Influence of the Acid-base Properties of Composite Membranes Inorganic Fillers on the High Temperature Performance of Direct Methanol Fuel Cells

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Introduction

Increasing interest has been recently devoted to high temperature direct methanol fuel cells. Composite perfluorosulfonic membranes based on recast Nafion containing ceramic oxides have been operated up to about 150 °C both in direct methanol and hydrogen-air polymer electrolyte fuel cells. Inorganic oxides inside a composite membrane enhance water retention at high temperatures extending the operating range of perfluorosulfonic membranes and reduce the cross-over effects. Most of the previous efforts have been addressed to technical aspects and limited attention has been devoted to an in-deep analysis of the basic operation mechanism of such materials. In the present work, various composite membranes based on recast Nafion containing inorganic nanoparticle fillers (SiO_2, SiO_2 with adsorbed phosphotungstic acid, ZrO_2, Al_2O_3) varying by their surface chemistry and acid-base characteristics have been prepared and investigated in DMFC devices. It has been observed that the surface acid-base properties of the inorganic fillers play a fundamental role in determining the conductivity characteristics and fuel cell performance at high temperature.

Experimental

The ceramic oxide fillers have been purchased from Cabot (SiO_2), Aldrich (Al_2O_3), synthesised at Rome Tor Vergata University (ZrO_2) or prepared at the ITAE Institute (SiO_2-PWA). The pH of slurry was measured at room temperature by an ATC compensated pH probe (Orion). The slurry was composed by 0.5 g powder per 0.1 liter of bi-distilled water. The slurry was stirred for about one day in presence of nitrogen bubbling up to obtain a steady-state pH value. The membranes were prepared by using a recast procedure. The thickness of the membranes was about 100 µm. Fuel cell experiments were carried out in a 5 cm^2 single cell (GlobeTech, Inc.). 2M aqueous solution of methanol and oxygen were preheated at 85°C and fed to the cell. The catalyst employed for methanol oxidation was 60% PtRu (1:1)/Vulcan (E-TEK), whereas a 30% Pt/Vulcan (E-TEK) was used for oxygen reduction. The platinum loading for all the electrodes was 2 mg cm^{-2}.

Results and discussion

The inorganic fillers selected for the composite membranes are characterised by different surface chemistry and acid-base behaviour. The acid-base characteristics have been investigated by determining the pH of slurry. Silica and Zirconia oxides showed acidic characteristics, with pH of slurry of 4.75 and 5.35 respectively. Alumina oxides showed basic (pH=8.15) and neutral (pH=7.5) properties. The acidic properties of the silica oxide have been further increased by adsorbing PWA on its surface (pH=2.54). All composite membranes show low resistance values in the range between 90°-145°C. The cell resistance progressively varies from 0.13 to 0.05 ohm cm^2 at 145 °C as the pH of slurry of the oxide filler decreases from 8.15 to 2.5. The DMFC polarisation characteristics at 145 °C (Fig. 1) closely reflect the trend observed in the cell resistance values. Significantly lower potential losses are observed in the ohmic controlled region of the polarisation curves for the membranes containing acidic fillers. Interestingly, in the activation controlled region, at low current density, smaller potential losses are recorded for the acidic with respect to neutral or basic oxide-fillers based membranes. An exponential increase of cell resistance and a linear decrease of maximum power density as a function of the pH of slurry of the inorganic fillers are observed in Fig. 2. Such trends indicate that the acid-base behaviour of the oxide filler plays a key role in determining the cell performance. Clearly, these oxide materials (including the one containing PWA adsorbed on the surface) do not possess elevated intrinsic protonic activity at 145 °C as well as their low weight content (3%) does not allow to justify a significant contribution as proton conductor. Their effect is mainly due to the hygroscopic characteristics and the large surface area which enables suitable water adsorption on the surface enhancing the water retention properties of the membranes.

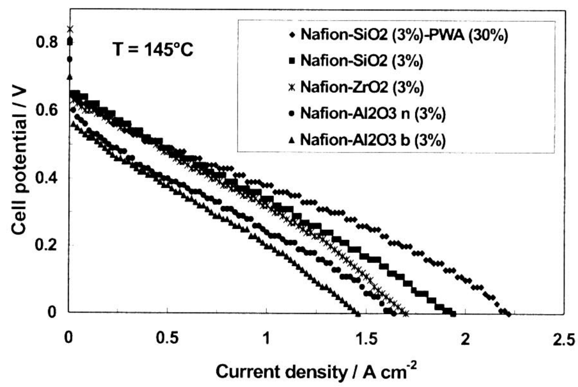

Fig. 1. Comparison of the polarisation curves at 145°C for the DMFCs based on various membranes.

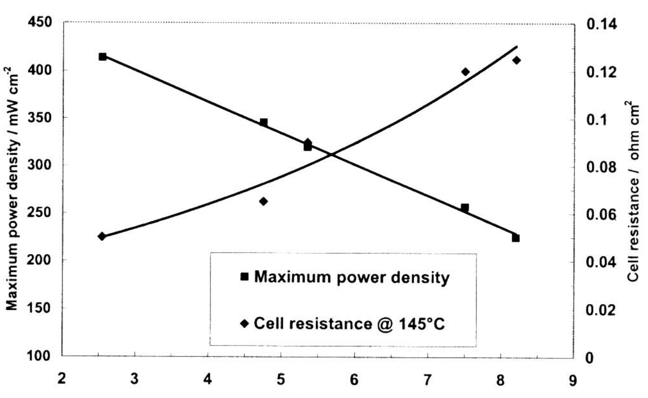

Fig. 2. Variation of cell resistance and power density as a function of the pH of slurry of the inorganic filler for composite membrane-based DMFCs at 145°C.