PEM Fuel Cells with Pd Nonporous Anode

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Introduction

A new non-porous anode has been developed which can be used effectively for CO-containing feed stream in H_2/O_2 fuel cell as well as for direct methanol fuel cell (DMFC). In the hydrogen fuel cell, it is desirable to develop anode materials which have lower affinity for CO, while maintaining their activity for the oxidation of hydrogen. Platinum, the most active metal for the hydrogen oxidation reaction, is unfortunately extremely sensitive to carbon monoxide, and thus, a number of binary and ternary electro-catalysts such as Pt-Ru and Pt-Ru-Mo have been developed to obtain better performance for CO-containing anode feed. These alloys are more effective than Pt in oxidizing the adsorbed CO with dissociated water into CO_2. Here, it is proposed to use nonporous anode capable of extracting hydrogen at low partial pressure from hydrocarbon containing feed streams. This process consists of distinct steps: hydrogen dissociation (Tafel step), hydrogen atom diffusion, hydrogen atom electro-oxidation into protons and electrons (Volmer step), proton diffusion through PEM and oxygen reduction at cathode.[1-3] A mathematical model has been developed for the whole fuel cell process based on the kinetics on electrode surfaces, and transport of hydrogen atom and proton through the non-porous anode and proton exchange membrane, respectively.

The model

A model accounting mass balances, transport of reaction species and electrochemical kinetics is developed to understand the mechanisms involved in the nonporous anode hydrogen fuel cells. The total overpotential for the MEA is the sum of the overpotentials from H_2 diffusion, H_2 dissociation, H atom diffusion, H_2 oxidation, H^+ transport through PEM, and O_2 reduction.

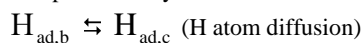Hydrogen Atom Diffusion Electrode (HADE)
i) Dissociation of H_2
The H_2 gas adsorbs on the surface of palladium film, which may have been catalyzed with Pt, for example,

$$H_2 + 2S \rightleftarrows 2H_{ad,b} \quad \text{(Tafel Step)}$$

[1]

ii) H atom diffusion
The diffusion of dissociated hydrogen through the Pd film may be represented by

$$H_{ad,b} \rightleftarrows H_{ad,c} \quad \text{(H atom diffusion)}$$

[2]

The rate of diffusion of hydrogen through the solid membrane is governed by the diffusion coefficient that is dependent on its chemical composition (α-phase or β-phase Pd) and to the concentration gradient across the membrane and to its thickness. Figure 2 shows concentration gradients in Pd layer. Table 1 and 2 show the diffusion coefficients and equilibrium hydrogen concentrations.

iii) Hydrogen Oxidation Reaction (HOR)
For the formation of a proton and electron from a hydrogen atom

$$H_{ad,c} \rightleftarrows H^+ + e^- \quad \text{(Volmer)}$$
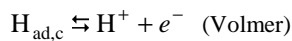
[3]

The limiting current density may be approximated as

$$i_{AL} = \frac{nF}{L_{Pd}} \left[D_\beta (C_0 - C_1) + D_\alpha C_2 \right] \quad [4]$$

where D_α and D_β represent the diffusion coefficient of hydrogen atom in Pd for α and β phase, respectively. The

overall performance of H_2 diffusion anode fuel cells can be theoretically understood based on the models developed here.
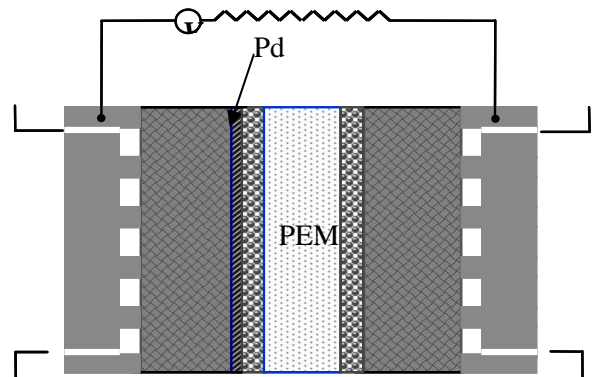

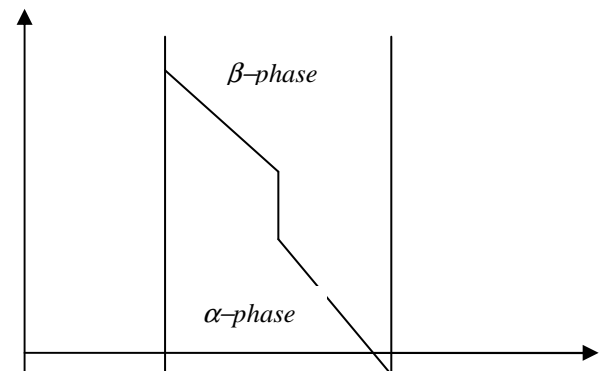Figure 1. Schematic diagram of Pd nonporous anode fuel cells.

Figure 2. Schematic diagram of the concentration of hydrogen atom in Pd layer of hydrogen diffusion anode fuel cells.

Table 1. Diffusion coefficients of hydrogen atom (cm^2/sec) in α and β phase Pd at different temperature.

$T(^0C)$	30	50	80	200
D_α	3.9×10^{-7}	5.3×10^{-7}	1.47×10^{-6}	1.11×10^{-5}
D_β	2.93×10^{-6}	3.42×10^{-6}	5.83×10^{-6}	1.68×10^{-5}

Table 2. Data for hydrogen concentration [g H/cc Pd] where C_0 is the concentration of hydrogen atom in the β phase in equilibrium with 1 atm. of H_2 and C_1 is the concentration of β phase in equilibrium with C_2 in the α phase.

Temp (ºC)	C_0	C_1	C_2
30	0.0703	0.0555	0.0035
40	0.0693	0.0536	0.0040
50	0.0684	0.0531	0.0045
60	0.0674	0.0526	0.0050
70	0.0664	0.0516	0.0060
80	0.0664	0.0506	0.0070
200	0	0	0.0030

References
1. H. G. Oswin, and S. M. Chodosh, *Advances in Chemistry Series*, **47**, 61 (1965).
2. H. G. Oswin, and N. Y. Elmsford, *US Patent*, 3092517 (1963).
3. H. G. Oswin, *US Patent*, 3375140 (1968).

[38]