

IV.B.3 High-Temperature Polymer Membranes

*Deborah Myers (Primary Contact), Suhas Niyogi, Seong-Woo Choi,
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

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:

- E. Distributed Generation Durability
- O. Stack Material and Manufacturing Cost
- P. Component Durability
- Q. Electrode Performance
- R. Thermal 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 >150°C
 - Retention of water at temperatures to 150°C
- Candidate materials include the following:
 - Dendritic macromolecules
 - Polyaryl ether dendrimer chosen due to high thermal stability
 - Cross-link or attach to polymer backbone (e.g., polyepichlorohydrin (PECH)) to render water insoluble
 - 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 dendronized polymer membranes with proton exchange capacities of 4.0 meq/gram, thermal stabilities up to 190°C, and proton conductivities of 0.022 S/cm (98°C and 22% RH) and 0.1 S/cm (76°C and 6% RH)
- Fabricated water-insoluble inorganic-organic hybrid polymer membranes mixed with Nafion[®] with thermal stability up to 300°C and a proton conductivity of 0.35 S/cm at 80°C and 5% RH

Future Directions

- Complete characterization of G2, G3, and G4 dendronized polymers with PECH backbone of 100K and 700K molecular weight
- Cross-link PECH-dendronized polymers to improve mechanical properties
- Cross-link dendrimers to form dendrimeric network
- Develop film-forming techniques for inorganic-organic hybrids not relying on Nafion[®]
- Fabricate and test membrane electrode assemblies (MEAs) using newly-developed high-temperature membranes

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% relative humidity (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 <100°C (typically 80°C) 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 relative humidity and temperatures above 100°C is to utilize sulfonated polyaryl ether dendrimers (which are highly branched macromolecules) and inorganic/organic composites.

The polyaryl ether dendrimers and their constituent 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 dendritic building blocks would render them soluble in water, however. Our approach to forming water-insoluble membranes is to cross-link the dendrimers or attach their constituent dendrons to water-insoluble polymer backbones, such as polyepichlorohydrin.

Silica was chosen as the inorganic component of the inorganic/organic composite materials to improve the water retention of the membranes at temperatures >100°C. The other component of the composite is a cyclic organic molecule with a high density of sites for functionalization with proton-conducting sulfonate groups. The organic component was chosen to have a high thermal stability (>300°C) and low cost.

Results

Our efforts this year have been focused on synthesizing significant quantities of the polyaryl ether dendrons up to generation four (four levels of branching), Figure 1, and attaching them to water-insoluble polymer backbones, such as polyepichlorohydrin (PECH). We have successfully fabricated water-insoluble membranes from the generation two (G2) and generation three (G3)

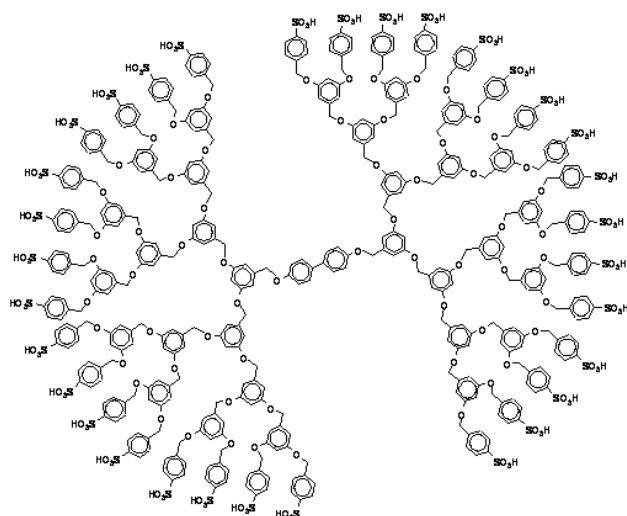


Figure 1. Structure of the Generation Four (G4) Polyaryl Ether Dendrimer

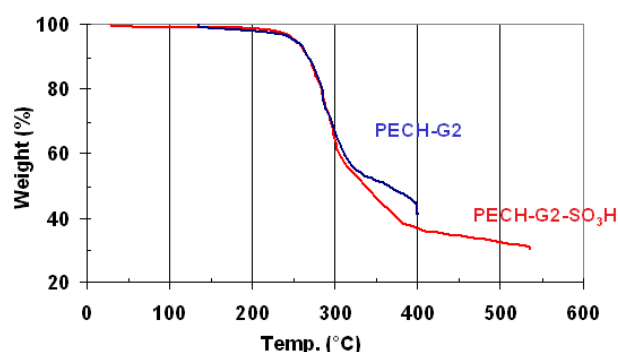


Figure 2. Thermogravimetric Analysis of the Dendronized Polyepichlorohydrin Polymer, with and without Sulfonation, Showing that the Materials do not Decompose at Temperatures <190°C

dendrons attached to 100,000 and 700,000 molecular weight (MW) polyepichlorohydrin. The G2-PECH (MW = 100,000) material was too brittle for film formation and the G3-PECH (MW = 100,000) too tacky. A blend of the two materials had good film-forming characteristics. Films were also cast from the G2-PECH (MW = 700,000) material. Thermogravimetric analyses of these materials, Figure 2, show that they are stable up to 190°C. Titration of the acid groups in these two materials showed them to have cation exchange capacities of 4.0 milliequivalents/gram, over four times that of

Nafion[®] 1100 (0.91 milliequivalents/gram). Table 1 shows the conductivity of the G2/G3-PECH (MW = 100,000) film measured at temperatures from room temperature to 98°C at a constant humidifier temperature of 61°C. The G2-PECH (MW = 700,000) membrane was found to have a short-term conductivity of 0.101 S/cm at 76°C and 6% RH. Further conductivity measurements of these materials were not possible due to mechanical deformation of the films under the low humidity/high temperature conditions.

Table 1. Conductivity of Dendronized Polyepichlorohydrin (G2/G3 polyaryl ether dendrite) at a Constant Humidifier Temperature of 61°C

Temperature (°C)	Relative Humidity (%)	Conductivity (S/cm)
21	100	0.031
56	100	0.081
73	59	0.036
98	22	0.022

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 an inorganic-organic hybrid material with an equivalent weight of ~600. Films were formed from the hybrid by blending with Nafion[®] solution (70 wt% Nafion[®], 14 wt% organics, 16 wt% silica). As shown in Figure 3 the inorganic-organic hybrid films exhibited higher proton conductivity than Nafion[®] in testing up to 80°C, even under low relative humidity conditions. This high conductivity was found to be stable over the four-day duration of the tests. Film-forming techniques for the inorganic-organic hybrids that do not rely on Nafion[®] are being investigated.

Conclusions

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

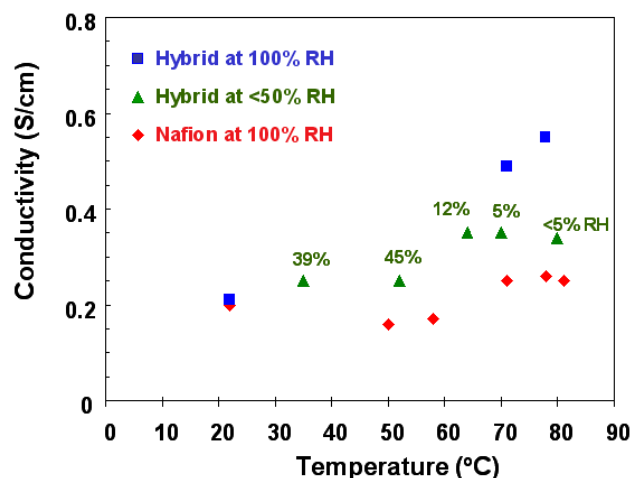


Figure 3. Measured Conductivity of an Inorganic-Organic Hybrid Membrane at 100% RH and Below (Shown for comparison is the conductivity of Nafion[®] measured at 100% RH.)

- Dendronized polymer membranes have high cation exchange capacities and high proton conductivity with reduced dependence on relative humidity as compared to Nafion[®] 1.
- Inorganic-organic hybrid membranes made from cyclic organic compounds and colloidal silica have high thermal stability and higher proton conductivity than Nafion[®] when fully humidified and under nearly dry conditions (<5% RH).
- 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%.

References

1. G. Alberti, M. Casciola, L. Massinelli, and B. Bauer, *J. Membrane Sci.*, **2001**, 185, 73.

FY 2004 Publications/Presentations

1. "Proton Conducting Membrane for Fuel Cells," Daniel G. Colombo, Michael Krumpelt, Deborah Myers, John P. Kopasz, Patent Application 20030035991.
2. "High Temperature Polymer Membrane Development at Argonne National Laboratory," Seong-Woo Choi, Suhas Niyogi, John Kopasz, Romesh Kumar, and Debbie Myers, presented at the High Temperature Membrane Working Group Meeting, October 17, 2003, Orlando, FL.
3. "High Temperature Polymer Membrane Development at Argonne National Laboratory," Seong-Woo Choi, Suhas Niyogi, John Kopasz, Romesh Kumar, and Debbie Myers, presented at the fall 2003 Workshop of the International Energy Agency's Advanced Fuel Cell Implementing Agreement Polymer Electrolyte Fuel Cell Annex, November 7-8, 2003, Miami Beach, FL.

Special Recognitions & Awards/Patents Issued

1. "Proton conducting membrane for fuel cells", U.S. Patent Application 20030035991, patent pending.