VII.B.2 High-Temperature Polymer Membranes

Deborah Myers (Primary Contact), Suhas Niyogi, and Romesh Kumar
Argonne National Laboratory
9700 S. Cass Avenue
Argonne, IL 60439-4837
Phone: (630) 252-4261; Fax: (630) 252-4176; E-mail: myers@cmt.anl.gov

DOE Technology Development Manager: Nancy Garland
Phone: (202) 586-5673; Fax: (202) 586-9811; E-mail: Nancy.Garland@ee.doe.gov

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Projected End Date: Project continuation and direction determined annually by DOE

Objectives

- To develop a proton-conducting polymer electrolyte material for use in fuel cells operating at 120-150°C and low humidities
- To investigate use of dendritic macromolecules attached to polymer backbones, cross-linked dendrimers, and inorganic-organic hybrids as candidate materials

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:

- A. Durability
- B. Cost
- D. Thermal, Air and Water Management

Approach

- Fabricate and test membranes using materials with the following properties:
  - High density of proton-conducting sites to facilitate proton transfer with reduced water mediation
  - Thermal stability to >150°C
  - Retention of water at temperatures to 150°C
- Candidate materials are:
  - Dendritic macromolecules
    - Polyaryl ether dendrimer chosen due to high thermal stability
    - Attach to polymer backbone (e.g., polyepichlorohydrin [PECH]) to render water-insoluble and to allow film formation
  - Inorganic-organic hybrids
    - Inorganic component improves water retention at high temperatures
    - Organic component can be functionalized at several sites for a variable charge density and distribution

Accomplishments

- Fabricated water-insoluble polymer electrolyte membranes from generation two to four polyaryl ether dendrons attached to a polyepichlorohydrin polymer backbone
- Improved the thermal and dimensional stability, the film-forming capability, the water-insolubility, and the proton conductivity of dendronized polyepichlorohydrin films through cross-linking
- Determined that dendronized polyepichlorohydrin is stable towards oxidizing conditions - established by the Fenton's test
- Determined that dendronized polyepichlorohydrin absorbs more water than Nafion® under high humidity conditions (30 wt% vs. 20% at 97% relative humidity, RH) and retains more water under low humidity conditions (12 wt% vs. 6 wt% at 40% RH)
- Fabricated and characterized proton-conducting water-insoluble inorganic-organic hybrid polymer membranes using a non-Nafion® binder

Future Directions

- Improve dimensional stability and proton conductivity of dendronized polymers at high temperatures
  - Improve film processing to insure complete removal of plasticizing/conductivity masking solvent
  - Optimize dendrimeric network with better cross-linker for dendronized materials
  - Evaluate polybenzimidazole and other film-forming polymers as backbones
  - Incorporate ionic liquids into membrane to improve conductivity and dependence on water
- Improve dimensional stability and conductivity of inorganic/organic hybrid films
  - Increase content of sulfonated organic component
  - Improve homogeneity of dispersed, proton-conducting phase
- Fabricate and test membrane-electrode assemblies using the most promising materials

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Introduction

The state-of-the-art electrolyte material for the polymer electrolyte fuel cell, perfluorosulfonic acid (PFSA), requires humidification to conduct protons. PFSA membranes require close to 100% RH for proton conductivity high enough for the fuel cell application (~0.1 S/cm) [1], dictating humidification of the reactant streams. This requirement limits the operating temperature of the fuel cell to <100ºC (typically 80ºC) and adds complexity, size, weight, and cost to the fuel cell power system. Proton-conducting membrane materials with reduced need for external humidification and the ability to operate at temperatures above 100°C would vastly simplify the fuel cell system and advance the development of fuel cell systems for automotive and stationary applications.

Approach

Argonne's approach to developing membrane electrolytes with high proton conductivity at low RH and temperatures above 100ºC is to utilize sulfonated polyaryl ether dendrimers (which are highly branched macromolecules) and inorganic/organic composites.

The polyaryl ether dendrons were chosen as membrane building blocks because they have a high density of proton-conducting functional groups, are thermally stable, and are expected to be stable in the fuel cell environment. The high density of ionic groups on the dendrons renders them soluble in water. Our approach to forming water-insoluble membranes is to attach their dendrons to water-insoluble polymer backbones, such as polyepichlorohydrin.

The inorganic/organic composites are fabricated from a hygroscopic inorganic material and an organic component with multiple sites for functional groups. Initially, silica was chosen as the inorganic component to improve the water retention of the membranes at temperatures >100°C. The organic component is a cyclic organic molecule with a high

density of sites for functionalization with proton-conducting sulfonate groups; it was chosen to have a high thermal stability (>300°C) and low cost.

Results

In FY 2005, we completed the preparation of generation two to four dendritic polyelectrolytes using a polyepichlorohydrin backbone and sulfonating the outer aromatic moieties (Figure 1). The dendronized polyepichlorohydrin was cross-linked prior to sulfonation. Cross-linking improved the thermal and dimensional stability, film-forming capability, water insolubility, and proton conductivity of the materials. We determined that these materials are stable towards oxidizing conditions, as established by the Fenton's test. As shown in Figure 2, it was also determined that these materials absorb more water than Nafion® under high-humidity conditions (30 wt% vs. 20% at 97% RH) and retain more water under low-humidity conditions (12 wt% vs. 6 wt% at 40% RH). Further improvements in the dimensional stability of these materials at temperatures >80°C are needed. This will be addressed by increasing the degree of cross-linking of the polyepichlorohydrin polymer backbone and by attaching the dendrons to alternative thermally stable polymers, such as polybenzimidazole. During the course of our investigations, we also determined that controlling the degree of sulfonation of these materials is difficult, thus limiting their reproducibility. During FY 2006, we will develop a reproducible technique to control the amount of sulfonic acid groups on the dendrons, with special emphasis on their long-term stability under fuel cell operating conditions.

Several inorganic-organic hybrid membranes were fabricated this year. The sulfonated organic component was blended with colloidal silica in formaldehyde to form a gel consisting of the organic component chemically bonded to the silica surface. This gel was freeze-dried to form the hybrid material with an equivalent molecular weight of ~600. Membranes were prepared using commercial polymer emulsions as the supporting material, replacing the Nafion® binder we used in FY 2004, and their physical properties were measured. These materials exhibited encouraging proton conductivity given the low content of the proton-conducting

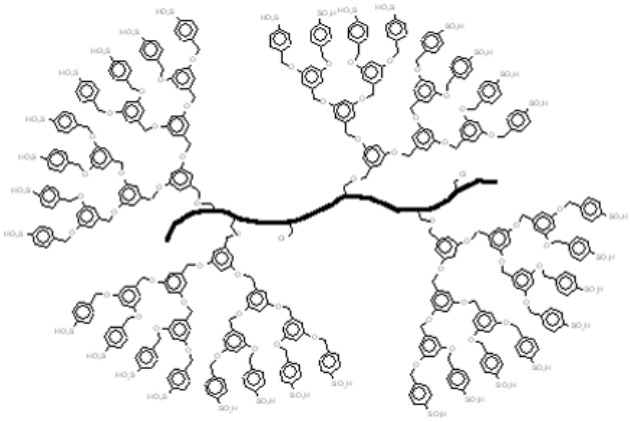

Figure 1. Structure of the Generation Three (G3) Polyaryl Ether Dendronized Polyepichlorohydrin

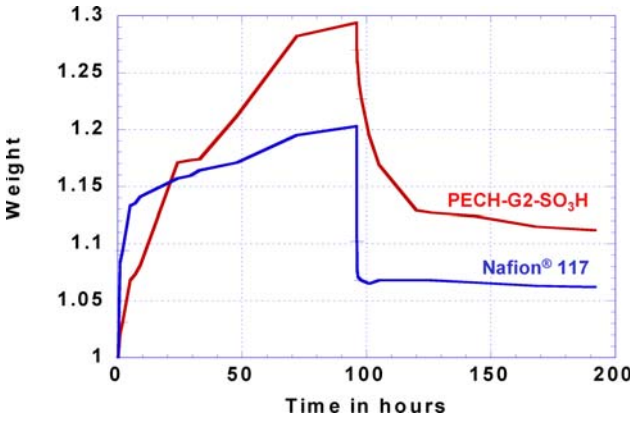

Figure 2. Water Absorption at High RH Conditions (25°C and 97% RH) and Desorption Under Low RH Conditions (25°C and 40% RH) for PECH-G2-SO_3H as Compared with Nafion® 117 (The two polymers are of comparable equivalent weight.)

organic component and the inhomogeneous dispersion of this phase. In FY 2006, we will focus on increasing the fraction of the proton-conducting component in the blend, improving its dispersion, and improving the high-temperature mechanical properties of the films through the use of alternative binders.

Conclusions

- Highly sulfonated dendrons can be formed into water-insoluble proton-conducting membranes by attachment to water-insoluble polymer backbones

- Dendronized polymers are thermally and oxidatively stable up to 150°C and retain nearly 30% more moisture than Nafion® under low RH
- Cross-linking of the polyepichlorohydrin polymer backbone improves the thermal and mechanical stability and the proton conductivity of the dendronized polymer
- Inorganic-organic hybrid membranes made from cyclic organic compounds and colloidal silica have high thermal stability and encouraging proton conductivity, given their high equivalent weights
- The mechanical properties of these materials are being improved by cross-linking and by utilizing new polymer matrices to allow high, sustained proton conductivity at temperatures >80°C and RH <25%

FY 2005 Publications/Presentations

1. "High-Temperature Polymer Electrolyte Fuel Cell Electrolytes Based on Dendronized Polymers," Seong-Woo Choi, Suhas Niyogi, Romesh Kumar, and Deborah Myers, presentation and extended abstract, 206th Fall Meeting of the Electrochemical Society, Honolulu, Hawaii, Oct. 3-8, 2004
2. "High-Temperature Polymer Electrolyte Membranes Based on Dendritic Macromolecules and Organic/Inorganic Hybrids," Seong-Woo Choi, Suhas Niyogi, Deborah J. Myers, and Romesh Kumar, poster and extended abstract, 2004 Fuel Cell Seminar, San Antonio, Texas, Nov. 1-5, 2004
3. "High-temperature Polymer Electrolyte Development at ANL," International Energy Agency-Polymer Electrolyte Fuel Cell Annex, Fall, 2004 Workshop, Rome, Italy, Nov. 18-19, 2004