

LOW CROSSOVER POLYMER ELECTROLYTE MEMBRANES FOR DIRECT METHANOL FUEL CELLS

G.K. Surya Prakash, Marshall Smart, Anthony R. Atti, George A. Olah

Loker Hydrocarbon Research Institute and Dept. of Chemistry, University of Southern California Los Angeles, CA, 90089-1661

S.R. Narayanan, T. Valdez, S. Surampudi
Jet Propulsion Laboratory, California Institute of Technology Pasadena, CA 91109

Background

Direct Methanol Fuel Cells (DMFC's) using polymer electrolyte membranes are promising power sources for portable and vehicular applications.¹ State of the art technology using Nafion[®] 117 membranes (Dupont) are limited by high methanol permeability and cost, resulting in reduced fuel cell efficiencies and impractical commercialization.

Therefore, much research in the fuel cell field is focused on the preparation and testing of low crossover and cost efficient polymer electrolyte membranes. The University of Southern California in cooperation with the Jet Propulsion Laboratory is focused on development of such materials.

Interpenetrating polymer networks are an effective method used to blend polymer systems without forming chemical links.² They provide the ability to modify physical and chemical properties of polymers by optimizing blend compositions. We have developed a novel interpenetrating polymer network based on poly (vinyl - difluoride)/cross-linked polystyrene-sulfonic acid polymer composites (PVDF - PSSA). Sulfonation of polystyrene accounts for protonic conductivity while the non-polar, PVDF backbone provides structural integrity in addition to methanol rejection.

Precursor materials were prepared and analyzed to characterize membrane crystallinity, stability and degree of interpenetration. USC - JPL PVDF-PSSA membranes were also characterized to determine methanol permeability, protonic conductivity and sulfur distribution.

Membranes were fabricated into membrane electrode assemblies (MEA) and tested for single cell performance. Tests include cell performance over a wide range of temperatures (20 °C - 90 °C) and cathode conditions (ambient Air/O₂). Methanol crossover values are measured in situ using an in-line CO₂ analyzer.

Results and Discussion

We have developed a methodology that results in uniform IPN's with smooth surface morphologies. This is desirable as it improves interfacial contact with electrocatalytic layers during MEA fabrication.

Membrane conductivity values range from 0.040 S/cm⁻¹ to 0.120 S/cm⁻¹ depending on PSSA uptake and distribution. This is comparable to the reported value of 0.070 S/cm⁻¹

for Nafion and within the range necessary to ensure adequate proton conductivity.

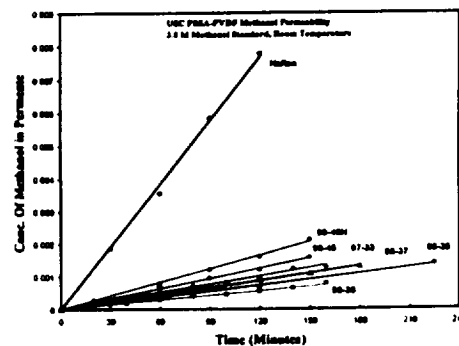


Fig. 1 Methanol permeation for various samples (20-25 °C)

Methanol diffusion coefficients are calculated from the results of methanol permeation measurements as shown in figure 1 and correlated to PSSA content and thickness. The results in figure 1 indicate USC - JPL membranes have permeation rates vastly lower than Nafion.

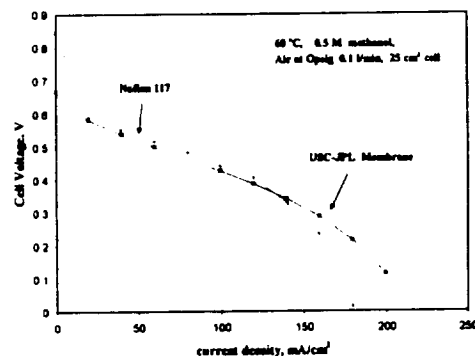


Fig. 2. Cell Performance at 60 °C, 0.50 M MeOH 0.10 L/min Ambient Air

These low crossover membranes feature comparable cell performance vs. Nafion under low stoichiometric conditions, as shown in figure 2. They also have greatly reduced methanol crossover values compared to Nafion at various operating cell temperatures. Methanol crossover values (OCV) range from 33 mA/cm² at 60 °C (Nafion = 90 mA/cm²) and 43 mA/cm² at 90 °C (Nafion = 160 mA/cm²).

TGA thermal analysis of USC - JPL membranes determined there is no appreciable degradation of these materials below 200 °C. Membrane samples heated to 200 °C for 15 - 30 minutes have retained conductivity following rehydration.

References:

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- 2) L. M. Sergeeva, L.A. Gorbach *Russian Chemical Reviews* 65 (4) 345-354 (1996)