

V.G.17 Poly(cyclohexadiene)-Base Polymer Electrolyte Membranes for Fuel Cell Applications

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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 and 120°C), and meet the following DOE 2010 performance criteria:

- Cost: \$25/kW_e
- Durability with cycling: 5,000 hours at an operating temperature $\geq 80^\circ\text{C}$
- Survivability: -40°C
- Thermal cyclability in the presence of condensed water
- Area specific resistance: 0.02 Ohm-cm²
- Hydrogen crossover: 2 mA/cm²
- Oxygen crossover: 2 mA/cm²
- Inlet water vapor partial pressure: <1.5 kPa
- Operating temperature: $\leq 120^\circ\text{C}$

Accomplishments

- Synthesized crosslinked and sulfonated PCHD films, characterized them, and measured their thermal and mechanical properties and proton conductivity. A range of membranes of crosslinked (5 ~ 10 mol%) and sulfonated (10 ~ 45 mol%) PCHD was tested. Proton conductivity has reached as high as 130 mS/cm at room temperature, 258 mS/cm at 80°C, and 330 mS/cm at 120°C.
- The proton conductivity of the crosslinked and sulfonated PCHD membrane XPCHD-1001-SPCHD-0105 measured at BekkTech was 108.5 mS/cm at 80.3% RH and 120°C, and 24.4 mS/cm at 48.9% RH and 120°C. Therefore, the Year 2 milestone of demonstrating conductivity of 0.07 S/cm at 80% RH and 120°C has been met.
- Poly(vinylidene fluoride-b-1,3-cyclohexadiene) multi-block copolymers and poly(α -methylstyrene-co-cyclohexadiene) statistical copolymers were synthesized. They are to be further functionalized by reactions such as crosslinking, fluorination, and sulfonation so that Type 2 and Type 3 fuel cell membranes can be made.

Objectives

- Synthesize, derive, and characterize a range of homopolymer and copolymer materials incorporating poly(cyclohexadiene) (PCHD) that conduct protons at low (25-50%) relative humidity (RH) and at temperatures ranging from room temperature to 120°C.
- 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.
- Improve high temperature water retention and mechanical durability of these materials.

Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program

- Investigations of the thermal, mechanical, and electrical properties of Type 1 membranes have been conducted. The thermal stability of these materials is outstanding and improved in systematic fashion by crosslinking, sulfonation, and aromatization.
- Growth of inorganic nanoparticles within the hydrophilic domains of Type 1 membranes is underway.



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 (i.e., conductivity = 0.1 S/cm at 50% RH and 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. This team 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). Most of the synthesis work so far has focused on the synthesis

and optimization of the Type 1 membranes. The mechanical and thermal properties of these materials are characterized by dynamic mechanical analysis (DMA), thermogravimetric analysis (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 and membranes degraded via the OCV testing 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 (Figure 1). These materials require the polymerization of 1,3-cyclohexadiene, followed by crosslinking of PCHD in membrane form 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 synthetic procedures, these problems have been almost entirely overcome. The synthesis focus is now on Type 2 and Type 3 membranes.

Proton Conductivity. A broad range of membrane compositions was prepared and characterized for their proton conductivity, thermal and mechanical properties. The goal of this effort is to understand the relationship between the proton conductivity and thermomechanical behavior of these membranes as they relate to fuel cell performance. Conductivity values of these membranes are reported in Table 1. The membranes can be divided into three categories based on low, medium, and high conductivity. The broad range in values shows the capability of varying conductivity through varying reaction conditions in the production of membranes. The results seen here reflect different degrees of sulfonation among samples resulting from variations of reaction conditions.

Proton conductivities of the membranes were measured at room temperature by soaking them in water. This particular test was meant for rapid screening. A sample mounted in the four point probe conductivity cell (Bekkttech) was immersed in water. Before impedance measurements, performed in the frequency range 1 kHz to 1 MHz, the samples were soaked in water for 24 h.

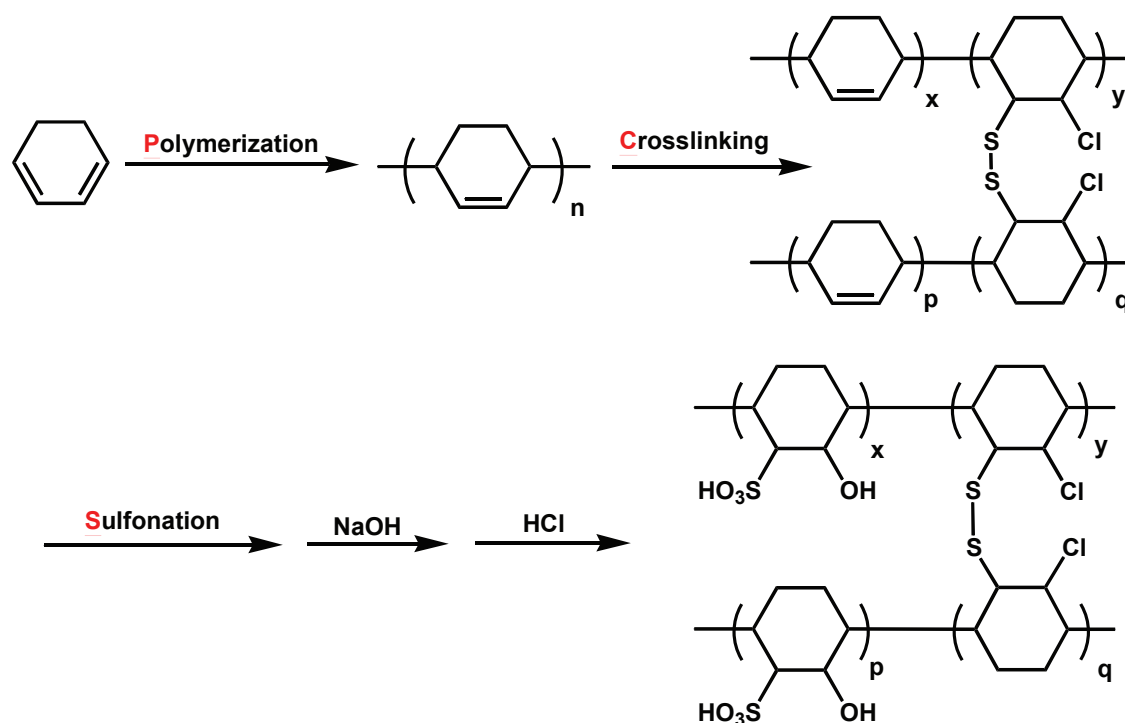


FIGURE 1. Synthetic Strategy to Type 1 Membranes

The Z' intercept from the Nyquist plot was taken, in the usual way, as the membrane resistance to compute conductivity.

Based on the results of these measurements of conductivity, Mays optimized macromolecular chemistry for high conductivity, the macromolecular chemistry for high conductivity was optimized, although other

TABLE 1. Conductivity Values of Different XPCHD_SPCHD Membranes Prepared Through Different Reaction Conditions

Sample	Conductivity (S/cm)
XPCHD_901_SPCHD_104	0.004 (low)
XPCHD_902_SPCHD_109	0.006 (low)
XPCHD_902_SPCHD_113	0.006 (low)
XPCHD_1001_SPCHD_103	0.005 (low)
XPCHD_902_SPCHD_103	0.032 (medium)
XPCHD_902_SPCHD_104	0.064 (medium)
XPCHD_902_SPCHD_114	0.043 (medium)
XPCHD_902_SPCHD_105	0.132 (high)
XPCHD_902_SPCHD_107	0.112 (high)
XPCHD_902_SPCHD_108	0.135 (high)
XPCHD_501_SPCHD_103	0.099 (high)
XPCHD_803_SPCHD_203	0.112 (high)

important properties, mainly durability, must now be considered. All membranes displayed high conductivity compared to Nafion[®] (≈ 0.07 S/cm) under the same conditions, as seen in Table 2. Many of the membranes reported in Tables 1 and 2 gave a minimum conductivity value of 0.09 S/cm, which is higher than that of Nafion[®] at the same conditions (0.067 S/cm).

Our goal, as per the DOE target, is proton conductivity > 0.1 S/cm at 50% RH at 120°C. Our results are very encouraging with regard to meeting our objectives in achieving the DOE target. The proton conductivity of the crosslinked and sulfonated PCHD

TABLE 2. Conductivity Values of Different XPCHD_SPCHD Membranes Prepared by Recent, More-Optimized Reaction Conditions

Sample	Conductivity (S/cm)
XPCHD_1001_SPCHD_106	0.09
XPCHD_1001_SPCHD_112	0.09
XPCHD_1001_SPCHD_113	0.09
XPCHD_1001_SPCHD_115	0.12
XPCHD_1001_SPCHD_116	0.10
XPCHD_1001_SPCHD_118	0.09
XPCHD_1001_SPCHD_120	0.12
XPCHD_1001_SPCHD_122	0.09

membrane XPCHD-1001-SPCHD-0105 measured by BekkTech was 108.5 mS/cm at 80.3% RH and 24.4 mS/cm at 48.9% RH at 120°C. Therefore, the Year 2 milestone of demonstrating conductivity of 0.07 S/cm at 80% RH at 120°C has been met. However, the final conductivity requirements specified by DOE (conductivity = 0.1 S/cm at 50% RH and 120°C) has not yet been met.

Thermogravimetric Analysis. TGA studies were performed on these materials to determine their thermal degradative stability in N₂ 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 2 shows mass loss (in N₂) vs. temperature up to 800°C for membranes prepared with different reaction conditions. Degradation of these materials is a multi-step process which reflects the complexity of these chemical structures that includes SO₃H groups and crosslinks as well as chemical heterogeneity along the backbone itself. Major mass loss does not occur until ~200°C for all membranes. Hence, these materials are stable with regard to thermal degradation and rather cohesive with regard to molecular bonding.

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_902, 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

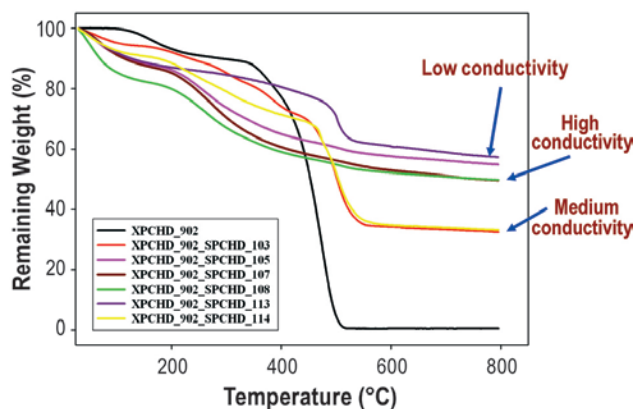


FIGURE 2. TGA thermograms of membranes prepared with recent optimized reaction conditions compared to a sample from previous batch.

SO₃H 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.

Figure 2 shows somewhat of a correlation between conductivity and thermal stability. The conductivity values of the samples were in a narrower range, as seen in Table 1, and also exhibited similar thermal degradation behavior. The unsulfonated sample curve (black) has catastrophic failure at an earlier temperature. This similarity in thermodegradative behavior could reflect similar complexity in chemical structures for membranes with closer values of conductivities which would have similar degrees of SO₃H group interactions. These degradative transitions are generally above fuel cell operating temperatures but the results are diagnostic of good material cohesion that could express itself in terms of mechanical durability at lower temperatures.

Molecular motions in different membranes have been uncovered by DMA and a number of clear signature relaxations are seen in the tanδ vs. temperature (T) curves in Figure 3. Three distinct peak regions with different degrees of broadening can be observed for all membranes. The degree of broadening is diagnostic of the degree of microstructural heterogeneity on the scale of the given relaxation.

There is a small peak, or sometimes shoulder, below 0°C. The corresponding storage modulus (E') vs. temperature behavior in this range shows a drop, or material softening. Very low temperature peaks often reflect short ranged molecular motions, such as the β relaxation in glassy polymers. Given the nature of the PCHD polymers and their modifications, the only fragments in which these short range motions might occur would be in the -CH-S-S-CH- crosslinks and/or motions of -CH-Cl side chains. Further investigation is needed to determine which of these is occurring.

There are two strong overlapping peaks between 0 and 100°C. The highest temperature relaxation is subsiding in the region of desired fuel cell operating temperature. These peaks have different widths for the different samples. We are investigating the nature of these relaxations that are also characterized by the fact that all the corresponding storage modulus vs. T curves *begin to rise*, indicating sample stiffening, rather than drop in this temperature range. This E' behavior might rule out this relaxation as being a glass transition. Perhaps the increase in temperature is driving some chemical reaction that is making the material stiffer and this would be beneficial for high temperature fuel cell operation. Also, the relaxations between 0 and 200°C seem to get broader as the number -SO₃H groups

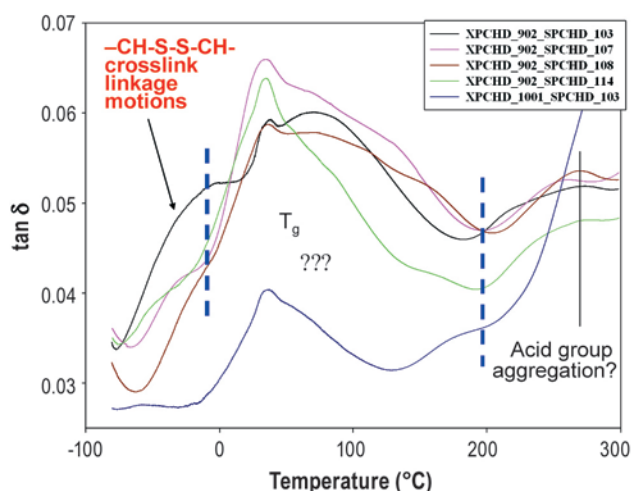


FIGURE 3. DMA curves of some of the membranes shown in Table 1.

increases; this is also reflected in their corresponding conductivity values. This trend might suggest progressive hydrogen bonding interactions among the $-\text{SO}_3\text{H}$ groups which would form physical crosslinks.

Another small peak appears above 200°C for all samples. Based on studies of other ionomers, this peak arises from the disruption of SO_3H group aggregates, based on studies of other ionomers. This could provide beneficial material cohesion at high membrane operating temperatures. It is interesting that the peak above 200°C shifts to lower temperature for the sample with lower conductivity (XPCHD_1001_SPCHD_103) compared with the other samples having medium to higher conductivities. This could reflect a lower degree of aggregation for the sample with lower conductivity and lower $-\text{SO}_3\text{H}$ group concentration.

Further studies must include membranes that are hydrated because incorporated water will likely shift at least some of these transitions and the molecular motions associated with these transitions are expected to influence water transport and proton conductivity. It is important to investigate the nature of high temperature transitions as they are directly implicated in mechanical degradation with regard to relative humidity and temperature cycling in fuel cells (structural hysteresis and micro-crack formation).

Conclusions and Future Directions

Work in year 2 has focused on optimizing the chemistry of the Type 1 membranes. A range of membranes with various degrees of crosslinking and sulfonation have been 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% RH and room

temperature). The year 2 milestone of demonstrating conductivity of 0.07 S/cm at 80% RH and 120°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 and 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 and have established the high temperature stability ceiling of these materials. Proton conductivity tests were performed to rank the feasibility of the various membrane compositions. Future interests include:

- Further optimization of crosslinking and sulfonation conditions for Type 1 membranes to obtain both high proton conductivity and good mechanical strength.
- Perform broadband dielectric spectroscopic studies of type 1 membranes to probe the nature molecular motions that are active at fuel cell-relevant temperatures and the coupling of these motions to water and proton transport.
- Determine the viscoelastic properties of Type 1 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 from Type 1 membranes and test their performance and expose them to OCV tests to check their durability and lifetime. Chemically degrade Type 1 membranes via Fenton's reagent. Characterize degraded samples via both chemical and OCV procedures using broadband dielectric spectroscopy.
- Crosslink and sulfonate poly(vinylidene fluoride-*b*-1,3-cyclohexadiene) multi-block copolymers to make Type 2 fuel cell membranes.
- Fluorinate and sulfonate poly(α -methylstyrene-co-cyclohexadiene) statistical copolymers to make Type 3 fuel cell membranes.

Special Recognitions & Awards/Patents Issued

1. A provisional patent has been filed on the Type 1 PCHD membranes.
2. Presented a Keynote Lecture on our work at the Purdue Hydrogen Symposium.
3. Presented an invited Highlands in Chemistry Lecture at Virginia Tech on our work.

FY 2008 Publications/Presentations

1. “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.
2. “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.
3. “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.
4. “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.

References

1. Williamson, D. T.; Mather, B. D.; Long, T. E. J. Polym. Sci.: Polym. Chem. 2003, 41, 84.
2. Natori, I.; Natori, S. Macromol. Chem. Phys. 2006, 207, 1387.