Development of New Polymer Electrolytes for Operation at High Temperature and Low Relative Humidity

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Case Western Reserve University

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Project ID # FC6

Overview

Timeline

- Project start 10/04
- Project 9/05

Barriers

DOE Technical Barriers for Components

- **O. Stack Material and Manufacturing Cost**
- **P. Durability**
- **Q. Electrode Performance**
- **R. Thermal and Water Management**

Budget

- Total project funding
  - DOE: $1.65M
- Funding received in FY04: $1.65M
- Funding for FY05: $0.8M

Participants

- **Pivovar, LANL**
- **Kerr, LBNL**
- **Tasaki, Mitsubishi**
- **Irvin, NSWC**
- **Coughlin, Umass-Amherst**
- **McGrath, Virginia Tech**
- **DesMarteau, Clemson**
- **Weiss, Uconn**
- **Nair, Foster-Miller**

Objectives

- The objective of this work is the development and deployment of new membranes for PEM fuel cells, targeting operation at low RH and/or T > 100^{o}C
- This project includes 'proof-of-concept' activities: goal is to find ways of achieving conduction under demanding conditions without worrying about all aspects (e.g. long-term durability)--

Some work is exploratory--we're looking for answers!

However, we try when possible for realism!!!

Approach (1)
Program Elements

- New membrane development
- Extensive property testing
- Formation of MEAs
- Fuel Cell testing

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Approach (2)
Development of New Membranes

- Rational development strategy
  - Combine diagnosis and physical chemistry studies with synthetic effort
  - Understand functional role of 'significant structures' operating at various length scales
  - Synthesis motivated by building block approach to improve or develop functions
  - Synthesis sometimes carried out 'just' for insight
  - Develop new analytical tools, deploy old tools to maximize insight gained
  - Iterate

Approach (3)
Testing and MEAs

- Physical Properties Testing
  - Transport: conductivity, diffusivity
  - Physical properties
  - Polymer durability

- MEAs
  - Overcome surface properties; Nafion vs. new polymer in CL

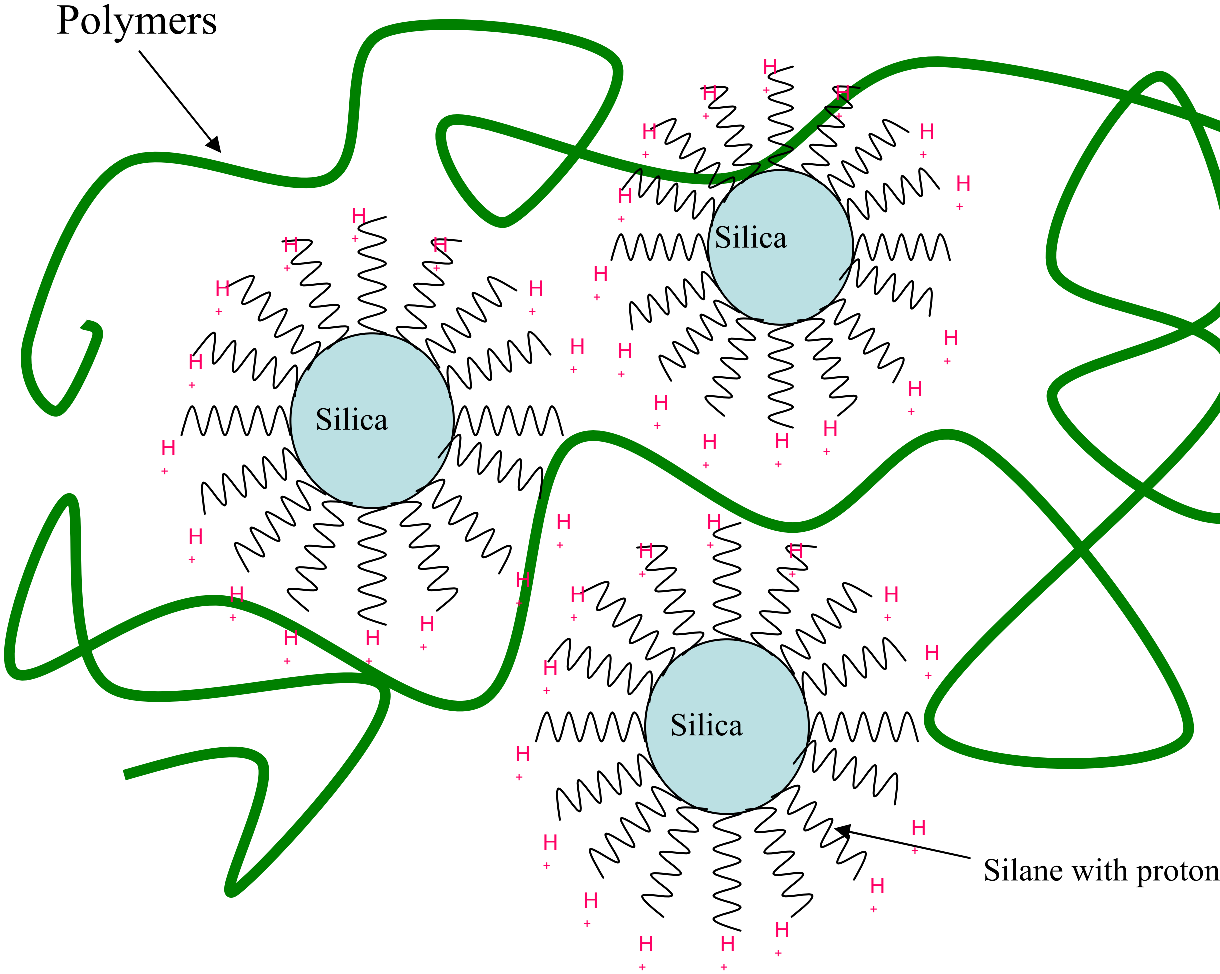
- Fuel Cell Testing
  - Performance of new materials, longevity

Technical Accomplishments/ Progress/Results

- Improvement of > 1 order of magnitude in conductivity of network structures, multiblocks, with decent low RH performance (Case)
- First fuel cell tests of Multiblock Polymers (Case, Va. Tech)
- Demonstration of good performance of C_{60} doped polymers (Mitsubishi)
- Synthesis, testing of ‘strong acid’ systems (NSWC, Case)
- Development of new materials based on polymer versions of ionic liquids, multi-site bases (LBNL, LANL)
- New fast proton conduction mechanism under study, implemented in first materials (Case)
- Transport limitations separated: morphology vs. basic interactions, leading to elimination of class of materials

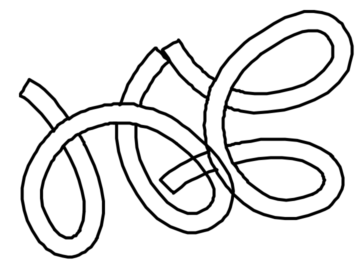
Network of Acid-modified Silica Particles

Building Silica/Polymer composite membrane

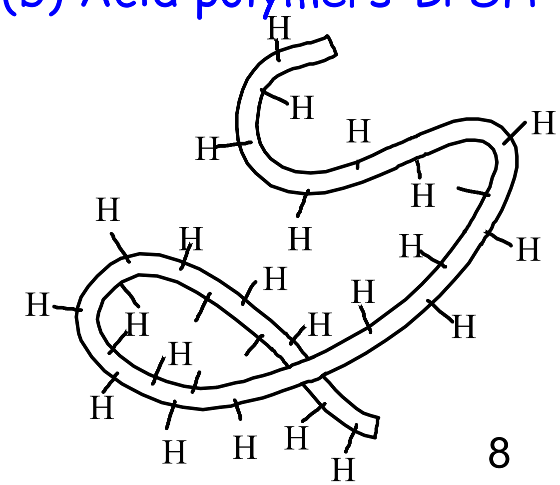


Form network in polymers
Polymer Types

(a) Proton free polymer-PVDF



(b) Acid polymers-BPSH

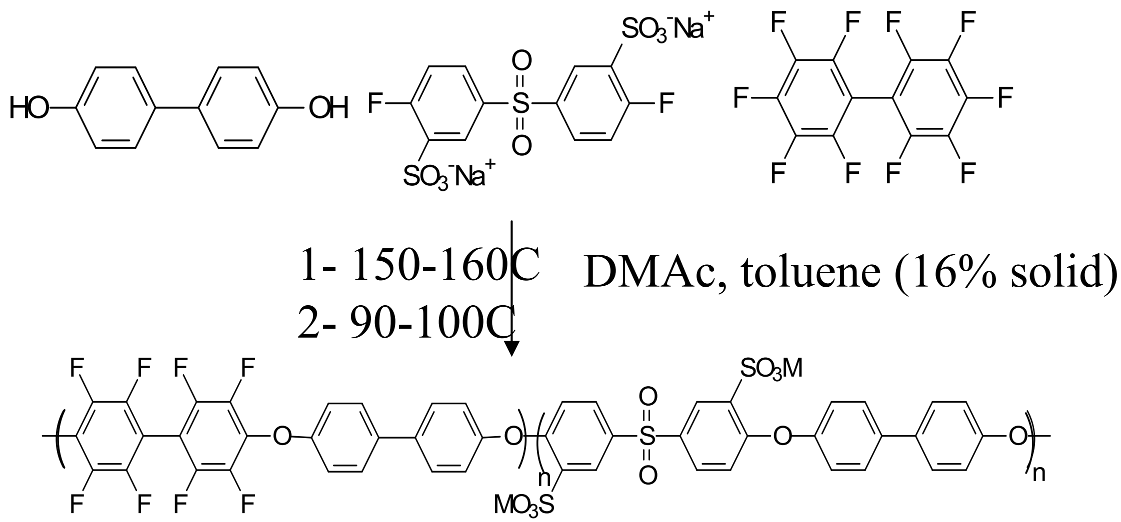


Network Structures: Progress

- Improvement in processing methods, binder composition, particle dispersion leads to dramatic increase in conductivity, from < 10^{-3} S/cm to > 10^{-2} S/cm @ 90^{o}C, 20% RH.

- Next steps: new network formation approach

Mixed Hydrophilic and Hydrophobic Block Copolymers as H+ Conductors



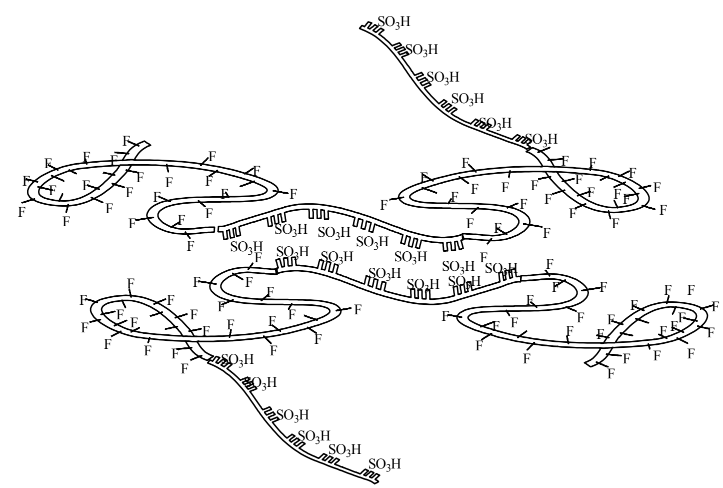
Yield: 99%, IEC (calc.): 1.29 meq/g

Several compositions prepared to date

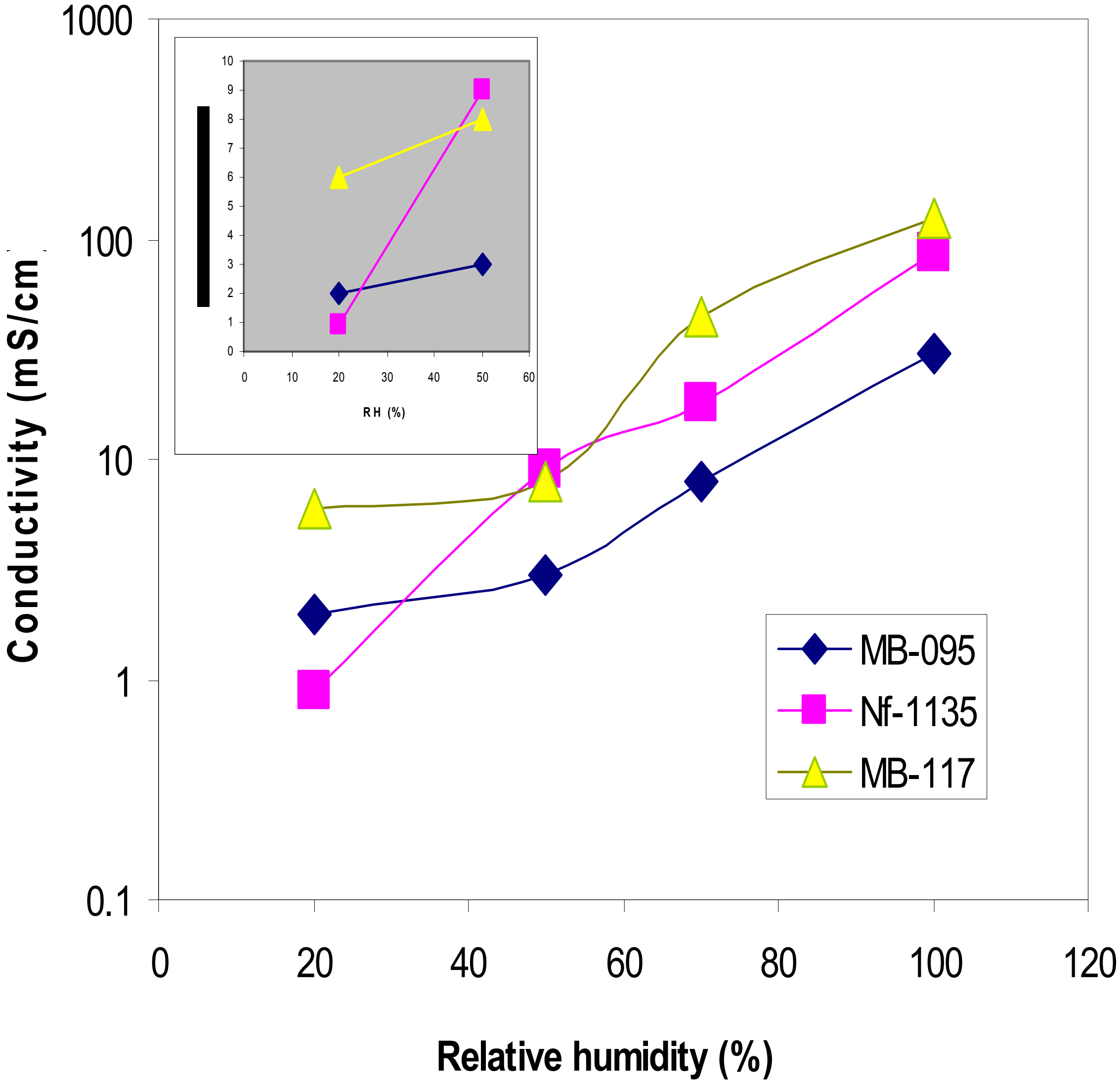
Organized structures yield higher conductivity

Next Steps: Designed Materials!!

- Huge array of possible polymers, acid groups, morphologies
- Introduce compatibilizers
- Tailor acid group orientation
- Introduce small molecule additives



Multiblock Polymer results



Non-optimized system has Conductivity on the order of 10^{-2}S/cm @ 20°C, 20% RH,

0.08 S/cm @ 60°C, 30% RH!!!

First MEAs tested in cells; Surface problems lead to high resistance.

Heterocycle Based Proton Conductors

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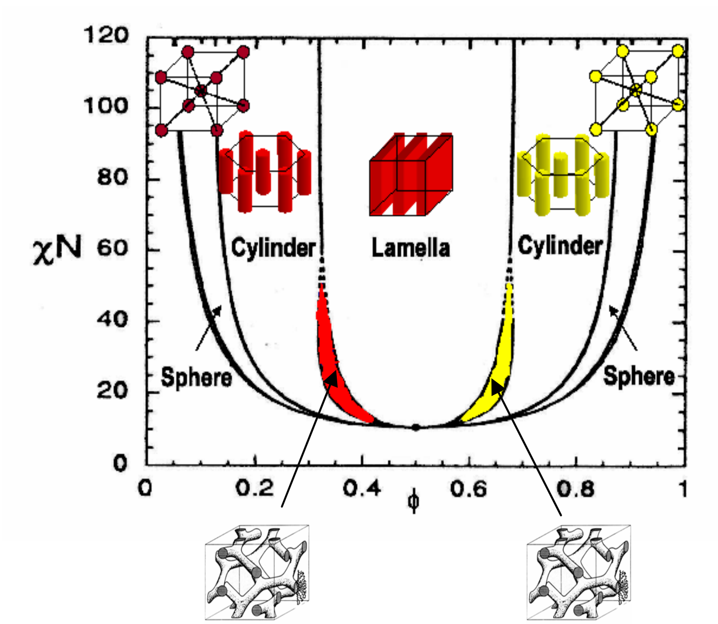
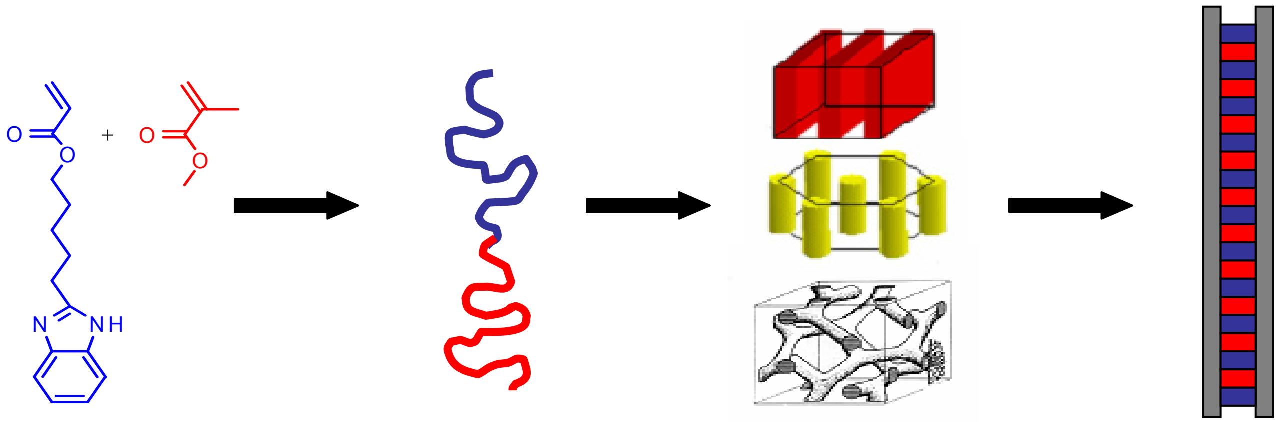
- High temperature (120 ºC +) proton conduction via heterocyclic proton donor/acceptors
- Explore novel molecular and polymeric architecture, and morphology effects on proton conduction
- Targeted continuous morphologies to mimic existing moderate temperature systems



Gyroid (bicontinuous phases)

- Morphology of block copolymers can be tailored by varying the volume fraction of each segment
- Such control is achievable by living chain growth polymerization methods
- Mechanical properties and conductivity can be balanced to create robust membranes

Heterocycle Based Proton Conductors

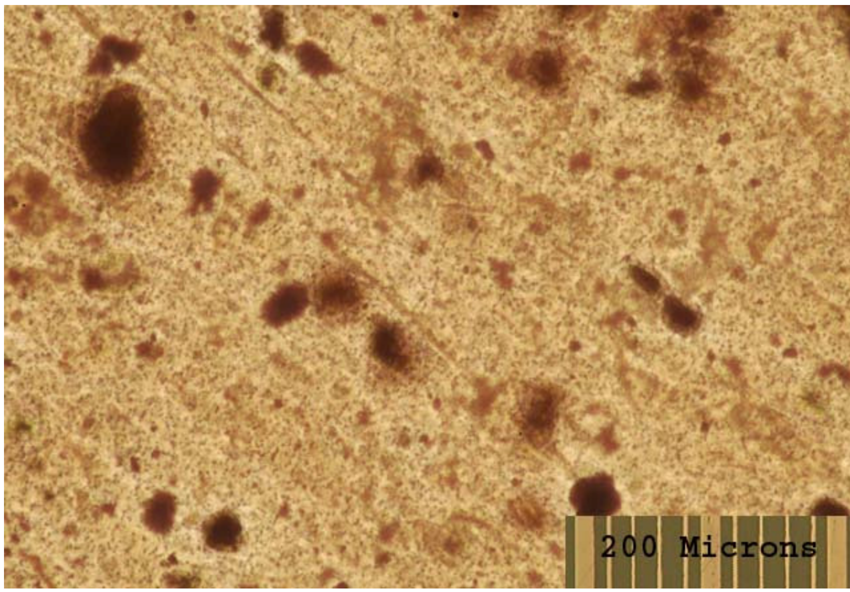


Monomer(s)	Block Copolymer	Bulk Morphology	Membrane Electrode Assembly
Ångstrom (10^{-10} m)	Nanometer (10^{-9} m)	Micrometer (10^{-6} m)	Millimeter (10^{-3} m)
Synthesize model protogenic monomers with heterocyclic groups	Well defined block copolymers through controlled polymerizations	Tailored morphologies (lamellar, cylindrical, gyroid) produce proton conducting channels	Membranes and MEA's that balance conductivity and structural integrity

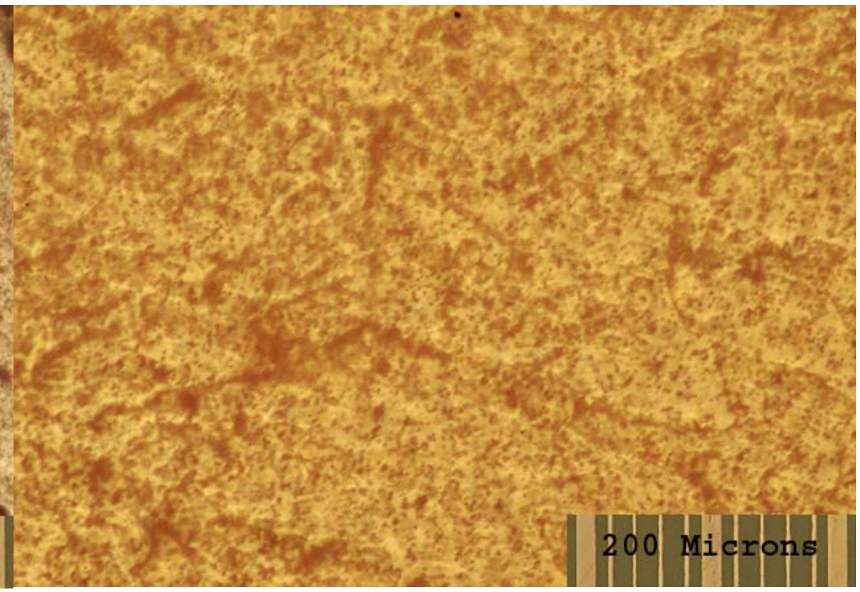
- Synthetic route to acrylate monomers identified
  - Radical polymerization accomplished
  - Membranes prepared and ready for testing to obtain baseline conductivity
- Beginning exploration of feasible living polymerization methods
- Determine effect on conductivity by preparing monodisperse homopolymers and block copolymers using several "hydrophobic" co-monomers

C_{60} Doped Polymers

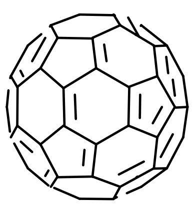
Morphologies of Fullerene–Nafion Composite Membranes



1 wt% C_{60} –Nafion Composite

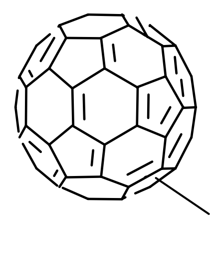


1 wt% $C_{60}(OH)_n$–Nafion Composite



+ Nafion

C_{60}

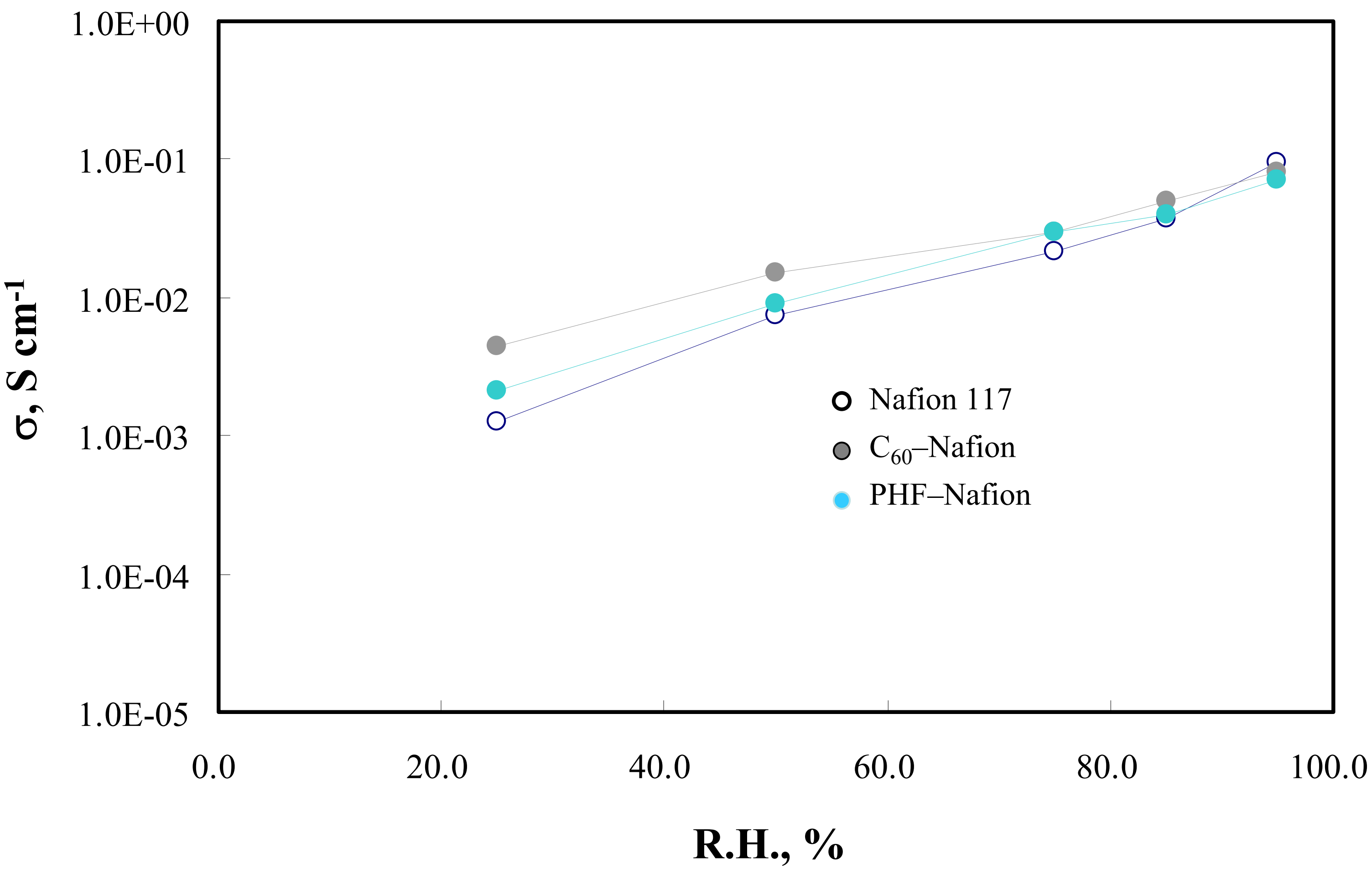


+ Nafion

polyhydroxy fullerene

C_{60} Doped Polymers

Fullerene–Nafion Composite Membranes

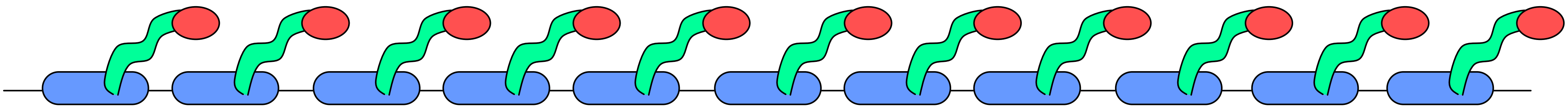


under N_2 gas flow

T = 30 °C

Advanced High Temperature Fuel Cell Membranes

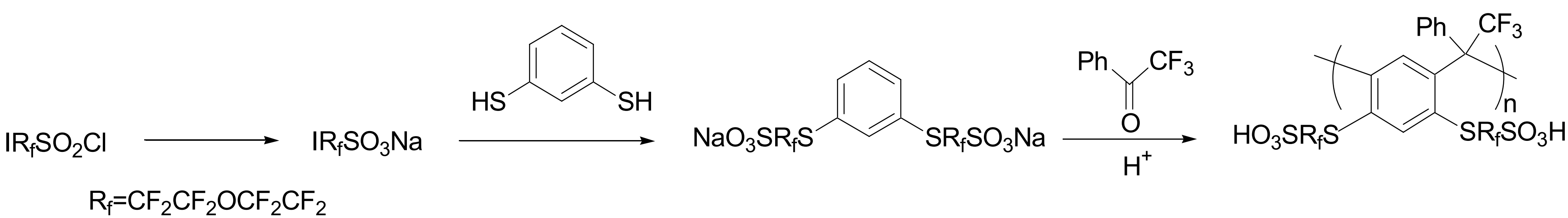
Dr. Jennifer Irvin, Naval Air Warfare Center Weapons Division, China Lake, CA



- Synthesis of new monomers
  - Aromatic repeat for rigid, stable backbone
  - Flexible perfluorinated spacer for aggregation and chemical stability; initial modeling shows 4-6 repeats ideal
  - Sulfonic acid end groups for conductivity
- Polymer synthesis
  - Polyethers, polyetherketones, polyethersulfones, polycarbonates, polysulfides, polybenzimidazoles, and/or polybenzoxazoles for chemical and thermal stability
- Membrane characterization
  - Membranes will be supplied to Prof. Tom Zawodzinski at CWRU for characterization

Irvin: Technical Accomplishments/Progress

- Identified potential target polymers and synthetic routes
- Conducted initial modeling experiments to determine ideal flexible spacer length (ca. 4 units) for aggregation
- Extensive monomer synthesis attempts: original target architecture is extremely difficult to generate, but an alternate route has been found that appears to be successful:



• Initial polymer produced in this fashion is water soluble; structural modifications are underway to produce insoluble polymers

Sulfonimide Proton Conducting Fuel Cell Membranes*

Objective

This research is to develop a sulfonimide proton conducting fuel cell membrane for operation at 120^{o}C and low (25%) relative humidity. The first phase has focused on investigating the high temperature hydrolytic stability of sulfonimide groups using NMR spectroscopy.

Background

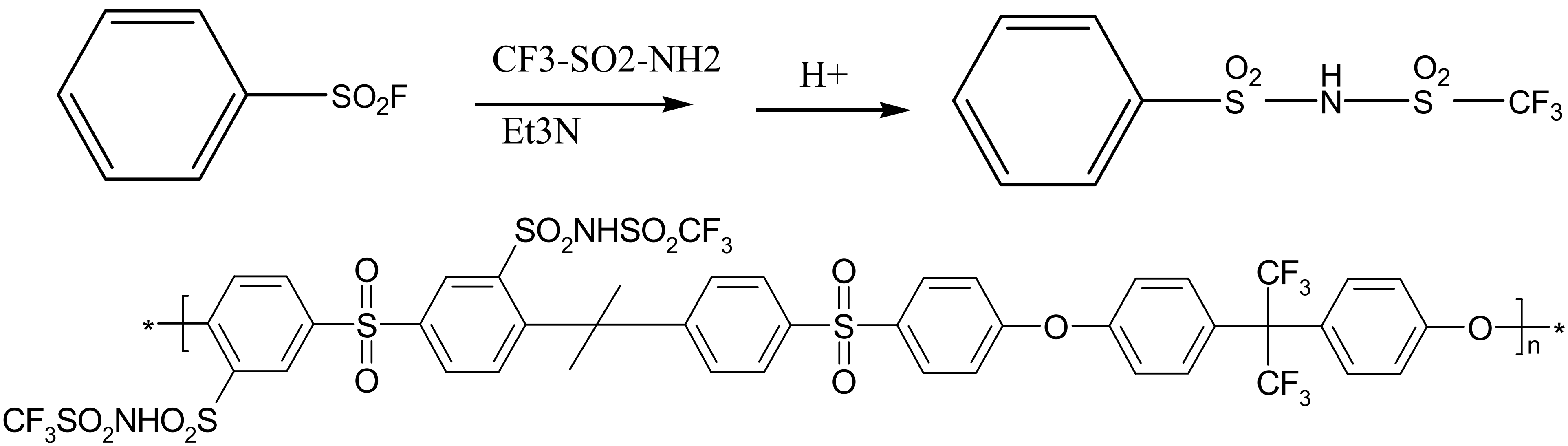
Water retention (important for proton conduction and hence fuel cell performance) is largely dependent on chemical structure and morphology.

Sulfonimides, for their strong gas-phase super-acidity, and capacity to promote facile fuel cell reactions at catalyst/ionomer interfaces, have proved to be promising membrane materials for fuel cell applications.

***Thomas L. Kalapos, Hossein Ghassemi, and Thomas A. Zawodzinski, Jr., Department of Chemical Engineering, Case Western Reserve University**

Stability of Ar-TFSI Compounds

- Benzenesulfonyl(trifluoromethylsulfonyl) amide was synthesized as a model compound.
- *NMR:* Spectra to date indicate that the compound is hydrolytically stable up to 200^{o}C.
- *TGA:* Both acid and salt forms of sulfonimide don't exhibit significant weight loss up to 400^{o}C. The acid form shows strong hydrophobicity even up to 200^{o}C.
- New polymer synthesized….



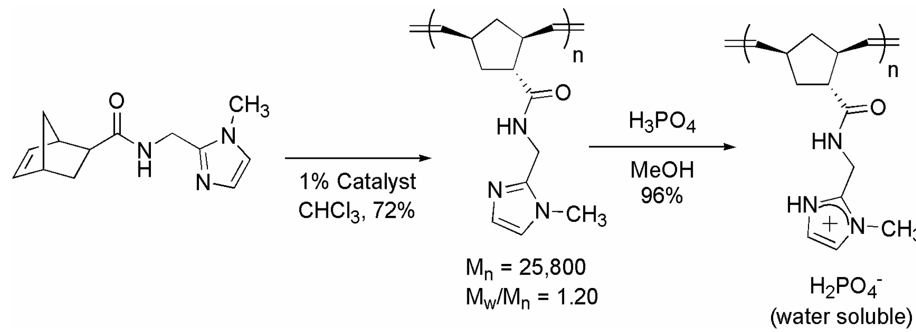
High Temperature/Low RH Ionomers based on Ionic Liquids

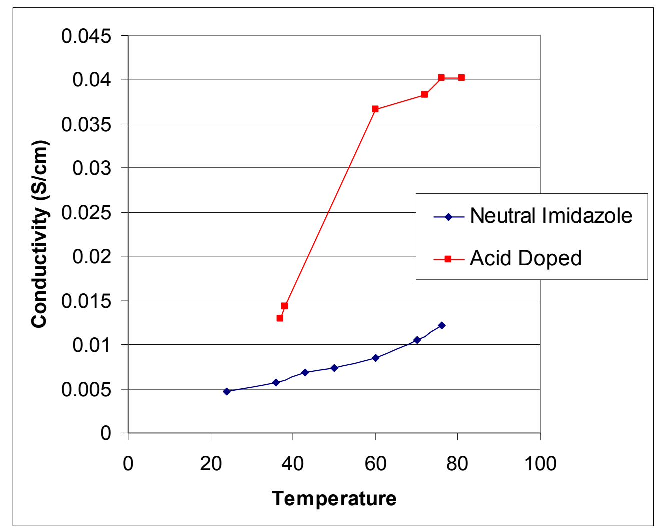
Los Alamos National Laboratory

- Investigate ionic liquid analogues with free protons such as imidazolium cations and dihydrogen phosphate ($H_2PO_4^-$) or bisulfate (HSO_4^-) anions capable of proton conduction

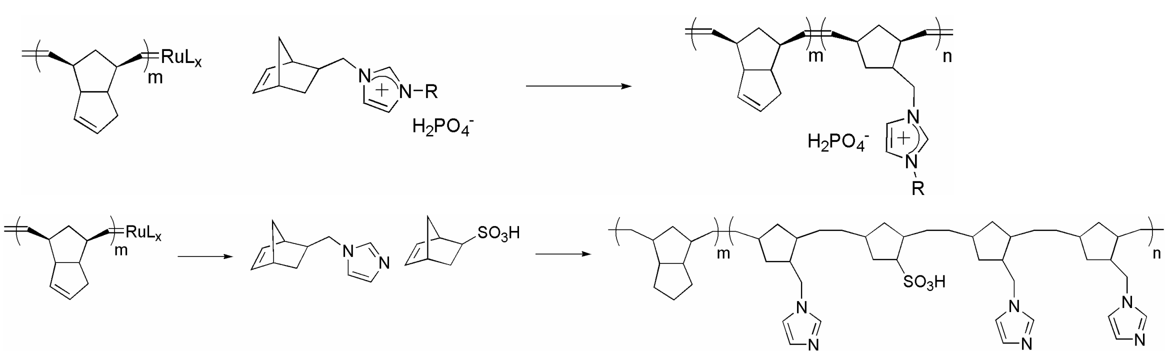
- Advantages of ionic liquids are
  - Thermally stable (up to 300 ˚C)
  - Stable to oxidation and reduction
  - Essentially no vapor pressure
  - High intrinsic ionic conductivity

- Investigate conduction limits of these materials, incorporate the most promising candidates into polymeric materials.





Future Directions: Block Copolymers

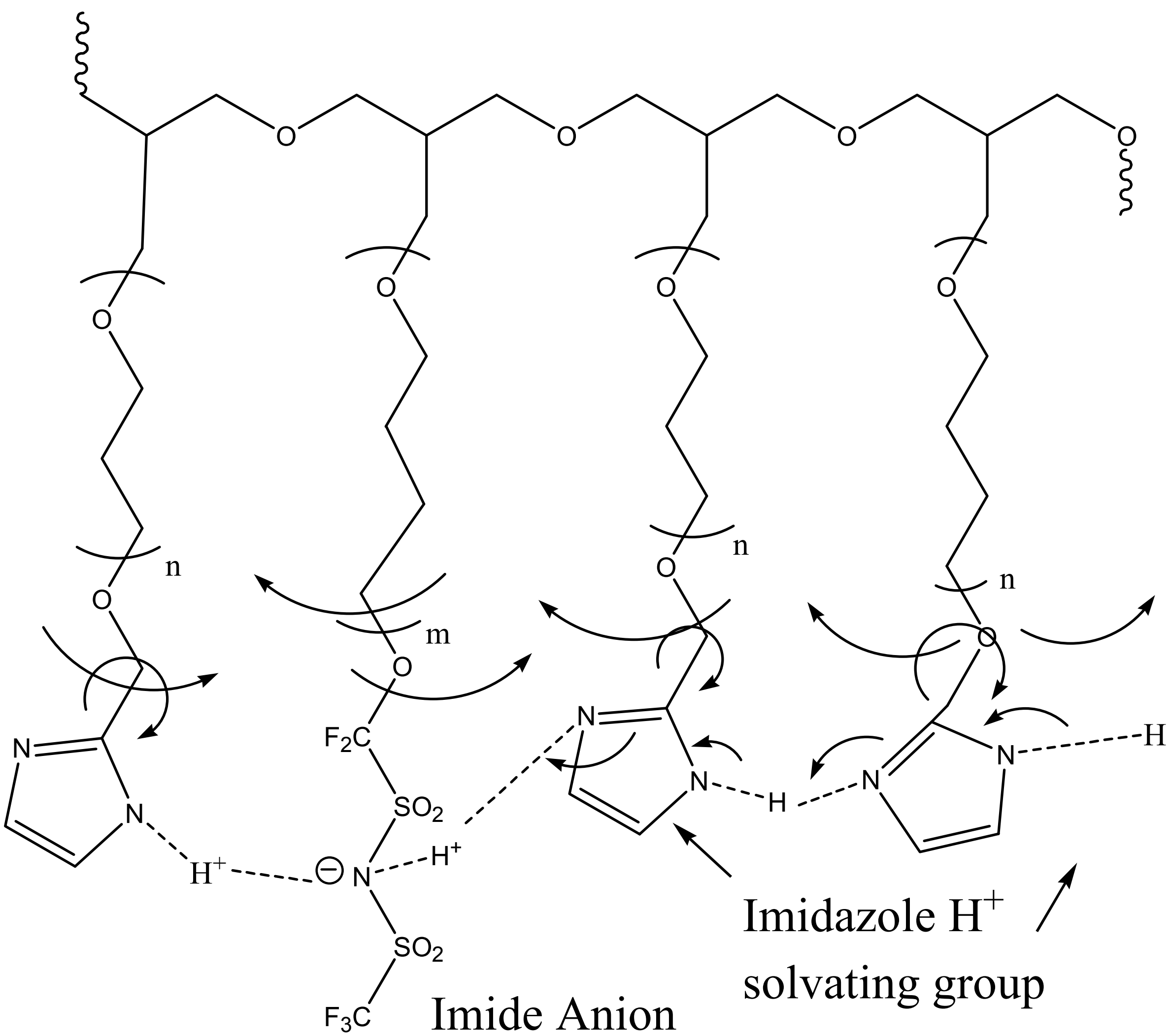


- Initial studies (above) show reasonable conductivities even under dry conditions (acid doped sample) and good thermal stability.

- Future work involves making block copolymers and incorporating acid functionality into the polymer backbone.

Kerr, LBNL: New Polymer Architectures for Imidazole

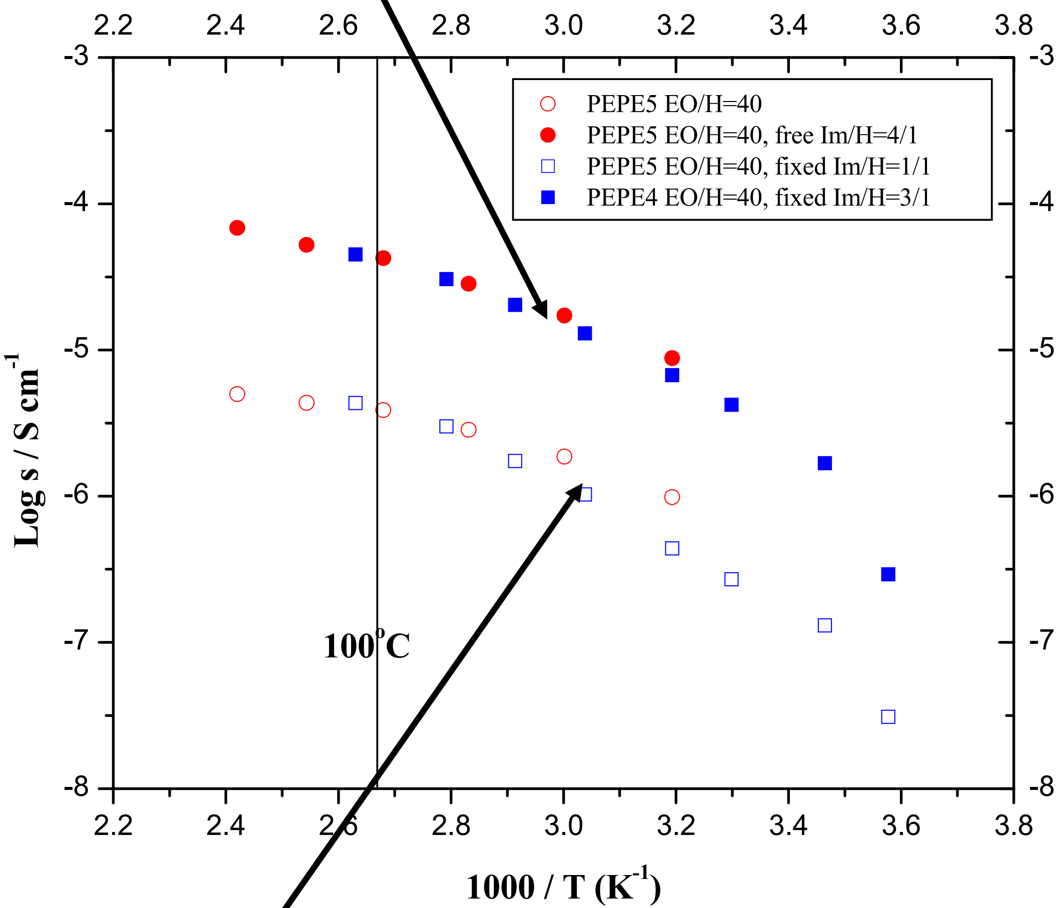
Solvating groups, Anion Mobility, Flexibility – only H+ moves!



- Attach anions and solvating groups by grafting –control nature and concentration.
- Use nature (pdo/bdo) and length of side chain
to control chain mobility.
- Backbone (PE, polystyrene, polysiloxane) and cross-link density to control mechanical & morphological properties.
- Morphology promotes Grotthuss mechanism.
- Degradation results in release of small fragments
- facilitates failure analysis.

Kerr, LBNL: Comparison of conductivities of free and tethered imidazole proton conductors. Tethered alkylsulfonic acid groups.

Conductivity of free and tethered imidazole equal



With no excess imidazole over acid groups conductivity is same as no imidazole.

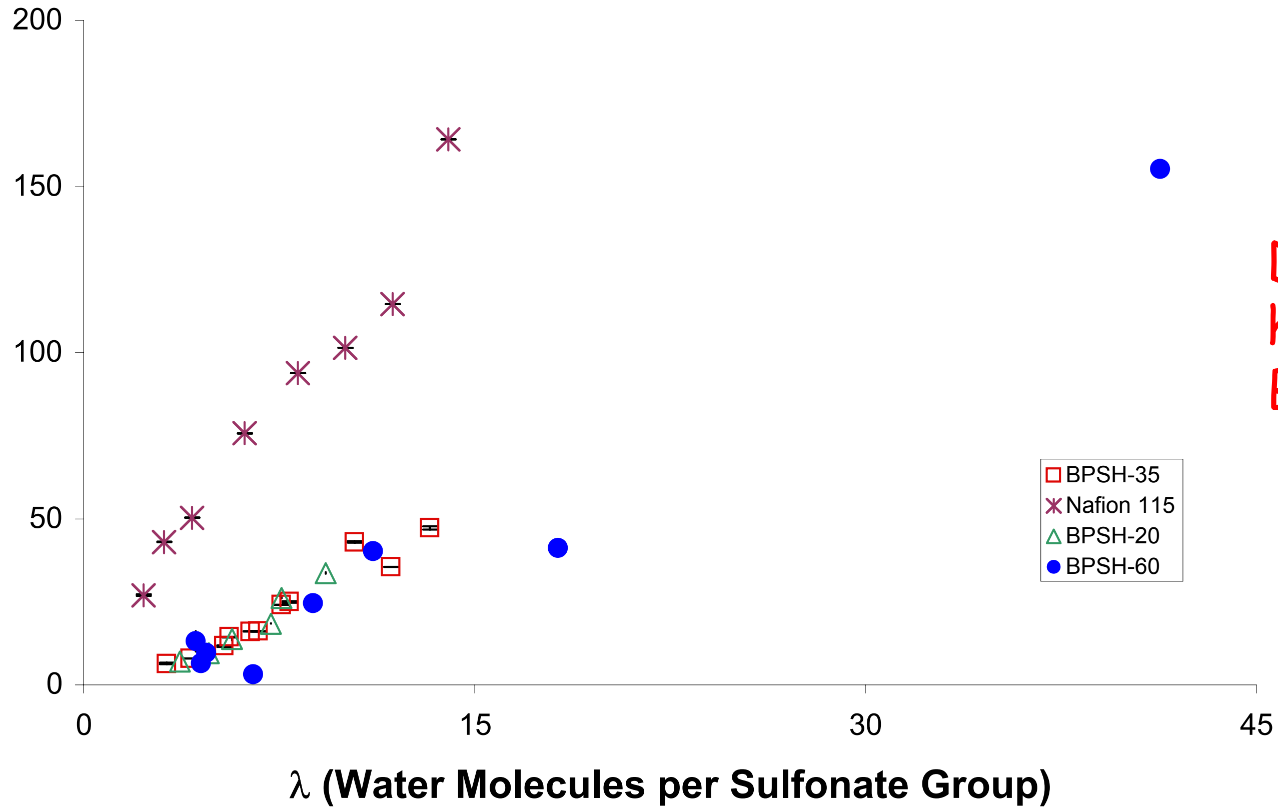
- Conductivity of N-tethered imidazole polymer equal to the conductivity of the polymer doped with free imidazole solvent.
- **Conductivity limited by mobility of the anion.**
- Relative concentration of Imidazole to acid group is critical.
- Increase conductivity by optimiz-ation of tether length, acid/base concentration, nature of the acid group (Fluoroalkylsulfonylimides vs. Alkylsulfonate) and by morphology control.

➔ **Road Map to solvent-free conductivity above 10^{-2}S/cm exists.**

New Conduction Mechanism

- Case developing new approach to water-free conduction of protons using a particualr type of additive
- First work
  - additive is totally insoluble
  - Un-optimized conductivity: >0.01 S/cm at T~150^{o}C, dry conditions
- Next steps
  - Investigate under lower T conditions etc.

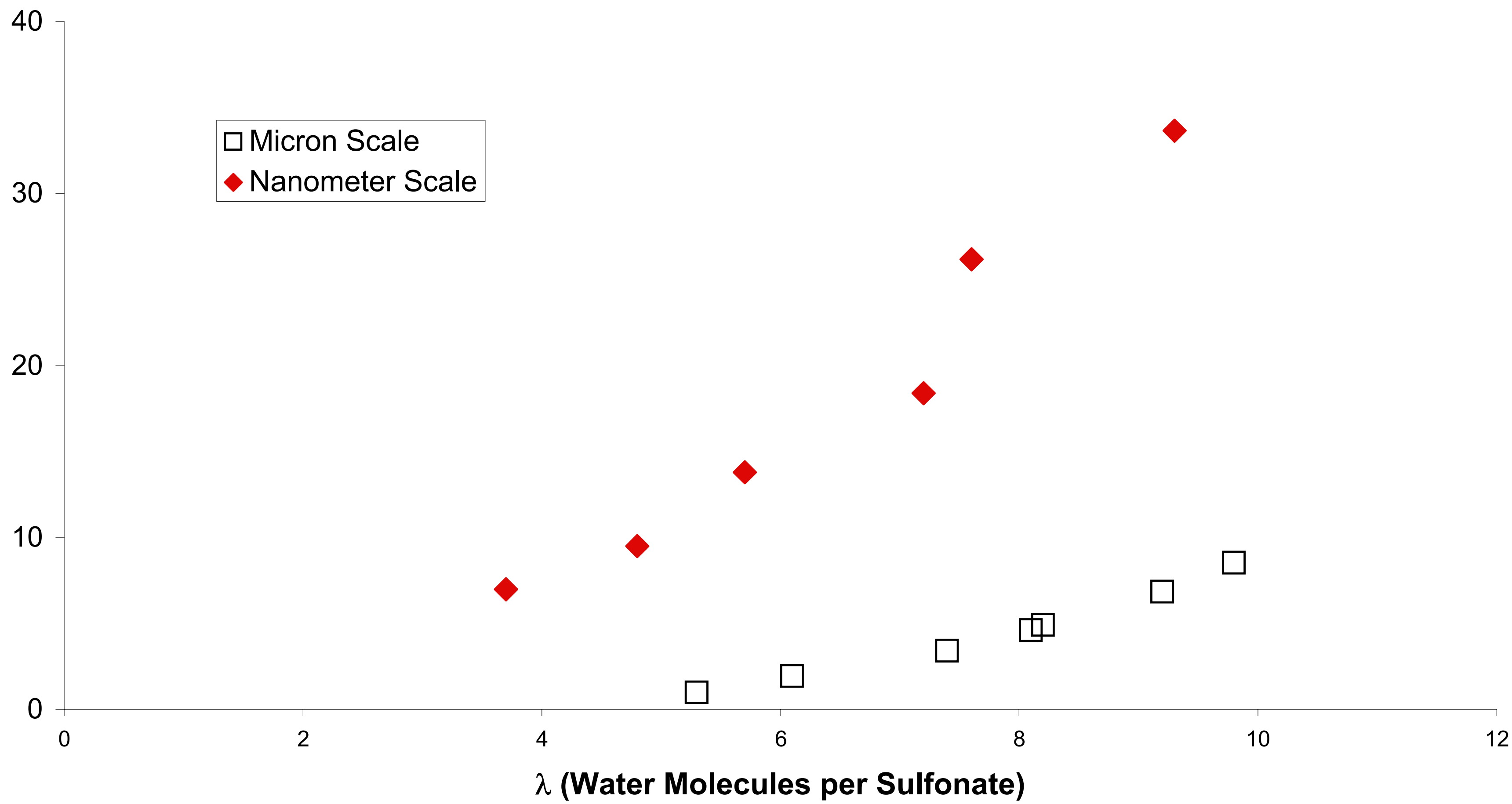
Limitations on Transport
Nano-Scale Diffusion from NMR



Dw in Nafion much higher than that in BPSH series

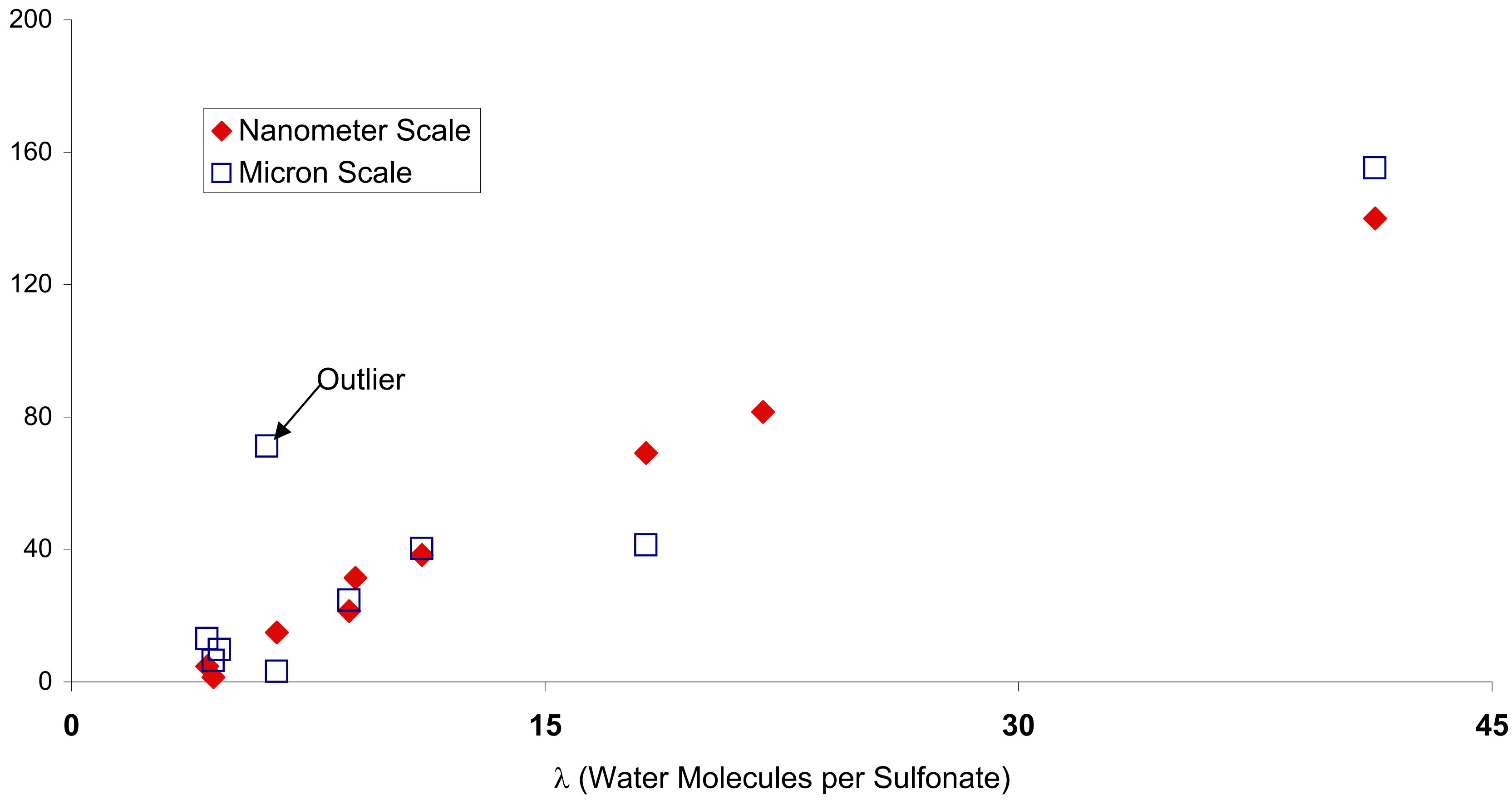
BPSH has the same nanometer scale motion regardless of the sulfonation level

Diffusion Length Scale Comparison, BPSH-20



Diffusion coefficients diverge with increasing λ.

Diffusion Length Scale Comparison, BPSH-60



Similar trend and values over the entire λ range.

Summary of Transport Influences

- **Morphology strongly influences long range transport in BPSH-20, not in BPSH-60**

- **Primary controlling factor in BPSH-60: local interactions between water and acid groups**

- **Nafion vs BPSH: motion much slower in BPSH at all length scales for equivalent water content**

Limiting Factor: Acidity of Functional Groups

- PASAs probably out of question for low RH

General Summary

- **Several promising strategies in hand**

- **Substantial progress on preparation and processing of diverse conductor types**

- **Iteration beginning with team concept**

Responses to Previous Year Reviewers' Comments

- Stability of polymers is an issue (several cases)
  - Response: The materials discussed here are sometimes prepared to assess the viability of a conduction mechanism only; the expectation is that more stable backbones could be developed later.
  - Increased emphasis on durability aspects; testing added as a standard expectation; methods under development for aromatics at Case; beyond Fenton's test
- Higher degree of focus on low RH
  - Response: Materials are now being prepared with low RH conduction as a specific target.

Future Work

- Continue multi-faceted synthesis effort with increased sample ‘circulation’, feedback on physical properties etc.

- Culminate synthetic efforts in MEA preparation, fuel cell testing as appropriate