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Novel Melt-Extruded Nanocomposite PEMs Based on Sulfonfyl Fluoride PFSA and Imidazole-Grafted Silica Nanoparticles for Low RH Operation

A. Mokrimi*, S.M. MacKinnon, A. Siu, L. Robitaille
Industrial Materials Institute – National Research
Council of Canada

75, De Mortagne, Boucherville (Qc) J4B6Y4 Canada
asmae.mokrimi@imi.nrc-nrc.gc.ca

Hybrid membranes are commonly generated by *in situ* precipitation of the inorganic material within a preformed ionomer membrane or in a polymer solution. Alternatively, melt-extruded hybrid proton exchange membranes (PEMs) are a new class of membrane materials with many desirable properties for fuel cell applications. It has been demonstrated that extruded PEMs show outstanding durability compared to solvent-cast and reinforced membranes (10,000 humidity cycles for melt-extruded Ion Power™ N111-IP, vs. 4,500 cycles for the solvent-cast DuPont™ NR-111, and 6,000-7,000 cycles for the micro-reinforced Gore™ Primea® membrane)(1). Furthermore, the use of solvent-free, melt-processing technologies allows a much more uniform dispersion of inorganic fillers as well as easier and continuous membrane production, resulting in a significantly reduced manufacturing time and cost.

Perfluorosulfonic acid resins (PFSA) are today's benchmark materials for PEMs for fuel cell applications (2). These materials exhibit outstanding stability and a proton conductivity of 0.1 S/cm at 80°C when fully humidified. However, their proton conductivity significantly depends on the membrane water content. Their performance drops dramatically at higher temperatures and/or low humidification. Our approach focuses on the unique combination of functional inorganic fillers with melt-processing methods with the objective to manufacture low cost, advanced nanocomposite PEMs with improved properties for operation in low relative humidity conditions.

In this work, functional nanoparticles have been synthesized by grafting N-containing heterocycles such as imidazole groups onto silica-based inorganic supports of different particle sizes (Figure 1). Silica nanoparticles with diameters in the range of 60-120 nm were synthesized via a sol-gel process from tetraethylsiloxane under base catalysis. Highly nucleophilic groups were introduced using appropriate amino-modified silane reagents. The immobilization of imidazole groups on the surface of the nanoparticles was achieved by reacting primary amine groups of the modified silica particles with aldehyde derivative of imidazole.

Figure 1. SEM images of silica nanoparticles of different diameters (60, 80 and 120 nm) synthesized by a sol-gel process.

Nanocomposite PEMs were prepared using melt-processing technologies, by blending the grafted and ungrafted nanoparticles with an extrusion grade of Nafion® in the sulfonfyl fluoride form. After converting

the ionomer matrix to the acid form, the resulting hybrid membranes are fully characterized mechanically, physically and electrochemically (TEM, DSC, DMTA, IEC, WU, conductivity measurement at controlled T and RH, fuel cell testing).

Figure 2. TEM image of melt-extruded nanocomposite PEM.

The development of hybrid membranes typically results generally, in both a reduction of fuel crossover and an improvement of mechanical and thermal stability in the hydrated state but, at the same time, in a loss of proton conductivity mostly due to a poor dispersion of the fillers in the membrane. Our approach produces hybrid fuel cell membranes with substantially better properties than commercially available Nafion (3). The nanocomposite electrolytes showed very efficient dispersion of the inorganic fillers (Figure 2), an overall improvement in hydrolytic stability and improved conductivities between 10^{-2} to 10^{-3} S.cm⁻¹ at 80°C over the entire humidity range from 100 to 30%. In this paper the results obtained from *in-situ* electrochemical characterization of a series of nanocomposite membranes will be presented. Figure 3 shows the preliminary results obtained for NRE-212 reference and nanocomposite PEM with 5wt% of 120nm SiO₂ inorganic filler. Composite PEM shows higher OCP, improved voltage and power density.

Figure 3. I-V and power density curves measured for NRE-212 and nanocomposite PEM with 5wt% of 120nm SiO₂ inorganic filler

References.

1. T. Greszler, DOE Hydrogen Program review meeting, September 2006.
2. Nafion®, Flemion®, and Aciplex® families are commercial products from DuPont, Dow Chemical, Asahi Chemical, Asahi Glass Company respectively.
3. A. Mokrimi, A. Siu, L. Robitaille, L. Gonzalez, and F. Sanchez. ECS Trans., 33 (1), 823 (2010).