V.M.9 Poly(cyclohexadiene)-Based Polymer Electrolyte Membranes for Fuel Cell Applications

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Objectives

- Design, synthesize and characterize new non-Nafion® polymer electrolyte membrane (PEM) materials that conduct protons at low (25-50%) relative humidity and at temperatures ranging from room temperature to 120ºC.
- To achieve these objectives, a range of homopolymer and copolymer materials incorporating poly(cyclohexadiene) (PCHD) will be synthesized, derivatized, and characterized.

Technical Barriers

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

(A) Durability
(B) Cost

Technical Targets

This project is targeted toward the development and characterization of PEMs that can meet conductivity requirements specified by DOE (conductivity = 0.1 S/cm at 50% relative humidity at 120°C), as well as achieving lower cost and meeting other 2010 performance criteria:

- Cost: $20/m^2
- Durability with cycling: 2,000 hours at an operating temperature >80°C
- Survivability: -40°C
- Thermal cyclability in the presence of condensed water
- Area specific resistance: 0.02 Ohm-cm^2
- Hydrogen crossover: 2 mA/cm^2
- Oxygen crossover: 2 mA/cm^2
- Inlet water vapor partial pressure: <1.5 kPa
- Operating temperature: ≤120°C

Accomplishments

- Synthesized crosslinked and sulfonated PCHD films, characterized them, and started to measure their thermal and mechanical properties and proton conductivity. A membrane of crosslinked, aromatized (90 mol%), and sulfonated (13 mol%) PCHD was tested. Water uptake was 5.3 wt%. Proton conductivity was measured for this membrane using a four-point fixture immersed in water (J. Sayre, Battelle): 1.2 E-02 S/cm at room temperature and 2.8 E-02 S/cm at 80ºC.
- Synthesized crosslinked, aromatized, and sulfonated PCHD films, characterized them, and started to measure their thermal and mechanical properties and proton conductivity. A membrane of crosslinked, non-aromatized, and sulfonated (47 mol%) PCHD was tested. Water uptake was 4 wt%. Proton conductivity: 1.6 E-02 S/cm at room temperature and 3.6 E-02 S/cm at 80ºC. The Year 1 milestone of synthesis of six different crosslinked type membranes (Type 1 membranes) with variation in molecular weight, crosslink density, extent of aromatization, and degree of sulfonation, has been met.
- Work has been initiated on the synthesis of the first multiblock PCHD-based block copolymers (Type 2 materials) and sulfonated and fluorinated statistical copolymers (Type 3 materials). This meets the second Year 1 milestone.

- Study of the thermal, mechanical, and electrical properties of the Type 1 membranes are under investigation in Professor Mauritz's laboratory. The thermal stability of these materials is outstanding and is improved in a systematic fashion by crosslinking, sulfonation, and aromatization.
- Growth of inorganic nanoparticles within hydrophilic domains of Type 1 membranes is underway.

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Introduction

The goal of this project is to create and develop fuel cell membranes having sufficiently high proton conductivity at high temperatures, as well as high chemical and mechanical durability. PCHD is of interest as an alternative PEM material due to its ring-like structure, which imparts superior mechanical and thermal properties, and due to the fact that PCHD can readily be incorporated into a range of homopolymer and copolymer structures. Furthermore, PCHD can be aromatized, sulfonated, or fluorinated, allowing for tuning of key performance properties such as conductivity, hydrophilicity, permeability, morphology, thermal stability, crystallinity, and cost. The basic building block, 1,3-cyclohexadiene, is a hydrocarbon monomer that could be inexpensively produced on a commercial scale (pricing typical of other hydrocarbon monomers).

To further manipulate and optimize the properties of the PCHD-based membranes, inorganic modification will be carried out through polymerization of metal alkoxides within hydrophilic regions of the membranes via sol-gel reactions. Such modification can improve mechanical and thermal properties of the membrane and also shows great promise for addressing thermal and water management issues. Thus, these membranes are expected to meet conductivity requirements laid out in this DOE solicitation at elevated temperatures (conductivity = 0.1 S/cm at 50% relative humidity at 120ºC).

Approach

A potentially inexpensive monomer, 1,3-cyclohexadiene, can be polymerized to yield a range of novel polymers and copolymers incorporating an unsaturated six-membered ring into the polymer backbone. Mays' group is synthesizing a range of homopolymer and copolymer materials incorporating PCHD. Type 1 membranes are composed of crosslinked, sulfonated, and optionally aromatized PCHD. Type 2 membranes are block copolymers of aromatized and sulfonated PCHD with poly(vinylidene fluoride), while Type 3 membranes are sulfonated

and fluorinated statistical copolymers of PCHD and poly(α-methylstyrene).

Most of the synthesis work so far has focused on the synthesis and optimization of the Type 1 membranes. The mechanical and thermal characteristics of these materials are under investigation, and strategies for growing nanoscale metal oxide nanoparticles within the membranes (to improve proton conductivity and thermal properties) are being developed. A working hypothesis is that relaxations, i.e., long and short range polymer motions, interact with water cluster dynamics and thereby affect proton hopping along hydrogen bonded water molecules.

Results

Most of the synthesis work to date has focused on the Type 1 membranes (Figure 1). These materials require the polymerization of 1,3-cyclohexadiene, followed by crosslinking of PCHD in membrane form, and aromatization and sulfonation of the materials. Initial materials synthesized were brittle, membranes were not flat, and high sulfonation levels were hard to achieve. Through modification of the synthesis procedures, these problems have been almost entirely overcome. The synthesis focus is now on Type 2 and Type 3 membranes.

Characterization of the Type 1 membranes is underway. The results of thermo-degradative stability tests (in N_2) for Type 1 samples are in Figure 2. This figure shows the evolution of the stability of materials after each reaction modification: crosslinking $\rightarrow$ sulfonation $\rightarrow$ aromatization. Stability increased by almost 200ºC in proceeding from ~300ºC for the uncrosslinked material to ~500ºC for the final crosslinked, sulfonated and aromatized membrane. Initial degradation around ~120ºC is observed in all samples. Williamson et al. also observed the early degradation and attributed the lower temperature weight loss to depolymerization [1]. However, if this process was depolymerization, it should not stop until the entire polymer degraded because it requires lower energy once initiated. Mays et al. reported that this initial weight loss is dependent on molecular weight; the lower the molecular weight, the higher the weight loss [2]. Their thermogravimetric analysis-mass spectrometer (TGA-MS) results revealed that the main fragments during the initial degradation were around 56 and 80, which correspond to butyl groups and the monomer unit [2]. These observations support the premise that the initial weight loss below 300ºC could be probably due to the loss of chain ends and/or some repeating units.

The amount of char left at $\cong$ 600°C increased with sulfonation and aromatization (35% remaining). Overall, this material seems to be very stable up to 300°C which is far beyond temperatures in fuel cells.
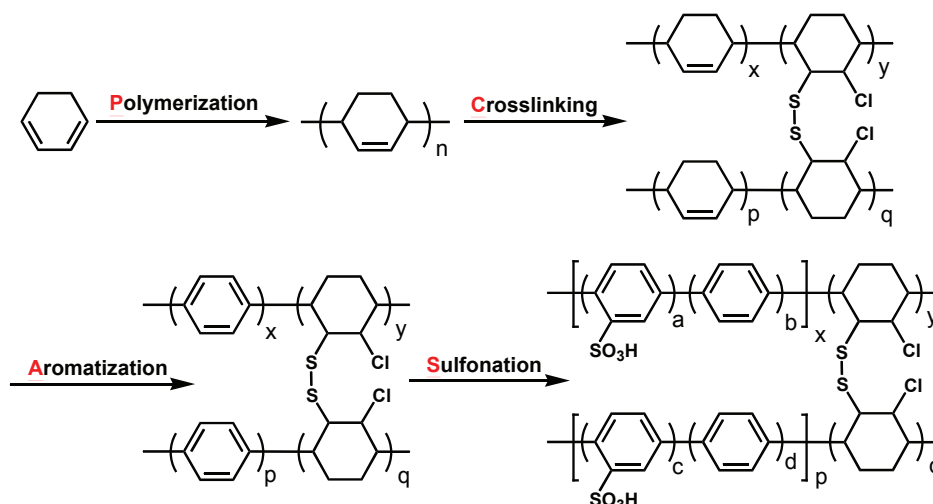
FIGURE 1. Synthesis Strategy to Type 1 Membranes

It is interesting that, while degradation of the final material might be considered a multi-stage process owing to the complexity of these chemical structures that includes SO_3H groups and cross-links as well as chemical heterogeneity along the backbone, the degradation profile after the final (aromatization) step is not multistage.

A comparison of the TGA curve of Figure 2 with that of a Nafion® 112 acid form membrane, revealed that the experimental membrane is more stable than Nafion®, which might be attributed to the bulky aromatic groups. On the other hand, there is gradual mass loss preceding catastrophic degradation at ~400°C.

Both proton conductivity (σ) and polymer relaxation data are being extracted from dielectric loss (ε") vs.
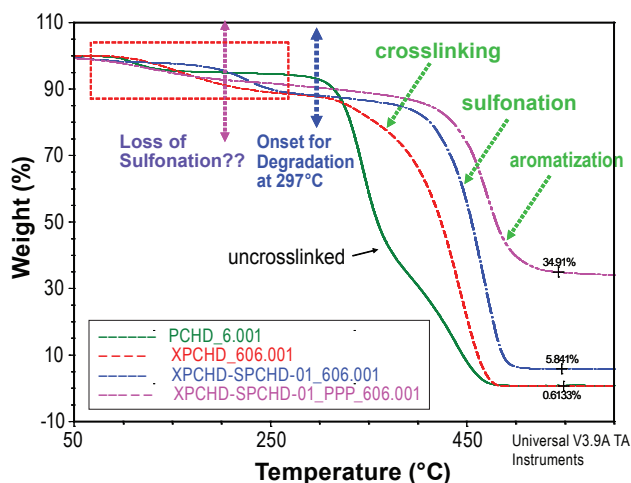

FIGURE 2. TGA Curves for Different Reaction Steps for Type 1 Membranes

frequency (f) spectra of membranes using the powerful technique of broadband dielectric spectroscopy (DS). Commonly, σ is determined in a separate experiment using a four-point probe and polymer relaxations are investigated separately using dynamic mechanical analysis. We obtain both data in a single experiment to identify coupling between the two processes.

The four-point probe method can be criticized in that it measures conductivity in the film in-plane direction rather than perpendicular to the plane. Also, the lines of the non-uniform electric field are more concentrated near the surface where the membrane water concentration is higher than in the middle. In the DS method, the uniform field is perpendicular to the plane. The DC conductivity can then be obtained by subtracting the contribution of membrane/electrode polarization at the lowest frequencies. After the DC contribution is subtracted from the total spectra, polymer relaxations can be isolated and analyzed using the Havriliak-Negami equation and distributions of relaxation time can be extracted. This analysis is being cultivated also with regard to membrane durability, particularly with regard to peroxide degradation. Shifts in the distribution of relaxation times are related to shifts in polymer membrane molecular weight distribution.

Efforts are under way to carefully control the amount of water (number of H_2O molecules/SO_3H group) in the membranes so that conductivity and relaxation behaviors can be related to hydration microstructure.

Conclusions and Future Directions

Work in Year 1 has focused on optimizing the chemistry of the Type 1 membranes. A number of promising membranes have been synthesized and are

currently being synthesized. Both Year 1 milestones were met.

- Optimization of sulfonation and aromatization conditions for Type 1 membranes.

  Characterization of Type 1 membranes:

  - Proton conductivity measurements. Key issue: need flatter, more flexible films.
  - Continue to establish dynamic mechanical, creep, stress relaxation, and nanoindentation data for undegraded samples. Key issue: need samples improved handling integrity.
  - Dielectric spectroscopic analysis of polymer chain motions as related to proton transport and degraded structures.

- Inorganic (mainly silicate) modification of Type 1 membranes to elevate the maximum temperature of water retention for high temperature fuel cell operation and investigate the possibility of having $^{\bullet}$OH (from peroxide decomposition) scavenger functionality on nanoparticle surfaces.

- Degrade Type 1 membrane materials via Fenton's reagent and characterize samples using the above methods.

- Synthesis of additional Type 2 and Type 3 materials.
- Aromatization and sulfonation of multi-block copolymer membranes.
- The two best Type 1 membranes will be submitted for conductivity testing by the University of Central Florida by the end of 2007.

FY 2007 Publications and Presentations

1. "New Polymeric Materials Derived from 1,3-Cyclohexadiene", J. Mays, invited lecture at the Symposium on Functional Polymer Based Materials, Jena, Germany, April 3–4, 2007.

2. "Poly(cyclohexadiene)–Based Polymer Electrolyte Membranes for Fuel Cell Applications", J. Mays, S. Deng, M. Hassan, and K. Mauritz, presented at the 2007 DOE Hydrogen Program Annual Merit Review, Arlington, VA, May 14–17, 2007.

References

1. Williamson, D. T.; Mather, B. D.; Long, T. E. J. Polym. Sci., Part A:. Polym. Chem. 2003, 41, 84.

2. Hong, K.; Huang, T.; Britt, P. F.; Pyda, M; Mays, J. W. Polymer Preprints 2005, 46(1), 843.