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Performance Evaluation of Fluorenyl and Non-fluorenyl Containing SPEEKK Polymers as Hydrogen and Methanol Fuel Cell Membranes

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Three polymers previously engineered for polymer electrolyte membrane fuel cell applications were evaluated as membranes in hydrogen and methanol fed fuel cells. This was done in an effort to improve upon the high temperature (>100°C) and methanol fed performance of perfluorinated ionomers such as Nafion. The polymers tested were: fluorenyl-containing sulfonated poly(aryl ether ether ketone ketone)s, 50% sulfonated content (p-SPFEEKK), and the para and meta isomers of non-fluorenyl-containing polyetherketones with pendant (3-methyl-4-sulfonic acid)phenyl groups (Me-p-SPEEKK and Me-m-SPEEKK). The synthesis and thorough characterization of these polymers including FTIR, TGA, water uptake, swelling, and proton conductivity have been presented elsewhere[1-3].

Membrane electrode assemblies were made by spraying a Nafion ionomer containing catalyst ink directly onto the membranes. Catalyst layers consisting of 20% Pt on Vulcan XC72 at 0.5 mgPt/cm^2 were used on the anodes and cathodes for hydrogen testing and on the cathodes for methanol testing. The anodes for methanol testing consisted of 50:50 PtRu, (4mg/cm^2). SGL carbon 35BC paper electrodes were used as gas diffusion layers in the fuel cell assembly. Fuel cell characterization was performed at 40, 60, 80 and 100°C. Gases fed to the fuel cell were maintained at 100% RH relative to the fuel cell temperature. Hydrogen testing was performed using both air and oxygen as the oxidants. Methanol testing was performed using only air as the oxidant. The gas flow rates were held constant at 200 slpm. Methanol solutions were varied from 0.5, 1, 2, and 3M, and were pumped at a constant flow rate of 1ml/min. Backpressure of 20 psig was maintained on both sides of the fuel cell. Alcohol permeability measurements were taken using a membrane separated diffusion cell with a differential refractometer used for measuring concentrations4. The permeability of methanol, ethanol, and n-propanol were evaluated for each polymer and Nafion. The low sulfonation content of the p-SPFEEKK was chosen to maintain high oxidative stability. Its low conductivity of 36mS/cm^2 (80°C) qualifies it only for DMFC use although hydrogen fuel cell tests were also conducted. This membrane exhibited very low methanol permeability of $4.4*10^{-7}$ cm^2/sec as compared to $3*10^{-6}$ for Nafion 115. The lower permeability resulted in a higher open circuit voltage of

0.69V at 80°C, 3M methanol using the hydrocarbon membrane compared with 0.57V when using the Nafion 115 membrane. Despite the higher open circuit voltage, the fuel cell performance was limited by its low proton conductivity. When using 3M methanol feed, at 80°C and 0.35V, Nafion 115 achieved 148mA/cm^2 while the p-SPFEEKK only achieved 55mA/cm^2. The polymers Me-p-SPEEKK and Me-m-SPEEKK were chosen because of their high proton conductivity. The high methanol permeability of these membranes makes them more suitable for hydrogen fuel cell applications. The methanol permeabilities were measured to be 3.8*10^{-6} cm^2/sec for Me-p-SPEEKK and 5.6*10^{-6} cm^2/sec for Me-m-SPEEKK. The similar permeability for Me-p-SPEEKK and Nafion 115 resulted in nearly identical DMFC performance, while the Me-m-SPEEKK performance suffered from higher methanol crossover. Hydrogen fuel cell tests show small but significant performance improvements over Nafion 115 when using Me-m-SPEEKK. At 0.65V and 80°C using oxygen the MEA made using Nafion 115 achieved 720 mA/cm^2 while the MEA made using Me-m-SPEEKK achieved 840 mA/cm^2.

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