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

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

Approach

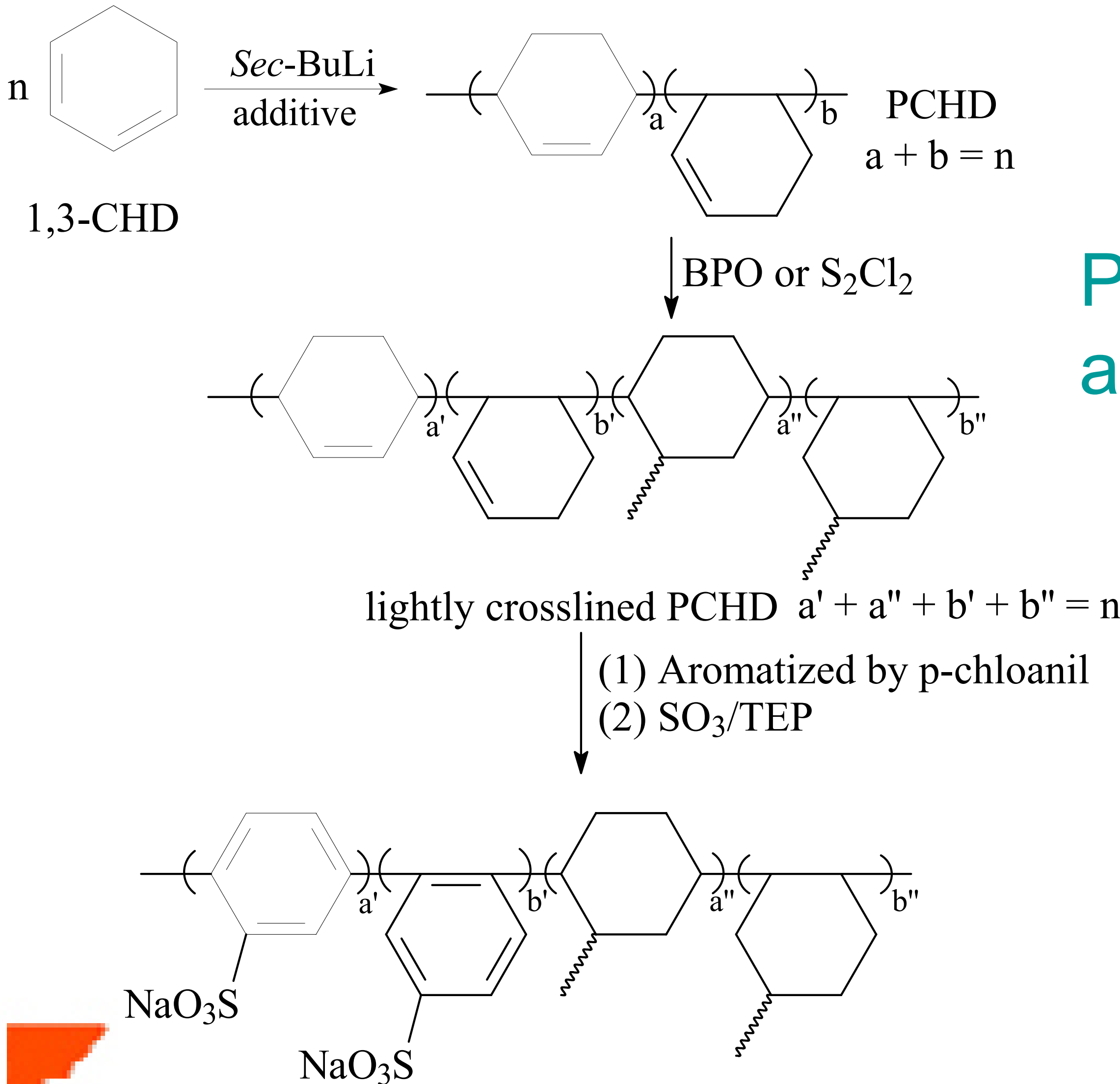
- 1,3-Cyclohexadiene is a potentially inexpensive monomer that can be polymerized to yield a range of novel polymers and copolymers
- Poly(cyclohexadiene (PCHD) incorporates an unsaturated 6-membered ring into the polymer backbone, which imparts superior mechanical and thermal properties
- PCHD can be 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.

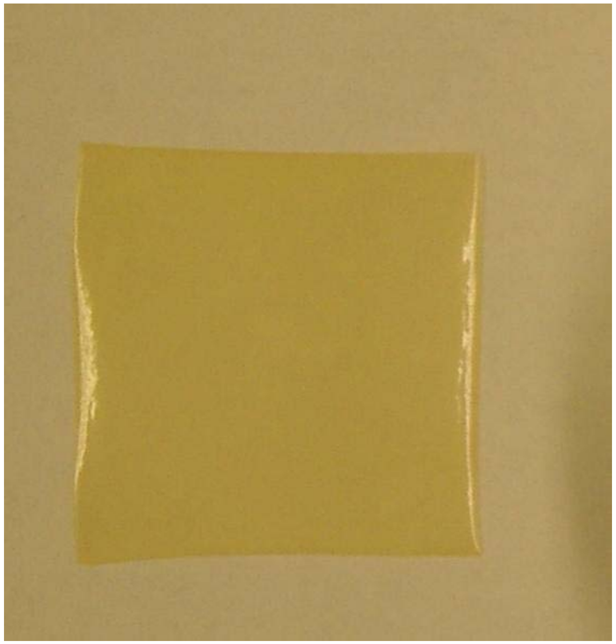
Accomplishments Slides (con't)

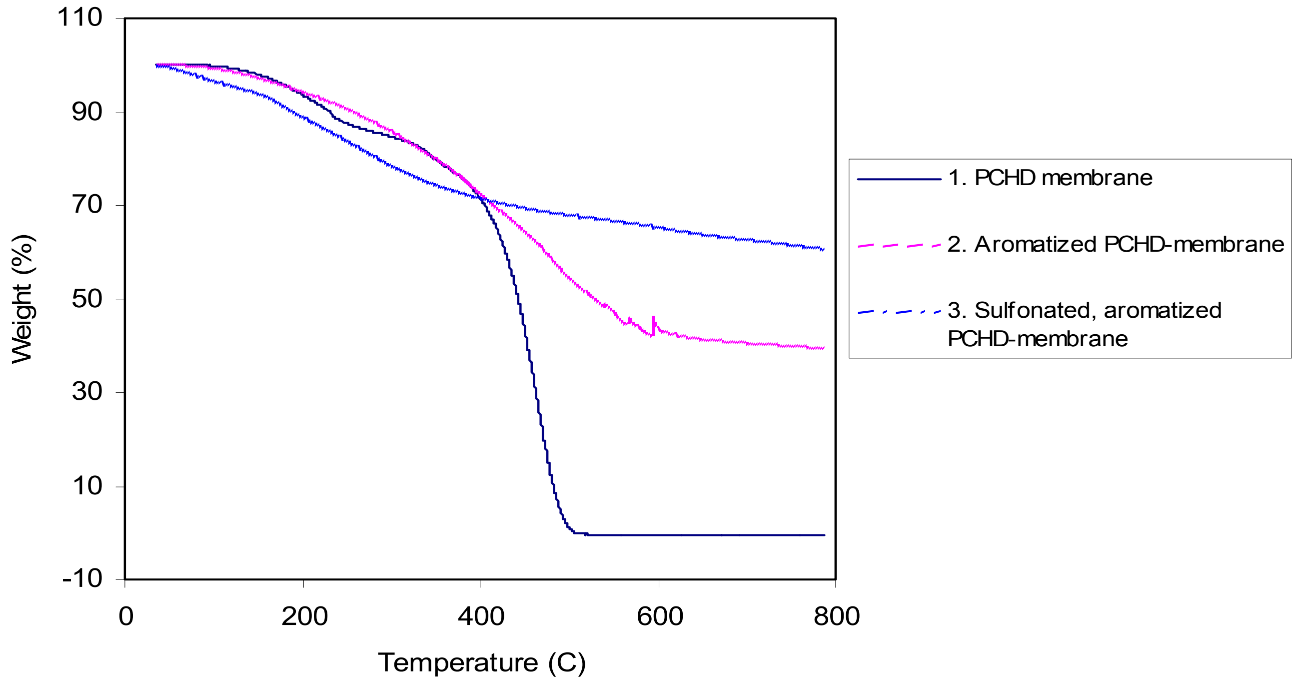


Polymer Synthesis and Modification

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 E-02 S/cm at room temperature and 2.8 E-02 S/cm at 80 ºC.

- 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 80 ºC.

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 menbranes 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 ºC yielded results of 0.028 – 0.036 S/cm, below the Year 3 goal of 0.1 S/cm at 50% RH and 120 ºC but encouraging for a first attempt.
- Chemical modifications and sol-gel chemistry will be used to optimize these membranes in the coming year.