New Polyelectrolyte Materials for High Temperature Fuel Cells

John B. Kerr
Lawrence Berkeley National Laboratory (LBNL)
Collaborators:
UC Berkeley (UCB)
Los Alamos National Laboratory (LANL).
3M Company

June 11, 2010

Project ID #
FC 033

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

Overview

Timeline

- Project start – February 2007
- Project end –March 2011
- Percent complete – 75%

Budget

- Total project funding
  - DOE share $6,000k
  - Contractor share - in-kind (up to $1,000k) plus NSF studentships (UCB)
- Funding received in FY0

  - $1550k
- Funding for FY10 - $1550k

Barriers

E. System Thermal and Water Management.

A. Durability

B. B. Stack Material and Manufacturing Cost.

C. Electrode Performance.

Team/Partners

- Jeff Reimer, Nitash Balsara, Rachel Segalman(UCB/LBNL), Adam Weber (LBNL).
- Yu Seung Kim, James Boncella (LANL)
- Steve Hamrock (3M Company)

Relevance - Long Term Objectives

- Develop knowledge that leads to materials that can meet the performance needs at acceptable cost.
- Fuel Cells that operate efficiently without external humidification and at operating temperatures between -40°C and 120°C.
  - Durable water-free membrane materials that meet the 2015 DOE targets as set out in the Multi-Year R&D Plan.
    - Conductivity: 0.1S/cm at operating temperatures ($\leq$ 120°C) and inlet water vapor partial pressures <1.5 kPa.
    - Durability with cycling > 5000 hours at > 80°C.
    - Oxygen and Hydrogen cross-over currents $\leq$ 2mA/cm^2.
  - Durable MEAs with rated power at 1,000 mW/cm^2 and less than 5% performance degradation over lifetime.

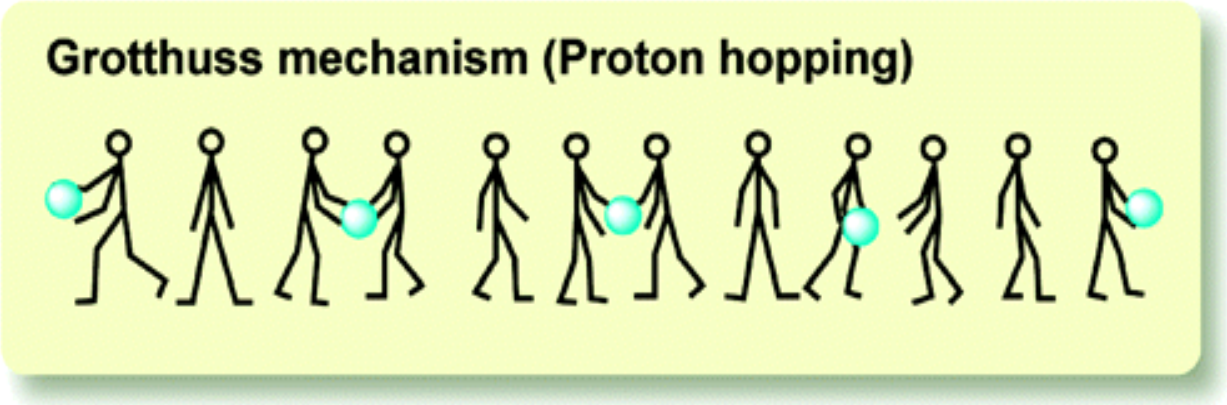
Project Objectives

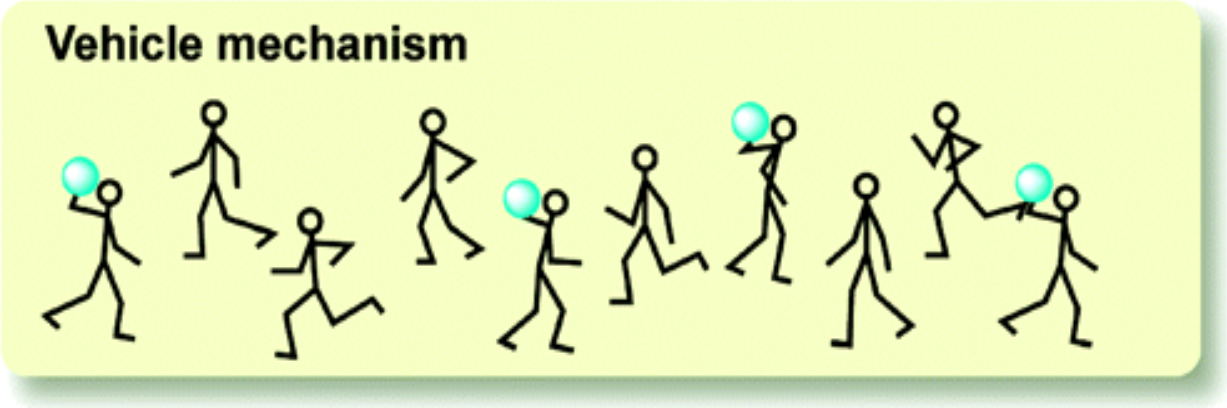
- Investigate the feasibility of polyelectrolyte proton conductors that do not require additional water to achieve practical conductivities (0.1 S/cm at 120°C, 25% RH).
  - Prepare and test proton conducting materials based on heterocyclic bases (imidazole) and acids (sulfonates, sulfonylimides) – ionic liquids, doped polymers.
  - Prepare and test solid polyelectrolytes at low water levels (25-50% RH) – most solvent and all acid groups tethered to the polymer backbones.
- Determine stability of these materials to oxidation and strong acids.
- Fabricate and test MEA's.
  - Determine gas crossover

Approach – Go/No-go Decisions

Month/Year/Status	Milestone or Go/No-Go Decision
March/09/ Completed 11/09	**Milestone:** Complete correlation of conductivity with polymer structure and morphology. Estimate conductivity limit of tethered base materials. Determine conductivity of membrane at 0 to 25% RH and the full range of temperature (-40 - 120°C) and compare to target of 0.1 S/cm in the absence of free solvents. **Go/No-Go Decision Criteria:** How close to 0.1 S/cm at 0 to 25% RH and the full range of temperature (-40-120°C) is possible without free solvents?
March/11/ On Track	**Milestone:** Durability **of** Imidazoles, other heterocylic bases and tethered imidazoles determined under fuel cell test conditions. **Go/No-Go Decision Criteria:** 1) Rate of reaction of imidazoles, other heterocyclic bases and polymers containing heterocylic bases with reactive oxygen is no greater than the rate of degradation of 3M PFSA 2) The presence of inhibitor/scavenger molecules has been shown to slow the reaction rate of imidazoles by at least a factor of two.
March/11/ On Track	**Milestone:** MEA fabrication methods developed with Task 1 polymers and/or polymer blends to provide satisfactory performance with Pt catalyst electrodes – 0.5V at 0.5A/cm^2 at 120°C, <25%RH **Go/No-go Decision Criteria:** Do the heterocyclic bases poison the Pt catalyst, i.e. failure to perform is due to electrode kinetics not mass transport or conductivity.

Approach - Proton Transport





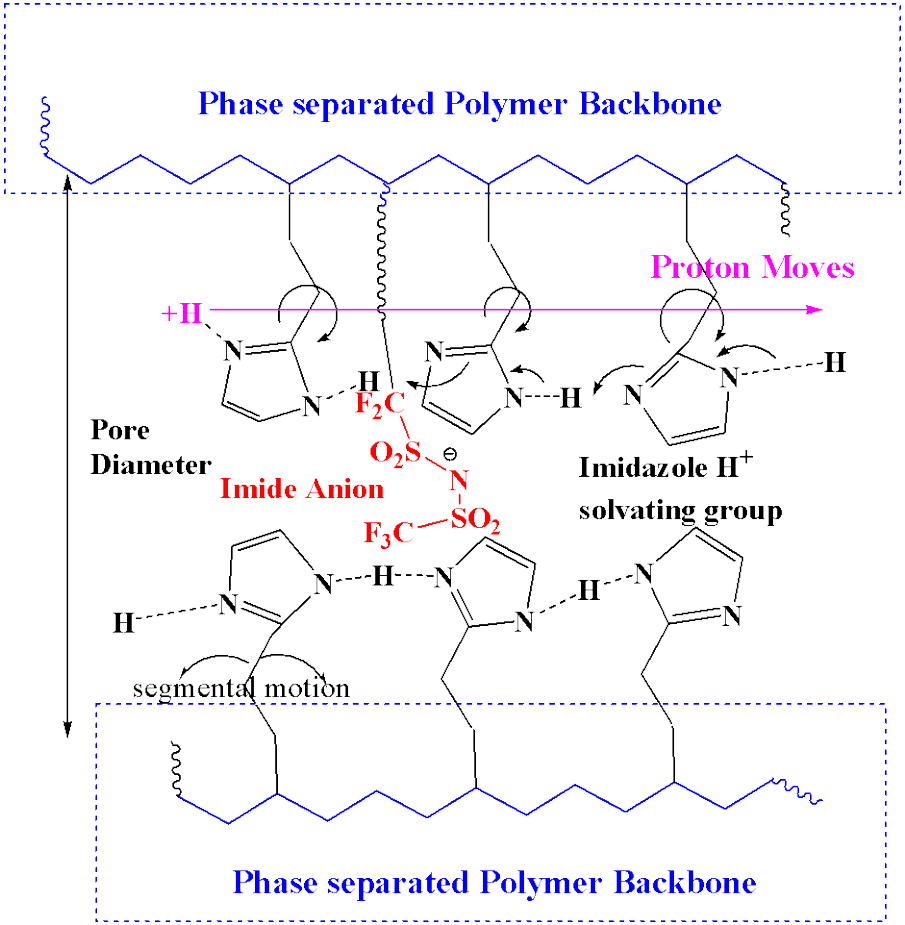
Grotthuss-type transport is necessary to reach 0.1S/cm at 120°C and practical conductivities at lower temperatures.

Grotthuss transport requires some degree of solvent organization (e.g. H-bonding in water or imidazoles) and a containment matrix.

Vehicle & segmental motion mechanisms require too much energy for 0.1S/cm.

Acknowledgement: K.D. Kreuer *et al*, Angewandte Chemie Int. Ed. Engl.(1983), No.3, 208.
Illustration from Macromolecules, 41 (2008), 3739

APPROACH to Material Design of Polymers to support Grotthuss Transport.



Tether heterocyclic bases (e.g. imidazoles) and acid groups to polymers

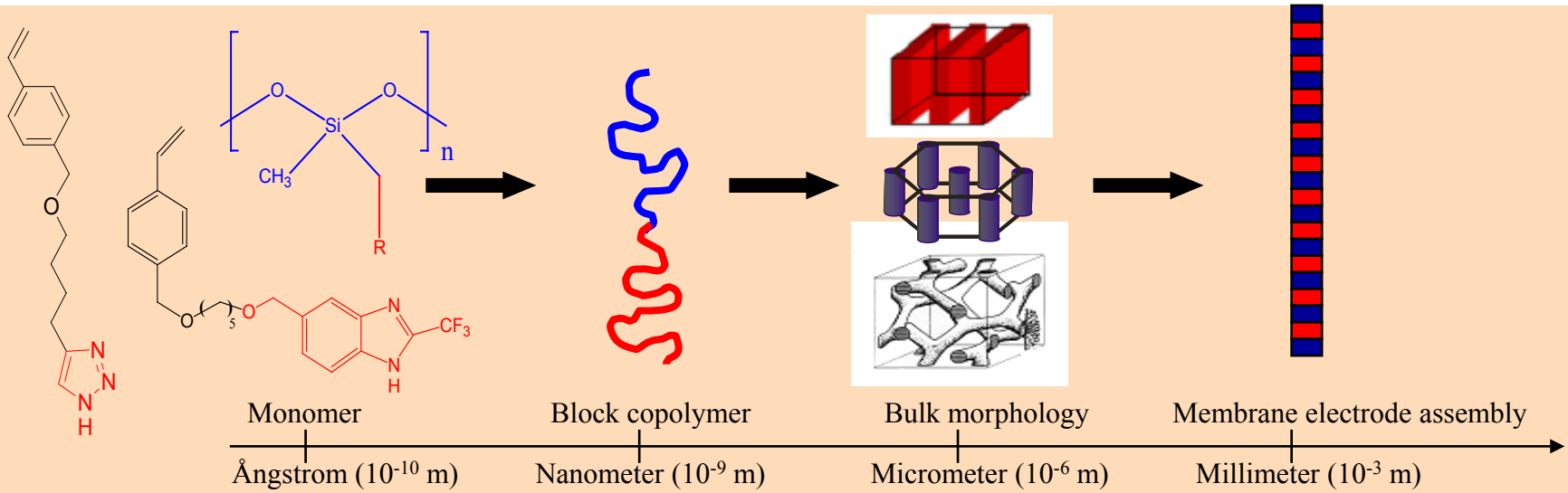
Determine optimum acid/base ratios from ionic liquid and polyelectrolyte doping studies.

Provide appropriate phase separating polymer backbone to facilitate solvent organization (Grotthuss transport).

Keep imidazole tether short to increase organization, prevent tether disrupting proton transport and maximize concentration.

Approach

Block Co-polymers for Morphology Control to Provide Connective Channels?



Synthesize model protogenic monomers with heterocyclic groups

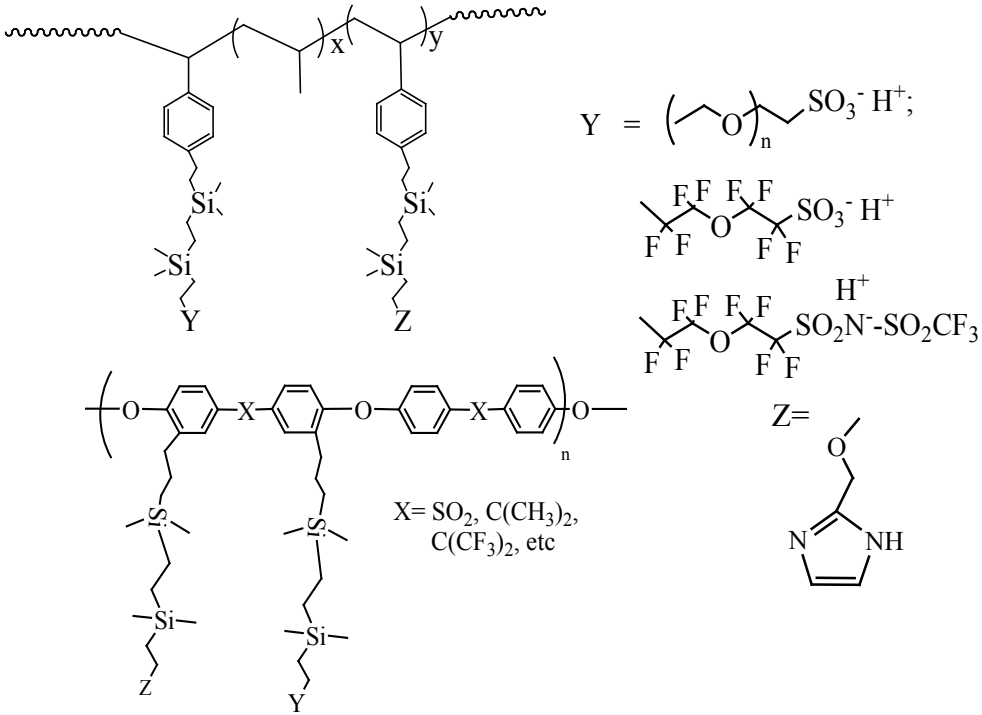
Well defined block copolymers through controlled polymerizations

Tailored morphologies (lamellar, cylindrical, gyroid) produce proton conducting channels

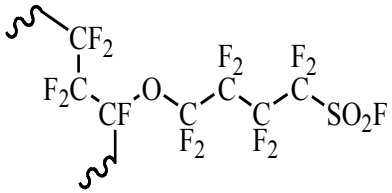
Membranes and MEA's that balance conductivity and structural integrity

Acknowledgement: Brian Coughlin, U. Mass, Amherst

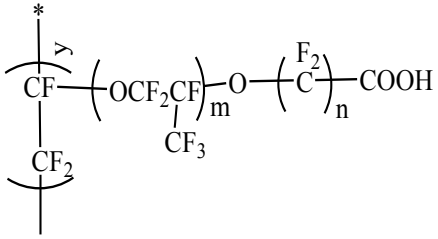
Approach – Synthesis of the Membrane Materials. Three Backbones, Many Side Chain Variations



Polystyrene and Polysulfone backbones provide for phase separation and the possibility for block copolymers to vary the morphology. Side chains can be varied to provide acid/ base ratios and vary tether length and flexibility. Base polymers are commercially available.



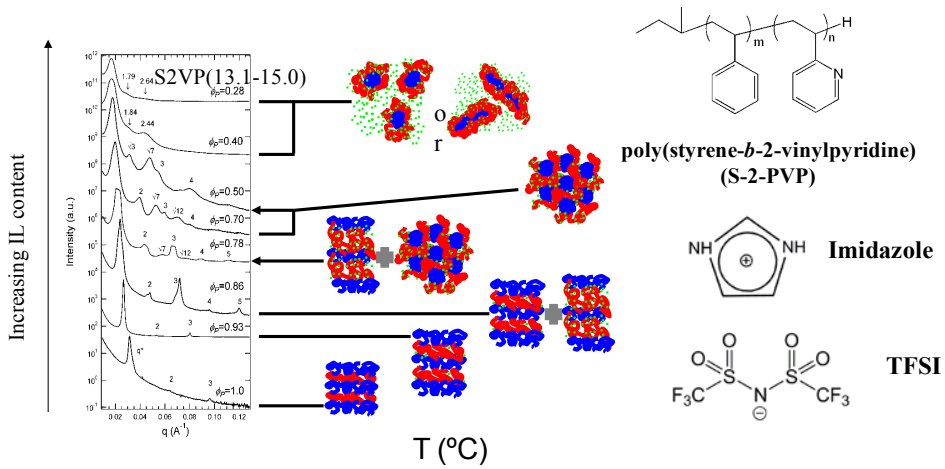
Perfluorinated precursors – generate sulfonic acid, imide acid and attach heterocylic bases.



Membranes and MEAs have been prepared from similar polymer materials.

Ionic Liquid Models in Polymer Matrices

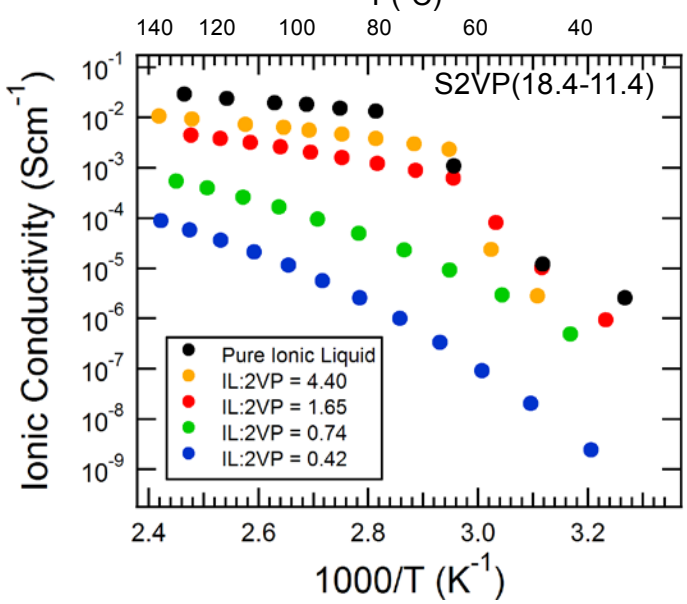
SAXS of Ionic Liquid-block copolymer



poly(styrene-*b*-2-vinylpyridine)
(S-2-PVP)

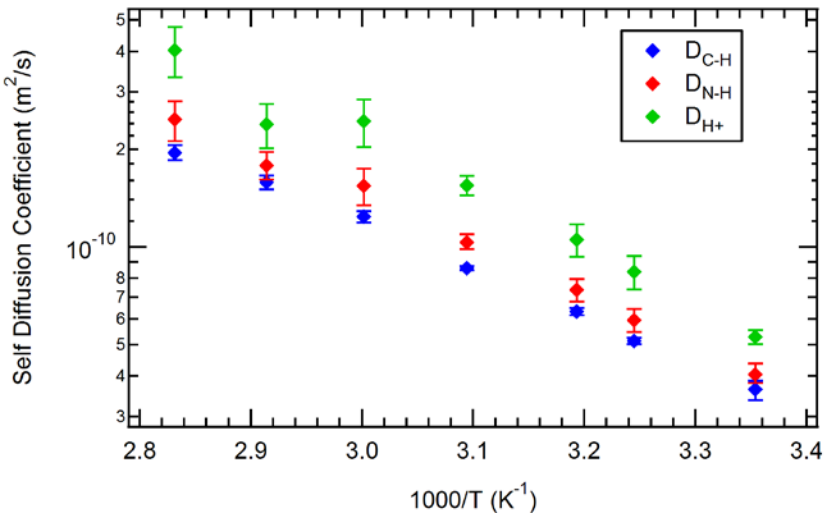
Imidazole

TFSI



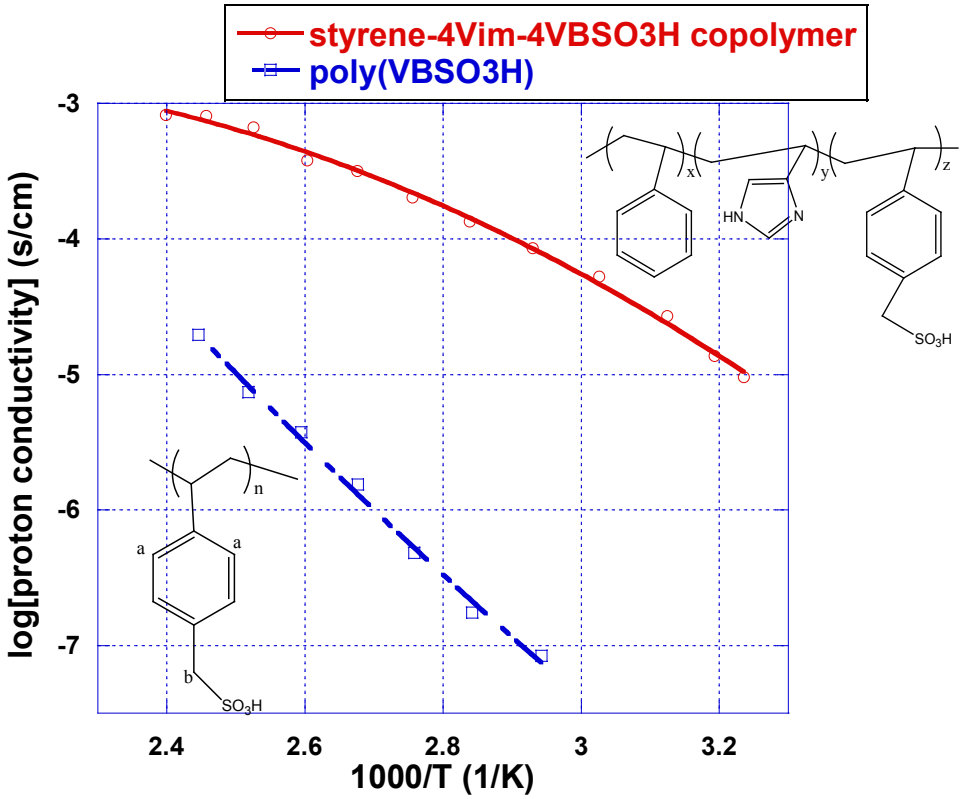
Conductivity of Ionic Liquids in block copolymer

Ionic liquid partitions into pyridine phase. Conductivity shows low E_{act} for ionic liquid which increases with polymer fraction. PGSE NMR measurements show evidence for Grotthuss transport for IL but segmental motion dominates as polymer fraction increases.



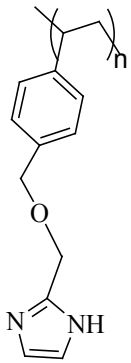
^{1}H PGSE NMR measurements of C-H and N-H self diffusion coefficients of ionic liquid alone. Faster H^+ diffusion indicates Proton hopping

Imidazole Co-polymers

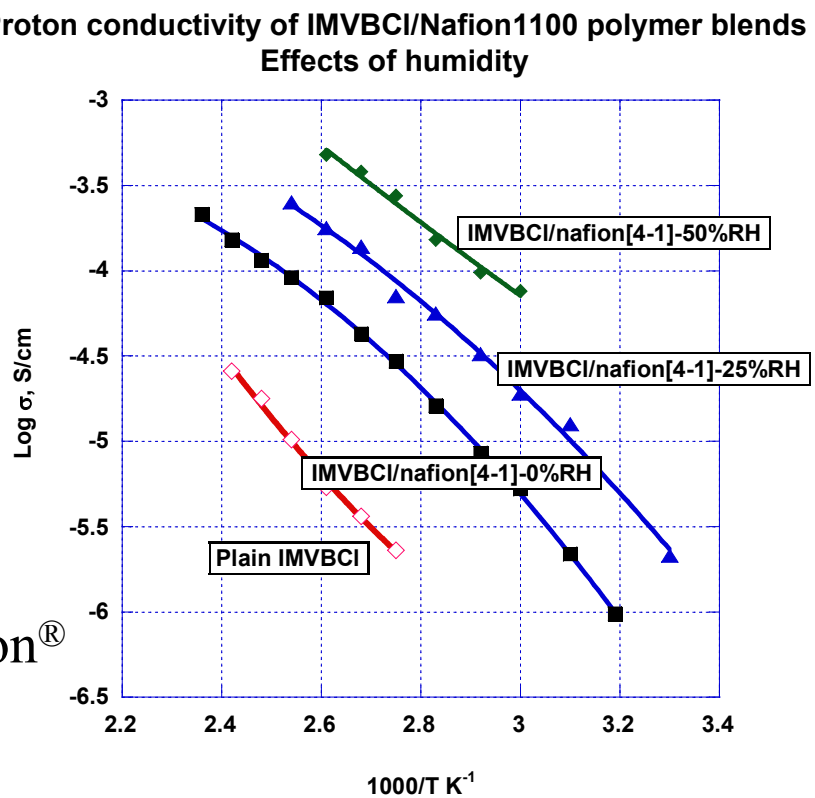


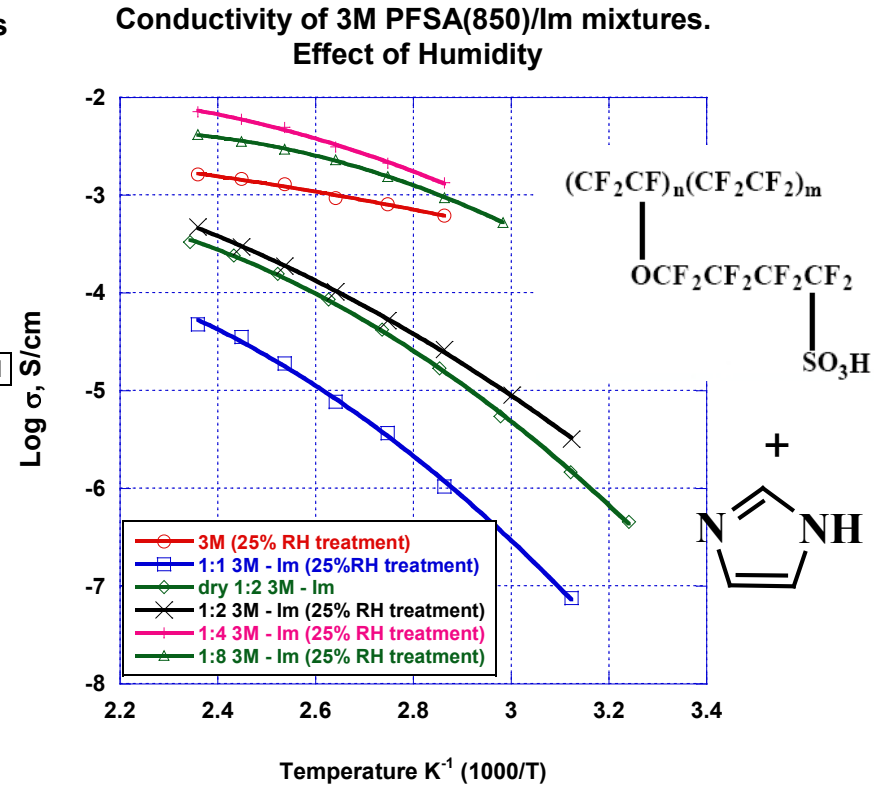
- Ratio of Styrene:imidazole: sulfonic acid was 4:5:1
  Acid EW ~1000
- Conductivities measured in through plane mode under dry conditions.
- Temperature dependence of conductivity indicates segmental motion control.

Proton Conductivities of Blends of Polymers and Free solvents.



Plus Nafion®





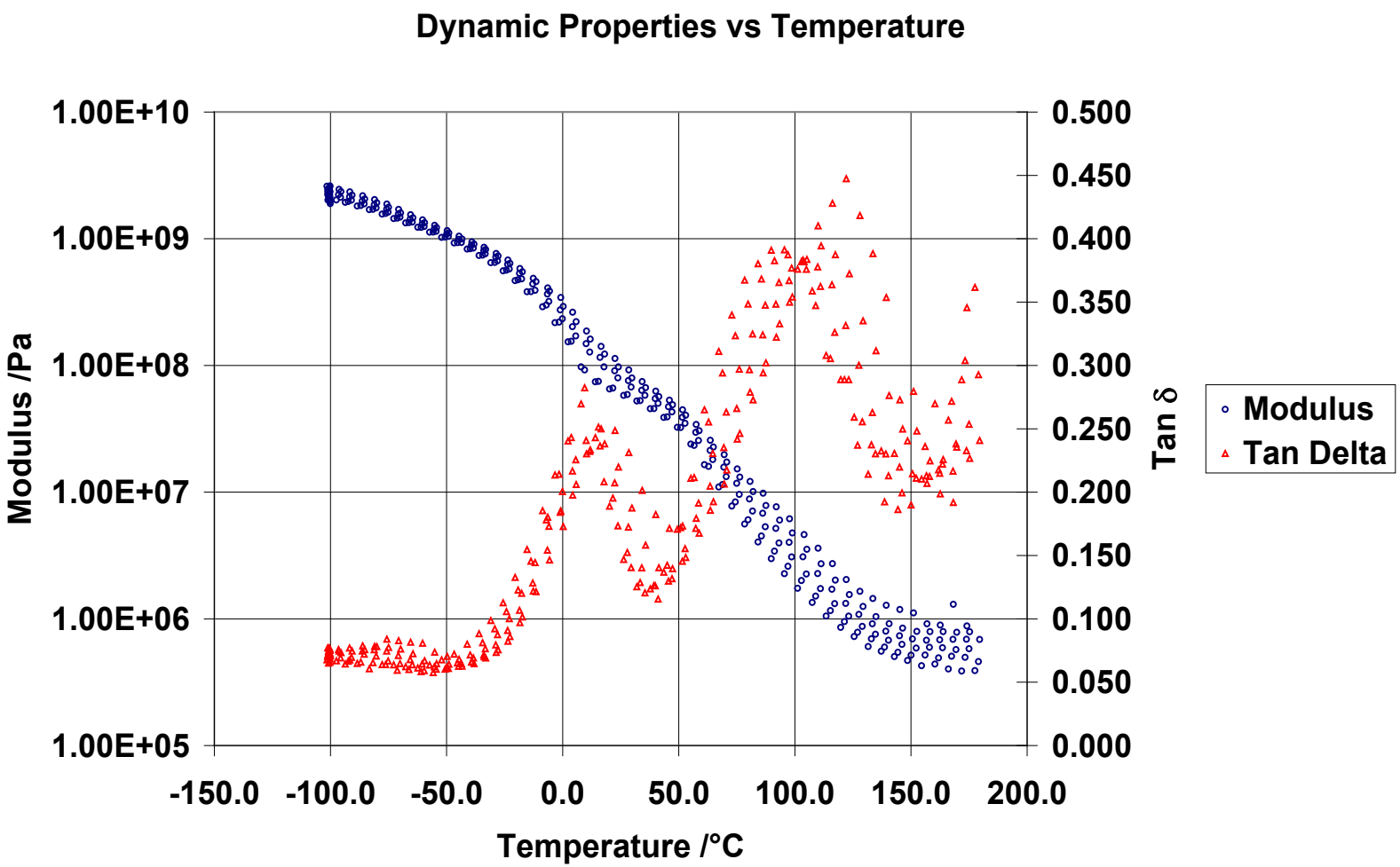
Effective Acid EW ~ 2,000

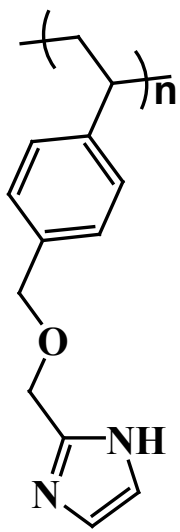
Thermal and Mechanical properties

•IMVBCl : Nafion® - 4:1 blend -IMVBCl polymer is thermally stable up to 200°C and has reasonable mechanical stability when blended with Nafion®.

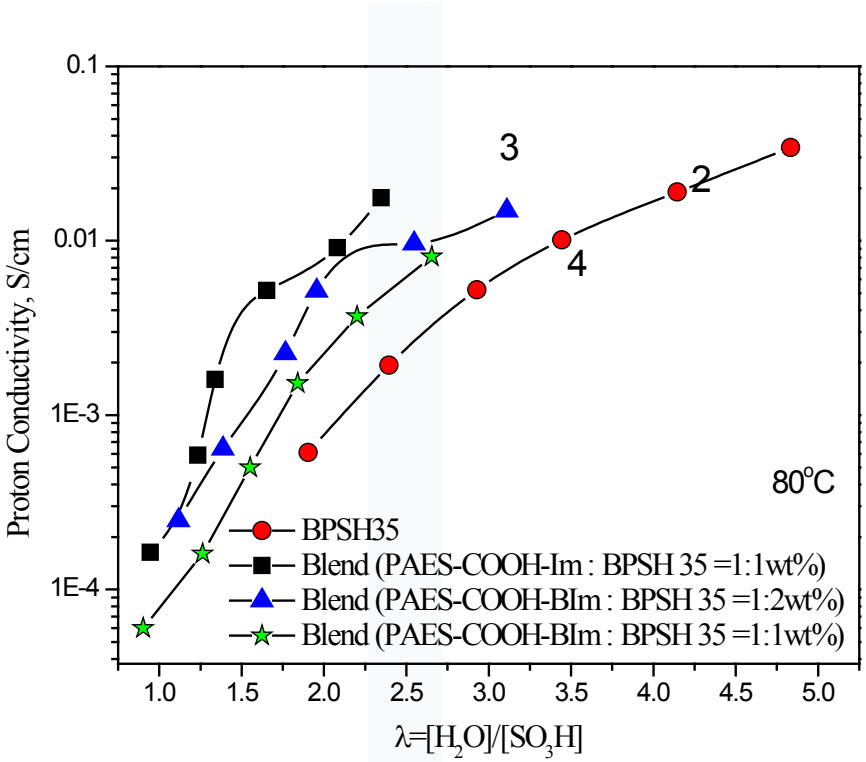
•IMVBCl plasticizes Nafion®.

•Temperature changes proton conductivity and mechanical properties





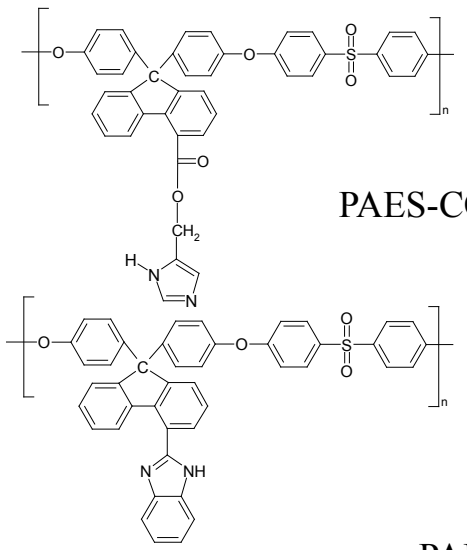
Proton Conductivities of Blend Membranes



Proton Conductivity at λ = 2

1 - 0.61 mS/cm
2 - 5.1 mS/cm
3 - 9.1 mS/cm
4 - 1.5 mS/cm

BPSH 35 (IEC = 1.54 meq./g)



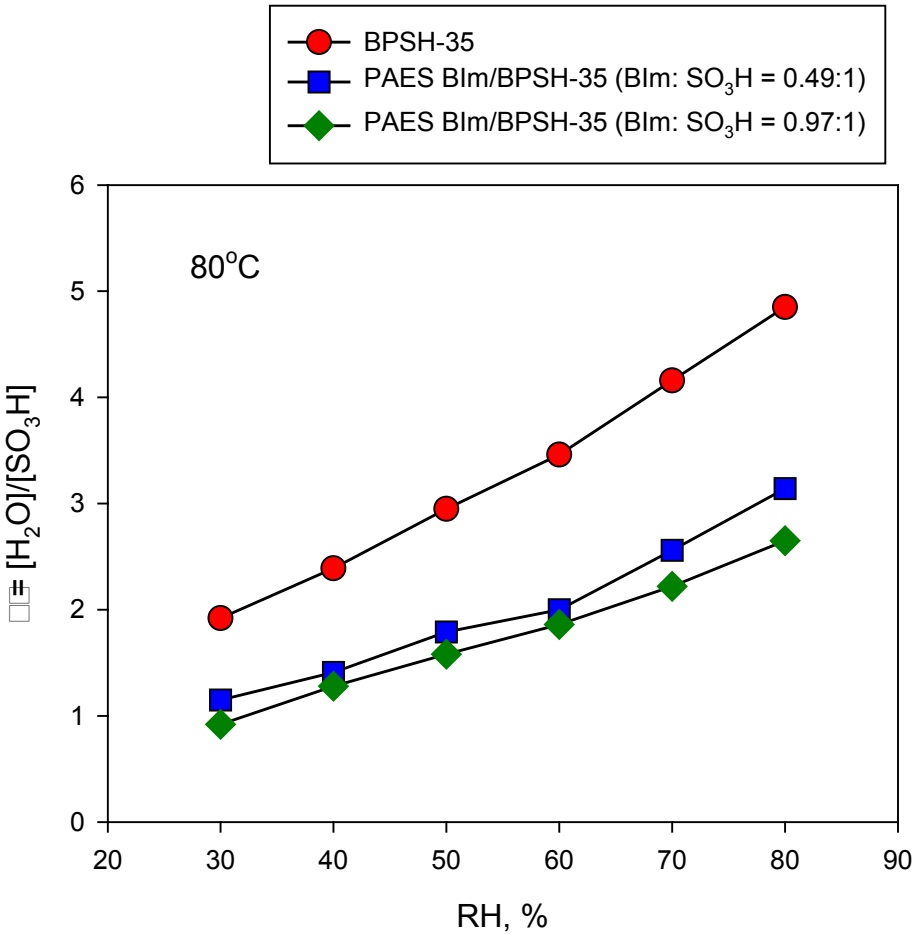
PAES-COOH-Im

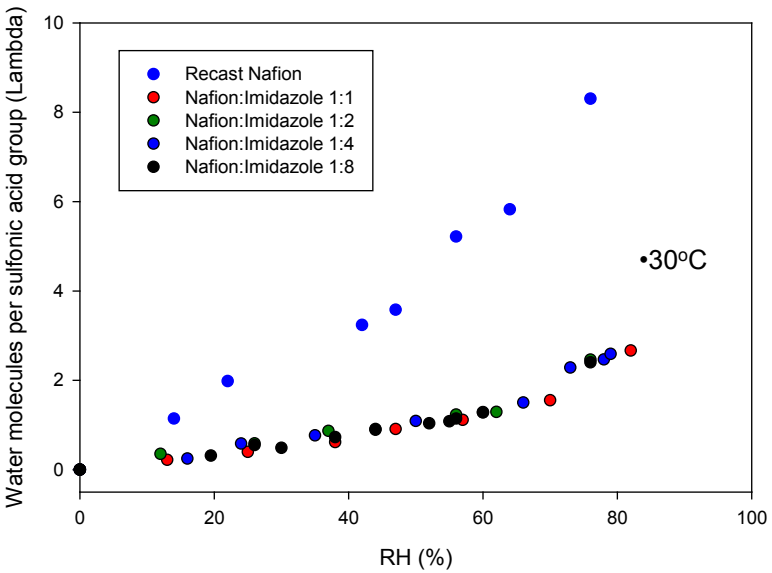
PAES-COOH-BIm

➢The blend membrane with same water molecules per sulfonic acid group (λ) showed high proton conductivity compared to pure sulfonated polymer.

14

Effect of Imidazole Polymers on Water Uptake



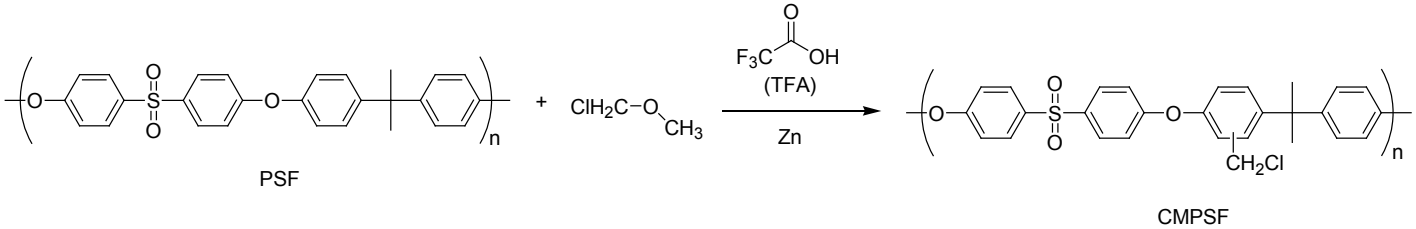


- Water vapor uptake suppressed by presence of imidazole.
- Membrane blends with imidazole or (imidazole tethered polymers) reject water.

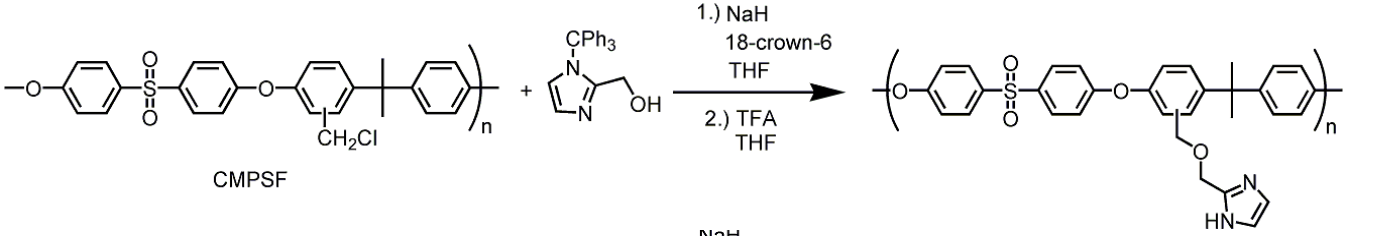
Nafion is a registered trademark of E.I. du Pont de Nemours and Company

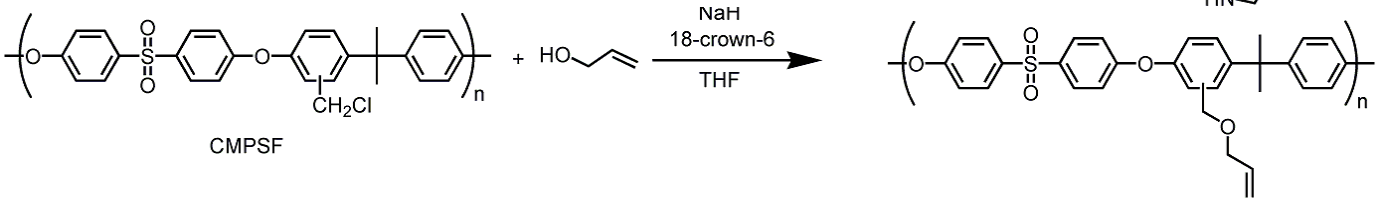
Polysulfone Modification

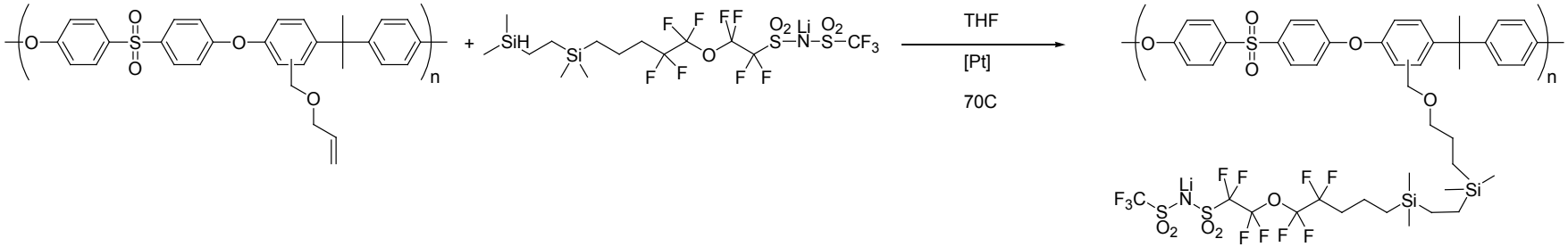
- Chloromethylation via an electrophilic substitution



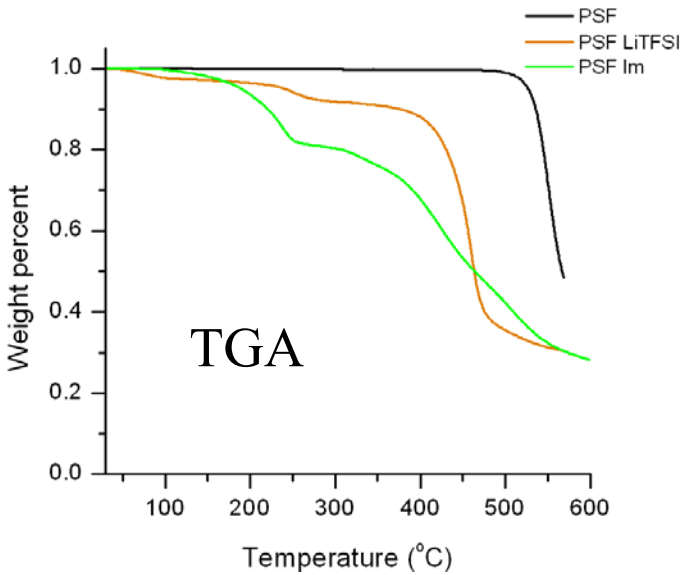
- The polymer was functionalized via ether linkages with imidazole or allyl groups

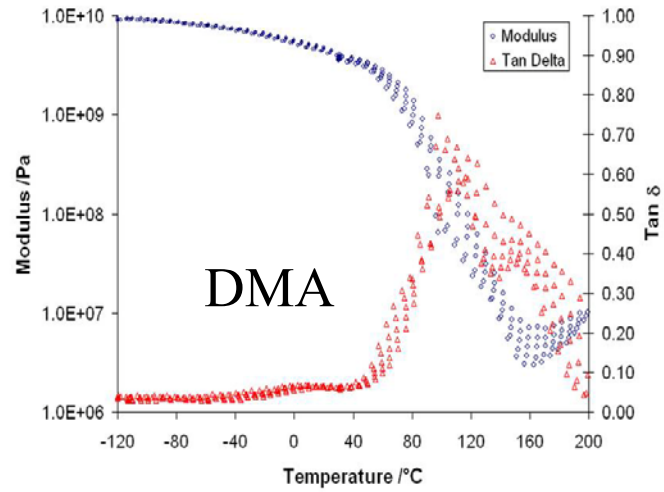


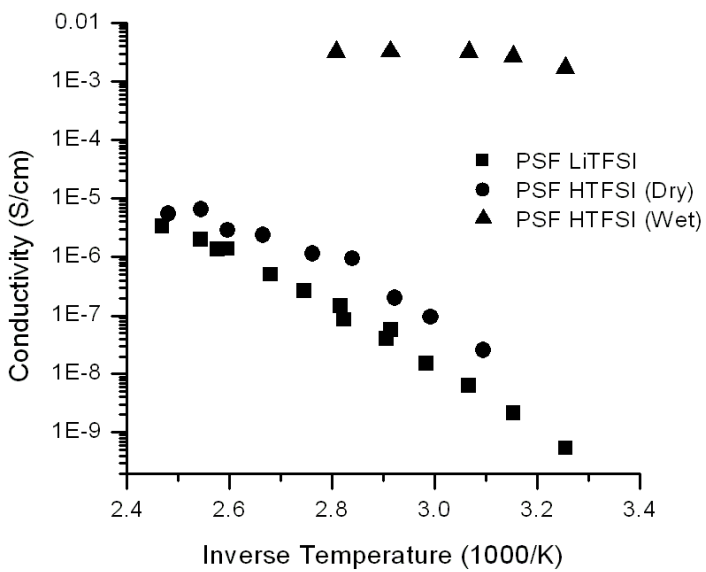




Characterization



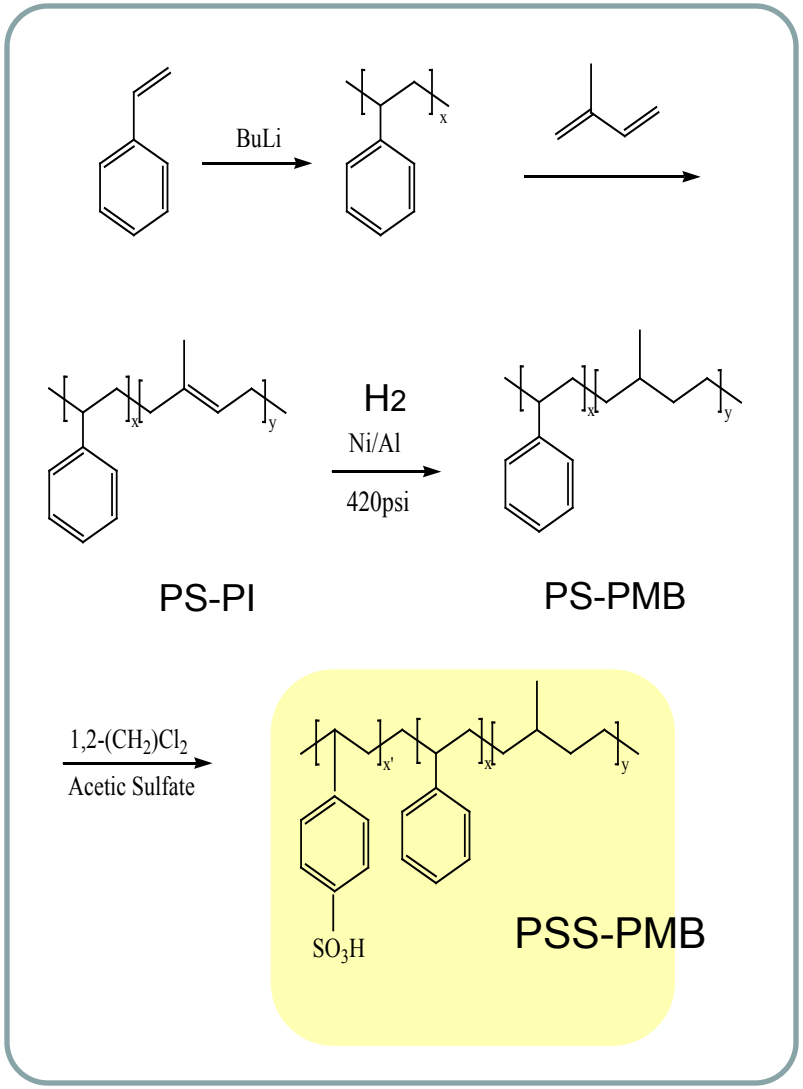




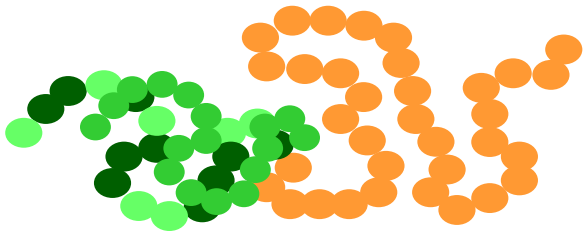
Conductivity

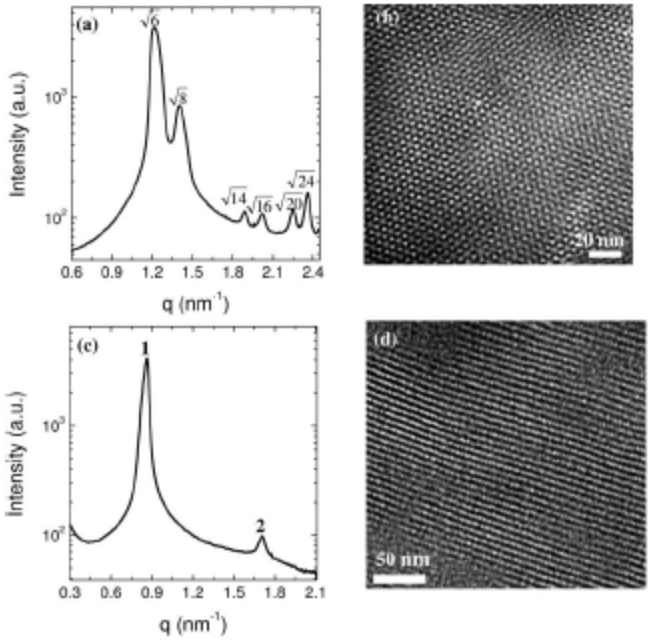
- TGA shows thermally stable polymer (PSF LiTFSI).
- DMA (Dynamic mechanical analysis) shows a strong material with thermal transitions at ~0°C and 100° C
- Conductivity of lithium form is similar to protic form in dry state and the conductivity is poor since there is no solvent present to dissociate the cations.
- Addition of solvent results in a large increase in conductivity. Conductivity and mechanical measurements are under way on blends with imidazoles and imidazole-containing polymers.

Block Copolymers For Morphology Control



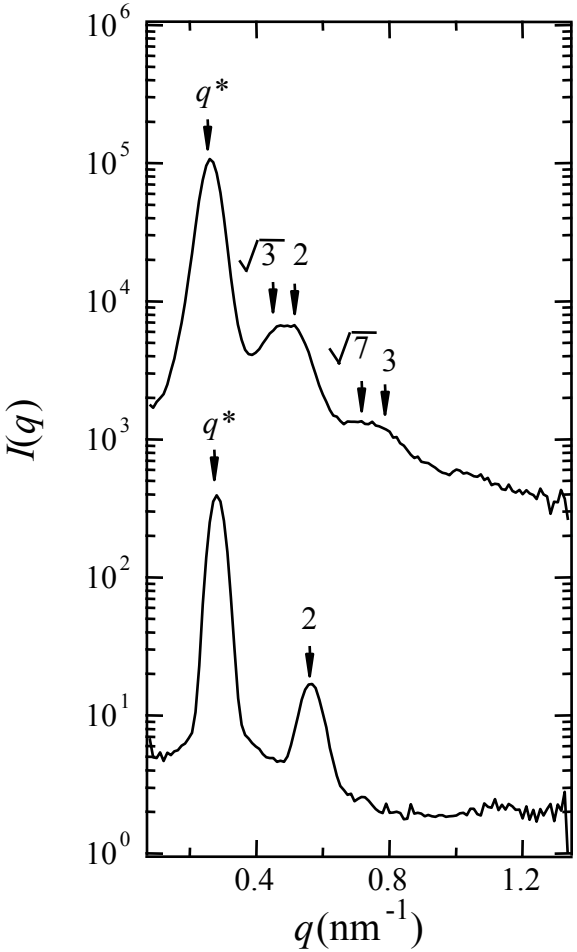
- Styrene: S
- Styrene Sulfonic Acid: SSA
- Hydrogenated Isoprene: MB





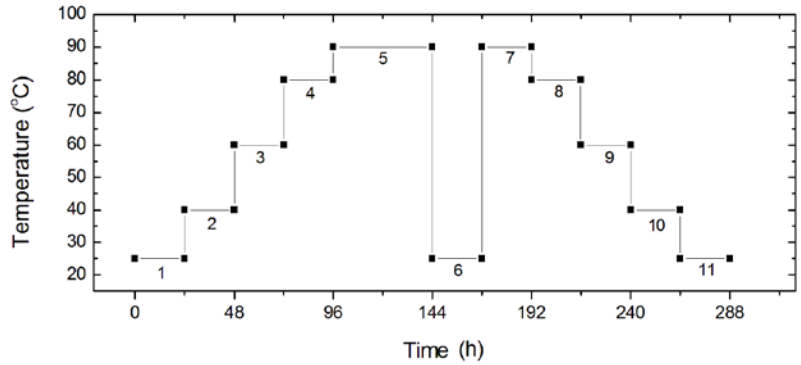
Morphology and Conductivity in the Hydrated State

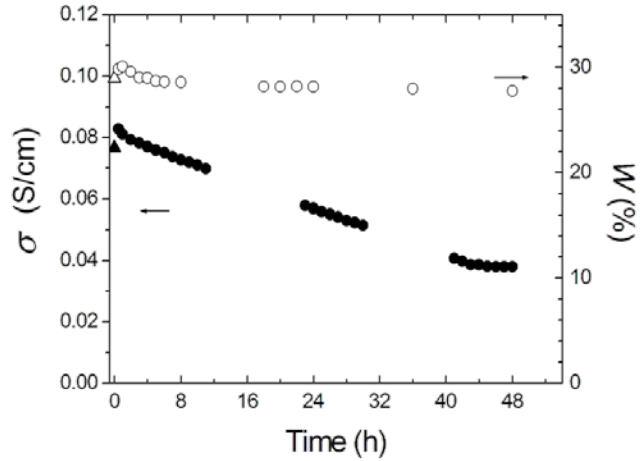
SANS at RH = 90%



60°C

25°C





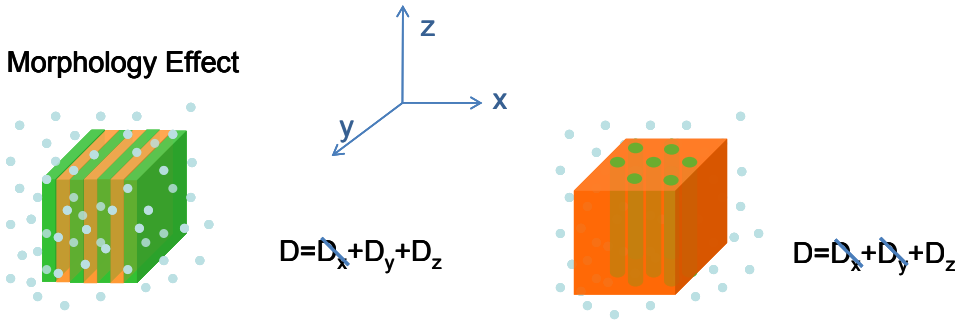
90°C Step 5

Conductivity drops and stays down

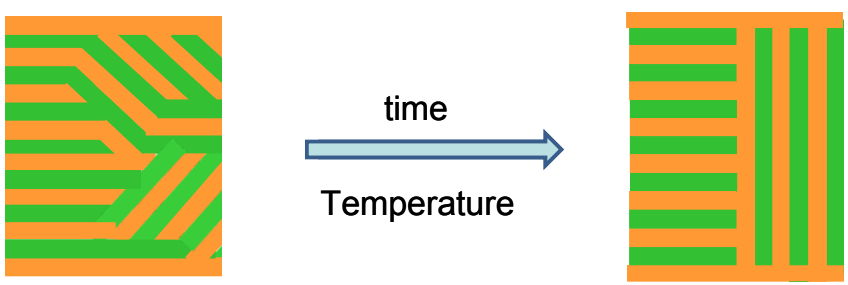
Time Dependence of Morphology

Morphologies respond quickly with temperature, humidity (& current?).

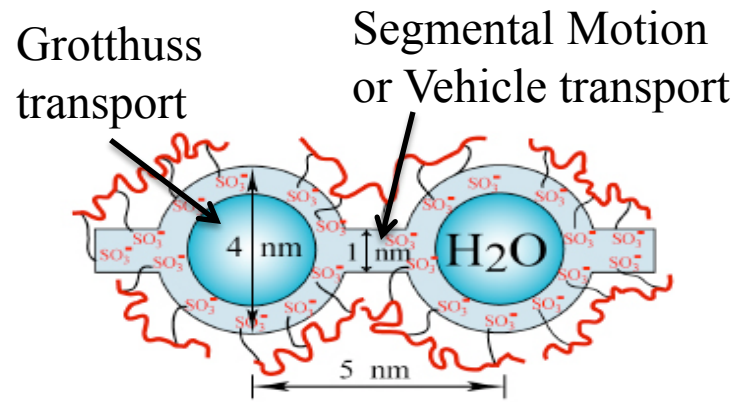
- Morphology Effect



- Connectivity Effect

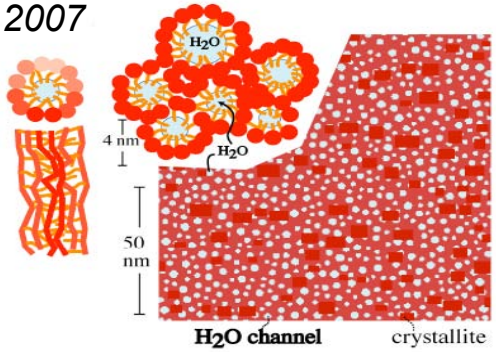


Morphologies are dynamic and change with conditions.

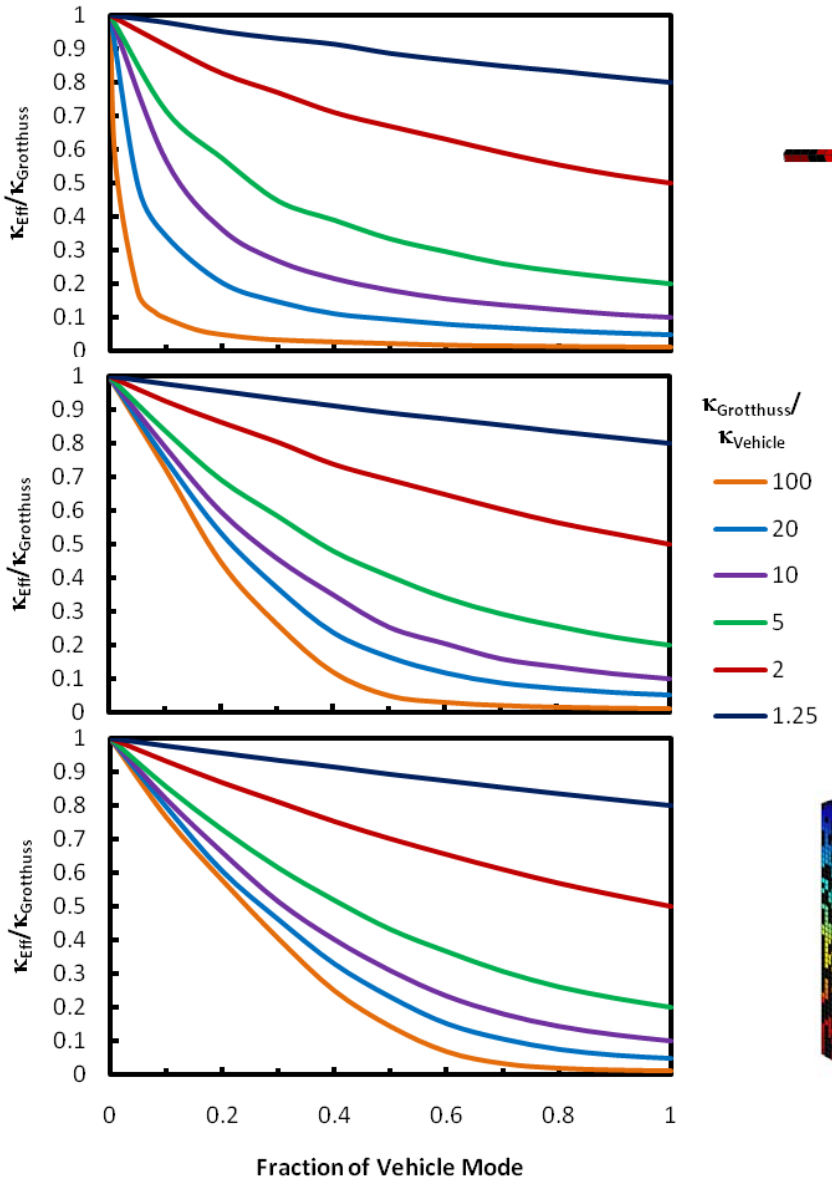


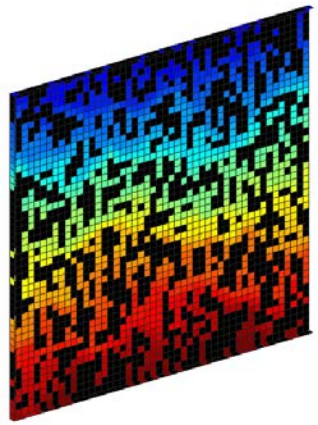
Gierke, et al,1981&1983

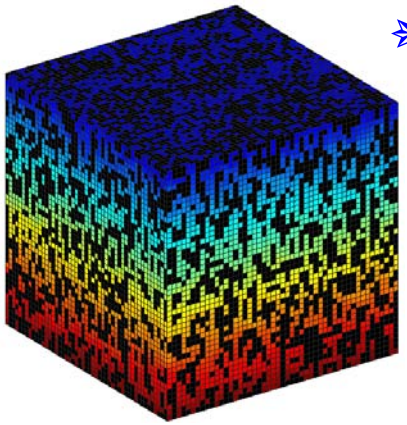
Schmidt-Rohr, et al, 2007



Conduction Network Modeling (Random)







- 1D: Series Conduction
  - Only a few vehicle sites greatly reduce overall conductivity
  - Same as single pore

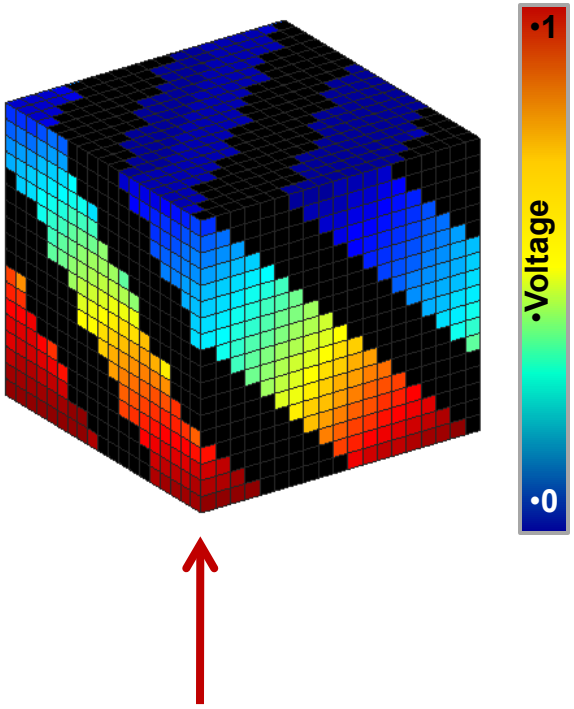
- 2D: Parallel Conduction
  - The ability to bypass vehicle sites enhances ion conductivity but percolation limitations remain

- 3D: Parallel Conduction
  - Additional paths around vehicle sites improves conductivity further and percolation threshold is increased over 2D

Conduction Network Modeling (Lamellar)

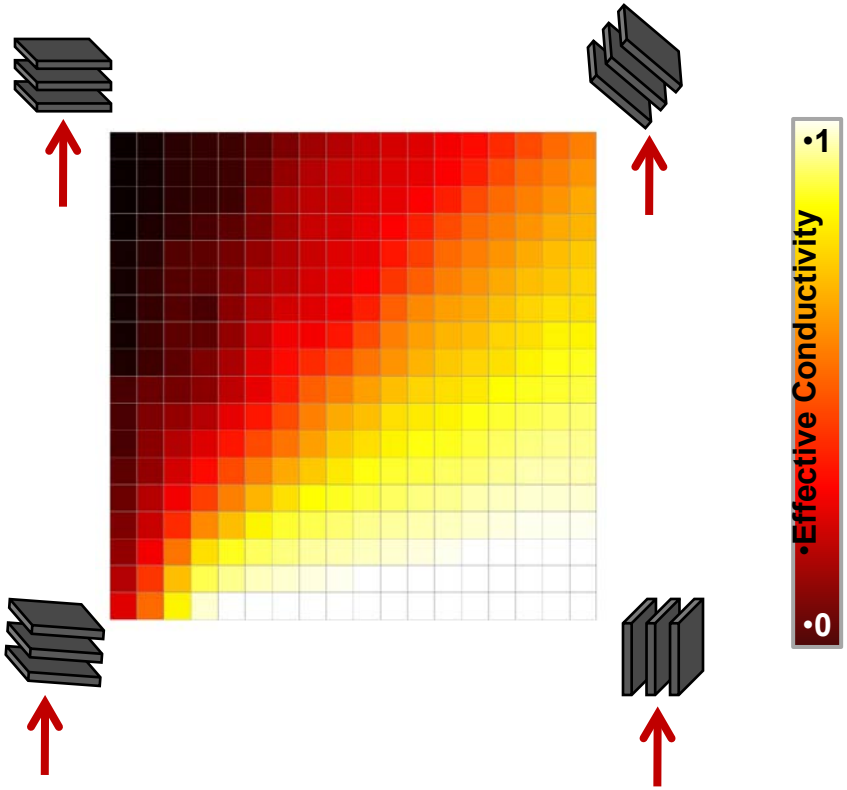
- Incorporate morphology into the modeling

•Simulation with Non-Conducting Lamella in Domain



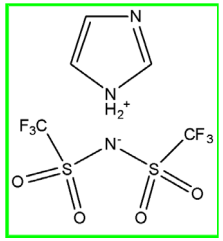
•Applied Voltage

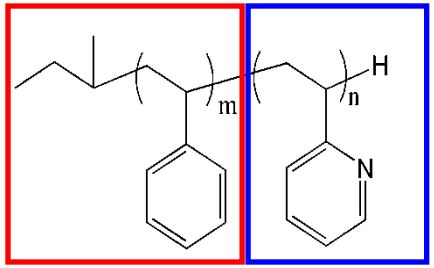
•Conductivity vs. Lamella Orientation

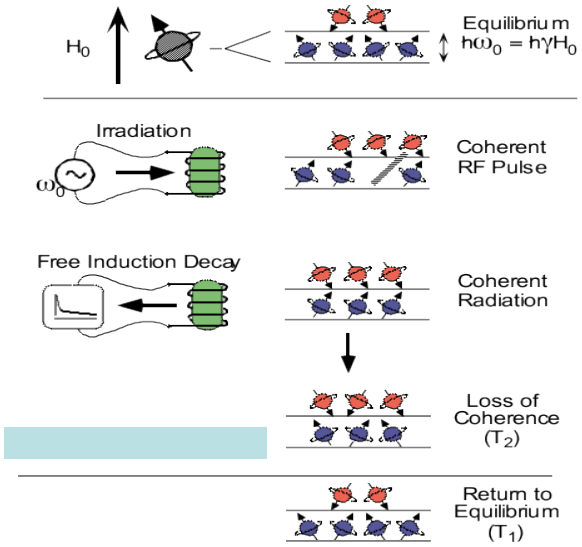


^{1}H 15kHz MAS NMR

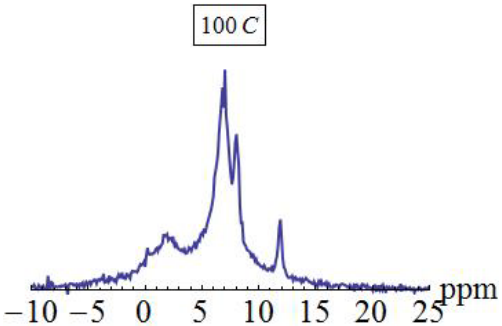
Relaxation Data to Characterize Polymer Dynamics

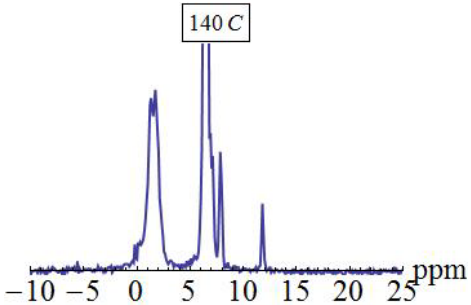


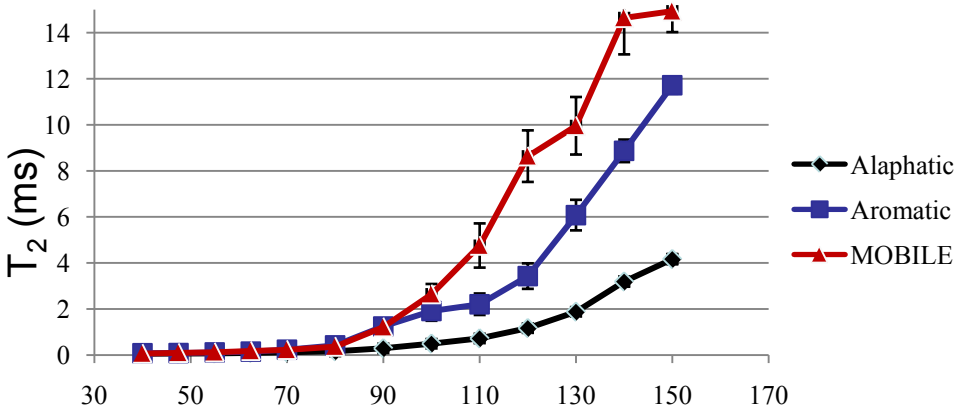




74% Copolymer 26%IL



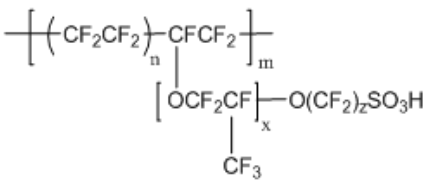




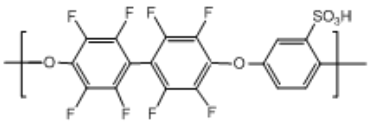
Temperature

Non-Nafion® Electrode Development For High Temperature Membranes - Effect of Hydrophobicity

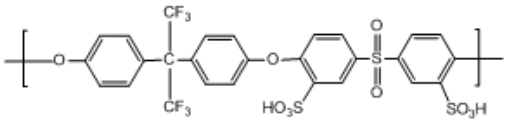
PFSA



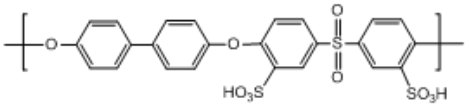
Decafluoro based Polyaromatic



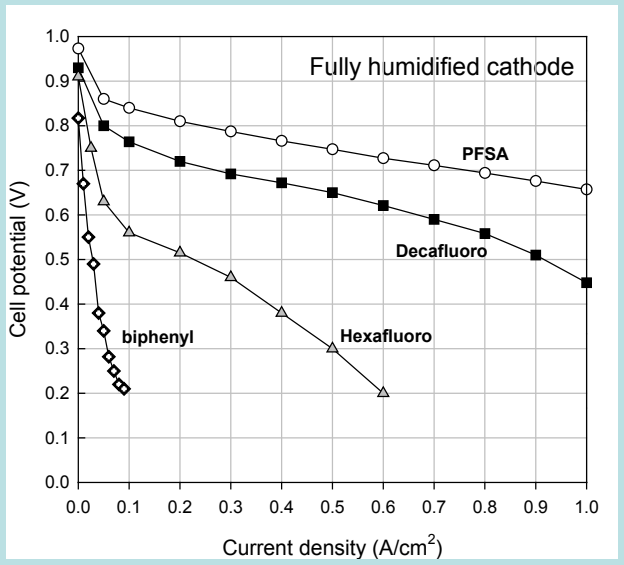
Hexafluoro bisphenol based Polyaromatic

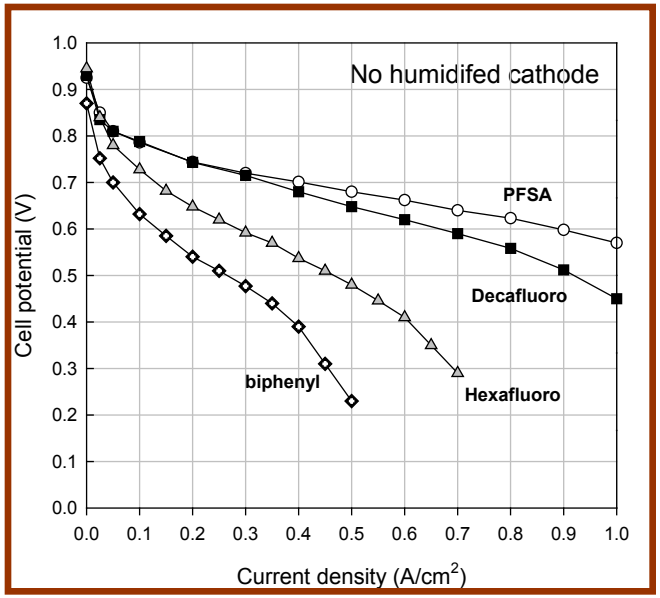


Biphenyl based Polyaromatic



Courtesy: Profs. McGrath (VT) and Lee (GIST)





Los Alamos NATIONAL LABORATORY

Collaborations

Between LBNL, LANL and 3M –frequent web-based conference calls are used to share results, discuss issues and plan experiments. Exchange of samples and reciprocal staff visits are integral to the program and increase as production of suitable material increases.

- **LBNL collaborations.**
  - Advanced Light Source and SLAC (SAXS beam-line use)- regular use
  - Molecular Foundry (polymer characterization and AFM) – daily use.
  - Oak Ridge Neutron Source (SANS).
  - NIST Neutron Source (Quasi Elastic Neutron Scattering) - pending
- **LANL collaborations.**
  - Dr. Michael Guiver (Canada NRC): Provide poly(arylene ethers) through DOE Technical Assistant Program: Polymer Synthesis
  - Dr. Bruce Orler and Rex Hjelm (LANL): Los Alamos Neutron Science Center through DOE Applied Science Program: Electrode Analysis

Future Work

- **Synthesis to provide material for testing (LBNL/LANL/3M)**
  - Attach imidazoles to available materials –Polysulfones, Polystyrenes, PFSA and PFCA – prepare blends with acid materials (with 3M) to give fully tethered materials that can be fabricated as membranes and incorporated into MEAs.
  - Prepare block copolymers that can be doped or functionalized with imidazoles and acid groups and whose morphology can be studied to help understand the connectivity issue and to help achieve the conductivity goals of 0.1S/cm at 120°C at < 25% RH.
- **Polymer Dynamics in bulk and as composites.(LBNL/LANL)**
  - Conductivity, NMR and Neutron relaxation measurements as function of temperature and humidity for both bulk and filled polymers.
  - Model Conductivity usiand extend MD collaborations with U. of Utah
- **Oxidative stability studies (LBNL/LANL/3M)**
  - Test oxidative stability of synthesized polymers with Fenton chemistry, use model studies to help identify released fragments and measure rates of polymer fragmentation. Test polymer blends in MEAs for stability. Go/No-Go decision.
- **Test MEAs.**
  - Fabricate & test composite electrodes and MEA's if practical conductivities(>0.01S/cm at 30°C) are achieved (LANL). Meets third Go/No-Go decision (FY10)

Summary

- Conductivity of polyelectrolyte systems that contain no mobile solvents appears to be too low unless a high degree of connectivity is achieved through the membrane.
- Connectivity though the membrane is very difficult to achieve and to maintain.
- Conductivities of imidazole-containing systems are improved considerably by the presence of some water in the system. Modeling shows that increasing the segmental motion transport by plasticization of the polymer increases the overall conductivity but also increases the loss of connectivity.
- Polymer dynamics is of critical importance.
- Synthesis of polymers with tethered imidazoles has been achieved with several different polymer backbones – polystyrene, polysulfone, polypropylene oxide and with different side chain lengths.
- Studies of proton conducting ionic liquids show that they support Grotthuss transport and morphological control in block copolymers can maintain high conductivities at lower temperatures.
- Composite electrode and MEA fabrication methods have been developed for hydrocarbon polyelectrolytes in anticipation of the availability of material for testing.