

Water Uptake and Conductivity of Composite Membranes Operating at Reduced Relative Humidity

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Proton exchange membrane fuel cells (PEMFCs) operating with perfluorinated sulfonic acid membranes have demonstrated high power densities at low temperatures (50-80°C). Increased operating temperatures for low temperature fuel cells can improve CO tolerance with increasing temperature, an important characteristic when running on hydrogen from reformed fuels, as well as improving kinetics of the methanol oxidation reactions for direct methanol fuel cells. The ability for perfluorinated sulfonic acid membranes and composites based upon these membranes to maintain acceptable performance under conditions of reduced relative humidity is examined.

Previous studies at Princeton and elsewhere have demonstrated the efficacy of composite inorganic-perfluorosulfonic acid membranes in improving fuel cell performance at higher temperatures, where humidification of the reactant gases occurs at temperature equal to or below that of the fuel cell [1,2]. These studies have suggested that composite membranes have improved water retention and proton conductivity at reduced relative humidity. Better characterization and other performance evaluation of these composite membranes can help to verify this hypothesis as well as lead to an improved understanding of the physical parameters necessary for this improved performance.

Water uptake measurements and conductivity measurements were made in a barometric sorption vessel as a function of temperature and relative humidity. Several composite membranes were tested based upon extruded Nafion films (e.g. 115) and recast Nafion.

Experimental - A barometric sorption vessel (400 cm³) was constructed and used to quantify water uptake of a membrane sample[3]. 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[1].

Results - Membrane water content increases with

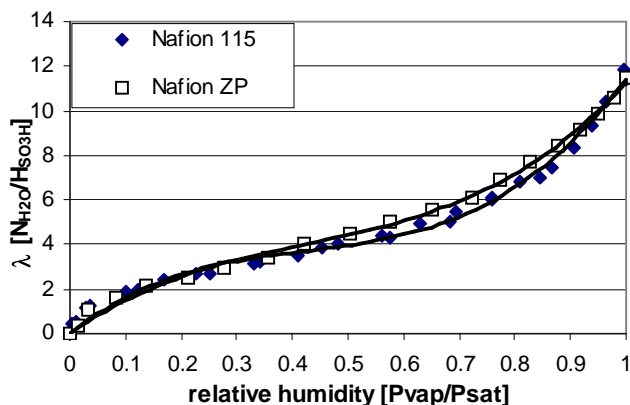


Figure 1: Nafion 115 and Nafion Zirconium Phosphate membrane water content vs relative humidity at 80°C.

increased relative humidity. The following figure shows the variation in the water content $\lambda (N_{H_2O}/N_{SO_3H})$ with

increasing relative humidity (P_{vap}/P_{sat}). The water sorption isotherm in figure 1 can be fit by a cubic polynomial. The comparison between the Nafion and Nafion composite membrane shows virtually identical water uptake per sulfonate except for slightly higher uptake by the composite membrane around a relative humidity of 65%.

Specific conductivity increases significantly with relative humidity and can vary over 4 or 5 orders of magnitude as water content increases to a fully saturated membrane. The variation of specific conductivity vs relative humidity can be modeled with a power law relation.

$$\sigma = \sigma_s (RH)^\alpha$$

where σ_s is the saturated membrane conductivity (at 100% RH) and α is a variation exponent.

Figure 2 shows the results of combining the membrane conductivity data with the membrane water uptake data. The semilog plot shows two distinct regions of exponential conductivity increase with increasing water content. At low water content, conductivity increases rapidly as the membrane water increases. At higher water contents above 4, conductivity increases less with additional water.

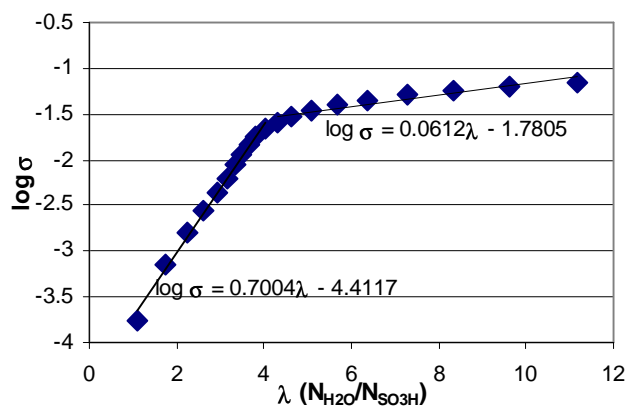


Figure 2: membrane conductivity variation with water content for Nafion 115 membrane.

Conclusions- The performance of both PEMFCs and DMFCs can be improved by operating at higher temperatures. Composite membranes can be synthesized to increase proton conductivity relative to unmodified Nafion membranes over a range of relative humidity. Increasing temperatures will lead to improved electrochemical kinetics and reduced CO poisoning but, unless accompanied by increased humidification, will also lead to water loss and reduced conductivity. This study seeks to quantify and compare the variation of protonic conductivity of Nafion and Nafion based composite membranes with temperature and relative humidity.

References:

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