V.B.2 High-Temperature Polymer Electrolyte Membranes

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Objective

To develop a durable proton-conducting membrane electrolyte based on dendronized polymers for use under low humidities and at temperatures from -20ºC to 120°C.

Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section (3.4.4.2) of the Hydrogen, Fuel Cells, and Infrastructure Technologies Program Multi-Year Research, Development, and Demonstration Plan:

(A) Component Durability
(B) Cost
(C) Electrode Performance
(D) Thermal and Water Management
(I) Hydrogen Purification/Carbon Monoxide Cleanup

Technical Targets

This project is addressing the following DOE 2010 technical targets for polymer electrolyte membranes by developing materials with a high concentration of sulfonate groups and attaching them to stable polymer backbones:

- High, sustained proton conductivity (0.1 S/cm) at <120ºC and <1.5 kPa water vapor pressure
- Proton conductivity of 0.01 S/cm at temperatures as low as -20°C
- Low oxygen and hydrogen cross-over (equivalent to 2 mA/cm²)
- Low cost, $40/m²
- Durability of 2,000 operating hours at >80°C
- Survivability to -40°C

Accomplishments

- Demonstrated a conductivity of >0.1 S/cm at 60°C and 100% relative humidity (RH) for dendronized polyepichlorohydrin
- Improved stability and control over placement of sulfonate groups using an alternative dendron, which
  - is stable to >200°C
  - retained 3 H_2O/SO_3 at 150°C
- Improved dimensional and thermal stability of polymer backbone by attaching dendrons to polybenzimidazole (PBI) as functional groups, not separate inclusions

Introduction

The state-of-the-art electrolyte material for polymer electrolyte fuel cells, perfluorosulfonic acid (PFSA), requires humidification to conduct protons. Membranes made with PFSA require close to 100% RH to achieve proton conductivity high enough for fuel cell applications (~0.1 S/cm), dictating humidification of the fuel and oxidant streams. This requirement and the thermal stability of PFSA limit the operating temperature of the fuel cell to <100ºC (typically 60–80ºC), while adding to the complexity, size, weight, and cost of the fuel cell system. Proton-conducting membrane materials with reduced need for external humidification and the ability to operate at temperatures above 100°C would simplify the fuel cell systems and advance their development for automotive and stationary applications.

Approach

Our approach to developing such polymer electrolyte materials is to use sulfonated polyaryl ether dendrons (highly branched macromolecules – Figure 1). The polyaryl ether dendrons were chosen as the building blocks because they have a high density of proton-conducting functional groups, they are thermally stable, and they are expected to be stable in the fuel cell environment. When fully sulfonated, the high density of ionic groups on the dendritic building blocks renders them soluble in water. Therefore, we attach their constituent dendrons to a water-insoluble polymer backbone, such as polyepichlorohydrin (PECH in Figure 1).

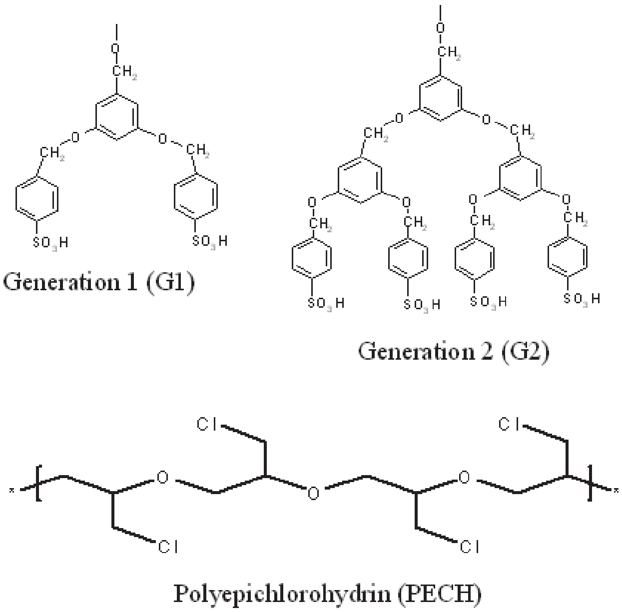

FIGURE 1. Structure of Generations One and Two Polyarylether Dendrons and Polyepichlorohydrin

Results

Multiple membranes of sulfonated generation-two (G2) dendrons attached to PECH were prepared and characterized this year. These films were found to be thermally stable up to 180°C. High proton conductivities were achieved with these membranes at 100% RH up to 70°C. The reproducibility of these high conductivities has been difficult, however, possibly due to inadequate control over sulfonation of the aromatic rings. Other issues with this material are the long-term hydrolytic stability of the sulfonate groups attached directly to the aromatic ring, and dimensional stability at >70°C.

An alternative dendron generation-one (Alt-G1), shown in Figure 2, was synthesized to address the control of sulfonation of the conventional dendrons and the hydrolytic stability of the sulfonate groups. In the alternative dendron, the sulfonate groups are attached to the aromatic rings through propyl or propyloxy groups, and a sultone is used to alkylate the methylol group on the dendron, thus avoiding strong sulfonation conditions. The alternative dendrons have been attached to PECH at various ratios of dendron to backbone unit. These ratios and the resulting properties of the materials are:

- 1 PECH/1 Alt-G1: 5.0 meq acid/g; water soluble
- 3 PECH/1 Alt-G1: 1.2 meq acid/g; cross-linked, non-film-forming
- 6 PECH/1 Alt-G1: 0.4 meq acid/g; cross-linked, non-film-forming

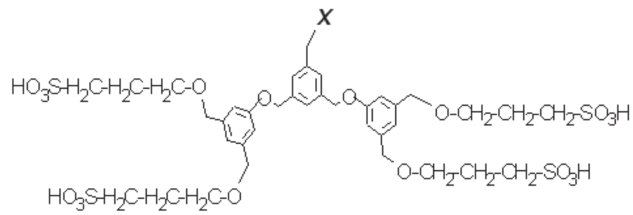

FIGURE 2. Structure of the Alternative Dendron, Alt-G1

In thermal gravimetric analyses, these materials were found to be more thermally stable than the conventional dendrons attached to PECH, with no degradation observed up to 200°C. They were also found to retain more water at high temperatures and low relative humidity than the conventional materials, as shown in Figure 3.

In an attempt to address the dimensional stability issue, the G1 dendron was attached to a PBI backbone (15 mol%). This film is thermally stable; however, sulfonation after dendronizing the PBI was found to remove the dendrons from the backbone polymer.

Conclusions and Future Directions

Conclusions

- High proton conductivities can be achieved with polymers comprised of sulfonated dendrons
- Molecular modeling results show that dendronized polymers have improved low relative humidity properties as compared to PFSA [1]

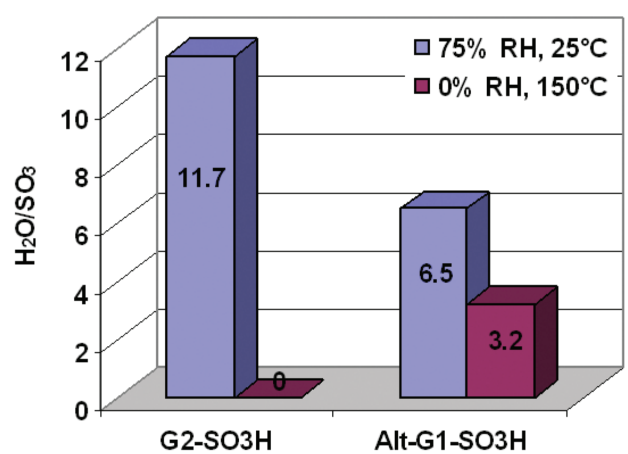

FIGURE 3. Water uptake at (a) room temperature and high RH conditions, and (b) 150°C and low RH conditions, for G2 sulfonated polyarylether dendron and the sulfonated alternative dendron. Water uptake is given as the number of water molecules per sulfonate group.

- Improved control over sulfonation of dendrons, water retention, and thermal stability can be achieved using alternative dendrons developed at Argonne
- Enhance stability and acidity of sulfonate groups using spacers between sulfonate group and benzene ring (e.g., propyloxy or fully- or partially-fluorinated ethers)

Future Work

- Continue work on sulfonation of dendronized PBI, begin work on fluorinated backbones
- Begin molecular modeling of dendronized polymers with proposed fluorinated backbones (collaboration with Caltech)
- Further improve stability of dendrons by using aromatic polyether dendrons, dendritic polybenzimidazole, and dendritic polysulfonates

Special Recognitions & Awards/Patents Issued

1. D. Colombo, M. Krumpelt, D. J. Myers, and J. P. Kopasz, "Improved Proton Conducting Membranes for Fuel Cells," U.S. Patent 6,977,122, issued December 20, 2005.

References

1. S. S. Jang, S.-T. Lin, T. Cagin, V. Molinero, W. A. Goddard, *J. Phys. Chem. B,* **2005**, *109*, 10154.