

Poly(cyclohexadiene)-Based Polymer Electrolyte Membranes for Fuel Cell Applications

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May 16, 2006

This presentation does not contain any proprietary or confidential information



Project ID #: FCP 3



Overview

Timeline

- Start: April 2006
- End: April 2011
- 1% complete

Budget

- Total project funding
 - DOE share \$1.5M
 - Contractor share \$500K
- Funding received in FY05: \$300K
- Funding for FY06: \$300K

Barriers

- Barriers addressed
 - Thermal stability of PEMs
 - High temperature, low RH proton conductivity
 - Cost

Partners

- Univ. of Southern Mississippi
- ORNL
- Battelle

Objectives

- 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 °C.
- To achieve these objectives, a range of homopolymer and copolymer materials incorporating poly(cyclohexadiene) (PCHD) will be synthesized, derivatized, and characterized.



Approach

- 1,3-Cyclohexadiene is a potentially inexpensive monomer that can be polymerized to yield a range of novel polymers and copolymers
- Poly(cyclohexadiene (PCHD) incorporates an unsaturated 6-membered ring into the polymer backbone, which imparts superior mechanical and thermal properties
- PCHD can be aromatized, sulfonated, or fluorinated, allowing for tuning of key properties such as conductivity, hydrophilicity, permeability, morphology, thermal stability, crystallinity, and cost.



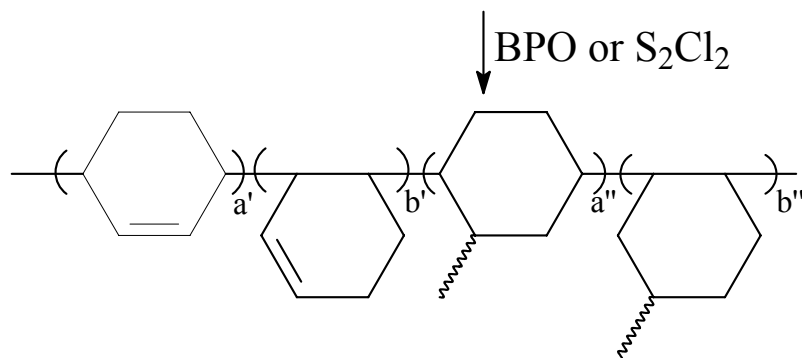
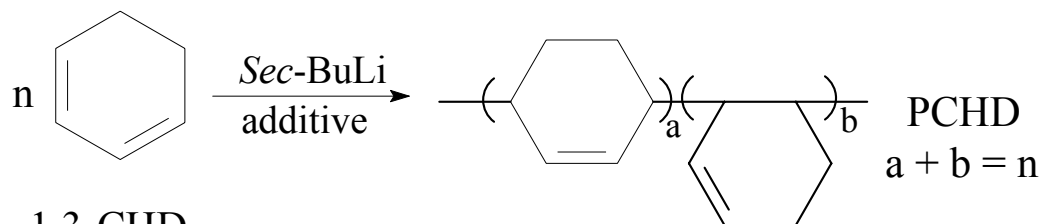
Technical Accomplishments/ Progress/Results

Official notification of funding was received on April 11, 2006. Despite this short time frame, we have:

- Synthesized crosslinked and sulfonated PCHD films, characterized them, and started to measure their thermal properties and proton conductivity.
- Synthesized crosslinked, aromatized, and sulfonated PCHD films, characterized them, and started to measure their thermal properties and proton conductivity.

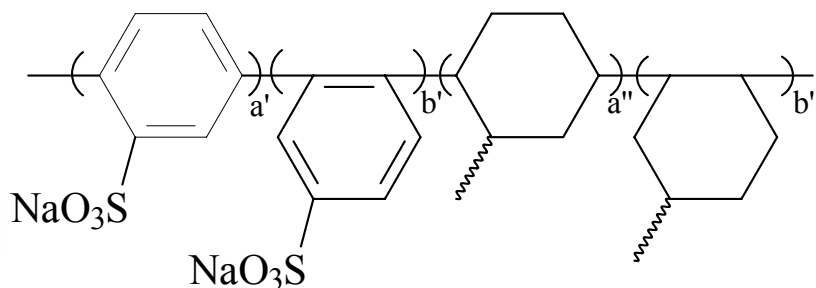


Accomplishments Slides (con't)



lightly crosslined PCHD $a' + a'' + b' + b'' = n$

- (1) Aromatized by p-chloanil
- (2) SO₃/TEP

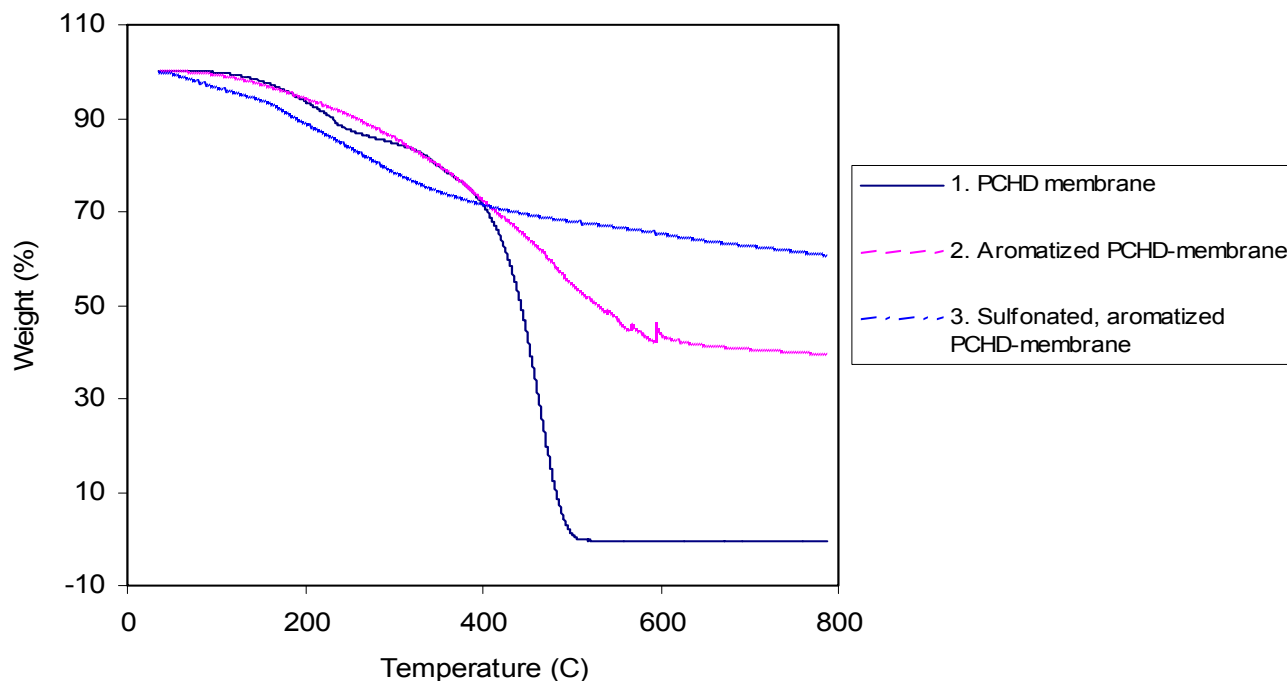
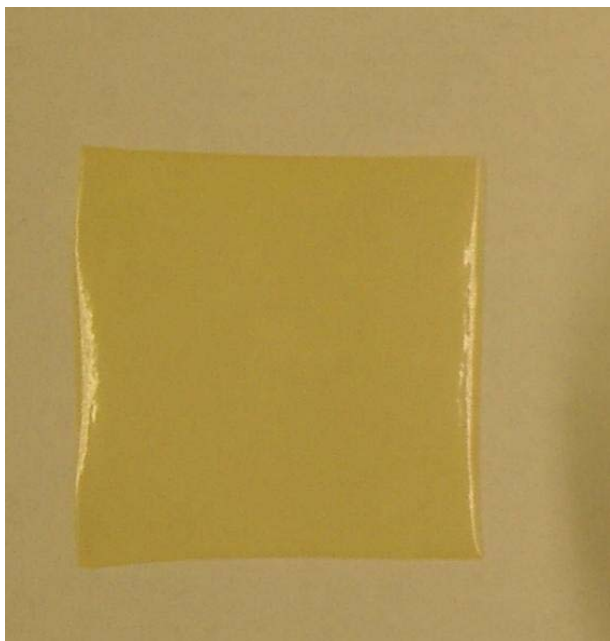


Polymer Synthesis
and Modification

aromatization is optional
or may be controlled



Accomplishments Slides (con't)



Left: A photograph of a cross-linked 2.5''X2.5'' PCHD membrane; Right: TGA curves 1) for the cross-linked PCHD membrane, 2) after aromatization, 3) after aromatization and sulfonation

Accomplishments Slides (con't)

- Materials were characterized by FT-IR, SEM, and elemental analysis
- 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 4-point fixture immersed in water (J. Sayre, Battelle): 1.2×10^{-2} S/cm at room temperature and 2.8×10^{-2} S/cm at 80 °C.
- A membrane of crosslinked, non-aromatized, and sulfonated (47 mol %) PCHD was tested. Water uptake was 4 wt %.
- Proton conductivity: 1.6×10^{-2} S/cm at room temperature and 3.6×10^{-2} S/cm at 80 °C.

Future Work

- A milestone by the end of Year 1 is the synthesis of additional PCHD-based membranes, as described above, with optimization of molecular parameters, including extent of aromatization and degree of sulfonation. These membranes will be thoroughly characterized.
- Sol-gel chemistry will be used to grow hydrophilic nanophases within the membranes.
- Materials synthesis work will expand to incorporate fluorinated species through post-polymerization chemistry and copolymerization.



Summary

- Work is just beginning but already we have demonstrated the feasibility of creating water swell-able, thermally stable membranes based on PCHD, a potentially cheap building block.
- PCHD structure and properties may be widely varied through choice of polymerization conditions and through post-polymerization chemistry.
- Initial preliminary measurements of proton conductivity at 80 °C yielded results of 0.028 – 0.036 S/cm, below the Year 3 goal of 0.1 S/cm at 50% RH and 120 °C but encouraging for a first attempt.
- Chemical modifications and sol-gel chemistry will be used to optimize these membranes in the coming year.

