then it becomes possible to estimate the effect of interparticle distance (related to the diameter particle) on the flux density as shown by figure 2.

If the system is under kinetic limitation ($u < 10^{-2}$), the dimensionless flux density does not depend on the geometrical ratio a/d, so proving that the interparticle distance a/d has no effect. However when diffusion becomes predominant, the flux density clearly depends on parameter a/d. Namely, it strongly decreases from a plateau value when a/d becomes smaller than 10.

As a conclusion, it can be stated that under diffusion control, when the interparticle distance becomes smaller than 10 times the particle diameter, the apparent specific activity significantly decreases.

Case 2

The second geometrical case concerns a fraction of particle disposed on a carbon plane under a thick Nafion[®] layer. Diffusion limitation will be only considered here. The aim of this study is to point out the effect of the contact angle θ between the carbon substrate and the particule in order to estimate the corner effect.

It appears that if the contact angle is equal to 90° corresponding to the case of one hemispherical particle, the dimensionless flux density is the same as for an isolated sphere, so showing that there is no noticeable effect of the substrate. Nevertheless, when the contact angle decreases down to 0° , the dimensionless flux density slightly decreases.

So there is an effect due to the contact angle between the particle and the substrate, although the corner effect remains smaller. This fact clearly establishes that the entire particle active surface area is not available.

Case 3

The purpose of the third case is to study diffusion toward a two-dimensional network of hemispherical particles under a thin film layer for a mixed diffusion and kinetic control. Here the flux density is again computed as a function of parameters u and a/d as shown on figure 3.

On one hand, under kinetic limitation as for the first modelling, the flux density does not depend on the interparticle distance and thus no more on the catalyst loading. Otherwise it is noticed that kinetics mask the whole geometrical effect. On the other hand, if diffusion becomes predominant, the flux density depends on the loading and the geometric effects are quite the same as for two isolated particles. When the

dimensionless ratio a/d decreases from 10, the flux density strongly decreases while it remains constant for a/d values higher than 10 (figure 3). Nevertheless, the most important point is that the flux density is the same as for an isolated sphere for the large values of a/d, while the effective diffusion is close to planar diffusion for small values of a/d (figure 4). Consequently it appears not only an interparticle distance effect but moreover a concentration diminution due to the increasing of catalyst loading on the surface.

To conclude about the interparticle effect, such an effect is easy to be explained. On one hand, when a particle is well separated from the neighboring particles, then the full active surface area is available for the reactant which is undergoing to a spherical diffusion to the individual particles. On the other hand, if the particles are close together within some critical region, a mutual influence on diffusion occurs, so limiting the available active surface area.

Case 4

The three previous systems provide interesting information concerning the mass transfer, but their major inconvenient is a relevant description limited to the neighboring of the substrate and consequently to very thin layers. So a more realistic geometric model is required for modelling the behavior of the active layers. Such a modelling is possible from a three dimensional hexagonal network of particles, the symmetry of which allows again a two-dimension mathematical treatment. Moreover the results forecasted from this modelling can be compared to the flooded model and to a modified flooded model which takes into account the local spherical diffusion in the particle vicinity (see appendix). The comparison between these three models is described by figure 5 from the evolution of the effectiveness factor with parameter u.

If kinetics are predominant ($u>10^2$), no difference appears between the results provided by the three models. In opposition when diffusion becomes the limiting step ($u<10^{-2}$), similar predictions are only obtained from computations with FLUX-EXPERT[®] and analytic calculations from the modified flooded model which both conclude to a stiffer decreasing of the effectiveness factor than with the flooded model. This strong difference is due to the fact that the local geometry is not taken into account for stating the classical flooded model while actually the accumulation of catalyst under a particle form induces a spherical diffusion limitation and probably a shielding effect of particles).

A parametric study performed with the FLUX-EXPERT[®] software, shows that, if the layer active thickness L or the real surface area / geometric area ratio γ increases the effectiveness factor ε decreases as forecasted by the flooded model (figures 6 and 7) as the results given by the flooded model. In other respects, for constant values of L and γ , the effectiveness factor ε increases if interparticle distance a increases (figure 8) due to the diminution of the mutual interaction between particles.

CONCLUSIONS

This study demonstrates an geometrical effect on the flux density due to the interparticle distance, the corner effect and the catalyst loading. This effect acts as a function of the dimensionless parameter u = 2 D/k d.

If considering the concrete case of oxygen/hydrogen fuel cells, the oxygen reduction is controlled by kinetics ($u<10^2$), thus the geometrical effect is masked at the cathode. However, the hydrogen oxidation is controlled by diffusion ($u<10^2$) and so depends on the geometric characteristics of the active layer. Consequently the tendency to increase the Pt/C ratio induces new limitations at the particle level only for the anode.

NOMENCLATURE

- a interparticle distance (m)
- b Tafel slope (V.dec⁻¹)
- C concentration in the electrolyte phase (mol.m-³)
- d mean particle diameter (m)
- D diffusion coefficient within the electrolyte phase $(m^2 s^{-1})$
- e layer thickness (m)
- F Faraday constant (96500 C.mole⁻¹)
- i current density (A.m⁻²)
- k kinetic constant (m.s⁻¹)
- L active layer thickness (m)
- n total number of electrons involved in the electrochemical reaction
- S catalyst specific area (m².kg⁻¹)
- W catalyst loading (kg.m⁻²)
- γ real catalyst area / geometric area ratio (m².m⁻²)
- η local overpotential (V)
- φ flux density (mole.m⁻².s⁻¹)
- σ ionic conductivity within the electrolyte phase (S.m⁻¹)
- θ contact angle between the particle and the substrate (°)
- i index referring to the electrolyte membrane-particle interface
- o index referring to the gas-electrolyte interface

APPENDIX

<u>Appendix 1:</u> Analytical solution for an isothermal sphere buried in semi-infinite medium having an isothermal surface (7):

The heat flow density φ is given by :

$$\varphi = \frac{\kappa \ \Delta T}{d/2} \left(\frac{1}{1 - d/4e} \right)$$
[18]

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where κ is the thermal conductivity, ΔT the temperature difference and e the distance between the sphere center and the isothermal surface.

By analogy the mass flow density is expressed form the concentration difference ΔC as :

$$\varphi = \frac{D \ \Delta C}{d/2} \left(\frac{1}{1 - d/4e} \right)$$
[19]

<u>Appendix 2</u>: Flooded model and modified model equations :

For the flooded model, the flux density is defined by the relationship :

$$\varphi = \frac{D C_o}{Z_d} \tanh \left(\frac{L}{Z_d} \right) C_o$$
 [20]

with $Z_d = \sqrt{D/K}$, where L is the active layer thickness of electrolyte and K (s⁻¹) the reaction rate constant for a first order reaction.

The one final difference between the classical flooded model and the modified one consists in using a modified reaction rate constant K including local spherical diffusion expressed as (8):

$$K = \frac{\gamma k}{L} \left(\frac{2 D_d}{k + 2 D_d} \right)$$
[21]

instead of :

$$K = \frac{\gamma k}{L}$$
[22]

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Figure 1: Geometrical case under study



Figure 2: Dimensionless flux density to 2 isolated spherical particles vs. dimensionless geometrical ratio under mixed diffusion and kinetic control.



Figure 3: Dimensionless flux density to a 2D hexagonal network of spherical particles vs. dimensionless geometrical ratio under mixed diffusion and kinetic control.



Figure 4: Dimensionless flux density to a 2D hexagonal network of hemispherical particles vs. dimensionless geometrical ratio under diffusion control.



Figure 5: Effectiveness factor for the same active layer (L=200 nm, γ = 3,12 m².m⁻²) and a 3D hexagonal network of particles (d= 2nm) vs. dimensionless parameter u



Figure 6: Effectiveness factor for a 3D hexagonal network of particles (d= 2 nm, γ =6,3 m².m⁻²) vs. dimensionless parameter u and active layer thickness L



Figure 7: Effectiveness factor for a 3D hexagonal network of particles (L=200 nm, d= 2nm) vs. dimensionless parameter u and real catalyst area/geometric area ratio γ



Figure 8: Effectiveness factor computed to a 3D hexagonal network of particles (L= $400 \text{ nm}, \gamma=6,3 \text{ m}^2.\text{m}^2$) vs. dimensionless parameter u and for 10, 16, 40 nm.

HIGH PERFORMANCE ELECTRODES FOR HYDROGEN/AIR PEMFC OPERATING AT ATMOSPHERIC PRESSURE

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Proton Exchange Membrane Fuel Cells (PEMFCs) are in an advanced state of development. However, the weight, volume, and cost of this type of systems are still limiting factors to their commercialization. In order to overcome some of these constraints, work has been conducted to attain high performances in hydrogen/air PEMFC, working at atmospheric pressure. The electrodes were prepared by either the spray or the dry method, and contained a platinum loading varying between 2 and 6 mg/cm². The influence of the PTFE content in the electrode, both for the anode and cathode, as well as of the concentration of platinum supported on carbon on the PEMFC performance were investigated. The optimization of the composition and structure of the electrode catalyst layer led to performance such as 0.35 W/cm² at cell voltage of 0.7 V.

INTRODUCTION

High power density and high energy efficiency PEMFC development has been the objective of many investigations during the last 15 years and PEMFC power plants are now very close to reaching this goal as well as commercialization. The increased interest in this type of power source is due to its potential for meeting the power requirements needed for electric traction. However, further decreases of the weight and volume of the fuel cell stacks and auxiliaries are required. One way to decrease the weight and increase the specific power of such system is to operate it at atmospheric pressure, but without significant loss of performance. This would eliminate auxiliaries, such as a compressor, and also would lead to a lighter stack. The aim of this work is to develop high performance electrodes for PEMFCs, which can operate at current densities higher than 0.3 A/cm² at cell voltage of 0.7 V, with hydrogen and air as reactants and at atmospheric pressure. Previous investigations at the Center for Electrochemical Systems and Hydrogen Research (1, 2) indicate that such PEMFC performance could be achieved by using electrodes with a high percent of platinum content on the carbon support, by optimizing the electrode structure, and by minimizing the ohmic losses in the proton conducting membrane electrolyte.

EXPERIMENTAL

Methods of Electrode Preparation

Two methods of electrode preparation were used. The first one - the spraying method consists of spraying a suspension of uncatalyzed or catalyzed carbon particles in water/alcohol mixtures to form the gas-diffusion and active layers respectively on the heated, Teflonized carbon cloth substrate (3). The second one - the dry method consists in casting the dry powdered materials on the carbon cloth, and subsequently cold pressing of this powdered material/carbon cloth composite to form the electrode.

Membrane and Electrode Assembly (MEA) Preparation

These electrodes (hydrogen and oxygen) were impregnated with Nafion 117 solution (5 wt % in alcohol) by brushing. The amount of proton conducting polymer deposited in the electrodes was about 0.6 mg/cm². The Nafion impregnated electrodes were hot pressed onto the proton conducting membrane. The membranes, used in this work, were Aciplex S 1104, Nafion 115 and Nafion 112. The thickness of the first two membranes in the dry state was approximately 120 μ m, the thickness of the third membrane was 50 μ m.

Single Cell Electrochemical Tests

The performances of all MEAs were investigated in 5 cm² geometrically active area single cells. Those cells were connected to the fuel cell test stations, equipped with controls for the current density, cell voltage, electrode potentials, gas pressures, and cell temperature, as well as gas humidification bottles. All experiments were performed at constant gas flow. The steady state current-voltage dependencies were recorded by using a computerized data acquisition facility. The experiments were carried out at 70 °C cell temperature and at atmospheric pressure of the reactant gases unless otherwise specified.

RESULTS AND DISCUSSION

Power Density Limiting Factors

Most of the limitations of a PEMFC operating at atmospheric pressure are due to (i) the low concentration of O_2 in the gas phase which reduces further the cell voltage, (ii) the slow diffusion of O_2 dissolved in the electrolyte, to the electrocatalyst particles in the active layer, and/or (iii) O_2 diffusion through the substrate diffusion layer which in all

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probability contains water droplets or films and a nitrogen blanket. In order to overcome these problems, previous studies have shown that the thickness of the active layer should be reduced and the electrocatalyst loading of the electrode increased. This goal can be achieved by using a higher concentration of platinum supported on the high surface area carbon. Another way of improving the electrode performance is to vary the PTFE content in order to optimize the water management in the active layer.

Influence of Methods of Preparation

The effect of the different methods of electrode preparation on the PEMFC performance is illustrated in Figure 1. The platinum loading of the electrodes was 2.5 mg Pt/cm². The gas-diffusion layers consisted of 4 mg/cm² of acetylene black Teflonized with 30% PTFE. Four different ways of preparation of the active layer were used: (i) spraying of Pt/carbon catalyst/30% FEP suspension, drying and rolling (4) (spray); (ii) spraying of initially Teflonized Pt/carbon catalyst suspension, drying, and pressing(Teflonized spray); (iii) spraying of Pt/carbon catalyst mixed with Teflonized (30% PTFE) acetylene black, drying and pressing (spray/dry); (iv) dry-casting of Pt/carbon catalyst mixed with Teflonized (30% PTFE) acetylene black and pressing (dry). The results showed that there is no significant influence of the method of electrode preparation on the electrode performances for current densities up to 800 mA/cm². Thus it was decided to use the dry method of preparation for subsequent experiments because this method is relatively easy to use, fast, and without any loss of the platinum electrocatalyst during fabrication.

Influence of Platinum Loading

The influence of the platinum loading in the electrode on the PEMFC performance was studied by using supported platinum on carbon electrocatalysts consisting of 40, 60 and 80 wt % platinum. The amount of supported electrocatalysts was kept constant at 6.6 mg/cm², while the platinum loading of the electrodes were 2.64 mg/cm² (40% Pt/C), 3.96 mg/cm² (60% Pt/C), and 5.12 mg/cm² (80% Pt/C). The particle sizes of the platinum and the related estimated thickness of the active layers of the electrodes are presented in Table I. The PEMFC performances are shown in Figure 2. The highest and lowest Pt-loaded electrodes have the same electrochemical activity at low current densities (less than 100 mA/cm²) but at the high current densities the highest platinum loaded electrode gave the best results. The electrode with 3.96 mg Pt/cm² had the highest electrochemical activity and the same slope in the linear region as the electrodes with the smallest amount of platinum loading. The slope in the linear region was lower for the PEMFC with electrode containing 5.12 mg Pt/cm². These results can be better explained by the Tafel plots for the PEMFC in the three cases (Figure 3) and the resulting electrode kinetics, mass transport, and ohmic parameters (Table II) estimated using a non linear least square fit of the experimental data to the empirical equation [1](5).

$$\mathbf{E} = \mathbf{E}_{i} - \mathbf{b} \log(\mathbf{i}) - \mathbf{R} \mathbf{i} - \mathbf{m} \exp(\mathbf{n} \mathbf{i})$$
[1]

where E is the cell potential, i the current density, R the ohmic resistance and m and n are parameter describing the mass transport effects in the PEMFC. The electrode with the 60% Pt/C has the highest electrochemical activity, while the electrochemical activities of electrodes with 80% Pt/C and 40% Pt/C are significantly lower. Because the weight of the active layer in the electrode was maintained constant (8 mg/cm²), its thickness was different and depended on the specific gravity of the supported catalyst; the thickness of the active layer decreased in the order 40% Pt/C, 60% Pt/C, 80% Pt/C. The amount of Nation impregnated in the active layer was practically constant (0.6 mg/cm^2) and the extent of Nafion penetration into the active layer was also constant. The thickness of the impregnated laver and the surface area of the Pt-catalyst (Pt particle size) are the main factors which determine the platinum utilization in the electrodes (6). The highest electrochemical activity is obtained in electrodes with 60% Pt/C catalyst, showing that this is the best compromise "thickness/Pt utilization/Pt particle size". In the case of electrodes with 40% Pt/C, the lower electrochemical activity is due to a lower Pt utilization, caused by a thicker active layer (insufficient Nafion penetration into the active layer). In the case of electrodes with 80% Pt/C the low electrochemical activity can be explained by the lower surface area of platinum particles (Table I). At higher current densities. PEMFCs with electrodes having thicker active layers, exhibit higher slopes in the linear region of cell potential (E) versus current density (i) plot, which is probably caused by the higher ohmic resistance in the Nafion impregnated active layer. On the contrary, electrodes with 80% Pt/C catalyst (thinner active layer) show a better conductivity, leading to a lower slope of the PEMFC E vs. i plot. These results illustrate that it is possible to design PEMFC electrodes, by varying the Pt concentration on carbon, to attain high power densities and cell potentials.

Influence of PTFE Content in Active Lavers of Electrodes

The amount of PTFE in the electrodes was varied by using different ratio of Pt supported on carbon electrocatalyst/Teflonized acetylene black. The latter has 30% Teflon. For total active layer weight of 8 mg/cm^2 , the ratios 4:1, 7:1 and 9:1 parts by weight 60% Pt/C : 30% Teflonized acetylene black were investigated. These ratios correspond to 6.00%, 3.75%, and 3.00% of PTFE in the entire active layer respectively. The goal of these experiments was to investigate the effect of PTFE content which was lower than 10%, which amount was found to be optimal from a previous investigation (4). In Figure 4 are shown the E vs. i plots for MEAs with different PTFE contents. The results show that decreasing the PTFE content below 6% leads to a poorer performance, caused, probably, by higher gas diffusion hindrance in the active layer of the electrode. This can be explained by the decreased volume of the hydrophobic, reactant gas permeable, porous regions in the active layer, which has a

negative influence on the electrode performance, especially when air at atmospheric pressure is used as the cathodic reactant.

Influence of Proton Conducting Membrane on PEMFC Performance

The influence of the proton conducting membrane on the performance of PEMFCs is illustrated in Figure 5. These results are in good agreement with results, obtained earlier (6). The thinnest membrane, Nafion 112, provides the best performance because of its lower ohmic resistance. On the other hand, the E vs. i plot for PEMFC with the Aciplex S membrane is better than that with Nafion 115 membrane despite the thickness being the same in both cases. This is due to the lower equivalent weight of Aciplex S membrane (EW=1000) compared to the Nafion 115 membrane (EW=1100) and hence the higher ionic conductivity of the Aciplex-S material. It must also be noted that the PEMFC with the Nafion 112 membrane shows a departure form linearity in the E vs. i plot at a considerable higher current density than in the PEMFCs with Nafion 115 and Aciplex-S membranes, confirming our previous conclusions that mass transport of protons and/or water can also explain the region of the E vs. i plot in which there is a departure from linearity.

CONCLUSIONS

This study is still at an early stage, but interesting results have already been obtained, showing that the optimization of the structure of the electrode and the composition of the active layer could lead to significant improvements in cell performance. The attained performance so far is 0.7 A/cm^2 at cell voltage of 0.65 V with air at atmospheric pressure as reactant. This demonstrates that, it is possible to reach power density of 0.5 W/cm^2 at an efficiency close to 60 % based on the lower heating value (LHV) of the hydrogen/oxygen reaction in a PEMFC operating with air at atmospheric pressure. Concerning the catalyst, this study was conducted with very high platinum loading (up to 6 mg Pt/cm²). We expect that further optimization of the electrodes will lead to a decrease of Pt loading, to less than 2 mg Pt/ cm², without loss of performance.

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Table I Dependence of Pt particle size and active layer thickness of electrode on percent of Pt in supported electrocatalyst and Pt loading

Catalyst type Pt/C, %	Electrode Pt loading [mg Pt/cm ²]	Pt particle size [nm]	Active layer thickness, µm
40	2.64	3.9	17
60	3.96	8.8	10
80	5.12	25	8.0

Table II Electrode kinetic, mass transport and ohmic parameters for PEMFCs with electrodes with different Pt loading. Parameters were calculated using the empirical equation [1] which shows excellent fit of experimental E vs i data (5)

Pt loading	E _o , mV	R, Ω	b,	m, mV	n
			mv/dec		
5.12	933	0.266	48	-3.89	0.00008
3.96	1051	0.209	48	73.02	0.001
2.64	950	0.298	63	0.40	-0.004



Figure 1 Cell potential vs. current density plot for PEMFCs with electrodes prepared by different methods. Membrane - Aciplex S, thickness 100 μm, cell temperature 70 °C, ambient pressure, reactants hydrogen/air. Symbols - experimental data, lines - fit to empirical equation [1]



Figure 2 Cell potential vs. current density plot for PEMFCs with electrodes containing different platinum loading. Membrane - Aciplex S, thickness 100 μm, cell temperature 70 °C, ambient pressure, reactants hydrogen/air. Symbols experimental data, lines - fit to empirical equation [1]

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Figure 3 Tafel plot for PEMFCs, using experimental data in Figure 2



Figure 4 Cell potential vs. current density plot for PEMFCs using electrodes with different PTFE content. Membrane - Aciplex S, thickness 100 μm, cell temperature 70 °C, ambient pressure, reactants hydrogen/air. Symbols experimental data, lines - fit to empirical equation [1]



Figure 5 Cell potential vs. current density plot for PEMFCs with different proton conducting membranes. Electrode Pt loading 3.96 mg/cm², cell temperature 70 °C, ambient pressure, reactants hydrogen/air. Symbols - experimental data, lines - fit to empirical equation [1]

PEM FUEL CELL STACK DEVELOPMENT BASED ON MEMBRANE-ELECTRODE ASSEMBLIES OF ULTRA-LOW PLATINUM LOADINGS

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We are attempting to scale-up our single cell technology, based on ultra-low platinum loadings, to develop a polymer electrolyte membrane (PEM) fuel cell stack for stationary power generation. We describe initial work on scale-up to a manifolded single cell based on a 100 cm² active area, with the intention of combining multiples of such cells to create stacks. The cells, which are fed by pressurized H₂ and air, utilize membranes catalyzed by ultra-low platinum loadings (0.14 mg Pt/cm²) and metal serpentine channel or screen flow-fields to minimize costs, while maintaining desirable power density. We describe some initial promising results from testing of stainless steel screens as flow-fields in such cells, achieving 0.5 W/cm² under mild flow and pressurization conditions.

INTRODUCTION

For some years, there has been substantial interest in PEM fuel cells for transportation applications. More recently, this interest has further extended to stationary power, ¹⁻⁴ which has long been the domain of higher temperature fuel cell technologies such as phosphoric acid or molten carbonate. While there may be some efficiency losses in coupling the PEM fuel cell to a reformer system compared to its higher temperature counterparts, the perceived advantages of the PEMFC are its quick start-up, high current densities and non-corrosive electrolyte. To date, these systems typically utilize membranes with platinum loadings of 4 mg/cm²/electrode and areas greater than 200 cm². In order to compete in the stationary power market, costs would most likely need to be less than \$1000/kW for an entire system. Lower platinum loadings are an important factor in meeting such cost projections. Using low-platinum loading technology developed at Los Alamos, ^{5,6} we are attempting to produce moderately-sized stack components that provide sufficient power output at a fraction of the platinum content (and cost) of present-day PEM fuel cell stacks.

Most stationary applications will likely require relatively high power yields, which suggests the use of large active areas. On the other hand, some applications, such as uninterruptable power supplies (UPS), home-based stationary power¹ or private transportation systems, require the supply of high voltages but only modest power output. For this reason, as much as the desire to minimize materials and costs, a relatively modest active area of 100 cm² was chosen as the initial stage for this development effort. Additional strategies in this program include exploring the use of alternative flow-field materials and configurations to simplify fabrication and lower costs, minimize unit cell thickness for the same reasons, as well as to lower ohmic losses and system weight, and simplification and/or automation of cell fabrication.

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EXPERIMENTAL

Membrane-Electrode Assemblies

We have experimented extensively with low platinum loading catalyzed membranes in small, single cells.^{5,6} These membrane-electrode assemblies (MEAs) are for the most part based on "thin-film" catalyst layers, in which an "ink" of catalyst and ionomer is applied directly to the membrane. The resulting catalyzed membranes are relatively robust and have been demonstrated on the small, single cell level to maintain high performances for thousands of hours and withstand numerous cycles of either start-up/shut-down or freeze/thaw conditions. In most cases, these MEAs have been fabricated by hand-painting the ink directly onto the membrane or onto hot-press decals.

The scale-up to cells much larger than our typical laboratory single cells prompted the development of an automated process to reliably and efficiently produce large catalyzed membranes. This was achieved by the use of a computer controlled standard X-Y analog chart recorder to apply the catalyst ink directly to a membrane or to decals that would later be transferred to the membrane by hot-pressing. Ink is supplied to the chart recorder pen by a pulse-free peristaltic pump drawing ink from a magnetically stirred vial. A schematic of the system is depicted in Figure 1.

To catalyze a membrane, the membrane is held in place on a heated vacuum table installed on the modified X-Y recorder. The pump and pen tubing are primed with ink. The operator interfaces with the computer program to align the pen settings properly. When given the approval, the program drops the chart recorder pen, starts the ink pump, and controls the pen to sweep over the desired electrode area in a serpentine pattern. When the pattern is complete, the pump turns off and the pen is raised. The amount of ink applied depends upon the pump speed, pen sweep-rate and size of the increment between sweeps. Total time to ink a 100 cm² area on one side of a membrane or one decal is about 2 minutes, which translates to an application of approximately 14 mg of platinum for a loading of about 0.14 mg Pt/cm².

Though both direct application of ink and the decal method produce comparable results, the decal method is preferable because it is much less time consuming and more convenient for producing large quantities of assemblies. Several decals can be inked in rapid succession, dried en masse in an oven and stored until needed for hot-pressing to a membrane.

When compared to other fabrication techniques we have experimented with, this simple process has several advantages such as 1) carefully controlled and uniform addition of the ink, 2) minimal wastage and cleanup (as compared to spraying or silk-screening), and lastly, 3) adaptability. Because the computer controls the printing area, the same unit can be adapted to any size or shape of electrode by varying the program.

Cell components

Although to this point we have experimented only with single cells, the hardware is designed for multiple cells with the requisite internal manifolding and sealing. The endplates and cell plates are rectangular to accommodate manifolding above and below the square 100 cm^2 active area in an effort to minimize unutilized space. The ratio of the active area to the endplate area is approximately 40%, which is reasonably high for the modest active area involved. The endplate dimensions are approximately 15 cm by 20 cm and are secured by 14 tie-bolts about the periphery in the conventional manner. A minimum

thickness of about 6 cm is required for the single cell, which includes endplates, current collector and cooling plates, and a unit stack cell (flow-fields, MEA, and seals).

We have used a variety of flow-fields in our scale-up work, including titanium or stainless steel serpentine-channel plates and stainless steel screens. Stainless steel screens were also used as cooling plates. The serpentine hardware consisted of metal sheets about 1.25 mm thick that were machined on one side with the serpentine open-faced channels. These were designed to be used back-to-back, sandwiching a stainless steel screen to form a combination bipolar/cooling plate. Typical MEAs consisted of catalyzed NafionTM 112 (DuPont) situated between E-TEK (Natick, MA) carbon-cloth gas diffusion style backings. In general, the catalyzed membranes were prepared using the decal method described above. The inks used contained 5% Nafion solution (1100 eq. wt. from Solution Technologies, Mendenhall, PA), 20% platinum on Vulcan XC-72 (E-TEK), and any of a number of appropriate solvents.

Cell testing

The test station for the 100 cm² cells contains a Hewlett-Packard 6050A load box with two 120 amp modules, a 208 V power supply to bias the cell against the load box such that low cell voltages can be attained, reactant humidification equipment, gas flowmeters, back-pressure regulators, temperature controllers, and control relays for actuating the cell's heating and cooling equipment. The test station also contains internal safety features that will shut down the cell under various conditions (loss of gas flow, or extreme cell temperatures, for example). Additionally, the load boxes are interfaced to a MacIntosh (Apple) computer so that experimental data, such as polarization curves, may be obtained using programs written with Labview (National Instruments) software.

The cells were typically operated on H₂/air at 3/3 atm (30/30 psi). Air flow-rates were approximately two times stoichiometric (i.e. 50% utilization) at 1 A/cm². Hydrogen flow varied but was typically slightly over stoichiometric at maximum current density. Occasionally, oxygen was used as a diagnostic aid. To provide water to the cell, the gases were externally humidified at temperatures ranging from 90 - 115° C for H₂ and 40 - 100° C for air. The cell temperature was generally maintained between 70 - 80° C to obtain optimum performance. For the majority of single cell work, the cell was air-cooled by an external fan. Multiple cells necessitated the use of internal water cooling. Water-was circulated through the cell via a cooling plate and upon exiting the cell was circulated through a fan-cooled radiator to maintain proper temperature.

RESULTS AND DISCUSSION

Initial development work was conducted using serpentine channel flow-fields because we obtain our highest performances in our conventional LANL test cells (5 cm² and 50 cm²) using such flow-fields machined into graphite blocks. Pressure drop is a concern in large-scale systems with their higher gas flows, thus the single channel pattern (Figure 2). The seven channels are arranged in a parallel flow scheme and are close to equal in length, as is advocated by Ballard.^{2,7} This general type of configuration should minimize water accumulation in the flow-channels while permitting a relatively low pressure drop. Pressure drops measured across the 7-channel plate at the 2 x stoichiometric flow-rate were 0.25 atm (4 psi) or less. Compared to previous work⁷, it should be mentioned, however, that the 7-channel scheme is not an optimized flow-field configuration.

Titanium was chosen as the original flow-field material because of its high conductivity, the possibility of nitriding the surface to make it corrosion resistant² and its availability in thin sheets, which could be machined with various patterns. It may also be of interest for transportation applications because of its relative lightness. In single 100 cm² cells with acid-etched titanium serpentine flow-fields and MEAs of ultra-low platinum loadings, current densities of 1.1 - 1.15 A/cm² (110 to 115 A) were attained at 0.5 V as shown in Figure 3. The high frequency resistances of these cells were approximately 0.09 Ω cm². This compares rather favorably with the 5 cm² laboratory cells, where the lowest resistances attained with thin-film catalyzed Nafion 112 MEAs are on the order of 0.065 Ω cm². Typical current densities at 0.5 V for the 5 cm² test cells are at best 1.4 A/cm² with Nafion 112 MEAs at $H_2/air = 3/3$ atm. Though some loss in performance occured with scale-up, the results obtained with the 100 cm^2 titanium cell were very encouraging. In particular, the ultra-low platinum, titanium serpentine plate cells produced 0.5 W/cm² at 0.7 V or 0.2 W/cm² at 0.8 V, which is within the range of stationary power requirements. Maximum performance of the cells was obtained with surprisingly high humidifier temperatures of about 115/80°C for the anode/cathode. Despite the high humidification levels and the observation that the polarization curve in Figure 3 starts to drop at relatively low current densities, flooding of the cathode compartment was not otherwise apparent.

Though acid-etched titanium proved to be a reasonable flow-field material in terms of short-term performance, there were many practical obstacles to continuing its use in the cells. Because titanium is a very hard material, it was not possible to machine the plates without first annealing the metal. Even with annealed plates, machining the intricate sevenchannel serpentine pattern was extremely time consuming and costly (end mills kept breaking due to the material's hardness). The machining cost of the titanium flow-fields was approximately \$750 per plate. Clearly, this is not acceptable for practical applications. Additionally, the annealing process creates an oxide layer on the titanium that must be removed by acid etching to attain acceptable contact resistances.

We then replaced the titanium with stainless steel. Researchers elsewhere⁸ have reported the use of stainless steel as a replacement for graphite in fuel cell stacks. They report no significant differences in cell performance in switching from graphite to stainless steel flow-fields. Additionally, they observed no corrosion of the stainless steel after 1000 hours of testing. Thus, for stationary power applications, where stack weight is not as critical as for transportation, the ruggedness of stainless steel as well as its low cost relative to graphite or titanium, make it an attractive material for practical use.

On the other hand, we observed a loss in performance in changing from titanium to stainless steel serpentine flow-fields. As also shown in Figure 3, at 0.5 V, current densities ranged from $0.90 - 1.0 \text{ A/cm}^2$ and performance in the kinetic region of the polarization curve dropped off from 0.85 V at 0.1 A/cm^2 for titanium to 0.82 V for stainless steel. While the loss of current density at 0.5 V was apparently due to higher resistances with the switch to un-etched stainless steel, the reasons for the loss of kinetic activity were not clear.

Even though the stainless steel flow-fields performed adequately, machining the narrow serpentine channels proved to be nearly as difficult and as expensive as for titanium. While lower cost alternatives to machining of the stainless steel are worth considering, we were interested in pursuing some alternative flow-field schemes such as porous⁹ or screen materials. Researchers at Sandia Livermore Laboratory (CA) and

elsewhere¹⁰ have experimented with the use of simple metal screens as flow-fields. As mentioned above, our original cooling plate design was based on a stainless steel woven screen. The combination of its apparent success and the previous work inspired us to pursue the use of screens as flow-fields. Among the advantages screens possess are that they require no special machining, are readily available in a variety of thicknesses and mesh sizes, and are inexpensive. To attain a bipolar plate structure, 0.25 mm (10-mil) thick stainless steel "barrier" plates would be used to separate the anode and cathode screen flow-fields in adjacent cells within a stack. In the single cells the same plates were used to protect the gold-plated copper current collector plates from indentation by the screens.

The use of the screen flow-fields presented new challenges in optimizing the gas flow pattern through the screen, sealing the cell, and attaining enough compressive force on the backings to achieve good interfacial contacts. Some idea of the uniformity of gas flow through a screen flow-field was obtained by appropriately fixturing a stainless steel screen and an E-TEK backing in a clear Plexiglass test fixture. Humidified air at 3 atm was flowed through the cell at the equivalent rate of two times stoichiometric at 1 A/cm². Water vapor tended to condense on the relatively cool Plexiglass such that the flow-field appeared cloudy. Large droplets from condensation and slugs of water that had accumulated in the feed line would occasionally pass through the flow-field and temporarily clear the condensate from the face of the Plexiglass. In this manner, stream lines would become apparent that would reflect the general reactant flow. The streamlines suggested that gas flow accessed all parts of the stainless steel screen fairly uniformly. In addition, we observed that water channeled directly through the flow-field without extensive pooling or flooding. Lastly, the pressure drops necessary to attain the desired flows and water removal were less than those required with the 7-channel serpentine flow-fields. In general, the behavior of the stainless steel screen flow-field as observed in the Plexiglass test fixture was much better than we had expected.

When installed into the electrochemical cells, the screen flow-fields initially provided poor performances. One of the difficulties was that the applied cell compression forced the E-TEK backings into the screens, which caused not only unacceptable pressure drops, but also compromised the integrity of the backing structures. The solution was to employ a combination of screens. The backing was protected from the large mesh size, relatively thick screen that served as the actual flow-field by a fine stainless steel screen. Pressure drops of 0.15 atm (2 psi) for air and < 0.07 atm (1 psi) for H₂ at the standard flow-rates were obtained. Even with the additional screens, the unit cell thicknesses were still less than 3 mm. Further changes in sealing of the MEA to prevent cross-over and acid-etching of the stainless steel before use to remove oxide coatings improved the cell performances to 1.0 A/cm² at 0.5 V, as is depicted in Figure 4. Somewhat high cell resistances of 0.14 Ω cm² were obtained, which may account for an excessive voltage drop of about 50-70 mV at 1 A/cm². This resistance is high compared to the titanium serpentine cells and primarily arises from the numerous stainless steel interfaces in the cell. On each side, there are interfaces between the collector plates and the barrier plate, as well as three more interfaces between the two screens and the backing. As in the case of the stainless steel serpentine hardware, however, the 100 mA/cm² cell voltage was lower than with the titanium serpentine flow-fields. The kinetic losses are apparent in the iR corrected polarizaton curves of Figure 4. Otherwise, the screen flow-fields provided near equal performance to the serpentine hardware, suggesting that the reactant access throughout the active area was equally effective. While it is conceded that our serpentine channel design is probably far from optimized, the relative performance of the simple screen configuration is

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very encouraging and offers much promise for this simple flow-field scheme. One of the challenges, though, will be to obtain and maintain good interfacial conductivities.

If it is eventually possible to maintain a performance of roughly 50 W at 0.5 V per cell output in a stack, a thickness of approximately 3 mm per unit cell (flow-fields, seals, MEA and cooling plate) would result in a 1 kW stack of 20 cells that is only 6 cm thick, not including endplates. The maximum power density of this configuration would be about 1kW/liter. Naturally, including the endplates and the corresponding increase in footprint lowers this value substantially. For example, a 5 kW stack would then yield about 0.4 kW/liter.

CONCLUSIONS

Ultra-low platinum loading of large surface area membranes was achieved by the use of a computer-controlled chart recorder to apply a uniform layer of catalyst "ink" to the membrane surface or a decal. Advantages of this method include the controlled application of the ink to reproducibly catalyze membrane surfaces with a certain desired platinum loading and the adaptability to catalyze different sizes or shapes of electrodes.

Combining the use of low-platinum loaded MEAs with titanium serpentine flowfields, produced cells that yielded 0.5 W/cm² at 0.7 V, which is within the realm of practical use for stationary power applications. A major barrier to the continued development of the titanium cell is the difficulty in machining the 7-channel serpentine flow-field pattern and relatively high associated costs. Though similar flow-fields made from stainless steel did not perform quite as well as the titanium plates, it may be possible to improve their performance by pretreating the metal to lower contact resistance. Additionally, newer fabrication technologies based on state of the art lithography techniques may provide plates that are inexpensive to produce on a mass-production scale.

Cells based on stainless steel screen flow-fields, in combination with low-platinum loaded MEAs, produced outputs of about 50 W at 0.5 V, which compared favorably with the titanium serpentine plate cells (55 W at 0.5 V). Though there was some loss in performance, the advantages gained by the use of screens (availability in various thicknesses and mesh sizes, low cost, elimination of machining, lighter weight, etc.) are attractive as a practical alternative to serpentine plates. With a maximum power density of about 50 W/cell at 0.5 V, the screen flow-fields provide a relatively inexpensive and light-weight PEM fuel cell configuration. Further refinements of the system should increase the maximum power and also improve the power densities at cell voltages of more relevance to stationary power applications.

Future work will include further single cell development with an emphasis on improving interfacial conductivites, improving backing components⁹ and implementing higher activity Pt alloy catalysts. In addition, multiple cell development, building on the results obtained above, will be initiated. Particular areas of concern in stack work will be the ease of fabrication of cell components and improving humidification schemes. Additional concepts to improve system efficiency, such as dead-ended H₂ feeds or low pressure cathodes, will also be explored.

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FIGURES



Figure 1. Computer controlled process for applying a uniform layer of catalyst ink to either a membrane or a decal blank positioned on a heated vacuum table.


Figure 2. 7-channel serpentine flow-field design machined into about 1.25 mm thick metal plates. Channels are ca. 0.8 mm wide and 1.0 mm deep with 0.8 mm wide ribs.



Figure 3. Polarization curves comparing the performances of fuel cells with 100 cm² titanium (Ti) and stainless steel (SS) serpentine channel flow-fields. Conditions are H₂/air = 3/3 atm, T_{cell}= 80° C, 50% air utilization at 1 A/cm², and MEAs with 0.14 mg Pt/cm²/electrode.



Figure 4. Cell and iR corrected polarization curves comparing the performances of titanium (Ti) serpentine channel and stainless steel (SS) screen flow-fields. Conditions are the same as in Figure 3.

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THE EFFECT OF THE FLOW DISTRIBUTOR ON THE PERFORMANCE OF PEM FUEL CELLS

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ABSTRACT

The effects of the design parameters of the flow distributor on the performance of the proton exchange membrane (PEM) fuel cell are studied in terms of the current density generated in the air cathode. Laplace's equation with boundary conditions that account for the shoulder area design is used to describe the gas transport through the electrode layer. Based on the computed results studied for the effects of the effective oxygen diffusion coefficient, aspect ratio, and current load, the current generated in the cathode side can be limited by as much as 45% as compared with a gas distributor design which has no shoulder area.

INTRODUCTION

With the promise of lower temperature, very high current density, and noncorrosive operation with lower sensitivity of orientation, proton-exchange-membrane (PEM) fuel cells are receiving increasing attention for, particularly, vehicular power application (1). Like other types of fuel cells, PEM fuel cell performance is limited by the activation, ohmic and concentration polarization (2). Activation polarization represents energy losses that are associated with the electrode reactions. Ohmic polarization represents the summation of all the ohmic losses within the cell, from electronic conduction through the electrodes, contacts and current collectors to ionic transportation through the electrolyte. The development of the perfluorosulphonic acid electrolyte membrane with platinum loading as an electrocatalyst has made it possible to reduce greatly the limitations from activation and some of the ohmic polarization (3, 4). With these new developments, many researchers started to focus on understanding and reducing the concentration polarization of the PEM fuel cells.

The concentration polarization represents the energy losses associated with mass transport effects. For instants, the performance of an electrode reaction may be inhibited by the inability of the reactants to diffuse to or products to diffuse away from the reaction site. Significant mass transport limitations occur in the electrode and active catalysts layers. However, it has been demonstrated that losses due to the transport of the reactant gas through the anode and cathode catalyst layers are insignificant at practical operating current density (5). Therefore, the main mass transport limitation of the reacting gases is in the electrode layers. The electrode layers serve the following functions: gas transport from the flow distributor to the catalyst layer, and electron transport from the catalyst layer to the current collector. Also, the presence and transport of liquid water generated at the cathode catalyst layer cause significant complexity to the gas transport in the cathode of the cell. However, this topic will be covered in future works.

Most studies on the mass transport limitations by the electrode layers have been investigated with the assumption that the reactant gas is provided uniformly from the flow distributor to the whole electrode surface area (3, 5, 6, 7, 8). However, the reactant gas diffusion to the catalyst layer on top of the shoulder of the flow distributor is hindered by the shoulder area of the flow distributor. Figure 1 shows a schematic of the cross-sectional view of an electrode of a typical PEM fuel cell. This shoulder area, which is essential for the electronic transport from the electrode to the current collector, affects the cell performance by changing the ohmic polarization. Therefore, it is important to investigate the effects of shoulder area on the transportation of the reactant through the electrode layer and the ohmic resistance of the flow distributor. Moreover, the area ratio between flow channel and shoulder needs to be optimized for both gas transport and electrical requirements. Note that larger shoulder area means smaller electrical resistance.

In this paper, the effect of the gas distributor design parameters on the performance of cathode electrode layer of the PEM fuel cells is studied at various load conditions.

MODEL DEVELOPMENT

The oxygen gas transport through the air cathode electrode is simulated. Gas transport from the flow channels to the catalyst layer is by diffusion, which is driven by concentration gradient. A steady-state, two-dimensional diffusion equation is used to describe the concentration (c) distribution of the oxygen gas in the electrode layer. See the model region shown in the schematic in Figure 1. It is assumed that the morphology of the electrode layer is uniform and identical in both directions such that the effective diffusion coefficient is invariant of position.

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$$\frac{\partial^2 c}{\partial x^2} + \frac{\partial^2 c}{\partial y^2} = 0 \quad \text{for } 0 < x < l, \ 0 < y < h$$
^[1]

At the points x equal zero and l, symmetric concentration profiles are assumed. Uniform concentrations and zero y-direction flux of oxygen are used for the electrode surface contacting the channel and the shoulder, respectively. At the reaction surface (y = h) the oxygen flux in the y-direction is related to the current density generated along the x-direction,

$$D_{eff} \frac{\partial c}{\partial y} = \frac{I(x)}{nF}$$
^[2]

The Butler-Volmer equation is used to describe the current distribution along the electrode and membrane interface, I(x),

$$I(x) = \frac{I_0 c(x, y = h)}{nFC_{ref}} \exp\left(\frac{\alpha F}{RT}\eta\right)$$
[3]

and the following boundary conditions apply:

at
$$x = 0, \frac{\partial c}{\partial x} = 0$$
 for $0 < y < h$ [4]

at
$$x = l$$
, $\frac{\partial c}{\partial x} = 0$ for $0 < y < h$ [5]

at
$$y = 0, c = c_0$$
 for $0 < x < l - s$ [6]

$$\frac{\partial c}{\partial y} = 0 \qquad \text{for } l - s \le x < l$$
 [7]

at
$$y = h$$
, $\frac{\partial c}{\partial y} = \varphi c$ for $0 < x < l$ [8]

where:

$$\varphi = \frac{I_0}{nFD_{eff}c_{ref}} \exp\left(\frac{\alpha F}{RT}\eta\right)$$
[9]

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 I_{θ} is the exchange current density for the oxygen reduction reaction, D_{eff} is the effective diffusion coefficient, α is the transfer coefficient for the reaction, n is the number of electrons involved in the reaction, s is the length for the shoulder, l is the combined length of the channel and shoulder, h is the height of the electrode, F is Faraday's constant, and η is the electrode over-potential (8).

The equations given above are solved by a finite difference method proposed in reference (9). Once the concentrations of the reactant gas along the reaction interface are known, the current densities (I(x)) along this interface are calculated from Equation 3, and the average current density (I_{avg}) is estimated by integrating the current density generated along the x-direction using Simpson's Rule.

RESULTS AND DISCUSSION

The model is used to study the effect of the gas distribution design on the performance of an air cathode. Figure 2 shows a typical gas concentration profile through the electrode layer with the condition of h/s = 0.2, (l-s)/s = 0.5, $D_{eff} = 0.03$ cm²/s, and $\eta = 0.2$ V. The region above the channel area shows higher oxygen concentrations than that above the shoulder. The concentration of the gas decreases linearly as y increases. Also, it decreases dramatically within the region beyond the interface between channel and shoulder (x = 0.05) as x increases.

The gas distribution in the electrode is changed by varying the current load. Various current loads can be simulated by adjusting the electrode over-potential parameter, n. The investigated range (between 0.1 to 0.2 volt) of the electrode overpotential parameter is determined based on normal operation conditions for PEM fuel cells (8). Figure 3 shows the effect of the shoulder on the current density profiles generated along the reaction interface (y = 1) at h/s = 0.2, (l-s)/s = 0.5, $D_{eff} = 0.03$ cm²/s and various over-potentials. Note the lower current densities along the reaction interface on top of the shoulder. Also, at higher over-potentials, the differences between the current generated at the channel side and shoulder side are greater, and the current densities near the interface between channel and shoulder (x = 0.05) change rapidly. Figure 4 shows the Iave/Imax ratio over the over-potential range of 0.1 to 0.2 V. The maximum current density, I_{max} , represents the current density without the shoulder. The ratio I_{avg}/I_{max} represents the ratio between the performance with and without the shoulder and is used here to illustrate the effect of the presence of the shoulder. At lower over-potentials, the effect of the presence of the shoulder on the cell performance is not significant. However, at higher over-potentials, the effect of the shoulder area becomes significant. In other words, the hindrance on the current generation by the shoulder area increases at higher current loads.

The effective diffusion coefficient of oxygen in the electrode layer is affected by the porosity and the tortuosity of the electrode layer (3). Also, the morphology of the electrode layer can be affected by the present of the liquid water that is generated by the electrode reaction and electroosmosis at the reaction interface. Different values of the effective diffusion coefficient of oxygen are used to simulate the effect of electrode morphology as well as water conditions of the system. Figure 5 shows the effect of the effective diffusion coefficients ranging from 0.03 to 0.09 cm²/s at five different current loads for h/s = 0.2 and (l-s)/s = 0.5. As expected, as the effective diffusion coefficient decreases, hindrance by the shoulder area increases as shown by the decreasing I_{avg}/I_{max} ratio.

Figure 6 shows the effect of the aspect ratio (h/s), the ratio between the electrode thickness and the length of the shoulder, at (l-s)/s = 0.5 and $D_{eff} = 0.03$ cm²/s. As the aspect ratio increases the average current density generated along the reaction interface approaches closer to the maximum current density. In other words, the hindrance on the current generation by the shoulder area decreases. As the aspect ratio increases the diffusion length of the gas increases and the difference in the diffusion distances between the region above the channel and that above the shoulder becomes less significant. Therefore, oxygen gas is more uniformly distributed. However, the maximum current density attainable decreases.

The effect of the channel and shoulder ratio ((l-s)/s) is shown in Figure 7 for different current loads with the conditions of h/s = 0.2 and $D_{eff} = 0.03$ cm²/s. As the channel ratio decreases, the effect of the shoulder increases, and this effect becomes more significant at higher current loads. Note that at higher channel to shoulder ratios, the electrical resistance is higher. The optimized channel to shoulder ratio must account for the gas transport as well as the electrical resistance requirements.

CONCLUSIONS

The effects of the shoulder area of the flow distributor were studied in terms of the current density generated at the reaction interface. Two dimensional Laplace's equation was used to simulate the oxygen transport through the air cathode of a PEM fuel cell. The boundary conditions were specified to account the presence of shoulder and channel area of the flow distributor. The effects of current loads, effective diffusion coefficients, aspect ratio of the electrode, and channel to shoulder ratio were investigated. At low current loads with high diffusion rates, aspect ratio, and channel ratio, the effect of the presence of the shoulder was negligible as expected. However, at high current loads, low diffusion rates, and low aspect ratio, the diffusion hindrance from the shoulder became significant, resulting in losses in performance by as much as 45 %. Also, it was

quantitatively demonstrated that the shoulder effect in terms of current generation decreased as the channel to shoulder ratio increased.

From this analysis, it could be concluded that the diffusion hindrance by the shoulder of the flow distributor could significantly affect the performance of a fuel cell. This hindrance effect increased with increases in the current load and decreases in the effective diffusion coefficient, aspect ratio of electrode thickness and the shoulder length, and channel to shoulder ratio.

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Figure 1. Schematic of the cross-sectional view of one electrode of a PEM fuel cell.



Figure 2. Concentration distribution of the reactant gas within the electrode.



Figure 3. Profiles of the current distribution along the reaction interface at various current loads.







Figure 5. Effect of the diffusion coefficent on the ratio between average current density and maximum current density.









WATER MANAGEMENT IN LARGE SCALE PEFC STACK

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Removal of product water is a problem in polymer electrolyte fuel cells (PEFCs) that operate at less than 100°C. As water vapor pressure increases along gas flow in a cell, the difficulty of removing product water also increases in downstream of the flow. This problem is negligible in case of small-area electrode, but it becomes serious in large-area electrode. The means we have taken to solve this problem is to make intentionally temperature difference between gas inlet and outlet in the cell. This method effectively prevented the large-area electrode of 600cm² and 2000cm² from the condensation of water vapor in the cell. We have added a theoretical explanation for the effect of the temperature difference method.

INTRODUCTION

Since PEFCs are usually operated at lower temperature than the boiling point of water, the issue of water management is very important in stable operation. Condensed water in electrodes hinders gas diffusion, and stuffed water in gas grooves causes ill distribution of gas. There are two approaches to remove water efficiently. One is to remove condensed water by capillary force using some hydrophilic materials. Another way is to prevent water vapor from condensing by adjusting cell temperature. We have examined the latter method, which makes intentionally temperature difference between gas inlet and outlet in the cell.

EXPERIMENTAL

In order to make intended temperature difference, the structure of cooling water flow path in a separator was designed as shown in Figure 1. Cell temperature was changed by controlling temperature and flow rate of cooling water passing through the grooves which made a right angle with gas passages. A 6-cell stack with 600cm^2 electrodes, as shown in Figure 2, and a 2-cell stack with 2000cm^2 electrodes were used in the

experiment. Both anode and cathode catalyst layers contained 2.6 mg/cm² of Pt black. The anode feed gas was pure H_2 , and the cathode feed gas was air. Operating conditions are shown in Table 1.

RESULTS

Figure 3 shows the effect of cell temperature at gas inlet (T_i) on cell voltage in 600cm² electrode cells operated at 0.2MPa abs. Cell temperature difference between gas inlet and outlet (ΔT) was fixed at 7°C. Each cell voltage was corrected into the deviation from maximum cell voltage in the figure. The cells gave stable voltage in the range of 66 to 68°C (T_i) except for No.2 and No.4 cells.

Figure 4 shows the effect of ΔT on cell voltage at constant T_i (66°C). High cell voltage was obtained in the 5 to 7°C of ΔT except for No.4 cell. Different behavior of No.2 and No.4 cells is considered to be due to ill distribution of gas. These experimental results give that the optimum temperature in 600cm² cells is T_i =66 to 68°C and ΔT =5 to 7°C.

Figure 5 and 6 show the case of 2000cm^2 electrode cells. Maximum cell voltage was obtained at $T_i=69^{\circ}\text{C}$ and $\Delta T=3$ to 5°C. Since the 2000cm^2 , 2-cell stack was operated at low pressure (0. 1MPa abs), the effect of temperature difference is less remarkable than that in the 600cm^2 stack.

MODEL DEVELOPMENT

Model Description

A theoretical model has been developed to calculate T_i and ΔT for various operating conditions. The schematic view of the model is shown in Figure 7. In this model, the contribution of anode on water removal was represented by a parameter α that is the ratio of product water removed through cathode to total removed water. The ratio α was determined experimentally. The anode polarizations is ignored because pure H₂ is used for anode feed gas. Assuming that the partial pressure of water vapor at cathode reaction site is equal to the saturated water vapor pressure at the cell temperature, the pressure difference of water vapor between the reaction site and the gas passage, $\Delta p(x)$, can be expressed as:

$$\Delta p(x) = P_w(T(x)) - P\left\{\frac{V_w(x)}{V_w(x) + V_A(x)}\right\}$$
[1]

where x is the distance from the gas inlet $(0 \le x \le L)$, P_W is the saturated pressure of water vapor, T is the cell temperature, P is the total pressure, V_W is the flow rate of water vapor in air, V_A is the flow rate of dry air. V_W and V_A are the functions of x, and can be expressed as:

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$$V_{W}(x) = V_{W0} + \frac{\alpha}{2F} \int_{0}^{x} i(t)dt$$
[2]

$$V_{A}(x) = V_{A0} - \frac{1}{4F} \int_{0}^{x} i(t)dt$$
 [3]

where V_{W0} and V_{A0} are the flow rate of water vapor and air at inlet, α is the ratio of product water removed through cathode. $\Delta p(x)$ in equation [1] can be written as:

$$\Delta p(x) = \Delta p_0 \left(\frac{T(x)}{T_0}\right)^{1.75} \left(\frac{P}{P_0}\right) \left(\frac{i(x)}{i_0}\right)$$
[4]

where temperature T_0 , pressure P_0 , and current density i_0 are selected value as standard conditions of calculation. Δp_0 is the calculated pressure difference of water vapor from T_0 , P_0 , i_0 , and the thickness of cathode. Equation [4] implies variation of diffusion coefficient by temperature and pressure.

Calculation of Optimum Temperature Distribution

The temperature distribution T(x) can be obtained by solving equation [1] to [4]. Ti and ΔT is given by Ti = T(0) and $\Delta T = T(L) - T(0)$. Figure 8 shows the contour of computed T_i as a function of dew point of air and total pressure at 0.4A/cm². ΔT can be also calculated as shown in Figure 9. The computed temperatures corresponding to the operating conditions in Table 1 are T_i =65.9°C / ΔT =7.2°C (600cm²), T_i =68.5°C / ΔT =2.8°C (2000cm²), which agree with the experimental results in Figure 2 to 5.

Optimum temperature distribution can be obtained from these figures. High pressure or low temperature requires large ΔT . High utilization of air or high current density also needs to enlarge ΔT from equation [1] to [4].

CONCLUSIONS

A temperature difference method operated effectively to remove product water from cathode in the experiments of 600 and 2000cm² electrode cells. The optimum cell temperature and temperature difference can be calculated from water vapor pressure in inlet air, total pressure, and current density. The computed optimum operating temperature shows good agreement with the experimental results.

Table 1 Operating Conditions		
600cm ²	2000cm ²	
0.4A/cm ²	0.4A/cm ²	
0.2MPa	0.1MPa	
25%	25%	
72%	36%	
57°C	65°C	
	perating Cond 600cm ² 0.4A/cm ² 0.2MPa 25% 72% 57°C	



Fig.1 Schematic Illustraton of Cooling Water Flow



Fig.2 6-Cell Stack with 600cm² Electrode



Fig.3 Cell Voltage vs. Cell Temperature at Gas Inlet (600cm²)



Fig.4 Cell Voltage vs. Cell Temperature Difference between Gas Inlet and Outlet (600cm²)



Fig.5 Cell Voltage vs. Cell Temperature at Gas Inlet (2000cm²)



Fig.6 Cell Voltage vs. Cell Temperature Difference between Gas Inlet and Outlet (2000cm²)



Fig.7 Schematic View of Model



Fig.8 Calculated Contour of Inlet Cell Temperature T_i at 0.4A/cm²

Fig.9 Calculated Contour of Temperature Difference between Gas Inlet and Outlet ΔT at 0.4A/cm²

DEVELOPMENT AND PERFORMANCE OF GASKETLESS STACK FOR PROTON EXCHANGE MEMBRANE FUEL CELLS

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ABSTRACT

The gasketless stack for proton exchange membrane(PEM) fuel cells was developed by using O-ring. Incorporation of O-ring makes it possible not only to obtain the perfect sealing and non-mixing of reactants gases but to fabricate the stacks less expensive and more convenient. The stack performance of 250 mÅ/cm² at 0.7 Volt was attained at 3 bar with the E-TEK electrode and Nafion 115 membrane by using the pure hydrogen and oxygen. It exhibited reasonably uniform cell-to-cell performance and stability.

INTRODUCTION

Among various electric power generating technologies utilizing non-petroleum fuels such as methanol, ethanol, natural gas and hydrogen, fuel cells provide advantages over conventional technologies. These advantages include high generation efficiency and superior characteristics with regard to environmental considerations. Numerous efforts have been made, therefore, for the fuel cells development as future generation technology. Proton exchange membrane fuel cell(PEMFC) is a fuel cell of special interest due to its high attainable power density at the lowest operating temperature. Recently it has been considered as a promising power source for electric vehicles[1,2].

The use of the solid polymer electrolyte in fuel cell enables one to remove problems encountered when liquid electrolytes were utilized. Problems of managing electrolyte and corrosion, for example, are minimized by replacing liquid electrolyte to solid polymer. PEMFC also enables the relative simplicity of stack design and the ruggedness of system. One of the key technological impediments associated with development of PEMFC is the water and heat management inside stack. Numerous efforts have been made concerning the distribution of reactants gases and the removal of reaction products such as water and heat[3,4,5].

It is surprising that the literatures on gas scaling are rather scare in spite of its critical importance in stack fabrication. Most of previous works employed the thermoplastic gaskets for gas scaling[6]. Gasket materials include Viton, rubber,

styrene-butadiene copolymers and silicon. It is author's understanding, however, that gaskets-incorporated stacks are prone to gas leak and/or gas crossover problems especially when they are operated in a pressurized condition. Moreover electrolytic membrane should be sufficiently large enough to ensure a close contact between gasket and membrane. Taking into account of the price of the membrane, it makes stack cost high since the membrane in contact with gasket is essentially unused.

This study presents the stack design and its performance. This stack was made of unit cells which does not have gaskets for scaling. Korea Gas is now producing stacks of unique design(KGPF-3) where reactant gases are fed by internal manifolders to the bipolar plates of series-parallel design. Gas scaling in this stack is achieved by incorporating double O-rings instead of gaskets.

EXPERIMENTAL

Membrane/Electrode Assembly Fabrication

A membrane-electrode assembly(MEA) is a basic building block of fuel cell stack. MEAs, having an active area of 289 cm², were fabricated from Nafion 115(thickness : 127 μ m) membranes and low Pt-loaded(0.4 mg Pt/cm²) E-TEK electrode. Prior to use in the MEA, membrane was cleaned and treated to make it a proton conductor. The electrodes were impregnated with 5% Nafion solution so that the MEA may attain high enough power density. The amount of impregnated ionomer(dry weight) was varied up to 1.9 mg/cm². Upon completion of membrane and electrode treatments, they were assembled and hot pressed at varying pressure(1~3 metric ton) and temperature(80~190°C) for about 3 minitues. The procedure of MEA fabrication is shown in Fig. 1.

Stack Fabrication

A 30-cell PEM fuel cell stack(KGPF-3) was fabricated in this study. The geometric area of reaction area was 289 cm²(17cm x 17cm). The stack consists of membrane/electrode assembly, bipolar plate and end plate and cooling plate. The later three plates are made of resin-impregnated graphite. The bipolar plates were designed so that the reactant and product gases are manifolded internally and fed to individual cells by series-parallel flow pattern. Cooling plates were placed in every four cells and fed with water. Fig. 2 shows the stack assembly which consists of tie plate(1), end plate(2), bipolar plate(3) and membrane/electrode assembly((4, (5), (6)). Four holes(8) located at the corner of the bipolar and cooling plate(3) are internally connected to the inside ribbed surface of bipolar plate and act as inlets and outlets of reactant and product gases. Grooves are machined to place O-rings(7). Five O-rings were incorporated into individual cells : one to separate the active area from the gas flow channels and the others to seal reactant and product gases.

Performance Test

The performance tests of stack were conducted using test stations. Test

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stations were equipped with humidification chamber, mass flow controllers, back pressure regulators and temperature controllers(Fig. 3). Hydrogen and oxygen were used as reactant gases. Both gases were humidified by passing them through the humidification chambers whose temperature was maintained at the predetermined level.

The gas flow rate was changed with current density in order to maintain it as a constant factor times gas utilization rate($1.5 \times$ stoichiometric). Stack potential vs. current density measurements were made over a temperature range of 50 to 80 °C and a pressure range of 1 to 3 atm.

RESULTS AND DISCUSSION

Design Feature of KGPF-3

The optimum fuel cell operating condition was already identified with several publications [1,7]. Gas temperatures should be maintained higher than the cell temperature in order to supply enough vapor for membrane humidification. It is identified that the best gas temperatures are 5°C and 10°C higher than the cell temperature, for oxygen and hydrogen respectively, irrespective of the cell temperature. Power output of fuel cell could be further increased via pressurized operation. Enhanced performance with increasing cell temperature was observed up to 70°C, whereas the latter showed no appreciable effect above 70°C. This observation might be attributed to the increased vapor pressure with increasing temperature which dilutes inlet gas composition [8].

Pressurized operation of polymer electrolyte membrane fuel cell is very important because of better gas distribution and membrane humidification but has exposed problems of gas tightening and scaling. Gaskets have been widely used for gas tightening and scaling. Use of gaskets, however, exposes several problems which are stated below

Most importantly, gasket-scaled stack, sometimes, can not secure gas scaling. Experience of this laboratory have shown that gas scaling by gaskets became difficult especially for the cells of large active area(>200 cm²). Planar deformation of thin graphite plates upon machining into the bipolar plates is responsible for this observation. Difference in the thermal expansion coefficients of gasket material and membrane causes considerable stress in repeated halt-operation cycles. This stress is concentrated at the inside border of gasket where gasket where gasket at the inside border of the contact. Membrane clectrode, both were attached on top of the membrane, are in contact. Membrane stress.

Fuel cell stacks which were fabricated utilizing O-rings, instead of gaskets, enable pressurized operation without above mentioned problems.

Stack Performance

Three individual stacks having 10 unit cells were fabricated separately. Each 10-cell stack was tested at least for 7 days in order to identify any fabrication

flaws. This test included not only the gas leak and cross-over at high pressure but also the basic performance such as open circuit potential and i-E characteristics at low current density. Upon completion of pre-test, 10-cell stack was added to previously tested stack. Component cells exhibiting poor performance were replaced by fresh cells during stack-to-stacking procedure. In fabricating the final stack, composed of 30 unit cells, cooling plates were incorporated into every four cells.

The potential vs. time plots, at constant current density, are shown in Fig. 4. Although the increase in the operating temperature and pressure resulted in the enhanced performance, results at 60° C and 1 bar (hydrogen and oxygen) are presented. As shown in this figure stack exhibited an excellent stability with time. Effect of the cell temperature on stack performance is shown Fig. 5. This study was conducted with 20-cell stack by maintaining the 1 bar pressure. This trend is almost same as that of the unit cell, that is, the increase in the open circuit voltage and on the exchange current density with increasing cell temperature[8]. Fig. 6 shows the effect of the operating pressure on 20-cell stack performance. The observed performance enhancement upon increasing the operating pressure from 1 to 3 bar is rather smaller than expected. This is a discrepancy between unit cell and stack performance behavior where the former exhibits significant performance enhancement upon pressurized operation.

Current-potential performances of each and every constituting cells in the 20-cell stack were monitored. Although some cells showed impaired performance at high current density operation, cells exhibited reasonably uniform performance even long time after fabrication(Fig. 7). Cell-to-cell consistency was maintained for the 30-cell stack(Fig. 8). This 30-cell stack, named KGPF-3, is currently under operation. The power capacity of this stack is 1.2 KW at 60 $^{\circ}$ C and 1 bar (Fig. 9) and the total operation time has exceeded 2500 hours. This stack has been demonstrated that there are no internal cross-over and external leakage problems. This stack has an ability to produce about 2 KW power at the higher pressure and temperature.

CONCLUSIONS

Korca Gas is developing proton exchange membrane fuel cell stack. We have identified several important features in developing PEMFC stack which is listed below ;

- Optimum conditions for PEMFC operation has been identified. Temperature of inlet gases higher than the cell temperature is required to humidify the membrane electrolyte. Pressurized operation becomes feasible when O-ring, instead of gaskets, are utilized.
- Cell stack(KGPF-3 : 1 KW power) is fabricated and is currently under testing. It exhibits reasonably uniform cell-to-cell performance and stability. The unique features of this stack include incorporation of O-rings, internal manifolding of reactant gases, series-parallel design of bipolar plate and water

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cooling.

• We have demonstrated that the stack does not experience internal cross-over and external leakage of reactant gases even after 2500 hours operation.

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Fig. 1. The procedure of MEA fabrication.



Fig. 2. Proton Exchange Membrane Fuel Cell Stack Assembly





Fig. 4. Performance data of PEMFC muti-cell stack at T_{stack}=60°C, P_{H,'O,}= 1bar. E-TEK electrode(0.4mg Pt/cm², area 289cm²) and Nafion #115 membrane.



Fig. 5. Effect of temperature on performance PEMFC 20-cell stack plot. E-TEK elctrode(0.4mg Pt/cm², area 289cm²) and Nafion #115 membrane, P_{H2.02}=1bar.







Fig. 7. 20-cell stack current distribution & Individual potential vs. No. of cell from H₂ inlet plot. E-TEK electrode(289cm² area, 0.4mg Pt/cm²) and Nafion#115 membrane. T_{stack}=60°C, P_{stack}=1 bar.



Fig. 8. 30-cell stack current distribution & individual potential vs. No. of cell from H₂ inlet plot. E-TEK electrode(289cm² area, 0.4mg Pt/cm²) and Nafion #115 membrane. T_{stack}=60°C, P_{stack}=1bar.



Fig. 9. 30-cell stack potential & power vs current plot. E-TEK electrode (0.4mg Pt/cm²,area289cm²) and Nafion #115 membrane, T_{stack} =60°C, $P_{\dot{H}_{r},o_{p}}$ =1bar.

EFFECT OF CONTACT PRESSURE AT Pt-POLYMER ELECTROLYTE INTERFACE ON OXYGEN REDUCTION REACTION

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In order to clarify the interface reaction between electrode/solid polymer electrolyte, the effect of the contact pressure between Pt electrode and polymer electrolyte(Nafion®) on oxygen reduction reaction(ORR) on Pt electrode has been studied at room temperature by the electrochemical methods (cyclic voltammetry, potential sweep and chronoamperometry) using a straingauge.

The current of ORR at a fixed potential depended on the contact pressure. At low oxygen overpotential where the activation controlled the reaction the ORR current increased with the increase of contact pressure because of the suppression of the formation of Pt oxide. On the other hand the limiting current of ORR where the reaction was controlled by the diffusion of reaction species decreased with the increase of the contact pressure owing to the suppression of oxygen flux in the polymer electrolyte.

INTRODUCTION

The polymer electrolyte fuel cells(PEFC) are started again to develop extensively since they can operate at relatively low temperature(close to room temperature) and have high power density and are easy to handle compared to other fuel cells¹). This was originally developed for the space use(Gemini Program). At that time the ability of PEFC is not enough compared to other fuel cells. Several years ago the announcement of Dow membrane changes the situation of PEFC for its high power density(current density)²). The breakthrough of basic material causes the great technical innovation. The special attention is paid for the application of PEFC to the moving power source, especially to the automobiles.

However, they have several technical problems to be solved before commercialization. The decrease the usage of Pt amount in catalyst, the water management in the polymer electrolyte, and the poisoning of the electrode by carbonaceous materials(especially CO) are thought to be primary major technical problems. Besides them the large overpotential of the oxygen reduction reaction(ORR) at the cathode exists. Oxygen electrodes generally causes this kind of problem in any electrochemical system especially at

low temperature. The active electrode material for the oxygen reduction is inevitable for a high performance PEFC. Presently, Pt or Pt based alloys on dispersed carbon are used since they are relatively active for oxygen reduction and stable with the polymer electrolyte that is thought to be a strong acid.

The catalytic activity of ORR at the cathode is affected by several other factors. The contact pressure between the cathode and the polymer electrolyte is one of them, since the characteristics of polymer electrolyte would be affected easily by the pressure(force) from outside. If the pressure were weak, the ORR could not proceed thoroughly since enough reaction interface could not be obtained. If the contact pressure were very strong, the reaction would be affected by the deformation of the polymer electrolyte. The deformation might cause the changes of the ionic conductivity or the diffusivity of the reaction species in the electrolyte.

In this work the effect of the contact pressure(or force) between the polymer electrolyte and the Pt cathode has been studied fundamentally by the electrochemical method using the pressure controlling devise.

EXPERIMENTAL

The solid state electrochemical cell that was used for the reaction cell³). Figure 1 shows the schematic drawings of the experimental cell where the contact pressure between the working electrode and polymer electrolyte can be controlled. The working electrode and the counter electrode were contacted on both sides of the polymer electrolyte. The electrolyte was Nafion[®] 117. The polymer electrolyte was washed in 5 wt% H₂O₂, 0.5 M HCl, and ultra pure water at 80°C before use. The contact pressure was changed by the turning of the screw of the micrometer head that was connected to the working electrode. The pressure was measured with the straingauge transducer that was placed on the top of the micrometer head.

At first spherical Pt electrodes were used for the working electrodes whose diameter were 0.45, 0.80 and 1.7mmØ that were made by melting Pt wires. The surface of the electrodes were polished with alumina polishing powder and washed in pure water with ultrasonic washer. In order to minimize the effect of oxygen diffusion through the polymer electrolyte, Pt microelectrode(0.3mmØ disk) was used for the cathode working electrode that was made by mounting Pt wire in acrylic housing with epoxy resin. The surface of Pt cathode was coated by polymer electrolyte using $10\mu l$ of 5% Nafion®- alcohol solution and dried in air at room temperature. The counter electrode was Pd plate with small holes with the current collector of Pt mesh. The reference electrode was the dynamic hydrogen electrode(DHE)⁴) that was made by the thermal decomposition of Pt salt on 1.5 mmØ Ti. The current density for the DHE was 1 mA/cm².

The oxygen gas was humidified by bubbling through the water whose temperature was kept same as the reaction cell. The ORR on the Pt electrode was studied at room temperature using the apparatus by the potential sweep method, the cyclic voltammetry and the chronoamperometry^{5,6}).

RESULTS AND DISCUSSION

Figure 2 shows the dependence of the net current of ORR on the spherical Pt electrodes at the potential of 0.3V vs.DHE on the contact force between Pt electrode and the polymer electrolyte. The current was obtained by the potential sweep from 1.3 V at the sweep rate of 0.01 V/s. The current increases on larger size Pt electrode and becomes constant value at high contact force. Figure 3 shows the dependence of the contact area of the Pt electrodes on the contact force that was obtained from the peak current of the Pt oxide reduction at the cyclic voltammogram from 1.5 V to 0.05 V at the sweep rate of 0.1 V/s in nitrogen atmosphere. The contact area increases sharply at small contact force. At high contact force the increase of the area becomes small, where the deformation of the polymer electrolyte would take place.

Combined the results of Fig.2 and Fig.3, the real current density of ORR can be calculated and plotted in Fig.4. With 0.45 and 0.80 mmØ electrodes the current density increases at small contact force and gets the maximum at 100 gf and 200 gf, respectively. At higher contact force the current density decreases gradually. If the ORR at Pt/polymer electrolyte interface were independent of the contact force, the current density should stay constant and be independent of contact force. The result of this work is different. The ORR would be affected by the contact force not only by the reaction area but by the other factors.

The surface of Pt electrode might be divided into two regions. One is active for ORR and the other is inactive. On Pt electrode Pt oxide is present as well as Pt metal in oxygen containing atmosphere. Generally, Pt oxide is inactive for electrode reactions compared to Pt metal. In the polymer electrolyte both the hydrophobic area and the hydrophilic area exist. The hydrophilic area would be more active for ORR. These phenomena were mixed and the current density got the maximum in Fig.4. The inactive area increases gradually at higher contact force in this case.

Figure 5 shows the results of the potential sweep $(1.1 \sim 0.3 \sim 1.1 \text{ V vs. DHE})$ in oxygen atmosphere on the 0.3mmØ Pt microelectrode that was mounted in epoxy resin. The sweep rate was 2 mV/s and the contact pressures were 0, 1.4, 2.8, 4.2, 5.7 and 7.1 kgf/cm⁻². These results are in the same figure. The starting and the terminal potential of each sweep is 1.1V. The reduction current starts about 1.0 V and gets the limiting around 0.7 V in each sweep. Since this kind of reduction current did not appear without oxygen, this reduction current would correspond to the oxygen reduction current. Although the shape of the curves are almost same, the absolute values(current) of sweeps are different.

Namely, the oxygen reduction current increases as the contact pressure increases in the low oxygen overpotential region(1.0 \sim 0.9 V). On the other hand, the limiting current that is controlled by the diffusion process of the reaction species in the polymer electrolyte decreases as the contact pressure increases.

Figure 6 shows the relation between contact pressure and the peak potential and the peak current of Pt oxide reduction on the Pt microelectrode that were obtained by the cyclic voltammograms in nitrogen atmosphere. The peak potential is independent of the contact pressure. However, the peak current decreases as the contact pressure increases. The ohmic contact between the Pt electrode and the polymer electrolyte did not change since the peak potential does not change. The electric quantity of hydrogen desorption peak at the cyclic voltammogram on Pt micro electrode is independent of the contact pressure. That means the reaction area did not change with the contact pressure.

Taking into account of these facts, the reduction of the Pt oxide reduction current with the contact pressure does not owe to the reduction of the active reaction area but to the increase of the hydrophobic area of the polymer electrolyte at the electrode surface. The increase of hydrophobic area causes the decrease of water content in the polymer and suppress the Pt oxide formation at the electrode/polymer interface. The oxide free Pt is more active for ORR than Pt oxide. This would be the reason for the increase of ORR current at higher contact pressure at low oxygen overpotential.

In order to obtain the transport properties of reaction species the chronoamperometry was studied using the Pt microelectrode in oxygen atmosphere. The initial potential was 1.1 V vs. DHE that was stepped to 0.3 V and the response current was measured up to 10 s. The obtained current decreased with time. The current was proportional to (time)-0.5 and the diffusion coefficient and the solubility of oxygen in the polymer electrolyte were obtained. Figure 7 shows the dependence of these factors on the contact pressure. As the contact pressure increases, the diffusion coefficient of oxygen decreases and the solubility increases.

Considering these results the water concentration gradient might be formed in the polymer electrolyte. The diffusion characteristics of oxygen in the polymer electrolyte would be affected by the water content. In this work the diffusion coefficient of oxygen was also measured with semi-dried electrolyte and with the electrolyte in water using the same method. The diffusion coefficient is highest in water and lowest with semi-dried membrane. The diffusion of oxygen in phosphoric acid increased at higher content of water owing to the increase of the viscosity of the electrolyte?). The decrease of water content in the polymer electrolyte means the decrease of the diffusivity of oxygen in the electrolyte. This might be a reason for the decrease of the limiting current on the Pt microelectrode at higher contact pressures.

CONCLUSION

The oxygen reduction kinetics on Pt electrode at the polymer electrolyte interface were studied in related to the contact pressure between electrolyte and electrode. At low oxygen overpotential the ORR current increased at higher contact pressure due to the suppression of the formation of Pt oxide. At high oxygen overpotential the limiting current of ORR decreased at higher contact pressure because of the decrease of the diffusivity of oxygen in the polymer electrolyte.

In order to apply these concept to the polymer electrolyte fuel cell the results of low oxygen overpotential is important. In this sense the catalytic activity of oxygen cathode might increase at higher contact pressure. However, the polymer electrolyte deforms or is destroyed easily at high contact pressure. A suitable contact pressure should be found by studying of the wider range of contact pressure.

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Fig.1 Schematic drawings of the cell.

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W/g

Fig.2 Dependence of net ORR current at 0.3V on contact force.



Fig.3 Dependence of Pt active surface area on contact force.



Fig.4 Dependence of net ORR current density at 0.3 V on contact force.




Fig.6 Dependence of peak potential and current of Pt oxide reduction on contact pressure.



Fig.7 Dependence of diffusion coefficient and solubility of oxygen in polymer electrolyte on contact pressure.

FABRICATION AND EVALUATION OF ELECTRODES FOR POLYMER ELECTROLYTE FUEL CELLS

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ABSTRACT

In this work, the development and results on the electrochemical studies of low catalyst loading gas diffusion electrodes for polymer electrolyte fuel cells are reported. The single cell data were analyzed employing the current knowledge derived from theoretical models of the electrode structure and of the fuel cell system.

INTRODUCTION

Recent developments in polymer electrolyte fuel cells (PEFC) led to a growing interest in this system, particularly for transportation applications. Perhaps the major breakthrough accomplished lately on this fuel is the improvement on the design, composition and loading of platinum in the gas diffusion electrodes (1-3).

This work reports single results obtained with low catalyst loading gas diffusion electrodes developed on the basis of the concept proposed by Gottesfeld and co-workers (3), combined with the standard approach of Srinivasan and co-workers (2). Studies on these electrodes involve the effect on the fuel cell operation of the structure and composition of the diffusion and catalyst layers on the electrodes and the effects of the membrane thickness, cell temperature and reactant pressure.

EXPERIMENTAL

The electrodes were prepared by a combined filtration/brushing procedure using carbon supported catalysts (E-Tek Inc.), carbon powder (Vulcan XC-72, Cabot), a carbon cloth substrate (PWB-3, Stackpole), a polytetrafluoroethylene (PTFE) suspension (Teflon T-30, DuPont), and a Nafion[®] solution (5 wt.%, Aldrich). PTFE and carbon powder were used to prepare the diffusion layer which was deposited on both sides of the carbon cloth by filtration. The catalyst layer was made by brushing an ink formed with the supported catalyst and the Nafion[®] solution in isopropanol. Membrane and electrode assemblies

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were prepared by hot pressing the electrodes onto a purified Nafion[®] membrane. The electrodes were prepared with different thicknesses and PTFE contents in the diffusion layer and with varying Nafion[®] and catalyst loadings in the catalyst layer. Employed catalysts were 10, 20, 30, 40, 60 and 80 wt.% Pt/C and 20 wt.% Pt alloy/C (50 atom% of Pt-Cr, Pt-V, and Pt-Co).

In this work the thickness of the diffusion layer is expressed in terms of the thicknesses of the PTFE/C layers applied to the carbon cloth, which were measured from separate films deposited on a filter paper. The PTFE contents are expressed in terms of the weight percentage of PTFE to the total weight of the PTFE/carbon mixture. The catalyst and Nafion[®] loadings are expressed in milligrams of the materials per square centimeter in the catalyst layer.

The polarization experiments were carried out under galvanostatic conditions with humidified reactants in a conventional single cell set-up with an electrode area of ca 5 cm². Cyclic voltammetries were performed at 25 °C in the same cell, with the probe electrodes supplied with nitrogen and the counter and reference (RHE) electrodes supplied with hydrogen. The scan rate was 50 mV s⁻¹. Unless otherwise stated the standard conditions for polarization measurements were: 0.4 mgPt cm⁻², H₂/O₂ 1/1 atm, Nafion 117 membrane, and 80/95/90 °C for the temperatures of cell/hydrogen humidifier/oxygen humidifier, respectively.

RESULTS AND DISCUSSION

The analysis of the experimental polarization results was made using the semiempirical equation proposed by Srinivasan and co-workers (4,5) for the representation of the cell potential (E) versus current density (i) characteristics:

$$E = E^{\circ} - b \log i - Ri$$
 [1]

where

$$\mathbf{E}^{\mathbf{o}} = \mathbf{E}^{\mathbf{r}} + \mathbf{b} \log \mathbf{i}_{\mathbf{o}}$$
 [2]

Here, E^r is the reversible potential for the cell, b is the Tafel slope and i_o is the exchange current density of the oxygen reduction reaction (ORR) in the Pt/C catalyst, and R represents the total contributions of the linear polarization components which include the charge transfer resistance of the hydrogen oxidation reaction (HOR), the resistance of the electrolyte in the cell and the linear diffusion terms due to diffusion in the gas phase and/or in the thin film (5). In the above equation it is assumed that the resistance of the electrolyte is not dependent on current density which is a good approximation for moderate values of current densities (6).

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The fittings of the above equation to the experimental results were made by a nonlinear least square method using the experimental data obtained for the cell potentials above 0.8 V for which the expected Tafel slope of the ORR in the Pt/C catalyst is 2.303(RT/F) (7) and the diffusion limitation in the gas phase and/or in the thin film, if present, is linear (5). Only in a few cases the fittings were carried out for potentials below 0.8 V for which the Tafel slope should be 2x2.303(RT/F) (7). Table 1 presents the calculated kinetic parameters E°, b and R resulting from some of the fittings.

On the basis of the above procedure and also from the predictions of the theoretical models of the PEFC (4-6) and of the gas diffusion electrodes with respect to the ORR (8), the analysis of the polarization diagrams was made taking into account the following facts:

- (i) a possible kinetic change of the ORR on the Pt/C catalyst due to the change of oxygen coverage on the platinum surface, occurring at around 0.8 V and appearing as a change in the Tafel slope of the polarization diagram from b = 2.303(RT/F) for potentials above 0.8 V to b = 2x2.303(RT/F) for potentials below 0.8 V (6);
- (ii) the existence of diffusion limitations in the gas channels in the diffusion and the catalyst layers of the electrodes, and in the thin film of the electrolyte covering the catalyst particles, leading to pseudo resistive effects at moderate current densities and the appearance of limiting currents at high current densities in the polarization diagrams (4,5,8);
- (iii) the influence of the effective surface area for the electrochemical reactions on the behavior of the electrodes which usually shift the above limiting effects to higher current densities.

Fig. 1 shows the cell potential vs. current density characteristics at 80 °C for the single cell with the electrodes with 10 wt % Pt/C presenting different thicknesses of the diffusion layer (40 % PTFE). The corresponding values of the kinetic parameters E°, b and R are presented in Table I. As expected, because the catalyst layers are the same, similar values of E° were obtained for the different electrodes, indicating that the value of i_o (eq. [2]), and thus the electrochemical active areas, are the same in all cases. The values of b are somewhat higher but still close to the value for the ORR on smooth platinum (2.303(RT/F)) at 80 °C, indicating a very small effect of the structure of the diffusion layer of the electrodes on the polarization behavior. In the range of 65 to 35 µm, the values of R slowly decrease with decreasing thickness of the diffusion layer, which is an evidence that there is a small decrease of the linear diffusion component. This can be due to a decrease of the path for the gas diffusion or to a lesser influence of flooding problems. Below 35 µm there is an increase of R probably related with to problems of electrical contact between the carbon particles. From these results it is concluded that the kinetic behavior of the electrodes with respect the HOR as well as the resistance in the membrane are the same in all cases. All these trends on the behavior of E°, b and R were similar for electrodes with 20 and 30 wt.% Pt/C. Thus, as a final conclusion it is observed that for all electrodes there is an optimum diffusion layer thickness, below which there are losses due

to poor electrical contact and above which diffusion effects due to flooding can be detected.

The study of the effect of PTFE content in the diffusion layer was carried out for the 35 and 50 μ m diffusion layer electrodes, in the range of PTFE content from 50 to 10%. Fig. 2 and Table I show the results obtained for the 20 wt.% Pt/C in the catalyst layer and 35 μ m thickness of the diffusion layer. These results show that no additional diffusion effects are detected even for a PTFE content as low as 10 %. However, it is observed from Fig. 2 that a small increase in the electrode performance occurs when the PTFE content is diminished from 50 to 10%. Most probably, this effect is due to improved water transport, and thus better humidification of the polymer electrolyte.

The polarization results and kinetic parameters obtained for the electrodes presenting different Pt/C ratios, keeping constant the catalyst loading, are presented in Fig. 3 and Table I. As in the previous cases, the values of b at potentials above 0.8 V are all close to 2.303(RT/F) at 80 °C. An exception was found for the electrode with 80 wt.% Pt/C which, due to the smaller active area, only showed the second linear region corresponding to potentials below 0.8 V. When loaded with proportional amounts of Nafion[®], the values of E° are similar for 10, 20, 30 and 40 wt.% Pt/C, indicating that the active areas are essentially the same for all these electrodes; with 60 wt.% Pt/C there is a decrease in E°, indicating a decrease in the active area. Finally, with 80 wt.% Pt/C the corresponding value of E° could not be obtained because the active area is so small that there were not enough experimental data to carry out the fitting for cell potentials above 0.8 V. The values of R for 10 to 40 wt.% Pt/C are practically constant, indicating that the membrane resistance and the HOR polarization are the major factors contributing to the values of the linear polarization term. For higher Pt/C weight ratios there is an increase of the values of R, most probably due to an increase of the linear diffusion component as a consequence of the decrease of the electrochemical active area. The increasing tendency to reach limiting diffusional currents observed in Fig. 3 for the electrodes with 60 wt.% Pt/C provide further evidence for this explanation.

The study of the effect of Nafion[®] loading in the catalyst layer was conducted for electrodes with 10, 20 and 30 wt.% Pt/C, for amounts of Nafion[®] ranging from 0.4 to 2.6 mg cm⁻². Fig. 3 presents the polarization results for the electrode with 10 wt.% Pt/C loaded with 1.3, 2.2 and 2.6 mg cm⁻², and Table I shows the corresponding kinetic parameters. In addition Fig. 4 presents some cyclic voltammograms obtained for these electrodes. From Table I it is observed that two regions of Tafel slopes are observed for the smaller Nafion[®] loadings, which is the typical behavior of the ORR on the Pt catalyst. On the other conditions the second linear region was not observed because it appears together with the diffusion limitations.

For Nafion^{\oplus} loadings below 1.75 mg cm⁻² a decrease in E^{\circ} and an increase in R are observed indicating a diminution of the active area and possibly an increase in lectrolyte

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resistance. Both phenomena are related to too small an amount of Nafion[®] impregnated into the electrode, which is insufficient to provide adequate electrolytic conductance inside the catalyst layer, leading to a low platinum utilization and high ohmic drop. In fact, with lower Nafion[®] loadings there is also the possibility for the gases to reach directly the membrane and then to cause a cross-over phenomenon, which may contribute to the decrease of E[°]. For the highest Nafion[®] loading (2.6 mg cm⁻²), the increase in R, compared with the value for the optimum condition, is possibly related to too large an amount of Nafion[®] blocking the gas penetration and leading to the appearance of linear diffusion components. In Fig. 3 it is seen that for the smaller Nafion[®] loadings and for high current densities (or for potentials well below 0.8 V) limiting currents are present. This is clearly related to the smaller active area under such conditions, as observed from the hydrogen adsorption/desorption charges in the cyclic voltammograms of Fig. 4.

Table I shows the effect the catalyst loading on the kinetic parameters for the electrode with 20 wt.% Pt/C containing proportional amounts of Nafion[®] in the catalyst layer. In the range 0.1 to 0.4 mgPt cm⁻², the effect of the catalyst loading on the anode was negligible. Regarding the oxygen electrode, several expected phenomena were observed as a function of the platinum loading: (i) the values of E^o show that the major effect of the decrease of the catalyst loading is a consistent diminution of the electrochemical active area, although for loadings above 0.2 mgPt cm⁻² the effect is not crucial for the fuel cell performance and (ii) the linear polarization terms are the same for loadings down to 0.2 mgPt cm⁻² but increase for 0.1 mg Pt cm⁻². This indicates the appearance of linear diffusion components, which is related to the decrease in the electrochemical active area.

Figs. 5 and 6 show the ORR polarization results and the cyclic voltammograms obtained for the electrodes with the Pt-V, Pt-Co and Pt-Cr (50-50 atom%) electrocatalysts loaded at 0.4 mg cm⁻² in the catalyst layer. Compared with pure platinum with the same load, all the alloy catalysts showed inferior performance for the single cell operation (Fig. 5). Because the values of b and R are essentially the same (Table I), these effects of the Pt-alloy catalysts can be only attributed to a diminution of the electrochemical active area, which is confirmed by the values of E° and the cyclic voltammograms of Fig. 6. However, it is important to note that the performances of the alloy electrodes are very much equivalent to those obtained for the electrochemical activity is completely indifferent to the presence of such metals. For Pt/Co, although the active area is smaller, the polarization curve is similar to that of pure Pt at low current densities which is an indication of a reasonable electrocatalytic activity. This has been also observed for phosphoric acid fuel cells (9).

Fig. 7 and Table I show the effect of the thickness of the membrane for the electrode with 15 % PTFE in the diffusion layer and 20 wt.% Pt/C, 0.1/0.3 (anode/cathode) mgPt cm^{-2} in the catalyst layer. Since the electrodes are the same in all cases, the dispersion in the values of E°, especially the high value obtained for the membrane with 125 μ m cannot

be attributed to a change in the active area, but must rather be related to an effect of impurities or to other experimental factors not considered in the formulation of equation (1). As expected, a decrease in the values of R with decreasing membrane thickness is observed. It should be recalled that the contributions for the linear polarization terms are related to a contribution of the resistance of the membrane added to the values arising from the polarization resistance of the hydrogen oxidation reaction and the linear diffusion resistance. Taking the resistivity of the membrane as 6.0 Ω cm at 80 °C (6) it is calculated that the contributions of the membrane resistance to the R values should be 0.03, 0.08, and 0.11 Ω cm² for the thicknesses of 50, 125 and 175 μ m, respectively. Comparing the above values with those presented in Table I, it is observed that the sum of the linear diffusion component with the HOR polarization is ca. 0.1 Ω cm² for the two thinner membranes. The same calculation made for the 175 µm membrane gave inconsistent results, denoting that the membrane resistance, obtained under conditions of fuel cell operation, is not linear with the thickness. This probably arises as a consequence of a non uniform water distribution due to proton dragging and back diffusion (6), which is more severe for the thicker membrane.

Figure 8 and Table I present the effect of temperature on the fuel cell behavior and on the kinetic parameters obtained with the electrode with 15 % of PTFE in the diffusion layer, and 20 wt.% Pt/C, 0.1 mgPt cm^{-2} , in the catalyst layer. The only significant effect is a decrease of the values of R with increasing temperature due to the decrease of the membrane resistance. Also, Fig. 8 shows an increase in limiting current with increasing temperature indicating that diffusion problems are less important. This is associated to a decrease of the flooding of the catalyst layer by liquid water, especially in the oxygen electrode (3).

The effect of the partial pressure of oxygen at 80 °C is presented in Figure 8 and Table I for the electrode with 20 wt.% Pt/C, 0.1 mgPt cm⁻² in the catalyst layer and with a diffusion layer with 15% PTFE and 50 μ m thickness. The increase in E° observed in Table I for increasing gas pressure is a consequence of the increase of the reversible potential of the fuel cell reactions (as predicted by the Nernst equation) combined with an increase of the exchange current density of the oxygen reduction reaction (i_o) due to the increase of the gas solubility. Finally, the values of R indicate the presence of linear diffusion component only at the smaller partial pressures. Fig. 8 shows that the observed limiting current densities are not directly proportional to the oxygen pressure. It thus appears that the experimental polarization responses are in contradiction to Henry's law, which may be associated to the appearance of a flooding problem by liquid water, introduced in the gas channels in the catalyst or diffusion layers, which is more crucial when the gas is supplied at higher pressures.

CONCLUSION

The best performance with the locally developed electrodes was obtained with 30 wt.% Pt/C, 0.4 mgPt cm⁻² and 0.7 mg Nafion[®] cm⁻² in the catalyst layer and 15% PTFE and 50 μ m thickness in the diffusion layer, for both the cathode and the anode (Fig. 3). However, it was also observed that the platinum requirement can be diminished to values close to 0.2 mgPt cm⁻² in the cathode and 0.1 mgPt cm⁻² in the anode, without significant loss of the characteristics.

Regarding the theoretical interpretation of the cell characteristics two main observations can be made: (i) the Tafel slopes for the ORR are all close to 70 mV dec⁻¹, for potentials above 0.8 V. In some cases a second Tafel slope of ca. 120 mV dec⁻¹ is found for potentials below 0.8 V. Within this picture the Pt/C catalysts show a behavior with respect to the ORR equivalent to a smooth Pt surface; (ii) most of the electrodic systems present limiting currents and some of them also show linear diffusion components arising from diffusion limitations in the gas channels and/or in the thin film of electrodyte covering the catalyst particles. These are the only structural parameters of the electrode which affect the polarization behavior.

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ELECTRODE	E°/V	b / V dec ⁻¹	$R / \Omega cm^2$
Thickness of diffusion layer $(\mu m)^{(a)}$			
15	0.959	0.083	0.34
25	0.959	0.082	0.30
35	0.958	0.076	0.27
50	0.957	0.076	0.30
65	0.962	0.078	0.35
% PTFE in the diffusion layer(b)			
10	0.962	0.072	0.26
20	0.976	0.073	0.28
30	0.964	0.076	0.29
40	0.966	0.076	0.29
50	0.967	0.076	0.29
Pt/C weight ratio (%)(c)			
10	0.958	0.076	0.30
20	0,965	0.075	0.28
30	0.963	0.071	0.30
40	0.960	0.078	0.30
60	0.915	0.072	0.39
80	-	(0.116)	0.66
Nation [®] loading (mg cm ⁻²) ^(d)			
0.87	0.861	0.078 (0.126)	0.89
1.33	0.900	0.078 (0.121)	0.38
1.75	0.953	0.075	0.34
2.20	0.958	0.076	0.30
2.60	0.957	0.068	0.38
Pt loading (mgPt cm ⁻²); anode/cathode(e)			
0.1/0.1	0.914	0.068	0.35
0,1/0.2	0.949	0.071	0.27
0.1/0.3	0.960	0.067	0.27
0.1/0.4	0.968	0.067	0.28
0.4/0.4	0.970	0.065	0.29
Alloy catalyst $^{(f)}$			
Pt-Co	0.973	0.072	0.33
Pt-Cr	0.947	0.073	0.32
Pt-V	0.933	0.073	0.33

Table I - Kinetic parameters obtained from the fitting of equation (1) to the experimental polarization results for the different electrodes and experimental conditions. The values of b between parenthesis were obtained at potentials below 0.8 V. Except when mentioned, the conditions were: 0.4 mgPt cm², H₂/O₂ 1/1 atm, T = 80 °C, Nafion[®] 117 membrane.

Table I - cont

Membrane thickness (µm)(g)			
50	0.945	0.064	0.13
125	0.964	0.065	0.19
175	0.957	0.065	0.29
Temperature of operation (oC) ^(h)			
50	0.913	0.085	0.66
60	0.918	0.078	0.51
70	0.916	0.073	0.39
80	0.914	0.068	0.35
Hydrogen/Oxygen (partial) pressure (h))		
1/0.2	0.900	0.072	0.50
2/0.6	0.929	0.071	0.43
1/1	0.914	0.068	0.35
2/5	0.963	0.070	0.30

(a) electrodes with 10 wt.% Pt/C, 2.2 mg cm⁻² of Nafion[®] in the catalyst layer and 40 % PTFE in the diffusion layer.

(b) electrodes with 20 wt.% Pt/C, 1.1 mg cm⁻² of Nafion[®] in the catalyst layer and 35 μm for the thickness of the diffusion layer.

(c) electrodes with 2.2, 1.1, 0.73, 0.55, 0.37, and 0.28 mg cm⁻² of Nafion[®] in the catalyst layer, respectively. Diffusion layers with 40% PTFE and 35 μm thickness.

(d) electrodes with 10 wt. % Pt/C, 40 % PTFE in the diffusion layer with a thickness of 35 μm.

(e) electrodes with 20 wt% Pt/C and proportional amounts of Nafion[®] in the catalyst layer taking as reference 1.1 mg Nafion[®] cm⁻² for the 0.4 mgPt cm⁻² electrode. Diffusion layer with 15% PTFE and 50 μm thickness.

(f) electrodes with 0.4 mgPt-alloy cm⁻². Electrodes with 20 wt.% Pt-alloy/C in the catalyst layer. Diffusion layer with 15% PTFE and 50 μm thickness.

(g) electrodes with 20 wt.% Pt/C, 0.1/0.3 mgPt cm⁻² (anode/cathode). Diffusion Layer with 15 % PTFE and 50 μm.

(h) electrodes with 20 wt.⁹ Pt/C 0.1 mgPt cm⁻² (cathode and anode). Diffusion Layer with 15 % PTFE and 50 μm.

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Fig. 1 - Cell potential-current density plots for H_2/O_2 1 atm PEFC single cells at 80 °C for the 10 wt.% Pt/C, 0.4 mgPt cm⁻², 2.2 mg Nafion[®] cm⁻² electrodes with several thicknesses of the diffusion layer (40 % PTFE): (+) 15; (o) 35; (Δ) 65 µm. Hydrogen humidifier at 95 °C; oxygen humidifier at 85 °C. Nafion[®] 117 membrane.



Fig. 2 - Cell potential-current density plots for H_2/O_2 1 atm PEFC single cells at 80 °C for the 20 wt.% Pt/C, 0.4 mgPt cm⁻², and 1.1 mg Nafion[®] cm⁻² electrodes with several PTFE contents in the diffusion layer: (+) 10, (O) 30 and (Δ) 50 % PTFE. Diffusion layer with 35µm thickness. Hydrogen humidifier at 95 °C; oxygen humidifier at 85 °C. Nafion[®] 117 membrane.



Fig. 3 - Cell potential-current density plots for $H_2/O_2 1$ atm PEFC single cells at 80 °C for the electrodes prepared with several Pt/C (wt.%) - Nafion loading (mg cm⁻²): Diffusion layer with 40% PTFE and 35 µm thickness: (\Box) 10 - 1.3; (∇) 10 - 2.2; (O) 10 - 2.6; (Δ) 60 - 0.4. Diffusion layer with 15% PTFE and 50 µm thickness: (+) 20 - 1.1; (\diamond) 30 - 0.7. Hydrogen/oxygen humidifiers at 95/85 °C;. Nafion[®] 117 membrane.



Fig. 4 - Cyclic voltammetry obtained at 25 °C for the electrodes with 10 wt.% Pt/C, 0.4 mgPt cm⁻², and several Nafion[®] loadings in the catalyst layers: (a) 1.3; (b) 2.2; and (c) 2.6 mg cm⁻². v = 50 mV s⁻¹. Diffusion layer with 15% PTFE and 50 μ m thickness. Nafion[®] 117 membrane.



Fig. 5 - Cell potential-current density plots for H_2/O_2 1 atm PEFC single cells at 80 °C for the 20 wt.% Pt-alloy/C for the several alloy catalysts with optimized Nafion loadings: (\Box) Pt; (∇) Pt-V; (Δ) Pt-Co, (O) Pt-Cr. Diffusion layer with 50 μ m and 15% PTFE. Hydrogen humidifier at 95 °C; oxygen humidifier at 85 °C. Nafion[®] 117 membrane.



Fig. 6 - Cyclic voltammetries obtained at 25 °C for the electrodes with the different alloys loaded to the catalyst layers: (a) Pt/C; (b) Pt-Co/C; (c) Pt-V/C and (d) Pt-Cr/C. v = 50 mV s⁻¹. Nafion[®] 117 membrane.



Fig. 7 - Cell potential-current density plots for H_2/O_2 1 atm PEFC single cells at 80 °C for the 20 wt.% Pt/C, hot-pressed to Nafion[®] membranes with several thicknesses: (□) Nafion[®] 112 (50 µm); (o) Nafion[®] 115 (124 µm) and (Δ) Nafion[®] 117 (175 µm). Electrodes with 0.1/0.3 mgPt cm⁻² (anode/cathode) and proportinonal amounts of Nafion[®] taking as reference 1.1 mg cm⁻² for 0.4 mgPt cm⁻². Diffusion layer with 15 % PTFE and 50 µm thickness. Hydrogen humidifier at 95 °C; oxygen humidifier at 85 °C. Nafion 117 membrane.



Fig. 8 - Cell potential- current density plots for PEFC single cells at 80 °C for the 20 wt.% Pt/C, 0.1 mg Pt cm⁻² at several cell temperatures and gas pressures (H_2/O_2) : (\Box) 50 °C, 1/1 atm; (o) 80 °C, 1/1 atm; (Δ) 80 °C, 2/5 atm and (∇) 80 °C, 1/0.2 atm. Diffusion layer with 15 % PTFE and 50 μ m thickness. Nafion 117 membrane.

ALTERNATIVE FLOW-FIELD AND BACKING CONCEPTS FOR POLYMER ELECTROLYTE FUEL CELLS

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New concepts for potentially low cost flow-field and electrode backing components for polymer electrolyte fuel cells are investigated. The primary motivation for the new configurations is to enhance cell performance on air by minimizing the oxygen diffusion barrier. This is accomplished with the use of porous flow-fields and unusually thin backings.

INTRODUCTION

Current flow-field technology for polymer electrolyte fuel cells (PEFCs) typically consists of grooved, serpentine flow-fields through which the gaseous reactants flow. A cross-section schematic is shown in Figure 1a. In order to bridge the open faced channels of the flow-field, a relatively rigid structure is required to facilitate the transition from the flow-channel to the catalyst layer, while ensuring gas transport uninhibited by excessive liquid water. This component is frequently described as the gas diffusion layer and will be referred to here as the backing. In an air electrode, the oxygen must diffuse through the backing in order to reach the catalyst layer. As the current density of the fuel cell is increased, this diffusion barrier lowers the effective concentration of oxygen at the catalyst layer and the performance of the electrode suffers. If the ribs in the flow-field are themselves non-porous, then the reactants must also diffuse laterally through the backing to reach the catalyst in the regions centered over the rib. It can be appreciated that two strategies can be implemented that would minimize the diffusion pathway. The first is to use much narrower ribs in the flow-field, which essentially suggests the use of a macroporous network for the flow-field, and the second is to minimize the thickness of the gas diffusion layer so the barrier to oxygen diffusion is minimized. The combination of the two concepts is shown in Figure 1c. Another possibly useful configuration is basically a compromise of the two and it is shown in Figure 1b. We describe here our recent efforts to implement the use of thin backings and/or macroporous materials in these two configurations.

Cost is another motivation for exploring alternative flow-field and backing components. Currently, fuel cell gas diffusion structures are made by hand in small quantities at relatively high costs. While automation would decrease the cost, the use of carbon papers or cloths in the structures will always add a component of complexity to the process. On the other hand, substantial quantities of thin, carbon black/polymer composite films are manufactured very cheaply for a large variety of uses by a number of companies on automated machinery. It should be only a matter of optimizing the components and processes to potentially attain very inexpensive, mass produced, backing materials based on such composite films.

The conventional technology for fuel cells consists of (machined) graphite bipolar plates. Efforts are being made to replace this expensive component with lower cost, more easily formed materials such as Kynar/carbon black composites which can be molded directly into the shape of a bipolar plate, given a suitable design. Unfortunately, this last material is, like graphite, relatively brittle and a certain amount of breakage may occur, especially in the case of thin unit cells. Perhaps some of these difficulties could be alleviated with the use of macroporous flow-field materials that are relatively durable and low cost and would not require extensive machining. It should be mentioned that metal hardware is attracting greater attention and some of our efforts in this regard are discussed elsewhere in this volume.¹

THIN BACKINGS

Conventional PEFC backings

The hardware and electrode structures discussed here are primarily relevant for catalyzed ionomeric membranes, such as those we describe as "thin-film" catalyzed membranes.² These are low platinum loading (typically 0.12 to 0.18 mg Pt/cm² or even less at the anode) 5 - 7 μ m thick catalyst layers formed by the application of a catalyst/ionomer solution "ink" to the membrane. Catalysts are 20 wt% Pt on Vulcan XC-72 from E-TEK (Natick, MA). With these catalyst layers, the backing materials used are microporous, hydrophobic, electronically conducting structures similar to "gas-diffusion" electrodes, except that they are uncatalyzed. Our conventional backing material is ELAT from E-TEK which is effectively a carbon black/PTFE impregnated carbon-cloth approximately 350 - 450 μ m thick. Other commercially available gas diffusion-type structures are based on carbon paper instead of carbon cloth, but we typically obtain better performance with the latter. The role of our backings is to a certain extent analogous to that of the PTFE/carbon paper^{3,4,5} typically used to back wet-proofed PTFE/Pt-black electrodes such as those originally developed by GE for PEFCs. Both types of backings supply electronic contact and gas access to the respective catalyst layers. However, in the case of the hydrophilic (non-PTFE) thin-film catalyst layers,² the backings serve the important additional function of a microporous water barrier. If a macroporous (ca. 30 µm pore size) PTFE/carbon paper backing is used in conjunction with the thin-film electrodes, a "flooding" situation quickly occurs. Some results and possible explanations for the dissimilar thin film and PTFE/Pt-black backing requirements are provided in Ref. 6. In any case, the need of a backing structure significantly affects the transport losses in fuel cells operating on air.⁷ We are interested in minimizing these losses in order to maximize fuel cell performance on air, possibly at lower pressures.

Porosity and tortuosity: possible backing performance enhancement

Modeling of fuel cell performance is useful to understand the limitations of the conventional backings and to predict what performance enhancements are possible. The most relevant parameters are the porosity and the tortuosity. A rough estimate of the porosity, ε , of the conventional backing using the material density and eventual geometry provides a value of about 0.4. The Carman tortuosity factor, τ , is defined as the square of the ratio between effective tortuous gas path length and backing thickness, and can be derived from ac impedance measurements. The low frequency loop in the ac impedance of an air electrode results from the dynamic lag of the oxygen partial pressure in the cathode catalyst layer with respect to changes in current density. The characteristic frequency, ω_B ,

of the backing can be measured as the frequency of the maximum imaginary component for this spectral feature, and can be shown⁸ to be equal to:

$$\omega_B = \frac{D_{ON}}{\tau \ \ell_B^2} \quad , \tag{1}$$

where D_{ON} is the O₂-N₂ binary diffusion coefficient and ℓ_B is the effective backing thickness (with geometry taken into account⁸).

Because the backing portion of the impedance spectrum is well separated from the higher frequency loop determined by kinetic and ionic resistance and condensed phase diffusion effects, the estimate of backing layer tortuosity is not dependent on estimates of these latter parameters.⁸ Rather, the tortuosity estimate is only dependent on D_{ON} and the gross geometry of the backing. In this manner, we determine the tortuosity factor of the E-TEK backing structure from ac impedance spectra to have a value of around 7. The diffusion pathway is then $\tau^{1/2}$, or about 2.6 times as great as the backing thickness. While this is a relatively high value, one might expect significant tortuosity from the microporous backing as it primarily consists of a hot-pressed and sintered mixture of relatively high surface area carbon black and colloidal PTFE solution. Many of the gas passages formed are likely to be dead-ended, bottle-necked, or severely convoluted.

With knowledge of the porosity and the tortuosity, it is now possible to predict what sorts of effects much thinner backing layer structures could potentially have on cell performance. Figure 2 is a simulation of the increase in performance that could be obtained if a conventional backing with a 300 μ m effective thickness is replaced by one only one tenth as thick. Both of the thicknesses are for uniform reactant access across the backside of the backings, so the effects would be somewhat different for channeled flow-fields. As can be seen, the mass transport limitations are significantly less with the thinner backing resulting in higher limiting current densities. Even in the maximum power region (about 0.5 V), significant improvement is evident. Other factors that are not addressed in this figure are possible improvements in performance that might occur with the thinner backing when the cells are operated at low pressure, or relatively close to stoichiometric flow, or if the reactant distribution is not perfectly uniform throughout the cell. A caveat to the performance improvements promised by Figure 2 is that it assumes that the properties of the conventional backings will be replicated on the much thinner scale.

Bilayer backings used with conventional flow-fields

The use of thin backings with conventional, serpentine channel flow-fields is problematic because the thin materials do not have the structural integrity or rigidity to span our 0.8 mm wide channels. In addition, the gas permeation to those areas of the backing covered by the ribs will be severely limited by the narrow diffusion path through the thin backing material. A compromise that partially provides the benefits of a microporous structure and sufficient structural integrity to span the ribs is to combine a thin microporous backing layer with a thicker, more rigid, macroporous structure to form a bilayer backing. A cross-section schematic of this configuration is shown in Figure 1b. The structural component will unfortunately add thickness to the structure, but the value of its tortuosity factor should be close to unity, so a 300 μ m thick open layer should effectively present a gas transport barrier similar to that of a 100 μ m thick microporous structure. However, this simple picture is not a completely accurate portrayal of the conditions in the operating fuel cell. The above model and simulations do not account for effects of liquid water

permeation through and accumulation in the backings. We have reason to believe that the primary difficulty in the bilayer backing occurs at the interface between the micro- and macroporous structures. Water that has squeezed through the microporous structure may tend to accumulate at the interface in the much larger pores. The hydrophobic/hydrophilic nature of the macroporous support material may then be expected to affect the accumulation of the water.

In Figure 3 are shown polarization curves for test cells with bilayer backings on the cathode side that consist of thin microporous films combined with 250 µm thick Spectracarb 2050 (Spectracorp, Lawrence, MA) carbon paper. In one case, the carbon paper is hydrophobized with FEP120 (DuPont) and the other one is hydrophilized with 2% diluted Nafion[™] solution (Nafion is a product of DuPont, 5% Nafion solution is from Solution Technology, Mendenhall, PA). Both cells are run under identical humidification conditions of anode/cathode humidifier temperatures of 105/70°C. The limiting current density of the cell with the hydrophilic backing support is somewhat greater than that of the hvdrophobic support, whose rapid voltage decay suggests a "flooding" condition. We suggest that the "flooding" is primarily attributable to water trapped at the bilayer interface, and is thus corrected to a certain extent when the macroporous support is hydrophilic. This conjecture is further supported by the observation that the limiting current densities for both cells increase and are similar when the cells are poorly humidified. However, the lower current density performances are sufficiently erratic and poor with low humidification that such conditions are not desirable for normal cell operation. Optimization of the components of such bilayer backings may provide an attractive alternative to conventional backings from the aspects of reproducibility, performance and cost. Nevertheless, in order to obtain the minimal transport-loss suggested by the simulation in Figure 2, a support/flow-field structure is required that eliminates the diffusion barrier due to the structural component, which suggests the use of porous flow-fields.

POROUS FLOW-FIELDS

Damiano⁹ introduced the use of porous flow-fields in place of ribbed flow-fields in phosphoric acid fuel cells. Relatively thick layers of fibrous carbon paper or bonded particles are incorporated into the design of the gas-diffusion electrodes conventionally used in phosphoric acid fuel cells. The thicker carbon paper component serves as the flow-field because the reactants are forced to flow laterally through this component, not unlike Figure 1c. There is no remaining need for a machined serpentine flow-field. In this way, the strategies listed above for minimizing the reactant diffusion pathway are realized for phosphoric acid fuel cells.

For our macroporous flow-field structures, we typically use resin bonded carbon papers such as provided by Toray (Japan) or Spectracorp. These are roughly 70% porosity, 30 µm mean pore diameter fiber boards of various available thicknesses that can withstand as much as 20 atm of compression without crushing. Possible other "porous" flow-field structures may consist of carbon or metal foams or sintered particles. Although not discussed here, we have also experimented with woven metal screens,¹ based on work done at Sandia Livermore and elsewhere.¹⁰

One of the difficulties with macroporous flow-fields is the inherently high pressure drop that is generated when appreciable amounts of gas are forced through relatively thin and long porous flow-fields with pores only about 30 μ m in diameter. To this point, the

solution has been to use thick porous flow-fields.⁹ There are a couple of drawbacks to this approach. First, the use of thicker flow-fields results in thicker unit cells and hence lower stack power densities. Furthermore, the gas flows more readily channel, especially in the case of PEFCs where water may accumulate and block off regions. Lastly, the high current density region is concentrated along the edge where the reactant stream enters the cell. Since the majority of heat is generated in this region, cooling a stack becomes more problematic and the high current density regions tend to flood.

Radial porous flow-fields

As mentioned above, one of the difficulties with porous flow-fields is that the pressure drop incurred from forcing the gas reactants through relatively small pores (about 30 μ m diameter) of the flow-field is considerably greater than through grooved channels. Another difficulty with using macroporous flow-fields in single cell hardware is in providing the manifolding that allows the reactants to be channeled through the structure without short-circuiting around the periphery of the flow field.

We circumvented both of these difficulties in early experimentation by using a radial flow geometry, in which inner and outer rings are machined into the standard graphite blocks and reactant flow is passed between the rings through a circular porous flow-field. The scheme is shown in Figure 4. Because the gases must flow through the overlying flow-field to reach the other ring, no short-circuiting around the flow-field is possible and the only gasketing required is around the periphery of the flow field. Pressure drops are also relatively low because of the relatively short distance through which the flow must traverse. Further advantages of the radial flow scheme are that the electrode region subjected to the "fresh" (oxygen rich) air is distributed around the periphery, and hence the regions of higher current density and water production are also widely distributed. In the case of the square flow-field mentioned above, the high current production would only be along the front edge, leading to excessive heat build up and/or flooding in this area. Unfortunately, the radial flow-field design is not very amenable to stacks, because manifold penetrations are needed that run up through the center axis, and also the low pressure drop is obtained only up to a certain size. The design has some utility for portable, low-power, ambient-pressure, fuel cell stacks.¹¹

Flow-field pressure tests

The primary factors in flow-field design are uniformity of reactant flow and magnitude of cell pressure drop. A trade-off occurs with the latter in that the uniformity of the reactant flow in a two-phase flow system is often improved in designs with a high pressure drop. In addition, an even flow distribution across many parallel cells in a stack is more readily attained with higher cell pressure drops. However, high pressure drops are undesirable because of the increase in compression costs and correspondingly lower system efficiency.

In order to quantify the level of the pressure drop and to visualize the dynamics of the accumulation of water in the macroporous flow-fields, a test rig was fabricated. The rig consisted of Plexiglas plates into which manifolds for a 50 cm^2 cell were machined. Air flows equivalent to 2 times stoichiometric flow at a current density of 1 A/cm² were fed to the rig for various thicknesses and types of flow-field material. A back pressure regulator was used to maintain the down stream pressure at 3 atm (30 psig). The air feed was sparged through a humidifier bottle upstream of the test rig and heated to 70° C in order to simulate the two-phase (gas/water) flow often encountered in actual cell

conditions. Immersion of the rig in a room temperature bath resulted in substantial condensation of the humidified stream in the rig. The behavior of the two-phase system could be visually monitored through the clear Plexiglas plates. The pressure drop across the cell was measured using a Magnehelix differential pressure gauge.

The pressure drop over a 1.5 mm (60 mil) thick Spectracarb 2050 flow-field using the humidified feed was on the order of about 0.06 atm (1 psi) as shown in Figure 5. When the flow-field was suddenly subjected to slugs of water that tended to collect in the inlet plenum, the pressure drop might momentarily spike several times higher. One of the apparent difficulties with the relatively thick flow-field was that water would collect in various areas and force the reactant flow to channel, typically down one side. One possibility we explored to alleviate this difficulty was to use thinner flow-fields. Not only would these increase the flow shear force to prevent water accumulation, but a thinner unit cell could be realized. With the use of a 0.25 mm (10 mil) thick flow-field of the standard Spectracarb 2050 material, the amount of channeling decreased, but was not eliminated, and the corresponding pressure drops increased to about 0.34 atm (5 psi), as is shown in Figure 5. Pressure drops should probably be somewhat less than 0.1 atm in practical systems to minimize compression losses. On the other hand, higher cell pressure drops simplify balancing the flows over many cells in a stack.

Hydrophilic flow-fields

We realized when we first started work on porous flow-fields that water accumulation would be a difficulty, as was evident in the channeling we saw in the Plexiglas test rig. One approach to minimize water clogging areas of the flow-field was to hydrophilize the flow-field material in order to wick water away before it could accumulate. The hydrophilization process used for pressure drop testing was to polymerize either aniline or pyrrole in situ on the flow-field material. In some formulations, the polyaniline (PANI) rendered the flow-fields quite hydrophilic and these could withstand several hours of boiling in water with no weight loss or loss of hydrophilicity. When hydrophilized flow-fields were examined in the test rig, the amount of water accumulation was substantially suppressed and, most interestingly, the pressure drops across test cells would also decrease, by about 10% to as much as 40% for some material/thickness combinations (some of the data are shown in Figure 5). Conceivably, the addition of the hydrophilizing material allowed the water to move through the finer, wicking component of the structure without accumulating and blocking the flow-channels. Because the polymerization process was not highly reproducible, we eventually resorted to hydrophilizing the flow-fields by dipping the material in 2% Nation solution as mentioned in an earlier section. Flow-fields treated with the Nafion solution are interesting in that they are not "instantaneously" hydrophilic as are the polyaniline or pyrrole structures. However, when in the presence of water for some time, they eventually attain a hydrophilic state. This may possibly be beneficial in that the flow-field structure may initially resist trapping water, but if it does, it eventually wicks it away.

Interdigitated macroporous flow-fields

A possible solution to lowering the high pressure drops is to combine the macroporous flow-field with channels in such a manner as to provide the optimal compromise of the two flow-field configurations. This can be achieved by using interdigitated channels to deliver the reactant gases throughout the macroporous flow-field structure, which overlays the channeled substrate. The general scheme is depicted in Figure 6. The channels are formed as a series of interdigitated fingers, with one set of

fingers supplying the reactants and the second set removing the exhausted gas. In order to get from one set of fingers to the other, the reactants must pass through the macroporous flow-field, thus achieving the advantages provided by such structures. One can readily appreciate that the pressure drop can be decreased substantially, and that much larger active areas can be accommodated with only minimal pressure drop increases.

Figure 5 also shows the decrease in pressure drop achieved with interdigitated (ID) channels. The experimental conditions were the same as described previously. The distances used between the interdigitated fingers for the 0.25 mm thick porous flow-fields were 3, 5, and 10 mm. The interdigitated channels were machined into an underlying plate and were 0.8 mm wide and deep. In the thicker porous flow-fields, the interdigitated channels can be machined directly into the relatively thick porous flow-field. This configuration may have cost and simplicity advantages in practical cells. As can be seen, merely introducing the interdigitated channels lowered the pressure drops by at least an order of magnitude. Decreasing the finger separation from 10 to 3 mm further lowered the pressure drop about a factor of two. When viewed in the clear Plexiglas test rig, the flow appeared to be uniform, although the visual test is not the best indication of uniform reactant distribution. Curiously, the pressure drops increased in the two cases in Figure 5 where the macroporous material was hydrophilized with PANI. If no channeling was occurring in the non-coated cases, then hydrophilizing the flow-fields may only serve to increase the water uptake and effectively decrease the porosity. Figure 5 shows that in the case of the 1.5 mm thick porous flow-field, the introduction of interdigitated channels decreased the pressure drop to a very low value.

There may be other possible advantages to interdigitated flow-field schemes. For example, from the perspective of stack design, it would be desirable to achieve uniform current densities throughout the active area. This is not easily accomplished because the region around the reactant inlet will provide the highest current densities. In the interdigitated scheme, the high and low current density regions are centered on the widely distributed feed and effluent fingers, respectively. This may help to alleviate large variations in the temperature and water content distributions.

Interdigitated flow-fields with thin backings

In addition to the transport improvement attained by the elimination of the nonporous ribs of serpentine flow-fields, porous flow-fields have the additional advantage of supporting the backing material across its entire surface as is shown in Figure 1c. While this has advantages with conventional gas diffusion backings by providing uniform pressure against the membrane/electrode assembly, Figure 1c demonstrates that it becomes possible to support a very thin backing.

A 10 cm² cell with a 0.25 mm thick hydrophilic porous flow-field overlying interdigitated channels and a 25 μ m thick hydrophobic gas diffusion backing was tested with a thin-film catalyzed developmental Dow membrane. In Figure 7, this cell is compared to a 5 cm² cell with standard backings (effectively about 300 μ m thick) and serpentine flow-fields. All other conditions are similar (approximately 0.13 mg Pt/cm² thin film catalyst layers on developmental. Dow membrane, etc.) As can be seen, the limiting current density with the thinner backing is substantially greater. If the curves are iR corrected (Figure 8), the low current density performances of the two are roughly equal, and the thinner backing gains a substantial advantage in the important mid-range area. The lower current density performance in this cell was not particularly good because the cell with the thinner backing tended to dry out. This difficulty is hopefully due to the backing

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material properties, and not to its thinness. This belief is somewhat supported by results obtained when as-received thin backings of this type are treated in a number of ways before use.

CONCLUSION

The use of catalyzed membranes separates the functions of catalyst layer and backing and thus permits a greater degree of flexibility in backing and flow-field components. One possibility discussed here is the use of unusually thin backings which promise increased reactant transport in air electrodes and, hence, higher performances. While yet further development of the thin backing materials is required for optimal performance, substantially higher limiting current densities are demonstrated. When thin backings are used in a bilayer configuration in combination with a more open, structural component, performances of conventional backings are attained with materials that are machine made and very inexpensive compared to conventional gas-diffusion-type backings.

The thin backings should, however, provide optimal performance when used with macroporous flow-field structures so as to minimize the diffusion barrier. While porous flow-fields provide uniform support and reactant access across the backing, the use of such materials often result in uncomfortably high pressure drops and poor reactant flow distributions. One solution, described here, is to use interdigitated channels in conjunction with the porous flow-field to lower pressure drop and improve the reactant distribution. Channels formed in the macroporous material would eliminate the need for machined graphite bipolar plates. Hence, macroporous flow-fields may cost advantages in addition to possible performance advantages.

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FIGURES



Figure 1. Cross-section schematics depicting a) conventional flow-field with gas-diffusion style backing, b) conventional flow-field with a bilayer (micro- and macroporous) backing, and c) macroporous flow-field supporting a thin microporous backing.



Figure 2. Simulations depicting the increase in performance that might be expected if the effectively 300 μ m thick conventional backing is replaced with one one-tenth as thick with similar properties. Simulation conditions: H₂/air = 3/5 atm, T_{cell}= 80°C.

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Figure 3. Bilayer backing configuration with conventional, serpentine flow-fields. Cell conditions: 5 cm^2 , H₂/Air = 3/5 atm, T_{cell} = 80°C, 0.18 mg Pt/cm² thin film catalyst layers on a developmental. Dow membrane.



Figure 4. Single cell radial flow hardware for experimentation of porous flow-fields. Configuration provides low pressure drop and simplified sealing.



Figure 5. Pressure drops over 50 cm² macroporous flow-fields with no channels (NC) or interdigitated channels (ID). "t" = macroporous material thickness, "w" = spacing between channels. Polyaniline (PANI) renders the flow-fields hydrophilic.



Figure 6. A schematic for a reactant flow-field scheme that combines the use of interdigitated flow-channels with an overlying macroporous flow-field structure.

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Figure 7. Experimental comparison of cells with conventional and with thin backings. The respective hardware are 5 cm^2 , serpentine flow-fields and 10 cm^2 , interdigitated porous flow-fields.



Figure 8. iR corrected polarization curves of the cells described in Figure 7.

DESIGN OF FLOWFIELDS FOR FUEL CELLS

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A flowfield design applicable to Proton Exchange Membrane(PEM) fuel cells was modeled. The effect of various geometrical design parameters on the gas distribution and the flowfield pressure drop for a circular electrode was studied. Local flooding in the electrode was simulated to study its effect on the gas distribution.

INTRODUCTION

The average performance of a cell in a fuel cell stack is usually poor compared to that of a single cell. One main reason for this is the inter cell flow variations. These variations can be mitigated by allowing a large pressure drop between the inlet and outlet manifolds. This approach is expensive since it involves a cost penalty for the turbo-charger used in the post processing. It is economical if the fuel cell operates under flowfield pressure-drop control that essentially involves much smaller pressure drops for the reactant gases.

An understanding of the flow behavior in a single cell is required in order to predict the inter cell flow variations in a stack. The flowfield should ideally offer a low pressure drop for gas flow, must offer a uniform distribution of the gas for a wide operating range and should not generate large pressure gradients or highly skewed reactant distribution upon local flooding. The design variables in this case are the flowfield pattern design (a discrete parameter), depth of grooves, inlet and outlet port design for the flowfield.

In this study a circular flowfield with a rectilinear network pattern of grooves and channels is modeled. The flowfield geometry is given in figure 1. In our nomenclature, the flow channels/grooves parallel to the fluid flow are termed *grooves* and those perpendicular to the flow are *channels*. The main design variables are the channel and groove widths (H and V respectively) and the depth of these grooves/channels (DP). The material between the grooves and channels constitutes an obstruction to the flow and their sizes or effective projected areas are fixed by the strength of the flowfield material and the sealing load provided through the endplates.

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ANALYSIS

The flowfield is circular and of diameter 7". The gas stream is assumed to be humidified air at 180 F. The total flowrate of air is calculated based on the specified oxygen utilization for a current density of 1000ASF. The temperature is assumed to be constant across the horizontal plane of the electrode. The gas flow is treated as steady-state incompressible fluid flow. Thus, the density variations due to the temperature and pressure effects are neglected. This is reasonable if the pressure variations are not high. The expansion and contraction effects are not included in the analysis. For low Reynolds number flows, as in our case, the skin friction is much greater than these effects [1] and therefore they may be neglected. The validity of the above assumptions need to be verified by comparing the model results with experimental data.

The consumption of oxygen is assumed to be uniform across the electrode in thus the current density variations are neglected. This is not strictly correct. The introduction of the non-uniform current density distribution highly complicates the problem. This is because current is limited by the membrane resistance and cathode overpotential that are not directly dependent on the oxygen partial pressure. Including the non-uniform current density variation in the analysis requires the governing equations for the whole cell to be solved in three dimensions. Since this is just an exploratory study for a single flowfield pattern design i.e., a rectilinear network of grooves, such an analysis is not warranted.

Considering the groove or channel as a pipe of rectangular cross-section the relation between the pressure difference and the flowrate is given below [2].

$$q = \frac{4ba^3}{3\mu} \cdot \frac{-\Delta h}{\Delta x} \cdot \left[1 - \frac{192a}{\pi^5 b} \sum_{i=1,3,5,\dots} \frac{\tanh(\frac{i\pi b}{2a})}{i^5}\right]$$
[1]

Here 2a is the width and 2b the depth of the groove or channel. The equivalent diameter approach is not used here as this introduces large errors when the flow is laminar.

The mass conservation equation at the node (i, j) is given by,

$$-ql_{ij} - q2_{ij} + ql_{i+1j} + q2_{ij+1} + Q_{ij} = 0$$
[2]

:-1

Referring to figure 2, $q l_{ij}$ is the flowrate of the gas from the node (i-1, j) to (i, j) in the direction parallel to the gas flow. Similarly $q l_{i+1j}$ denotes the flowrate of the gas from the node (i, j) to (i+1, j). It could be seen that q1 is in the direction of the flow of the gas through the cell i.e., flow through the *grooves* and q2 is in a direction perpendicular to it i.e., flow in the *channels*. Q_{ij} is the consumption of the gas at the node (i, j) and is taken as positive by

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convention. The boundary conditions are specified by the $Q_{i,j}$ which is fixed for the inlet and outlet nodes. All the flow rates are in cu. ins /s. The water produced by the oxygen reduction is assumed to be in the vapor form. The inlet flow is Q cu .ins/s and the outlet flow is specified by the oxygen utilization.

The flowrate pressure difference relation is written in the form as given below to eliminate the flowrates from the conservation equation.

$$ql_{ij} = kl_{ij} (h_{i-1j} - h_{ij})$$
 [3a]

$$q_{ij} = k_{ij} (h_{ij-1} - h_{ij})$$
 [3b]

where $h_{i,j}$ is the gas pressure at the node (i, j). The proportionality constants $kl_{i,j}$ and $k2_{i,j}$ are found using equation [1] and is as given below.

$$kl_{ij} = \frac{ql_{ij}}{-\Delta h}$$
 [4]

The mass conservation equation is written in terms of the pressures $(h_{i,j})$ at each node by substituting equations similar to equations [3a], [3b] and [4] for $q_{1_{i+1,j}}$ and $q_{2_{i,j+1}}$.

$$-kl_{u}h_{i-1j}-k2_{u}h_{u-1}-kl_{i+1j}h_{i+1j}-k2_{u+1}-h_{u+1}+(kl_{u}+kl_{i+1j}+k2_{u}+k2_{u+1}).h_{u}+Q_{u}=0$$
[5]

This forms a set of NH x NV simultaneous algebraic equations, where NH and NV are the number of channels and grooves respectively. The above set of equations is solved for the nodes inside the circle by the successive over relaxation technique in which the influence of the circular boundary can be easily accounted for.

The effect of local flooding is simulated by turning off the conductances $k l_{ij}$, $k 2_{ij}$ to zero within a fixed area of about 1.35 sq.in (3.5 % of total area) at various locations in the flowfield i.e., near the inlet, center of the flowfield etc.

DISCUSSION

Effect of Flowfield pattern design

For the base case (Table 1), the pressure drop is about 5000 Pa and the gas distribution is nearly uniform with a slight non-uniformity near the inlet and outlet regions (figure 3a). Comparing figures 3a and 3b it is seen that, increasing the channel width does not result in dramatic improvement in the gas distribution. This may be because increasing the channel width within the constrained size of the flowfield reduces the number of channels. It is to be stressed that this type of behavior depends on the numerical value of the parameters since at a much smaller values of the channel widths a small increase in H will substantially improve the distribution.

When the width of the groove (the trench parallel to the flow direction) is increased with a view of decreasing the pressure drop a substantial decrease in the gas pressure drop (of about 4000 Pa) results as shown in figure 3c. But the gas distribution is not uniform in the direction perpendicular to flow. Therefore, these parameters can be optimized for minimum pressure drop with an acceptable non-uniformity in the reactant distribution.

Effect of groove depth

The variations of the flowfield pressure drop with flowrate is given in figure 4a. It is seen that the pressure drop increases linearly with flowrate as expected for any poiseuille flow. But the variation of pressure drop with the depth of the groove is highly nonlinear in the range studied. It seems from figure 4a that a groove depth of 0.03" may be optimal for the base case, as increasing the depth to 0.05 does not significantly decreases the pressure drop. A smaller the groove depth is always preferred as the ohmic losses associated with the flowfield is reduced. Also the bipolar plates with the flowfield constitute a large fraction of the weight and volume of the fuel cell. Thus higher energy and power densities can be obtained with a smaller flowfield depth.

The gas distribution (figure. 4b), is represented by the total flowrate of the gas at three random points on a line perpendicular to the general direction of gas flow (line connecting the inlet and the outlet). In the ideal case of uniform distribution, the resultant graph should be a straight horizontal line. It is seen that the distribution is more uniform at lower flows and at small groove depths. The more uniform distribution at smaller groove depths can be explained as due to the increased pressure drop offered by the smaller groove depths.

Effect of oxygen utilization

At a constant current density, decrease in utilization of oxygen implies a higher gas flowrate. Thus the effect of utilization is similar to gas flowrate with a net gas consumption or generation in the flowfield. Thus a decrease in the utilization results in increasing flow and hence a larger pressure drop, figure 5a. The effect on distribution is also similar i.e, decreasing utilization leading to non uniform distribution figure 5b.

Effect of local flooding

For the case where flooding is simulated near the inlet, the presuure contours are given in figure 6b, the gas distribution is highly non uniform with a large area being blocked by a small flooded site. In this case the current would have to take a longer path parallel to the electrode surface. This entails large losses as the cell components are typically very thin and hence have high electrical resistances. Flooding near the center also has a similar effect but not as large an effect as that for flooding near the inlet. But flooding near the outlet did not make a significant impact on the gas distribution. In all these cases the pressure drop was not significantly affected as the flooded area was very small, 3.5% of the cell area.

CONCLUSION

The effect of important design parameters on the flowfield pressure drop and reactant distribution was studied. It was found that in a rectilinear network of grooves and channels, an increase in the groove width parallel to the gas flow yields low pressure drop. But this results in a highly nonuniform distribution of the gas across the electrode. An optimum groove depth that minimizes the ohmic losses, weight and volume of the fuel cell stack and offers acceptable pressure losses exists. Local flooding occurring in very small areas can effectively block a much larger part of the electrode. Flooding near the inlet has a particularly severe effect on the gas distribution.

ACKNOWLEDGMENTS

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Figure. 2 Solution Methodology



Table 1. Parameters for the base case simulation

Diameter of flowfield,D	7"	
Groove width,V	0.01"	
Material between grooves, DV	0.04"	
Channel width,H	0.05"	
Material between channels,DH	0.4"	
Current density	1000 ASF	
Composition of inlet air:		
Oxygen	0.12 mol %	
Nitrogen	0.48 %	
H2O vapor	0.4 %	
Oxygen Utilization	0 %	
Temperature	180 F	
Inlet gas flowrate	0.3 acfm	
Inlet and Outlet port geometry	2.5" along the circumference and diametrically opposite to each other.	

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3d. H=0.05, V=0.02








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DIAGNOSTIC INFORMATION FROM AC IMPEDANCE MEASUREMENTS ON POLYMER ELECTROLYTE FUEL CELLS

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ABSTRACT

The ac impedance spectra of polymer electrolyte fuel cell cathodes measured under various experimental conditions are analyzed. Impedance spectra of the air cathode contain two features: a higher frequency loop or arc determined by interfacial charge transfer resistance and catalyst layer properties and a lower frequency loop determined by gas phase transport limitations in the backing. The lower frequency loop is absent from the spectrum of cathodes operating on neat oxygen. Properties of measured impedance spectra are analyzed by adapting a recently developed polymer electrolyte fuel cell model to probe the effect of ac perturbation. Comparison of model predictions to observed data is made by simultaneous least squares fitting of a set of spectra measured for several cathode potentials. General diagnostic criteria for sources of loss in PEM fuel cells are described. These are derived from experimental impedance spectra and the effects of perturbation of model parameters. Three different types of losses caused by insufficient cell hydration to do with interfacial kinetics, proton conductivity in the catalyst layer and conductivity in the membrane, are clearly resolved in these impedance spectra.

INTRODUCTION

Polymer electrolyte fuel cells (PEFC) are energy conversion devices capable of delivering high power densities. They have attracted considerable research effort in recent years, particularly in the context of potential transportation applications¹. PEFC performance is limited by losses caused by factors related to membrane, electrode, and hardware components. A depiction of one half of a PEFC, emphasizing components considered in the model described herein, is shown in Fig. 1. Previously reported work from this group and others has aimed at characterizing the water uptake and the water and proton transport properties of membranes used in these devices ²⁻⁵, and at modeling membrane losses in operating fuel cells⁶. We have previously described a detailed model of the dc polarization characteristic of the PEFC air cathode⁷. Together, the modeling chapters described in Ref. 6 (membrane model) and 7 (cathode model) provide a complete description of losses observed for a well humidified PEFC operating on pure hydrogen.

Losses at fuel cell cathodes, particularly when the fuel cell is using air as oxidant, are significant and could originate from: (1) limited interfacial kinetics; (2) limited protonic conductivity through the catalyst layer and (3) limited effective permeability of oxygen in the catalyst layer. In addition, the gas diffusion backing is responsible for significant oxygen transport losses in the case of air cathodes. Electrode behavior in PEFCs is quite complex and is influenced by several factors, including electrode composition and structure⁸⁻⁹ and the hydration level within the catalyst layer¹⁰. It has been recognized that a high-performance electrode will allow good gas access to the electrocatalyst as well as sufficient protonic conductivity within the catalyst layer⁷. The hydration conditions within the fuel cell have a profound influence on electrode performance. In the model system of an ionomer covered Pt microelectrode, poor hydration has been shown by Uribe et al.¹⁰ to re-

sult in very poor oxygen electrocatalysis. On the other hand, excess liquid water leads to "flooding" of the electrode and, consequently, poor transport of gas through the electrode. Understanding the losses stemming from inappropriate electrode humidification is thus a key to optimizing electrode and ultimately fuel cell performance.

Electrode structures in PEM fuel cells have evolved from hot-pressed Pt black/PTFE composites on a membrane¹¹ through Nafion-impregnated catalyzed gas diffusion electrodes employing carbon-supported Pt (Pt/C) particles as electrocatalyst^{12,13}, to the recently developed ultra-low platinum loading electrodes utilizing a composite layer of ionomer and Pt/C particles bonded to the membrane and backed by a gas-diffusion (backing) layer ^{8,9,14}. The latter sequence of cell elements is depicted in Fig. 1 for the PEFC cathode . The last mentioned electrode type delivers excellent performance, particularly when considered on a catalyst weight basis.

Effects of membrane, interfacial kinetics and electrode transport losses on the PEFC polarization characteristic have been considered in detail in Refs. 6 and 7. Here we discuss the use of impedance spectroscopy to study cell and, particularly, air cathode characteristics in PEFCs. The ac response provides an additional source of information. As shown below, some features are more emphasized and better resolved in the dynamic response of the PEM fuel cell than under steady state. The electrodes studied were thin-film catalyst layers¹⁴ cast on the ionomeric membrane with gas diffusion backing layers inserted behind the catalyst layer (Fig. 1). This configuration lends itself to effective diagnostics because the catalyst layer and gas diffusion domains are well defined and separated. A more detailed version of this work has been submitted for publication¹⁵.

EXPERIMENTAL

The fuel cells tested were standard 5 cm² single cells employing Asahi Membrane C polymer (PFSA) electrolyte separators. In the standard configuration, used for all tests described here unless otherwise noted, the electrodes consisted of a thin film catalyst layer, 0.13 mg Pt/cm², prepared as previously described¹⁴, with an E-TEK gas diffusion backing added on each side. Cells were run at 80°C with anode and cathode feed streams humidified by passage through a sparging bottle.

The current densities attainable in these cells were several A/cm², leading to absolute currents up to 15 A. A scheme of the instrumental system is given in Ref. 7. We have recorded the spectra measured using a Macintosh computer with National Instruments LabVIEW software. This system was interfaced to a HP-6060A which served as electronic load for the fuel cell and could handle currents up to 60 A with a 10 kHz bandwidth. To

circumvent the HP 6060A minimum load impedance of 30 m Ω , an additional power supply is connected in series to allow the applied fuel cell voltage to be set as low as 0 V. The frequency response analyzer (FRA) used was a Voltech Model TF 2000. The cell and current shunt voltages were processed through matching bandpass filters of 0.03 to 10000 Hz in Stanford Research SR 560 differential amplifiers. The ac generator from the FRA drove through an isolation pad the external program input to the electronic load. To maximize the bandwidth of the system, the HP-6060A was operated in constant voltage mode below 100 Hz and in constant current mode above that frequency.

All ac impedance spectra reported herein were measured between the fuel cell cathode and the fuel cell anode. Negligible difference in response was seen when measuring cathode impedance relative to the anode or relative to a reference RHE placed on the side of the anode. We have thus assumed negligible voltage loss and negligible impedance at the anode at all currents measured and have performed all measurements reported here in cell cathode vs. cell anode mode. Typically, a dc polarization curve was recorded prior to the ac run to allow us to determine the dc current corresponding to each iR-corrected cell voltage.

The iR-corrected cell voltage is assumed to be equal to the potential of the cathode vs. RHE.

AC IMPEDANCE MODEL

The physical model used to obtain equations for ac impedance of a PEFC is based on a previously published steady state, one-dimensional model for the gas-diffusion backing and the cathode catalyst layer⁷. To adapt the steady state model for the description of dynamic processes in the PEFC cathode, the dynamics of a changing O₂ concentration in the backing and in the catalyst layer and of charge stored in the interfacial capacitor within the catalyst layer have been added. We have also considered effects of a local O₂flux-limiting barrier around individual catalyst particles, but have found that it was not needed to explain the data.

Figure 1 shows schematically the backing and catalyst layers in the cathode and illustrates some of the nomenclature used herein. In the ac modeling of cathode performance, we must consider these two regions of the cathode and their coupling. Fractional distance is represented by the variable y through either the backing (distance/ ℓ_B) or the catalyst layer (distance/ ℓ). The assumptions and nomenclature used here are similar to those in Ref. 7. These include:

- uniform effective ionic conductivity σ in the catalyst layer
- uniform effective oxygen diffusion coefficient D in the catalyst layer
- negligible electronic resistance throughout the electrode
- uniform porosity in backing with gas transport following Stefan-Maxwell equations and with water vapor assumed saturated.

Treatment of the last item is different in this paper than in Ref. 7. There, we considered binary flow of oxygen through nitrogen with the partial pressures reduced by the water vapor but without considering that saturated water vapor is dragged by the flowing oxygen. Ternary flow of all three components, oxygen, nitrogen and water vapor, are considered here, providing a more rigorous treatment.

- For the ac model, we use these additional assumptions:
- · uniform double layer capacitance within the catalyst layer
- uniform O₂ storage capacity throughout the catalyst layer

We now describe sequentially our modeling approach for the backing and the catalyst layer dynamic behaviors. Some of the details of this approach have been further refined as compared with the approach in Ref. 7.

<u>Backing: Porosity and Tortuosity</u>: The gas diffusion backing consists of 100- to 200 Åcarbon particles mixed with a colloidal PTFE solution, pressed into carbon cloth and sintered. As prepared, dry E-TEK backing material has a porosity of about 0.75 to 0.8 and also varies in thickness from about 350 to 450 μ m. When compressed in the assembled cell the thickness is 180 μ m and the porosity is estimated to be 0.4. A characteristic frequency of gas interdiffusion in the backing can be measured from the low frequency arc in the air electrode impedance spectrum. We find the characteristic frequency of the backing

 $\omega_B = \frac{D_{ON}}{\tau \ell_B^2}$ is a function of τ , the torusity factor of the backing, but not of ε_B , the effective

porosity of the backing which leads us to a good estimate of the tortuosity factor (τ ~7) that

corresponds to effective average path lengths roughly 2.6 $(\tau^{1/2})$ times the backing thickness. Melted and resolidified PTFE around the carbon could well provide such a tortuous path for diffusion

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<u>Geometric Considerations</u>: Our model is one dimensional and assumes uniform flow over the cell cross section (see Fig. 1). However, the ribbed flow field supplying air to the gas diffusion backing defies this assumption. In our typical fuel cell, the flow field ribs occlude half the flow area with strips whose width are about three times the thickness of the backing. This constriction will cause the local flux to increase and will cause greater concentration drop than will a uniform flow. For steady state flow the ribbed geometry can be replaced with an open geometry of 300 μ m effective backing thickness that drops the concentration an equivalent amount. We have now modeled two-dimensional simple diffusion in the ribbed geometry and calculated the dynamic transfer function for change in average O₂ concentration at the catalyst layer with respect to a change in flux. We have concluded from this calculation that we could apply backing transfer functions for a 300- μ m-thick uniform geometry, instead of the 180 μ m thick actual, ribbed geometry.

<u>The ternary gas system (oxygen, water, nitrogen</u>) We have developed the dynamic equations to determine the transfer function with respect to the current density of oxygen mole fraction at the cathode backing/catalyst interface for the ternary system of saturated water vapor, nitrogen and oxygen. We assume that both equilibrium saturation and isothermal conditions are maintained under ac perturbation. Under saturation the partial pressure of water remains fixed but there is a water vapor flux dragged along by the O₂ flux that slightly modifies the solution. We used the Stefan-Maxwell equations and the continuity equation with boundary equations that state the O₂ flux does not vary at the flow channel side and that there is no N₂ flux at the catalyst layer side. We were able to show that the exact solution can be approximated by an equation having the same functional form as for thin-film diffusion but forced to match the low and high frequency ends of the exact solution. The equations of the backing transfer function are detailed in another paper.¹⁵

Catalyst Layer

In the catalyst layer four differential equations in the thickness variable and in time, representing respectively ohmic losses, current generation from interfacial electron transfer and double layer charging, Fick's law diffusion of O2, and conversion of O2 flux to proton flux, were used. Variables were local cathode overpotential η , ionic current density I, O₂ concentration ratio C/C*, and O₂ flux. We assume a Tafel dependence of the kinetic current density on overpotential and use a fixed Tafel slope of 85 mV/decade. The equations include the transfer function of backing outlet partial pressure with respect to current density from the backing equations. The equations, first solved for steady state, were linearized, LaPlace transformed and solved in the frequency domain for the impedance, the ratio of the transformed overpotential at the catalyst layer/membrane interface to the transformed current density. The boundary conditions at the backing side of the catalyst layer, were a unity perturbation in overpotential, zero ionic current density, zero change in O₂ concentration ratio to concentration at the backing side. At the membrane side the O_2 flux was zero. Again the detailed equations and their method of solution are described elsewhere¹⁵. The parameters in the model that can be estimated by fitting to measured impedance data are: i*Ar, the current density per cm² Pt @ 0.9V vs. RHE times the effective Pt surface area per unit geometric surface area; C*D, the O2 concentration at catalyst layer inlet times the effective O2 catalyst layer diffusion coefficient; and Rcl, the catalyst layer ionic resistance.

RESULTS AND DISCUSSION

<u>Analysis</u>

A standard practice in interpreting ac impedance plots has been to fit measured data by a complex least squares method to an analog electrical circuit of equivalent resistors, ca-

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pacitors, constant phase elements, finite or infinite Warburg impedances, and so forth, whose values hopefully represent interpretable physical variables. When the model is described by partial differential equations, as in the case of our PEFC cathode model, interpretation by equivalent circuit becomes more difficult and the model equations themselves should replace the equivalent circuit. In the catalyst layer portion of our model, O₂ concentration and overpotential vary continuously through the layer because of reactant diffusion and distributed ionic resistance. Double layer capacitance and O₂ storage exist throughout the layer. While distributed systems with uniform resistance and capacitance can be represented by finite Warburg impedances, the more complex system dealt with here is not so amenable to this representation.

Normally, individual impedance spectra recorded at one potential are fitted separately and an evaluation of parameters at each separate potential is made. We modified our fitting code (originally obtained from B. Boukamp¹⁶) to allow *simultaneous fitting of many spectra at once*. This provides a strong test of the model. For each separate spectrum, the corresponding cathode overpotential and the measured current dependent membrane resistance (high frequency resistance) were used in the fit, and a constant Tafel slope was assumed. The other parameters were assumed to be independent of potential. We could also separately fit each spectrum and could freeze the value of any of the parameters, which allowed forcing some parameters to be the same at all potentials while fitting individual spectra. We expect certain model parameters such as ionic resistance in the catalyst layer, double layer capacitance, catalyst surface area, and O₂ permeability to be independent of interfacial potential difference to first order. Some changes in these elements caused by local production of water might occur in reality, but as long as the model does not specifically include such effects we prefer to hold these parameters independent of interfacial potential difference when fitting impedance data taken at a range of cell cathode potentials.

Modeling Base Case Results

Figure 2a shows measured impedance data for the standard test cell (see Experimental). Figure 2b shows a simultaneous fit to the model of spectra obtained at six cathode potentials. There are 5 points logarithmically spaced per decade of frequency. Clearly, the model captures the qualitative features of the impedance response of the cell. Table 1 gives values for the model parameters that generated the best simultaneous fit to the six spectra.

Table I. Parameters Evaluated from a Simultaneous Fit of Impedance Spectra Measured at Six Potentials. A fixed Tafel slope of 85 mV/decade was used.

Π_{CL} $\Omega \text{ cm}^2$	C D X 10 ¹⁰	A _r i mA/cm ² -atm	$\sqrt{\tau}$	mF/cm ²	x 10 ³
0.106	12.30	32.80	2.778	13.70	16.40

It is interesting to compare the cathode parameters evaluated from such simultaneous fits to several impedance spectra (Table I) to the cathode parameters evaluated by us previously from a family of steady-state polarization curves measured with a range of cathode feed streams compositions⁷. The corresponding values derived in Ref. 7 were: R_{CL} =0.06-0.36 ohm cm², Ari^{*}=30-90 mA/cm² and C^{*}D = 40-190 x10⁻¹⁰ mol/cm-sec-atm

(the tortuosity factor, τ , and the double layer capacitance, C_{DL}, are obtainable only from the impedance measurements). The numbers are similar albeit not identical, some of the difference originating from differences in efficiency of local humidification within the catalyst layers in different cells and some reflecting the level of uncertainty in the analysis of such a

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multiparameter system. In any case, previous conclusions on a significant loss due to limited protonic conductivity within the catalyst layer, on the high catalyst utilization in such thin-film catalyst layers and on the rather high gas permeability in such catalyst layers (see Discussion in Ref. 7) are well confirmed by these ac impedance results.

Typical features of the impedance spectrum of a PEFC.

Having executed a simultaneous fit to several spectra measured for a PEFC, we have now obtained a realistic base set of cell parameters (actually, cathode parameters). We will use these parameters (Table I) to discuss typical features of impedance spectra observed for PEFC air cathodes. We will do that by changing individual cathode parameters and evaluating the effects of such changes on three impedance spectra recorded at cathode potentials of 0.81, 0.76 and 0.58V. These three potentials represent low, intermediate and high cathode overpotential regimes.

Generic impedance spectra for the fuel cell cathode include two arcs, a higher frequency arc reflecting the combination of an effective charge transfer resistance and a double layer capacitance within the catalyst layer and a lower frequency arc reflecting mass transport limitations in the gas phase within the backing. The effective charge transfer resistance is largely determined by the rate of the interfacial oxygen reduction process, but also by the protonic conductivity and oxygen permeability limitations within the catalyst layer. As highlighted by the three measured spectra in Fig. 3(a), the dual-feature spectrum shows the following trends with increase in cathode overpotential. At low overpotentials (0.81V), the backing impedance is relatively negligible and only the higher frequency semi-circle shows, terminating at the high frequency end with a 45° branch that reflects coupling of the distributed ionic resistance and distributed capacitance in the catalyst layer. As the overpotential increases, the diameter of the higher frequency arc decreases, reflecting the increasing driving force for the interfacial oxygen reduction process (see spectrum at 0.76V vs. spectrum at 0.81V). However, the diameter of this higher-frequency arc eventually reaches a minimum value and subsequently grows again as the overpotential is further increased (0.58V spectrum vs. 0.76V spectrum). Such increase in effective charge transfer resistance at the higher cell current densities occurs when the O₂ concentration drops within the catalyst layer as a result of oxygen transport limitations.

With increased overpotential, the second, lower frequency spectral feature grows in Fig.3a, reflecting the diffusion limitations in the backing layer that both statically and dynamically affect the O₂ partial pressure at the backing/catalyst layer interface. At the highest overpotentials, this lower frequency arc comes to dominate the impedance spectrum in the case of an air cathode. The features of this lower frequency loop are affected by the porosity and tortuosity of the backing layer. For a cathode operating on neat oxygen, the low frequency loop is completely absent from the impedance spectrum. The absence of the low frequency feature in this case is a straightforward demonstration that this spectral feature arises from a gas-phase, mass-transfer barrier in the backing of an air cathode.

We can now explore the effect of variation of the key cathode parameters on the impedance spectrum. This exercise will help in arriving at diagnostic uses of ac impedance spectra of PEFC cathodes. To arrive at the calculated curves shown in Fig. 3b-f, one model parameter is changed each time from its value in the base case (Fig. 3a). Parameters for the base case (a) and the five variations of individual parameters (b-f) are listed in Table II. Frequencies run from 0.1 to 10,000 Hz, with 5 points per decade.

Table II. Parameter Variations for Fig. 3.

Case	RCL	C*D	A _r i*	$\ell_{\rm B}$	CD
	$\Omega \text{ cm}^2$	X 10 ¹⁰	mA/cm ² -atm	μm	mF/cm ²
а	0.106	12.3	32.80	300	13.70
b	0.005	12.3	32.80	300	13.70
С	0.106	36.9	32.80	300	13.70
d	0.106	12.3	98.4	300	13.70
е	0.106	12.3	32.80	1	13.70
f	0.005	12.3	32.80	1	13.70

The effect of decreasing the catalyst layer resistance is shown in Fig. 3b. Two expected effects of decreasing catalyst layer resistance are observed: (1) the disappearance of the -45° angle of approach to the real axis at high frequency and (2) the overall resistance associated with the high frequency loop becomes smaller. More surprisingly, the overall resistance associated with the low frequency loop increases dramatically at the highest overpotential. Because the decreased catalyst layer resistance allows better catalyst utilization at high current densities, the backing losses become greater at the same cathode potential, reflected by a steeper slope of the steady state polarization curve. Comparison of the (b) curves to the (a) curves demonstrates that improved catalyst layer conductivity has a beneficial effect in the medium range of overpotentials but does not help with the limiting current dictated by the backing.

The effect on the impedance spectra of increasing oxygen permeability through the catalyst layer is shown in Fig. 3c. Of particular interest is, again, the behavior in the intermediate overpotential domain. The low frequency resistance, RIf, is substantially decreased in this regime. This clearly shows that mass transport effects within the catalyst layer are significant at intermediate overpotentials. Again, this leads to higher value of R_{lf} at the highest overpotential (0.58V) because of backing limitations.

The effect on the impedance spectra of increasing the parameter A_r i^{*} is shown in Fig. 3d. As would be expected, this has the effect of significant decrease in Rif at the lowest overpotential. The higher current density obtained at a given overpotential is also reflected in a lower "turnaround overpotential" (R_{1f} is now larger at 0.76V than at 0.81V), since the higher current density exacerbates the effect of R_{cl} on the magnitude of the high frequency loop.

Figures 3e and 3f show the effect of eliminating completely the transport barrier in the backing on the impedance spectra. These curves indicate what is expected with pure O₂ feed to the cathode. They exhibit two important features. Only one (higher frequency) arc shows in the spectrum and the value of R₁ at the highest overpotentials is much smaller. The latter is expected since the ac response is most sensitive to backing effects at the highest overpotentials.

<u>Further Information on PEFCs from Impedance Studies</u> We now turn to further cell impedance studies that illustrate problems associated with both poor humidification and overly thick backing layers.

<u>Cell Humidification Effects</u>. We have probed effects of water supply by varying cell humidification conditions and determining the ac impedance spectra. Figure 4a shows spectra taken at the same cathode overpotential, 0.82 V, with two different cathode humidification conditions: first with "normal" cell humidification of the cathode and anode and second with the cathode humidifier bypassed (i.e. dry air supply). At such low cathode overpotentials, the impedance spectrum includes only the arc associated with interfacial impedance and catalyst layer transport effects. As shown here, at a potential of 0.82V good humidification of the cathode gas stream results in this cell in a high frequency cell

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resistance (membrane + contacts) of 0.12 Ω cm², and a faradaic additional resistance of 0.50 ohm cm.² At the same potential, a dry air stream into the cathode increases the high frequency cell resistance to $0.45 \,\Omega \,\mathrm{cm^2}$, whereas the low frequency resistance increases quite dramatically to 2.5 Ω cm.² As clearly observed in Fig. 4a, in the case of dry air supply to the cathode, the high frequency impedance loop has a clearly developed branch of an angle of 45°, as expected from protonic conductivity limitations within the catalyst layer. However, the increase of the overall diameter of the impedance loop is above and beyond the effect of the 45° branch, reflecting a significant increase in interfacial ORR impedance caused by low levels of water in the cathode catalyst laver¹⁰

These spectra thus reveal that lack of sufficient humidification of the cathode air stream brings about cell losses because of three different factors, which are well resolved in the impedance spectrum: an increase in membrane (high frequency) resistance, an increase in the resistance of the ionomeric component within the catalyst layer (significant branch of 45^o develops), and an increase of the interfacial impedance for oxygen reduction (ORR) reflected by the increase of the overall diameter of the impedance loop. While the increase in membrane resistance is expected and quite well understood, the effects of insufficient humidification on the conductivity within the catalyst layer and on the interfacial kinetics have been less extensively treated and these impedance data demonstrate them very clearly. In a steady state polarization characteristic, only an overall increase of the slope dV/dI will be observed, corresponding to the sum total of these three separate effects.

Figure 4b demonstrates the effect of hydration mode on the high frequency (membrane) resistance in the cell. Clearly, the strongest effect of enhanced membrane resistance originates from lack of anode humidification, easily understood from the increased resistance near the anode expected as a result of electroosmotic drag⁶.

Figure 4c shows the dependence of the diameter of the high frequency impedance loop, Rif, on cathode potential (iR-corrected cell voltage). In the case of the humidified air stream, the average slope of this semi-logarithmic plot is close to 90 mV/decade, which is in agreement with Tafel slopes derived for the ORR at a well defined, well humidified Pt/recast Nafion interface¹⁰. In the case of dry air, however, not only are the values of RIf much higher, but the Tafel slope also increases to about 160 mV/decade. The results in Fig. 4c emphasize the fact that, especially at low cell current densities, efficient hydration of the cell is required to achieve maximal PEFC cathode performance.

Backing Layer Thickness Effects. To demonstrate the effect of the backing layer on air cathode performance, we compared the steady state performances and the impedance spectra for air cathodes in two PEFCs. In one cell we used a carbon cloth backing compressed to 180µm thick, as ordinarily employed in our cells. In the other cell we employed a "sandwich" of two such cathode backing layers, with an overall compressed thickness of 360µm. The thin film catalyst layer structure makes the separation of backing and catalyst layer experimentally simple, an important prerequisite for this study.

In Fig. 5, the effects of doubling the backing layer thickness on polarization curves and on the ac impedance spectra of the air cathode are shown. The polarization curves corresponding to cells employing single and double backing, are shown in Fig. 5a and b. It is evident that the addition of a second backing layer has a marked deleterious effect on the performance of the cell, manifested in a sharp decrease in the limiting current density obtained. (Note the change in current density scale between Fig. 5a and b.)

Figure 5c shows the ac impedance spectra recorded at 0.81 V. At this low overpotential, at which ORR kinetic limitations predominate, the cathode performance is somewhat improved with the double backing. In contrast, in Fig. 5d, showing the ac impedance spectra recorded at a polarization at which mass transfer is limiting (around 0.35 V), the

size of the impedance loop for the double backing case is significantly larger than for the single backing case. The results for the two different cathode polarizations (Fig. 5c and 5d) can be reconciled by considering that the extra backing essentially traps water in the cathode. Increased liquid water content in the cathode with the thicker backing, tending to excess at higher current densities, is indicated by several observations for the cell employing the thick backing layers: (i) the steep fall of the voltage at 0.7 A/cm² (Fig. 5b); (ii) the increased electrode impedance at high cell current (Fig. 5d); and (iii) the lower interfacial impedance at low current densities (Fig. 5c). At low polarizations, where the kinetics of the oxygen reduction reaction are reflected in the impedance spectrum, the impedance is somewhat less in the double backing case because of the beneficial effect of extra water in the catalyst layer. This accords well with the results of Uribe et al., ¹⁰ which highlighted the necessity of sufficient water for good kinetics at the Pt/ionomer interface. At higher fuel cell polarizations, the excess water inhibits mass transfer through the backing layer(s), effectively decreasing the porosity of the backing.

We conclude that more effective liquid water removal is an important advantage of thinner backing layers, leading to enhanced currents at low air pressures. Attempts to further minimize the thickness of the air cathode backing are being pursued in our group.

Diagnostics from Impedance Spectra and Modeling.

To summarize the information presented here, we distill the findings of our modeling and experimental work into a set of diagnostic features characterizing sources of losses PEFCs.

The simplest possible behavior of the impedance spectrum of a PEFC cathode arises when the only loss is caused by interfacial kinetics of the oxygen reduction (ORR) process. Under such conditions, a single semicircular loop or arc is expected at each potential with a diameter determined by the local value of the faradaic resistance. The diagnostics for interfacial kinetics being the only source of cathode loss are therefore: a single semicircular impedance loop with decrease of the diameter with decreased applied potential, which is in agreement with the potential dependence of the ORR interfacial rate constant, as measured at well defined Pt/ionomer interfaces (e.g., bulk Pt/ionomer microelectrodes).

When the diffusion coefficient of oxygen in the catalyst layer is low, allowing only limited permeability through the catalyst layer, semicircular "kinetic loops" are still expected at each potential. However, the rate of fall of the diameter of the loop with potential will be decreased significantly. For example, to lower it by a factor two requires lowering the cathode potential from 0.80 V to 0.72V under pure kinetic control, whereas with slower diffusion through the catalyst layer it would require lowering the potential from 0.80V to 0.55V. This behavior is equivalent to an increase of the apparent Tafel slope. The qualitative diagnostics for limited permeability through the catalyst layer are thus a decrease with overpotential of the diameter of the semicircular plot, which is slower than expected from ORR measurements at well defined Pt/ionomer interfaces.

If the protonic resistivity of the catalyst layer contributes significantly to cathode loss, the impedance loop terminates at high frequency with a well defined 45^o branch. The presence of such a 45^o branch is the diagnostic criterion for a significant contribution of protonic resistivity in the catalyst layer to cathode losses. It should be emphasized that all the losses originating from the catalyst layer affect only the "kinetic loop", which is the higher frequency loop in the impedance spectrum of the PEFC.

Losses in the backing correspond to a transfer function with lower characteristic frequencies. As a result, the presence of a second, low frequency loop in the impedance spectrum indicates significant losses associated with oxygen diffusion through nitrogen in the backing. This second loop shows only in the spectrum of air cathodes, not in the spectrum of neat oxygen cathodes.

The remaining important feature for which we sought explanation is the variation of the diameter of the higher frequency loop with potential. It first decreases with overpoten-

tial, but then starts to increase again as the overpotential increases beyond some value. This feature arises from the combination of conductivity and mass transport limitations within the catalyst layer. Both oxygen and protons must be available at the catalyst site for the ORR to occur. Restriction of access of either decreases the observed rate of the reaction, causing an increased kinetic (higher frequency) loop at higher overpotentials.

It is important to remember that we have provided here a fit to impedance data for one polymer electrolyte (single) cell, which we regard as average in performance. Some variability of the spectra from cell to cell is observed, but different cells based on similar catalyst and backing layers do generate similar spectra under similar operating conditions.

CONCLUSION

We have provided here a combination of experimental and modeling results which illustrate the effects of polymer electrolyte fuel cell components and operating conditions on the impedance spectra of such cells. This has led to a set of diagnostic criteria for evaluating PEFC losses. The resolution in the frequency domain of the overall change in cell impedance helps to resolve, and to quantitatively evaluate individual contributions to PEFC losses, such as the lowering of electrocatalytic activity in the cathode, the lowering of catalyst layer conductivity and the lowering in membrane conductivity -- all three effects arising together from low humidification levels in the air feed stream. Such resolution cannot be achieved from steady state measurements alone. We have shown that an effective way to analyze such impedance spectra is by a simultaneous fit of spectra obtained at several potentials. The cathode parameters evaluated with this approach agree with parameters derived from steady state measurements with a range of cathode freed streams in Ref. 7.

Some general conclusions on PEFC characteristics, reached from this investigation of their dynamic response are as follows:

(1) High catalyst utilization is achieved with thin-film ionomer//Pt/C composite catalyst layers.

(2) Limited protonic conductivity combined with finite O₂ permeability in the catalyst layer contributes significantly to the cathode impedance in the medium current density domain. (3) A major contribution to air cathode impedance at higher current densities arises from transport limitations in the gas phase in the backing. These limitations are well resolved as a separate, low frequency feature in the impedance spectrum which is absent in the spectrum of a cathode operating on neat oxygen, where the gas phase transport limitations are lifted. (4) The cathode impedance spectra show that the tortuosity in the backing could be significant. Instead of the previous interpretation for families of steady state polarization curves, which was based on an assumption of very limited backing porosity¹⁰, the impedance results suggest a combination of a porosity of about 0.4 and tortuosity factor of about 7

 $(\sqrt{\tau} \approx 2.6)$ in the backing layer of the cathode in a PEFC operating under pressure and at 80° C.

(5) Cell humidification has a profound effect on several cell components. The effects of insufficient humidification on electrocatalysis and on catalyst layer (protonic) conductivity may actually exceed the most commonly considered effects on membrane conductivity.

It is our hope that the qualitative diagnostics and the examples of "generic" ac impedance spectra described herein for PEFCs will enable workers in this field to determine some performance characteristics of their fuel cells essentially at a glance from measured ac impedance spectra.

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Figure 1: Schematic illustration of various regions considered in fuel cell modeling.



Figure 2 (a) Measured impedance of a PEM fuel cell with Membrane C operating with 5 atm air, 3 atm H₂ for various cathode potentials; cell operating at 80°C, anode humidifier T=105°C, and cathode humidifier T=80°C. (b) Simultaneously fitted impedances for data in (a). Fit parameters are summarized in Table I.



Figure 3: Top (4 panels): Calculated ac impedance spectra for base case and several cases with individual model parameters varied; parameters used to calculate these curves are summarized in Table II.



Figure 4: Effect of cathode humidification on cell performance: (a) Typical impedance spectra in the kinetic region for cells with well humidified (cathode humidifier T=80°C) and dry (cathode humidifier bypassed) cathodes. (b) Effect of cell humidification on the high frequency resistance at different iR-corrected cell voltages. (c) Effect of cell humidification on the diameter of the cathode impedance loop in the kinetic regime.



Figure 5: Effects of multiple backing layers on cell performance: IR-corrected polarization curves for cell with (a) single and (b) double backing layers; cell operating at 80° C, anode humidifier T= 105° C, and cathode humidifier T= 80° C. Impedance spectra (c and d) for cells with single and double backing layers: (c) kinetic regime (0.81 V) and (d) mass transport limiting regime (0.39 V).

THROUGH-THE-ELECTRODE MODEL OF A PROTON EXCHANGE MEMBRANE FUEL CELL

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A one dimensional model for a proton exchange membrane fuel cell was developed which makes use of independently measured parameters for predicting single cell performance. Optimization of catalyst layer formulation and properties are explored. Impact of temperature and cathode pressure upon system performance is investigated.

INTRODUCTION

Development of a comprehensive mechanistic model is essential for understanding fuel cell performance and the variables which impact operation. Both through-the-electrode and down-the channel models have been developed to leverage our experimental effort toward improving membrane electrode assemblies (MEAs) and defining optimum operating conditions.

Water management is key to optimal fuel cell operation. High water activity is desired to obtain maximum ionic conductivity of the membrane and catalyst layers. A significant improvement in conductivity is apparent when liquid water is in contact with the ionomer. (1) On the other hand, the presence of liquid water in the backing layer and catalyst layers will decrease gas phase transport to catalytic sites.

Recent models of proton exchange membrane (PEM) fuel cells include electrode kinetics, electro-osmotic transport of water and component diffusion through the backing and cathode catalyst layer. Bernardi et al. developed a comprehensive model from fundamental transport properties (2). Springer et al. included diffusion limitations which arise in the backing layer at the cathode (3). Kinetic resistance at the anode was neglected. Nguyen et al. developed a down-the-channel model to account for mass and heat transfer between the electrode and gases in the channel (4). A simplified treatment of transport through the MEA was implemented.

The purpose of the through-the-electrode model is to apply known properties and relationships to first validate with experimental data and then predict fuel cell behavior. Key factors include water saturation and transport within backing layers and reaction kinetics within the cathode catalyst layer. Using this validated model, the impact of cell temperature and operating pressure will be explored. In addition, use of the model to aid in design of the catalyst layer is demonstrated.

MODEL DESCRIPTION

A schematic illustration of a PEM fuel cell is shown in Fig. 1. A cation-conducting polymer membrane is located between two catalyst layers. This structure is in turn placed next to diffusion backing layers between two flow fields. Hydrogen diffuses through the backing layer to the anode catalyst layer where

$$H_2 \Rightarrow 2H^+ + 2e^-$$
[1]

Protons, formed in the reaction, migrate through the cation conducting membrane to the cathode catalyst layer and are consumed by the following reaction

$$\frac{1}{2}O_2 + 2H^+ + 2e^- \Rightarrow H_2O$$
[2]

The difference in electromotive force for electrons produced at the anode and transferred to the cathode converts chemical energy to electrical energy, in a process not limited by the Carnot cycle.

The model attempts to treat the cathode in detail. Kinetics of the oxygen reduction reaction at the cathode is five orders of magnitude slower than hydrogen oxidation in acidic electrolyte. As a result, kinetic resistance at the anode is neglected. Oxygen transport in the cathode requires detailed representation. The presence of liquid water, produced at the cathode, reduces the pore volume available for oxygen diffusion.

Components of the model consist of water transport through the MEA, oxygen diffusion through the cathode backing layer, ionic resistance in the membrane, and transport and kinetics within the cathode catalyst layer. The description of the model is divided into two sections: (a) gas and water transport through the entire MEA structure and (b) cathode catalyst layer kinetics and transport.

Membrane and Backing Transport

Diffusive transport through both the anode and cathode backing layers is modeled to obtain the water activity at ionomer interfaces and oxygen concentration at the cathode catalyst layer / backing interface. Within the backing layers, the Stefan-Maxwell equation defines diffusive compositional changes (5)

$$\frac{dx_i}{dz} = \sum_{j=1}^n \frac{1}{C D_{ij}^{eff}} \left(x_i N_j - x_j N_i \right)$$
^[3]

where for ideal gases

$$C \approx \frac{P'}{RT}$$

and N_i is the flux of species i in the z direction, D_{ij}^{eff} is the effective binary diffusion coefficient of the pair i-j in the porous medium and C represents the molar gas concentration, P^t, total pressure, T, absolute temperature, and R, the ideal gas constant.

Two classes of water activity profiles can arise and are illustrated in Fig. 1. In Case 1, high relative humidity in the cathode flow channel leads to saturation of gas in the backing layer at the dashed line (a). Water is transported in the liquid phase on the left side of this line through the backing and catalyst layer. The presence of liquid water in the catalytic

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layer and high water activity in the membrane tends to increase ionic conductivity. On the other hand, the presence of liquid water in the backing layer can reduce the available oxygen partial pressure in the catalyst. These two factors lead to a conflicting impact upon fuel cell performance. In Case 2, low relative humidity in the cathode channel yields improved gas phase transport in the cathode backing but lowers ionic conductivity of the ionomer phase.

Depending upon whether liquid water is present, water transport in the cathode backing occurs by different mechanisms. Eq. [3] describes the mole fraction water when water is transported in the gaseous phase. If liquid water partially floods the porous structure, the mole fraction of water in the gas phase is constant and is determined by its vapor pressure. No water is then transported in the vapor phase. Liquid water saturation variations interact with capillary pressure to move liquid water through the backing. In addition, the presence of liquid water lowers the gas phase porosity to reduce the effective oxygen diffusivity.

Water transport in the membrane results from the sum of electro-osmotic transport and diffusion. (7) While electro-osmotic drag is always from the anode to the cathode, diffusion follows the concentration gradient and may occur in either direction as illustrated in Fig. 1. The applicable equation for net water transport is

$$N_{H_2O}^{net} = N_{H_2O}^{diff} + \frac{I_z n_d}{F}$$
 [4]

where I_z is the total current density through the cell and n_d represents the electro-osmotic drag coefficient. For the 1-D case, the diffusion equation may be written as

$$N_{H_{2}0}^{diff} = -\mathcal{D}_{H_{2}0}^{m,w} \frac{dC_{H_{2}0}^{m,w}}{dz_{m,w}}$$
[5]

where subscript or superscript m designates membrane, d indicates dry and w shows a wet basis. The derivative in Eq. [5] may be expressed in terms of membrane water content, λ , which is defined as moles of H₂O per equivalent of SO_1^-

$$\frac{dC_{H_2O}^{m,w}}{dz_{m,w}} = \left(\frac{dC_{H_2O}^{m,w}}{d\lambda}\right) \left(\frac{d\lambda}{dz_{m,w}}\right)$$
[6]

Use of λ instead of concentration simplifies integration. Rearrangement of Eq. [6] and substitution of Eqs. [4] and [5] yields

$$\frac{d\lambda}{dz_{m,w}} = -\frac{\left(N_{H_2O}^{net} - \frac{I_{\delta_r} n_d}{F}\right)}{\mathcal{D}_{H_2O}^{m,w} \left(\frac{dC_{H_2O}}{d\lambda}\right)}$$
[7]

which describes the gradient of water content in the membrane with position.

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Use of the diffusion equation is complicated by changes in membrane dimensions with water activity. Assuming that there is no excess volume of mixing between the ionomer and water, a relationship may be derived which describes the change in dimensions with water content. Molar concentration of water on a wet volume basis can be expressed as

$$C_{H_2O}^{m,w} = \frac{a\lambda}{(c\lambda+1)}$$
[8]

where

and $\rho_{m,d}$, represents the density of the dry membrane, E_m , the equivalent weight of the ionomer, ρ_w and M_w , the density and molecular weight of water, respectively. Assuming that the membrane expands equally in all directions, we can also derive the following relationship between wet and dry membrane thickness

$$z_{wet} = (c\lambda + 1)^{1/3} z_{dry}$$
[10]

After substitution of the derivative of Eq. [10] into Eq. [7] we obtain

$$\frac{d\lambda}{dz_{m,d}} = -\frac{\left(N_{H_2O}^{net} - \frac{I_{\delta_c} n_d}{F}\right)(c\lambda + 1)^{1/3}}{\mathcal{D}_{H_2O}\left(\frac{dC_{H_2O}}{d\lambda}\right)}$$
[11]

where the derivative of Eq. [8] yields

$$\frac{dC_{H_2O}}{d\lambda} = \frac{a}{\left(c\lambda + 1\right)^2}$$
[12]

Through Eq. [11], membrane water content may be calculated.

Effective transport properties for both diffusion and ionic conduction are dependent upon porosity. Formation resistivity, R_0 , is related to bulk resistivity, R_w , of the conducting phase by

$$R_0 = F_R R_W$$
[13]

where the formation resistivity factor, F_{R} , is defined as

$$F_R = \frac{a}{\phi^m}$$
[14]

In this expression, ϕ represents porosity, *a* is a coefficient which varies from 0.6 to 2.0 and m is the cementation factor or tortuosity factor that ranges from 1 to 3 (6). This type of relationship represents ionic conductivity of brine saturated rocks which vary widely in pore characteristics. For sandstone rock, which approximates the types of porosity found in MEA electrodes, the Humble formula sets m = 2.15. (6) Thus, effective transport properties may be approximately related to bulk properties by:

$$\kappa^{eff} = \phi^2 \kappa \qquad D_{ii}^{eff} = \phi^2 D_{ii} \qquad [15]$$

Solution for the water distribution through the MEA structure is obtained by integrating from the anode channel to the cathode catalytic layer and from the cathode channel to the cathode catalytic layer. The mole fraction of components is calculated in both the anode and cathode channels. For a given current density, a net flux of water is assumed through the anode backing and membrane. Eq. [3] is used to calculate the gas composition through the anode backing. Binary diffusion coefficients needed in Eq. [3] are calculated from Chapman-Enskog kinetic theory for the gaseous state at low density (5).

At the anode backing / membrane interface, the mole fraction of water is converted to water content in the membrane interface by the following expression (7)

$$\lambda_{(30^{\circ}C)} = 0.043 + 17.81a - 39.85a^2 + 36.0a^3 \quad 0 < a \le 1$$
[16]

where $a = x_w P' / P_{sut}$. Since this correlation was obtained for membranes treated in boiling water, the relation is assumed to hold to 100°C.

Membrane properties include electro-osmotic drag coefficient, water diffusion coefficient and ionic conductivity. Recent water content and electro-osmotic drag measurements indicate (8)

$$a_w$$
(water vapor) ≤ 1 $\lambda \leq 14$ $n_d = 1.0$
 a_w (liquid water) $= 1$ $\lambda = 22 to 25$ $n_d = 2.5$

Data for the diffusion coefficient for water in the membrane was obtained from Zawodzinski et. al. (1). The data was correlated in the form given below:

$$\mathcal{D}_{H,0} = C_1 + C_2 (1 - \exp(-C_3 \lambda))$$
[17]

Water diffusivity is adjusted from 30°C by the following equation:

$$\mathcal{D}(at \ T_{cell}) = \mathcal{D}(30^{\circ}C) \left[\frac{E_a}{R} \left(\frac{1}{303} - \frac{1}{273 + T_{cell}} \right) \right]$$
[18]

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where $E_a/R = 2416$ (9). The potential loss in the membrane and catalytic layer is calculated from the ionic conductivity. Conductivity data from Zawodzinski et al.(1) is fitted with the equation

$$\kappa_i = C_i^{\kappa} \left[C_i^{\kappa} + C_i^{\kappa} \left(1 - \exp\left(-C_i^{\kappa} \lambda\right) \right) \right]$$
[19]

where C_T is the temperature coefficient for temperatures other than 30°C where $C_T = 1.0$. While complete curves have not been measured as a function of temperature, membrane conductivity in liquid water is available for NAFION® 117 and DOW ionomers (1). The data is fitted by

$$C_r^{\kappa} = C_r^{\kappa} + C_s^{\kappa} T$$
[20]

Water content is integrated by Eq. [11] through the membrane to the cathode catalytic layer where the water content is assumed to be constant.

Water content is again estimated for the cathode catalyst layer, but starting at the cathode flow channel. As shown in Fig. 1, gas composition through the cathode backing is integrated with Eq. [3] to the catalyst layer. In this case, however, water condensation can occur at some plane in the backing. From this point toward the catalyst layer, a constant water mole fraction is defined with a lower gas saturation to account for the presence of liquid water.

At the cathode layer / catalyst layer interface, Eq. [16] is again applied to obtain the water content of the ionomer. If the water content after integrating in both directions agrees, convergence is obtained. If they differ, a new net water flux is assumed and the calculation is repeated until convergence is obtained.

The procedure is complicated by non-ideal behavior at the gas - ionomer interface. NAFION® in contact with water vapor at unit activity yields $\lambda = 14$. Liquid water with the same activity produces $\lambda = 22$. Contact angle measurements show that membrane surface wettability is different for the two cases (10). Small-angle neutron scattering techniques indicate the presence of high kinetic resistance to water transport at the interface for water vapor (11). Thus, it is assumed that a step change occurs at the interface. Concentration gradients within the membrane are unaffected.

Cathode Catalyst Layer

A conceptual representation of the catalytic layer is given in Fig. 2. The catalyst layer is represented as a uniform structure with catalyzed carbon black particles covered with a continuous ionomer film. Oxygen reaches the catalyst by diffusion through void volume within the structure. Assumptions for the model include a uniform water content of the catalyst layer, a uniform distribution of components within the layer, and low electronic resistance.

Derivation of the equations describing the current distribution, potential distribution, oxygen flux and oxygen concentration are similar to those by Springer et. al. (12). Four governing equations are as follows:

$$\frac{dI_z}{dz} = A_v i_a^{\dagger} \left\{ \exp\left(\frac{\alpha_c F \eta}{RT}\right) - \exp\left(\frac{-\alpha_a F \eta}{RT}\right) \right\}$$
[21]

$$\frac{d\eta}{dz} = \frac{I_z}{\kappa^{eff}}$$
[22]

$$\frac{d(N_{o_1})}{dz} = \frac{-1}{4F} \frac{dI_z}{dz}$$
[23]

$$\frac{d(C_{o_1})_g}{dz} = -\frac{N_{o_1}}{D_{o_1}^{eff}}$$
[24]

where

$$i_{o}^{*} = i_{o}^{ref*} \left(\frac{C_{O_{2}}^{f}}{C_{O_{2}}^{f,ref}} \right)$$
 [25]

and A_v is the catalyst surface area per unit volume of catalyst layer. Since the catalyst layer is assumed to be grain supported, expansion of ionomer with hydration is neglected. Equation [25] assumes that the proton concentration is constant at the catalyst interface. While oxygen diffusion in the "z" direction occurs in both the gas phase and ionomer, fluxes are greater in the gas phase. Thus, diffusion in the ionomer is neglected.

The catalyst is assumed to be covered with an ionomer film to facilitate proton transfer. Calculations indicated that if this film was uniformly distributed over the carbon support, the mass transfer limiting current for oxygen diffusion through the film would be greater than 10 amp/cm^2 of geometric area. Thus, oxygen diffusion through ionomer is neglected.

Concentration of oxygen in the ionomer as a function of temperature was obtained from the work of Sakai et. al. (13). The molar concentration of oxygen in ionomer, $C_{O_1}^f$, was defined as being proportional to the molar concentration of oxygen in the gas phase, $C_{O_2}^k$. The proportionality constant was in turn made a function of temperature.

Four unknowns, namely I_{z} , η , N_{o_2} , and C_{o_2} are described by equations [21] to [24]. Boundary conditions are based upon known values of variables. Before integration is begun, the current density, I_{g_2} , for the electrode is assumed. Since the water saturation through the MEA has been obtained, ionic conductivity can be calculated. Boundary conditions thus become:

$$z = 0 I_z = 0 [26]$$

$$\frac{d\eta}{dr} = \frac{I_{\delta}}{r_{c}^{eff}}$$
[27]

$$I_s$$

$$z = 0 N_{o_2} = \frac{I_\delta}{nF} [28]$$

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 $z = \delta_c$

$$z = 0$$
 $C_{0,} = C_{0,}^{z=0}$ [29]

Solution of Eqs. [21] to [24] involves the use of a Runga-Kutta integration routine with adaptive stepsize control (14). A "shooting" method is implemented where an overpotential is assumed at z = 0 and integration is performed to $z = \delta_c$. The "shooting" procedure is repeated until the condition specified by Eq. [27] is met.

Cell voltage is then calculated as $V = V_{oc} - I \cdot AR_m - \eta_c(z = \delta_c)$. V_{oc} is calculated from the free energy of reaction at temperature and pressure. (Cell voltages are generally calculated at currents greater than 0.01 amp/cm² so corrections for electrode corrosion currents, organic impurity oxidation, and hydrogen diffusion and reaction at the cathode may be neglected.) The membrane resistance AR_m is calculated by integrating over the membrane thickness by the following equation:

$$AR_{m} = \int_{0}^{\delta_{m}} \frac{dz_{w}}{\kappa(\lambda)} = \int_{0}^{\delta_{m}} \frac{(c\lambda+1)^{1/3} dz_{d}}{\kappa(\lambda)}$$
[30]

where c is defined in Eq. [9].

Two Tafel slopes have been measured for oxygen reduction on platinum. Parthasarathy, et al (15) found that at potentials greater than 0.75 to 0.8 volts vs the dynamic hydrogen reference electrode, oxygen reduction occurs on a Pt-oxide covered surface. Below this potential, an oxide-free surface is proposed.

Early simulations with data from Parthasarathy et al. (15) yielded high kinetic resistance at low current densities. A subsequent paper by Parthasarathy et al. (16), which explored the effect of pressure upon kinetics, yielded exchange current densities that were ten times larger than in the former paper. Parthasarathy et al. attributed related phenomena to organic contamination (17). Thus, exchange current densities from the later paper were used along with the temperature dependence from the first paper.

Electrode parameters derived from the indicated references are given in Table I. The transfer coefficients were calculated from the mean value of Tafel slopes measured from 30 to 80°C. The catalyst surface area $A_{\rm v}$ was calculated from the measured catalyst layer thickness and a platinum surface area on carbon of 100 m² / gm Pt. Reference values were calculated at 80°C. Volume fractions of void and ionomer were obtained from the measured catalyst layer thickness and the ink formulation.

EXPERIMENTAL

A single cell and reference test stand were designed and constructed to provide tight control on operating parameters. Key components included mass flow control of gas streams, humidification with HPLC pumps and vaporizers and balances to weigh recovered anode and cathode water. Cell temperature was controlled by water circulation through heat exchangers within the single cell. A data acquisition and control system allowed unattended operation with programmed gas stoichiometries and humidification (18,19). High frequency resistance of the MEA was measured at 1 khz by a 4 probe method.

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Membrane electrode assemblies (MEAs) were assembled by a procedure similar to that described by Wilson et. al. (20) Two decals were coated with a carefully controlled thickness of catalyzed ink in the TBA form and dried in an oven. One decal was placed on each side of the membrane, generally NAFION 112, and pressed under carefully controlled conditions. The catalyzed membrane was then sandwiched between two pieces of Teflonated graphite paper and placed in the test cell. Active area was 46.5 cm².

RESULTS AND DISCUSSION

Single cell performance was measured as a function of temperature, pressure, anode and cathode humidification levels. A comparison between the measured performance and modeling results is given in Fig. 3. Cathode stoichiometry is represented by calculating an mean effective oxygen concentration. The only parameters adjusted to obtain this match are the gas saturation in the catalyst layer and cathode backing. These variables induce a slight downturn at high current density. The measured high frequency resistance was consistently higher than the calculated value. The calculated value only included resistance from the membrane. The difference may be attributed to interfacial resistance and a portion of the ionic resistance of the catalyst layer.

A model with independently defined parameters can aid in studies on the effect of MEA structure upon performance. Two key parameters in MEA optimization include carbon black packing density and NAFION® to carbon ratio within the catalyst layer. Carbon packing density is determined from micrographs of MEA cross sections after testing is complete. A series of simulations were run to explore the relationship between cell voltage and cathode catalyst loading. Cases included three thicknesses of catalyst layer at 5 different carbon packing densities.

In Fig. 4, cell voltage at 1 amp/cm² increases at carbon packing density increases from 0.5 g/cm³. After reaching a maximum, a decrease is performance is predicted. At higher packing densities, A_v increases to improve kinetics. A decrease in void fraction increases the ionomer volume fraction which in turn improves ionic conductivity through Eq. [15]. As packing density continues to increase, a point is reached where the void fraction reduction begins to impact oxygen diffusion through the catalyst layer. A downturn in performance is then predicted.

Good performance is predicted even at low catalyst loading. For instance, for a 5 μ M layer, 0.59 volts is predicted at 1 amp /cm². This value may be compared to the experimental results by Ferreira et al. who found that at a Pt loading of 0.05 mg/cm², 0.56 volts was obtained at 1 amp/cm² with 1 atm air (21). Thus, reasonable agreement is obtained, particularly when the differences in air pressure and unknowns in Ferreira's MEA structure, are considered.

Inferences may also be made concerning the relative performance of supported platinum catalysts and platinum black at low catalyst loadings. Platinum surface area of a 20% Pt /C catalyst is approximately 100 m²/gm Pt compared to around 30 m²/gm for platinum black (22). Higher performance might be expected for the supported catalyst at the same loading. This indeed appears to be true at catalyst loadings below 0.2 mg/cm². Other factors tend to predominate at higher catalyst loadings. Carbon occupies space which may be better utilized by ionomer to increase ionic conductivity or void volume to improve oxygen access. The advantage that platinum black holds above 0.5 mg/cm² may be

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partially lost through the use of carbon with higher platinum loadings. Lower Pt surface area, however, reduces potential gains.

The ionomer to carbon ratio was explored as another laboratory adjustable variable. The weight of carbon was used in the ratio since it correlates with pore volume available for ionomer addition in a grain supported structure. Fig. 5 illustrates that at low current densities, the benefits of ionomer addition reach an asymptote. A mass transfer limit is not reached. At high ionomer loadings, mass transfer limitations are reached at higher current densities. It should be noted that ionomer addition may also impact wettability characteristics of the structure. While carbon surfaces, formed at elevated temperature, tend to be hydrophobic, ionomer in contact with liquid water is hydrophilic. Additional ionomer may be expected to increase liquid water saturation. Compared to model predictions, a mass transfer limit is anticipated at lower ionomer loadings.

Operating temperature and pressure affect system performance. As shown in Fig. 6, a slight improvement in cell voltage is predicted at elevated temperature. Higher reference exchange current densities, ionic conductance, and gas diffusivity tend to increase performance. Above 100°C, a reduction in performance is generally observed at lower pressure (23). As the boiling point of water at pressure is approached, the oxygen mole fraction is reduced significantly by dilution with water vapor. Similar behavior is predicted at lower to make the oxygen mole fraction is reduced significantly by dilution with water vapor.

Cell voltage is dependent on cathode pressure. A series of simulations was performed to explore the effect of cell pressure and air stoichiometry upon performance. Stoichiometry is represented by lowering the average oxygen concentration in the cathode channel. This approach was found to be approximately correct (3). While higher total cathode pressure is expected to improve oxygen transport and kinetics, other factors reduce its effectiveness. First, the diffusivity of oxygen is inversely proportional to pressure. In addition, water condensation, that reduces oxygen transport, is facilitated by higher pressure.

To approximate the effect of air compression upon overall system performance, cell voltage may be reduced by an amount equivalent to the compression penalty. Fig. 7 illustrates the predicted net cell voltage versus cathode pressure and air stoichiometry. It is apparent that at an air stoichiometry of 3, atmospheric pressure operation would be preferred. At lower stoichiometries, cell voltage is less sensitive to pressure. Below an air pressure of 2 atm, other factors such as humidification requirements and equipment size may become predominant factors. It should be noted, however, that water rejection behavior of an MEA can also affect the optimum pressure.

CONCLUSION

A through-the-electrode model, based upon independently measured or calculated parameters, has expanded our ability to predict the impact of variables upon PEM fuel cell performance. After model validation, it was found that cell performance increases with carbon backing density up to a maximum. As indicated in the literature, moderate performance is predicted at Pt catalyst loadings below 0.1 mg/cm². Finally, platinum black electrodes are predicted to compete effectively with supported catalysts at loadings above 0.2 to 0.5 mg/cm².

Increased operating temperature at two atm pressure is predicted to increase cell performance up to about 100 °C. As the boiling point of water is reached, performance drops because of reduced oxygen mole fraction. Higher air pressure also improves cell performance. Once a voltage penalty is subtracted to account for compression costs, maximum system performance appears to occur between 1 and 2 atm pressure at air stoichiometries less than 3.

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Parameters for the Cathode Catalytic Layer Table I.

Parameter	Tafel Slope ~60 mv/decade at 80°C	Tafel Slope ~120 mv/decade at 80°C	
Cathodic transfer coefficient for O ₂ electrode, α_c Exchange current density at reference O ₂ concentration. $i_c^{rg/+}$	0.86 (15) 4.9E-7 (15,16)	0.52 (15) 1.3E-5 (15,16)	
Catalyst surface area per unit volume, cm^2/cm^3 , A_v Anodic transfer coefficient for O ₂ electrode, α_a Reference concentration of O ₂ in jonomer mole/cm ³	1.40E+5 0.54 (24) 1.21E-5		
$C_{O_{2}}^{ref}$ Volume fraction ionomer Volume fraction void Ratio of Oxygen concentration in ionomer to gas	0.17 0.53 0.07 (13)		
phase, $C_{O_1}^f / C_{O_2}^g$		(/	



Figure 1. Schematic illustration of a proton exchange membrane fuel cell .

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Figure 2. Schematic illustration of the Cathode Catalyst Layer.



Figure 3. Validation of model with experimental results, temperature: 95°C, H₂/air pressure: 1.8 atm, anode RH: 100%, anode stoich: 1.5, cathode RH: 96%, cathode stoich: 3.3, gas saturation - catalyst layer /cathode backing 0.4 / 0.65.



Figure 4. Predicted fuel cell performance for 20% Pt on Vulcan XC-72 and platinum black catalyst, membrane: NAFION® 112, temperature: 95°C, H₂/air pressure: 1.8 atm.



Figure 5. Predicted cell voltage versus ionomer to carbon ratio, 20% Pt /C, membrane: NAFION® 112, carbon packing density: 0.6 gm/cm³, Temp: 95°C, air/H₂ pressure: 1.8 atm, catalyst gas saturation: 0.4, backing gas saturation: 0.6.



Figure 6. Predicted impact of cell operating temperature upon cell voltage, H_2 / air pressure: 1.8 atm, Anode RH: 100%, cathode RH: 96%, catalyst gas saturation: 0.4, backing gas saturation: 0.6.



Figure 7. Predicted impact of operating pressure and cathode stoichiometry upon cell voltage corrected for air compression penalty, 80°C, 70% Adiabatic Compressor Efficiency

CHARACTERIZATION OF PEM FUEL CELL MEMBRANE-ELECTRODE-ASSEMBLIES BY ELECTROCHEMICAL METHODS AND MICROANALYSIS

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ABSTRACT

Characterization of Membrane Electrode Assemblies (MEAs) is used to help optimize construction of the MEA. Characterization techniques include electron microscopies (SEM and TEM), and electrochemical evaluation of the catalyst. Electrochemical hydrogen adsorption / desorption (HAD) and CO oxidation are used to evaluate the active Pt surface area of fuel cell membrane electrode assemblies. Electrochemical surface area measurements have observed large active Pt surface areas, on the order of 50 m²/g for 20% weight Pt supported on graphite. Comparison of the hydrogen adsorption/desorption with CO oxidation indicates that on the supported catalysts, the saturation coverage of CO/Pt is about 0.90, the same as observed in H₂SO₄. The catalyst surface area measurements are about 66% of the Pt surface area calculated from the 30 Å average particle size observed by TEM. The electrochemical measurements combined with microanalysis of membrane electrode assemblies, allow a greater understanding and optimization of process variables.

INTRODUCTION

Electricity is the most convenient and widely-used form of energy. However, electrical energy cannot be stored cheaply in large quantities, and in order to provide practical and flexible electrical energy sources, conversion of energy must be carried out to and from another form. Conservation of fuel in energy conversion processes is essential for economical feasibility and has been the major consideration in development of energy conversion technology. Environmental consciousness has also become more of an issue in recent years, and is driving new technologies. Both considerations motivate the development of fuel cells for energy conversion processes.

Proton exchange membrane (PEM) fuel cells generally use platinum catalyzed proton exchange membranes for hydrogen conversion into electrical energy and have shown high power densities. The hydrogen / oxygen electrode reactions occur in the catalyst layer of the membrane-electrode assembly (MEA) which is the efficiency and kinetically limiting region of the fuel cell. For useful fuel cell production, MEAs must be optimized for high proton transfer, hydrogen oxidation and oxygen reduction kinetics, and low platinum catalyst loadings. The production of MEAs for PEM fuel cells can be accomplished by many different methods, ¹⁻⁶ with each production technique presenting many process variables which need optimizing. Because testing of these MEA's is a long and complex process with many fuel cell operating variables to be examined, optimization of production variables can be a tedious procedure.

Characterization of MEAs in various phases of the production process can help reduce the testing time required for MEA evaluation. The use of electrochemical techniques such as hydrogen adsorption and desorption, and carbon monoxide oxidation complement microscopic analysis techniques such as scanning electron microscopy (SEM) and energy

dispersive spectroscopy (EDS). These techniques can be used for characterization of the MEA to determine the characteristics of the catalyst layer and membrane interface. Transmission electron microscopy (TEM) is a valuable technique to examine the individual Pt particle size and Pt distribution on the supporting graphite. Examination of the catalyst layers (anode and cathode) in all dimensions helps illustrate whether the production process has been successful in producing a catalyst with desired uniform properties. In this work, electrochemical and electron microscopies to characterize MEAs are used to assist device optimization of MEA's, thus reducing testing time and furthering our understanding of the MEA variables.

EXPERIMENTAL

MEA's were produced using techniques similar to those used by Wilson & Gottesfeld.^{1,2} Pt catalysts presented in this study were obtained from ETEK corporation and were 20%, 40%, 60% weight Pt supported on graphite and platinum black. The MEA was placed in a single cell test apparatus as shown in Fig. 1, similar to the cell used for fuel cell testing of the MEA. The polycarbonate blocks have facilities for gas distribution, voltage and current takeoff and cell temperature regulation. The graphite flowfield inserts have milled grooves on one side to distribute properly the reactant gases to the MEA. The graphite paper, used for current collection and gas distribution, was impregnated with a Teflon® suspension. The active area of the MEA examined was 47.5 cm², which is large enough to simulate flowfield patterns of full size MEAs. The hydraulic press was operated at 60 psi to compress the gasket assembly for leak proof operation. This cell can be operated as an operating fuel cell using hydrogen and oxygen (or air), or as in the case of this study, to evaluate the activity of the platinum catalyst. All measurements described here were made at room temperature.

The active surface area of the catalyst was measured by evaluating the hydrogen adsorption/desorption and relative carbon monoxide oxidation. For these measurements, the fuel cell cathode was exposed to nitrogen while the anode was exposed to hydrogen. The gases fed to the cell were humidified. The cathode was made the working electrode and the anode was used as both the reference and counter electrode. The double layer capacitance from the voltammogram was subtracted followed by integration of the hydrogen adsorption/desorption region from 0.0 to 0.45 V. The values for hydrogen adsorption and hydrogen desorption were integrated separately, and have generally agreed within 10%. To alleviate problems caused by excess hydrogen evolution, the reported values were calculated by integrating the hydrogen desorption region. Polarization effects at the counter electrode were neglected since the hydrogen oxidation reaction at the fuel cell anode is nearly reversible. For CO oxidation experiments, 5% CO (or 5% CO₂) was added to the cathode gas feed. After exposure to carbon monoxide or carbon dioxide, the anode was purged with nitrogen to remove all of the gas phase CO or CO₂ before the electrochemical measurements were made. The electrochemical measurements were made using a Pine AFCBP1 Bipotentiostat interfaced with a Macintosh via Labview for data acquisition.

The TEM measurements were made using a Philips CM30 Analytical TEM with a 300 kV electron beam. The catalyst samples were dispersed in petroleum ether, and applied to a commercially available TEM substrate. The SEM measurements were made on a CAMSCAN SEM interfaced with a KEVEX EDS system. The MEA cross-sections were prepared by drying the membrane, mounting in epoxy and polishing to 0.1 μ m alumina. The samples were then coated with either graphite or gold to form a conductive surface coating.

RESULTS & DISCUSSION

TEM Catalyst Characterization

TEM Catalyst Characterization For reduction of catalyst loading, a high surface area Pt catalyst is required. To achieve the highest Pt utilization possible, small Pt particles are required. To achieve this, Pt has been supported on high surface area graphite. The Pt particles should be uniform without large agglomerations of Pt, with the smallest possible particle size. Fig. 2 is a transmission electron micrograph of 20% Pt supported on graphite commercially available from ETEK. Mostly uniform Pt particle size was observed for the ETEK catalyst, with an average particle size of about 30 Å. Particle size generally ranges from about 20 Å to 40 Å, although some larger Pt particle, is 75 Å in the longer direction. The edges of supporting graphite are labeled and there are large areas where no Pt particles are apparent. Since the electrons in TEM go through the entire sample, the particles are best examined at the interface where graphite particles are next to regions where no material is present, such as Particle A, where graphite particles are next to regions where no material is present, such as Particle A, to keep volume effects to a minimum. Other areas of graphite show larger concentration of Pt particles, which could be due to a large volume of catalyst material imaged. For an average particle size of 30 Å, the platinum catalyst has a surface area of 93 m^2/g . These TEM measurements tend to agree with measurements made by x-ray diffraction taken by ETEK which measured a surface area of $88 \text{ m}^2/g$ for 30% weight Pt.⁷ The measured Pt surface area by these methods assumes that the entire Pt particle is active, even though the Pt particles are supported on carbon.

Electrochemical MEA evaluation:

Electrochemical MEA evaluation: Electrochemical voltammetry of poly-crystalline and crystalline platinum surfaces have been examined in detail,⁸⁻¹⁶ however little has been published on the electrochemical voltammetry of Pt supported catalysts.^{17,18} Hydrogen adsorption and desorption (HAD) occur essentially reversibly on the platinum surface in the region from 0.0 to 0.4 V_{RHE}. The potential region from 0.4 to 0.5 V is termed the double layer region, as there are negligible Faradaic currents present. During cathodic sweeps, at > 1.0 V_{RHE} oxygen adsorption occurs which is reduced during the anodic sweep at 0.65 V.

The surface area of the platinum can be evaluated by integration of the hydrogen adsorption or desorption according to the following:

$$H^+ + e^- \leftrightarrow H_{ad}$$

(1)

To obtain the platinum surface area, a charge of $210 \,\mu\text{C/cm}^2$ was used to correspond to a monolayer of hydrogen.³¹ A charge transfer of $210 \,\mu\text{C/cm}^2$ correlates to a monolayer of hydrogen adsorption on the Pt(100) surface which appears to be the predominant exposed surface,³² and also correlates to equal distribution of the three low index surfaces.³³ The value of 210 μ C/cm² has been used as a conventional standard for polycrystalline Pt.³¹

The cyclic voltammograms of MEAs with differing weight % Pt catalysts supported on graphite are shown in Fig. 3. The voltammograms have been normalized for the loading of Pt used in the MEAs so that a direct comparison of the charge transfer per unit weight of platinum can be made easily. Fig. 3a is the voltammogram for 20% Pt supported on graphite and has a surface area of 61.1 m²/g of catalyst. While this is a large active surface area, it is almost only a 66% of the value calculated by TEM (or XRD) measurements. The simplest explanation of this discrepancy is that a portion (33%) of the pt surface area is used to hend the Pt particles to the graphite support. Pt surface area is used to bond the Pt particles to the graphite support. Figures 3b, 3c and 3d are for 40% Pt, 60% Pt and Pt black and have active surface areas of 27.4, 20.7 and 33.2 m²/g respectively. These results are summarized in Table 1.

MEAs utilized by our group typically require several hours of operation before stable high performance is achieved. This is termed the 'burn in' period. This effect has also been observed when making the hydrogen adsorption/desorption measurements. Fig. 4 shows the cyclic voltammogram as a function of time for a newly prepared MEA. As the MEA is potentially cycled, the Pt hydrogen adsorption/desorption and oxygen oxidation/reduction features slowly start to appear. The amount of hydrogen adsorption/desorption gradually increases over time, perhaps due to removal of organics in the catalytic ink due to oxidation. The first curve (Fig. 4a) is after the MEA has been cycled for 1 hour. The Pt features are apparent, but are not as well defined as generally observed. After 2.5 hours the Pt features are more pronounced, and the amount of HAD is greater. Initially the MEA show essentially no hydrogen adsorption or hydrogen desorption. The third curve, shows a greater amount of hydrogen adsorption which occurred after the MEA was reversed, so that the opposite side was used as the working electrode. This side also showed a gradual increase in the amount of hydrogen adsorption / desorption, although it reached a higher limiting value more quickly. This possibly indicates that the lower amounts of observed HAD could be due to organic species which are gradually removed from both the catalyst layer and the membrane.

Fig. 5 shows the voltammogram of an MEA anode and cathode after testing in a single cell test apparatus. The MEA was used for electrolysis, i.e. in reverse bias to simulate regenerative fuel cell operation. The cathode (a) shows markedly higher hydrogen adsorption than the anode (b). The anode catalyst surface area has been reduced by a factor of 4, from 30.1 m²/g observed for the cathode to 8.1 m²/g for the anode. This decrease in active catalyst area was also evident from the decrease in performance observed after reverse biasing of the MEA. Subsequent SEM analysis (see Fig. 7d) shows that the thickness of the anode catalyst layer has been greatly reduced by the reverse biasing of the electrode. This result indicates that this type of MEA may not be suitable for electrolysis.

The voltammogram of a MEA with 60% Pt (same as Fig. 3c) after (a) exposure to CO and (b) exposure to CO₂ for five minutes is shown in Fig. 6. The hydrogen adsorption in Fig. 6a is essentially completely blocked as evidenced by the initial curve from 0.0 to 0.4 V. On the following cathodic sweep to 1.5 V, carbon monoxide is oxidized from the Pt surface beginning at about 0.8 V. After oxidation of the carbon monoxide, hydrogen adsorption occurs on the following anodic sweep. The amount of adsorbed carbon monoxide can be calculated via the following reaction:

$$CO_{ad} + H_2O - CO_2 + 2H^+ + 2e^-$$

(2)

The charge required to oxidize a monolayer of carbon monoxide corresponds to $Q_{CO} = 484 \ \mu C/cm^2$ (for Pt(111).²⁰ Using Q_{CO} to calculate the catalyst surface area yields 14.8 m²/g for Fig. 6a. This is only about 70% of the surface area observed by integration of the HAD. Results of the surface area calculations for different catalysts appear in Table 1. From the values in Table 1, we see that the ratio of the surface area calculated by CO oxidation to HAD ranges from 0.72 to 0.93, with three values at 0.90 ± .03. Evaluation of the saturation coverage of CO on crystalline platinum surfaces has been the subject of recent discussion, ¹⁹⁻²⁵ and the saturation coverage of CO on Pt has been measured to be 0.70 in HClO4, and 0.90 in H₂SO4. ^{20,24} The values in Table 1 agree with the saturation coverage of 0.90 observed in H₂SO4. The CO coverage on the 60% Pt catalyst probably did not reach saturation, and thus a lower value was obtained.

Real world applications of PEM fuel cells often require operation on fuels other than pure hydrogen. Fuels considered are typically reformed hydrocarbons, which result in a feed gas of H_2 and CO_2 . Fig. 6b shows that exposure to carbon dioxide forms a species similar to carbon monoxide. However after 5 minutes exposure to carbon dioxide only a small portion of the platinum surface is covered (as evidenced by the amount of

hydrogen adsorption present). If the exposure time to CO_2 is increased, a greater portion of the Pt surface is poisoned. However the coverage does not seem to reach that obtained by direct contact with CO. To evaluate the coverage of the reduced CO2 adsorbed species, by differentiate with CO. To valuate the coverage of the coverage of the determined. However, there is conflicting evidence as to whether the reduced CO₂ species is COH^{26-28} or $CO.^{29-30}$ Oxidation of CO is a two electron process, while oxidation of a COH species is a 3 electron process:

(3)

$$COH_{ad} + H_2O --> CO_2 + 3H^+ + 3e^-$$

If oxidation of the reduced CO_2 species is assumed to be a two electron process, the highest coverage obtained by exposure of the MEA to CO_2 was about 0.70. For a three electron process the coverage obtained would be 0.47. The reduction of CO_2 apparently does not fully poison the Pt surface whether the species is oxidized through a 2 or 3 electron process. This also agrees with the fact that hydrogen adsorption / desorption is still observed at the highest coverages of CO₂.

SEM and EDS MEA Characterization SEM and EDS were used to characterize the cross-sectional properties of the MEA and catalyst layer. This characterization includes not only this physical uniformity of the MEA, but the elemental distributions throughout the catalyst layers of the MEA. A scanning electron micrograph (SEM) backscattered image of a cross-section of a membrane-electrode assembly is shown in Figure 7a. The image shows the anode (a) and cathode (c) catalyst layers, and the proton exchange membrane (b). In a backscattered SEM image, materials with higher atomic numbers appear brighter. The membrane has SEM image, materials with higher atomic numbers appear brighter. The membrane has sulfur present, thus is brighter than the background of the sample mounting epoxy, but not as bright as the platinum present in the catalyst layer. The catalyst layers are made of diffuse catalyst particles, much smaller than the resolution of the image. A different experimental catalyst ink formulation is shown in Fig. 7b. The catalyst layers appear uniform except for a bright particle present in the top catalyst layer, which indicates a higher concentration of platinum. This was confirmed by EDS (energy dispersive spectroscopy) point analysis. This particle appears to about 30 μ m in diameter, and it has poor adhesion between the particle and the rest of the catalytic layer. The poor adhesion is more apparent at higher magnifications. EDS confirmed that the other elemental constituents of the catalytic layer are not as concentrated inside the particle as the rest of the catalytic layer, so the particle was probably present in the catalytic ink before it was applied to the membrane. to the membrane.

A different region of the same MEA as in Fig. 7b is shown in Fig. 7c. Particles that appear dark in the backscattered image and have only about 60% of the platinum as the rest of the catalyst layer. These particles have good adhesion to the rest of the catalytic layer, and the other elemental constituents of the catalyst layer appear uniform inside the particle. These particles appear to have formed after the catalytic ink was formed, or were at least partially solubilized during the mixing process of the catalytic ink.

Fig. 7d is a micrograph of a MEA after testing in a single cell apparatus, and is the same MEA used for the HAD of Fig. 5. This particular MEA was used to examine not only normal fuel cell operation for power production, but was operated in a reverse bias mode, to simulate regenerative fuel cell operation. As can be seen in the micrograph, the anode catalyst layer has mostly been removed due to the reverse bias operation, and the remaining anode catalyst does not have good contact to the membrane.

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CONCLUSIONS

MEA characterization has reduced the time required for fuel cell testing by improving our understanding of the MEA production variables. Use of electrochemical evaluation and electron microscopies have been used to characterize MEAs and the catalyst layers of the MEAs.

Electrochemical surface area measurements have observed large active Pt surface areas, about 60 m²/g for 20% weight Pt supported on graphite. Comparison of the hydrogen adsorption/desorption with CO oxidation indicates that on the supported catalysts, the saturation coverage of CO/Pt is about 0.90, the same as observed in H₂SO₄. The catalyst surface area measurements are about 66% of the Pt surface area calculated from the 30 Å average particle size observed by TEM.

MEA cross-sectional characterization by SEM and EDS has helped to identify process variables which lead to uniform catalytic layers. SEM and EDS characterization has also identified large catalyst particles in experimental formulations, and identified whether the particles appear to have been solubilized in the ink before application to the membrane. SEM analysis has also identified degradation of MEA catalyst layers under certain operating conditions.

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	20% Pt [m ² /g Pt]	40% Pt [m ² / g Pt]	60 % Pt [m ² / g Pt]	Pt Black [m ² / g Pt]
HAD	61.1	27.4	20.7	33.2 30.0
CO Oxidation	56.6	24.4	14.8	30.0

Table 1: Measured Surface Areas by CO Oxidation and HAD.



Fig 1. View of single cell testing hardware.



Fig. 2: Transmission Electron Micrograph (TEM) of Pt catalyst. Pt particle A is 20 Å. Pt particle B is 75 Å.



Fig 3: Cyclic voltammogram of the fuel cell cathode showing hydrogen adsorption and desorption and platinum oxidation and reduction. Catalyst used was (a) 20% wt Pt / graphite, (b) 40% wt Pt, (c) 60% wt Pt and (d) Pt black. Scan rate : 20 mV/sec. The reference electrode used was the counter electrode (anode).

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Fig 4: Cyclic voltammograms showing increasing hydrogen adsorption / desorption as MEA is repeatedly cycled. After cycling for (a) 1 hour, (b) 2.5 hours and (c) switching MEA sides and cycling for 1 hour. Catalyst used was 20 wt % Pt / graphite. Scan rate : 20 mV/sec. The reference electrode used was the counter electrode (anode).



Fig. 5: Cyclic voltammogram of MEA (a) before reverse polarization and (b) after reverse polarization. Sweep rate : 20 mV/sec.



Fig. 6: Cyclic voltammogram of MEA after (a) 5 %CO in gas feed of cathode (b) 5% 'CO₂' in gas feed of cathode. CO/CO₂ dosing time : 5 min. Sweep rate : 20 mV/sec



Fig. 7a: Scanning electron micrograph of catalyzed membrane. Image was taken in backscattered mode. Catalytic layer appears to be uniformly distributed, without large particles.



Fig. 7b: Backscattered scanning electron micrograph of catalyzed membrane. Experimental catalyst ink formulation shows a catalytic layer with a bright particle of high Pt concentration.



Fig. 7c: Backscattered scanning electron micrograph of catalyzed membrane. Experimental catalyst ink formulation shows a catalytic layer with dark particles of low Pt concentration.



Fig. 7d: Backscattered scanning electron micrograph of catalyzed membrane. MEA was tested in electrolysis mode for regenerative operation.

FACTORS AFFECTING THE PERFORMANCE OF PROTON EXCHANGE MEMBRANE FUEL CELLS

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Several of the many factors affecting the performance of a proton exchange membrane (PEM) fuel cell have been examined in an effort to better define the improvements needed for the production of a practical vehicular power system. The presence of either CO or CO_2 in the fuel gas, as would be produced in a reformed methanol stream, were found to be detrimental to performance, with CO levels of even 10 ppm causing major losses in cell output. Repeated freezing and thawing was found to have no effect on the performance of a single cell PEM fuel cell, even when the cell was cooled to -78 °C. The load following capability of a fuel cell stack was measured and determined to be at least 2 orders of magnitude faster than what is needed for vehicular applications.

INTRODUCTION

Early in the next century light-duty and heavy-duty vehicles for transportation are likely to be powered with hydrogen/air fuel cells rather than with the conventional internal combustion engine, because fuel cells can lead to a reduction in emissions and noise as well as an increase in energy conversion efficiency (1). The proton exchange membrane (PEM) fuel cell is the strongest candidate electrochemical power source for electric vehicles capable of attaining the performance levels of the highly advanced internal combustion engine-powered vehicles.

The PEM fuel cell operates at a maximum temperature of 95° C (at reasonable pressures) and, at present, relies on the use of platinum-based electrocatalysts, the loadings of which are continually being reduced (< 0.1 mg Pt cm⁻²) (2). For fuel cells operating in aqueous electrolytes (below 200°C, depending on the chosen electrolyte technology), including PEM cells, hydrogen is the most active common fuel that can be used. However, to be of practical use for power generation, a fuel cell must be capable of

using an available fuel, such as methanol or natural gas. In consequence, the hydrogen required for low temperature fuel cells will be supplied by reforming, followed by watergas shift of readily available and transportable fossil-derived fuels.

For transportation applications, it has been proposed that the hydrogen required for PEM fuel cells will be produced by the on-board reforming of methanol (3). There are two processes for this that are currently receiving significant attention. These are the steam reforming process (3,4), as represented by Equation 1, and the partial oxidation

$$CH_3OH + H_2O \longrightarrow 3H_2 + CO_2$$
 [1]

process (5), as illustrated in Equation 2. The steam reforming process has the advantage

$$CH_3OH + \frac{1}{2}O_3 \rightarrow 2H_3 + CO_3 + heat$$
 [2]

of producing three moles of hydrogen from each mole of methanol, but the process is endothermal necessitating the addition of heat to the reactor and requires the addition of substantial amounts of water to the fuel. The partial oxidation process uses the methanol directly, and is exothermal but produces a fuel gas with a substantially lower hydrogen content. Both produce a mixture of hydrogen and carbon dioxide with variable amounts of carbon monoxide and other gases.

The steam reforming of methanol results in the production of approximately 24-25 vol% CO₂ and CO at levels of the order of 200 ppm to 2 vol% in the H₂-based gas mixture from the reformer output, depending on operational conditions. This concentration of CO in the gas stream exiting from the reformer can be readily lowered to values of the order of 50 ppm by passing the gas mixture through a catalytic reactor, that is selective for the oxidation of CO in the presence of hydrogen. However, a selective oxidation catalyst and reactor operating conditions capable of producing CO at levels less than 50 ppm are not readily available.

The partial oxidation process, using air as the oxidizer, produces a fuel gas that is roughly 40 vol% H_2 , combined with 10 vol% CO_2 and 20 vol% CO. (The balance of the mixture is N_2 with a small amount of water vapor.) The CO can largely be converted to additional hydrogen with the water gas shift reaction, as shown in Equation 3.

$$CO + H_2O \rightarrow H_2 + CO_2$$
 [3]

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This produces a fuel gas with a CO content similar to that of steam reformed methanol, but with a higher inert gas content (5).

The steam reforming process is generally acknowledged to produce a fuel gas with a higher hydrogen content, which contributes to higher total system efficiencies. The partial oxidation process has two advantages however. The process can be cold started faster, and since it does not require any feedback from the fuel cell (as steam reformers using unspent anode gas for heating do) it can respond faster to changes in power demands. The partial oxidation process is also more amenable to the use of other fuels, including both ethanol and hydrocarbons (6).

The presence of the oxides of carbon (CO₂ and CO) in the H₂ fuel stream to be fed to PEM fuel cells used as power sources for electric vehicles gives great cause for concern with regard to the power densities that can be delivered under such circumstances. The presence of CO₂ as a component in the H₂ gas mixture can give rise to poisoning of the surfaces of Pt electrocatalysts due to the formation of "reduced CO₂" (7,8). Carbon dioxide interacts with adsorbed hydrogen on platinum to form COOH species. This can further react with more adsorbed hydrogen to form a COH species. Both of these species poison platinum electrode surfaces and inhibit the hydrogen oxidation reaction. Further, the presence of low levels of CO in the hydrogen fuel gas stream will severely degrade the performance of anodic platinum electrocatalysts, since CO acts as a poison to platinum electrodes operating in the range of potentials 0.0 - 0.5 V (NHE) at temperatures less than 130°C in acidic electrolytes (9,10). Thus, one of the objectives of the work undertaken in this investigation was to determine the effects of CO₂ and CO₂ plus various concentrations of CO in H₂ fuel streams on the performance of a PEM fuel cell using air as oxidant.

A practical PEM fuel cell power source installed in an electric vehicle located in northern regions of the U.S. during winter months will be subjected to multiple freeze/thaw cycles, corresponding to periods of vehicle inactivity/vehicle in service. Since it is known that the PEM electrolyte layer and the PEM impregnated electrocatalyst layers in each cell contain significant amounts of water it might be expected that fuel cells subjected to multiple freeze/thaw cycles may undergo various forms of degradation leading to a decay in fuel cell performance. Possible degradative processes taking place as a result of the formation of ice particles within membrane and electrode structures may include: (i) rupture of the PEM electrolyte layer leading to gas leaks from the anode compartment to the cathode compartment or vice versa; (ii) delamination at the electrocatalyst layer/membrane electrolyte interface giving rise to a reduction in the intimate contact required between electrocatalyst particles and the PEM electrolyte, and (iii) delamination at the electrocatalyst layer/gas diffusion layer interface which may cause an increase in electrical resistance and less effective gas distribution within electrode structures. Thus the second objective of the work carried out was to determine

the effect of multiple freeze/thaw cycles on the performance of PEM fuel cells operating on pure hydrogen/oxygen as reactants.

Another challenge to a fuel cell in vehicular use is load following. In normal commuting an automobile engine is frequently and repeatedly called on to go from idle to a significant fraction of maximum power in a few seconds, or less. While fuel cells are known to be efficient at load following, the limit of their response rate is not clearly defined. A third objective of this work was to determine how fast a relatively large PEM fuel cell can be brought to full power.

EXPERIMENTAL

All fuel cell data were collected using a Lynntech Model 1000 Fuel Cell Test System (11). This is a fully automated microprocessor controlled instrument which logs all cell operating data, including temperatures, directly to disk for processing. This processing can be carried out on the same unit, while data collection continues, or off-line using a separate computer. For the rapid start experiments a storage oscilloscope (Tektronix Model 2212) was used to record the data and a rapid triggering power supply with a clean step function output was used to control the load bank.

For CO₂ and CO tolerance measurements, performance characteristics were obtained from a 25 cm² active electrode area single cell PEM fuel cell. Six fuel gas compositions were used in these experiments; (i) pure H₂; (ii) H₂ + 25 vol% N₂; (iii) H₂ + 25 vol% CO₂, and (iv) H₂ + 25 vol% CO₂ + 10, 28, or 94 ppm of CO with air as oxidant. In all cases, gas flows were adjusted to maintain a stable 2:1 stoichiometry for the hydrogen fuel.

The freeze/thaw cycling data were collected using a similar single cell PEM fuel cell operating on pure H₂ and O₂. Freezing to -10 °C was accomplished using a standard laboratory freezer. For extreme low temperature testing (-78 °C), a standard ice chest was used, with dry ice as the coolant. The entire test cell was frozen in all cases.

The rapid start data were collected using a two-cell short fuel cell stack, with a significantly larger active electrode area, 300 cm^2 (10 cm x 30 cm). This fuel cell stack was mounted on the test system in the normal manner. The storage oscilloscope was attached to read the stack current in parallel to the test system and the fast triggering power supply was connected to operate the system's load bank. (The standard load bank in this test system was designed with microsecond switching capability.)

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RESULTS AND DISCUSSION

Gas Composition Effects

One effect that is present in any fuel cell operated with a fuel gas that is not pure hydrogen is a Nernstian voltage loss due to the dilution of the gas. While this value is small (9.6 mV for a 50% reduction in hydrogen concentration), it is none the less real, and must be considered as part of the baseline in evaluating any other effects in a mixed gas system. The magnitude of this effect is illustrated in Figure 1. This figure shows the effect of replacing pure hydrogen with a mixture containing 75 vol% H₂ and 25 vol% N₂. The 25 vol% level was selected to simulate the inert gas (CO₂) concentration present in ideal steam reformed methanol. As expected the loss in performance is small.

In principle, CO₂, with no fuel value, should be equally inert at the anode of a CO₂-rejecting PEM fuel cell. Unfortunately, as has already been recognized, this is not the case (12). As pointed out earlier, the same platinum catalyst that serves as an oxidation catalyst for the hydrogen also serves to catalyze the reaction of CO₂ with the adsorbed hydrogen to form surface species which poison the active sites on the surface of the platinum catalyst. This is clearly shown in Figure 2, which contains polarization curves obtained with the same membrane and electrode assembly (M&E) operating on pure hydrogen, hydrogen diluted with nitrogen, and hydrogen diluted with CO₂. If the CO₂ were truly inert, the curves for hydrogen diluted with nitrogen and hydrogen diluted with CO₂ is the result of the chemical interactions occurring between the gas and the adsorbed hydrogen on the surfaces of the highly dispersed platinum electrocatalyst particles.

The effect of CO content in the hydrogen fuel gas stream on the performance of carbon-supported high surface area platinum electrocatalyst is shown in Figure 3. Carbon monoxide is much more detrimental to the performance of the cell compared to CO_2 , even though it is present at much lower concentrations. The CO poisoning effect, as evidenced by the lower hydrogen oxidation currents, increased with increasing CO content in the hydrogen gas fed to the cell. The presence of only a small amount (10 ppm) of CO gives rise to a significant decline in the performance of the fuel cell.

The performance of PEM fuel cells having carbon-supported platinum as the anodic electrocatalyst was observed also by other investigators (13,14) to be lowered considerably, even in the presence of very low levels of CO (<5 ppm) in the hydrogen fuel stream, particularly at high current densities (>500 mA cm⁻²). For CO concentrations greater than 1 ppm, at the relatively low operating temperature (75-95° C) of the PEM fuel cell, platinum electrocatalysts rapidly lose their activity and are unable to support the

high current densities necessary for acceptable power-to-weight or power-to-volume ratios.

To maintain high power densities over extended periods of time, the concentration of CO in the reformate gas must be maintained at levels less than 1 ppm. In addition to selective catalytic oxidation of CO in the reformer output, a number of alternative methods have been considered. Pressure swing absorption and gas-permeable membrane separation, which require very high pressures to achieve the necessary separation, are impractical for transportation applications (3). Two approaches which are attractive include the already-mentioned selective oxidation over a supported platinum catalyst (1) and direct injection of a small amount of air (or oxygen) to the fuel cell anode, along with the hydrogen fuel gas stream (13).

An alternative approach to avoid the degradation in performance of PEM fuel cells, brought about by the presence of CO and other small organic molecule contaminants, is to develop contamination-tolerant anode electrocatalysts. Some success in this direction has been reported recently for a Pt-Ru alloy with a Ru surface composition of ~ 50 atom% Ru (15) and for a Pt₃Sn alloy electrocatalyst (16). In the case of the former alloy material, a uniquely active state of OH_{ads} on Pt-Ru pair sites supported a bifunctional mechanism for the CO electrooxidation process and brought about a shift in the CO electrooxidation current of -0.25 V compared to pure platinum. The potential for the onset of CO oxidation on a Pt₃Sn alloy electrode with a Sn surface concentration of ~ 20 atom% was ~ 0.5 V lower than for pure platinum and ~ 0.15 V lower than for the Pt-Ru alloy.

Freeze/Thaw Cycling of a Fuel Cell

The effect of freezing on the performance of a PEM fuel cell was determined over a wide range of freezing conditions. This was accomplished by placing a complete single cell fuel cell, the performance of which had previously been characterized, in a standard laboratory freezer and leaving it for 24 hours. Upon thawing and restarting the performance was unchanged, as illustrated in Figure 4.

This was followed with nine additional cycles of freezing and thawing, with the time spent in the frozen state varied from a few hours to a few days and the rate of thawing varied from an hour to a day. In one experiment, the cell was started while still frozen. While the cell had no significant output until it thawed (at about -3 °C), when the cell heated up to normal operating temperature it performed as before. As shown in Figure 5, these treatments had no effect on cell performance. These cycles were followed by a more extreme test, freezing the cell, and then packing it in dry ice for 24 hours at -78 °C. This exposure had no more of an effect on cell performance than did freezing it at -10 °C.

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This immunity to freeze damage is in agreement with a recent publication where a similar test was carried out, although under less extreme conditions (17). It is clear that PEM fuel cells can stand up to the rigors that are likely to be encountered in service during extremely cold weather conditions.

Load Following with a Fuel Cell

The results of the load following tests are shown in Figures 6 and 7. For normal vehicular service, going from idle to full power in half a second is more than adequate. When the start-up of a PEM fuel cell is viewed on a time scale of a half second, as presented in Figure 6, the stack appears to respond instantly. However, when the time scale is expanded by two orders of magnitude, as demonstrated in Figure 7, it can be seen that the response is fast, but not instantaneous. The actual time from applying the trigger signal until the stack reached its full sustainable power level, considered to be the level at the extreme right in Figure 7, was 0.34 msec. This is an average value for eight tests, with the individual tests varying from 0.25 to 0.40 msec. These results are in good agreement with data obtained from a similar PEM fuel cell under pulsing conditions (18). In this case, full power was achieved in approximately 0.2 msec after applying a pulse to the fuel cell.

Figure 7 shows the current rising through a maximum, and then dropping back to the steady state value. This is a very repeatable phenomenon. It is the result of the delay in gas moving through the gas diffusion electrode to the active region. At the moment of start-up the entire electrode structure is filled with gas to the back pressure level and a substantial amount of current can be drawn without any significant motion on the part of the gas. As the gas closest to the active region is consumed, it has to be replaced. This requires gas motion. The right-hand portion of Figure 7, where the current gradually declines to a steady state value, represents the transition from the consumption of the gas stored in the electrode structure to the consumption of the gas that is being fed to the electrode.

CONCLUSIONS

PEM fuel cells have long been known to meet the environmental requirements for the next generation of light duty vehicles. The questions that remain are concerned with attaining the performance characteristics currently met by internal combustion (IC) engines. The results described here demonstrate that in at least two areas these characteristics can easily be met, or exceeded.

A fuel cell power source can go from idle to full power faster than an IC engine, or any power source that relies on the motion of mechanical parts. While the twelve

freeze/thaw cycles carried out here do not simulate even one full winter, the complete lack of degradation observed in these cycles, where any significant problems would be expected to show up, indicates that thermal cycling under freezing conditions should not be a major issue.

The fuel content question is somewhat more problematic. If a reformer system is to be used, it will be necessary to either suppress the CO concentration well below 10 ppm (in the fuel feed), or find an effective replacement CO-tolerant electrocatalyst for platinum. While great strides are being made in the latter area, there is still no complete solution.

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Figure 1. Cell potential-current density profiles for a 25 cm² active area single cell PEM fuel cell. M&E assemblies consisted of Nafion[®] 112 and low platinum loading electrodes (20 wt% Pt on C; 0.4 mg of Pt cm⁻²). Fuel and oxidant gases were: (\bullet), 100% H₂ / Air; (\blacksquare) 75% H₂ - 25% N₂ / Air. Fuel gases were flowed through the cell at twice stoichiometric at a pressure of 30 psi. Air at a pressure of 30 psi was flowed through the cell at four times stoichiometric. The cell temperature was 90°C.



Figure 2. Cell potential-current density profiles for a 25 cm² active area single cell PEM fuel cell. M&E assemblies consisted of Nafion® 112 and low platinum loading

electrodes (20 wt% Pt on C; 0.4 mg of Pt cm⁻²). Fuel gases used: (•), 100% H₂; (•), 75% H₂ - 25% N₂; (•), 75% H₂ - 25% CO₂ were flowed through the cell at twice stoichiometric at a pressure of 30 psi. Air at 30 psi was used as oxidant in each run and was flowed through the cell at four times stoichiometric. The cell temperature was 90°C.



Figure 3. Cell potential-current density profiles for a 25 cm² active area single cell PEM fuel cell. M&E assemblies consisted of Nafion® 112 and low platinum loading electrodes (20 wt% Pt on C; 0.4 mg of Pt cm⁻²). Fuel gases used: (•), 100% H₂; (•), 75% H₂ - 25% CO₂; (·), 75% H₂ - 25% CO₂; (·), 75% H₂ - 25% CO₂ - 10 ppm CO; (•), 75% H₂ - 25% CO₂ - 28 ppm CO; (•), 75% H₂ - 25% CO₂ - 94 ppm CO were flowed through the cell at twice stoichiometric at a pressure of 30 psi. Air at 30 psi was used as oxidant in each run and was flowed through the cell at four times stoichiometric. The cell temperature was 90°C.



Figure 4. Effect of freezing on the performance of a single cell PEM fuel cell having an active electrode area of 25 cm². The M&E assembly consisted of Nafion[®] 115 and unsupported Pt black (4 mg of Pt cm⁻²) electrocatalyst on gas diffusion electrodes.



Figure 5. Effect of freeze/thaw cycling on the performance of a single cell PEM fuel cell. This is the same cell as in Figure 4, but after additional freeze thaw cycles, including 24 hours packed in dry ice.



Figure 6. Digitized oscilloscope trace showing a 300 cm^2 fuel cell stack powering up from open circuit to about 1 A/cm². The lower trace is the triggering signal (left-hand scale) and the upper trace is the current from the cell (right-hand scale). On this time scale it appears instantaneous.



Figure 7. The same event and display as shown in Figure 6, but with the time scale expanded by two orders of magnitude. The actual time from trigger signal to achieving the sustained current is 0.34 msec.

ADVANCED COMPOSITE POLYMER ELECTROLYTE FUEL CELL MEMBRANES

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A new type of reinforced composite perfluorinated polymer electrolyte membrane, GORE-SELECTTM (W. L. Gore & Assoc.), is characterized and tested for fuel cell applications. Very thin membranes (5-20 μ m thick) are available. The combination of reinforcement and thinness provides high membrane conductances (80 S/cm² for a 12 μ m thick membrane at 25°C) and improved water distribution in the operating fuel cell without sacrificing longevity or durability. In contrast to non-reinforced perfluorinated membranes, the x-y dimensions of the GORE-SELECT membranes are relatively unaffected by the hydration state. This feature may be important from the viewpoints of membrane/electrode interface stability and fuel cell manufacturability.

INTRODUCTION

To a large extent, the evolution of the polymer electrolyte fuel cell (PEFC) is linked to ionomeric membrane advances. Perhaps the single most significant advancement in PEFC membrane technology was the replacement of the polystyrene sulfonate based membranes, as used in the Gemini program, with perfluorinated membranes that provided substantially improved durability, longevity, and performance.¹ These perfluorinated membranes, such as NafionTM 117 (from DuPont), were originally developed for chlor-alkali or other non-fuel cell applications. Aside from some incremental advances tailored towards fuel cell applications, the membrane products from DuPont, Dow and Asahi Glass employed at present for fuel cell applications are fundamentally similar to the perfluorinated membranes introduced in the 1960's. Although some advantages were gained by lowering the membrane equivalent weights (EW), perhaps the most substantial improvements in fuel cell performance were realized by simply thinning the membranes.^{3,4} The advantages gained with this simple strategy include lower membrane resistance, lower material utilization (which obviously relates to costs), and improved hydration of the entire membrane. The latter is facilitated by the enhanced back-diffusion of water from the cathode side of the membrane to the anode side, the latter of which tends to become dehydrated as a result of the electroosmotic drag.² However, there is a limitation to the extent to which such membranes can be thinned because of difficulties with durability and reactant cross-over.

Conceivably, some of these difficulties could be alleviated using reinforced membranes. Fluoroionomer membranes reinforced with woven polytetrafluoroethylene (PTFE) are used in industrial electrochemical membranes (such as Nafions 324 or 417). The relatively coarse weave of the woven PTFE reinforcements results in membranes that are much too thick for high fuel cell performance. Some experimental non-woven

PTFE/fluoroionomer composite membranes have been formulated for fundamental ion transport studies^{5,6} and for investigations of other properties relevant to chlor-alkali^{7,8} and fuel cell⁹ applications.

Advancements in materials and processing technology have resulted in the introduction of a new series of PTFE/fluoroionomer composite membranes from W. L. Gore and Associates, Inc. under the GORE-SELECT trademark. Samples of these membranes were provided in nominal thicknesses of about 5, 10, and 20 μ m. The membranes were supplied with either 900 or 1100 EW ionomeric components.

MEMBRANE CHARACTERIZATION

The GORE-SELECT reinforced membranes are transparent, very much like the nonreinforced Nafion or developmental Dow membranes. The membrane appears to be uniform and homogeneous. Nevertheless, some of the physical properties of the membrane reflect a preferred orientation, as is observed with the extruded Nafion 117 product.

Membrane	<u>EW</u>	<u>Thickness</u> (µm)	Ionic <u>Fhickness Conductivity Con</u> (μm) (S/cm) (S	
Nafion 117	1100	200	0.14 ^a , 0.10 ^b	5-7
Nafion 112	1100	60	0.10 ^b	17
Dev. Dow	800	100	0.15 ^b	15
GORE-SELECT	1100	20	0.052 ^a , 0.053 ^b	26
GORE-SELECT	1100	5	0.028 ^a	56
GORE-SELECT	900	12	0.096 ^b	80

Table I. Membrane ionic conductivities and conductances.

^a z-direction, sulfuric acid immersed sample measured with a four-point probe

^b x-y direction, high-frequency measurement for membrane immersed in deionized water.

Ionic Conductivities

For comparison, the ionic conductivities of several thicknesses of GORE-SELECT membranes and various other commercial membranes were measured using four-point probe and high-frequency response methods. All membrane samples were boiled for at least 30 minutes in deionized water prior to use. Transverse (z-direction) ionic conductances of sample membranes were obtained using a standard "Kelvin" four-point probe (Palico Model 9100-2) in which the membrane samples were immersed in 1 M sulfuric acid maintained at 25° C. Longitudinal (x-y) conductances of the membranes in the fully hydrated state were provided by the real axis intercept of a 1 Hz to 10 kHz impedance spectrum using a Solatron 1260 Frequency Response Analyzer.¹⁰ Results for several thicknesses of GORE-SELECT membrane are compared to values obtained for

developmental Dow and Nafions 112 and 117 in Table I. Although the conductivities of the higher equivalent weight GORE-SELECT membranes are much lower than the unreinforced Nafion membranes, the conductances are significantly higher due to the thinness of the reinforced membranes. The similarities in the x-y and the z direction conductivities for the 20 μ m thick GORE-SELECT membrane suggest that the material is relatively isotropic, so far as ionic conductivity is concerned. However, it should be noted that sulfuric acid imbibed in the membranes during the four-point probe experiments may have influenced the measured conductivities.

Water Content and Hydraulic Permeability

Water contents of several commercial and GORE-SELECT membranes are listed in Table II. The water contents of the GORE-SELECT membranes are surprisingly high compared to the other commercial membranes considering they possess a substantial nonionic reinforcement component. The water content variations within the GORE-SELECT membrane values roughly correspond to the differences in the EW's.

Membrane	EW	<u>Thickness</u> (µm)	Water Uptake ^a (%)	Hydraulic <u>Permeation</u> b (Relative Rate)
Nafion 117	1100	200	34	1.0
Nafion 112	1100	60	34	3.3
Dev. Dow	800	100	56	4.0
GORE-SELECT	1100	20	32	3.7
GORE-SELECT	900	12	43	12.9

Table II. Membrane water content and hydraulic permeability.

^aExpressed as percent of membrane dry weight.

^bHydraulic permeability relative to Nafion 117

Table II also shows that the hydraulic permeability of the 20 μ m thick 1100 EW GORE-SELECT membrane is about 4 times as great as Nafion 117, much as might be expected for a composite material that is about one-ninth as thick. On the other hand, the permeability of the 12 μ m thick 900 EW membrane is somewhat higher than expected based on the 20 μ m thick membrane results. Indeed, the general trend across all types of membranes suggest that the lower equivalent weight (and corresponding higher water uptake) enhances the water transport, after factoring in the relative thicknesses.

Shrinkage

The x and y direction dimensional stabilities of the GORE-SELECT and Nafion 117 membranes were measured upon dehydration using a Thermomechanical Analyzer 2940. A predetermined force was applied to 25.4 mm by 3 mm samples that were first fully hydrated by boiling in deionized water for 30 minutes. A quartz probe in contact with the samples detected the changes in sample dimensions during drying. The amounts of shrinkage are noted in Table III.

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Membrane	<u>Thickness</u> (µm)	Direction (%)	Machine Direction (%)
Nafion 117	200	-11.80	-10.55
GORE-SELECT	20	-2.95	-2.90

Table III. Membrane shrinkage upon dehydration.

Tensile strengths

The tensile strengths of membrane samples were measured using an Instron Model 1122 instrument, in accordance with ASTM D 638-91. Membrane samples were oven dried, tested, fully hydrated by boiling in deionized water and then retested. Table IV provides the average normalized stresses at maximum load for the various sample conditions.

Nafion 117 and GORE-SELECT tensile strengths are fairly similar in the dried state. Upon hydration, however, the Nafion 117 ionomer loses over half of its strength due to the "plasticization" of the membrane by the rather substantial water component. While the ionomeric component of the GORE-SELECT membrane would be similarly compromised, the loss in the hydrated membrane strength is quite modest because the reinforcement component of the membrane is unaffected by the presence of water.

	Table IV.	Membrane	tensile	strengths.
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		Transverse Direction			Machine Direction		
Membrane	<u>Thickness</u> (µm)	<u>Dry</u> (Pascals	$\frac{Wet}{10^7}$	<u>Loss</u> (%)	<u>Dry</u> (Pascals	$\frac{Wet}{x \ 10^7}$	<u>Loss</u> (%)
Nafion 117	180 - 200	2.47ª	0.95 ^b	62	2.98 ^a	1.39 ^b	53
GORE-SELECT	20 ^c	2.39	1.77	26	3.44	3.25	6

^a Based on a 180 µm dry thickness.

^b Based on a 200 µm fully hydrated thickness

^c Thicknesses are relatively invariant to hydration state.

FUEL CELL TESTING

Several of the available membrane thicknesses were tested in 5 cm² fuel cell hardware. The single-cell components, hardware, testing equipment, and membrane catalyzation process for low platinum loadings (< 0.2 mg Pt/cm²/electrode) are for the most part similar to those described previously.¹¹ A 20 µm thick GORE-SELECT membrane, with an 1100 EW ionomeric component, was catalyzed in this manner with 0.14 mg Pt/cm²/electrode. Polarization and high frequency resistance curves for the cell operating on H₂/Air after about 210 hours of continuous operation are shown in Figure 1. Typical humidification conditions of anode/cathode humidifiers of 105/80°C were used. Under these conditions, Figure 1 suggests that the cell evidently dried out slightly at low

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current densities, but quickly recovered with the increase in current density. Fairly quickly, the cell resistance stabilized at a low value of only 0.06 Ω cm², of which, Table I suggests that about 0.04 Ω cm² is attributable to the membrane. Shortly after the data for Figure 1 were acquired, a testing equipment mishap terminated the test (after about 240 h total)

More extensive testing was accomplished with a 12 µm thick, 900 EW (ionomeric component) GORE-SELECT membrane with a GORE-CARBEL[™] carbon composite cathode that was catalyzed with 0.2 mg Pt/cm² at W. L. Gore and an anode prepared at Los Alamos. Polarization curves for varying reactant pressures are shown in Figure 2. At the higher pressures, about 0.8 W/cm² maximum power was attained. Even at a low cathode air pressure of only 1.2 atm, the cell yielded a commendable 0.45 W/cm². Life test performance (ongoing 3000 h), as indicated by the current density at a continuous 0.5 V $(T_{cell} = 80^{\circ}C, H_2/Air = 2.8/4.2 \text{ atm})$, is shown in Figure 3. Long term performance of the cell has been quite good and the high-frequency cell resistances were also stable and uniformly below 0.06 Ω cm². The early variations in the current density evident in Figure 3 are primarily due to variations in the humidification conditions. In this cell, lower levels of humidification than are typically optimal for 5 cm² cells provide improved performance when operating under maximum power conditions. For example, the increase in performance evident at about 700 h resulted after the cathode humidifier temperature was decreased from 80° to 25°C. In contrast, lowering the anode humidifier temperature substantially below 90°C does impair the performance of the cell. It still may be possible to realize a non-humidified system with these membranes on a larger scale, since we find that larger cells invariably require less external humidification than these 5 $\rm cm^2$ ones.

Concerns of excessive reactant cross-over or membrane failure are common with such thin membranes. Even minute defects could become potential failure sites in very thin membranes. While routine testing for pin-holes eliminates some difficulties, composite membranes have a natural advantage in minimizing weak spots. In the limited testing accomplished, the cells with the 12 and 20 μ m GORE-SELECT membranes, catalyzed with thin-film catalysts layers by either the Los Alamos process¹¹ or at W. L. Gore, demonstrated reasonable open circuit voltages of at least 0.92 V and did not experience membrane failures. An even thinner membrane, 5 μ m thick, is available but only limited testing has thus far been accomplished.

DISCUSSION

For the most part, the fuel cell membranes currently under consideration for commercial products are not particularly thin because of concerns about durability and cross-over in the operating cell. However, these types of high performance membranes are not reinforced and depend upon the entanglement of the ionomer chains for their structural integrity. Naturally, mechanical properties are compromised when the membranes are well hydrated and heated somewhat, such as might be expected in fuel cell applications. While it is possible to obtain good, long term cell performance with some of the thin, non-reinforced, perfluoroionomer membranes,¹¹ they are clearly more susceptible to cross-over and failure than their thicker brethren. On the other hand, in the case of a reinforced membrane, the structural element is relatively unaffected by heat and hydration and can provide a stable base for the ionomeric element. Table IV demonstrates the increase in strength of a fully hydrated membrane over that of the

relatively robust 1100 EW Nafion product. This advantage is not only relevant for the operating fuel cell but also in membrane/electrode assembly fabrication and cell assembly.

A significant advantage of the reinforced GORE-SELECT products is that the dimensional stability of the membranes in the x-y plane is relatively unaffected by the hydration level of the membrane, as is shown in Table III. This may be important in types of fuel cell electrodes in which the catalyst layer is bonded to a relatively rigid structure that will not easily accommodate variations in the membrane hydration state and may tend to delaminate. The x-y stability may be even more advantageous from a manufacturing point of view. A membrane that maintains the same dimensions independent of the hydration state should simplify the manufacturing process, increase part consistency, and improve product reliability.

While there may be some material consumption factors, the primary motivation for developing thin membranes is to enhance fuel cell performance. This is realized by not only a decrease in the membrane resistance but also by more effective water management within the membrane. As shown in Table I, the conductances of the GORE-SELECT membranes are substantially higher than Nafion 117, the baseline material for comparison. Although Table I also demonstrates that the inherent bulk conductivities of the GORE-SELECT membranes are relatively low, their high membrane conductances are made possible by the extreme thinness of the membranes. Table IV suggests that water transport is not adversely affected by the presence of the reinforcement component. Good water transport is also indicated in the operating cells by a lack of increase in the cell resistance with current density, as is shown in Figure 1.

CONCLUSION

Conventional high performance fuel cell membranes require that both structural and electrochemical functions be achieved by a single material. As is observed in the chlor-alkali industry, there are advantages to using membranes with distinct structural and functional components. This dual-component advantage has apparently been realized for fuel cells with the GORE-SELECT membranes. The thin, yet durable, membranes made possible by the composite construction provide the high ionic conductances and enhanced water transport necessary for high performance fuel cells. Other desirable properties include minimal dimensional changes during hydration/dehydration cycles and the maintenance of good mechanical properties in the fully hydrated membrane.

ACKNOWLEDGEMENTS

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FIGURES



Figure 1. Polarization and high-frequency resistance curves for a 0.14 mg Pt/cm² catalyzed 20 µm thick, 1100 EW (ionomeric component) GORE-SELECT membrane. T_{cell} $= 80^{\circ}$ C, H₂/Air = 2.8/4.2 atm.

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Figure 2. Polarization curves for a 0.20 mg Pt/cm² catalyzed 12 μ m thick, 900 EW (ionomeric component) GORE-SELECT membrane at various reactant pressures. $T_{cell} = 80^{\circ}$ C.



Figure 3. Life test current density at 0.5 V of the cell shown in Figure 2. $T_{cell} = 80^{\circ}C$, $H_2/Air = 2.8/4.2$ atm.

A H₂/O₂ FUEL CELL USING ACID DOPED POLYBENZIMIDAZOLE AS POLYMER ELECTROLYTE

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ABSTRACT

Phosphoric acid doped polybenzimidazole (PBI-poly[2,2'-(mphenylene)-5,5'-bibenzimidazole]) has been investigated for use in a H_2/O_2 fuel cell. The prototype fuel cell test results show that the PBI fuel cell worked quite well at 150°C with atmospheric pressure hydrogen and oxygen which were humidified at room temperature. No membrane dehydration was observed over 200 hours operating. The maximum power density of this prototype fuel cell was 0.25 W/cm² at current density of 700 mA/cm². Further improvement of the cell performance is to be anticipated by properly impregnating the electrode structure with the polymer electrolyte. The advantage of the H₂/O₂ fuel cell using PBI as polymer electrolyte is that the cell design and the routine maintenance can be significantly simplified because of the low electro-osmotic drag number and good proton conductivity of the PBI membrane at elevated temperature.

INTRODUCTION

Fuel cells employing a solid polymer electrolytes such as perfluorosulfonic acid polymer electrolyte (Nafion[®]) have been receiving more and more attention due to their promise for high energy density power plant for both stationary or mobile applications. The main features of the polymer electrolyte fuel cell (PEFC) are pollution free operation, less corrosion and high power density. During the last five years, many efforts were made to decrease the noble metal catalyst loading and improve the conductivity of the polymer electrolyte[1-4]. Gottesfeld et. al.[1,2] and Taylor et. al.[3] reported that the catalyst loading can be deceased to as low as 0.05-0.15mg/cm² with a fuel cell performance similar to that of a high loading PEFC (4mg/cm² Pt). Since the Nafion[®] type of polymer electrolytes usually have a large electro-osmotic drag number, water is moved from the anode side to the cathode side when cell is operating, resulting a large cell voltage loss due

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to the dehydration of the membrane. In order to adequately hydrate the membrane, these cell must be operated under intensive gas humidification (reactant gas saturated at 100-105°C), though the cell operating temperature is 80°C. Therefore the water management is critical for these PEFC to achieve a high energy efficiency. There are several modeling and experimental studies published[5-9] that discuss the issues of the water and heat management of this kind of PEFC.

There is a motivation to increase the cell operating temperature in order to enhance the reaction kinetics and depress the electrode poisoning, for instance, when using impure reformed hydrogen or when the fuel is methanol. For such an application, a new polymer electrolyte which can be operated at elevated temperature is required. Savinell et. al [10] proposed that the polybenzimidazole (PBI) can be used in PEFC as a polymer electrolyte when the PBI was doped with a strong acid such as phosphoric acid or sulfuric acid. PBI is a basic polymer (pKa=5.5) and it can be easily doped with a strong acid to form a single phase polymer electrolyte. The doping level, for instance, could be as high as five phosphoric acid molecules per polymer repeat unit. The results of the NMR spectroscopy show that phosphoric acid sorbed inside the PBI membrane is relatively immobilized as compared to free phosphoric acid. The solid-state NMR spectra reveals that there is an interaction between PBI and phosphoric acid[11]. The acid doped PBI membrane exhibits good proton conductivity, low gas permeability, excellent oxidative and thermal stability, and good mechanical flexibility at elevated temperature (200°C). The most interesting feature of the PBI is that it has an almost zero electro-osmotic drag number[12], compared to the drag number of 0.6-2 for Nafion[®] membrane[13,14]. This means that when the protons transport through the PBI membrane, they do not carry water with them. This unique feature of the PBI allows the PBI fuel cell to be operated under a high temperature and a low gas humidification without membrane and anode dehydration. Since a PBI fuel cell does not have the water management problem, the cell design and the routine maintenance can be significantly simplified. These properties of acid doped PBI polymer electrolyte are promising for applications of PEFC, including the hydrogen/oxygen fuel cell and the direct methanol fuel cell.

This paper presents the results of a H_2/O_2 fuel cell employing the acid doped PBI membrane as the polymer electrolyte. The PBI fuel cell was operated at 150°C using hydrogen and oxygen or air at atmospheric pressure. The effects of the gas humidification, and air on the cell performance were examined. The stability of the electrodes and the polymer electrolyte were examined in tests of several hundred hours duration. Different methods to prepare membrane/electrode assemblies were evaluated for the hydrogen electrode and the oxygen electrode, respectively.

EXPERIMENTAL

Polybenzimidazole (Hoechst Celanese) films were cast from a solution of the high molecular weight (HMW) PBI (25,000 amu) in dimethylacetamide (DMAc). The films

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were then doped by immersion in a 11M phosphoric acid solution for at least 24 hours. The resulting doping level is approximately five phosphoric acid molecules per polymer repeat unit. The film thickness after doping were about 0.008 cm.

E-TEK electrodes (The Electrosynthesis Co., Inc.) with a Pt loading of 0.5mg/cm^2 on carbon and homemade Pt black electrodes with Pt loading of 2mg/cm^2 were used. The membrane/electrode (M&E) assemblies were formed by hot pressing the electrodes on an acid doped PBI membrane at 150° C, 2.2×10^4 kPa for 10 min. The M&E assemblies were then impregnated with phosphoric acid by adding few micro-liters of 5M H₃PO₄ solution on the gas backing side, and letting the acid solution penetrate into the electrode structure. The function of added acid is to soften the PBI/electrode interface to make ionic contact when the electrode is heated to 150° C. Since the ionic conductivity of the electrode is important to the electrode performance, several other methods to form M&E assembly were tested to investigate the effect of the polymer loading within the electrode structure on the electrode performance.

One method to add electrolyte to the electrode structure is to impregnate the electrode with 10% PBI solution (HMW PBI in DMAc with 2% LiCl). To help the PBI solution penetrate into the electrode structure, the electrodes were placed in 10% PBI solution under vacuum at room temperature, and then repressurized to 1 atm. They then were dried under vacuum at room temperature. Electrodes impregnated with 10% PBI solution increased in weight by 12%. Two impregnated electrodes were attached to an undoped PBI membrane with a small amount of solvent DMAc and pressed at 100°C and 8.8×10^3 kPa for 2 min to form M&E assembly. Finally the M&E assembly was immersed in DI water for four days to extract LiCl, and then whole M&E assembly was doped with H₃PO₄.

In a second method, instead of impregnating electrodes first, the electrodes were directly glued on a undoped PBI membrane with 12% PBI solution (HMW PBI in DMAc with 2% CH₃COOLi) at 100°C and 8.8×10^3 kPa for 2 min to form the M&E assembly. It is expected that when the electrodes are glued directly onto the PBI membrane, some of PBI solution will penetrate into the electrode structure. Like the first method, the salt was then extracted with DI water for four days and then the M&E assembly was doped with H₃PO₄. In both the first method and the second method, the PBI membranes are doped after forming M&E assembly. While doping the M&E assembly with H₃PO₄, the PBI membrane formed wrinkles due to its expansion upon adsorbing acid and water. Therefore these methods may not be suitable to prepare large M&E assemblies.

The third method eliminates membrane expansion. The electrodes were first brushed by a dilute PBI solution (HMW PBI in DMAc with 2% CH₃COOLi). After the electrodes were impregnated with PBI solution, they were dried at 80°C for 2 hours and then the lithium salt was washed out by boiling the electrodes in DI water. The electrodes

were kept in clean DI water four days. Before the electrodes were hot pressed onto a PBI membrane, they were doped with 5M H₃PO₄. Then the electrodes were hot pressed on an acid doped PBI membrane at 150°C, 2.2×10^4 kPa for 10 min. Since this method uses doped PBI membrane to form the M&E assembly, it significantly reduces the stress between electrodes and membrane. This method appears to be more suitable for preparing large size electrodes.

All the electrochemical experiments were carried out in a single cell test station. A drawing of the single cell is shown in Fig. 1. The fuel cell hardware consisted of two PTFE blocks supported by two stainless steel plates at the outside. The gas distribution channels and feed-throughs were machined into the PTFE blocks. The whole construction was held together by four threaded studs with nuts at each end. At the anode side, a small hydrogen fed gas diffusion electrode (E-TEK electrode 0.5 mg/cm² Pt on carbon) was used as the reference electrode and was found to operate satisfactorily. The potential of this reference electrode was assumed to be equivalent to the reversible hydrogen electrode (RHE), and all potentials reported are with respect to this reference electrode. The whole fuel cell hardware was placed in an oven and heated to 150°C. The reactant gases were humidified by bubbling through distilled water at room temperature or the temperature as specified. The pressures of the reactant gases were one atmosphere. The cell resistance was measured by a current interrupt method. All of the electrode polarization curves reported in this paper are iR corrected.

RESULTS AND DISCUSSION

1. Gas humidification effect

A typical cell polarization curve and iR free polarization curve for a one atmosphere pressure hydrogen/oxygen fuel cell are shown in Fig. 2. This PBI fuel cell demonstrates quite good performance even at a high operating temperature and a low gas humidification. It shows a maximum power density of 0.25 W/cm² at 700 mA/cm². The cell resistance of this fuel cell was about 0.45 ohm cm², corresponding to a membrane conductivity about 0.0167 ohm⁻¹ cm⁻¹. This value is consistent with the conductivity of PBI membrane measured by the four probe AC technique[10]. The cell resistance of the PBI fuel cell is large if compared to the cell resistance of a well hydrated Nafion membrane fuel cell at 80°C (0,1-0,2 ohm cm²)[8]. However, on consideration of the high operating temperature and low humidification, the performance of the membrane is quite significant. Moreover, the cell resistance could be further reduced by decreasing the membrane thickness because of the good mechanical properties of the PBI polymer film. The experiment demonstrates that the cell resistance is independent of gas humidification. According to electro-osmotic drag measurements[12], the water drag number is nearly zero. This unique feature of the PBI membrane allows the fuel cell to be operated at a very low humidification level. Under most conditions, the water produced at an operating cathode is sufficient to maintain the conductivity of the PBI membrane. One fuel cell was

operated with dry hydrogen and oxygen at a current density of 200 mA/cm^2 for over 20 hours with no performance decay observed. However, it was found that upon a slight increase of the humidification temperature of the hydrogen from room temperature to 48°C, the performance of the anode and cathode improved at high current density (see Fig. 3). This result indicates that increased humidification level of the electrode improves the ionic conductivity of the electrode. Thus, more active catalyst surface of the electrode is utilized for reaction.

2. Stability of the cell performance

Multi-hour discharge tests were conducted on PBI/electrode assemblies to investigate the stability of the PBI membrane and electrodes. In these tests, the cell voltage was kept constant, and the current density and the cell resistance were measured. A typical cell performance is shown in Fig. 4. Except for the first few hours, the cell performance is quite stable over 200 hours. The polarization curves of hydrogen and oxygen electrodes before the test and after 200 hours test are shown in Fig. 5. These curves show that the performance of oxygen electrode became better after 200 hours, and the performance of the hydrogen electrode was slightly degraded. In the first few hours, the cell performance slowly improved probably due to the water produced at the cathode which enhanced the membrane conductivity and the ionic conductivity of the electrodes. The cell resistance for this fuel cell was between 0.4-0.55 ohm cm² during the 200 hour test.

3. Air effect

Since air is a more realistic oxygen source, a PBI fuel cell was tested using air instead of oxygen. The cell performance is shown in Fig. 6. The open circuit potential of the cell decreases from 1.015V with oxygen to 0.970V with air. The cell voltages of this PBI fuel cell with oxygen or air are about 0.54V and 0.41V at a current density of 250 mA/cm², respectively. The cathode polarization curve with air parallels that with oxygen. An approximately 80 mV potential loss when using air instead of oxygen was observed because of the lower partial pressure of the oxygen in air.

4. The effect of the polymer electrode impregnating method on electrode performance

For a good gas diffusion electrode, it not only needs high catalytic activity and high electronic conductivity, but also requires high ionic conductivity. The latter may become more important in high temperature operation due to the decrease of the ionic conductivity of polymer electrolyte. In the conventional method of preparing the PBI M&E assembly, a small amount of phosphoric acid was added to the electrode structure to increase the ionic contact of the electrode/membrane. It was expected that the electrodes loaded with PBI polymer will have more stable performance and longer life time. Our simulation results[15,16] also show that for an agglomerated gas diffusion electrode there

is an optimal polymer loading for best electrode performance. Therefore, several methods to making M&E assembly were developed as described in the experimental section. These M&E assemblies were evaluated electrochemically as a hydrogen electrode and an oxygen electrode.

Figure 7 and Figure 8 show the electrode performance of these different assemblies for hydrogen oxidation and oxygen reduction, respectively. The performance of the electrode prepared by the first method (impregnated 10% PBI solution) was not as good as the electrode only impregnated with H₃PO₄ for both oxygen reduction and hydrogen oxidation. Since in this electrode PBI solution is added under a vacuum, the amount of the PBI in the electrode structure may be too much so that the electrode performance is limited by the mass transport of the reactant gases. The electrode prepared by the second method shows improved performance for hydrogen oxidation at high current density, but only slightly improved for oxygen reduction. It can be expected that when electrodes are glued by PBI solution, a small amount of PBI solution will penetrate into the electrode structure dependent on the viscosity of the PBI solution. The improved electrode performance is believe to be due to improved ionic conductivity within the electrode structure. The only disadvantage of this method is that the polymer loading is not reproducible and that the stress between the membrane/electrode interface is introduced due to acid doping after making the M&E assembly.

The third method was developed to eliminate the problem of membrane/electrode stress. Two different PBI solutions were used to impregnate the M&E assembly. For low polymer loading (0.3mg/cm²), 1% PBI solution was used and for high polymer loading (0.9 mg/cm²), 2% PBI solution was used. From Figures 7 and 8, it can be seen that the performance of the electrode impregnated with 1% PBI solution is not as good as that of the electrode impregnated only with H₃PO₄. However, the performance of the electrode impregnated with 2% PBI solution (0.9 mg/cm²) is better than any other electrodes for both hydrogen oxidation and oxygen reduction. The overpotential of this electrode decreases about 60-100 mV for hydrogen and oxygen in comparison to the electrode impregnated only with H₃PO₄. The lower performance of the electrode impregnated with 1%PBI solution could be caused by strong adsorption of PBI on catalyst surface. Since 1% PBI solution has a low viscosity, it can be easily penetrated into the electrode and be adsorbed on the active catalyst sites thus causing poor performance. Cyclic voltammetry of these electrodes indicate that the PBI polymer strongly adsorbs onto active surface sites and thus blocks the reaction. These results suggest that the electrode structure should be impregnated with only a small amount of PBI so that the electrode will have good ionic contact with the PBI membrane and will stabilize the phosphoric acid in the electrode structure, but will not block too many active catalyst sites. Using a PBI solution with proper viscosity to impregnate the electrode appears to be critical.

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SUMMARY

Phosphoric acid doped polybenzimidazole has been investigated for use in a H_2/O_2 fuel cell. Prototype fuel cell test results show that a PBI fuel cell works quite well at 150°C and with low gas humidification without membrane dehydration occuring for over 200 hours. Impregnating the M&E assembly with polymer electrolyte is critical to improving electrode performance. Since these results obtained from the non-optimal electrode structures, it can be expected that the cell performance could be further improved by optimizing the electrode structures and operating conditions. These preliminary results clearly demonstrate the new opportunity offered by acid doped PBI membranes and the potential benefits in the simplification of the cell design and the cell maintenance when an acid doped PBI membrane is used as the polymer electrolyte.

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Fig. 1. Schematic of single cell with an electrode area of 1cm².



Fig. 2. Cell polarization curve and iR free polarization curve from a PBI fuel cell. E-TEK electrodes (0.5 mg/cm² Pt on carbon). Hydrogen: 1 atm, humidified at 48°C and oxygen: 1 atm, humidified at 28°C. Cell resistance: 0.45 ohm. Cell operating temperature: 150°C.



Fig. 3. Polarization curves from a PBI fuel cell. E-TEK electrodes (0.5 mg/cm2 Pt on carbon). Oxygen: 1 atm, humidified at 28°C. Hydrogen: 1 atm, humidified at 28°C and 48°C, respectively. Cell operated at 150°C.



Fig. 4. Cell performance of PBI H_2/O_2 fuel cell at constant cell voltage 0.55V and 150°C. Anode: E-TEK electrode (0.5 mg/cm² Pt on carbon); Cathode: homemade electrode (2 mg/cm² Pt); all gases humidified at room temperature, 1 atm.



Fig. 5. Polarization curves of a PBI fuel cell before and after 200 hours of operation. Anode: E-TEK electrode (0.5 mg/cm² Pt on carbon); Cathode: homemade electrode (2 mg/cm² Pt); all gases humidified at room temperature, 1 atm. Cell operated at 150° C.



Fig. 6. Cell performance of a PBI H_2/O_2 fuel cell with oxygen or air. Anode: E-TEK electrode (0.5 mg/cm² Pt on carbon); Cathode: homemade electrode (2 mg/cm² Pt); all gases humidified at room temperature, 1 atm. Cell operated at 150°C.



Fig. 7. Polarization curves of hydrogen oxidation from electrodes impregnated with polymer electrolyte using different methods. E-TEK electrodes (0.5 mg/cm² Pt on carbon), hydrogen humidified at room temperature, 1 atm. Cell temperature 150°C.



Fig. 8. Polarization curves from oxygen reduction for electrodes impregnated with polymer electrolyte using different methods. E-TEK electrodes (0.5 mg/cm² Pt on carbon), oxygen humidified at room temperature, 1 atm. Cell temperature 150°C.

ELECTRO-OSMOTIC DRAG COEFFICIENT OF WATER IN POLYMER ELECTROLYTES AT ELEVATED TEMPERATURES

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ABSTRACT

The electro-osmotic drag coefficient of water in two polymer electrolytes was experimentally determined as a function of water vapor activity and current density for temperatures up to 200 °C. The results show that the electro-osmotic drag coefficient varies from 0.2 to 0.6 in Nafion[®]/H₃PO₄ membrane electrolyte, but is essentially zero in a phosphoric acid doped PBI (polybenzimidazole) membrane electrolyte over the range of water vapor activity considered. The near zero electro-osmotic drag coefficient found in PBI indicates that this electrolyte should lessen the problems associated with water redistribution in PEM fuel cells.

INSTRUCTION

In order to assure long term stable cell performance, it is important to maintain an optimal chemical species distribution in solid electrolyte fuel cells. We are currently investigating the use of polymer electrolytes for direct methanol fuel cells operating at temperature exceeding $100 \, {}^{\circ}C^{1,2}$. It is believed that operation at these temperature can minimize the effects of catalyst poisoning associated with strongly adsorbed intermediates e.g., CO and/or impurities, and significantly enhance electrochemical performance by increasing the catalyst activity. In PEM (proton exchange membrane) fuel cells, it is particularly critical to manage the water content in the polymer electrolytes to maintain sufficient proton conductivity and avoid cathode flooding and anode dehydration.

The motion of water through a polymer electrolyte in a methanol/air fuel cell can be ascribed according to concentrated solution theory^{3,4} to the gradient in the chemical potentials of water and methanol, and to water drag due to the movement of protons (proportional to the DC current). This latter water drag is referred to as the "electro-osmotic drag" and is quantified in term of the electro-osmotic drag coefficient,

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 $\xi = N_{H_2O} / N_{H_2O}$, indicating the number of water molecules moving with each proton in the absence of concentration gradients.

The electro-osmotic drag coefficient in Nafion[®] membrane electrolyte has been previously determined by measuring the flux of water across the membrane at constant current and fixed water concentration in the membrane by exposing the membrane on both sides to liquid water^{5,6}. In another study, the electro-osmotic drag coefficient has been determined over a wide range of water content by measuring the open-circuit potential of a concentration cell⁷. The water content in the Nafion[®] 117 was controlled by equilibrating the membrane with various partial pressures of water. Both measurements^{5,6,7} were carried out at room temperature and the electro-osmotic drag coefficient in Nafion membrane electrolyte was determined to be about $1 \sim 3$.

This study describes a different approach for the measurement of the electroosmotic drag coefficient which is particularly suited for higher temperature where water is a vapor. The electro-osmotic drag coefficient of water in polymer electrolytes was determined here as a function of water vapor activity, current density, and temperatures up to 200 °C.

EXPERIMENTAL

Nafion[®]117 membranes (acid form, DuPont, film thickness of 0.018 cm and equivalent weight 1100) were first boiled in distilled water for 4 hours, then treated in 10% hydrogen peroxide (H₂O₂) at 80 °C for 12 hours to oxidize organic impurities in the membrane, and subsequently boiled in distilled water again for 4 hours. The membranes were eventually equilibrated with 85% phosphoric acid (H₃PO₄) at 150°C for 12 hours.

Following phosphoric acid equilibration, the samples of the Nafion[®]/H₃PO₄ membrane electrolyte were stored in phosphoric acid until use. This treatment yields a phosphoric acid content, measured after withdrawing the membrane from the solution and lightly squeezing and wiping off its surface with a blotting paper, equivalent to ≈ 2 moles of phosphoric acid per mole of sulfonic acid in the membrane. Nafion samples treated in this way remain conductive at temperatures in excess of 100°C without resorting to pressurized conditions¹.

PBI (polybenzimidazole) membrane samples, which were cast from a solution of the polymer in dimethylacetamide (membrane thickness of ~ 0.009 cm and repeat unit weight 308), were first boiled in distilled water for several hours to remove impurities, and then doped by immersion in 71% phosphoric acid for at least 16 hours at room temperature. This treatment yields a phosphoric acid content of about five phosphoric acid molecules per polymer repeat unit.

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For the purpose of the electro-osmotic drag coefficient measurement, two E-TEK gas diffusion electrodes were hot-pressed on both sides of Nafion[®]/H₃PO₄ or PBI membrane electrolytes at 130 ~ 150 °C. The diameter of the E-TEK electrode was 1.27 cm corresponding to an area of about 1.27 cm².

The electro-osmotic drag coefficient was measured in a specially designed closed volume cell, shown in Figure 1. The cell consists of two chambers, a 2200 cm³ reservoir and a 175 cm³ small chamber, separated by the membrane electrolyte with the E-TEK gas diffusion electrodes placed on both sides. The apparatus was placed inside an oven and connected to a gas manifold system so that the temperature, pressure and composition of the gas phase in contact with the sample could be controlled.

Initially, both chambers were evacuated at the prescribed temperature, and then filled with hydrogen to the desired pressure. Finally, sufficient liquid water and/or methanol was injected into the reservoir via a septum to yield a water and/or methanol vapor partial pressure that was significantly higher than that in the small chamber. The pressure change (increase) in the small chamber was monitored by a MKS pressure transducer within the oven, and the results (in the absense of current) used to determine the permeability coefficient.

When both the reservoir and the small chamber were at equal hydrogen and water vapor pressures, the two E-TEK gas diffusion electrodes were connected to a PAR Model 173 potentiostat/galvanostat and a stable DC current was passed through the membrane. Hydrogen was consumed at the reservoir side (oxidation) and generated at the small chamber side (reduction). As protons were transported across the membrane, water was also dragged through the membrane from the anode to the cathode. The pressure change in the small chamber, due to the contribution of hydrogen generated on the cathode and the water dragged across the membrane along with the protons, was monitored by the MKS pressure transducer within the oven. The pressure versus time results were used to determine the electro-osmotic drag coefficient. After the measurement, the cell was evacuated again and filled with hydrogen and water and/or methanol vapor for the next run.

RESULTS AND DISCUSSION

In the osmotic drag measurements outlined above, the back diffusion of hydrogen can be neglected since the permeability of hydrogen is much less than that of water $(P_m(H_2O)/P_m(H_2) > 30$ in PBI⁹). Assuming that the water and/or methanol vapor and hydrogen follow the ideal gas law, the molar flux of water vapor passed across the membrane from anode to cathode, $N_{\mu,O}$, is given by:

$$N_{H,O} = \xi \frac{I}{FA} - \frac{P_m(P_{s,H,O} - P_{R,H,O})}{V_{STP}h}$$
(1)

where F and I are Faraday's constant and the total current passed across a membrane of thickness h and an area A, respectively. P_m is the permeability of water, which was determined from the initial permeability measurement. V_{STP} is the standard molar gas volume. $P_{S,H,O}$ and $P_{R,H,O}$ are the water partial pressures in the small chamber and the reservoir (cathode side and anode side), respectively. ξ is the electro-osmotic drag coefficient defined as the number of water molecule dragged by each proton. The first term on the right represents the flux of water dragged by the migrating protons, i.e. due to the effect of electro-osmotic drag coefficient ξ , the second term is due to the back diffusion of water resulting from the increase in the water partial pressure in the small chamber, dP_{S,H_2O} , due only to water vapor transport between time t and t+dt is:

$$dP_{s,H_{2}O} = \frac{RT}{V_{s}} \left(\xi \frac{I}{F} - \frac{AP_{m}(P_{s,H_{2}O} - P_{R,H_{2}O})}{V_{STP}h} \right) dt$$
(2)

where R and T are the gas constant and temperature. V_s is the volume of the small chamber. The initial condition for equation (2) is:

$$t = 0, \quad P_{R,H,O} = P_{S,H,O} = P_{0,H,O}$$
 (3)

Using the ideal gas law, at constant temperature a mass balance of water vapor between the small chamber and the reservoir can be written as:

$$V_{S}(P_{S,H_{2}O} - P_{0,H_{2}O}) = V_{R}(P_{0,H_{2}O} - P_{R,H_{2}O})$$
(4)

where V_R is the volume of the reservoir. Substituting equation (4) into (2) yields:

$$dP_{S,H,O} = \frac{RT}{V_S} \left(\xi \frac{I}{F} - \frac{AP_m (V_S / V_R + 1) (P_{S,H,O} - P_{0,H,O})}{V_{STP} h} \right) dt$$
(5)

Solving Equation (5) for the change in the partial pressure of water in the small chamber and applying initial condition (3) yields:

$$\Delta P_{S,H_2O} = \zeta \frac{IV_{STP}h}{FAP_m(V_S/V_R+1)} \left(1 - exp\left(-\frac{RTAP_m(V_S/V_R+1)}{V_SV_{STP}h}t\right) \right)$$
(6)

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The electro-osmotic drag coefficient, ξ can be determined by fitting the experimental data to Equation (6).

Typical data from an experiment using a Nafion[®]/H₃PO₄ membrane are shown in Figure 2. Curve 1 represents the pressure change in the receiving small chamber. Line 2 represents the calculated pressure rise from hydrogen transported due to the current, *I*. Curve 3 (correlated by line 4) represents the pressure rise in the small chamber due only to water vapor transport and is obtained by subtracting line 2 from curve 1. The solid line 4, which yields the electro-osmotic drag coefficient, represents the curve fit of Equation (6) to the pressure increase due to water vapor transport (curve 3).

The electro-osmotic drag coefficients of water in Nafion[®]/H₃PO₄ membrane electrolyte measured and calculated by the procedure discussed above are shown in Figure 3. The water vapor activity was changed by either maintaining a constant temperature of 125°C and varying the water partial pressure, or by maintaining a constant water partial pressure around 46.6 kPa and varying the temperature from 125 to 185°C. The results indicate that the electro-osmotic drag coefficient in Nafion[®]/H₃PO₄ membrane electrolyte is a strong function of water content in the membrane electrolyte, since the water content increases as the water vapor activity increases and the water vapor activity alone controls the amount of water sorbed in the membrane⁸. At the same water vapor activity, identical electro-osmotic drag coefficients of water is expected regardless of the change of the temperature. The electro-osmotic drag coefficient varied from 0.2 to 0.6 over the range of water vapor activity studied. These values are significantly lower than those expected from the hydration number of the proton and less than the corresponding room temperature values that have been previously reported in the literature^{5,6,7}. At 30°C, it has been reported that the electro-osmotic drag coefficients for water equilibrated Nafion membrane was between 1 to 3. The small electro-osmotic drag coefficient obtained here may indicate that instead of a simple proton migrating mechanism, conductivity by a Grotthus proton hopping mechanism may take place under the present conditions.

As another check on the validity of our experiment, several trials were run with varying current densities. Figure 4 shows that the electro-osmotic drag coefficients remain essentially constant for various levels of applied current density.

In PBI membranes, the results show that the pressure change due to water (the total pressure change in the small chamber minus the pressure change due to the hydrogen) is near zero (Figure 5), implying that the electro-osmotic drag coefficient is near zero in PBI membrane electrolyte.

Several trials were run at different water and methanol vapor partial pressures, different phosphoric acid doping levels in the PBI membranes and at different current densities. Table 1 shows that the electro-osmotic drag coefficients are essentially zero in

each case. There is some scatter in the data shown in Table 1. This may be due to changes in the structure of PBI membrane which probably occurs during the measurement processes (crystallization in the absence of water and/or the formation of pyrophosphoric acid in the system) and measurement errors. However, the near zero water electro-osmotic drag coefficient found here reflects the dense, non-porous nature of the phosphoric acid doped PBI membrane and indicates that the conductivity mechanism in the PBI membrane is different from that in the Nafion[®]/H₃PO₄ membrane electrolyte. The near zero water electro-osmotic drag coefficient also implies that PEM fuel cells with PBI membranes should lessen the difficulties associated with water redistribution that are observed in conventional PEM fuel cells employing Nafion or other perfluorosulfonic acid polymer electrolytes. This result is consistent with the relative insensitivity to the humidification conditions that has been observed during fuel cell tests with doped PBI membranes².

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DC current mA/cm ²	H ₃ PO₄ Content mol%	Р _{н20+Сн30н} kPa	H ₂ O:CH ₃ OH	Drag coefficient
40	480	40	1:0	0
40	480	28.8	1:0	0.039
40	480	70	1:0	0.025
47	480	61.3	1:0	0.028
55	480	34.7	1:0	0
40	310	36	1:0	0
40	310	26.7	1:0	0
40	500	44	4:1	0.09
40	500	52.5	2.08:1	0.085
40	500	44.9	2:1	0.073
40	500	45.6	1:1	0.034
40	500	44.3	1:0	0.059
40	500	43.6	10:1	0.08
40	500	44.7	7.6:1	0
40	500	37.9	6.7:1	0
40	500	44	1:0	0
40	500	44.9	5:1	0
40	500	48.9	3.6:1	0
40	500	46.9	2:1	0
40	500	35.7	1:1	0
40	500	32.3	0:1	0

Table 1. Osmotic drag Measurement in phosphoric acid doped PBI membrane

All measurement were carried out at 150 °C and about 54 kPa hydrogen partial pressure in the cell.



Figure 1. Schematic diagram of the electro-osmotic drag measurement cell, consisting of a 2200 cm³ reservoir and a 175 cm³ small chamber



Figure 2. Electro-osmotic drag coefficient measurement in Nafion[®]/H₃PO₄ polymer electrolyte at 125°C. The pressure change in the small chamber is indicative of the electro-osmotic drag coefficient. (1) Total pressure change in the small chamber. (2) Expected pressure change in the small chamber due to H₂ electrolysis based on i = 40 mA/cm². (3) Pressure change due to water drag, (=curve 1 - curve 2). (4) Results fitted to Eq. 6 with $\xi = 0.45$. Electrode area is 1.27 cm².



Figure 3. The electro-osmotic drag coefficient, ξ , in the Nafion[®]/H₃PO₄ polymer electrolyte at various water vapor activities. The activity was varied by changing the temperature maintaining $P_{H,O} \sim 46.7$ kPa and by varying the water vapor pressure maintaining a temperature of 125°C. Error bars represent estimation of accumulated errors from experimental measurements and equipment sensitivity.



Figure 4. Electro-osmotic drag coefficient, ξ , in the Nafion[®]/H₃PO₄ polymer electrolyte at various current densities maintaining $P_{H,o} \sim 46.7$ kPa and a temperature of 125°C. For error bars description see Figure 3 caption.



Figure 5. Electro-osmotic drag coefficient measurement in PBI doped with 480 mol% H_3PO_4 at 155°C. The pressure change in the small chamber is indicative of the electro-osmotic drag coefficient. (1) Total pressure change in the small chamber. (2) Expected pressure change in the small chamber due to H_2 electrolysis based on i = 55 mA/cm². (3) Pressure change due to water drag (=curve 1- curve 2). Electrode area is 1.27 cm².

PERFORMANCE OF PEM FUEL CELLS WITHOUT EXTERNAL HUMIDIFICATION OF THE REACTANT GASES

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ABSTRACT

Operation of polymer electrolyte fuel cells (PEMFC) without external humidification of the reactant gases is advantageous for the PEMFC system. This is, because this mode of operation eliminates the need of a gas-humidification subsystem which is a burden the fuel cell system with respect to weight, complexity, cost and parasitic power. We investigated the possible range of operating conditions for a PEMFC using dry H_2 /air by applying a simple model and it was found, that dry air, passing at the cathode, may be fully internally humidified by the water produced by the electrochemical reaction at temperatures up to 70 °C. The water distribution in the cell operated on dry gases is dominated by the back-diffusion of product water to the anode. The dominating water back diffusion allows for internally humidifying also the hydrogen and prevents drying out of the anode. With optimized membrane-electrode-assemblies (MEA), self-humidified cells achieve similar performance as cells withs standard MEA's and humdified gases. The performance of single cells and small stacks is investigated.

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INTRODUCTION

Due to their in principle high power density and efficiency, polymer membrane electrolyte fuel cells (PEMFC) are one of the most promising power sources for future electric cars and buses [1-3]. However at the present time cost and weight of the PEMFC system still have to be reduced to make this technique acceptable for the transportation application. Work in the past decade has focused on both issues, e.g. cost was greatly reduced through the development of low platinum loading electrodes [e.g. 4-6] and simultaneously the power density was increased [e.g. 7, 8]. Still, the state of the art PEMFC systems are too heavy (> 5 kg/kW) and too expensive (> 5 k\$/kW) and more improvement is needed. In this work we address the problem of reducing the system weight and complexity by operating PEMFC without external humidification of the reactant gases. Operation of PEMFC systems in absence of external humidification will be beneficial for the cost and weight of the system as it eliminates the need of the gashumidification subsystem.

The performance of a PEMFC is strongly governed by the conductance of the membrane electrolyte. The conductivity of the membrane employed is a linear function of it's hydration state, i.e. the higher the hydration state, the better the conductivity [9]. Therefore, to prevent drying out of the membrane and to keep it in its most conductive state, traditionally the reactant gases have been humidified before entering the fuel cell. This procedure of external humidification of the gases has been applied on the scale of laboratory cells [e.g. 4, 7] as well as on the scale of commercial stacks [1,2].

However the external humidification of the reactant gases is a burden for the fuel cell system. It requires a gas-humidification subsystem which adds to the weight and depending on its layout also to the parasitic power of the fuel cell system. In today's commercial stacks, stack integrated gas-humidification systems account for about 20% of the stack volume and weight. Furthermore the humidified reactant gases transport latent heat into the cell which has to be removed by the cooling system. And the water transported into the cell, if in excess, can even reduce the performance by flooding pores in the gas diffusion electrodes. In multiple cell stacks the condensing water can cause problems by clogging channels and changing the gas pressure drop through individual cells. In our experience this is especially evident when operating fuel cell stacks at atmospheric gas pressure.

The absence of external humidification, i.e. operating the fuel cell or fuel cell stack on dry gases could therefore be an advantage because (i) no gas humidification subsystem is needed; (ii) no latent heat is transferred into the cell by water vapor; (iii) less condensed water is present in the system, which could affect the gas diffuison in the electrode backings or pressure drop in the cells.

The drawbacks of adding water to the fuel cell have been identified in earlier work and several ways of alternate humidification of the membrane were proposed.

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Water can be added through wicks [10] or hollow fibers [11], the membrane may be humidified by small catalyst particles imbedded into it's structure [12] or the membrane electrode assembly may be prepared by a special casting process [13]. However all these methods have certain disadvantages, they require more complicated cell structures or additional membrane preparation steps. The easiest approach would be to run a fuel cell, containing conventional membranes and electrode structures, on dry gases and rely for the humidification of the membrane on the water produced by the electrochemical reaction and to adjust the water management of the cell by choosing the appropriate operating conditions.

In this work the possibility of operating PEMFC without external humidification of the gases is studied and the characteristics of such cells examined. The water management of PEMFC run on dry gases is investigated in order to understand which are the important operating parameters. Further on the performance and long term behavior of such cells is measured.

EXPERIMENTAL

Standard membrane electrode assemblies (MEA) of 50 cm² were prepared from Nafion[®] 115 membranes (DuPont de Neimours, Favettville, PA) and commercial electrodes from E-Tek (Natick, MA) containing 0.4 mg/cm² platinum (20% Pt on C). Before use, the membranes were pretreated using a standard procedure. They were kept in 3 % H₂O₂ at 100 °C for 1 hour, then thoroughly washed and boiled for 1 h in pure water (18 M Ω , from Modulab Type I purification system). The membranes were then kept in 0.5 M H,SO, at 100 °C for 1 hour and again washed and boiled for 1 hour in water. The membranes were stored in the dark in pure water. Electrodes were impregnated with recast Nafion[®] of 1100 g/eq (Aldrich) by brushing. The amount of impregnation (dry mass) was kept in the range 0.6 - 0.7 mg/cm². The MEA was finally prepared by hot-pressing the electrodes for 90 s at 145 °C (at 2500 kp) onto the membrane. After the hot pressing the MEA was inserted into the cell fixture between two Teflon coated fiberglass gaskets. For the preparation of MEAs optimized for operation without external humidification, only the preparation of the electrodes was different. For the optimized MEAs, the active layer of the electrodes was prepared onto uncatalyzed electrodes from E-Tek by a proprietary procedure.

The single cell fixtures for testing 50 cm² MEAs were made from resin impregnated graphite (AXF-5Q from Poco Graphite Inc., Decatur, TX). For the distribution of the gases a "series-parallel" flow field was machined into the front side of the graphite blocks. The same flow field design has been used in many previous studies, also in other labs. Multi-cell stacks were built with identical graphite flow-fields of 50 cm² area as the single cells. The graphite bipolar plates had a thickness of 5.0 mm and the stack had internal manifolding for the reactant gases. A two cell stack was operated

without cooling, the four cell stacks had one cooling plate in the middle of the stack. Pressurized air was used as cooling medium.

The gases were dosed using electronic mass flow controllers (MKS Instruments, Andover, MA) calibrated at 25 °C. For calculations of relative humidity in the reactant gases, the volume flux was adjusted to the cell temperature using tables for air [14] and the ideal gas law for hydrogen. The electric parameters of the cell were controlled by an electronic load (HP 6050A) interfaced by a personal computer. For measuring automated current-voltage characteristics the cells were operated in constant current mode and points were recorded after the voltage change was less than 0.25 mV/s after the current change. Approximate measuring time per point was 20 - 30 s. For current densities of > 100 mA/cm² the flow of the gases was adjusted to constant stoichiometry of $\lambda_{\mu 2}$ =1.2 for hydrogen and $\lambda air=2.8$ for air. For current densities < 100 mA/cm², the flows were held constant at the 100 mA/cm² values. In experiments with elevated gas pressures, the pressures in the cell were regulated by valves in the gas streams, downstream of the cell.

The amount of water leaving the cell at the anode or cathode gas outlet was measured by condensing the water at the cell outlets in a cold trap and subsequent weighing of the cold trap. For these measurements the cell was operated in the constant current mode, so the total amount of product water produced could easily be calculated from the charge passed.

RESULTS AND DISCUSSION

Fundamental Aspects

The water content of a membrane in an operating fuel cell is affected by several parameters. One hand a transport of water through the membrane from the anode to the cathode side by electro-osmotic drag was observed [9, 15]. This drag was measured exsitu to be $0.9 - 2.9 \text{ H}_2\text{O}$ per proton for Nafion[•] 117 depending on the hydration state of the membrane. On the other hand back diffusion of water occurs down the concentration gradient which builds up in the operating fuel cell. The concentration gradient is established through the transport of water by the electro-osmotic drag and the production of water at the cathode from the oxygen reduction reaction. In situ measurements reported a net water drag of about 0.2 H₂O per proton, indicating that the back diffusion is substantial. More recent work has shown, that even a net flux of water to the anode may be achieved by employing proper operating conditions with respect to pressure drop and gas flow rates [16].

If it is possible to operate a fuel cell without a net water drag from the anode to the cathode, then in principle operating a PEMFC with dry gases is possible. To prevent

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drying out of the membrane the only caution to take is not to remove more water from the cell with the exiting gas streams, than is produced by the electrochemical process.

The amount of water removed from the cell by the reactant gases entering dry and exiting the cell with a 100 % relative humidity may be calculated and compared to the water produced by the electrochemical reaction. If the amount of water vapor leaving the cell is less than the product water, then in principle no net drying of the cell should occur. Because the stoichiometries of the gases can be confined to small values when the fuel cell is operated on pure hydrogen and oxygen the most critical situation is the operation of the cell on dry H/air. In Figure 1 the relative humidity of the exiting air (entering the cell dry) is plotted as a function of stoichiometries for different cell temperatures, assuming that all the all of the water is leaving the cell in the vapor phase. all water is drained from the cathode (no water loss at the anode) and atmospheric pressure in the cell. It can be deduced from these plots that the cell could indeed operate in a quite broad range without a net water loss. At 40 °C, only at an air stoichiometry of more than 4.8 the amount of product water will not be able to fully humidify the air. At 50 °C, 60 °C and 70 °C the (theoretically) critical air stoichiometries are 2.9, 1.8 and 1.2 respectively. These calculations indicate, that indeed a range of operating conditions should be available to run the PEMFC on dry hydrogen and air when no net water transport from the anode to the cathode occurs.

Figure 2 shows the current voltage characteristic of a PEMFC at 50 °C operated on humidified and dry gases to illustrate the cell performance in both modes. No special components were used to build this cell, i.e. it contains a Nafion^{\circ} 115 membrane and commercial electrodes with a platinum loading of 0.4 mg/cm² which have been impregnated with recast Nafion.

The performance in absence of the external humidification is lower. At 0.6V the current density is 30 % lower for the case without external humidification at atmospheric gas pressures. However this performance is stable over long terms, proving that the assumptions on the cell water management outlined above are valid. Figure 3 shows the current density at 0.61 V of such a cell over the period of more than 1800 hours. Some degradation of the performance is observed over this time, but it probably has to be attributed to other factors than drying out of the cell, e. g. we did not filter the air used.

In order to understand why the operation on dry gases is possible we have investigated the water distribution in a PEMFC. We have studied the location and amount of drainage of product water as a function of operating conditions such as flow rates of the anode and cathode gases, and cell temperature. In the cell operated with dry gases these measurements can be performed with a high accuracy as there is no interference with water transported into the fuel cell by any humidification process. The results in Figures 4 to 6 describe the distribution of the product water efflux in the PEMFC at 50°.

Figure 4 shows the dependence of the fraction of product water draining from the fuel cell on the anode side with changing air stoichiometry at constant hydrogen stoichiometries of $\lambda_{\mu 2} = 1.7$ and $\lambda_{\mu 2} = 4.4$. Surprisingly the amount of product water drained at the anode (and cathode) is almost independent of the air stoichiometry. Only a small decrease is observed at the anode side with increasing air stoichiometry. This means that the water distribution in the cell is almost independent of the air stoichiometry for the range investigated of $\lambda_{\mu 2} = 1.2$ to 4.5.

The picture changes completely if the hydrogen stoichiometry is varied and the air stoichiometry is held constant. The water removed from the cell at the anode side is a linear function of the hydrogen stoichiometry, i.e. the hydrogen efflux from the cell, as shown in Figure 5 for λ_{112} = 1.3 to 5.8. From the plot in Figure 5 the rate of water removal may be calculated to be $84 \pm 3 \text{ mg H}_2\text{O/I}$ hydrogen leaving the cell. The amount of 84 mg H₂O/I corresponds very nicely to the value for 100 % water vapor saturated hydrogen at 50 °C of 83 mg H₂O/I. This result shows, that hydrogen always leaves the cell with 100 % of relative humidity even at stoichiometries λ_{112} > 5 and very little or no liquid water is drained from the anode as liquid. These findings are important for the operation of the fuel cell with dry gases, they mean that the water loss at the anode may be controlled by the hydrogen stoichiometry. And although no (or only very little) liquid water is lost at the anode, still the possibility to drain water from the anode indicates that the anode is well humidified.

The data in Fig. 2 was measured at 200 mA/cm². The value of 54 ± 3 % of the product water removed at the anode at a hydrogen stoichiometry of $\lambda_{\mu2}$ =5.8 corresponds to a flux of water of 503 µg/s form the entire 50 cm² cell or a value of 10.1 µg/s·cm² if the flux is distributed homogeneously over the entire cell area. Although the assumption of homogeneity is only an approximation, as the gas fluxes and relative humidities change over the cell area, this measured value may be compared to theoretical values based on the ex-situ determination of D_{H20} in Nafion 117 of Zawodzinki at. al [17]. Flux is described by Fick's law as

$$flux = D_{H20} \left(dC_{H20} / dx \right) \tag{1}$$

Assuming a water diffusion coefficient at 50 °C of $D_{H20} = 5 \times 10^{6}$ cm²/s, a water concentration difference across the membrane of $\Delta C_{H20} = 5$ mMol/cm³ and a membrane thickness $\Delta x = 1.2 \times 10^{-2}$ cm, then a flux of 38 µg/s·cm² may be calculated. This value, which is about 4 times the highest experimental value observed, shows, that the high water removal rates at the anode are well within the theoretical limits for the concentration difference applied. The value of $\Delta C_{H20} = 5$ mMol/cm³ was assumed based on the results of Halim et al. [18] who found a sulfonic acid concentration of 1.0 mMol/cm³ in Nafion 117 and Springer et al. [19] who calculated a value of $\Delta C_{H20} = 5$ H₂O/SO₃ for a current density of 200 mA/cm². The present calculation shows, that even a considerable lower concentration difference would be sufficient for removing

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50% of the product water at the anode. These results imply, that the back diffusion of water to the anode is the dominant process in the distribution of the product water in PEMFC operated with dry gases.

The dependence of water drained at the anode as function of cell temperature is shown in Figure 6. The fraction of product water leaving the cell on the anode side is greatly increasing with the increase of the cell temperature, although the gas flows in the cell are constant for all temperatures. As shown in Figure 6, the water removed at the anode coincides very closely with the theoretical removal rate for 100 % humidified hydrogen at temperatures up to about 60 °C. Above 60 °C even more water is removed than theoretically possible in the gas phase, i.e. water is also drained as a liquid. At 75 °C, 25% of the water leaves the anode as a liquid. In addition to the increase of the water vapor pressure also the diffusion coefficient of water within the membrane increases with temperature [20] thus increasing the amount of water drainable at the anode with increasing temperature.

At Temperatures \geq 70 °C the cell is not in a stable operation mode. Under the applied constant current conditions the voltage of the cell decreases slowly during the course of the experiment (few hours), indicating that the membrane is drying out rapidly under these temperature conditions. The results also show, that the hydrogen efflux from cell becomes a more significant source of water loss from the cell with increasing temperature. This in turn means, that minimizing the hydrogen stoichiometry is an important design feature for PEMFC operated on dry H₂/air.

Optimization of Single Cells and Small Stacks

It was observed from Fig. 2, that if standard MEA's are employed, the performance of a single fuel cell is decreased by 25 - 30% at 0.6 V when operated on dry H./air, as compared to the conventional humidified operation. However several methods have been proposed to increase the performance of PEMFC when operated with dry gases. Either water was added to the MEA by other means than through the gas stream, such as through wicks [12] or hollow fibers [11]. Or the generation of water by small catalyst particles within the membrane was proposed. We have taken a different approach : instead of adding water to the cell, to replace losses, the water losses from the cell may be reduced by changes to the structure of the electrodes. It has been observed, that solubilized membrane material, when dried or made to form a gel, can have different characteristics than the parent membrane with respect to water content [21, 22]. The dried deposits can absorb more water. This property has been used by Dhar [13] to prepare MEAs with improved performance when operated on dry reactant gases. For many applications where low weight and hence high power density is important, operating a PEMFC Stack at or close to atmospheric pressure can be advantageous as the required parasitic power for the compression of the air and the size and weight of the

blower/compressor would be small. For this analysis we have put special emphasis on the operation at atmospheric pressure of the gases.

In Figure 7 the current voltage characteristic of PEMFC with standard and optimized MEA's, operated with humidified and dry gases are shown. It can be seen, that the optimized MEA's reach with dry gases the same performance as the standard MEA's with humidified gases. These results prove, that at least at the temperature of 50 °C, self-humidified cells can reach the same performance as externally humidified cells.

In single cells humidification is a simple procedure, and normally excess water in the cell has no adverse effects on the performance of the cell. The excess water is simply removed from the cell by the exiting gases. In multi-cell stacks humidification is a delicate problem, because if the stack is internally manifolded, excess water in the stack may have adverse effects on the performance. In an internally manifolded stack, the gas flow through each individual cell is determined by the pressure drop in the cell and the pressure drop in turn may markedly be affected by condensed water in the flow field channels of the cell. Unequal gas-flow through the cells is a consequence. The performance of a cell is strongly dependent on the gas-flow, particularly the air flow. The flow-performance relationship is not linear, especially for air-stoichiometries of $\lambda_{i} < 2$ as shown in Figure 8. Therefore, if the air flow is distributed unequally between the individual cells in the stack, the average performance of a cell in the stack is less, than the performance of a single cell. Without optimizing the humidification, i.e. using the same humidifier temperatures as for the single cell, this effect is very well apparent from Figure 9. The performance of the single cell is well above the average of a cell in the 4 cell stack. At 0.6 V, the current density in the stack is at average 35 % lower than in the single cell under identical conditions.

When dry gases are used however, and the fuel cell is self-humidifying, the problem of excess water, blocking channels in the flow fields is much less. This effect is demonstrated by the current voltage curves in Figure 10. The performance of the average cell in the 4 cell stack is very close to the performance of the single cell. These results indicate, that operating stacks in the self-humidified mode can reduce the problems of water management, and allow for operation of a stack at the same power density as a single cell, even at atmospheric gas pressures.

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CONCLUSIONS

The operation of PEMFC without external humidification of the gases was investigated. It was found, that cells with conventional membrane-electrode assemblies (MEA) can be operated with dry H₂/air if restrictions with regard to gas flow rates and cell temperature are respected. Stable long term operation was demonstrated at cell temperatures up to 60 °C. The level of performance with standard MEA's obtained is 25th 30% lower as compared to the conventional mode of operation with both gases humidified to super-saturation.

The water distribution in the fuel cell is dominated over a wide range of operating conditions (with respect to gas stoichiometries and current densities), by the backdiffusion of water from the cathode to the anode. This allows for internally humidifying also the hydrogen and prevents drying out of the anode.

The membrane electrode assemblies may be optimized for the self-humidified operation. With optimized MEA's and dry gases, the same performance as with standard MEA's and humidified gases can be obtained. Finally in self-humidified stacks, the problem of excess water and water removal is reduced. Therefore no performance losses are apparent due to the stacking of cells, even at atmospheric gas pressures. This is unlike the conventional humidified system, where substantial performance losses are observed.

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Figure 1: Calculated relative humitity of air exiting fuel cell at temperatures given, as function of the air stoichiometry. The results are based on the assuptions of atmospheric air pressure and that all product water is leaving the cell in the vapor phase at the cathode side.



Figure 2 : Current-voltage characteristics of 50 cm² H₂/Air fuel cell at 50 ° and H₂ / Air 1.0 / 1.0 atm, (**■**) operation without external humidification and (•) gases humidified : H₂ at 60 °C, air at 55 °C; Stoichiometries of gases are $\lambda_{tre} = 1.2$ and $\lambda_{tre} = 2.8$.



Figure 3 : Steady state current density of H₂/Air PEMFC operated on dry gases at indicated cell temperatures and 0.61 V cell voltage; hydrogen stoichiometry $\lambda_{\mu_2} = 1.2 - 1.4$; air stoichiometry $\lambda_{\mu_2} = 1.6 - 1.8$.



Figure 4 : Fraction of product water leaving the fuel cell at the anode side as a function of air stoichiometry at two different constant hydrogen stoichiometries. Operating conditions : Cell temperature 50 °C; current density 200 mA/cm²; gas pressures H₂/Air 1.0 / 1.7 atm.



Figure 5 : Fraction of product water leaving the fuel cell at the anode side as a function of hydrogen stoichiometry at constant air stoichiometry of ($\lambda_{ur} = 1.7$). Operating conditions : Cell temperature 50 °C; current density 200 mA/cm²; gas pressures H₂/Air 1.0 / 1.7 atm.



Figure 6: Fraction of product water leaving the fuel cell at the anode side as a function of cell temperature at constant stoichiometries of $\lambda_{H2} = 1.6$ and $\lambda_{u2} = 1.7$. Operating conditions : Current density 200 mA/cm²; gas pressures H₂/Air 1.0 / 1.7 atm. (•) Experimental values, (Δ) calculated values for 100 % rel. humidity of exiting hydrogen.



Figure 7 : Current-voltage characteristics of 50 cm² H₂/Air fuel cell at 50 ° and H₂ / Air 1.0 / 1.0 atm with standard and optimized MEAs. Stoichiometries of gases are $\lambda_{112} = 1.2$ and $\lambda_{1x} = 2.8$.



Figure 8 : Single Cell Voltage of H₂/Air fuel cell with standard MEA as function of air stoichiometry. Cell temperature 50 °C. Humidification temperatures as in Fig. 2.



Figure 9 : Current-voltage characteristics of 50 cm² H₂/Air fuel cell at 50 ° and H₂ / Air 1.0 / 1.0 atm; (•) single cell (**n**) average of 4 cell stack. Gases humidified : H₂ at 60 °C, air at 55 °C; Stoichiometries of gases are $\lambda_{n_2} = 1.2$ and $\lambda_{n_2} = 2.8$.



Figure 10 : Current-voltage characteristics of 50 cm² H₂/Air fuel cell at 50 ° and H₂ / Air 1.0 / 1.0 atm, (•) single cell (•) average of 4 cell stack. Gases suppled dry; Stoichiometries of gases are $\lambda_{H2} = 1.2$ and $\lambda_{H2} = 2.8$.

MEMBRANE MATERIALS FOR PEM-FUEL-CELLS: A MICROSTRUCTURAL APPROACH

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The effects of the hydrophobic/hydrophilic phase separation of hydrated sulfonated polymers on proton conductivity, water diffusion and the swelling behaviour is investigated by comparing data obtained on NAFION and a homogeneously sulfonated polyaryle membrane. Owing to the differences in the water distribution, intermolecular proton transfer rates are less surpressed, H_3O^+ is less trapped at its $-SO_3^-$ counter charge and the percolation for proton and water transport is improved for the phase separated NAFION compared to the homogeneous polymer. The heterogeneous polymer also shows superior morphological stability in the presence of water.

INTRODUCTION

Separator materials for PEM-fuel-cells have to meet a combination of requirements: High protonic conductivity, excellent electrochemical and chemical long term compatibility with the reducing and oxidising active masses including the electrocatalyst, low permeation of undissociated fuel gases and reasonable mechanical properties including a defined swelling behaviour in the presence of water are among the most important requirements. In a fuel cell operating under varying conditions they must be guaranteed at any instant.

The only polymeric membrane materials which are close to fulfil these requirements so far are NAFION and other related perfluorosulfonic polymers.

This paper presents an analysis of why such polymers show a unique combination of properties. In particular, it is shown that the hydrophilic/hydrophobic phase separation leads to a heterogeneous microstructure which combines morphological stability as a typical solid state property and high proton diffusivity as a typical liquid state property in different parts of the microstructure. This turns out to be a key to a deeper understanding of (i) the proton conductivity and water diffusion as a function of the water content and (ii) the swelling behaviour in water.

The results may be the basis for the development of alternative materials with properties similar to those of perfluorosulfonic polymers.

HYDRATION AND PHASE SEPARATION

Perfluorosulfonic polymers naturally combine an extremely high hydrophobicity of the perfluorinated backbone with an extremely high hydrophilicity of the sulfonic acid functional group ($-SO_3H$). In the presence of water, hydration preferentially takes place as a solvation of the acid groups, which goes along with proton transfer to the hydration water strongly hydrogen bonding to the oxygens of the $-SO_3^-$ groups. On the other hand, the dispersion of water in the polymer requires some hydrogen bond breaking with respect to bulk water because of the destabilising hydrophobic interaction with the perfluorinated backbone. In particular, this is the case for a

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homogeneous distribution of $-SO_3H$ groups and low water concentrations which do not allow the hydration clusters to bind together to minimise the fraction of broken hydrogen bonds. The degree of hydration for a given partial pressure is considered to be the result of the competition between these two effects.

In any real polymer the hydrated state does not strictly correspond to thermodynamic equilibrium, i.e. the minimum of the Gibbs free energy. A complete separation of the hydrophobic and hydrophilic parts of the polymer would minimise the unfavourable interface between the water of hydration and the polymer backbone and thus correspond to thermodynamic equilibrium. To what extend the hydrated polymer approaches equilibrium depends on its elastic and plastic properties and the history of the sample.

Perfluorinated polymers are generally soft materials with a low glass transition temperature (1) which allows some rearrangement especially of the polymer side chains in the presence of water. Thus, the hydrophilic parts may separate from the hydrophobic parts. Whereas the hydrophobic domain essentially keeps its elastic and plastic properties the water of hydration preferentially penetrating the hydrophilic domain further increases the softness of this part of the microstructure where it acts - so to say - as a plastiziser (2). Speaking in terms of relaxation times, the elastic properties of the material are expected to split into at least two different relaxation times upon hydration corresponding to the two separating domains. In real space, the material may approximately be considered a hydrophobic sponge with a highly hydrophilic inner surface, the pores and channels being filled with acidified water. In the case of NAFION these are considered to have an extension of some nanometers only.

This basic picture of the microstructure of hydrated perfluorosulfonic polymers has tentatively been sketched already by Gierke (3).

In the following, we will investigate the implications of this microstructure on properties relevant for the use as membrane materials in PEM-fuel-cells by comparing experimental data obtained on a phase separated polymer (NAFION, Du Pond de Nemour, equivalent weight 1100 g/mol) a homogeneously sulfonated polyaryle membrane (Hoechst, equivalent weight 720 g/mol (4)) and acidic aqueous solutions.

PROPERTIES

Proton Conductivity and Water Diffusion

Because of the morphological heterogeneities we will discuss the transport properties separately for different length scales.

In NAFION water moves almost freely on a nonometer scale and the water diffusion coefficient and proton conductivity has been suggested to be similar to that of bulk water on a molecular scale for highly hydrated NAFION, i.e. for high $[H_2O]/[-SO_3H]$ ratios (5,6). This is also indicated by activation enthalpies of the transport coefficients which are very close to those of aqueous solutions.

But this is no longer true for low degrees of hydration. For decreasing water contents the proton mobility decreases more than the water diffusion coefficient as being indicated by the ratio $\mathbf{A} = D_{\text{H2O}}/D_{\sigma}$ decreasing even below unity (fig.1) for two reasons.

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The first is also observed for proton conductivity of aqueous solutions of hydrochloric acid. A approaches unity for high acid concentrations, where proton mobility, chloride ion mobility and the water diffusion coefficient are almost equal. All charged species (H_3O^+ , Cl^-) and neutral solvent molecules (H_2O) move in a highly cooperative way (7). Proton transfer reactions along hydrogen bonds, which account for the high proton mobility in dilute solutions, are practically surpressed. This is due to the strong biasing of the hydrogen bonds in the electric field of the anions, which disturb the mean solvent symmetry, required for fast proton transfer in aqueous systems (8,9). Consequently, proton conductivity can only occur correlated with molecular diffusion, i.e. via the migration of hydrated protons (e.g. H_3O^+) (10). The second reason is probably due to the spatial dispersion of the proton counter charge, i.e. the -SO₃⁻ functional groups. As opposed to the situation in aqueous solutions, they are practically immobile in configurations given by the microstructure of the polymer. Although the diffusivity of different anions and cations fall into a very narrow range around the diffusion coefficient of water in aqueous solutions, the diffusion of ions is almost independent, i.e. there is no significant correlation between the motion of different ions. It is the very nature of a polar solvent with a high dielectric constant, that the electric field of solvated ions is almost completely shielded by the first solvation shell, thus efficiently surpressing correlated diffusion which might originate from direct coulomb interactions. Therefore, the similarity of iondiffusivities in aqueous solutions are reflecting the strong interaction with the common solvent (H₂O) rather than direct ion/ion interactions. In hydrated polymers, however, the dielectric properties of the water of hydration are expected to be different from that of bulk water, especially for low degrees of hydration. As already pointed out above, the dispersion of the water in the polymer must lead to an increased fraction of broken hydrogen bonds with respect to bulk water. As has been described in ref.9, breaking of hydrogen bonds in the hydrogen bond network of water leads to a significant strengthening of the remaining hydrogen bonds. This, together with the formation of additional strong hydrogen bonds with the -SO₃⁻ groups leads to a toughening of the water structure and thus to a decrease of the dielectric constant, i.e. a decrease of the electrostatic shielding of the -SO₃⁻ charge by the solvent. For low water contents, this may lead to some trapping of the hydronium ion at the immobile anionic counter charge as indicated by the decrease of A below unity (fig.1), i.e. the neutral water molecules exhibit a higher diffusion coefficient than the charged hydronium ions. This effect is expected to depend on the microstructure, in particular on the spatial distribution of the -SO₃⁻ groups.

For a homogeneous distribution of $-SO_3^-$ groups the water of hydration is more dispersed, i.e. less connected, than for a heterogeneous distribution, where the $SO_3^$ groups are concentrated in the hydrophilic domain of a phase separated polymer, thus allowing the water clusters to bind together already at low water contents. Owing to the smaller number of broken hydrogen bonds in the latter case, the properties of the water of hydration are anticipated to become similar to those of bulk water at lower water contents. The corresponding effect on the proton conductivity can clearly be seen in the evolution of A with the degree of hydration for a polymer with a homogeneous and a heterogeneous $-SO_3^-$ distribution. As can be seen from fig.1, the ratio A in the first case is lower than in the case of a phase separated polymer for all degrees of hydration. It should be noted that A in the latter case is still lower than A for an aqueous solution of hydrochloric acid. Compared to water diffusion the H₃O⁺
diffusivity is, as expected, more reduced for a homogeneously sulfonated than for a phase separated polymer.

Also the macroscopic transport properties of a phase separated polymer are advantageous over those of a homogeneously sulfonated polymer. As has been shown in ref.6 the activation enthalpies of proton conductivity and water diffusion in NAFION remain almost unchanged with decreasing degree of hydration while the absolute transport coefficients significantly decrease. The latter effect was ascribed to the water percolation within the hydrophilic domain of the polymer which reduces the transport coefficients on a macroscopic scale compared to a nanoscale. Of course this depends on the connectivity within the hydrophilic domain which is expected to be improved by the phase separation. This becomes apparent in the evolution of the proton diffusivity (D_{σ}) and water diffusivity (D_{H20}) as a function of the water content (fig.2). Both transport coefficients are significantly higher for the heterogeneous than for the homogeneously sulfonated polymer over the whole range of hydration. It should also be noted that the activation enthalpies of proton and water transport are slightly higher for the aromatic polymer than for the perfluorinated NAFION which probably reflects slightly increased solvent effects (9) induced by the higher static dielectric constant of the first polymer backbone (approx.2-2.1 compared to 3.2-3.3).

Despite the above discussed trapping effects, there is still a reasonable correlation between proton (hydronium) and water transport (fig.2). The major effect of the hydrophobic/hydrophilic phase separation on the transport properties, therefore, is to improve the percolation for the diffusion of water molecules and thus also for proton diffusivity.

Swelling Behaviour

As discussed above, the phase separation in the presence of water leads to the formation of a soft hydrophilic and a stiffer hydrophobic domain, the latter being expected to determine the overall morphological stability. If the local $-SO_3^-$ concentration in the hydrophilic domain exceeds a certain limit, this part of the microstructure is even expected to continuously swell and eventually dissolve in water. But this is prevented by the presence of the hydrophobic domain which, so to say, acts as a stable "container" for the water of hydration. As long as this "container" keeps its morphological stability its maximum water contents should be constant. Indeed, this is observed in the swelling behaviour of NAFION in liquid water (fig.3). At room temperature the water uptake is about 20 H₂O per -SO₃H which only slightly increases up to about 140°C, where the polymer starts to swell dramatically. This temperature probably indicates the softening of the hydrophobic domain.

As opposed to NAFION, the homogeneously sulfonated aromatic polymer with an approximately identical overall $-SO_3H$ concentration starts to swell irreversibly at significantly lower temperature (about 80°C) (fig.3).

OUTLOOK

The microstructural considerations presented may be the basis of a strategy for the development of new polymeric membrane materials. At the time of the development of NAFION perfluorinated polymers were the only ones with the desired high thermal and chemical stability. In the meantime, however, numerous nonfluorinated, polyaromatic high performance polymers have become available which can resist highly oxidising and reducing conditions (11). Some of them can easily be sulfonated by standard procedures, and the desired microstructure may be designed by controlled blending and cross linking.

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FIGURES



Fig.1

The ratio $A=D_{\sigma}/D_{HzO}$ for a heterogeneous phase separated and a homogeneously sulfonated polymer. The data for aqueous solutions of hydrochloric acid (7) are given for comparison.







Fig.3

Swelling behaviour in liquid water. (The samples were kept at each temperature for two hours before the weight gain was determined at room temperature.)

NEW HYDROCARBON PROTON EXCHANGE MEMBRANES BASED ON SULFONATED STYRENE-ETHYLENE/BUTYLENE-STYRENE TRIBLOCK COPOLYMERS

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Abstract

Commercially available styrene-ethylene/butylene-styrene triblock polymer (Kraton G1650) was partially sulfonated using a SO3/tricthyl phosphate reagent in a dichloroethane/cyclohexane mixed solvent. Films of the product were cast from lower alcohols to give elastic materials with different degrees of sulfonation (ca. 30-60%) as determined by titration. Transmission electron microscopy suggests that the cast films possess cylindrical sulfonated polystyrene domains. The films swell in water, with the extent of swelling being dependent on the sulfonation level. Ionic conductivities as high as 8.5×10^{-2} S/cm are obtained when fully hydrated, and compare favorably to those exhibited by hydrated, sulfonated fluoropolymers such as Nafion.

Introduction

Polymers with high protonic conductivities are potentially useful as proton exchange membranes (PEM's) in fuel cells. Among the earliest PEM's were sulfonated, crosslinked polystyrenes, and these were employed in fuel cells on the Gemini space missions.¹ More recently, interest has been directed to sulfonated fluorocarbon polymers, of which Nafion has been most extensively studied.²⁻⁷ This material has a high protonic conductivity (ca. 7 x 10⁻² S/cm at 30 °C)⁸ when hydrated and is chemically rather inert.

It has been proposed that Nafion possesses an inverted micellar structure, with spherical (ca. 40-50 Å diameter) clusters lined with sulfonic acid groups which are interconnected via ca. 10Å channels.⁹⁻¹¹ We sought to mimic this picture using inexpensive sulfonated, hydrocarbon-based block copolymers. Block copolymers in

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general can exhibit a rich array of microphase-separated morphologies depending on relative block sizes.¹² Such materials provide us with an opportunity to link good ionic (protonic) conductivity through water-swellable microdomains with low material cost and desirable mechanical properties. We note that selected block copolymers have been shown to be useful as alkali metal-based polymer electrolytes,¹³ although apparently no efforts have been directed toward obtaining high protonic conductivity based on hydrocarbon block polymers.

We selected Kraton G1650 for our studies as it contains a saturated carbon center block which should be inert to the sulfonation reaction, which in this case employs SO3/triethyl phosphate to achieve high levels of sulfonation without crosslinking.¹⁴ The reaction is summarized in Figure 1. The Kraton used in this study contains 29% by weight styrene and exhibits a microstructure of polystyrene phases intermediate between spheres and cylinders (ca. 150 Å in diameter) in an ethylene/ butylene-rich continuous phase.¹⁶ Sulfonation levels, based on the moles of styrene units sulfonated, ranged from 35-65% as determined by titration. We note that sulfonated, saturated Kratons have been disclosed in a patent,¹⁵ and that Weiss and coworkers¹⁶⁻¹⁸ have explored in detail the morphology and mechanical properties of lightly sulfonated (up to 12 mol% styrene units) Kraton G1650, the latter representing an interesting new class of ionomers. However, we are unaware of studies directed at highly sulfonated derivatives with the aim of obtaining highly proton conducting films.

Experimental

Kraton G1650 was acquired from Shell Chemical; dichloroethane (DCE) and cyclohexane were from Krackeler Scientific; triethyl phosphate (TEP) and sulfur trioxide (SO₃) were from Aldrich. All materials were used without further purification. Sulfonation of the styrene-ethylene/butylene-styrene (SEBS) triblock polymer was carried out in a batch mode using SO₃/TEP.¹⁴ The reaction vessel was kept slightly below 0°C and reaction times ranged from 60-90 min. After removing most of the cyclohexane and DCE, the residue was taken up into lower alcohols. Films were then cast from these solutions on glass under an IR lamp.

Titrations to determine the sulfonic acid content of the film were carried out using standardized sodium hydroxide solutions. Films were hydrated in deionized water and washed by placing the film in clean deionized water three times for one hour cach. About 0.15 g of film was placed in a small vial and approximately 12 ml of sodium chloride solution was added. After immersion for about 2 h, titrations to a phenolphthalein endpoint were carried out. Data are reported as mol% styrene units sulfonated. Samples for transmission electron microscopy (TEM) were first stained for 15 min in the presence of RuO4 vapor and then cryomicrotomed at -100°C using a Reichert-Jung Fc4 microtome. A 2000 FX high resolution transmission electron microscope was employed at a magnification of 275,000x.

Conductivity measurements were made on samples treated to remove any residual sulfuric acid from the sulfonation reaction. Samples were soaked in water for 30 min, and then dried under an IR lamp for 30 min, and this sequence was repeated twice. The conductivity of the membrane was measured by using a pair of pressure-attached high surface area platinum electrodes as described by Zawodsinski et al.⁸ The mounted sample was immersed in distilled, deionized water at room temperature (ca. 24 °C). Once the sample had completely hydrated, measurements were made from 1 Hz to 10KHz using a Solartron 1260 frequency response analyzer. Both real and imaginary

components of the impedance were measured and the real Z-axis intercept was closely approximated. The cell constant was calculated from the spacing of the electrodes (L), the thickness of the membrane and the area of the platinum electrodes (A). The conductivity (σ) was calculated using the equation

 $\sigma = L/RA$.

Results and Discussion

Films of sulfonated triblock polymer are yellow and relatively transparent as well as elastomeric. A transmission electron micrograph of a microtomed and RuO4-stained film (ca. 45% sulfonation) is shown in Figure 2 and reveals what appear to be cylindrical (ca. 150 Å diameter) sulfonated polystyrene domains in an ethylene/butylene matrix. We believe that at this high sulfonation level, relatively homogeneous sulfonated polystyrene domains are present rather than ionic clusters of sulfonated styrene repeat units within polystyrene domains as is the case in lightly sulfonated Kratons. ¹⁶⁻¹⁸

The films swell upon immersion in water, and the extent of swelling is as expected dependent upon the sulfonation level. These hydrogels retain their elastomeric character. We have no information on the organization or the sizes of the sulfonated domains upon hydration, but speculate that these are interconnected upon swelling and perhaps forming bicontinuous phases. X-ray and neutron scattering experiments are planned to address this important issue. The films remain relatively transparent upon hydration, suggesting that the water-swollen domains remain below ca. 400 nm in diameter.

Ionic conductivities of fully hydrated films having various levels of sulfonation are reported in Table 1. Samples having sulfonation levels greater than about 45% have conductivities comparable to Nafion (ca. 7×10^{-2} S/cm) under similar conditions.⁸ The amount of sulfonation within the polystyrene domains is well above the percolation threshold for ionic conduction of ca. 7 mol%, as recently determined by Yeager, Eisenberg and coworkers¹⁹ for sulfonated homopolystyrene. The high conductivity we observe indicates that the sulfonated domains are interconnected.

In summary, we have prepared highly proton conducting, elastomeric films by sulfonation of a styrene-ethylene/butylene-styrene triblock polymer. Several applications of these materials are being investigated, including their use as proton exchange membranes in fuel cells.

Acknowledgments

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Table 1

Conductivities of Sulfonated Block Polymers as a Function of Sulfonation Level

Percentage Sulfonation ^a	mmol/g ^b	Conductivity ^c (S/cm)
35	0.96	0.068
43	1.16	0.075
50	1.33	0.080
65	1.72	0.089

^aMole % based on styrene units, determined by titration. Data are averages of triplicate determinations.

^bMillimol sulfonic acid per gram of total polymer

^cImmersed in water, room temperature.

Figure 1: Sulfonation of Styrene/Ethylene-Butylene/Styrene Triblock Copolymer



Figure 2: Transmission electron micrograph of ca. 45% sulfonated Kraton G-1652 stained with RuO4. Magnification = 275,000x.



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ON DIRECT AND INDIRECT METHANOL FUEL CELLS FOR TRANSPORTATION APPLICATIONS

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Recently, we and others have achieved power densities in polymer electrolyte Direct Methanol Fuel Cells (DMFCs), which are only three times lower than those achieved with similar reformate/air fuel cells (RAFC). Comparisons of power densities, energy conversion efficiencies and projected costs reveal similar values for the DMFC and the methanol reformer + RAFC stack. We conclude that the DMFC could become the preferable methanol-fueled system due to its relative simplicity. However, important remaining DMFC issues are: improved anode catalyst activity, demonstrated long-term stable performance, and high fuel efficiencies.

INTRODUCTION

Polymer electrolyte fuel cell (PEFC) technology has advanced in the last few years to the point of being considered a viable option for primary power sources in electric vehicles. In the past, the systems considered in this context have been based on either hydrogen carried on board the vehicle, or the steam-reforming of methanol to generate a mixture of hydrogen and CO₂ as the fuel feed stream for the fuel cell stack. The latter system has been considered an attractive option because of the high energy density of the fuel (methanol), its availability and the relatively simple fuel distribution system required. However, the complexity and additional weight and volume associated with the reformer on board the vehicle have presented significant challenges in the implementation of this option. To date, the DMFC has not been considered a serious option for transportation applications due to its limited performance (low power density) in comparison to the RAFC.

Recent advancements in DMFC research and development have been quite dramatic, however, with the DMFC achieving power densities which are significant fractions of that provided by the RAFC. The more applied DMFC work, aimed primarily at the demonstration of enhanced stable performance of DMFC single cells or stacks, has been supported in the US by the DOE, Office of Transportation Technology, ARPA and the US Army. This type of work has taken place in several research institutes, including the Jet Propulsion Laboratory, Case Western Reserve University and Los Alamos National Laboratory, in collaboration with industries such as International Fuel Cells (IFC) and Giner, Inc. Similar efforts in Europe resulted in a demonstration at Siemens of a high-performance polymer electrolyte DMFC operating at temperatures above 120°C.

The recent strong advances in DMFC performance have been achieved without any breakthroughs in electrocatalysis, much the same way as in the previous cases of the hydrogen/air PEFC or the RAFC. The use of established Pt-Ru anode electrocatalysts and Pt cathode electrocatalysts in conjunction with polymer electrolyte DMFCs has resulted in very significant enhancements in DMFC performance when such cells are operated at

temperatures as high as 120-140°C, and particularly, as shown in this paper, when catalyst layer composition and structure have been optimized. Operation at elevated temperatures is facilitated in such polymer electrolyte fuel cells by the anode being continuously in contact with liquid methanol-water mixtures.

In the following section we describe recent experimental work at Los Alamos National Laboratory (LANL), which resulted in high performances of polymer electrolyte DMFCs. These recent results will be considered together with previously reported LANL results to comparatively evaluate (i) a polymer electrolyte DMFC stack and (ii) a system comprised of a methanol reformer and polymer electrolyte reformate/air fuel cell stack for transportation applications.

PROGRESS IN DIRECT METHANOL FUEL CELLS AT LANL

Membrane/Electrode Assemblies

Over the course of the DMFC development effort at LANL, a number of different methods were investigated for forming the membrane/electrode assembly (MEA) in cells based on NafionTM membranes (DuPont). These included conventional PTFE-treated wet-proofed electrodes, catalyst/ionomer inks applied to carbon cloth and thin-film catalysts formed by applying catalyst ink to transfer decals.¹ The various types of catalyst structures were then bound to the Nafion membranes by hot-pressing. The thin film catalysts bonded to the membrane by the decal method^{1,2} provided the best results in terms of catalyst utilization and cell performance. Such decal-formed thin-film catalyst layer structures have been used previously for H₂/air fuel cells in this laboratory and proved to provide the highest catalyst utilizations.

The protocol for forming the high performance DMFC assemblies described here is somewhat different than that for the H_2 /air cells. Nation 112, 115 and 117 membranes were cleaned and converted into the acid form by successively boiling the membranes for at least one hour in each of the following solutions: 3% H₂O₂, deionized (DI) water, 0.5 M H_2SO_4 , and then DI water again. Unsupported Pt-RuO_x (Pt:Ru = 1:1, sample designated RV30-30 from E-TEK, Inc., Natick, MA) was used for the anode catalyst and Pt-black (20 m^2/g , Johnson Matthey) was used for the cathode catalyst. Catalyst inks were prepared by adding 5% Nation solution (900 EW, Solution Technology, Inc.) to the water-wetted metal catalysts. Suitable dry ink compositions were 85 wt % Pt-RuO_x and 15 wt % Nafion for the anode ink, and 93 wt % Pt-black with 7 wt % Nafion for the cathode ink. To prepare the MEAs, appropriate amounts of anode and cathode inks were uniformly applied to 5 cm^2 Teflon decal blanks to give metal catalyst loadings of approximately 2.2 mg/cm^2 . The inked decals were then dried at 100°C, and the catalyst layers were transferred from the Teflon blank to the pre-dried Nafion membranes (45 min. on a 60°C heated vacuum table) by hot-pressing at 120° C and 105 atm for 120 s. After the decal blanks were removed, the MEAs were inserted into the fuel cell hardware, and sandwiched between two 5.5 cm² uncatalyzed carbon-cloth gas-diffusion backings from E-TEK. The reasons for the use of such backings are discussed briefly elsewhere.² The single-cell fuel cell hardware consists of nuclear-grade graphite blocks with machined serpentine flow channels, gold-plated copper current collectors, and stainless steel compression plates.³ The cell testing¹ and high-frequency resistance measurement⁴ systems have been described previously.

Specific activities (i.e., activities per mg Pt) of unsupported Pt-Ru anode catalysts are not as high as those described by Watanabe⁵ for Pt-Ru/C, or those we have obtained ourselves with commercially available Johnson-Matthey Pt-Ru/C catalysts (e.g. their FCA-6X).⁶ However, an unsupported, highly active Pt-Ru catalyst (as described by Kosek et al.⁷) provides a significantly higher overall anode performance. This is mainly due to the high catalyst utilization, enabled by effective simultaneous access of protons, electrons and methanol to a large number of active catalyst sites in thin layers of high site density. The overall loadings in such layers of unsupported Pt-Ru catalysts are indeed higher than those typically obtained for supported Pt alloy catalysts (1-4 mg/cm² vs. 0.1-0.5 mg/cm²). However, a key advantage that has permitted the relatively high performances of DMFC anodes with such unsupported catalysts is not just the higher loading, but the dense thinfilm catalyst layer structure, which permits high methanol and proton transport rates to a large number of active sites. For example, DMFC performance enhancement cannot be achieved by increasing the loading of a supported anode catalyst well above 0.5 mg/cm², because of an excessive catalyst layer thickness.

Our findings for DMFC cathode catalyst layers have been similar to those for the DMFC anode, in that catalyst/ionomer thin-films bonded to the membrane provided performances equal to or better than other (e.g., wet-proofed) electrode configurations. High loading, unsupported Pt-black thin-film catalyst layers were found superior to low-loading, supported Pt/C catalysts typically used in our H_2 fueled PEM cells. In this case, the advantages of the high loading, unsupported catalyst appear to enhance methanol tolerance, in addition to the high volume density of catalyst sites.

Single Cell Testing

1 <u>M</u> methanol solutions were pumped through the DMFC anode flow-fields at the relatively high flow-rates of 2 ml/min.⁸ The outlet flows could be controlled such as to impose a desired amount of back-pressure to ensure saturated vapor conditions at the temperature of operation, such that the membrane would be in contact with a liquid solution of methanol on the anode side. The mild pressures required to ensure a two-phase, liquid/vapor system on the anode side of the DMFC also provide a well humidified membrane, and thus, good protonic conductivity at temperatures as high as 130°C. The oxygen or air feeds to the cathodes were humidified to provide water vapor saturated gas at temperatures 0° - 10°C above the cell temperatures. Cell performances were evaluated over the range of 30° to 130°C.

Figure 1 shows polarization and high frequency resistance curves of DMFCs operated at 130° C with 5 atm oxygen cathodes using Nafion 112, 115, and 117 membranes. The best performance (670 mA/cm² at 0.5 V cell voltage) was obtained using the relatively thin (50 μ m) Nafion 112 membranes. The high-frequency (8 kHz) cell resistances for the three cells are also depicted in Figure 1. As the membrane thickness increases, cell resistance increases and cell performance decreases correspondingly. As a matter of fact, the iR-corrected polarization curves for the three different Nafion MEAs virtually overlay one another. Since the methanol permeation rate through the membranes is expected to be greater in the thinner membranes, the cathode should be handling higher fluxes of methanol. The similarity of the iR corrected polarization curves suggests that the cathodes are highly tolerant to such variations in methanol flux. The relative insensitivity of the cathodes does not indicate, however, that the fuel efficiency is unaffected, as the methanol permeation rate is indeed higher with the thinner barriers.⁹ Additional strategies, such as methanol barrier membranes or lean-feed DMFCs,⁹ will need to be implemented to maximize the total efficiencies of DMFCs.

As shown in Figure 1, the high-frequency cell resistivities of the DMFCs operating at 130°C were as low, or lower than those typically seen for conventional, well-humidified H₂/air cells operating at 80°C. Clearly, the membranes were well hydrated even at these elevated temperatures. This is most probably a result of the maintenance (by pressurization) of a liquid in the anode compartment. If, as expected, the methanol in the liquid feed wets (hydrophilizes) the anode backing, liquid water would come in direct contact with the membrane. Since the membrane uptake of water from the liquid is greater than that from the vapor, particularly at such higher temperatures, ¹⁰ a level of water content and hence, conductivity, is attained that could not have been possible if the membrane were equilibrated with water vapor alone. However, others¹¹ have operated direct methanol polymer electrolyte fuel cells at 130°C on vaporized water/methanol feeds.

All of the cells described here demonstrated reasonable performance stability. The performance of the Nafion 112 based cell dropped from 670 mA/cm² to 600 mA/cm² at constant 0.5V cell voltage after one week of running 4 hours each day. Longer term performance stabilities warrant further investigation.

Although the use of the neat oxygen cathode minimizes the oxygen reduction reaction (ORR) losses, most terrestrial applications require the use of an air cathode, preferably under modest pressure conditions. In a similar vein, high temperatures are of some concern because of cell longevity and increased pressure requirements. Figure 2 shows polymer electrolyte DMFC performances under conditions that may be more amenable to transportation applications. Air cathodes at only 3 atm were used instead of higher pressure oxygen and the cell temperatures were also set somewhat lower, at 110°C. Still, Figure 2 shows that with the Nafion 112 membrane/electrode assembly, a current of 370 mA/cm² at 0.5 V cell voltage was obtained with a 1M methanol feed. As shown in Figure 3, the peak power output of this type of DMFC was almost 400 mW/cm² for the oxygen cathode at 130°C.

Figure 4 depicts DMFC performances for various Nafion membranes with thinfilm catalyst layers as a function of cell temperature. Generally, the cells performed relatively poorly at cell temperatures below 80°C. As the cell temperatures were increased, significantly better cell performances were obtained, primarily due to the substantial improvement in anode kinetics. While even higher temperatures will further enhance the anode performance, 130°C is probably near the upper limit for the long-term stability of perfluorosulfonic acid membranes in contact with methanol/water mixtures.

To summarize this brief description of our newest DMFC results, we have shown that high polymer electrolyte DMFC performances can be obtained with MEAs prepared by the decal thin-film electrode fabrication method,^{1,2} using perfluorosulfonic acid membranes and unsupported Pt-Ru anode catalysts. Improvements over previously reported performances are attributable in part to cell temperatures well above 100°C, demonstrated to be feasible in slightly pressurized DMFCs, possibly due to the liquid (methanol/water) in contact with the anode side of the membrane. It is interesting to note that, because the anode feed can be kept in liquid state at such elevated temperatures, the polymer electrolyte DMFC is easier to operate than the hydrogen/air polymer electrolyte fuel cells at temperatures above 100°C. Another very important factor in achieving these high performances is the high catalyst utilizations achieved with optimal catalyst layer structures, as attained with thin-film electrodes bonded to the membrane. Such MEAs have provided the highest DMFC performance in cells prepared by us based on Nafion membranes. The

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apparently high methanol tolerance of our cathodes at higher temperatures suggests that the present performance is primarily limited by anode catalyst activity. With improved anode catalysts and less methanol permeable membranes, it should be possible to obtain yet higher cell performances and fuel efficiencies, using the same general fuel cell package.

DMFC STACK VS. METHANOL REFORMER + RAFC STACK

The significant increase in demonstrated DMFC performance, as shown above and by other research groups, 8,11 has brought the peak power density of the polymer electrolyte DMFC to a level which is only three times lower than that of the reformate/air fuel cell. Consequently, at this point, some simple calculations¹² reveal that the two options, (i) a DMFC stack and, (ii) a methanol reformer + reformate/air fuel cell (RAFC) stack, start showing comparable overall system characteristics.

Table I. Calculation of Energy Conversion Efficiencies for DMFC and RAFC Systems

Assumptions

• Methanol is either: (case 1) Converted directly in DMFC, or (case 2) Steam reformed to H₂ and converted in RAFC

Efficiency calculation

(case 1, DMFC) Total Eff. = $(\eta_v \circ \eta_{fuel})_{fc}$ = $[(V_{cell})_1/V^\circ MeOH/CO_2] \circ (\eta_{fuel,fc})_1$ (case 2, RAFC) Total Eff. = $\eta_{ref} \circ \eta_{prox} \circ \eta_v \circ (\eta_{fuel,fc})_2$ = $[(V_{cell})_2/V^\circ MeOH/CO_2] \circ (\eta_{fuel,fc})_2 \circ \eta_{ref} \circ \eta_{prox}.$

Conclusion

To achieve equal overall conversion efficiencies (MeOH to dc power):

 $(V_{cell})_1 = (V_{cell})_2 \cdot [(\eta_{fuel,fc})_2/(\eta_{fuel,fc})_1] \cdot \eta_{ref} \cdot \eta_{prox}.$

Assuming $(\eta_{\text{fuel,fc}})_1 = 0.90$, $\eta_{\text{ref}} = 0.72$ and $\eta_{\text{prox}} = 0.97$, then

$$V_{cell}$$
)₁ = 0.79 (V_{cell})₂.

i.e., same overall energy conversion for DMFC operating at 0.55 V and RAFC at 0.70 V.

Table I shows a comparison of overall system efficiencies. The overall efficiency of the DMFC is calculated as the voltage efficiency times fuel efficiency of the DMFC stack. The overall efficiency of the reformer+RAFC stack is calculated as a product of the energy conversion efficiency of the reformer, the efficiency of a preferential oxidation (prox) stage, the voltage efficiency of the RAFC stack and the fuel efficiency of the RAFC stack. The calculation shows that the overall energy conversion efficiencies: methanol chemical

energy to DC power of the two systems are comparable(43%) when a DMFC is operating at 0.55V and a RAFC is operating at 0.70V. This is true assuming:

(a) fuel efficiencies of 90% can be reached in the DMFC,

(b) the methanol reformer efficiency (hydrogen energy out/methanol energy in), is 72% (data from reformer manufacturer), and

(c) the overall efficiency of the PROX (hydrogen energy out/hydrogen energy in) is 97%. The fuel efficiency in the RAFC is assumed here 100%.

The main DMFC parameter that needs significant improvement to reach the level assumed above is the fuel efficiency, which to date is significantly smaller in polymer membrane DMFCs because of methanol cross-over. There are, however, some encouraging new results which show that the cross-over flux may possibly be decreased significantly (particularly at higher temperatures) by the use of lean methanol feeds to the anode, without sacrificing cell performance significantly. Adding this approach to possible membrane modifications aimed at lowering methanol permeability, the fuel efficiency of the DMFC could conceivably reach at higher temperatures the level of 90% assumed above.

This calculation, therefore, shows comparable overall energy conversion efficiencies for the two options, DMFC and reformer + RAFC, achieved at what may be described as typical operating voltages for each of the two types of fuel cells.

	DMFC ^a	RAFC ^b	
Stack Power Density (kW/kg)	0.25	1.0	
Stack Materials Cost (\$/kW)			
 Projected^c 	200	45	
• Today	2500	1500	
System Energy Density ^d (Wh/kg)	450	450	

Table II. Projecte	d DMFC and	RAFC Stack	And Syste	ms Characteristics
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a). Advanced fuel cell stack is 50 - 75% of total weight. b). Advanced fuel cell stack is 10 - 30% of total weight. c). Assuming drop in membrane cost by an order of magnitude. d). Assuming (1) Similar overall conv. efficiency of 40%, and (2) Range of 240 mile @ 20 kW, 40 mph. Results of (1) and (2) are: DMFC system: 55 kg MeOH, 100 kg stack, 100 kg BOP; RAFC system: 55 kg MeOH, 20 kg stack, 180 kg BOP

Table II uses some very rough estimates to compare three other key parameters for the two systems: DMFC and the reformer+RAFC stack, i.e., the power density, stack materials costs and system's energy density. Table II shows that the stack power density for the reformate/air fuel cell may be a factor three higher, but the stack is only 10-30% of the total weight of the system vs. 50-75% of the weight expected in the case of the DMFC. The stack materials costs per kW are projected four times higher for the DMFC, mainly because of the lower power density. However, it should be remembered that the DMFC stack cost is a much more major component of the total systems cost. The total system energy density for a 20 kW vehicle with a range of 240 miles is estimated to be similar for both options, around 450 Wh/kg. It should be realized that all of these estimates are very rough indeed, but they do seem to lend support to the following general conclusions:

Having obtained roughly one-third the maximum power densities of reformate/air fuel cells, the methanol/air cell shows promise in becoming a serious competitor to the onboard methanol reforming system for methanol-fueled transportation applications. For these two different systems for conversion of methanol to DC power, we have shown that:

(1) The mass or volume power density are quite similar for:

(i) a DMFC stack operating at 0.25 W/cm², and

(ii) a system comprising a methanol reformer+RAFC generating 1.0 W/cm².

(2) The overall energy conversion efficiency for the complete process of methanol chemical energy to DC electric energy, will be similar (43%) for a system with a RAFC operating at 0.70V and a DMFC operating at 0.55V, provided the fuel efficiency in the DMFC is raised to 90%.

(3) The cost per kW predicted for the DMFC is significantly higher, as long as the areal power density remains lower by a factor of about 3-4 and the catalyst loadings are not reduced significantly. However, the cost of the balance of plant is much higher in the case of the reformer-based system, lowering the cost differential between the two options significantly.

From the points made above, it seems that the DMFC could become a serious candidate for transportation applications, provided the following requirements are also met:

(1) Catalyst loadings are further reduced (or alternative anode catalysts developed),

(2) Long term stable performances (1000 hours time scale) are demonstrated, and

(3) Fuel efficiencies are actually increased to the 90% level.

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FIGURES



Figure 1. Polarization curves for 130°C, oxygen cathode DMFC based on thin-film catalyzed Nafion 112, 115 and 117 membranes. Anodes: 2.2 mg/cm² Pt-RuO_x, 1 <u>M</u> methanol at 2 ml/min and 3 atm. Cathodes: 2.3 mg/cm² Pt-black, 5 atm O₂ at 0.6 l/min.



Figure 2. Polarization curves for 110°C, air cathode DMFC based on thin-film catalyzed Nafion 112, 115 and 117 membranes. Anodes: 2.2 mg/cm² Pt-RuO_x, 1 <u>M</u> methanol at 2 ml/min and 1.8 atm. Cathodes: 2.3 mg/cm² Pt-black, 3 atm air at 0.6 l/min.

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Figure 3. Power density curves for the thin-film catalyzed Nafion 112 assembly operating at 130°C on oxygen and at 110°C on air as depicted in Figs. 1 and 2.



Figure 4. The increase in DMFC current density at 0.5 V with temperature for the thin-film catalyzed Nafion 112, 115, and 117 assemblies. Other conditions noted in Figure 1.

PERFORMANCE OF PEM LIQUID-FEED DIRECT METHANOL - AIR FUEL CELLS

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Abstract

A direct methanol-air fuel cell operating at near atmospheric pressure, low-flow rate air, and at temperatures close to 60° C would tremendously enlarge the scope of potential applications. While earlier studies have reported performance with oxygen, the present study focuses on characterizing the performance of a PEM liquid feed direct methanol-air cell consisting of components developed in house. These cells employ Pt-Ru catalyst in the anode, Pt at the cathode and Nafion[®] 117 as the PEM. The effect of pressure, flow rate of air and temperature on cell performance has been studied. With air, the performance level is as high as 0.437 V at 300 mA/cm² (90 °C, 20 psig, and excess air flow) has been attained. Even more significant is the performance level at 60° C, 1 atm and low flow rates of air (3-5 times stoichiometric), which is 0.4 V at 150 mA/cm². Individual electrode potentials for the methanol and air electrode have been separated and analyzed. Fuel crossover rates and the impact of fuel crossover on the performance of the air electrode have also been measured. The study identifies issues specific to the methanol-air fuel cell and provides a basis for improvement strategies.

Introduction

A liquid-feed type direct methanol fuel cell using proton-exchange membrane electrolyte was developed under an ARPA-sponsored program[1,2]. This fuel cell operates on aqueous solutions of methanol as fuel, and oxygen or air as the oxidant. The cell delivers as high as 0.5 V at 300 mA/cm² at 90°C and employs a Pt-Ru anode and a Pt cathode with Nafion[®] 117 as the electrolyte. Among the significant advantages of this cell are its overall simplicity, ease of removal of carbon dioxide produced from the anode stream, and inherent ability to maintain the membrane at high levels of hydration. A 5-cell stack based on this concept was recently constructed by Giner Inc. and was tested at JPL. The liquid feed direct methanol fuel cell is now being actively considered by DOE and DOD for stationary, portable, and transportation applications. In order that the direct methanol fuel cell become a viable power source for many applications and from an overall system standpoint, it is essential that the fuel cell operates on air as an oxidant near atmospheric pressures, at low air flow rates, and at low to moderate temperatures. Therefore, this study focuses on characterizing the performance of liquid feed direct methanol-air cells developed in house, in order to identify the causes that limit cell performance, and design appropriate modifications.

Experimental Approach

The approach included: a) characterizing and assessing the effects of flow rate, pressure and temperature on the cell performance, b) measuring individual electrode

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characteristics, and c) measuring the crossover rates of methanol. These investigations were carried out on JPL-developed components. The anode catalyst was Pt-Ru (prepared in house), and the cathode catalyst was Pt (fuel cell grade, Johnson Matthey). Specifically designed anode and cathode structures prepared on porous carbon substrate were bonded under heat and pressure to a pre-conditioned Nafion[®] 117 membrane to form a membrane-electrode assembly. The active area of the electrodes was typically 25 cm^2 unless stated otherwise. Each electrode had 4 mg/cm² of catalyst. The cells were characterized with respect to their overall electrical performance under various conditions of temperature and pressure of the oxidant. Substitution of hydrogen for air or oxygen at the cathode converts this electrode into a dynamic hydrogen electrode that can be effectively used as a reference to monitor the methanol fuel electrode. The ohmic resistance of the cell at 1 kHz was also measured. Polarization curves (corrected for ohmic resistance) for individual electrodes were obtained. Methanol crossover rates were measured by estimating the carbon dioxide content of the cathode exit stream using a Horiba VIA-510 analyzer.

Results and Discussion

Figure 1 presents the difference in performances of liquid feed direct methanol fuel cells operating on air and oxygen at 20 psig (2.36 atm) and 1 L/min of the oxidant. The loss in performance to the extent of 90 mV at 300 mA/cm², is attributed to a combination of mass transfer effects in the catalyst layer and porous backing of the cathode and is similar to that observed with the hydrogen-oxygen fuel cell[3]. The cell is capable of sustaining high current densities as in the hydrogen/air fuel cell. Results on the separation of the cell voltage into individual electrode potentials are presented herein later show that under conditions of high stoichiometric flows and pressures as high as 20 psig, the cell is limited in voltage over most of the current density range by the performance of the anode unlike in the hydrogen/air fuel cell. From Fig. 1 it is seen that the methanol -air fuel cell operating on excess air flow at 20 psig and 90 °C sustains 300 mA/cm² at 0.437 V, and with oxygen as the oxidant the cell voltage is as high as 0.520V.



Fig.1 : Performance of liquid feed methanol fuel cell on oxygen and air at 90°C,1 M methanol, active area 25 cm².

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To our knowledge, the performance shown in Figure 1 is the highest reported in the published literature under the specified conditions. On the basis of the ohmic resistance of the Nafion[®] 117 membrane, the cell voltage could be about 40 mV higher using a Nafion [®] 112 membrane with the penalty of increased crossover of methanol. The effect of temperature and pressure of air at high/low flow rates on the cell performance is presented in Figures 2 and 3. Results show that the effect of pressure on the cell voltage is more significant at low flow rates than high flow rates. Likewise, the effect of flow rate is less significant at higher pressures. The impact of working at ambient pressure on the cell voltage is the greatest at low flow rates and low temperature.



Fig. 2: Performance of direct methanol liquid feed fuel cell on air at 0 psig and 20 psig at 5 L/min and 60°C.



Fig. 3: Effect of pressure and temperature on the operation of direct methanol-air cells at air flow rate of 1 L/min.

These results demonstrate that a current density of 150 mA/cm² can be sustained at 0.4 V at 60° C, at ambient pressure and low flow rate (1L/min) of air. This performance level makes the methanol-air fuel as practical power source for many applications.

In order to determine the individual electrode contributions to the cell voltage at low flow rates and ambient pressure, a separation of the electrode potentials was accomplished as described above. These results are presented in Figure 4.



Fig. 4: Individual electrode potentials vs. dynamic hydrogen electrode in a direct methanol air fuel cell operating under ambient pressure air at 1 L/min and 1 M methanol

These results suggest that although the polarization at high current densities arises from the air electrode, the methanol electrode is the most significant contributor to the polarization at low/medium current densities. In order to improve the performance in the range of 100-300 mA/cm² significant improvement in the activity of the anode catalyst is required. At 60°C the overpotential at the anode is higher (by at least 75 mV) than the value at 90 °C throughout the range of current densities. Results shown in Fig.4 establish that significant cathode polarization is observed at 300 mA/cm² at 60°C at low flow rates

The steady state crossover rates for methanol have been measured by estimating the carbon dioxide content in the cathode stream. The crossover rate is expressed as a parasitic current density. The present technique for measurement of crossover rates yields much more consistent values compared to earlier measurements[4] and the present method is now considered the most direct and reliable of those tested so far. The crossover rate is found to decrease with increasing current density, and also increases with temperature. Results presented in Figure 5 is a comparison of the crossover rates at 60°C and 90°C. The decrease of crossover rate at high current density arises from the increased

utilization of methanol at high current densities. This supports the view that improving the utilization of methanol at the anode is a promising approach to achieving lower crossover rates. The impact of methanol crossover on the performance of the cathode is very significant. Improvements in anode performance can be completely offset by reduction in potential of the air electrode over a wide range of current densities.



Fig. 5 : Dependence of parasitic crossover current density on the operating current density of the direct methanol-air fuel cell operating on 1 M methanol and air at 20 psig, 5L/min.

The results presented in Figure 6 suggest that improvements in cathode performance to the extent of 50- 70 mV can be achieved by prevention of fuel crossover. Also, reduction of methanol crossover will allow the use of higher concentrations of methanol that will result in improved kinetics of methanol electro-oxidation.



Fig.6: Individual Electrode Potentials vs. dynamic hydrogen electrode for direct methanol -air fuel cell operating at 60 °C, 0 psig and 5L/min of air.

Conclusions

The liquid-feed direct methanol fuel cells developed at JPL perform at 0.437 V at 300 mA/cm² on air at 20 psig and 90°C; with oxygen, the cell voltage of 0.52 V has been obtained under identical operating conditions. The effect of flow rate on performance is very significant at pressures close to ambient. With the latest improvements in electrode structure, 0.4 V has been attained at 150 mA/cm² at 60 °C and air flows at 3-5 times stoichiometric. These performance levels make the methanol fuel cell extremely suitable for practical applications. Measurement of individual electrode potentials show that improvements to the anode catalyst activity can greatly enhance the performance at 60°C in the low to medium current density range, while improvement in the air electrode performance is also required at higher current densities. The decrease of crossover rate on applied load demonstrates that improvement of methanol utilization at the anode can reduce crossover rates significantly. Impact of the crossover of methanol on the cathode potential is shown to be about 70 mV. This study quantifies the scope for improvement in various parts of the cell.

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DEMS AND SINGLE CELL MEASUREMENTS OF A DIRECT METHANOL FUEL CELL

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The adsorption and oxidation of CH₃OH were studied in 1 M HClO₄ on porous Pt and Pt_xRu_y electrodes by means of Differential Electrochemical Mass Spectrometry (DEMS). The electrodes were made by potentiostatic co-deposition on porous Au substrates. It was found that Pt_{0.9}Ru_{0.1} shows the highest activity compared to pure Pt. For this composition the complete oxidation to CO₂ is favoured in contrast to other compositions which yield more amounts of formic acid. The oxidation of poisoning adsorbate species on Pt_{0.9}Ru_{0.1} is shifted 0.15 V to negative potentials in comparison to Pt. First results on the oxidation of gaseous CH₃OH/H₂O mixtures in a Proton Exchange Membrane Fuel Cell at T = 100 °C are presented. The catalyst loading of gas diffusion electrodes for anode and cathode was 1 mg/cm². With a Pt_{0.7}Ru_{0.3} anode catalyst and Pt as cathode catalyst current densities of > 0.1 A/cm² at 0.4 V were obtained.

INTRODUCTION

Methanol is considered a promising energy carrier for fuel cell systems in mobile and stationary applications. At present, the utilization of methanol in a Proton Exchange Membrane Fuel Cell (PEMFC) requires a reformer for hydrogen production and additional gas cleaning procedures for CO reduction of the fuel gas (1). In principle, the Direct Methanol Fuel Cell (DMFC) probably could avoid complicate fuel processing with its additional weight, volume and costs. Although the basic idea is known for many years the realization has only been demonstrated on a laboratory scale (2-4). The loading of the dispersed electrocatalyst supported on carbon in these demonstration systems was 4-5 mg/cm² and the power density achieved was 100 - 300 mW/cm². However, the amount of noble metal catalyst used for mobile application should be reduced to ≤ 1 mg/cm² whereas the power density should be further enhanced.

A basic concept of a complete DMFC system is illustrated in Fig. 1. Methanol and product water are mixed, evaporated and fed directly into the fuel cell. The heat necessary for methanol evaporation and cleaning of the anode exhaust gas can be provided by a catalytic converter. In such a way the advantage of a fuel cell system in terms of high efficiency and low emissions can be fulfilled. More focussed criteria for

the development of the main components of such a fuel cell system can be obtained by simulating a complete DMFC under various operating conditions (5).

The direct electrochemical oxidation of methanol in a PEMFC requires the development of optimized anode catalysts since the oxidation of CH_3OH on Pt that is presently the most active material leads to the formation of poisoning species such as CO, COH and CHO (6) on the electrode surface. In order to enhance the electrocatalytic activity of the anode towards the oxidation of CO and CH_3OH , PtRu alloys are being proposed as catalysts(7-9). The combination of cyclic voltammetry and Differential Electrochemical Mass Spectrometry (DEMS) (10) is a suitable method to study electrochemical reactions on porous electrodes. On-line mass spectrometry enables identification of volatile and gaseous reaction products formed during methanol oxidation in acid electrolytes. By varying the Pt to Ru ratio in the alloy the best composition for this reaction can be elucidated. In addition, single cell measurements with a PEMFC using carbon supported Pt and PtRu catalysts for the anode can give valuable information on the electrochemical activity of such alloys under practical conditions and can lead to a deeper insight into the process parameters of a complete fuel cell.

EXPERIMENTAL

DEMS measurements were carried out in an electrochemical flow cell attached directly to the vacuum chamber of the mass spectrometer. The electrolyte volume was approx. 2 ml. The working electrodes were prepared by sputtering first a gold substrate layer onto a hydrophobic ethylene-tetrafluoroethylene copolymer membrane (Scimat 200/40/60 from Scimat Ltd.; mean thickness 60 μ m, mean pore size 0.17 μ m, 50 % porosity). Pt and/or Ru were then codeposited from solutions of RuCl₃ and H₂PtCl₆ in 1 M HClO₄ at a constant potential of 0.05 V vs. RHE during 30 min. The surface composition of the Pt_xRu_y layers were determined by ZPS according to (11) while the composition of the bulk alloy was determined by EDAX. The analysis of each sample showed a good reproducibility of the preparation method. The comparison showed that the Pt concentration at the electrode surface was always higher than the corresponding solution composition. For the experiments described below PtRu alloys with Ru contents of <50 atomic % were investigated. To avoid possible surface segregation effects occurring during the experiments, always freshly prepared working electrodes were used.

For testing various Pt_xRu_y anode catalysts in a PEMFC, Membrane Electrode Assemblies (MEAs) were fabricated by hot-pressing gas diffusion electrodes (ETEK, Natick, MA) with a catalyst loading of 1 mg/cm² onto NafionTM 117. MEAs were mounted in a laboratory PEM single cell with Ti current collectors and stainless steel end plates. The active electrode area in all experiments was 4 cm².

The test station for characterization of PEM single cells is shown in Fig. 2 enabling the utilization of various fuels such as pure H_2 , reformate ($H_2/CO_2/CO$) and

CH₃OH. Methanol/water mixtures with various volume ratios are fed into an evaporator and then introduced into the single cell. The cell temperature was 100 °C. Oxygen was used at 2 bar_{abs}, whereas gaseous CH₃OH/H₂O were used at atmospheric pressure. After activation of the MEA the performance of a PEM single cell was first evaluated using H₂/O₂. Then the fuel gas was switched from pure H₂ to CH₃OH/H₂O mixtures.

RESULTS AND DISCUSSION

In order to evaluate the electrocatalytic activity of porous Pt_xRu_y electrodes towards methanol, the electrooxidation of CH_3OH in perchloric acid, the adsorbate formation and the adsorbate oxidation in methanol free $HClO_4$ solution were studied by means of DEMS.

Fig. 3 shows CVs of 1 M CH₃OH in 1 M HClO₄ and simultaneously recorded MSCVs for m/z = 44 and 60 for porous Pt and $Pt_{0.9}Ru_{0.1}$. The potential dependent mass signal of m/z = 44 in the positive going potential scan is due to CO₂ formation during methanol oxidation whereas the signal at m/z = 60 is assigned to the radical cation of HCOOCH₁ indicating the formation of formic acid as partial oxidation product of methanol. The ester formation is explained by a chemical reaction of HCOOH with excess CH₃OH in the solution (6). The onset potential for methanol oxidation at the Pt_{0.9}Ru_{0.1} electrode was observed to be about 0.15 V more negative as with pure Pt. This is the highest negative shift observed for all $Pt_{r}Ru_{v}$ electrodes studied. It should be mentioned that on a pure Ru electrode nor faradaic current due to methanol oxidation neither ion currents of possible reaction products could be observed. Therefore, Ru in acid electrolytes shows no reactivity for methanol oxidation. In a first approximation the relative distribution for CO₂ and HCOOH formation during oxidation can be determined by integrating the ion current for m/z = 44 and 60 for a complete potential cycle. Fig. 4 shows such relative amounts as a function of the Pt content in Pt_xRu_y. It can be seen that the ratio $Q_{(m/z = 44)}$ to $Q_{(m/z = 60)}$ has its maximum when the alloy contains about 90 % Pt. This indicates that the complete oxidation of CH₃OH to CO₂ is favoured on this alloy composition with respect to the formation of the partial oxidation product.

Considering the thermodynamics of the electrochemical methanol oxidation according to

 $CH_3OH + 3/2 O_2 = CO_2 + 2 H_2O$ $\Delta U = 1.21 V (at 25 °C) [1]$

cell performance comparable to the H_2/O_2 fuel cell should be possible. However, a significantly lower activity of methanol oxidation on Pt electrodes is obtained which is explained by the formation of strongly adsorbed intermediates. To study the influence of the Ru content in Pt_xRu_x alloys on the formation of these species, cyclic voltammetric

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curves of CH₃OH in HClO₄ on adsorbate free electrode surfaces were monitored. For this purpose, a complete potential scan in methanol free solution was recorded for checking the cleanness of the electrode. A potential of $U_{ad} = 0.05$ V vs. RHE was adjusted and 1 M CH₃OH solution was introduced into the flow cell followed by starting a positive going potential scan. Fig. 5 shows the CVs and the simultaneously recorded MSCVs for m/z = 44 on pure Pt and Pt_{0.9}Ru_{0.1}. In the potential range between 0.05 and 0.3 V anodic peaks were observed at 0.2 V for Pt and at 0.18 V for Pt_{0.9}Ru_{0.1} occurring only in the first potential scan. In this potential range no mass signals due to CO₂ were observed. CO₂ production on Pt and $Pt_{0.9}Ru_{0.1}$ commences at U > 0.35 V parallel to the increase of the faradaic currents in the CV. The anodic current in the range 0.05 - 0.3 V is explained by the formation an adsorbate layer having a higher oxidation state than methanol. On pure Pt, in-situ infrared spectroscopy has shown that the adsorbate layer formed consists of species such as linear bonded CO, COH and CHO (3). The highest anodic charge determined during the first positive going scan as seen in Fig. 5 was found for pure Pt. This adsorption charge decreases with increasing Ru content in Pt_rRu_v. On pure Ru no adsorbate formation was observed. Thus methanol adsorption occurs only on Pt sites agree with results reported in literature (9, 13).

In the next series of experiments the oxidation of the methanol adsorbate in CH₃OH free solutions was studied. After adsorption of methanol at $U_{ad} = 0.20$ V vs. RHE for 5 min. the methanol containing electrolyte was replaced completely by pure HClO₄ solution and the adsorbate was stripped in the first positive going potential scan. Fig. 6 shows the CVs and corresponding mass signals for CO₂ formation during oxidation of adsorbed methanol on pure Pt and Pt_{0.9}Ru_{0.1}. On Pt_{0.9}Ru_{0.1} the peak potential observed for the complete oxidation of the adsorbate to CO₂ is shifted by 0.15 V negative compared to Pt. This is the same shift as observed for the oxidation of dissolved CH₃OH as discussed above. This observation gives evidence that Ru promotes the oxidation of the poisoning intermediate during oxidation of methanol.

The mechanism of the electrochemical CH₃OH oxidation on Pt electrodes is regarded to consist of two parallel reaction pathways (12,14). This is first the direct oxidation of a weakly adsorbed CH₃OH molecule to CO_2 and partially oxidized products such as HCOOH. Using DEMS this product can be identified as HCOOCH₃ as illustrated in Figs.3 and 4. The second pathway is the oxidation of methanol via a strongly adsorbed intermediate partially blocking active site of the Pt surface. The adsorption is assumed to take place by dehydrogenation reactions forming different adsorbate species according to the following reactions

>	Pt-CH₂OH		$+ H^{+} +$	⊦ e⁻	[2]
>	Pt ₂ -CHOH		+ H+ +	⊦e⁻	[3]
>	Pt ₃ -COH		+ H* +	⊦e⁻	[4]
>	Pt-CO +	2 Pt	+ H* +	⊦e⁻	[5]
	> > >	$\begin{array}{llllllllllllllllllllllllllllllllllll$	$\begin{array}{ll}> & \text{Pt-CH}_2\text{OH} \\> & \text{Pt}_2\text{-CHOH} \\> & \text{Pt}_3\text{-COH} \\> & \text{Pt-CO} & + & 2 \text{ Pt} \end{array}$	$\begin{array}{rrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrr$	$\begin{array}{rrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrr$

The experimental findings obtained on porous Pt_xRu_y electrodes in $HClO_4$ solutions can be explained using a certain spatial distribution of sites for CH_3OH adsorption on PtRu first presented by Gasteiger et al. (9). In this model methanol is preferentially adsorbed on 3-fold Pt sites according reactions [2] - [4]. With a surface composition of around 90 % Pt and 10 % Ru these Pt ensembles are surrounded by one Ru atom on which water adsorption according

$$Ru + H_2O ---> Ru-OH + H^+ + e^-$$
 [6]

occurs at potentials more negative compared to Pt. The enhanced reaction rate for methanol oxidation on Pt_xRu_y is then promoted by adsorbed water on Ru according the bifunctional mechanism proposed by Watanabe and Motoo (15)

or

$$Pt-COH + Ru-OH \quad --- > Pt + Ru + CO_2 + 2 H^+ + 2 e^-$$
[7]

$$Pt-CO + Ru-OH \longrightarrow Pt + Ru + CO_2 + H^+ + e^-$$
 [8]

Figs. 7 and 8 present results on the direct electrochemical oxidation of methanol in a PEMFC. The MEA in the single cell was activated at a current density of 0.25 A/cm² with humidified H₂ and O₂ at 100 °C and 2 bar until reproducible current-voltage curves were obtained. After introducing gaseous CH₃OH/H₂O with a volume ratio of 1:5 into the test station the open cell voltage drops from 1.05 V for H₂/O₂ to values of about 0.7 V after a period of 5 min (see Fig. 7). In the case of H₂/CO mixtures as fuels, however, the observed open circuit cell voltage is the same as for pure H₂ (16). The decrease of the cell voltage of a PEMFC in the presence of CH₃OH is explained by the diffusion of methanol through the Nafion membrane and the formation of a mixed potential at the cathode. Assuming a membrane thickness 170 μ m, a diffusion coefficient of methanol in Nafion of D = 4 · 10⁻⁷ cm²/s can roughly be estimated according the cell voltage transient in Fig. 7.

Current-voltage plots the single cell using Pt, $Pt_{0.7}Ru_{0.3}$ and $Pt_{0.5}Ru_{0.5}$ as anode catalyst is shown in Fig. 8. The use of PtRu anode catalysts lead to an improvement of the power density of the PEMFC. As expected from the DEMS data, $Pt_{0.7}Ru_{0.3}$ shows a better performance as $Pt_{0.5}Ru_{0.5}$. Using low catalyst loading of 1 mg/cm² current densities of > 0.1 A/cm² can be achieved at 0.4 V. It should be mentioned that the operating conditions are not optimized and improvements of the cell performance are possible. For a Pt content of > 70 % a further enhancement of the power density is expected when regarding the experimental results obtained on porous Pt_xRu_y electrodes as discussed above. An additional aspect should be the catalyst loading. Literature data show higher performances at catalyst loading of $\ge 4 \text{ mg/cm}^2$ (2-4). However, for the possible application of a DMFC in mobile systems, it should be kept in mind that high catalyst loading lead to higher costs of such fuel cell systems.

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CONCLUSIONS

Adsorption and oxidation of methanol in 1 M HClO₄ solution were studied on porous Pt_xRu_y electrodes by means of cyclic voltammetry combined with on-line mass spectrometry. Beside CO₂ the formation of HCOOCH₃ coming from HCOOH was identified. The quantification of the product distribution showed that on $Pt_{0.9}Ru_{0.1}$ the complete oxidation of CH₃OH to CO₂ is favoured with respect to partial oxidation to HCOOH. The amount of poisoning adsorbate species decreases with increasing Ru content in the alloy. The onset potential of both oxidation of dissolved methanol and adsorbate oxidation is negative shifted by 0.15 V compared to pure Pt. The enhanced reaction rate for methanol oxidation on $Pt_{0.9}Ru_{0.1}$ was explained by the bifunctional mechanism.

Preliminary results on the direct electrochemical oxidation of gaseous CH_3OH/H_2O mixtures in a Proton Exchange Membrane Fuel Cell were presented. Membrane electrode assemblies were fabricated with catalyst loadings of 1 mg/cm². PtRu as anode catalyst improves the cell performance compared to a pure Pt catalyst. For a $Pt_{0.9}Ru_{0.1}$ catalyst current density of 0.1 A/cm² at 0.4 V were achieved.

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FIGURES







Figure 2:

Test station for performance evaluation of PEM single cells using H₂/O₂(air) or CH₃OH/O₂(air).



Figure 3:

Potentiodynamic profiles for electrooxidation of 1 M CH₃OH in 1 M HClO₄ at porous Pt and $Pt_{0.9}Ru_{0.1}$; dU/dt = 0.01 V/s

CV; MSCVs for m/z = 44 (CO₂ formation) and m/z = 60 (formation of HCOOCH₃).



Figure 4: Relative amount of m/z = 44 and m/z = 60 versus the Pt content in PtRu.

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Figure 5:

Potentiodynamic methanol adsorbate formation on porous $Pt_{0.9}Ru_{0.1}$ and Pt in 1 M HClO₄; dU/dt = 0.01 V/s; CV (top); MSCV for m/z = 44;

(-) first positive-going scan starting at 0.05 V; (---) supporting electrolyte.



Figure 6:

Oxidation of adsorbed methanol on Pt and $Pt_{0.9}Ru_{0.1}$ in 1 M HClO₄; dU/dt = 0.01 V/s; CV (top); MSCV for m/z = 44.

solid line: first positive-going scan starting at Uad; dashed line: second potential scan.



Figure 7:

Open circuit cell voltage of a PEMFC after switching the fuel gas from pure H_2 to H_2O/CH_3OH (vol. 5 :1) mixtures using a $Pt_{70}Ru_{30}$ anode catalyst.



Figure 8:

Single cell measurements for direct oxidation of methanol in a PEMFC with Pt, $Pt_{0.7}Ru_{0.3}$ and $Pt_{0.5}Ru_{0.5}$ as anode catalysts and pure Pt for the cathode; catalyst loading on both gas diffusion electrodes: 1 mg/cm².

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STUDIES ON METHANOL CROSSOVER IN LIQUID-FEED DIRECT METHANOL PEM FUEL CELLS

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Abstract

The performance of liquid feed direct methanol fuel cells using various types of Nafion membranes as the solid polymer electrolyte have been studied. The rate of fuel crossover and electrical performance has been measured for cells with Nafion membranes of various thicknesses and equivalent weights. The crossover rate is found to decrease with increasing thickness and applied current. The dependence of crossover rate on current density can be understood in terms of a simple linear diffusion model which suggests that the crossover rate can be influenced by the electrode structure in addition to the membrane. The studies suggest that Nafion EW 1500 is a very promising alternate to Nafion EW 1100 for direct methanol fuel cells.

Introduction

A liquid-feed type direct methanol fuel cell using proton-exchange membrane electrolyte was developed under an ARPA-sponsored program and is now being actively considered by DOE and DOD for stationary, portable, and transportation applications[1-3]. This fuel cell operates on aqueous solutions of methanol as fuel and oxygen or air as the oxidant and uses an ionically conducting polymer membrane such as Nafion[®] 117 as the electrolyte. This type of direct oxidation cell is fuel versatile and offers significant advantages in terms of simplicity of design and operation. In order to improve the performance of these cells, it is necessary to reduce the parasitic loss of fuel across the cell, termed "fuel crossover". The present study on fuel crossover focuses on Nafion[®] type membranes of various thicknesses and equivalent weight. The effect of applied current density on fuel crossover has also been studied.

Experimental approach

The membrane-electrode assemblies used in this study had an active area of 25 cm^2 . The anode consisted of 4 mg/cm² of Pt-Ru and the cathode of 1mg/cm² of Pt and were fabricated by Giner, Inc. The catalyzed electrodes were bonded to the various Nafion-type membranes supplied by Du Pont. Crossover rates were measured by estimating the carbon dioxide content of the cathode exit stream using a Horiba VIA-510 Analyzer. The

methanol concentration was maintained at 1M in all the experiments. Crossover rate is reported as an equivalent current density of methanol oxidation. Crossover rate was measured under open circuit and on load. Nafion types of various equivalent weights and thicknesses were investigated.

Results and Discussion

Results presented in Fig 1 show that membrane thickness has a significant impact on crossover. Increasing the thickness from 5 mils to 14 mils causes the crossover to reduce by about 40-50%. At the operating current density of 300 mA/cm², the reduction in crossover rate with thickness is about 10.5 mA/cm² per mil of reduction in thickness. This can be used as a value for first approximation in estimating crossover reduction by increasing membrane thickness.



Fig. 1. Effect of membrane thickness on crossover for Nafion EW 1100.

Under actual conditions of operation, the crossover rate decreases with increasing current density of operation. From Fig. 1 it is seen that this effect is similar for membranes of two different thicknesses. Initially, it was perceived that methanol crossover phenomena was controlled only by transfer of methanol through the membrane. However, the results shown in Fig.1 suggests that factors other than membrane thickness govern the effect of applied load on crossover. A phenomenological linear diffusion model for the steady-state conditions prevailing during fuel cell operation was presented earlier [4] and considered only membrane effects. This model can now be extended to include electrode effects is shown in Fig.2.


= applied current density

= crossover current density

- D_a = apparent diffusion coefficient in the electrode structure
- D_{mem} = apparent diffusion coefficeint in the membrane
- A = area
- F = Faraday
- n = number of electrons/ mole
- C' = concentration of MeOH at the inlet
- C = concentration of MeOH adjacent to the edge of membrane



The flux of methanol across the electrode structure is related to the total current as follows:

 $i_{app} + i_{cr} = nFAD_{el}(C^*-C)/\delta_{el}$

The flux of methanol due to crossover is given by, $i_{cr} = nFAD_{mem}C/\delta_{mem}$

Combining the above relations, $i_{cr}=nFAD_{el}\{1/(1+k)\}C^*/\delta_{el}-i_{app}\{1/(1+k)\}$ where $k=D_{el}\delta_{mem}/(D_{mem}\delta_{el})$

Fig.2: Phenomenological modelling of the crossover of methanol across the membrane electrode assembly

The methanol concentration is shown to vary from a known inlet value to an intermediate value on the fuel side and then finally to known zero concentration on the cathode. In the steady state all these concentration gradients are linear. The methanol consumption rate in the electrode in terms of the measured current and concentration gradient in the electrode structure is related to the methanol crossover rate through the membrane to yield an expression for crossover rate of methanol in terms of membrane and electrode properties and applied current. Such a model explains the apparent linear decrease in crossover rate with current density and suggests that the crossover can be reduced by altering the methanol permeabilities of the catalyst layer and electrode structure.

The electrical performance of fuel cells with 1100 EW membrane of various thicknesses (Fig.3) shows that the performance trend is probably determined by the combined effects of ionic conductivity and fuel crossover. As a result at higher thicknesses, the ohmic resistance of the cell could be determining the cell voltage, although there would have been some enhancement of the cell voltage due to reduced crossover.



Fig.3: Electrical performance of direct methanol fuel cells with Nafion 1100 membranes of various thicknesses.

Results presented in Fig. 4 demonstrate that high equivalent weight Nafion-types exhibit lower methanol permeability.



Fig. 4: Crossover rate in direct methanol fuel cells with Nafion membranes of different equivalent weight types

Electrical performance studies (Figure 5) on various membranes of different equivalent weights indicates a small reduction in voltage and increase in slope with increasing membrane equivalent weight.

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Fig.5: Electrical Performance of direct methanol fuel cells with Nafion 1500 and 1100.

These findings are consistent with the results of ionic conductivity measurements (Figure 6) suggesting that Nafion 1500 would be a promising alternate to Nafion 1100. The Nafion membrane consisting of a thin layer of EW 1500 and a thicker layer of EW 1070 shows an intermediate crossover rates and electrical performance.



Fig.6: Electrical conductivity of Nafion membranes of different equivalent weights.

The open circuit voltage of the cells with various membrane types correlated with the crossover rate as shown in Table 1.

Table 1:	Open circuit voltage of methanol/oxygen fuel cell		with 1 M methanol at 90°C
	MEMBRANE	CROSSOVER	

TYPE, EW	RATE,mA/cm2	OCV
1100	313	0.748
(1500/1070)	275	0.755
1200	227	0.766
1500	186	0.778

The cell voltage decreases with increasing crossover rate. Similar effects on the on-load voltage of the cell is to be expected.

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Methanol Cross-over in Direct Methanol Fuel Cells

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ABSTRACT

Transport rates of methanol in ionomer membranes exposed to methanol aqueous solutions were determined electrochemically in cells identical to direct methanol fuel cells (DMFCs) and by NMR measurements on the membrane equilibrated with the methanol solutions. We will compare the electrochemical and NMR results and discuss them in the context of temperature and membrane thickness effects on methanol crossover in DMFCs. In addition, we show results for CO₂ emission from the cathode of an operating DMFC as a function of cell current and methanol concentration in the feed stream, that indicate (1) at low concentrations, methanol cross-over can be lowered by methanol consumption in the anode; and (2) at higher concentrations, methanol is carried across the cell significantly by electroosmosis.

INTRODUCTION

Direct methanol fuel cells (DMFC) utilizing perfluorosulfonate ionomer membranes, such as Nafion[®], have received much recent attention. These fuel cells achieve simplicity in system design and cell operation relative to cells operating on reformed methanol, and can yield overall high energy efficiency. They are promising candidates for portable power sources as well as electric vehicle applications. Two major obstacles currently preventing wide-spread commercial applications of DMFCs are the low activity of methanol oxidation catalysts described to date and the phenomenon of methanol permeation through the membrane. Methanol cross-over not only lowers fuel utilization efficiency but also adversely affects the oxygen cathode performance, thus lowering cell performance. Since the methanol permeation rate is an important factor affecting the DMFC performance, it was measured in some investigations by monitoring CO₂ emission from the cathode during the DMFC operation^{1,2}. Some fundamental studies of methanol transport in membranes have also been published^{3,4}.

We have previously discussed the transport and related parameters required for complete characterization of membrane aspects of the DMFC⁴. These include water and methanol uptake by the membrane as a function of feed type and concentration, the diffusion coefficients of water and methanol in the membrane and their cross-coupling, and electroosmotic drag of each solvent associated with the protonic current. Here, we report a study of methanol partitioning and transport in Nafion[®] membranes, using both *in situ* and *ex situ* measurement methods. Nafion[®] and related poly (perfluorosulfonic) acid membranes have been extensively studied in the context of hydrogen fueled fuel cells⁵. Such studies represent a good starting point for understanding and optimizing membrane performance in DMFCs. We compare results of electrochemical permeation measurements across a cell of structure identical to that of a DMFC with data obtained from NMR measurements of methanol uptake and diffusion. In addition, we describe some recent measurements of cathode CO₂ emission in an operating DMFC which demonstrate interesting effects of DMFC current on methanol cross-over, measured in an operating DMFC.

EXPERIMENTAL

The cell components used in a DMFC and in the measurement of methanol permeation through the membrane are shown in Fig. 1. Nafion[®] membranes are pretreated as described elsewhere⁶. Electrodes consist of two distinct layers, a (gas diffusion) backing layer and a thin film composite layer of interspersed catalyst and ionomer.

The thin film catalyst layers on the Nafion[®] membranes were formed by using the decal method developed in this laboratory previously for H₂/air cell⁶. Unsupported catalysts (anode catalyst: Pt-RuOx, NRP 30-30 from E-Tek, Inc.; cathode catalyst: Pt black) were used. The catalyst compositions were optimized to ensure good electronic and ionic connectivity. This was achieved by adjusting the metal catalyst/Nafion[®] ratio of the ink mixtures, adding 5% Nafion[®] solution (900 EW., Solution Technology, Inc.) to the water-wetted metal catalysts. A suitable DMFC anode ink composition was 85 w.% Pt-RuOx and 15 w.% Nafion[®], and that of cathode ink was 93 w. % Pt and 7 w. % Nafion[®]. To prepare the membrane electrode assembly, anode and cathode inks were uniformly painted on two Teflon blanks (5 cm²) to a catalyst loading of 2 mg cm⁻². After drying at 100 °C, the catalyst layers were transferred to and bound to a dried Nafion[®] membrane (60 °C on vacuum table for 45 min.) by hot pressing at 125 °C and 1200 pounds for 120 s. After the Teflon blanks were peeled off the catalyst/membrane assembly, the cells were assembled in the order shown in Fig.1.

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For both voltammetric and potential step experiments, a HP6033A power supply (Hewlett Packard) was used in conjunction with our standard fuel cell test station. The power supply allowed potential control. Programs written in Labview (National Instruments) were used to control the experiments using a Power Macintosh computer.

The cell conditions used for methanol permeation experiments were the same as those used for a liquid-feed DMFC, other than the replacement of humidified oxygen by humidified nitrogen, and are listed in Table 1 for different cell temperatures. Methanol solution fed into the cell was at room temperature. At a cell temperature above 90 °C, it is necessary to raise the pressure applied to methanol effluent to prevent complete vaporization. Applying a higher pressure than that listed in Table 1 does not have noticeable effect on the methanol permeation rate. Using a higher N₂ humidification temperature than the cell temperature helps to keep the membrane adequately hydrated. At a sufficiently high methanol solution feed rate (>0.75 ml min.⁻¹), the limiting current i_{lim} was independent of methanol pumping rate. All experiments in this study were carried out at a methanol pumping rate of 2.5 ml min.⁻¹, which was well above the methanol flow rate limited current. The permeation of methanol was measured in such cells electrochemically by monitoring methanol electrooxidation at the "nitrogen electrode."

Tcell	PMeOH (psig)	Thum, nit (°C)	Pnitrogen (psig)
30	0	80	30
50	0	100	40
90	0	110	60
110	12	130	60
130	32	150	60

Table 1: Cell Conditions for Testing at Various Temperatures

For *ex situ* membrane transport measurements, a variety of methods based on those previously described in the context of water and proton transport studies were used^{5b-f}. For experiments probing methanol and water partitioning into the membrane, hydrated Nafion[®] 117 samples were immersed in a methanol/water mixture of appropriate composition at room temperature for several days and then emersed and loaded into an NMR tube. The total water plus methanol uptake was determined gravimetrically. ¹H NMR spectra were recorded on a Bruker AMX400 spectrometer operating at 400 MHz. Diffusion coefficients were measured for both the equilibrated membrane and the equilibration solution using the pulsed gradient spin-echo sequence. The NMR probe employed shielded gradients to minimize the effects of induced Eddy currents on the diffusion measurements. Protonic conductivities for membrane samples

immersed in methanol water mixtures were measured by high-frequency impedance using our previously described conductivity cell^{5b}.

Measurements of methanol transport through DMFCs under current were carried out by monitoring the IR absorbance of CO₂ in the gas stream emerging from the DMFC cathode. The gas stream was passed through a desiccant column into the gas IR cell. A minimum time of roughly 1 minute for equilibration of CO₂ in the system was observed and all sampling was done for longer than this time to ensure an accurate reading. IR spectra were recorded at room temperature with a Perkin-Elmer System 2000 spectrometer using a short pathlength gas cell.

RESULTS AND DISCUSSION

Electrochemical Measurements of Methanol Permeability Through DMFC-like Cells

For the electrochemical determination of permeation rates of methanol through the DMFC, the ordinary DMFC assembly shown in Figure 1 is used. The electrode which is ordinarily the cathode in the DMFC is exposed to an inert atmosphere and its potential is controlled in the voltammetric or potential step experiment. Fig. 1 shows schematically the transport processes involved and the electrode reactions occurring during the permeation experiments. It can be seen that the methanol electrooxidation current measured at the "nitrogen side" of the cell will depend on the methanol flux through the cell, as the counter electrode process--electroreduction of H⁺ to H₂ occurring on the "methanol side"--will not present any current limitation. Fig. 2 shows the voltammetric curves obtained by varying the potential at scan rates of 2 mV/sec. The current/voltage curves due to the methanol flux and electrooxidation are shown at various cell temperatures for a Nafion[®] 117 membrane. The methanol flux through the membrane is determined from the measured mass transport limited current, i.e. the plateau of the voltammogram. The methanol flux is seen to increase with temperature. Assuming that the Nafion[®] membrane is pinhole free, the observed i_{lim} from methanol permeation through the complete cell can be expressed, in general, as:

$$\frac{1}{i_{\lim}} = \frac{1}{i_{\lim,back}} + \frac{d}{nFAD_mC_m} + \frac{1}{nFAC X_f}$$
(1)

where, $D_m C_m/d$ is the methanol flux across the membrane, $i_{lim,back}$ is the limiting current equivalent of methanol flux across the (carbon cloth) anode backing, and C'X_f is a methanol flux across an interface, a measure of any interfacial barriers present in the cell.

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Figure 3 shows a plot of the reciprocal of the limiting currents obtained from these permeation measurements versus the thickness of the membrane for a series of Nafion[®] 1100 EW membranes at 30, 50, and 70 °C. This plot reveals a linear dependence of i_{lim}^{-1} on membrane thickness. Importantly, the zero intercept observed in this plot indicates that the rate of methanol transport through the cell is practically controlled by the membrane only (i.e. the middle term in Eqn. 1). The implication of this result is that neither the anode backing nor any interfacial barriers to methanol transport significantly affect the methanol cross-over rate in cells prepared as in this work. Cross-over is fully determined by the membrane.

The methanol flux obtained from the above permeation experiments can be further dissected into corresponding partition and diffusion coefficients, based on values of $C_m D_m^{1/2}$ obtained, according to the Cottrell relationship, from potential step experiments:

$$i = \frac{nFAC_m \sqrt{D_m}}{\sqrt{\pi t}}$$
(2)

The relatively small permeability of the membrane allowed us to observe, in the potential step experiment, Cottrell behavior for an extended time period (up to 10 sec) followed by steady state diffusion through the membrane, and thus to evaluate $C_m D_m ^{1/2}$. A typical Cottrell plot, obtained in response to a potential step from 0 to 0.85 V for a cell with a Nafion[®] 117 membrane operating at 90 °C, is shown in Figure 4.

We solve for D_m and C_m using $D_m C_m$ values obtained from the limiting currents and $C_m D_m^{1/2}$ values obtained from the Cottrell analysis. The results are summarized in Fig. 5 and Table 2. We see that between 30 and 90 °C the methanol concentration in the membrane ([MeOH]_m) in contact with a methanol solution remains unchanged, but starts to decrease above 90 °C (Fig. 5). This explains the slower increase in methanol electrooxidation current with temperature above 90 °C, observed in Fig. 2. The diffusion coefficients obtained are summarized in Table 2. The lower uptake of methanol at such elevated temperatures reflects the strong tendency of the PFSA membrane to lose solvent at temperatures exceeding the boiling point of the solvent.

 Table 2: Methanol Diffusion Coefficients from Electrochemistry Measurements at Various Temperatures, 1 M Methanol Liquid Feed

Temperature (°C)	Diffusion Coefficient (x 10 ⁵ , cm ² /sec)	
30	0.65	
50	1.1	
90	2.3	
110	4.3	
130	8.1	

There is a marked increase in the measured D's with temperature. Indeed, an Arrhenius plot of log(D) vs. T^{-1} yields an apparent activation energy of 5.8 kcal mol⁻¹. This number should be considered an effective value. In the actual cell, factors other than temperature changes (e.g. water content changes) also contribute to changes in the observed D and it is thus inappropriate to refer to this value as a pure activation energy. However, it does emphasize the point that methanol mobility within the membrane increases significantly with temperature.

Ex situ Measurements of Membrane Transport Properties

Methanol uptake and transport in membranes have been studied using NMR spectroscopic and PGSE diffusion methods applied to Nafion[®] 117 membranes equilibrated by immersion in solutions of 0.5-8 m methanol in water at 30 °C. These concentrations bracket the experimentally observed optimal methanol concentration (in water) in a liquid feed DMFC. NMR spectroscopic measurements allow us to estimate water to methanol ratios in the membrane. The relative amounts of water and methanol absorbed by the membrane from solutions of various concentrations were measured by comparing the NMR signal intensities of the water and methanol (CH3) resonances. In each case, the ratio of methanol to water concentrations found from these measurements is the same inside and outside the membrane. Thus, little preference is shown for methanol (or for water) uptake by Nafion[®] from methanol/water mixtures. It should also be added that the uptake of methanol is in addition to the uptake of water. There is no observable enhancement (or decrease) of the water uptake in the presence of methanol. These results are consistent with methanol concentration evaluated from the electrochemical measurements (Fig. 5) when the membrane porosity is taken into account.

Diffusion coefficients for water and methanol in solution and in the membrane were determined at 30 °C using the pulsed field gradient spin-echo NMR method. In this method, the latter half of the spin-echo is measured as a function of gradient strength. The Fourier transform of each half echo gives the spectrum with appropriate diffusional attenuation. This allows one to calculate the component self-diffusion coefficients for water and methanol. A concentration independent diffusion coefficient for methanol of 6 x 10^{-6} cm²sec⁻¹ has been measured for methanol at 30 °C in the methanol/water equilibrated samples. This value accords well with that measured by electrochemical means. The similarity of diffusion coefficients measured by the different methods, electrochemical and NMR, used here, is probably due to the low mole fraction of

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methanol in water. Under these conditions, it is reasonable to expect that the intradiffusion coefficient, D_{intra} , (from the NMR measurement) is similar to the chemical diffusion coefficient, D_{chem} , (from the electrochemical measurements). The NMR measurements are currently being extended to higher temperature regimes.

We also measured the conductivity of membranes immersed in the methanol/water mixtures as a function of temperature. The results are shown in Figure 6. A small decrease in the membrane conductivity was observed over a wide temperature range in the presence of the methanol.

<u>Diffusion, Electroosmosis and "Preconsumption" of Methanol</u> Separation of the diffusive and electrokinetic components of the methanol cross-over rate in the DMFC is critical. A strong effect of electroosmosis on methanol cross-over was shown by the work of Maricle et al.¹ where they demonstrated transport of 1 MeOH/H⁺ by electroosmosis through a cell in which a 1.5:1 H₂O/MeOH solution was used as liquid anode feed. Interestingly, the results of Maricle et al. correspond to essentially statistical partitioning of the drag between water and methanol if we assume a total solvent drag of 2.5 solvent molecules per proton, in line with our previously reported electroosmotic drag coefficient in Nafion[®] 117 membranes exposed to liquid water^{5e}. Assuming this statistical partitioning, we can estimate the influence of electroosmotic effects on the cross-over levels reported here from *in situ* electrochemical measurements. Roughly speaking, for 1M methanol, methanol would correspond to only 2% of the overall drag while 98% of the dragged solvent will be water. To a good approximation, then, migration of methanol is negligible relative to diffusion at such low concentrations of methanol.

The high methanol cross-over rates measured electrochemically through Nafion[®] 117 are not directly translated to cross-over fluxes in operating cells, particularly at higher cell temperatures. The important difference is that, unlike the case of the electrochemical cell shown in Fig. 1, methanol can be consumed to some extent in the anode of an operating DMFC (*vide infra*), thus lowering the methanol permeance. To determine the methanol flux through the membrane in an operating DMFC, as opposed to determining membrane properties *per se*, we must study output of CO₂ from the cell cathode under current, as described in the next section.

Methanol Transport Across the Cell in an Operating DMFC

We have determined the dependence of CO₂ emission from the cathode of an operating, liquid feed DMFC as a function of current density for a variety of feed

concentrations. The cell configuration was as follows: MeOH(aq)/Pt-Ru(2.6 mg/cm2) / Nafion[®] 117 / Pt black (2.7 mg/cm2)/Oxygen(humidified). It was operated at 90 °C. The results are shown in Figure 7. Because of difficulties with trapping of some CO₂ in the drierite column, the results are best regarded as qualitatively correct (with an offset on the equivalent current axis). Nonetheless, there are several intriguing features of this curve.

At low methanol feed concentrations, the CO₂ evolved from the cathode decreases substantially with current densities. This suggests that the methanol impinging on the anode is substantially consumed within the anode catalyst layer before crossing over through the membrane. Thus, it may be possible to operate the DMFC in a lean feed mode with high fuel utilization efficiency if a stable operating point at high current densities can be found and maintained.

At higher methanol feed concentrations ($C_{MeOH}\geq 2M$), the CO₂ emission from the cathode begins to increase with increasing current density. Under these conditions, electroosmotic transport of methanol through the cell becomes a significant player. Such results have been previously reported (for the 13 M point) by Maricle et al.¹. The overall implication of these results is that fuel utilization may degrade with current density for high methanol concentrations. These results also emphasize the previously observed optimal methanol concentration for maximum DMFC performance, reported by several groups to be below 4M.

Cross-over Implications in DMFCs

The principal penalty associated with methanol cross-over in DMFCs is a lower fuel efficiency. As the results reported above show, substantial permeation of methanol through the membrane occurs in cells using poly(perfluorosulfonic) acid membranes. Based on the linear decrease of methanol flux with membrane thickness (Fig. 3) and the steady state methanol flux values shown (Fig. 2), we estimate, for a 2 mil thick Nafion[®] membrane, a cross-over flux of up to 700 mA/cm² at 130 °C for a 1M methanol feed. Nonetheless, a DMFC using such a thin membrane under those conditions gives excellent performance at high current densities⁷. It is likely that the actual methanol cross-over rate is significantly less than the calculated amount because of significant methanol consumption within the anode at high current densities, as shown in Fig. 7. The electrochemical method used here estimates the methanol permeation rate only under open circuit conditions. The high DMFC performance at higher temperatures also suggests that, at 130 °C, the DMFC cathode performance is not severely degraded by methanol cross-over. These high performances are quite encouraging, but high fuel-oxygen

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recombination rates at open circuit would require an answer at the system design level if cross-over rates cannot be significantly lowered.

CONCLUSIONS

The primary results shown here are:

Methanol permeation rates between 50 -200 mA/cm² of equivalent current density are measured through a Nafion[®] 117 membrane in the temperature range 50-130 °C.
 In Nafion[®] membrane-based DMFCs, the methanol permeation rate at open circuit is linearly dependent on membrane thickness in a liquid feed cell, thus ruling out any other significant transport barrier.

(3) Concentration of methanol in the membrane starts to decline as the temperature is raised, but the diffusion coefficient increases rapidly, leading to an overall increase in permeation of methanol with temperature through a well-swollen Nafion[®] membrane.
(4) Measurements of methanol cross-over in operating DMFCs show significant consumption of methanol at the anode at 90 °C for feed concentrations of the order of 1M methanol. This suggests a possible cell operating mode ('lean feed') for improved fuel efficiency in polymer electrolyte DMFCs.

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Figure 1: Schematic showing permeation measurement method in DMFC configuration;
 (a) graphite blocks with cross-patterned flow field;
 (b) gas permeable backing, anode side;
 (c) anode thin film catalyst layer;
 (d) Nafion[®] membrane;
 (e) cathode thin film catalyst layer;
 (f) gas permeable backing, cathode side. For the permeation measurement, the humidified oxygen feed is replaced by humidified nitrogen feed and electrooxidation of methanol takes place at <u>e</u>. See text for more detailed descriptions.



Figure 2: Voltammetric curves at various cell temperatures for the oxidation of methanol permeating through a Nafion[®] membrane 117 exposed to a 1 M methanol feed on the anode side and humidified inert gas on the cathode side(see cell in Fig. 1).



Figure 3: Thickness dependence of methanol permeation rates, measured as in Fig. 1 and plotted according to Eqn. (1).



Figure 4: Cottrell plot of current transient data obtained from a potential step from 0 to 0.85 V for a Nafion[®] 117 membrane at 90 °C fed with 1 M methanol solution (see cell in Fig. 1).



Figure 5: Concentration of methanol in membrane, derived from voltammetric plus potential step experiments, as a function of cell temperature and methanol feed concentration. Cell configuration used is depicted in Fig. 1.

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Figure 6: Temperature dependence of conductivity of Nafion[®] 117 membrane immersed in aqueous solutions of methanol of various concentrations.



DMF02.b1

Figure 7: Dependence of methanol cross-over flux through a Nafion 117 membrane at 90 °C on DMFC current density for a range of anode liquid feed concentrations. The cross-over flux is expressed as an equivalent current density based on FT-IR measurements (absorbance at 2360 cm⁻¹) of the cathode CO₂ outlet stream, assuming complete oxidation to CO₂ of methanol arriving at the cathode. Permeation rates are not quantitatively accurate (see text).

CATALYTIC ACTIVITY OF A PT(111) ELECTRODE MODIFIED BY RUTHENIUM DEPOSITION: A COMBINED STM AND IR-SPECTROSCOPIC STUDY

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The structure of a Pt(111) electrode modified by Ru deposition is studied by STM and the CO electrooxidation on this electrode surface was monitored by IR spectroscopy. The STM images of the Ru-modified Pt(111) electrode in aqueous perchloric acid show islands of monoatomic height and about 3 nm in diameter. In situ IR spectroscopy of the CO stretching vibration shows distinct bands for CO adsorbed on Pt and on Ru. With increasing potential the vibrational bands assigned to CO adsorbed on Ru and on Pt decrease simultaneously at the potential of CO oxidation. A reaction mechanism assuming that the Ru islands act as nucleation centers for CO oxidation is proposed in order to explain the experimental results.

INTRODUCTION

Currently the development of a fuel cell based vehicle propulsion system is considered worldwide by several companies and research facilities using a polymer electrolyte membrane fuel cell (PEMFC) (see e.g. (1)). The fuel gas, a mixture of H_2 , CO_2 and CO_3 , is produced by a heterogeneously catalyzed steam reforming reaction of methanol. A major obstacle in the development of polymer electrolyte membrane fuel cells operated with a hydrogen-rich synthesis gas is the drastic deactivation of the anode electrocatalyst (such as dispersed platinum) caused by adsorption of carbon monoxide (2, 3). Therefore, the realization of the fuel gas to levels lower than 100 ppm CO or the development of new CO-tolerant electrocatalyst for the anode. The latter concept has triggered a renewed interest in bimetallic electrocatalyst such as Pt-Sn (4-6), Pt-Rh (7) and Pt-Ru (8, 9) that have been reported in the literature to show an enhanced electrochemical activity in the oxidation of hydrogen in H₂/CO fuel gas mixtures.

The promoter effect of these bimetallic electrocatalyst, and in particular that of Pt-Ru, has been explained by a preferential adsorption of water on the Ru surface sites at more negative potentials compared with platinum (the so-called bifunctional mechanism) (10) but a detailed understanding of the enhancement of catalytic activity is still lacking. Therefore, fundamental investigations performed on well-defined Pt-Ru model surfaces should provide a deeper insight into the relationship between surface structure and reactivity that is expected to further the development of better anode electrocatalysts.

Recently, UHV prepared and well characterized Pt-Ru alloys have been studied with respect to their catalytic activity for the electrooxidation of CO and methanol (11-15). A

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distinct dependence of the rate of CO electrooxidation upon surface composition of the alloys with an optimum Pt:Ru surface-atom ratio of 1:1 was observed. Our approach to investigate the electrocatalytic activity of structurally defined composite electrodes has been to deposit Ru on a Pt(111) single crystal electrode. The mostly ideal surface of the single crystal facilitates the surface characterization by STM, since structural modifications are readily observed. The characterization with respect to surface structure and composition is a prerequisite for the understanding of the electrochemical behavior of these Ru-modified electrocatalyst for the oxidation of methanol and CO before, but the interpretation of the observed enhancement in catalytic activity has been complicated by the unknown structure of the Ru deposits (8, 16).

In this study, relatively large (2 - 5 nm in diameter) structures are detected in the STM images, which are attributed to deposited ruthenium islands. From the STM measurements we conclude that our electrodes can be considered Ru "nano-clectrodes" deposited on a Pt(111) substrate. As will be discussed below, the electrode structure of our electrodes can be regarded as an intermediate surface structure between two limiting cases: pure Pt (e.g. as the (111) surface) and Pt-Ru alloys.

In addition, we use in-situ IR-spectroscopy in order to further elucidate the role of Ru surface atoms in the mechanism of CO electrooxidation on this Ru-modified Pt(111) single-crystal surfaces. IR spectroscopy of the stretch vibration of adsorbed CO and CO₂ provides detailed information regarding the bonding configuration and the onset of CO electrooxidation to CO₂. As it is well-known, CO adsorbs strongly on Ru and the reported CO-stretch frequency is lower by about 30 - 40 cm⁻¹ compared to CO on Pt (17). This frequency shift is large compared to the line width of the vibrational band and should therefore allow a distinction of Pt and Ru adsorption sites and enable an investigation of their respective functionality for CO electrooxidation.

EXPERIMENTAL

Surface preparation and electrochemical characterization

The Pt(111) crystal with 10 mm diameter was grown in the Institut für Festkörperforschung (IFF) and was oriented ($\pm 0.1^{\circ}$) and polished in the Institut für Grenzflächen- und Vakuumphysik (IGV), both of the Forschungszentrum Jülich (KFA).

At the beginning of the experiment, the crystal was flame-annealed, cooled in Ar and characterized with cyclic voltammetry using the hanging meniscus method in an electrochemical or in the spectroscopical cell. The cyclic voltammograms in 0.1 M HClO₄ were found to agree satisfactorily with previously published results (18). Ru deposition potentials ranging from 0.6 V to 0.2 V versus RHE. The deposition was performed by a potential step from 0.9 V vs. RHE where no Ru deposition occurs to the deposition potential. Deposition time was always 5 min. In this paper, we show measurements corresponding to deposition of Ru at 0.3 V, 0.4 V and 0.6 V versus RHE. The current transient during deposition at 0.3 V, 0.4 V, and 0.6 V, respectively. Different reference electrodes were used in the experiments (Ru deposition: Hg/Hg2SO4, STM measurements: a reversible hydrogen electrode (RHE)) but all potentials are

reported with respect to RHE. The electrolytes were prepared from suprapure HClO₄ and H_2SO_4 (Merck).

<u>STM</u>

The measurements presented here were performed with a commercial Besocke Delta-Phi STM, which was modified for electrochemical applications and interfaced to a self-built bipotentiostat. The STM was operated in an inert gas atmosphere of argon. Details of the setup are presented elsewhere (19).

The purpose of the STM-investigation was to access information on the morphology of the Ru-modified platinum surface. The most straightforward approach should be to monitor the process of Ru deposition on the platinum surface directly with the in-situ STM. It is known, however, that galvanic reactions can be affected by the tunneling tip. The influence of the tip has been observed to depend strongly on the substrate as well as on the deposition material (20). For ruthenium deposition on platinum, the tip influence is very pronounced (21), thus making this approach unsuitable for the present purpose. To circumvent this problem, another experimental route was followed. The electrodes were pretreated in a separate glass cell, thoroughly rinsed with water, and then transferred to the STM cell with an adhering drop of water protecting them against atmospheric contaminations. Then the STM was purged with Ar and the water was replaced by electrolyte solution. Subsequently the surface was imaged with the STM.

IR spectroscopy

Infrared spectroscopy was performed using a Bruker IFS 66V FTIR Spectrometer with a self-built cell attachment permitting measurements with evacuated IR optics. The spectroscopical cell was made from Duran glass and a CaF₂ window with 60° bevelled edges. IR spectra were accumulated during a continuous positive sweep at a scan rate of 0.5 mV/s. Typically, 400 scans at $\Delta \tilde{v} = 4 \text{ cm}^{-1}$ were taken for each spectrum corresponding to a measurement time of $\approx 90 \text{ s}$. The electrodes were prepared as described above, but then transferred to the spectroscopic cell with the surface protected by a drop of water. Then CO was adsorbed at a constant potential of U= 90 mV up to saturation coverage and subsequently the thin layer configuration for the spectroscopic measurement was established. The CO dissolved in the solution was removed by purging with Ar. For the calculation of the CO_{ads} signal a reference spectrum R₀ was chosen, which was obtained after complete oxidation of the CO_{ads} species.

RESULTS AND DISCUSSION

Cyclic voltammetry

Fig. 1 shows the cyclic voltammograms of the clean and two Ru-modified Pt(111) surfaces (dashed line) and of the electrooxidation of a monolayer of CO on these surfaces (solid line). The voltammograms were recorded at 20 mV/s. The electrode surfaces of fig. 1b and fig. 1c correspond to a Ru deposition at 0.6 V and at 0.3 V, respectively. The determination of Ru coverage on platinum electrodes by electrochemical methods is rather difficult, since the deposition process is poorly understood and the decrease of hydrogen adsorption reflects only indirectly the amount of Ru coverage on polycrystalline Pt based on the integration of the current wave attributed to OH adsorption on Ru and relating this value to the hydrogen adsorption charge. Since the hydrogen desorption and surface oxidation

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(OH adsorption) currents overlap and the OH adsorption current is not prominent in the cyclic voltammograms in Fig. 1, the effective surface area of the Ru deposit cannot be determined accurately. However, if the values of the Ru coverage as determined for polycrystalline Pt-Ru surfaces according to the method suggested by Watanabe et al. are assumed to be valid also for the Pt(111) surface, the Ru coverage of the electrode surface in fig. 1b and fig. 1c would be $\theta_{Ru} \approx 30\%$ and $\theta_{Ru} \approx 70\%$, respectively. As shown by STM images below, this somewhat arbitrary Ru coverage determination is qualitatively correct. A more detailed discussion of Ru deposition and the determination of Ru surface concentration will be given elsewhere (22).

We observe a peak potential of CO electrooxidation at $U_{OX} \approx 730 \text{ mV}$ on the uncovered Pt(111) surface which correlates with the onset of the current peak associated with OH adsorption on this surface (23) (dashed line, fig. 1a). On the Ru-modified surfaces (fig. 1b-c), a negative shift of $\approx 130 \text{ mV}$ for the CO electrooxidation potential is observed, but still only a single oxidation current peak is detected. For lower scan rates the CO electrooxidation peak shifts negatively. For a sweep rate of 0.5 mV/s, the recording rate of the potential-dependent IR spectra, a shift by -100 mV compared to the measurements in fig. 1a-c is found.

STM investigations

The preparation procedure described in the experimental section does not routinely yield clean, well-defined platinum single crystal surfaces. This is evident from fig. 2a, which shows the as-transferred Pt(111) surface without any Ru deposit. The typical terrace structure of the (111) surface with monoatomic steps can easily be recognized, but a moderate density of islands on the terraces indicates a non-negligible surface disorder, which may either result from insufficient flame annealing or from contamination of the sample during transfer.

Fig. 2b shows a Pt(111) surface with a Ru coverage of 0.3 according to WM and exhibits a striking difference to the unmodified Pt(111) surface. The surface is covered with small islands of 2 to 5 nm in diameter. The height of the islands is predominantly close to the height of monoatomic steps of the substrate. The defect density of the substrate given, it is unclear for an individual island whether it consists of Pt or Ru. From the comparison of fig. 2a and 2b one can, however, derive, that the density of Pt islands is almost negligible compared to the density of islands on the Ru-covered surface. The fraction of the surface which is covered by the islands has been estimated for several images, yielding values between 0.2 and 0.4 with a mean value of 0.25.

A Pt(111) surface with a Ru coverage of 0.7 according to the coverage determination method of WM is shown in fig. 2c. Islands similar to those in fig. 2b dominate the image, but with a considerably higher density. Due to this high density, it is impossible to distinguish the substrate from the deposit, thus one can not evaluate the images in terms of surface coverage. It is feasible, however, to estimate upper and lower limits for the coverage. From a comparison of fig. 2b and 2c it is obvious, that the respective coverages differ at least by a factor of two. An upper limit can be derived from the fact, that the monoatomic steps of the substrate can still be clearly seen on the Ru-covered surface. This indicates that the coverage is still in the monolayer regime.

IR spectroscopy

Fig. 3 compares IR reflection absorption spectra of clean Pt(111) (fig. 3a), Rumodified Pt(111) with a nominal Ru coverage of 0.3 (fig. 3b) and with a nominal Ru

coverage of 0.7 (fig. 3c) at about 400 mV. The spectra shown in Fig. 3 were obtained during a slow positive potential scan (0.5 mV/s) in a thin film configuration. The vibrational bands shown in this figure all exhibited a strong potential dependence and are therefore associated with CO adsorbates. For each spectrum the collection time was ≈ 100 s, therefore the potentials given in Fig. 3 refer to the mean values of the potential interval ($\Delta U = 50 \text{ mV}$). On the clean Pt(111) surface, the bands around 2070 and 1790 cm⁻¹ have been reported before and are assigned to CO_{ads} in a linear-bonded (on-top) and threefold hollow coordination (24). A 2:1 ratio for the integrated intensities of the 2070 cm⁻¹ to the 1790 cm⁻¹ band has been attributed to a (2×2)-3CO adsorbate structure as shown by a combination of STM and IRAS studies (25). In fig. 3b, apart from the absorption bands around 2070 cm⁻¹ and 1790 cm⁻¹, a new vibrational feature around 2010 cm⁻¹ is present. This third band has not been observed on the unmodified Pt(111) surface. For the surface with a high Ru coverage (fig. 3c), this band is very pronounced (its integrated band intensity is higher than that of the 2070 cm^{-1} band). Therefore, this band is most likely associated with a Ru-CO species. CO adsorbs readily on polycrystalline Ru electrodes and a CO vibrational band, assigned to linear-bonded CO, is observed around 2040 cm⁻¹ at saturation coverage (17). Coverage dependent lateral interactions between the adsorbed CO molecules lead to a lowering of \tilde{v}_{CO} with decreasing coverage and this effect has been observed very dramatically in UHV studies of CO adsorption on Ru(001) (26), where a coverage dependent variation of $\tilde{\nu}_{CO}$ between 1984 and 2061 cm⁻¹ was found. Since multiple-bonded CO has not been detected in UHV studies (26, 27) and since the typical frequency ranges for linear-bonded CO lie above 2000 cm⁻¹ we propose to assign the vibrational band around 2010 cm⁻¹ to CO linearbonded to Ru surface atoms. In the spectrum with the high ruthenium coverage (fig. 3c) the band around 1850 cm⁻¹ can be assigned to bridge-bonded CO adsorbed on platinum (24). Interestingly, no CO in a threefold coordination is present for this surface. As far as we know of, a ratio of integrated band intensity of 1:1 for the bridge band to the on-top band has not been reported before and we assume that the high density of Ru islands has disrupted completely the ordered (2×2)-3CO adsorbate structure. Likewise, the ratio of integrated intensities of the threefold hollow band to the on-top band diminishes from 1:2 on the clean Pt(111) crystal to 1:5 on the Ru-modified Pt(111) electrode with 0.3 coverage in fig. 3b. This preferential removal of the threefold hollow band in the spectra of the Rucovered Pt(111) crystals suggests the existence of a boundary region along the circumference of the Ru islands, where threefold-bonded CO is affected with higher probability than CO adsorbed in a linear or a bridge configuration.

Fig. 4 shows IR spectra measured during a positive sweep after adsorption of CO at 90 mV on a Ru-modified Pt(111) electrode with a coverage of 50 % according to WM. Again, the spectra show three potential-dependent bands; the bands around 2070 and 1790 cm⁻¹ are due to linearly bonded CO and triply bonded CO, respectively. The band around 2010 cm⁻¹ is assigned to linearly bonded CO on Ru. The band frequency of CO/Ru shifts at a rate of $\tilde{v}_{CO(Ru)}/dU=48$ cm⁻¹/V which is considerably higher than the tuning rate of the vibration of CO adsorbed on Pt (d $\tilde{v}_{CO(Pt)}/dU=27$ cm⁻¹/V in this study for linearly bonded CO). Nevertheless, this shift is similar to the value reported for the frequency shift of CO on a Ru electrode by Gutiérrez et al. (41 cm⁻¹/V) (17). Small differences in the tuning rate may be explained by coverage effects. CO_{ads} is oxidized to CO₂ at a potential of ~550 mV and within the resolution of our experiments ($\Delta U=50$ mV) the intensities of the vibrational bands of CO/Ru and CO/Pt decrease at the same potential. The simultaneous electrooxidation of CO/Ru and CO/Ru is in agreement with a single current peak in the cyclic voltammograms in Fig. 1.

The STM images in fig. 2 and the observation of two separate vibrational bands for CO bonded to Pt and to Ru both clearly demonstrate that relatively large Ru and platinum areas with their respective chemical properties are present. However, the cyclic voltammograms of the investigated electrodes are not a superposition of Pt and Ru, but reveal a pronounced promoter effect for CO electrooxidation with a single sharp current peak (fig. 1). The bifunctional mechanism of CO electrooxidation postulates a coadsorbed oxygen-containing species such as -OH. OH adsorption on pure Pt(111) is evident in the current peak at \approx 580 mV (23) (fig. 1a) and therefore the uncovered Pt(111) surface area is considered free of adsorbed OH at the onset of CO oxidation on the Ru-modified surfaces. Consequently, CO electrooxidation has to start on the Ru islands and along their periphery; the adjacent Pt sites can be considered active sites for CO electrooxidation (denoted Pt*). Furthermore, we have to assume a high mobility of the CO adsorbates on Pt in order to explain the single current peak. This way, the Ru islands act as nucleation centers for CO oxidation according to the following reaction scheme (1a-d):

a)
$$Ru + H_2O \longrightarrow Ru - OH + H^+ + e^-$$

b) $CO - Ru + OH - Ru \longrightarrow 2Ru + CO_2 + H^+ + e^-$
c) $CO - Pt^* + OH - Ru \longrightarrow Pt^* + Ru + CO_2 + H^+ + e^-$
d) $CO - Pt \longrightarrow CO - Pt^*$
[1]

Water adsorption takes place on the Ru island at low potentials [1a]. CO adsorbed on Ru and at Pt* is oxidized at sites in close proximity to a Ru-OH surface species [1b,c]. After initiation of the CO electrooxidation, CO adsorbed on Pt migrates to an active site Pt* (step [1d]) in close proximity to Ru (the adsorption site of the oxygen-containing species) and, subsequently, CO-Pt* is oxidized to CO₂ (step [1c]).

For polycrystalline Pt-Ru alloys, only one vibrational band has been reported, shifted to lower frequencies by about 15-30 cm⁻¹ as compared to polycrystalline Pt (28). This disparity to the results presented here is rationalized in terms of a homogeneous distribution of Ru and Pt atoms at the surface of the alloys. CO is either adsorbed only on platinum sites on the alloy surface with a low coverage or, more likely, the local binding configuration are averaged out by lateral interactions (dipole-dipole coupling). In this case, an intensity transfer from the low (CO/Ru) to the high frequency band (CO/Pt) occurs as well as a shift towards higher wavenumbers of the lower frequency band. This would also explain the observed asymmetry of the CO absorption band on Pt-Ru alloys.

In conclusion, the STM investigation showed that Ru on Pt(111), electrodeposited from 5 mM solution of RuCl₃ in H₂SO₄ at submonolayer coverages, forms islands of monoatomic height with diameters from approximately 2 to 5 nm. A variation of the Ru coverage results in a variation of the density of Ru islands, but does not affect their shape. Rough estimates of the coverage have been derived from the STM images and, for medium coverage, gave values slightly smaller than the evaluation according to the method of WM. Since STM is, however, not the most suitable technique for the detection of average surface properties, we consider this small deviation not significant.

IR spectroscopic studies of the CO stretching vibration exhibit distinct bands for CO adsorbed on Pt and on Ru. A band around 2010 cm⁻¹ is assigned to CO adsorbed on Ru in an on-top configuration. The vibrational bands assigned to CO adsorbed on Ru and on Pt persist in the potential range negative of the oxidation potential and diminish simultaneously upon oxidation. This shows that although CO adsorbs both on Ru and Pt, a promoting effect is operative which gives rise to a single oxidation process. These findings are consistent with the bifunctional mechanism if we postulate an initiation of CO oxidation on/or around the Ru islands in combination with a sufficient high mobility of the CO adsorbate on platinum. Therefore, these surfaces modified by Ru deposition may be considered an intermediate surface structure between pure Pt and Pt-Ru alloys.

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Fig 2. In-situ STM images of Pt(111) electrodes after transfer to the STM cell, measured in 0.1 M HClO₄ at a sample potential of 0.5 V vs. RHE with a tip potential of 0.8 V and a tunneling current of 0.4 nA. A) Blank experiment without predeposited ruthenium.
B) With predeposited ruthenium at a coverage of 0.3. C) With predeposited ruthenium at a coverage of 0.7.





- 90 mV; signal averaging of 400 scans at a resolution of 4 cm⁻¹.
- (a) Pt(111) without predeposited ruthenium.
 (b) With predeposited Ru at a coverage of 0.3.

(c) With predeposited Ru at a coverage of 0.7.

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Fig. 4. In situ IR spectra of a Ru-modified Pt(111) with a Ru coverage of about 0.5 in 0.1 M HClO₄ during a slow anodic scan (scan rate: 0.5 mV/s) after adsorption of CO at 90 mV; parameters as in Fig. 3.

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CONSIDERATIONS IN THE DESIGN OF A DIRECT METHANOL FUEL CELL SYSTEM FOR ELECTRIC VEHICLES

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ABSTRACT

Under an ARPA-sponsored program, the fuel cell team of Electrochemical Technologies Group at JPL has identified a Liquid-Feed Fuel Cell (DMLFFC) operating on aqueous solutions of methanol. This fuel cell operates using a Proton Exchange Membrane (PEM) at 90°C. State-of-art fuel cells for electric vehicles have been based on hydrogen or reformed methanol. High pressure is undesirable. Methanol reformers which are bulky, complex, and do not respond to load changes. The Direct Methanol, Liquid-Feed Fuel Cell (DMLFFC) can be fed from the fuel tank which is filled from a service station pump in much the same way as is done today with gasoline powered vehicles The operation of this design involves mixing of methanol with water and circulating directly through the anode chamber of the fuel cell. Oxygen or air serves as the oxidant. The products are water and carbon dioxide. This paper describes results of an initial conceptual design of a 5 kW DMLFFC system. The objective of the study was to develop and evaluate conceptual designs of a 5 kW DMLFFC system suitable for electric vehicle and other terrestrial applications. The approach consisted of : a) developing a conceptual system design, b) selecting operating conditions for assumed steady state operation, c) conducting sizing studies for the stack and other systems components including fuel supply subsystem, oxidant supply subsystem thermal and water effluent subsystem, sensors and control subsystem, and power electronics subsystem, and d) summarizing and assessing system design and performance.

INTRODUCTION

Significant progress has been made recently under an ARPA-sponsored direct methanol fuel cell development program. The fuel cell team led by JPL with Giner Inc. and the University of Southern California has identified a Liquid-Feed Fuel Cell (DMLFFC) operating on aqueous solutions of methanol. Several papers presented by JPL and Giner describe the system and its past performance ¹⁻³. This fuel cell makes use of a Nafion 117 Proton Exchange Membrane (PEM) operating at temperatures from 60 - 90°C. Using aqueous 3% methanol as the fuel, single 2" x 2" and 4" x 6" cells have operated at 90°C

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producing 300 mA/cm² at 0.5 V with 30 psig oxygen (0.4 V with air). It can also start up at room temperature at reduced levels.

State-of-art fuel cells for electric vchicles are based on hydrogen or reformed methanol. High pressure and hydrogen storage in general is undesirable and methanol reformers which are bulky, complex, and do not respond quickly to load changes. The DMLFFC can be fed from the fuel tank which is filled from a service station pump in much the same way as is done today with gasoline powered vehicles The operation of this design involves mixing of methanol with water and circulating directly through the anode chamber of the fuel cell. Oxygen or air serves as the oxidant. The only products are water and carbon dioxide.

THE INITIAL AND PROJECTED DESIGNS

This paper describes initial and projected conceptual designs of a DMLFFC system capable of delivering 5 kW. The objective of the study was to develop and evaluate systems suitable for electric vehicle and other terrestrial applications. The approach consisted of: a) developing an overall system concept, b) selecting operating conditions for assumed steady state operation, c) conducting sizing studies for the stack and other systems components including fuel supply subsystem, oxidant supply subsystem thermal and water effluent subsystem, sensors and control subsystem, and power electronics subsystem, and d) summarizing and assessing system design and performance. The operating conditions are given in Table I.

Table I: System Operating Conditions (Temperature: 5-40°C, RH: 0-100%, 1 Atm., constant load)

Operating Parameter	Initial Design	<u>Adv. Design</u>
Temperature (°C)	90	90
Pressure (psig)	30	30
Fuel	MeOH	MeOH
Fuel Conc. (%)	3	3
Fuel Mix Flow Rate (I/min	n.) 30	16
Air Flow Rate (g/sec)	30	20

These are the operating conditions initially found to produce the performance reported and those believed to be achievable in the near term with the same performance. An overview of the key system features is given in Table II. The system design concept is given in Figure 1.

FACTORS CONSIDERED

Number of Cells

The number of cells is determined by the voltage of each cell and the fact that a large number of cells have to be stacked in series to achieve the voltage and in parallel for the fuel and air feed. For consistency with transportation applications, the DMLFFC system

Initial Design	<u>Adv. Design</u>
320 V	320 V
40 V	40 V
112 kg	84 kg
1151	74 1
5 kW	5 kW
7 kW	7 kW
42 W/Kg	60 W/kg
44 W/I	67 W/I
18.4 %	35.5%
12.7%	27.1%
	Initial Design 320 V 40 V 112 kg 115 I 5 kW 7 kW 42 W/Kg 44 W/I 18.4 % 12.7%

Table II: System Design Overview (at 30 psi air and 90°C)

voltage was selected as 320V. To achieve the desired 320 V, at 0.4 V/cell, 800 cells would have to be assembled into a stack. This would be impractical. However, at the reasonably high current achieved, the larger cell area could be used to provide the current and therefore power necessary to drive up the voltage to enable the use of a converter. Using a cell stack of 100 cells to produce the 40 volts, a converter with >90% efficiency could provide the necessary 320 Volts. The lower number of cells would also serve to reduce the complexity of fuel and air flow.

Stack Efficiency

The major contributors to stack inefficiency were methanol crossover and polarization losses. For the initial design the cell voltage was 0.4 V at 300 mA/cm^2 which represents an efficiency of 32.2% based on the theoretical voltage of 1.24V. The second factor in efficiency is related to the methanol crossover, i.e., methanol migrating through the Nafion from anode to cathode where it reacts with the O₂ to form water and CO₂. This results in inefficient use of the methanol and a lower cell voltage. The loss of methanol through the membrane combined with the lower voltage results in a cell efficiency of 18.4\%. It was projected that the initial 0.4 V/cell performance could be improved in two ways; reduction of the crossover to 10% from 40% and reducing polarization at the anode and cathode. An increase in the cell voltage to 0.5V/cell combined with the lower crossover rate would increase cell efficiency from 18.4% to 36.4\%.

Mass and Volume

The major contributors to the overall system weight for the advanced system were found to be the stack subsystem and the air supply subsystem. The major improvements are due to the increase in the number of cells per inch also known as the "pitch" and the ability to operate at higher current density with increased voltage as described above.

The Subsystem weight estimates for the advanced system is given in Figure 2. and the volume in Figure 3. The subsystems that had the major impact on mass were the stack

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which decreased from 39 to 31% in the advanced design and the air supply subsystem increasing from 22 - 29% as the stack design improved. The electronics were estimated to be at ~20%. On the other hand the volume of the stack improved from 45 to 34%, the thermal, water and effluent subsystem was similar for both at ~30% and the fuel subsystem became a larger percentage of the total going from 17 - 26% in the advanced design.

Sensitivity studies shown in Figures 4 and 5 have shown that a marked reduction in weight and size as well as improvements in overall efficiency can be achieved by reducing crossover and lower operating pressure. Recent experimental advances have identified methods for reducing crossover and enabling operation at lower pressures.

The Air Supply Subsystem

The air supply subsystem was found to require very large parasitic power without power recovery. A schematic is given in Figure 6. To optimize performance required adequate flow of air into the stack and cells. The design called for air pressure of 20 - 30 psig with a flow rate of 20-30 liters/minute to achieve the reported performance. The goal was to minimize the power drain to less than 1.3 kW for the compressor system. Estimates for the compressor efficiency and turbine efficiency were 85% and 75-88% respectively. This resulted in weight of 24.6 kg and a volume of 2.8 liters. The incorporation of a turbo-compressor with recovery was found to necessary reduce parasitic power drain. In order to account for the additional parasitic loss, the stack was designed to deliver 7 Kw. The concerns included the fact that the turbine compressor is not off-the-shelf, that it requires two phase fluid dynamics, and effect of direct coupling over a range of operating conditions is not well known.

The Fuel Supply Subsystem

The goal for minimizing the parasitic drain for this subsystem was less than 150 W for the 7 kW stack and defined operating conditions. The assumptions included an inlet concentration of 1 molar with the outlet being a minimum of 0.8 molar methanol and the outlet temperature set at 90°C. It was also assumed that the fuel tank of 15 gal would contain high purity methanol which would drip into a water circulation tank initially containing deionized water and be diluted to 1 molar. A schematic of the fuel supply subsystem is given in Figure 7. The product high purity water from the cathode together with the unused methanol water mixture from the anode chamber would be returned to the circulation tank for further use. A sensor would be used to control the concentration of methanol in the tank was estimated that the circulation tank of 6 liters would be adequate for the circulation tank.

Thermal, Water and Effluent Management Subsystem

The objective of this effort was: a) to project the heat generation rates and design a cooling system, b) project water consumption and generation rates, c) design a water recovery system d) project CO_2 production rates, and e) determine how much methanol exits from in the fuel exhaust. These calculations were quite complex especially starting with a limited cell and stack measurements. A computer model of the subsystems within the system was

developed. It was the determined that a balance between the input and output of all species could be achieved under the operating conditions baselined.

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Figure 1. Schematic Diagram of the DMLFFC System

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Figure 6. Schematic of the Air Supply Subsystem



Figure 7. Schematic of the Fuel Supply Subsystem

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