V.D.4 Poly(cyclohexadiene)-Base Polymer Electrolyte Membranes for Fuel Cell Applications

Jimmy W. Mays
University of Tennessee
Department of Chemistry
Knoxville, TN 37996
Phone: (865) 974-0747; Fax: (865) 974-9304
E-mail: jimmymays@utk.edu

DOE Technology Development Manager:
Jason Marcinkoski
Phone: (202) 586-7466; Fax: (202) 586-9811
E-mail: Jason.Marcinkoski@ee.doe.gov

DOE Project Officer: Gregory Kleen
Phone: (303) 275-4875; Fax: (303) 275-4788
E-mail: Greg.Kleen@go.doe.gov

Technical Advisor: Walt Podolski
Phone: (630) 252-7558; Fax: (630) 972-4430
E-mail: podolski@cmt.anl.gov

Contract Number: DE-FG36-06GO16037

Subcontractor:
Professor Kenneth A. Mauritz,
University of Southern Mississippi (USM),
Hattiesburg, MS

Start Date: April 1, 2006
Project End Date: September 30, 2009

Objectives

- Design, synthesize and characterize new non-Nafion® polymer electrolyte membrane (PEM) materials that conduct protons at low (25-50%) relative humidity (RH) 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.
- Characterize thermal stability of these materials.
- Identify molecular relaxations that might impact mechanical properties, temperature ceiling for fuel cell operation, and water and proton transport and durability using dynamic mechanical and dielectric relaxation techniques.
- Inorganic, membrane in situ sol-gel modifications of membranes to improve high temperature water retention and mechanical durability.

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

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% RH at 120°C), as well as achieving low cost and meet the following DOE 2010 performance criteria:

- Cost: $25/kW$_e$
- Durability with cycling: 5,000 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

- Thinner crosslinked (5 ~ 10 mol%) and sulfonated (10 ~ 45 mol%) PCHD fuel cell membranes were synthesized and characterized with elemental analysis, dynamic mechanical analysis (DMA), thermogravimetric analysis (TGA), and proton conductivity. With thinner membranes, proton conductivity has reached as high as 156 mS/cm at room temperature and 100% RH, which is much higher than that of Nafion® NRE-212 (~70 mS/cm).
- Three diblock copolymers of PCHD and PEG (polyethylene glycol) with different weight percent PEG (5.0%, 10%, 9.5%) were synthesized and characterized.
- New types of fuel cell membranes were prepared by sequential crosslinking and sulfonation of polymer blends or block copolymers of PCHD and PEG.
- Addition of PEG made a big jump in proton conductivity at high RH (322 mS/cm *vs.* 156 mS/cm)

and also enhanced proton conductivities at low RH. Copolymerization causes another considerable jump in conductivity so that membranes have very impressively high conductivity (410 mS/cm) at 100% RH and higher conductivity than that of Nafion® NRE-212 even at RH as low as 20%.

- The proton conductivity of the crosslinked and sulfonated PCHD-PEG block copolymer membrane XPCHD_1009_SPCHD_102 measured at BekkTech was 82.5 mS/cm at 80.3% RH at 30ºC. Therefore, the Year 2 milestone of demonstrating conductivity of 70 S/cm at 80% RH at 30ºC has been met. However, the final conductivity requirements specified by DOE (conductivity = 0.1 S/cm at 50% RH at 120°C) has not been met yet and is our goal of on-going effort.

- The resulting membranes are thermal stable up to 200°C and resistant to chemical degradation. Moreover, they are also very flexible and have mechanical integrity.

- The cost of membranes can be as low as $10/m^2, about 1.5% that of Nafion® (about $800/m^2), making these membranes very attractive and commercially feasible for high-temperature fuel cell applications.

- Growth of inorganic nanoparticles within the hydrophilic domains of membranes is underway.

✧   ✧   ✧   ✧   ✧

Introduction

The goal of this project is to create and develop low-cost 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% RH at 120°C).

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 sulfonated PCHD with poly(vinylidene fluoride), while Type 3 membranes are sulfonated and fluorinated statistical copolymers of PCHD and poly(α-methylstyrene). Since Type 2 and 3 membranes involve fluorination, it would be fairly difficult to obtain membranes of low-cost. Therefore, most of the synthesis work so far has focused on the synthesis and optimization of the Type 1 membranes. In order to reach high proton conductivity, especially at low RH, very high degree of sulfonation should be and could be reached. In general, the higher the degree of sulfonation is, the higher the proton conductivity is. However, "over-sulfonated" membranes always had too weak mechanical strength. A delicate balance between degree of sulfonation and good mechanical strength much be obtained. Therefore, it is the maintaining of good mechanical strength that limits higher extent of sulfonation. This dilemma forced us to use PEG as an additive/plasticizer or synthesize a block polymer of PCHD and PEG to increase proton conductivity instead. It turns out that the addition of PEG did make a big jump in conductivity.

The mechanical and thermal properties of these materials are characterized by DMA, TGA, and strategies for growing nanoscale metal oxide nanoparticles within the membranes (to improve proton conductivity, mechanical durability and high temperature fuel cell performance by water retention) 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. Molecular motions of membranes are characterized by broadband dielectric spectroscopy and correlated to proton conductivity at different temperatures. Membrane electrode assemblies (MEAs) of the membranes are prepared and checked for their performance and durability via open circuit voltage (OCV) test. Membranes degraded chemically via Fenton's reagent as well as OCV degraded ones are analyzed with broadband dielectric spectroscopy to investigate their degradation mechanisms.

Results

Most of the synthesis work to date has focused on the Type 1 membranes. These materials require the polymerization of 1,3-cyclohexadiene, followed by crosslinking of PCHD in membrane form and sulfonation of the materials. Although sulfonated crosslinked PCHD membranes such as XPCHD_1001_ SPCHD_105 can obtain proton conductivity as high as 130 mS/cm at 100% RH (see our previous annual report), higher than Nafion® NRE-212 (68 mS/cm) under the same conduction, their conductivities drop so sharply with decreased humidity that the conductivities are lower than that of Nafion® NRE-212 at RH lower than 80%. Therefore, it is very critical to increase proton conductivity of our fuel cell membranes at low RH in order to meet DOE final conductivity requirement. Three different yet complementary strategies toward the conductivity goal have been taken:

- Creation of a thinner cross-linked PCHD membrane by using half amount of PCHD, followed by sulfonation.
- Creation of a cross-linked membrane from a polymer blend of PCHD and PEG, followed by sulfonation.
- Synthesis of a block polymer of PCHD and PEG, followed by sequential crosslinking and sulfonation (see Figure 1).

Characterization of Membranes

Optimization of Proton Conductivity of Crosslinked PCHD Membranes

Proton Conductivity. New membrane batches were prepared by Mays and characterized by Mauritz for conductivity, thermal and mechanical properties. Based on previous conductivity measurements, (DOE reports starting September 2007) Mays has been optimizing macromolecular chemistry for high conductivity and better sample mechanical integrity.

Proton conductivities were first measured at room temperature after soaking membranes in dionized water and then mounting them in a four point probe conductivity cell immersed in water. Before, electrical impedance measurements were performed in the frequency range 0.5 kHz to 1 MHz and samples were soaked in water for 24 h. The Z' intercept from the semicircle in Nyquist plots was taken as membrane resistance to calculate conductivity (σ).

Conductivities in Table 1 for new batch samples are higher than that of Nafion® under the same test conditions ($\cong 0.07$ S/cm). Some membranes have σ values up to 0.41 S/cm under these conditions. Addition of PEG is responsible for the large conductivity increase. Copolymerization gives higher values than blending PCHD with PEG and causes another considerable jump in conductivity.
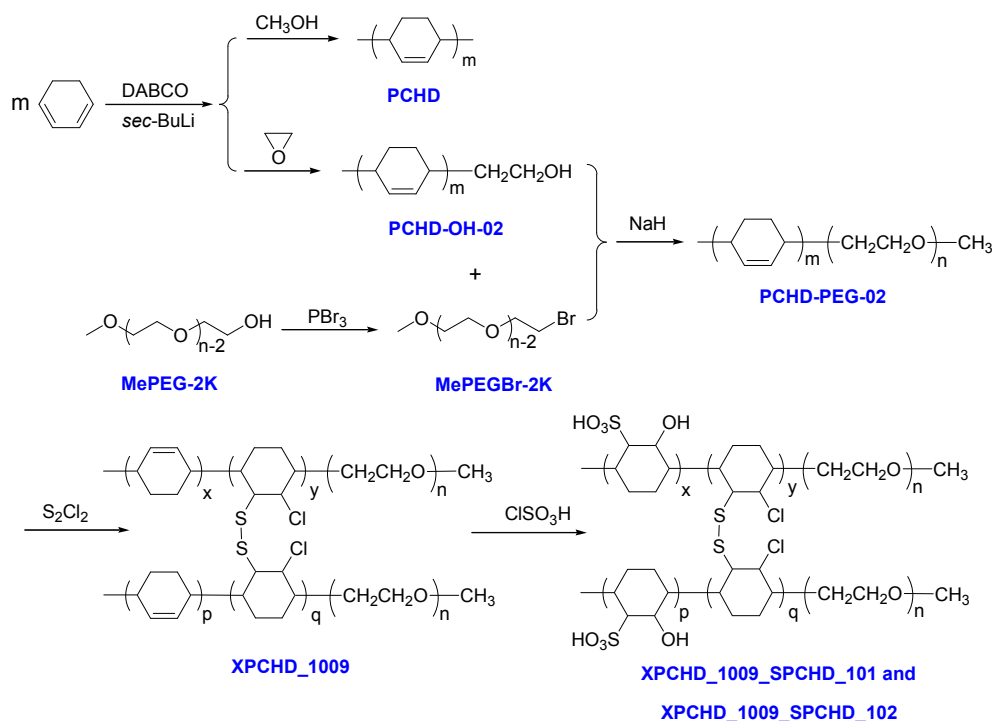

FIGURE 1. Synthetic Strategy to Type 1 Membranes

TABLE 1. Effect of blending vs. copolymerization of PEG (M_n = 2,000 g/mol) with PCHD on the conductivity of different membranes at room temperature and soaked in dionized water before measurements.

| Sample	Conductivity (S/cm)
XPCHD_902_SPCHD_108 (No PEG)	0.135
XPCHD_1005_SPCHD_104 (No PEG)	0.144
XPCHD_1005_SPCHD_105 (No PEG)	0.156
XPCHD_1007_SPCHD_101 [PEG(9.1 wt%) blended with PCHD]	0.136
XPCHD_1007_SPCHD_102 [PEG(9.1 wt%) blended with PCHD]	0.207
XPCHD_1007_SPCHD_103 [PEG(9.1 wt%) blended with PCHD]	0.256
XPCHD_1008_SPCHD_101 [PEG(16.7 wt%) blended with PCHD]	0.135
XPCHD_1008_SPCHD_102 [PEG(16.7 wt%) blended with PCHD]	0.322
XPCHD_1009_SPCHD_101 [PEG(5.3 wt%) copolymerized with PCHD]	0.410
XPCHD_1009_SPCHD_102 [PEG(5.3 wt%) copolymerized with PCHD]	0.380

Six membranes were sent to BekkTech for measurements of proton conductivity at various RHs (20 to 100%) and different temperatures (30, 80, and 120ºC) and the results are in Table 2. Without PEG, the proton conductivity could be slightly higher than Nafion® NRE-212 at high RH but much lower at low RH. For example, XPCHD_902_SPCHD_105 has σ = 125.77 mS/cm at 80% RH, slightly higher than that of NRE-212 (120.75 mS/cm). However, it has only half the conductivity compared with NRE-212 (18.13 vs. 36.96 mS/cm). By blending with PEG, not only do the membranes have higher proton conductivity at 80% RH,

but also have almost as high conductivity as NRE-212, for example XPCHD_1008_SPCHD_102. Membranes made from a block copolymer of PCHD and PEG had not only higher proton conductivity at 80% RH but also higher conductivity at 50% RH than Nafion® NRE-212. XPCHD_1009_SPCHD_102 had σ = 245.10 mS/cm at 80% RH (> 100% increase compared with NRE-212) and 57.6 mS/cm at 50% RH (56% increase compared with NRE-212). As shown in Figure 2a, XPCHD_1009_SPCHD_102 showed higher conductivity at all RH ranging from 100 to 20% than NRE-212 although it showed a slightly sharper decrease of conductivity vs. RH. The higher conductivity than NRE-212 at lower (50%) RH of our membranes is significant in terms of developing inexpensive non-Nafion® high temperature low humidity operable membranes.

Conductivity measurements at 120ºC and different RH for some membranes were also conducted at USM using the same protocol and instrument developed
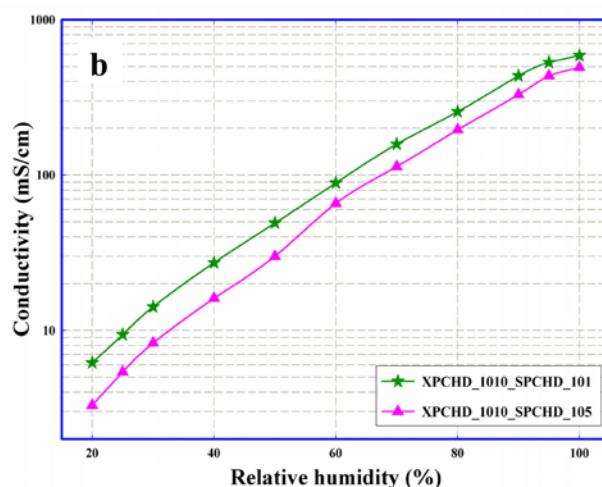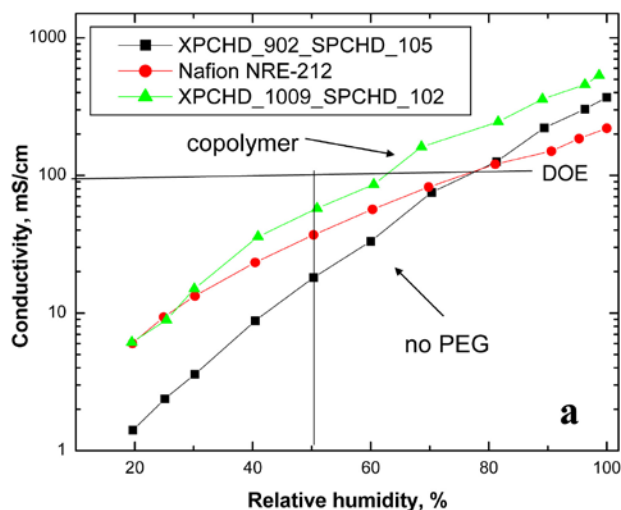

FIGURE 2. Proton conductivity at 120ºC vs. RH for different membranes measured at BekkTech (a) and at USM (b).

TABLE 2. Effect of blending vs. copolymerization of PEG (M_n = 2,000 g/mol) with PCHD on the conductivity at 120°C at lower (80% and 50%) RHs.

Sample	Conductivity (mS/cm) 80% RH	Conductivity (mS/cm) 50% RH
XPCHD_1003_SPCHD_102 (No PEG)	28.93	2.33
XPCHD_1001_SPCHD_105 (No PEG)	108.50	17.80
XPCHD_902_SPCHD_105 (No PEG)	125.77	18.13
Nafion® NRE-212	120.75	36.96
XPCHD_1007_SPCHD_103 [PEG(9.1 wt%) blended with PCHD]	149.00	24.10
XPCHD_1008_SPCHD_102 [PEG(16.7 wt%) blended with PCHD]	182.10	33.20
XPCHD_1009_SPCHD_102 [PEG(5.3 wt%) copolymerized with PCHD]	245.10	57.60

by BekkTech. Figure 2b showed $\sigma = 50$ mS/cm for XPCHD_1010_SPCHD_101, which was prepared by copolymerizing PCHD with PEG, confirming the conclusion that PEG copolymerization improves conductivity at 120°C and low RH. New samples have been prepared to achieve the DOE target ($\sigma > 0.1$ S/cm at 50% RH at 120°C) conductivity at 120°C but we have not yet measured their conductivities.

Water Uptake. Membrane water uptakes at different temperatures vs. RH were determined using an accurate vapor sorption analyzer (Q5000-TA Instruments). Figure 3 shows vapor pressure isotherms of PCHD (copolymer with PEG) based membranes measured at 25 and 80°C vs. a Nafion®112 membrane at 80°C.

The equilibrium uptakes are expressed in terms of average number of water molecules per sulfonic acid group. PCHD membranes absorb considerably more water than Nafion® at each RH at 80°C. The difference is even pronounced at low RH and 80°C which is significant for fuel cell applications. This enhancement is attributed to the influence of PEG in this specific sample and accounts for the higher conductivity although cross-linking is most likely another important factor. It is also interesting to see that the PCHD membrane uptake did not change with increasing temperature from 25 to 80°C.

Thermal Stability. TGA studies were performed on these materials to determine their thermal degradative stability in N_2 atmosphere (no thermo-oxidative effects present). While the temperatures reached in these tests are above fuel cell operating temperature, the degradation temperatures reflect
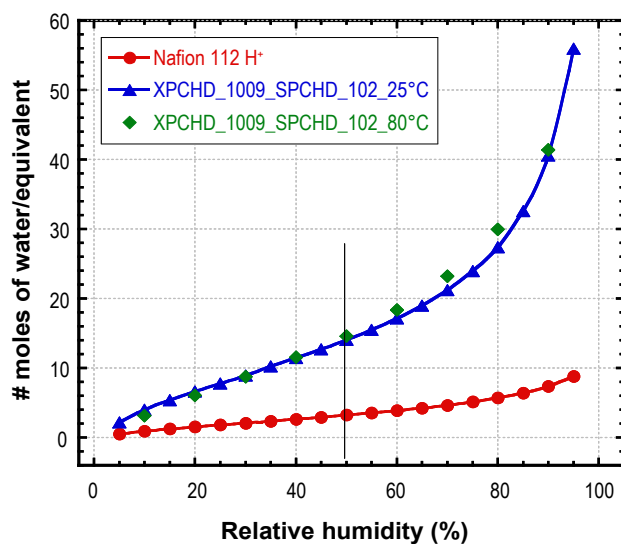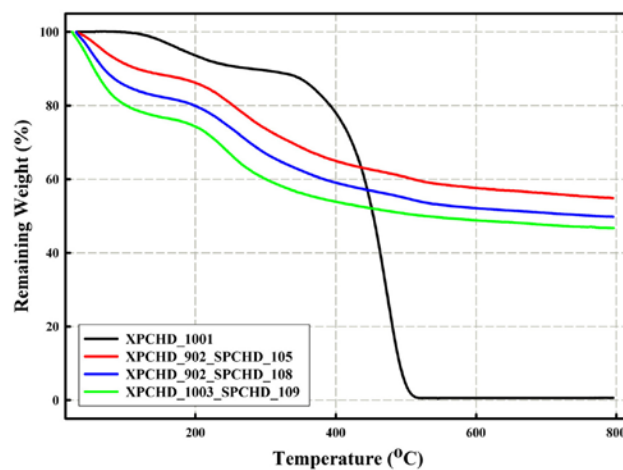
material cohesion that is related to membrane durability. The information reported here is part of an effort to understand the relationship between conductivity and thermodegradative behavior.
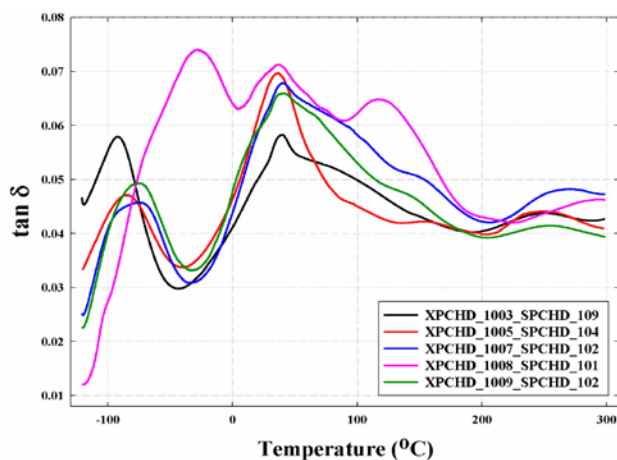
Figure 4 shows mass loss (in N_2 atmosphere) vs. temperature up to 800°C for some representative membranes. Assignment of thermal degradation mass loss events, based on related work reported in the literature [1,2], is as follows: for all samples, except unsulfonated XPCHD_1001, at ≈95°C, there is mass loss of ~5 to 20%. This initial loss is believed to be due to polymer chain depolymerization which proceeds until more thermally stable units on the polymer backbone are reached. The remaining backbone remains thermally stable until 200°C after which more chain depolymerization takes place. Between 200 and 400°C, membrane thermal stability depends on the strength of interactions among SO_3H groups and restrictive crosslinks. Then, the backbone shows more resistance to thermal degradation due to the formation of carbonized compounds, formed from the dehydrogenation of PCHD, which can also be regarded as graphitic compounds formed by the carbonization of phenyl units. This is the reason why most of the samples show a remaining mass of 50 to 60% at the high temperature of 800°C.

Dynamic Mechanical Analysis. Long and short range macromolecular motions in a new membrane batch were identified using DMA and the loss tangent (tan δ) vs. temperature (T) curves are seen in Figure 5. Many distinct peaks with different degrees of broadening can be observed for both membranes. The breadth of a peak reflects microstructural heterogeneity.

There is a small peak between -120 and -30°C tentatively assigned to local motions of –CH-S-S-CH- crosslinks plus motions of –CH-Cl and –CH-OH side chains because the shortest range motions, which are

FIGURE 3. Vapor pressure isotherm at 25 and 80°C for PCHD (copolymer with PEG) based membrane vs. Nafion®112 membrane measured at 80°C.

FIGURE 4. TGA Thermograms of Some Representative Membranes

FIGURE 5. Tan δ vs. T curves for new membranes compared to an earlier-synthesized membrane.

FIGURE 6. Storage modulus (E′) vs. temperature for membranes containing PEG vs. an earlier-synthesized membrane without PEG.

active at low temperatures, would seem to be possible in these groupings. A very broad peak exists between about -30 and 200°C which is thought to be the glass transition (T_g). This is active at fuel cell operating temperatures but would most likely shift to lower temperature with sorbed water. Based on assignments we reported earlier, crosslinked PCHD films showed T_g ~95°C. Finally, there is a small peak above 200°C which is suggested, based on studies of other ionomers, to be due to disruption of $-SO_3H$ group aggregates.

The glass transition peak is somewhat broad and there is more than one relaxation active. Perhaps hydrogen bonding interactions among the $-SO_3H$ groups which would form physical cross-links might be responsible for broadening the glass transition peak owing to microstructural/chemical heterogeneity. It is not clear, at this point, why the low temperature peak for the XPCHD_1008_SPCHD_101 sample shifts to higher temperature compared to other samples. The glass transition peak for XPCHD_1008_SPCHD_101 is divided into two peaks which is not understood. In comparing samples with (either blending or copolymerization) and without PEG; no change in the three peak positions is noticed although one might expect some plasticization due to the presence of PEG.

The corresponding change in storage modulus (E′) with increasing temperature is seen in Figure 6. The initial drop in E′ with increasing temperature resembles a glass transition, although it must be said that the drop is less than an order of magnitude. All membranes showed an *increase* in E′ beyond around 0°C, which must be explained because this indicates a material stiffening.

This behavior is hypothesized to involve SO_3H group associations which act as physical crosslinks. An increase in thermal mobility of these hydrogen bonding groups above T_g might impart sufficient mobility for
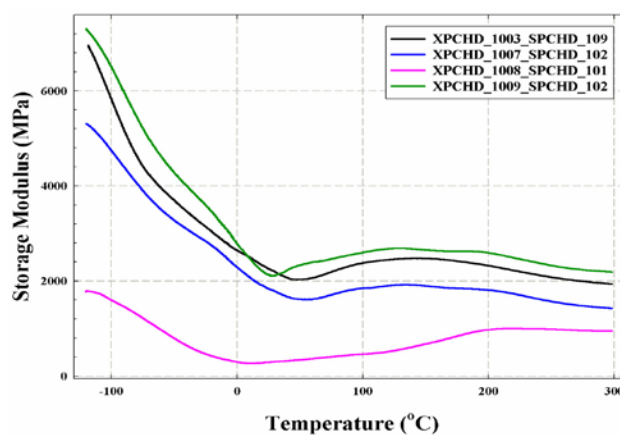
them to migrate to form larger energetically-favorable associations which increases E′ for the membranes with higher conductivities. The final drop in E′ (around 200°C) can be interpreted in terms of the subsequent dissociation of these acid group aggregates as also reflected by the transition peaks in Figure 5. This is of special interest for fuel cell membranes at a temperature around 100°C as mechanical stability is desired in that temperature range.

Conclusions and Future Directions

Work in Year 3 has focused on optimizing the chemistry of membranes based on PCHD homopolymers, polymer blends and block copolymers of PCHD and PEG. A range of membranes with various degrees of crosslinking and sulfonation have been synthesized and characterized for their conductivity, thermal and mechanical stability.

Blending and copolymerization of PEG with PCHD before crosslinking causes a big jump in conductivity most likely through plasticization. This increase was observed at low RH and 120°C in comparison with Nafion® membranes measured at the same conditions. Also, PCHD membranes retain more water than Nafion® at low RH and 80°C. The new batch of membranes have higher proton conductivity than that of Nafion® samples not only at high RH (≥80%) but also at low RH (50%). The fact that conductivity obtained for membranes made from a block copolymer of PCHD and PEG was higher than that of Nafion® samples at 50% RH and at 120°C is very encouraging and provides useful information in directing future synthetic efforts.

The Year 2 milestone of demonstrating conductivity of 0.07 S/cm at 80% RH at 30°C has been met. However, further effort is needed to meet the final proton conductivity requirements specified by DOE (conductivity = 0.1 S/cm at 50% RH at 120°C).

We have successfully characterized the thermal stability of these membranes as related to material cohesion that is important for high temperature fuel cell operation. Also, we have determined dynamic mechanical studies of thermal transitions that can be implicated with gas, water and proton transport as well as establish the high temperature stability ceiling of these materials. Proton conductivity tests were performed to rank the feasibility of the various membrane compositions.

Future directions include:

- Further optimize crosslinking and sulfonation conditions for Type 1 membranes to obtain both high proton conductivity and good mechanic strength.
- Change the composition of polymer blends and block copolymers to obtain ideal membrane morphology for higher proton conductivity at lower RH.
- Improve chemical stability by partial aromatization and inorganic sol-gel modification.
- Perform broadband dielectric spectroscopic studies of membranes to probe the nature molecular motions that are active at fuel cell-relevant temperatures and well as the coupling of these motions to water and proton transport.
- Determine the viscoelastic properties of membranes, such as creep, stress relaxation, and cyclic loading with a view toward mechanical durability.
- Once a higher degree of dimensional stability is imparted to these materials, we will render them more hydrophobic to have higher temperature water retention by growing, in situ, by sol-gel processes, inorganic oxide nanostructures. This will additionally improve the mechanical durability.
- Prepare MEAs and test their performance as well as exposing them to OCV test to check their durability and life time. Chemical degradation of type 1 membranes via Fenton's reagent. And then, characterization of degraded samples via both chemical and OCV procedures using broadband dielectric spectroscopy.

Special Recognitions & Awards/Patents Issued

1. "Copolymers of Fluorinated Polydienes and Sulfonated Polystyrene", CIP of USP 11/906,118 (patent pending).

2. We were recently awarded $75,000 by the Tennessee Technology Development Corporation to continue development and commercialization of these membranes for a variety of applications.

FY 2009 Publications/Presentations

1. "Novel Ion-Containing Polymers Via Post-Polymerization Chemistry: Synthesis, Morphology, and Mineralization Studies", J.W. Mays, invited lecture at the 7th Hellenic Polymer Conference, September 28 – October 1, 2008, Ioannina, Greece.

2. "Sulfonated Fuel Cell Membrane", J. Mays, S. Deng, K. Mauritz, M. Hassan, presented at the Tennessee Innovation Conference, Nashville, TN, November 20–21, 2008.

3. "Novel Charged Polymers: From Biomineralization to Fuel Cell Membranes", J.W. Mays, invited lecture at the University of Minnesota, Department of Chemical Engineering and Materials Science, December 2, 2008.

4. "Poly(cyclohexadiene)-Based Polymer Electrolyte Membranes for Fuel Cell Applications", J. Mays, S. Deng, M. Hassan, and K. Mauritz, presented at US Car, Detroit, MI, February 11, 2009.

5. "Poly(cyclohexadiene)-Based Polymer Electrolyte Membranes for Fuel Cell Applications", J. Mays, S. Deng, M. Hassan, and K. Mauritz, presented to Department of Energy, Washington, D.C., February 26, 2009.

6. "Novel Charged Polymers: From Biomineralization to Fuel Cell Membranes", J.W. Mays, invited Bayer Lectures on Polymers, Cornell University, Ithaca, New York, April 8, 2009.

7. "Poly(cyclohexadiene)-Based Polymer Electrolyte Membranes for Fuel Cell Applications", J. Mays, S. Deng, M. Hassan, and K. Mauritz, presented at the DOE Annual Hydrogen Review, Arlington, VA, May 18–21, 2009.