

V.B.22 Advanced Materials for Proton Exchange Membranes

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Technologies Program Multi-Year Research,
Development and Demonstration Plan.

TABLE 1. Fuel Cells Targets Addressed by this Project

Characteristic	Units	2005	2010	2015
Operating Temperature	°C	≤120	≤120	≤120
Inlet water vapor partial pressure	kPa (absolute)	25	1.5	1.5
Cost	\$/m ²	200	40	40
Durability with cycling				
At operating temp of <80°C	hours	2,000	5,000	5,000
At operating temp of >80°C	hours		2,000	5,000
Survivability	°C	-30	-40	-40

Approach

The polymer synthesis and processing groups at Virginia Tech (VT) will address the issue of higher temperature/lower humidity proton exchange membranes (PEMs) as advanced material components for fuel cells. The research will use thermally, oxidatively, and hydrolytically ductile, high T_g ion containing polymers based on poly(arylene ethers). Excellent durability has been achieved as demonstrated by the fact that the open circuit voltage (OCV) stability of these materials is significantly better than those of perfluorinated sulfonic acid state-of-the-art systems at 100°C, 25% humidity, under hydrogen-oxygen conditions. The improvement is related to the lower (by a factor of 10x) oxygen permeability in the glassy poly(arylene ether) disulfonated copolymers. Direct methanol fuel cells (DMFCs) using these membranes have demonstrated lifetimes exceeding 3,000 hours at 80°C with improved performance relative to the benchmark materials.

The synthesis part of the effort will focus on two important thrusts. The random copolymers will be reinforced with protonic conductive zirconium phenyl phosphonate (zpp) layered structures, which affords a ductile composite. The filler will contain controlled amounts of ordered sulfonic acid moieties to enhance conductivity. Additional efforts with mixed acid structures, which provide significant higher conductivity in the absence of moisture, will also be included. Techniques have been developed to reproducibly synthesize these materials. The composite membranes

Objectives

- Design polymer-based proton exchange membranes that operate at high temperature and low humidity
- Prepare a production process for the polymer membranes
- Supply samples for testing

Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

(B) Cost

Technical Targets

This project addresses the following Fuel Cells technical targets from Table 3.4.12 Membranes for Transportation Applications from the Fuel Cells section of the Hydrogen, Fuel Cells and Infrastructure

can be made either in solution or dispersion, and the resulting zpp will be water insoluble, unlike many other additives.

The second approach will continue and expand efforts at preparing alternating hydrophilic-hydrophobic multiblock copolymers derived from a hydrophilic aromatic oligomer with reactive phenoxide endgroups, coupled with a perfluorinated or hydrocarbon functional hydrophobic material, to produce multiblocks that are also ductile. Because of the long sequences, they can provide pathways for the hydrated proton complex to traverse the membrane more easily relative to random copolymers. Fundamental studies utilizing nuclear magnetic resonance (NMR) to establish diffusion coefficients of water along the channels of the cocontinuous system have shown that the block copolymers have very significantly higher diffusion coefficients, which can explain why the important end result of improved conductivity at lower relative humidities can be achieved. A number of copolymers have been prepared and characterized, and *it has been shown that in these copolymers conductivity is a function of relative humidity, and the copolymers have significantly better conductivity than the benchmark perfluorosulfonic acid.* A number of variables will be systemically studied to further optimize this promising behavior. The multiblock copolymers can also be filled with partially conductive zirconium salt.

The strong synthesis, polymer characterization and electrochemical characterization will be coupled with the development of a process to produce proton exchange membrane films of controlled thickness. Presently, batch processes for these films are employed, which are tedious and subject to reproducibility and thickness uniformity problems. An intensive combined experimental and modeling activity will be designed (most likely for the reverse roll coating process but possibly for the curtain coating process) which will relate coating thickness to the geometric, rheological, interfacial, and operating variables of the process. Once the film is cast on the web, then a model for calculating the time to remove the solvent as a function of web speed and heat transfer conditions will be developed. Based on this fundamental study, conditions for any experimental composition developed in this project can be readily established to produce model films that are 2 to 3 inches in width, pinhole-free, and controllable with respect to their thickness. In particular, 25-, 50-, and 75-micron (approximately 1, 2 and 3 mil) thick films will be featured. The resulting films will be subjected to similar mechanical and electrochemical testing as before.

FY 2006 Progress

This project is in the process of being initiated.