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

Jimmy Mays¹, Suxiang Deng¹, Mohammad Hassan², Kenneth Mauritz²
¹University of Tennessee
²University of Southern Mississippi
May 19, 2009

Project ID# fc_04_mays

This presentation does not contain any proprietary, confidential, or otherwise restricted information
Overview

Timeline
• Start: April 2006
• End: August 2009
• 99% complete

Budget
• Total project funding
  – DOE share $900K
  – Contractor share $300K
• DOE Funding for FY08: $300K

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

Partners
• Univ. of Southern Mississippi
• ORNL
Relevance

- The objective of this project is to synthesize and characterize novel non-Nafion® proton conducting membranes having reduced cost, improved durability, and high proton conductivity at elevated temperatures and low RH.
- To achieve these objectives, a range of homopolymer and copolymer materials incorporating poly(cyclohexadiene) (PCHD) will be synthesized, derivatized, and characterized.
- Successful completion of this project will result in the development of novel PEM membranes engineered to have high conductivity at elevated temperatures and low relative humidity.
Approach

• Anionic polymerization and post-polymerization chemistry will be utilized to synthesize novel thermally stable proton conducting membranes based on a potentially inexpensive hydrocarbon monomer, 1,3-cyclohexadiene.

• Thorough characterization of the membranes will be carried out to understand structure/property relationships.
Technical Accomplishments: PCS Approach

Chemistry was optimized over the past year.
Cross-linking of PCHD

$\text{PCHD-01} + S_2Cl_2 \rightarrow \text{XPCHD-0102}$

- ~ 5% cross-linked
- Very flat and thin (thickness less than 100 microns)
- Crack-free
- The quality of this membrane is crucial for the subsequent reactions

Membranes made by simple solution casting or melt pressing
Sulfonation: Formation of PEMs

XPCHD_803

Sulfonation

XPCHD_803_SPCHD_201

NaOH

XPCHD_803_SPCHD_202
Sodium Form

HCl

XPCHD_803_SPCHD_203
Acid Form
Photos of PEMs in Two Forms

- XPCHD_803_SPCHD_202
  - Sodium Form

- XPCHD_803_SPCHD_203
  - Acid Form
Proton Conductivity & Properties: PCS Approach

- early samples
- comparable to Nafion® in mid-RH range

Bekktech Data

Conductivity, mS/cm vs. Relative humidity, %

Sample Result at 80% RH, 30 °C: 40.9 mS/cm
DOE Milestone at 80% RH, 30 °C: 70 mS/cm
Temperature Derivative of Remaining Weight % from TGA Curves for XPCHD-SPPP_606 Sample

Improved thermal stability by crosslinking, sulfonation and aromatization
Can we further improve conductivity?

The synthesis of a block copolymer of PCHD and PEG: PCHD-PEG-02

![Chemical structure of PCHD-PEG-02](image)

**Synthesis of a Block Copolymer of PCHD and PEG: PCHD-PEG-02**

![Graph showing proton conductivity at 120°C vs. relative humidity](image)

Proton conductivity at 120°C vs. relative humidity
• Moisture adsorption/desorption for Nafion® at 80° C

- Also performed for PCHD- based membranes.

- TA Q5000SA

  - Also, water vapor uptake kinetics can be determined.

  - Plot equilibrium data ⇒
• More hydrated over entire RH range, including low RH.

• Can reduce water, increase durability w/ sol-gel titanate insertion.

Vapor Pressure Isotherm at 25 °C for PCHD (copolymer w/ PEG) based membrane vs. Nafion®112 membrane
• Vapor Pressure Isotherm at 80°C

• conductivity of Nafion®/titania < Nafion®
  - IEC unchanged
  - Mechanical modulus increased
  - FER results good
  - OCV results good
  - Polarization curves bad

• Water uptake lowered

• Similar *in situ*, sol-gel growth of titania particles in PCHD-based membranes scheduled
•Proton conductivity at 120° C vs. relative humidity

- better than Nafion® over practically entire RH range

• with 230 kPa (~145 kPaga) measured at
Viscoelastic studies

• DMA, stress relaxation, creep
• High temperature stability, glass transition, mechanical integrity of membranes
• Polymer molecular motions (relaxations) related to transport correlate w/ dielectric spectroscopy studies
• Mechanical durability: RH, temperature and current density cycling, contractile stresses in land-groove regions
• Tan $\delta$ vs. T curves for new membranes

- $-\text{CH-S-S-CH-}$
- $-\text{CH-Cl}$, $-\text{CH-OH}$

• FC operation

• Disruption of $-\text{SO}_3\text{H}$

• Aggregates?
• Storage modulus ($E'$) vs. temperature for membranes containing PEG vs. an earlier-synthesized membrane without PEG

- Post-stiffening – thermal – driven reactions? Acid group clustering?
- All modulus changes within an order of magnitude

• Action item:
  - Spectroscopic identification of possible chemical changes with heating.
Plans for the Future and Key Issues:

**Synthesis of membranes:**
- Further optimize the reaction conditions, especially sulfonation conditions, to obtain both high proton conductivity and good mechanical strength with high reproducibility.
- Synthesize more block copolymers of PCHD and PEG and find optimal composition and architecture in order to meet the final proton conductivity outlined by DOE.

**Characterization of membranes:**
- Determine mechanical (stress-strain, creep, stress relaxation) and dynamic mechanical properties related to high temperature stability, durability and fuel cell performance.
- Initiate dielectric spectroscopic analysis of polymer chain motions related to proton transport and degraded macromolecular structure.
- Determine proton conductivity and water sorption isotherms of membranes at different temperatures.
- Inorganic modification of membranes to elevate maximum temperature of water retention and mechanical stability for high temperature fuel cell operation.
- Degrade membrane materials via Fenton’s reagent and characterize samples using above methods.
- Test in fuel cell.

**Utility of membranes in other applications:**
- Lithium ion batteries?

SEEK A NEW FUNDING SOURCE
Summary

Novel promising, inherently inexpensive ion conductive membranes derived from hydrocarbon monomers have been developed. Materials containing short PEG blocks exhibit proton conductivity superior to Nafion® over essentially the entire RH range but fall just short of the DOE Year 3 target. We thank DOE for their support and plan to continue development of these membranes for applications including lithium batteries.