DEVELOPING HIGH-TEMPAERTURE, CO TOLERANT POLYMER ELECTROLYTE MEMBRANE FUEL CELLS

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Introduction

High temperature operation of polymer electrolyte membrane fuel cells is desirable to allow for operation using reformed hydrocarbon fuels which contain CO impurities. Elevated temperatures also improve fuel cell performance by improving reaction kinetics. However higher temperatures introduce greater challenges in maintaining hydration in the membrane and membrane-electrode interface which are necessary to allow for proton conductivity. Modification of the membrane and electrode interface by the impregnation of mesoscopic metal oxide particles has been found to allow for improved fuel cell performance at elevated temperatures. The structure and properties of these modified membranes are being studied through a combination of water uptake and conductivity experiments as well as small-angle x-ray scattering analysis.

Experimental

Modified Membrane Preparation. The membranes were pretreated to remove impurities. After pretreatment, the membranes were placed in a 2:1 by volume mixture of methanol and water for a few minutes. The membranes were then submerged in a 3:2 by volume mixture of tetraethoxysilane and methanol for a period of time depending on the desired silicon oxide content. The membranes were then dried at 100°C and treated again to remove impurities. Recast silicon oxide membranes were produced by mixing commercial 5%Nafion solution with isopropanol and a siloxane polymer solution. After formation, the recast membranes were also treated to remove impurities.

Active Layer Modification. The silica sol was prepared by mixing 2 ml TEOS (Tetraethoxy silane), 4.7 ml distilled water and 100 μl of 0.1 M HCl for 3 hours. Electrodes (E-TEK ELAT double sided, 20% Pt on C,0.4 mg/cm^2) are prepared by brushing 0.6 mg/cm^2 Nafion solution (5 % by wt) and required amount of the silica sol depending on the wt % of silica needed on the electrodes. Nafion 115 was used as the membrane. MEAs were prepared by hot pressing the electrodes and the membrane at 130^0 C for 1 min without pressure and applying 1 metric ton pressure for 1 minute.

Water Uptake and Conductivity Measurements. A barometric sorption vessel (400 cm^3) was constructed and used to quantify water uptake of a membrane sample[1]. The dry membrane is placed within the sorption vessel held at a given temperature and known quantity of water is introduced into the vessel through a septum. The membrane water uptake can be calculated by using a pressure transducer to determine the difference between the expected vapor pressure and actual vapor pressure. The conductivity is measured on the membrane in the longitudinal (in-plane) direction by an AC impedance spectroscopy two probe method using a PAR 273A potentiostat/galvanostat and a 5210 lock-in amplifier[2].

SAXS Analysis. The Cu-Kα x-rays were generated by a Philips XRG-3000 sealed tube generator source. The beam was slit collimated and the scattering was detected by an Anton-Paar compact Kratky camera equipped with a Braun OED-50M detector. Empty beam scattering, sample transmittance, and detector response were corrected for in the data analysis. The data reduction and desmearing procedures used are described in detail by Register [3].

Results and Discussion

Fuel Cell Data. Introducing metal oxides into the membrane and the active electrocatalyst layer have been shown to improve fuel cell performance at elevated temperatures as shown in **Figures 1 and 2**.

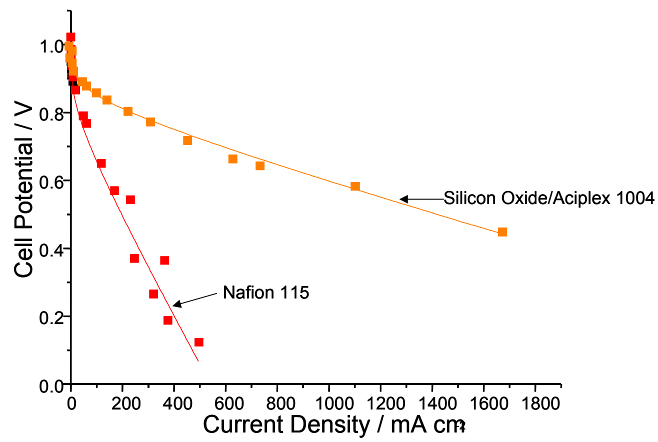

Figure 1. Cell Potential versus current density at a fuel cell temperature of 130°C.

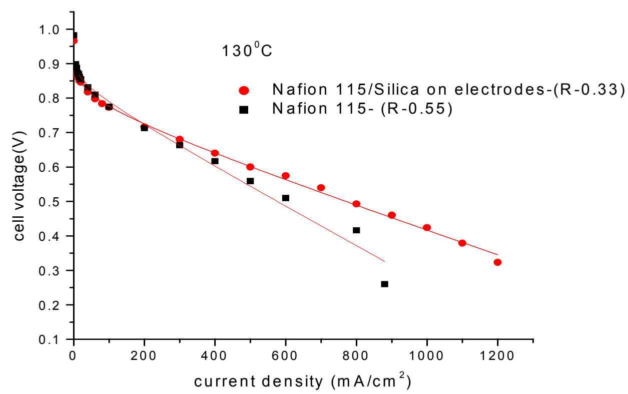

Figure 2. Performance curves of PEMFC with cell temperature 130^{0}C at 3 atm

Membranes containing silicon oxide lead to significant improvements of fuel cell performance at 130°C as can be seen in **Figure 1**. In the modification of the electrode membrane interface it was found that 6% by weight of silica provided the best results. Higher silica concentrations led to mass transport problems.

Water Uptake and Conductivity Results. The comparison between the Nafion and Nafion composite membrane shows higher uptake by the composite membrane around a relative humidity of 65% as shown in **Figure 3**.

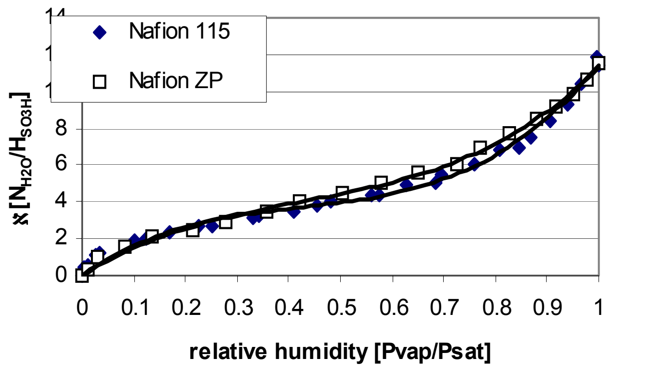

Figure 3. Nafion 115 and Nafion Zirconium Phosphate membrane water content vs relative humidity at 80°C.

As the water content of the membrane increases, the conductivity of the membrane rises exponentially as shown in **Figure 4**.

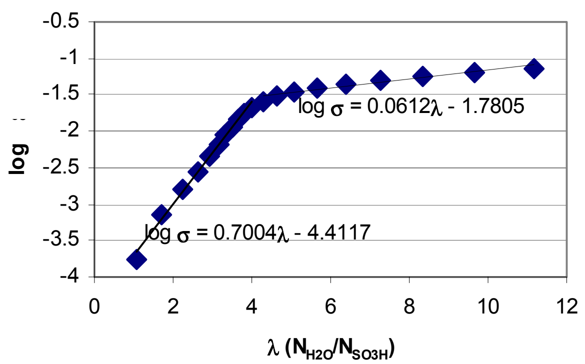

Figure 4. Membrane conductivity variation with water content for Nafion 115 membrane.

The semilog plot in shows two distinct regions of exponential conductivity increase with increasing water content. At low water content, conductivity increases rapidly as the membrane water increases. For a hydration state greater than 4 waters per sulfonate group, conductivity increases less with additional water.

SAXS Results. From the SAXS analysis, it was found that the Bragg spacing which represents the distance between ionic clusters increased with increasing water content in all cases as shown in **Figure 5**.

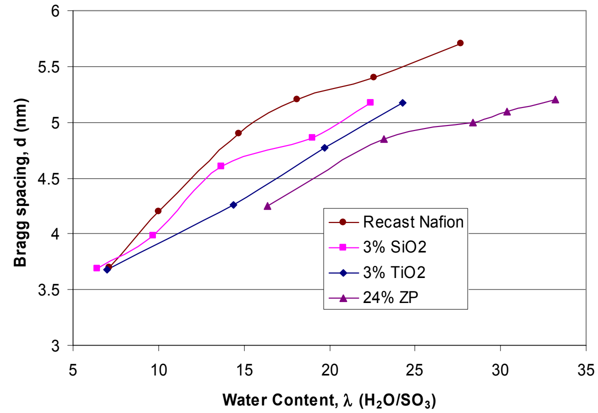

Figure 5. Comparison of Bragg spacing of composite membranes with pure Nafion at different levels of hydration

For a given water content, the Bragg spacing was lower for the composite membranes than for the control membrane. This indicates that the presence of the inorganic compound may inhibit the agglomeration of the ionic clusters to the extent that occurs in pure Nafion. Further experiments are in progress to find out how the characteristics of each compound effect the behavior of the composite membranes as they uptake water. This SAXS study provides information on the structural changes of the membrane during the uptake of water in the presence of inorganic compounds.

The reason that the inclusion of small amounts of metal oxide in the membrane and active layer lead to improved fuel cell performance is uncertain. It is believed that the improvement in fuel cell operation is due to a combination of effects including higher water uptake, improved conductivity and more, smaller ionic clusters.

References

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