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

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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

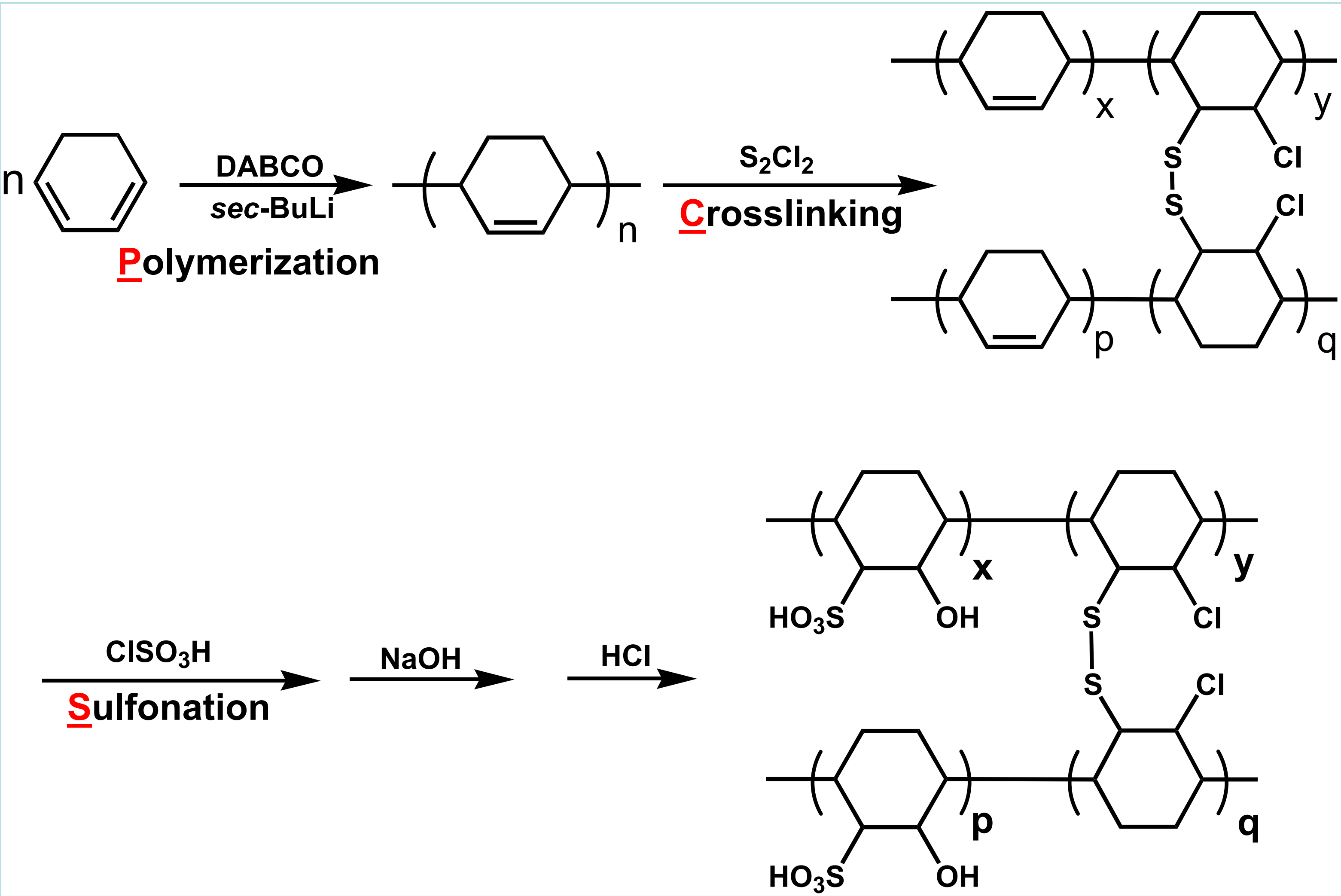
Relevance

- 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

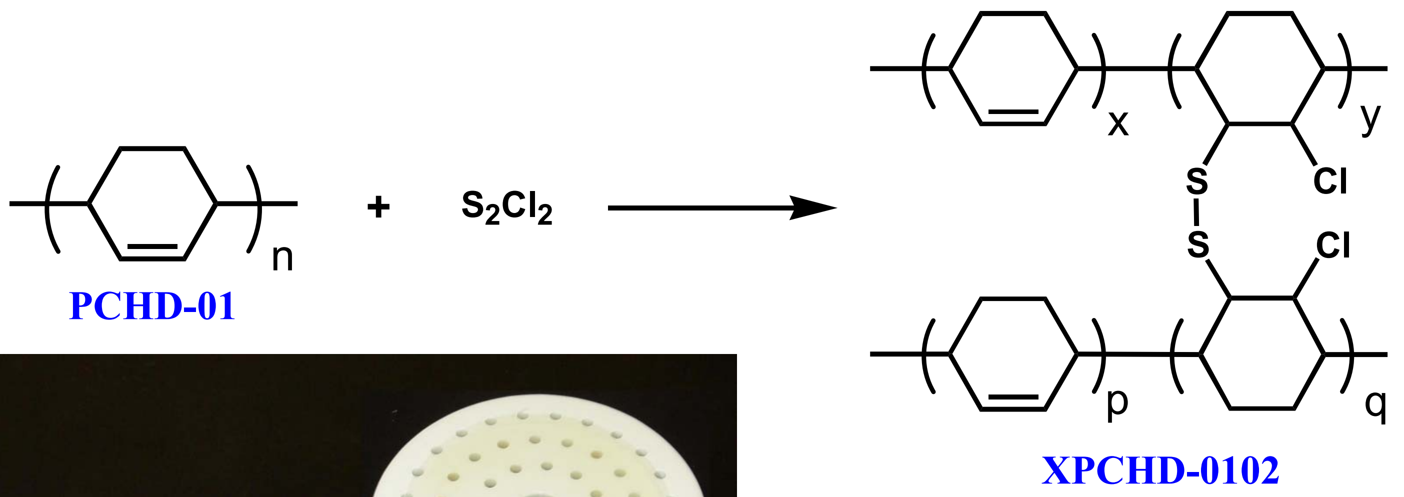
- Anionic polymerization and post-polymerization chemistry will be utilized to synthesize novel thermally stable proton conducting membranes based on a potentially inexpensive hydrocarbon monomer, 1,3-cyclohexadiene.
- Thorough characterization of the membranes will be carried out to understand structure/property relationships.

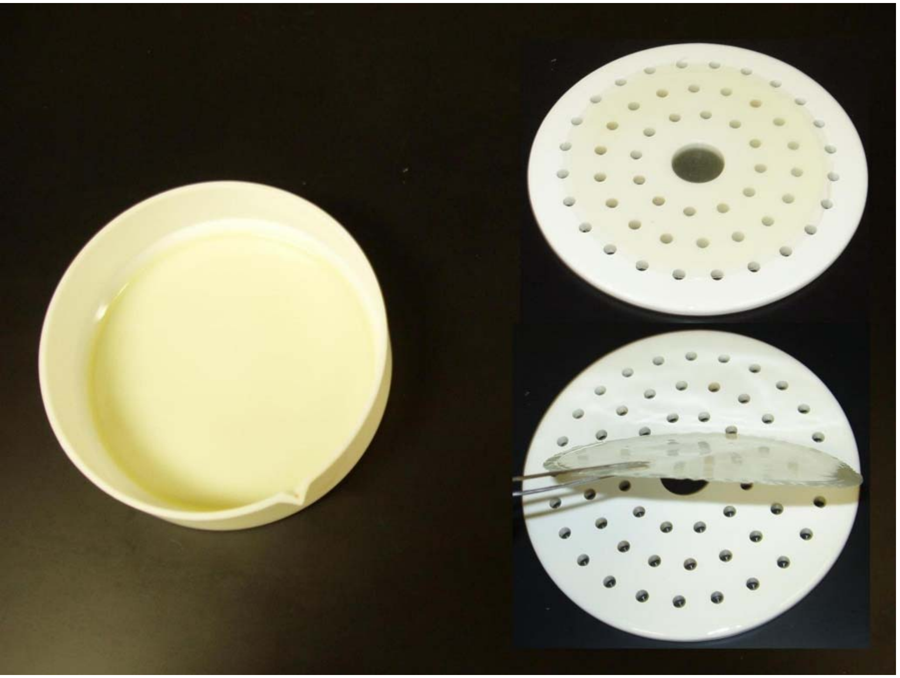
Technical Accomplishments: PCS Approach



Chemistry was optimized over the past year

Cross-linking of PCHD

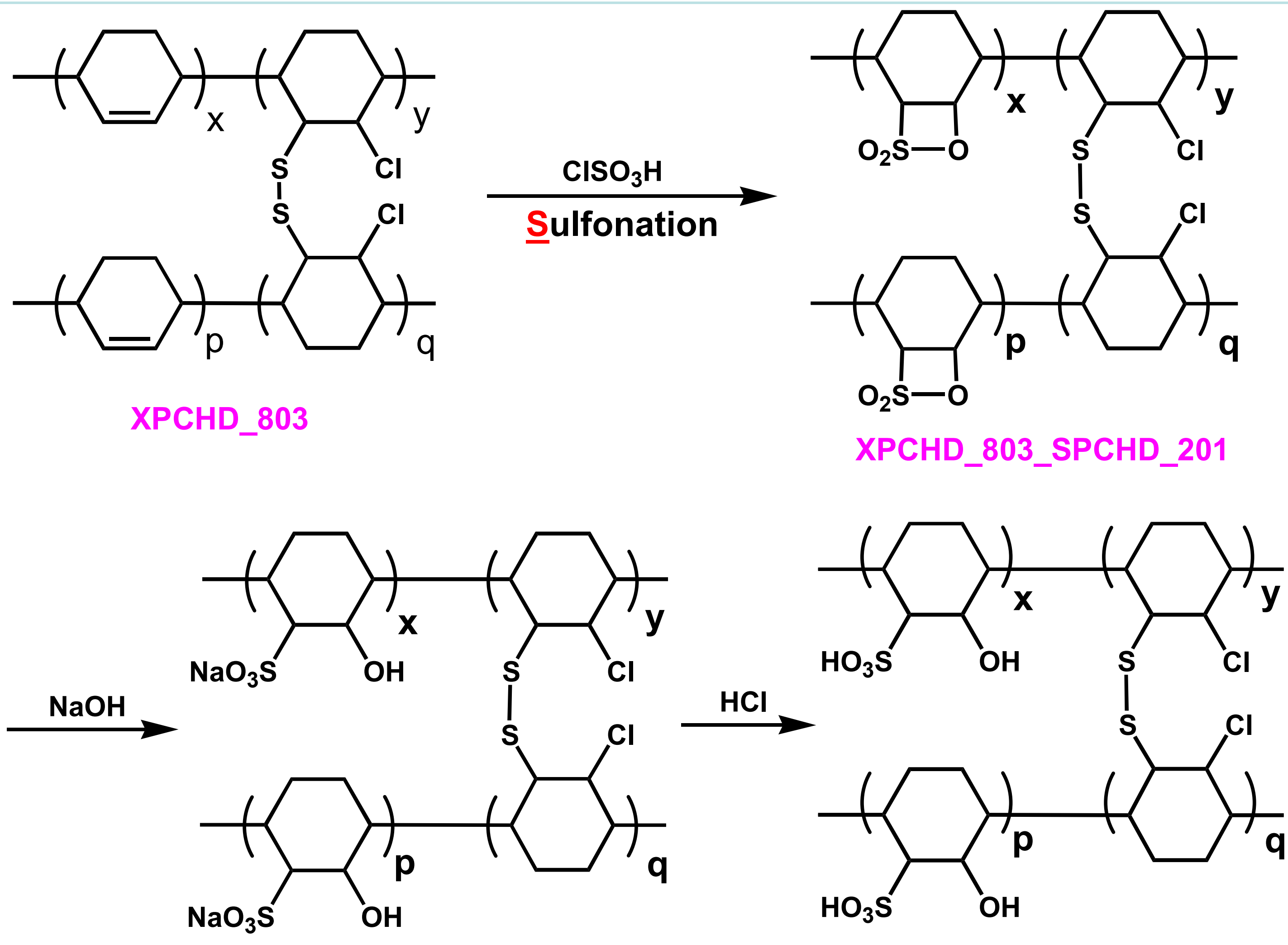




- ~ 5% cross-linked
- Very flat and thin (thickness less than 100 microns)
- Crack - free
- The quality of this membrane is crucial for the subsequent reactions

Membranes made by simple solution casting or melt pressing

Sulfonation: Formation of PEMs



XPCHD_803

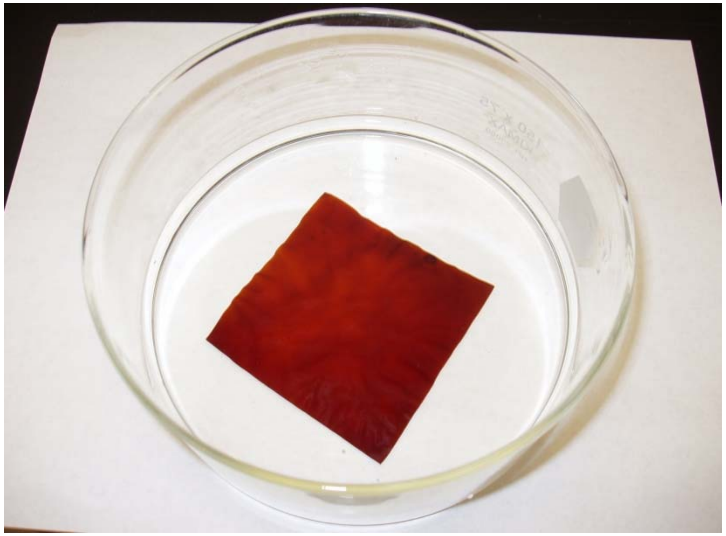
XPCHD_803_SPCHD_201

XPCHD_803_SPCHD_202
Sodium Form

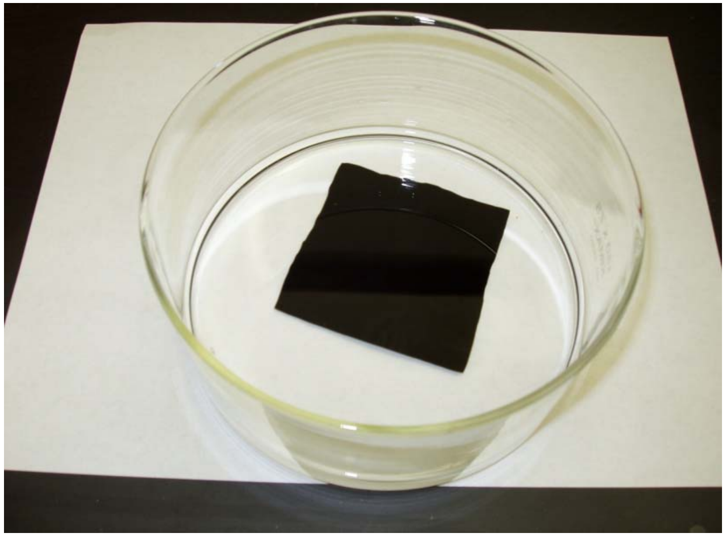
XPCHD_803_SPCHD_203
Acid Form

Photos of PEMs in Two Forms

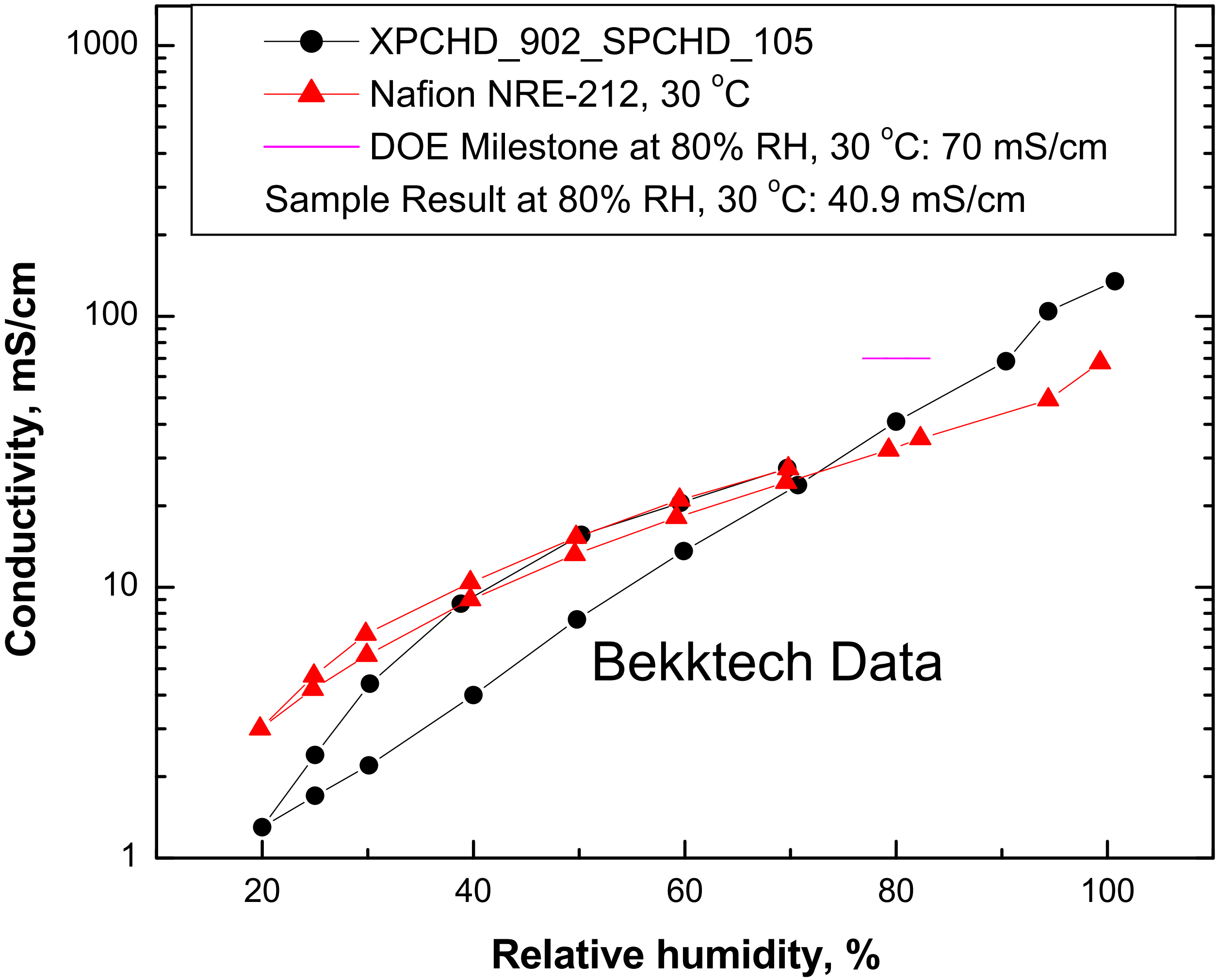
- XPCHD_803_SPCHD_202
  - Sodium Form



- XPCHD_803_SPCHD_203
  - Acid Form



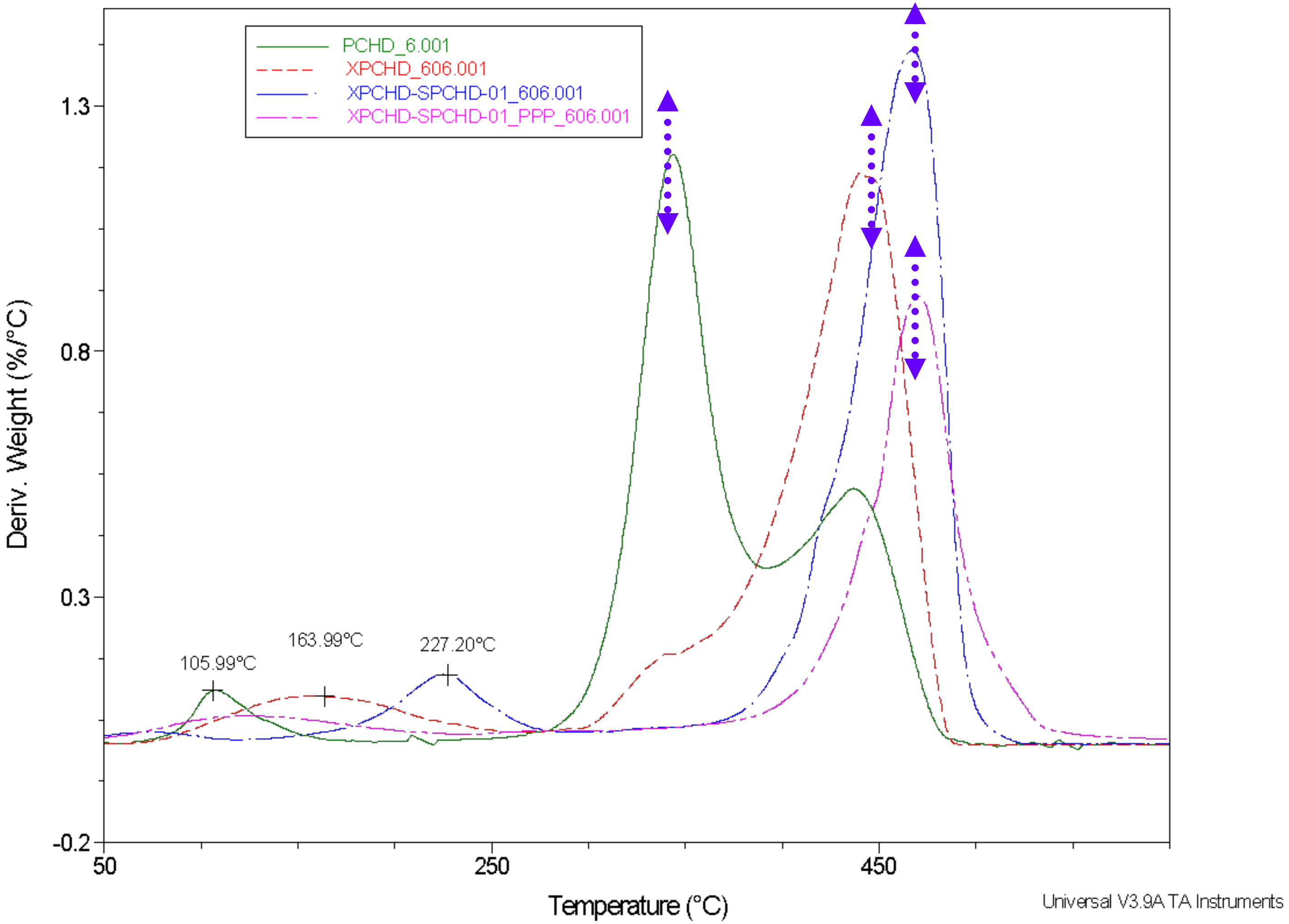
Proton Conductivity & Properties: PCS Approach



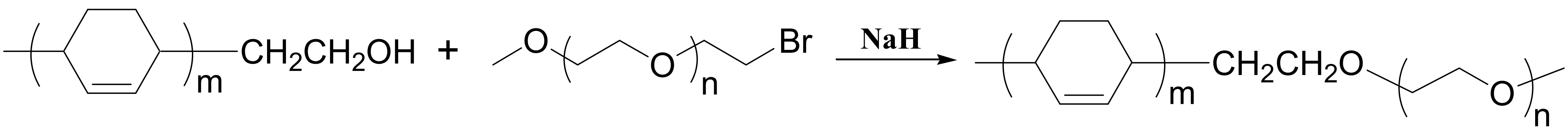
- early samples
- comparable to Nafion® in mid-RH range

Temperature Derivative of Remaining Weight % from TGA Curves for XPCHD-SPPP_606 Sample

Improved thermal stability by crosslinking, sulfonation and aromatization

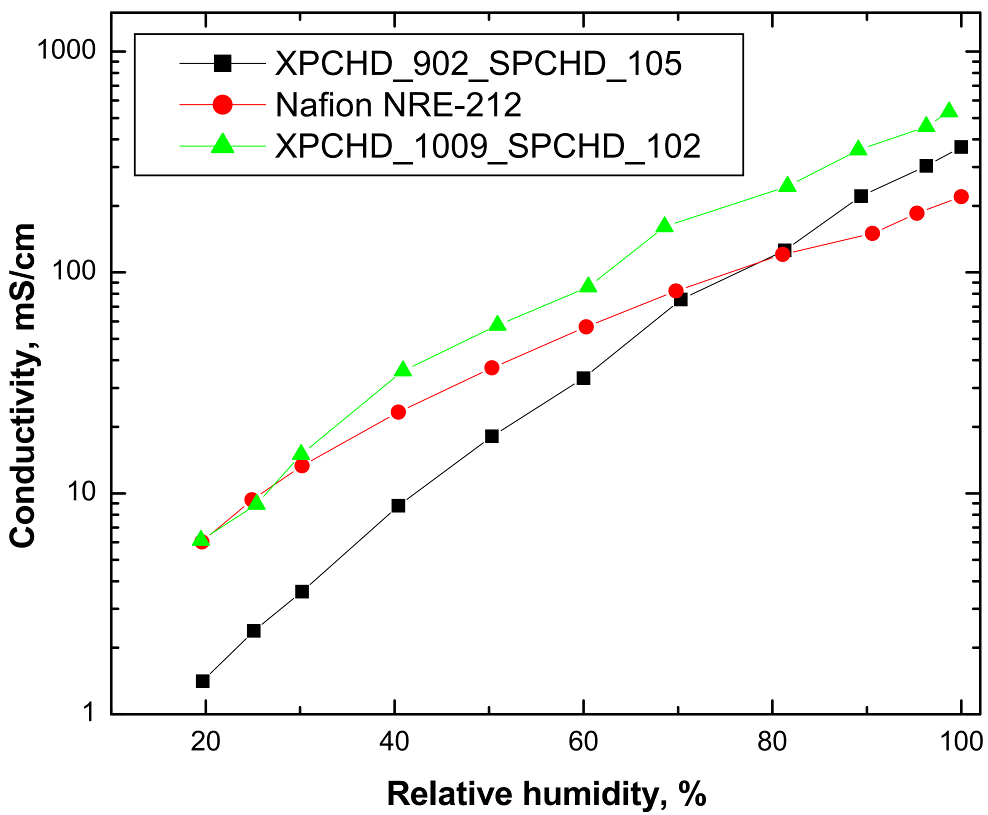


Can we further improve conductivity?



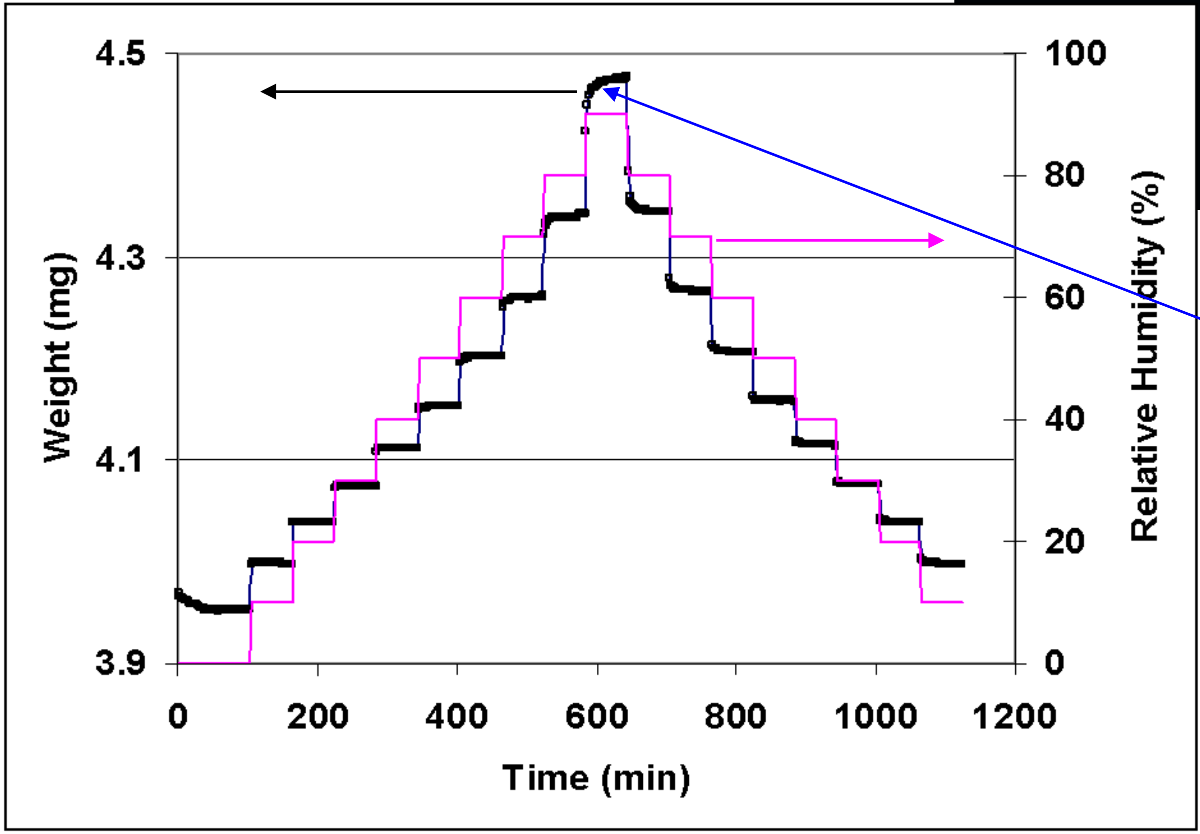
PCHD-OH-02 **MePEGBr-2K** **PCHD-PEG-02**

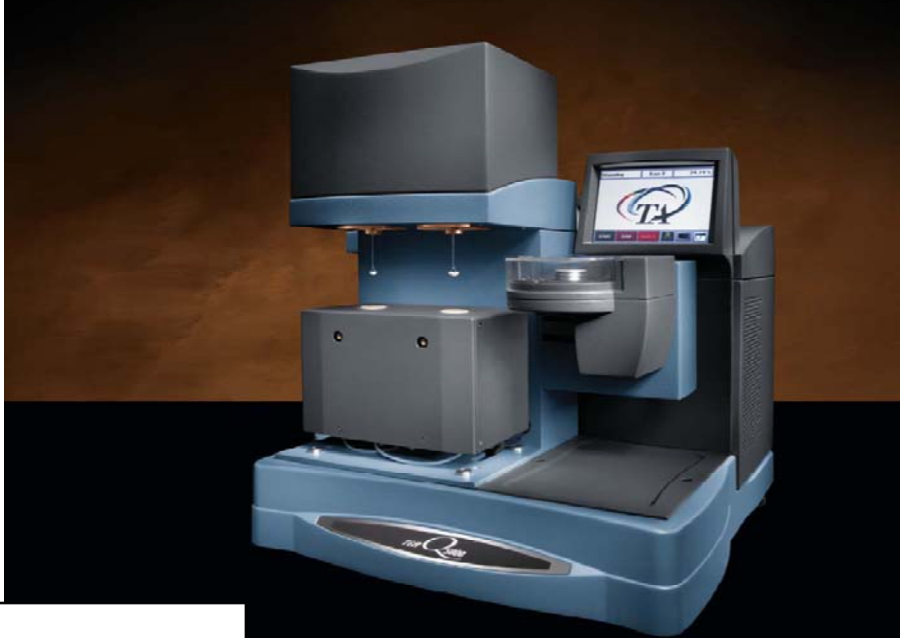
Synthesis of a Block Copolymer of PCHD and PEG: PCHD-PEG-02



Proton conductivity at 120° C vs. relative humidity

•Moisture adsorption/desorption for Nafion® at 80° C



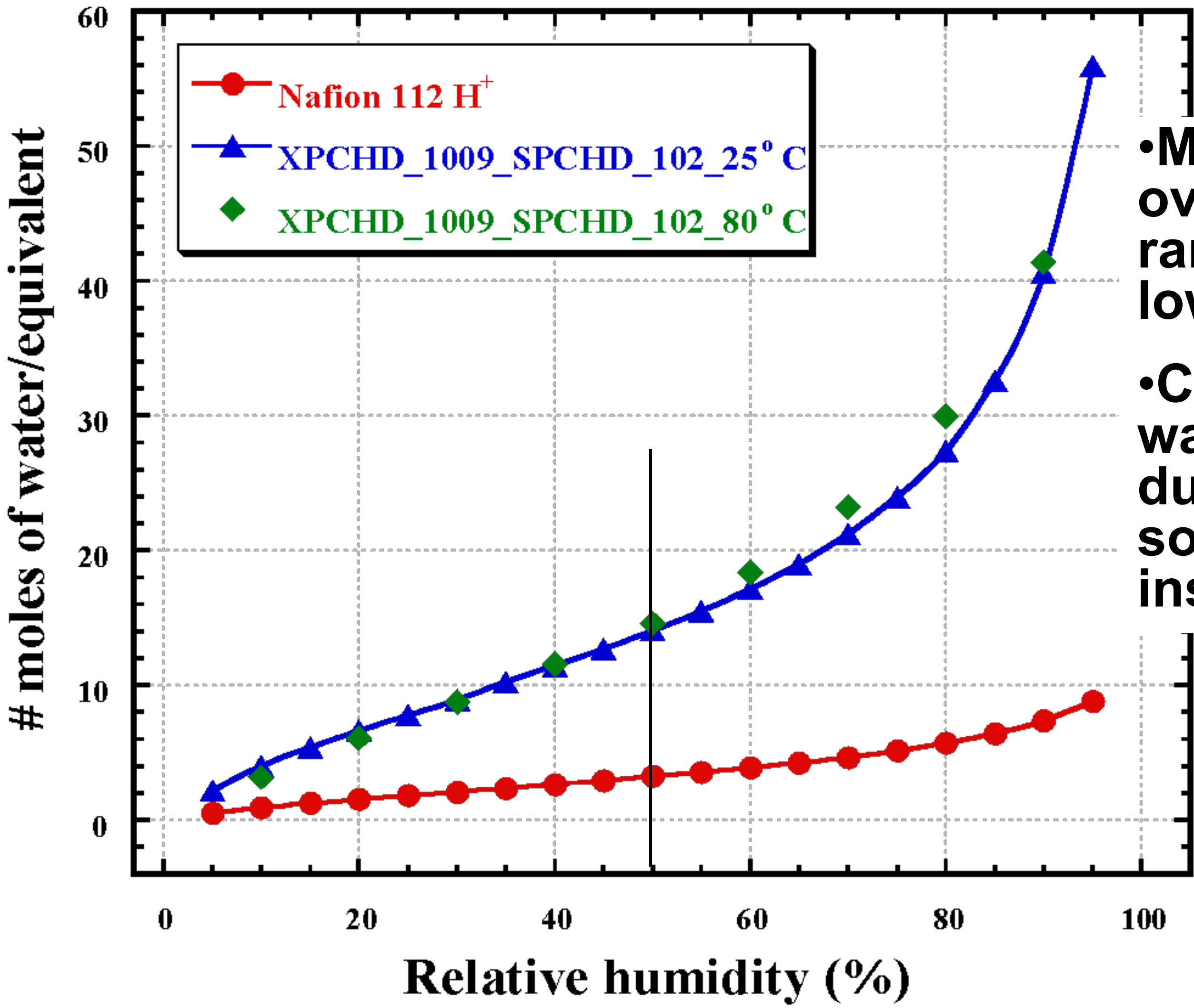


•TA Q5000SA

- also, water vapor uptake kinetics can be determined.
- Plot equilibrium data ⇒

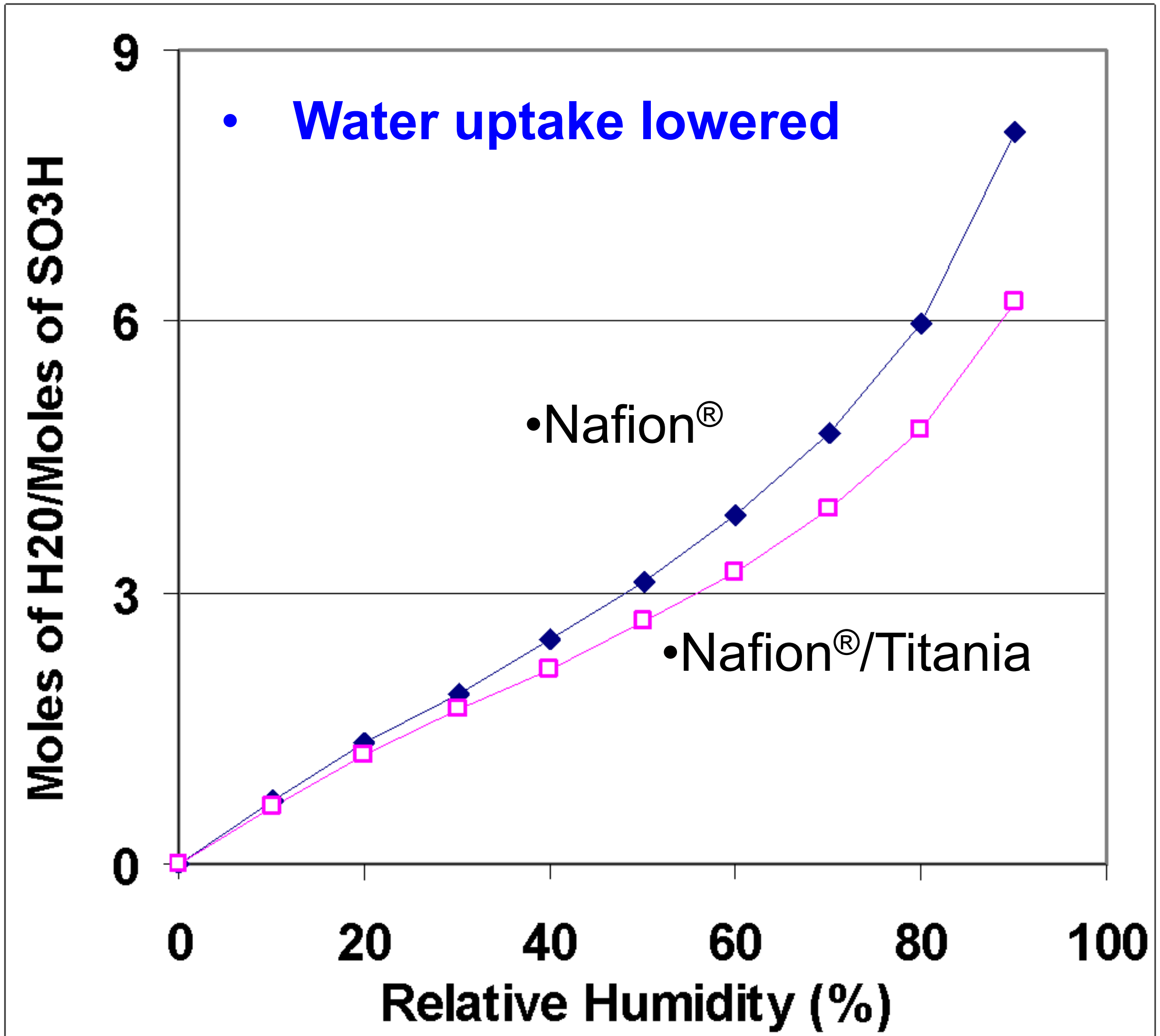
•- Also performed for PCHD- based membranes

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



- More hydrated over entire RH range, including low RH.
- Can reduce water, increase durability w/ sol-gel titanate insertion.

•Vapor Pressure Isotherm at 80° C



•conductivity of Nafion®/titania < Nafion®

-IEC unchanged

-Mechanical modulus increased

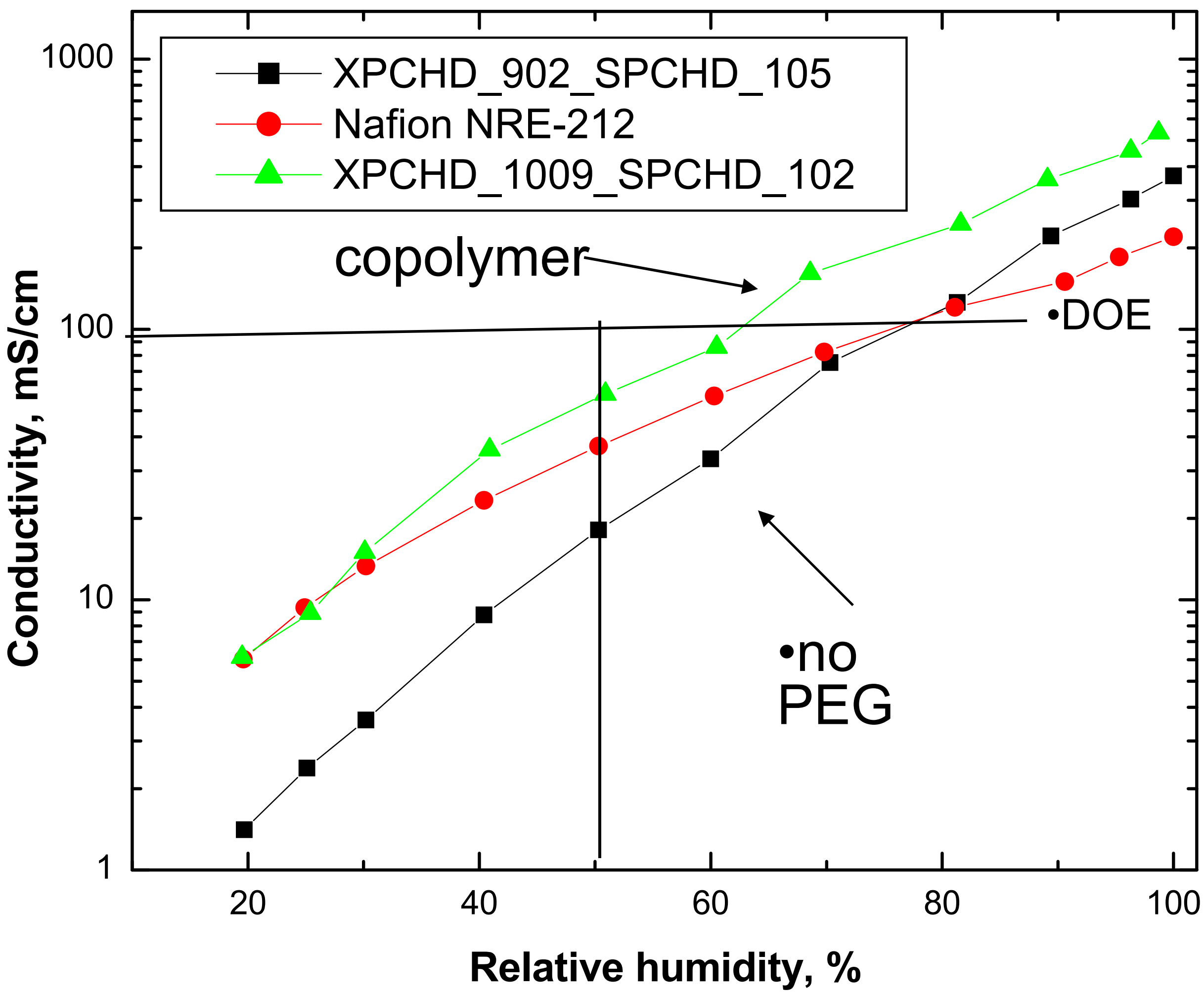
-FER results good

-OCV results good

- polarization curves bad

- **Similar i*n 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

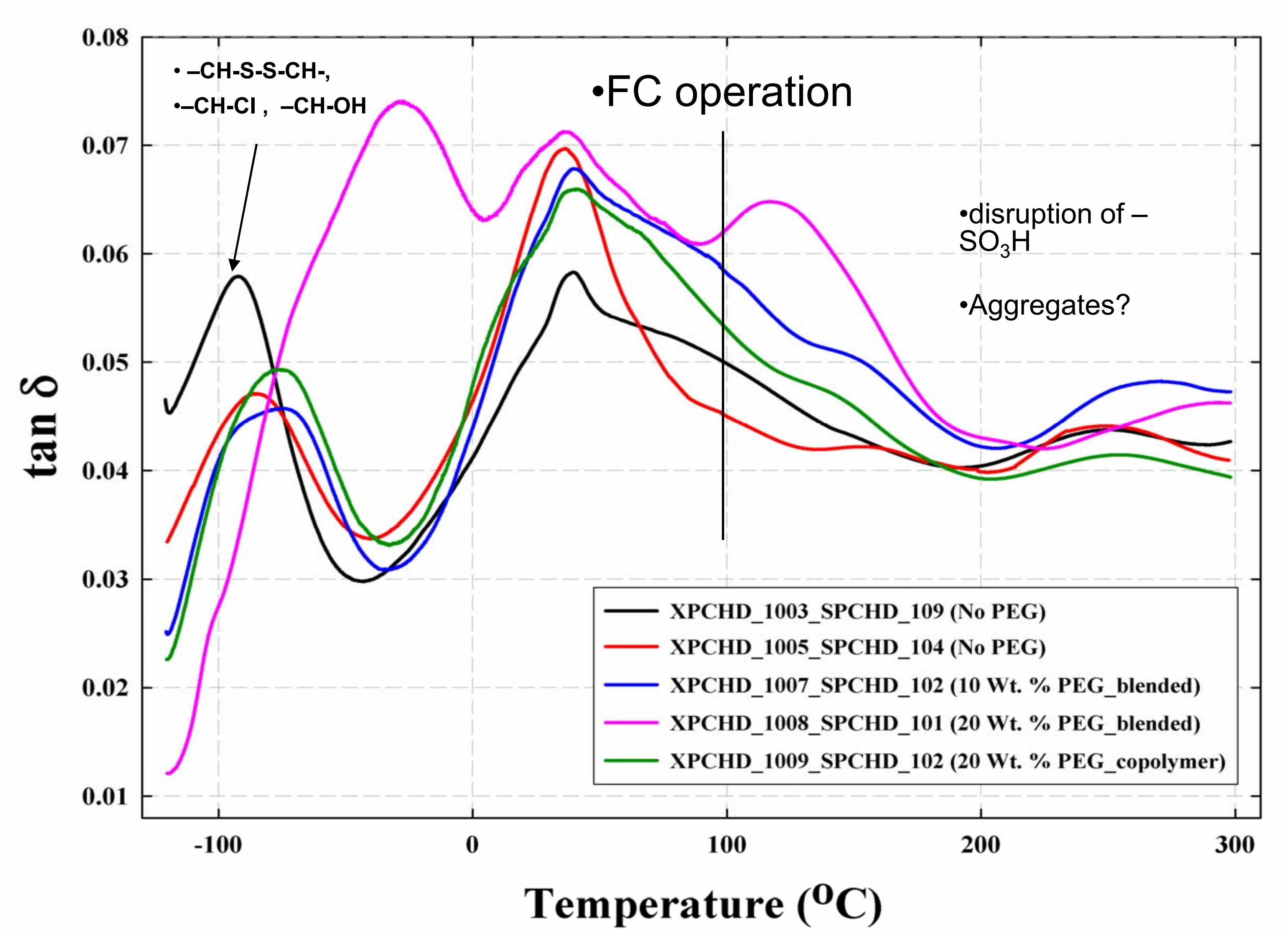
•w/ 230 kPa (~145 kPag) measured at

BEKKTECH LLC

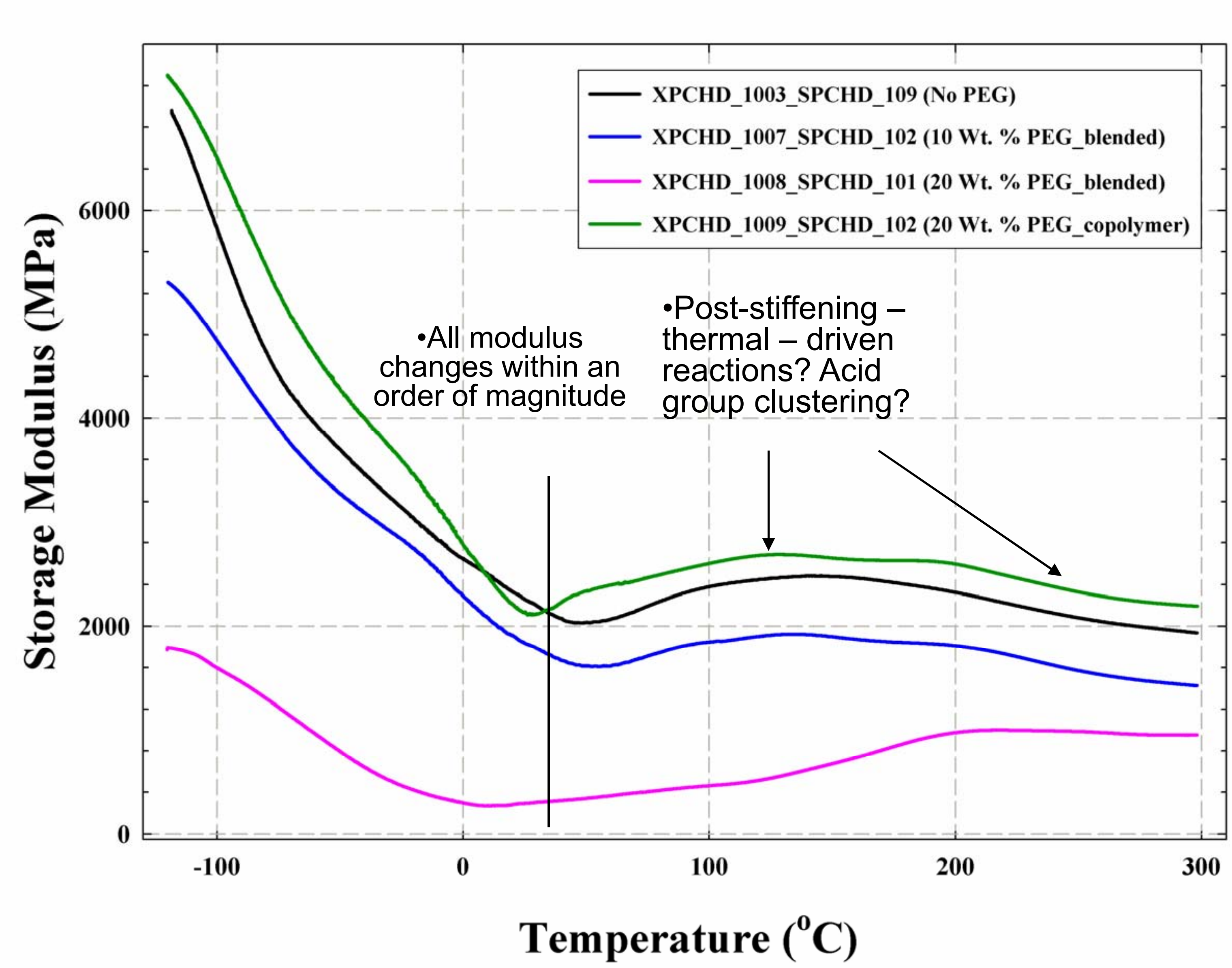
Viscoelastic studies

- 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 δ vs. T curves for new membranes



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



•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 thanks DOE for their support and plan to continue development of these membranes for applications including lithium batteries