Final Technical Report

Project Title: "Poly(cyclohexadiene)-Based Polymer Electrolyte Membranes for Fuel Cell Applications"

Project Period: April 1, 2006 to September 30, 2009
Date of Report: March 7, 2011

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Award Number: DE-FG36-06GO16037

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Executive Summary:

The goal of this research project was to create and develop fuel cell membranes having high proton conductivity at high temperatures and high chemical and mechanical durability. Poly(1,3-cyclohexadiene) (PCHD) is of interest as an alternative polymer electrolyte membrane (PEM) material due to its ring-like structure which is expected to impart superior mechanical and thermal properties, and due to the fact that PCHD can readily be incorporated into a range of homopolymer and copolymer structures. PCHD can be aromatized, sulfonated, or fluorinated, allowing for tuning of key performance structure and properties. These factors include good proton transport, hydrophilicity, permeability (including fuel gas impermeability), good mechanical properties, 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). Optimal material properties will result in novel low cost PEM membranes engineered for high conductivity at elevated temperatures and low relative humidities, as well as good performance and durability.

Comparison of Accomplishments with Goals and Objectives:

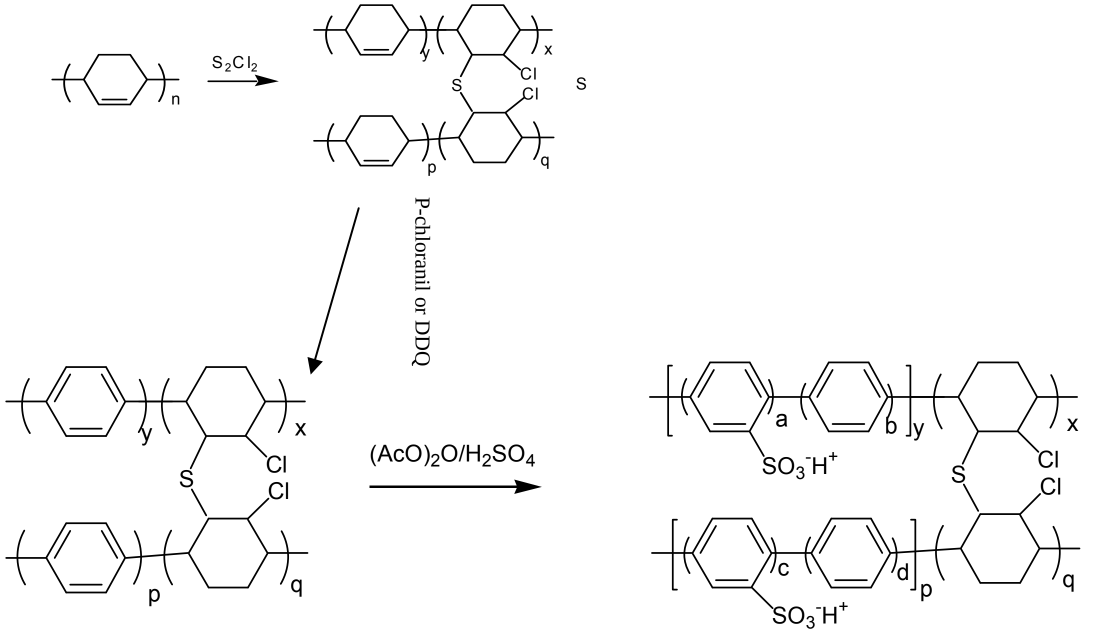
The primary objectives of this project were:

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

These two objectives have been achieved. Sulfonated and crosslinked PCHD homopolymer membranes exhibit proton conductivities similar to Nafion in the mid-RH range, are superior to Nafion at higher RH, but are poorer than Nafion at RH<50%. Thus to further improve proton conductivity, particularly at low RH, poly(ethylene glycol) (PEG) was incorporated into the membrane by blending and by copolymerization. Conductivity measurements at 120 °C over RH ranging from 20 to 100% using the BekkTech protocol showed much improved proton conductivities. Conductivities for the best of these new membranes exceed the DOE Year 3 milestone of 100 mS/cm at 50% RH at 120 °C. Further optimization of these very promising low cost membranes could be pursued in the future.

Summary of Project Activities:

Three types of non-Nafion membrane materials were proposed. Our initial focus was on sulfonated, crosslinked, and aromatized PCHD, synthesized as shown below.



The idea was to take advantage of the fact that aromatized 1,4-PCHD is poly(para-phenylene) (PPP), one of the most chemically and thermally stable organic polymers known. Our hypothesis was that sulfonation would create proton conducting channels, while maintaining good thermal and oxidative stability. Crosslinking would prevent the sulfonated PPP from dissolving and lock in the membrane morphology. Several of these materials were synthesized and characterized, and it was determined that the materials suffered from extreme brittleness and low sulfonation degrees.

Some work early on was also devoted to synthesis of poly(vinylidene fluoride-b-1,3-cyclohexadiene) [P(VDF-b-CHD)) multi-block copolymers by condensation polymerization of α,ω-difunctionalized PVDF telechelics and PCHD telechelics. Again the idea here was to aromatize the PCHD blocks and then sulfonate the resulting PPP blocks. The synthesis of these materials proved difficult (it was not possible to synthesize PCHD telechelics having the necessary functionality of 2). We also attempted to make random copolymers of CHD and α-methylstyrene, where the former could be fluorinated and the latter sulfonated. Differences in reactivity ratios of these two monomers made it very difficult to obtain the desired ranfdom copolymers. While these two classes of materials were being synthesized and evaluated, we also decided to evaluate membranes made by simply crosslinking and then sulfonating PCHD. These latter materials showed considerable promise. They were flexible and easy to handle and had proton conductivities similar to that of Nafion in the medium RH range (see Figure 1 where the USM sample is sulfonated crosslinked PCHD and NRE is Nafion). We thus abandoned work on other materials to focus on these.

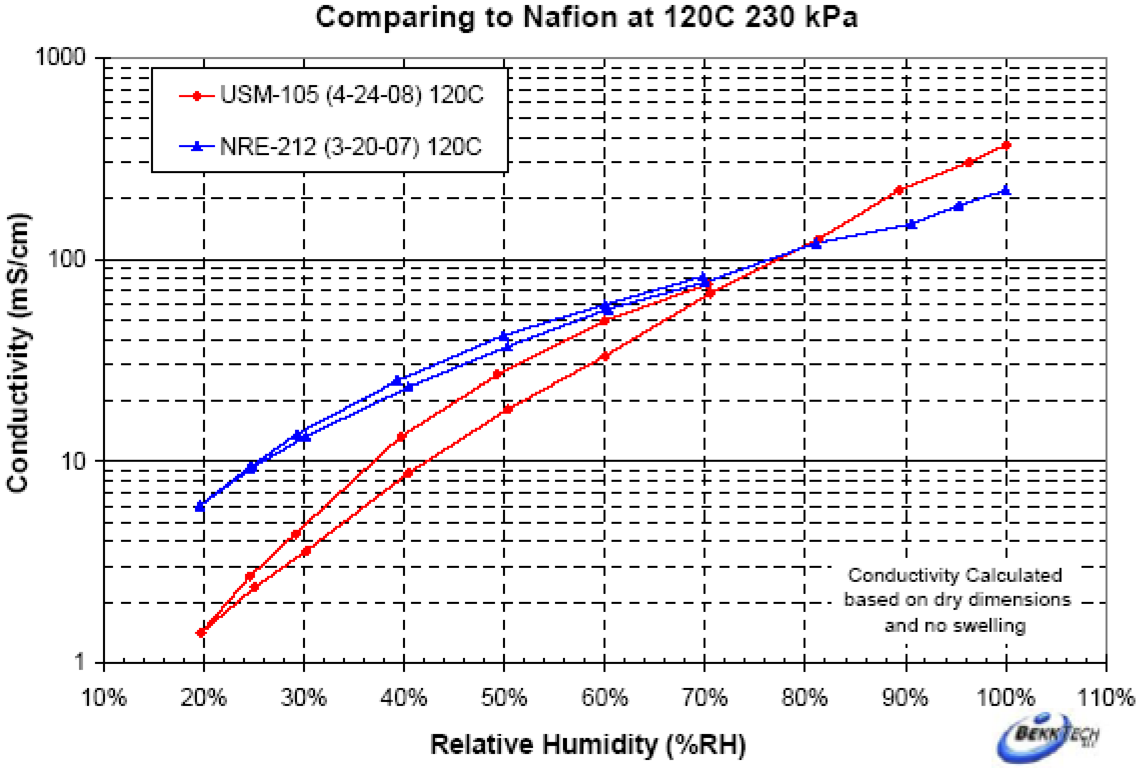


Figure 1. Proton conductivity vs relative humidity for Nafion and PCHD-based mmembranes.

A range of membranes with various degrees of crosslinking and sulfonation were synthesized and characterized for their conductivity, thermal and mechanical stability. Conductivities of some membranes were in fact much higher than that of Nafion measured at the same experimental conditions (100% relative humidity and room temperature). The Year 2 milestone of demonstrating conductivity of 0.07 S/cm at 80% RH at 120ºC was met. However, further effort was needed to meet the Year 3 proton conductivity requirements specified by DOE (conductivity = 0.1 S/cm at 50% relative humidity at 120 °C).

An important achievement was the synthesis and film formation of samples of very good mechanical integrity. This factor accelerated all of our physical testing activities. PCHD-based materials with higher degrees of sulfonation were characterized for proton conductivity, thermal-degradative stability and temperature transitions in relation to fuel cell operating temperatures, using dynamic mechanical analysis. There is a correlation between conductivity and thermal degradation which suggests that there is a common microstructural factor involved in both properties, most likely acid group aggregation that provides good proton hopping sites as well as material cohesion. This type of membrane has optimum conductivity as well as thermo-mechanical stability and mechanical integrity. The fact that conductivities obtained for new batch of membranes were higher than Nafion® samples, measured at the same experimental conditions, is very encouraging.

We successfully characterized the thermal stability of these membranes as related to material cohesion that is important for high temperature fuel cell operation. The membranes showed a small (10%) weight loss around 100 °C, probably loss of water, and were then thermally stable to 400 °C. Also, we determined dynamic mechanical studies of thermal transitions that can be correlated 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. Optimal materials had 5-10% crosslinking and around 40-45% sulfonation.

Although the crosslinked and sulfonated membranes described above have higher proton conductivity than Nafion® NRE-212 at relative humidity higher than 80% at 120 ºC, they have lower conductivity at relative humidity lower than 80% as their proton conductivity drops more sharply than Nafion NRE-212 as relative humidity decreases. Therefore, it is critical to increase proton conductivity of our novel fuel cell membranes at low relative humidity in order to meet DOE conductivity requirements. Two strategies toward the conductivity goal were explored:

1. Creation of a cross-linked membrane from a polymer blend of PCHD and poly(ethylene glycol) (PEG), followed by sulfonation.
2. Synthesis of a block polymer of PCHD and PEG, followed by sequential crosslinking and sulfonation

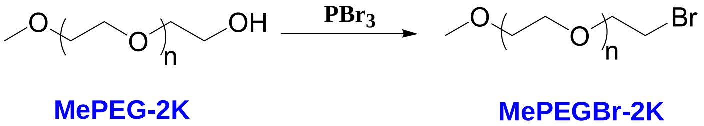
Ethylene oxide based materials are known to conduct Li^+ through segmental motions of the ethylene oxide units.[1] The Grotthus mechanism of H^+ conductivity is similar to Li^+ conductivity in these materials that rely on ethylene oxide segmental motions and the rate of polymer reorganization. As Ritchie and his coworker's study[2] suggests that PEG might increase the proton conductivity at lower humidity. Two parallel strategies of using a polymer blend and a block copolymer of PCHD and PEG were explored in order to enhance proton conductivity at lower humidity.

The fuel cell membranes made from polymer blends of PCHD and PEG exhibit a large jump in proton conductivity at room temperature and 100% relative humidity (0.322 S/cm for membrane XPCHD_1008_SPCHD_102 as compared with 0.138 S/cm for membrane XPCHD_1003_SPCHD_109). Even more impressively, the membrane XPCHD_1009_SPCHD_101 made from a block copolymer of PCHD and PEG has reached as high as 0.41 S/cm in proton conductivity. Moreover, the proton conductivity at lower relative humidity (50%) and at 120 ºC has been tripled (18.13 mS/cm for

XPCHD_0902_SPCHD_105 as compared with 57.6 mS/cm for membrane XPCHD_1009_SPCHD_102) and showed 56% increase when compared with that of Nafion® NRE-212 (36.96 mS/cm). This big jump of proton conductivity at lower relative humidity is significant and makes these material very promising in terms of meeting DOE Year 3 Milestone although the final conductivity requirement specified by DOE (conductivity = 0.1 S/cm at 50% relative humidity at 120 °C) has not yet been achieved with these materials.

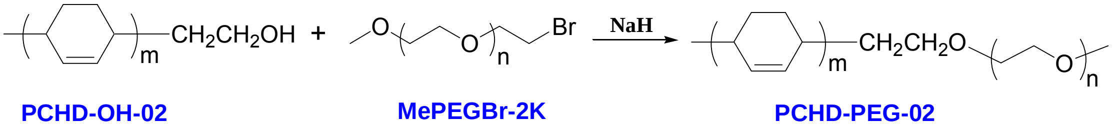
Preparation of PCHD/PEO Membranes

(1). Bromination of PEG (Mn: 2,000): MePEGBr-2K



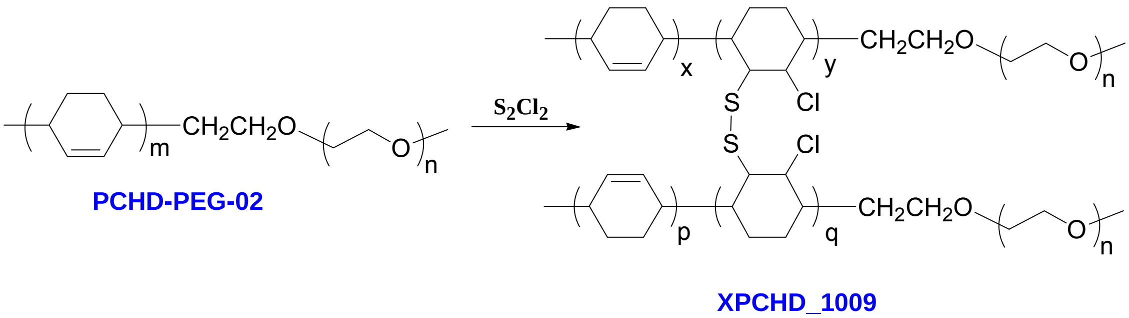
Under argon, about 2.0 g of PBr_3 was added dropwise into a solution of 5.0 g of poly(ethylene glycol) methyl ether $CH_3(OCH_2CH_2)_nOH$ (M_n: 2,000; Aldrich catalog #: 20,250-9) in 1,2-dichloroethane (~ 100 mL). The mixture was stirred overnight at r.t., poured onto water, and extracted with CH_2Cl_2. The extract was dried over $MgSO_4$ overnight. The drying agent was filtered off. The filtrate was concentrated and the residue was dried under vacuum.

(2). Synthesis of A Block Copolymer of PCHD and PEG: PCHD-PEG-02



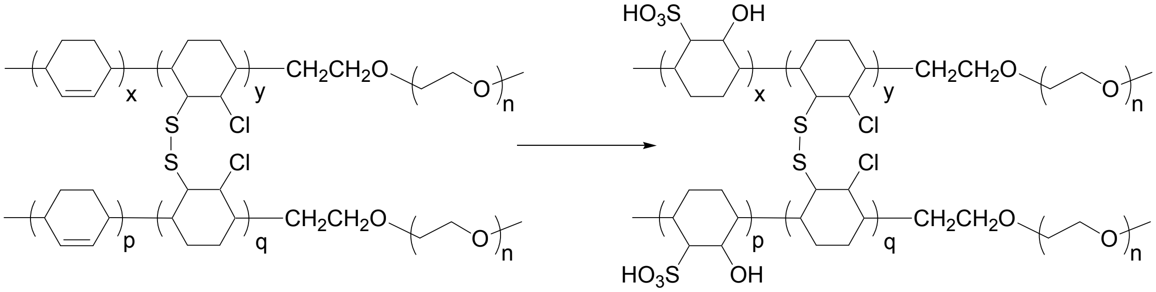
Under argon, to a solution of PCHD-OH-02 (M_n: 35.6 Kg/mol, 2.0 g) in THF was added 200 mg of NaH (60% dispersion in mineral oil) and then 0.2 g of MePEGBr-2K. The mixture was stirred overnight at room temperature and poured onto water. The polymer was collected by filtration and dried under vacuum.

(3). Membrane Casting: XPCHD_1009



To a solution of PCHD-PEG-02 (0.50 g) in toluene (10.0 mL), 0.10 g of S_2Cl_2 was added dropwise. The mixture was stirred at room temperature for about 1 hour, divided evenly and poured into 2 Teflon dishes of 100 mm in diameter. The solvent was evaporated off overnight and the membranes were peeled off with a spatula. Membranes were washed with hexane twice and dried between desiccator plates under vacuum. All membranes were very flat, uniform, and very flexible probably due to PEG.

(4). Sulfonation of Cross-linked Membranes: Formation of Fuel Cell Membranes



XPCHD_1009

XPCHD_1009_SPCHD_101

A cross-linked PCHD membrane was placed between two desiccator plates in a 2000 mL three-necked reactor. Appropriate volume of 1,2-dichloroethane was added to immerse the membrane and a sulfonating reagent. The molar ratio of sulfonating reagent to the double bond in PCHD ranged from 2.0 to 5.0. A typical ratio was 4.0. The membrane was sulfonated for about 2 h and then washed with methylene chloride. The membrane was hydrolyzed by immersing in THF about 15 min. and then water for about 1 hour. The membrane was washed with plenty of water and then dried between two desiccator plates under vacuum.

Characterizations of Membranes

Optimization of Proton Conductivity of Crosslinked PCHD Membranes:
A new batch of membranes was prepared and characterized for conductivity, thermal and mechanical properties. Based on previous measurements of conductivity, (DOE reports starting from Sep. 07) the Mays group has been optimizing macromolecular chemistry for high conductivity and better mechanical integrity of samples.

All membranes prepared recently under optimized conditions showed high conductivity compared to Nafion® (≅ 0.07 S/cm) under the same conditions, as seen in Table 1. Samples of the new batch of membranes were prepared by blending different levels of polyethylene glycol (PEG) with PCHD or copolymerizing both polymers as shown in Table 1. The number average molecular weight (M_n) of PEG used was 2000 g/mol.

The information reported here is part of an effort to understand the relationship between conductivity and the dynamic mechanical behavior of the membranes as correlated to variation in the chemistry used during synthesis. Proton conductivities were measured at r.t. after soaking membranes in DI 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 the samples were soaked in water for 24h. The Z' intercept from the semicircle in the Nyquist plot was taken, in the usual way, as membrane resistance to calculate conductivity (σ).

The conductivities in Table 1 for new batch samples are higher than that of Nafion® under the same test conditions ($\cong$ 0.07 S/cm). It is impressive to see some membranes with conductivity values up to 0.41 S/cm under these conditions. Addition of PEG seems to be responsible for the big jump in conductivity. Moreover, copolymerization gives higher values than blending PCHD with PEG and causes another considerable jump in conductivity.

A total of six membranes were sent to BekkTech (Loveland, Colorado 80537, USA) for measurements of proton conductivity at various relative humidities (from 20% to 100%) and different temperatures (30, 80, and 120 °C). The results are shown in Table 2. Without PEG, the proton conductivity could be slightly higher than Nafion® NRE-212 at high RH, but much lower than Nafion® NRE-212 at low RH. For example, XPCHD_902_SPCHD_105 has proton conductivity of 125.77 mS/cm at 80% RH, slightly higher than that of NRE-212 (120.75 mS/cm). However, it has only half the proton conductivity compared with NRE-212 (18.13 vs. 36.96 mS/cm). As shown in Figure 1, the proton conductivity of XPCHD_902_SPCHD_105 drops more sharply as the relative humidity decreases than that of NRE-212 does. As a result, the proton conductivity of XPCHD_902_SPCHD_105 is lower than that of Nafion® NRE-212 as the relative humidity is lower than 80%.

Table 1. Effect of blending vs. copolymerization of PEG (M_n = 2000 g/mol) with PCHD on the conductivity of different membranes.

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**

Table 2. Effect of blending vs. copolymerization of PEG (M_n = 2000 g/mol) with PCHD on the conductivity at 120 °C at lower (80% & 50%) relative humidities.

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**

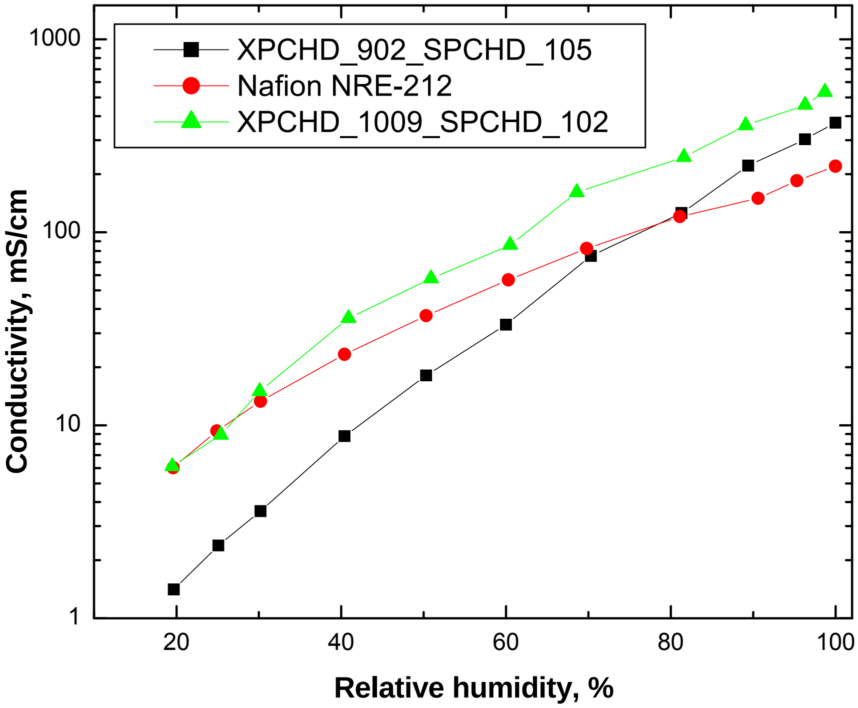


Figure 2. Proton conductivity at 120 °C vs. relative humidity curves.

By blending with PEG, not only do the membranes have higher proton conductivity at 80% RH, but also they have almost as high proton conductivity as Nafion® 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 proton conductivity at 50% RH than Nafion® NRE-212. The membrane XPCHD_1009_SPCHD_102 had proton conductivity of 245.10 mS/cm at 80% RH (more than 100% increase compared with NRE-212) and 57.6 mS/cm at 50% RH (56% increase compared with NRE-212). As shown in Figure 2, membrane XPCHD_1009_SPCHD_102 showed higher proton conductivity at all relative humidities ranging from 100% to 20% than Nafion® NRE-212 although it showed a slightly sharper decrease of proton conductivity *vs*. relative humidity. The higher proton conductivity at lower (50%) RH shown by our membranes than Nafion® NRE-212 is significant in terms of developing cheap non-Nafion® high temperature low humidity operable membranes, which is the main goal of DOE-funded fuel cell membrane projects. Therefore, the results showed in Table 1, Table 2, and Figure 2 along with good mechanical integrity of samples could be considered as a big success in optimizing the reaction conditions during preparation of these membranes although the final conductivity requirement specified by DOE (conductivity = 0.1 S/cm at 50% relative humidity at 120 °C) has not been met as yet.

Correlation of Proton Conductivity with Thermal / Mechanical Properties of Crosslinked PCHD Membranes:

Membrane water uptake at 25 °C vs. RH was determined using a very accurate vapor sorption analyzer (Q5000-TA Instruments). Water uptake vs. RH at 25 °C for XPCHD_1009_SPCHD_102 vs. Nafion 112 H^+ membranes is shown in Figure 3. The equilibrium uptakes are expressed in terms of moles of water per equivalent of polymer, or average number of water molecules per sulfonic acid group. PCHD membranes absorb considerably more water than Nafion® at each RH. The difference is even pronounced at low RH which is significant for fuel cell applications. This enhancement is attributed to the presence of PEG in this specific sample and accounts for the higher conductivity although cross-linking is most likely another important factor. More of these measurements are required for various PCHD membranes to draw firm conclusions on water uptake at different temperatures and RH for different membrane compositions as related to DOE targets.

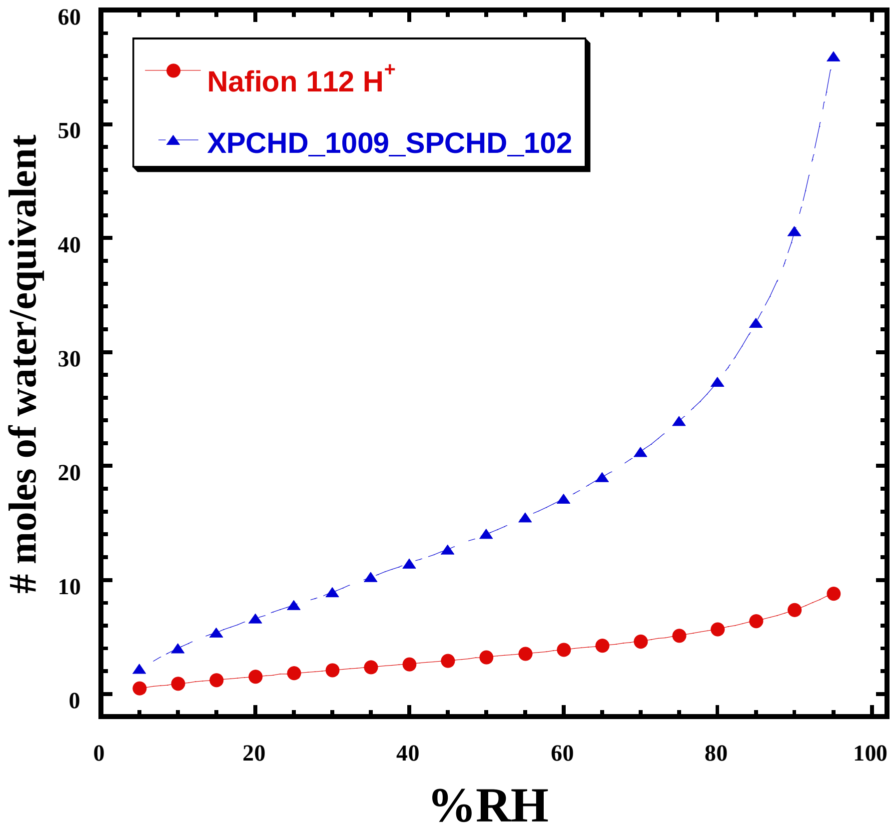


Figure 3. Equilibrium water uptake at 25 °C for a PCHD (copolymerized w/ PEG) based membrane vs. a Nafion®112 membrane

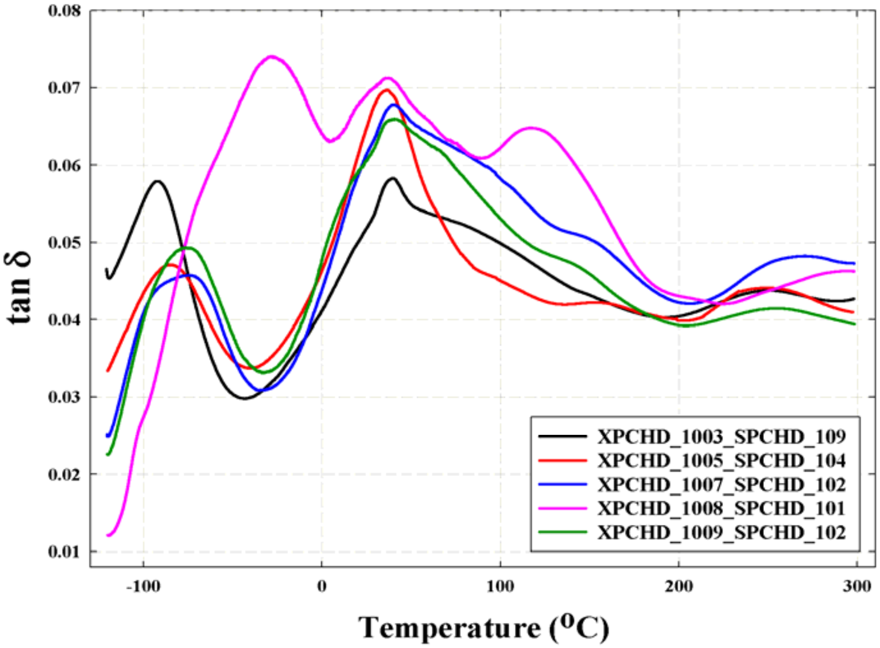


Figure 4. Tan δ vs. T curves for new membranes compared to an earlier-synthesized membrane.

Long and short range macromolecular motions in a new membrane batch were identified using dynamic mechanical analysis (DMA) and the loss tangent (tan δ) vs. temperature (T) curves are seen in Figure 4. 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^o 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 active at low temperatures, would seem to be possible in these groupings. A very broad peak exists between about -30 and 200^o 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^o C. Finally, there is a small peak above 200^o C which is suggested based on studies of other ionomers, to be disruption of –SO_3H 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 5. 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^o C, which must be explained because this indicates a material stiffening.

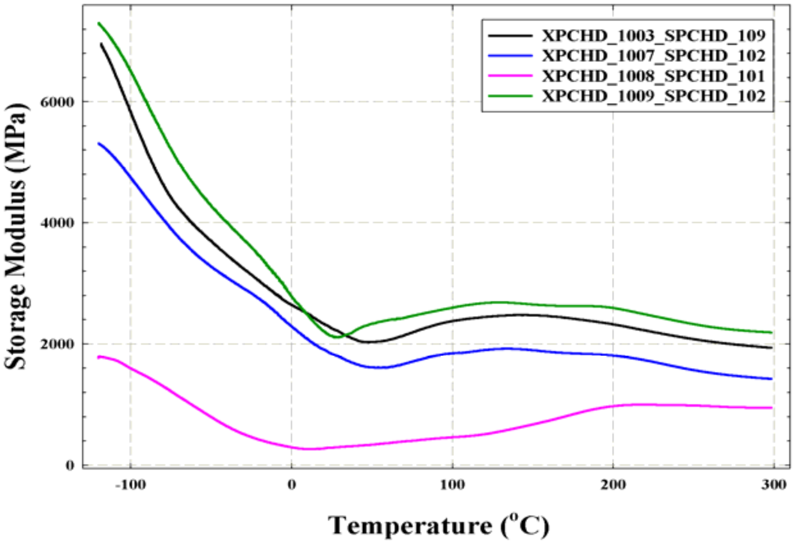


Figure 5. Storage modulus (E′) vs. temperature for membranes containing PEG vs. an earlier-synthesized membrane without PEG.

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 4. This is of special interest for fuel cell membranes at a temperature around 100° C as mechanical stability is desired in that temperature range.

Membranes with Nanochannels

Our next strategy was to explore the possibility of extracting out the low molecular weight PEG from blends with crosslinked and sulfonated PCHD in order to create hydrophilic nanochannels in the material. This was done by soaking the membranes in large quantities of deionized water for two days. Proton conductivity results are shown in Figure 6 and listed in Table 3.

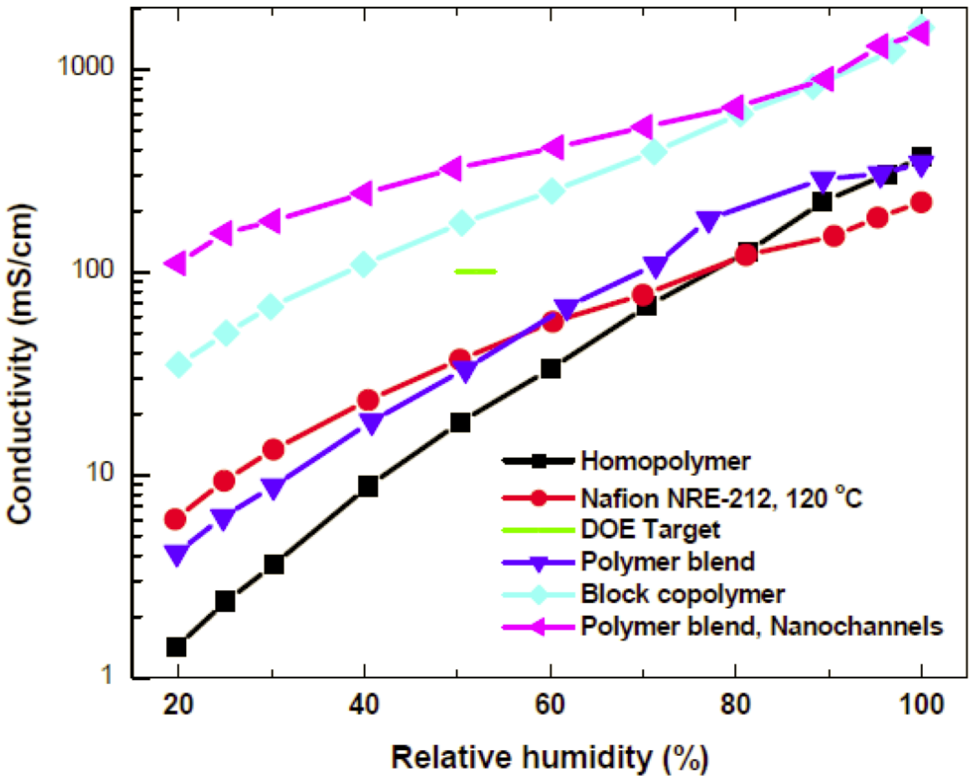


Figure 6. Proton conductivities of various membranes and DOE Year 3 goal.

Table 3. Proton conductivities of optimized sulfonated PCHD membranes

Sample at 120 °C	**Conductivity (mS/cm) 100% RH**	**Conductivity (mS/cm) 50% RH**
XPCHD_902_SPCHD_105 (Homopolymer)	**369.39**	**18.13**
Nafion® NRE-212	**120.75**	**36.96**
DOE Year 3 Milestone		**100.00**
XPCHD_1008_SPCHD_102 (Polymer Blend)	**342.10**	**33.23**
XPCHD_1012_SPCHD_106 (Block Polymer)	**1596.90**	**174.10**
XPCHD_1013_SPCHD_101 (Polymer Blend, Nanochannels)	**1499.60**	**322.44**

Except for XPCHD_902_SPCHD_105, all other membranes were made using a two-step sulfonation, i.e., room temperature about 1 hour and then 80 degree C about 1 hour with about 5 equivalents of ClSO3H. These sulfonation conditions also improved substantially the proton conductivity of block copolymer membranes (Figure 6 and Table 3), presumably by altering the amount of "addition" versus "substitution" type of sulfonation. Both the block copolymer sample and the nanochannel sample exhibit proton conductivities far exceed the DOE Year 3 goal of 100 mS/cm at 120 °C. At this point work was stopped on the project due to termination of DOE funding. Patent applications have been filed on these promising low cost proton conducting membranes.

Summary

In summary, four different types of non-Nafion membranes were synthesized and investigated in this project: 1. crosslinked, aromatized, and sulfonated PCHD ; 2. poly(vinylidene fluoride-b-1,3-cyclohexadiene); 3. random copolymers of CHD and α-methylstyrene; 4. crosslinked and sulfonated PCHD, with and without addition of PEG. The type 1 membranes suffered from extreme brittleness and were abandoned. Type 2 and 3 membranes were abandoned due to difficulties in their synthesis and successes with type 4 membranes.

The type 4 membranes are synthesized from a potentially inexpensive hydrocarbon monomer, resulting in potentially much less expensive membranes that are thermally stable to 400 °C. The type 4 membranes without addition of PEG met the Year 2 milestone of 0.07 S/cm at 80% RH at 120ºC was met. However, further effort was needed to meet the Year 3 proton conductivity requirements specified by DOE (conductivity = 0.1 S/cm at 50% relative humidity at 120 °C). By adjusting sulfonation conditions and incorporating PEG as either a block copolymer or as a polymer blend with sulfonated PCHD, the Year 3 milestone was achieved. Mechanical properties of these materials were characterized by DMA and dielectric spectroscopy, and thermal properties were explored by TGA and DSC. The materials have adequate thermal and mechanical stability for use as a fuel cell membrane. For PEG-modified materials the degree of hydration was seen to greatly exceed that of a Nafion® 112 membrane. This enhanced hydration, in turn, caused proton conductivities to greatly exceed that of Nafion®. This is attributed to plasticization that increases macromolecular mobility that, in turn, enhances water uptake and proton transport. The fact that the excellent conductivities obtained for these materials exceeded the DOE Year 3 Milestone (100 mS/cm at 120° C and 50% RH) is very encouraging. These results provide useful information to suggest future synthetic directions.

References

[1] Ratner, M. A. ; Shriver, D. F. *Chem. Rev.* **1988**, *88*, 109-124.
[2] Ghosh, B. D.; Lott, K. F.; Ritchie, J.E. *Chem. Mater.* **2005**, *17*, 661-669.

Products Developed Under the Award and Technology Transfer Activities:

Patent applications:

"Materials Comprising Polydienes and Hydrophilic Polymers and Related Methods", J. W. Mays, S. Deng, K. A. Mauritz, M. K. Hassan, and S. Gido, PCT/US2010/022556.

"Sulfonated Crosslinked Poly(1,3-cyclohexadiene) Membranes for Fuel Cell Applications", J. W. Mays, S. Deng, K. Mauritz, and M. Hassan, PCT/US10/022556.

Technical presentations:

"Poly(cyclohexadiene) – Based Polymer Electrolyte Membranes for Fuel Cell Applications", J. W. Mays, T. Huang, H. Zhou, and K. Mauritz, poster presentation at the 2006 DOE Hydrogen Program Review, Washington, DC, May 16 – 19, 2006.

"Poly(cyclohexadiene) – Based Polymer Electrolyte Membranes for Fuel Cell Applications", J. W. Mays, T. Huang, H. Zhou, and K. Mauritz, oral presentation at the High Temperature Membranes Working Group, DOE Hydrogen Program Review, Washington, DC, May 16 – 19, 2006.

"Poly(Cyclohexadiene)-Based Polymer Electrolyte Membranes for Fuel Cell Applications", S. Deng, M. K. Hassan, K. A. Mauritz, and J. W. Mays, invited poster presentation at the Polymers West Gordon Research Conference, Ventura, CA, January 7 – 12, 2007.

"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.

“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.

“Synthesis and Characterization of Poly(Cyclohexadiene)-Based Fuel Cell Membranes”, S. Deng, M. Hassan, K. Mauritz, and J. Mays, presented at the 20th International Symposium on Polymer Analysis and Characterization, October 1-4, 2007, Agios Nikolaos, Crete, Greece.

“Poly(1,3-Cyclohexadiene)-Based Proton Exchange Fuel Cell Membranes”, S. Deng, M. K. Hassan, J. W. Mays, and K. A. Mauritz, invited presentation at the Southeast Regional Meeting of the American Chemical Society (SERMACS), October 26, 2007, Greenville, SC.

“Novel Ion-Containing Polymers Via Post-Polymerization Chemistry” J. Mays, invited Highlands in Chemistry Lecture at the Department of Chemistry, Virginia Tech, Blacksburg, VA, March 14, 2008.

“Poly(cyclohexadiene)-Based Polymer Electrolyte Membranes for Fuel Cell Applications”, J. Mays, S. Deng, M. Hassan, and K. Mauritz, presented to the meeting of the FreedomCar and Fuel Cells Partnership, Detroit, MI, March 19, 2008.

“Novel Proton Conductive Membranes Derived from 1,3-Cyclohexadiene”, J. Mays, S. Deng, M. Hassan, and K. Mauritz, invited Keynote Lecture at the Purdue University Hydrogen Symposium 2008, West Lafayette, IN, April 24 – 25, 2008.

“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, June 9 – 11, 2008.

“Novel Proton Conductive Membranes based on Poly(Cyclohexadiene) Derivatives”, J. W. Mays, invited lecture at the UK Polymer Showcase, September 16 – 18, 2008, York, England.

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

“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.

“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.

“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, DC, February 26, 2009.

“Novel Charged Polymers: From Biomineralization to Fuel Cell Membranes”, J. W. Mays, invited Bayer Lectures on Polymers, Cornell University, Ithaca New York, April 9, 2009.

“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.

“Low Cost High Temperature Fuel Cell Membrane Based on Poly(1,3-cyclohexadiene) Homopolymers, Polymer Blends, and Block Copolymers”, S. Deng, J. W. Mays, M. K. Hassan, and K. A. Mauritz, presented at the Fall 2009 National Meeting of the American Chemical Society, Washington, DC, August 16 – 20, 2009.

“Novel Polymeric Materials Based on Poly(1,3-Cyclohexadiene)”, J. W. Mays, invited presentation at the Frontiers of Polymer Science Symposium held in honor of the Retirement of Professor Roderick Quirk, University of Akron, Akron, OH, May 13-14, 2010.

“Novel Polymeric Materials Based on Poly(1,3-Cyclohexadiene)”, J. W. Mays, invited presentation at Dow Chemical, Freeport, TX, July 29, 2010.

“High Performance Proton Conducting Membranes for Fuel Cells”, J. Mays, presented at the Energy Partnership Forum, University of Tennessee, Knoxville, September 8, 2010.

“Novel Polymeric Materials Based on Poly(1,3-cyclohexadiene)”, J. Mays, invited presentation at the Army Research Laboratory, Aberdeen, MD, September 21, 2010.

Networks Fostered:
This project allowed us to develop a strong collaboration with the group of Professor Mauritz at USM and facilitated student exchanges between the two institutions.

In addition, we were able to obtain funds from the Tennessee Technology Development Corporation to continue our work on proton conducting membranes.