New Polymeric Proton Conductors for Water-free and Elevated Temperature Fuel Cells

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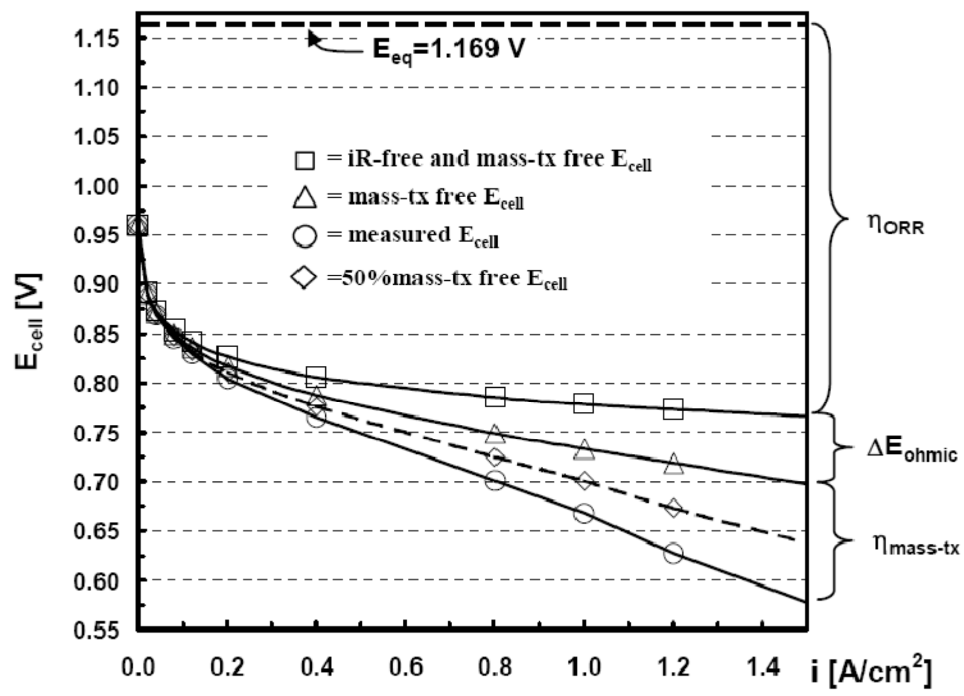
The need to replace water in PEM Fuel Cells

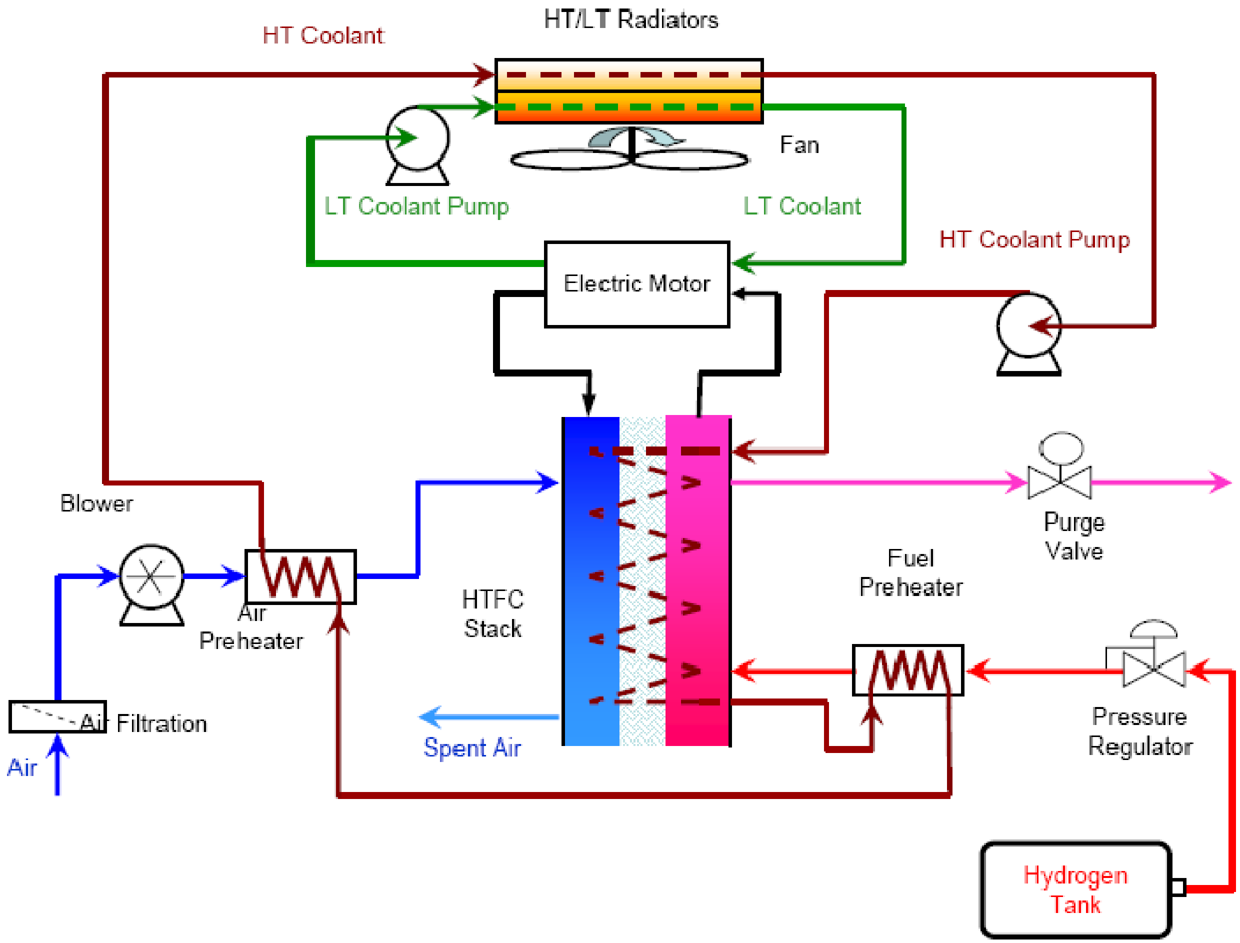
- Nafion PEM cells operate at 85^{o}C, >90% RH
  - complex water management system
- Nearly 50% of energy is converted to heat
  - Complex heat management system
- Water causes swelling of membrane
  - Unacceptable Mechanical Stress.



- Freezing of Water damages membrane and electrodes

Long Term Goal

Argonne 2015 FCS Configuration



Changes from FCS 2010

MEA
- Non PM catalyst
- HTM

AMS
- BMM

WMS
- None

TMS
- Standard radiator

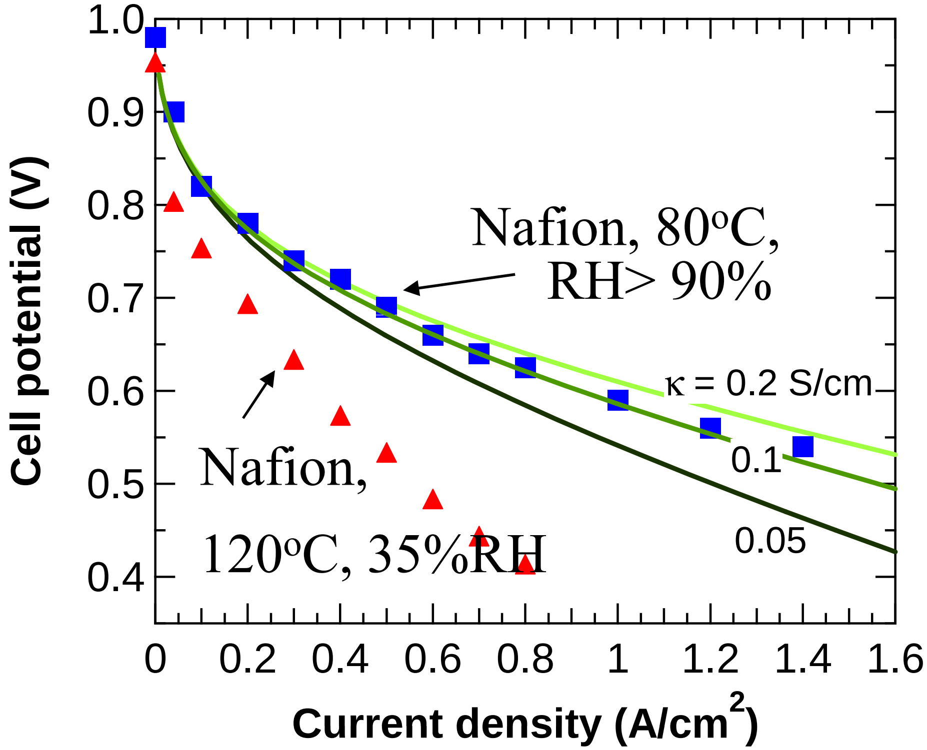
FMS
- FC quality H_2
- Dead-ended

Approach - Objectives

- Investigate the feasibility of solid polyelectrolyte proton conductors that do not require water to achieve practical conductivities (0.1 S/cm at 120^{o}C).
  - Prepare and test proton conducting materials based on heterocyclic bases (imidazole) and acids (sulfonates, sulfonylimides) – ionic liquids, doped polymers.
  - Prepare and test solid polyelectrolytes where only the proton moves - solvent and acid groups to the polymer backbone.
- Determine stability of these materials to oxidation and strong acids.
- Fabricate and test MEA's.
  - Determine gas crossover

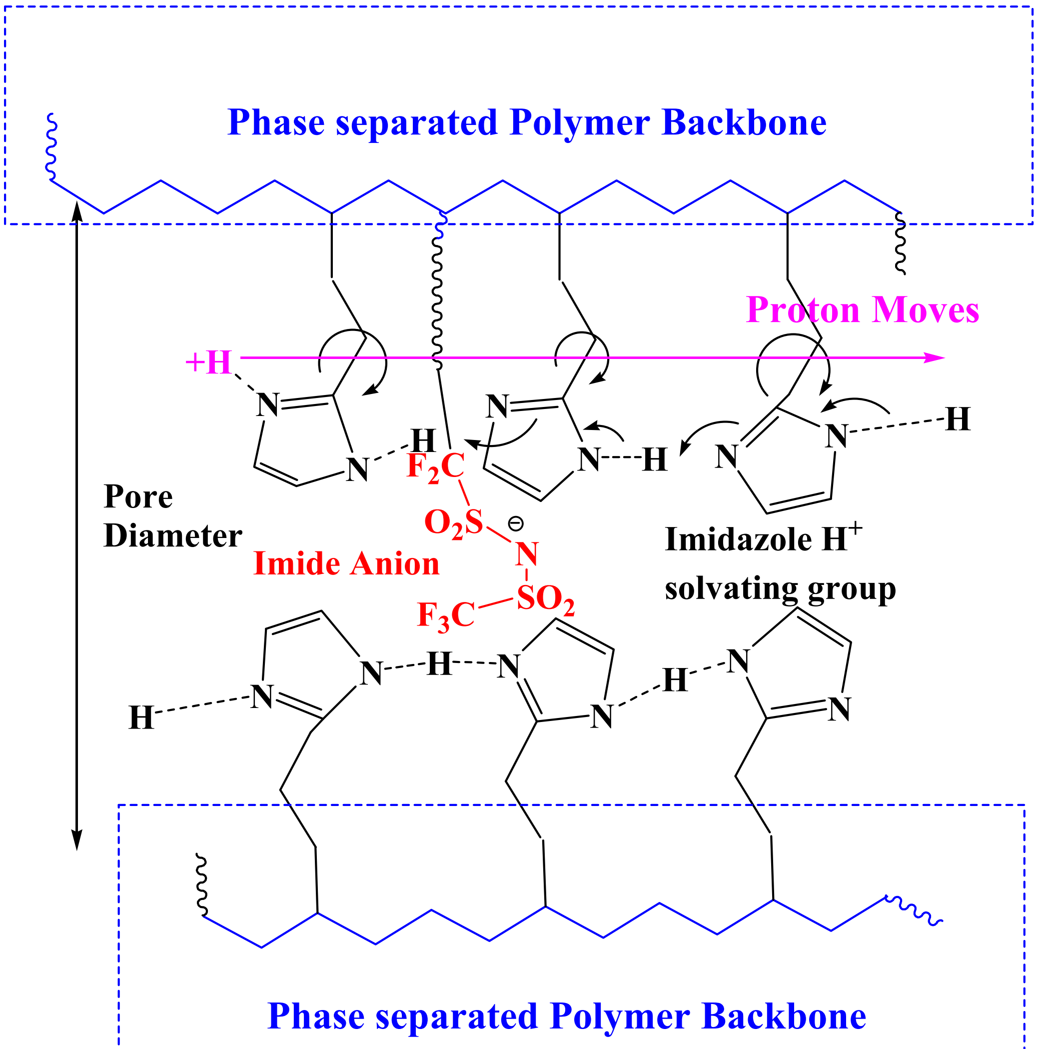
Check the Goals - Modeling

- **Assumptions**
  - **Dry inlets at 120°C**
  - **All property expressions the same**
  - **Only property change is the membrane conductivity in the separator and the catalyst layers**



- **Diminishing returns for higher conductivity**
  - **Limited by kinetics**
- **System simplification could allow for a lower conductivity goal**

APPROACH to Material Design of Polymers to support Grotthuss Transport.



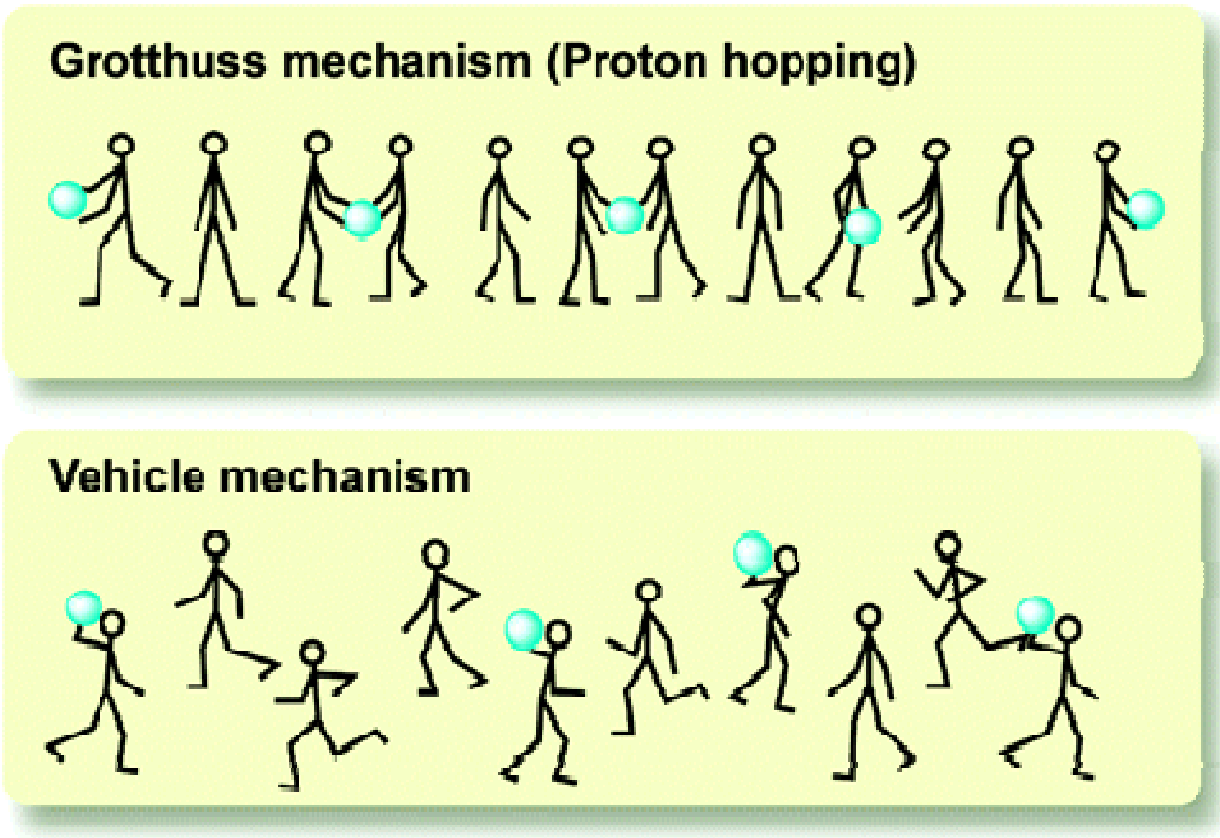
Tether imidazoles and acid groups to polymers

Determine acid/base ratio from ionic liquid studies.

Provide phase-separating polymer for solvent organization to facilitate Grotthuss transport.

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

Approach - Proton Transport



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

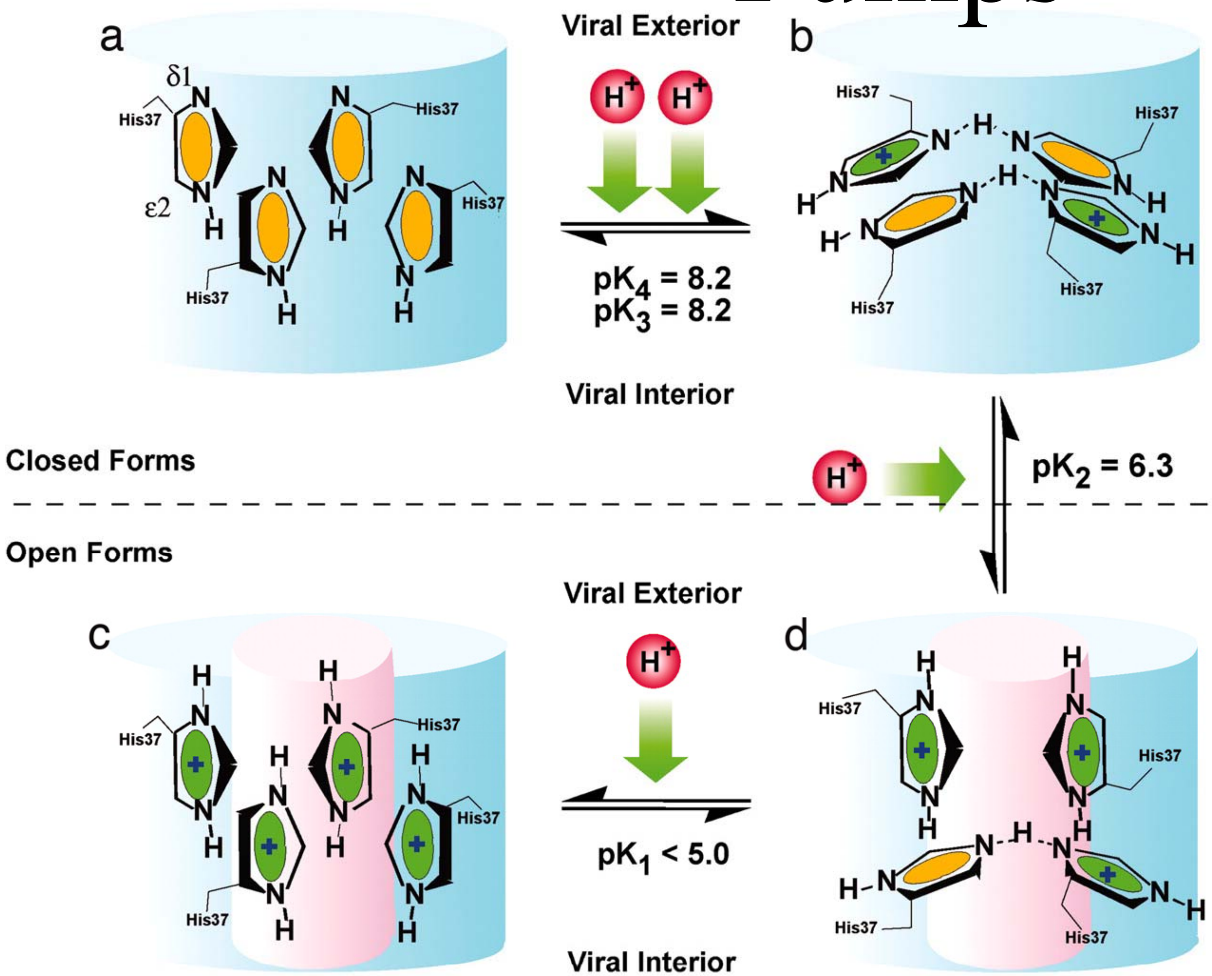
Grotthuss transport requires some degree of solvent organization (e.g. H-bonding).

Vehicle mechanism & segmental motion mechanism require too much energy.

Acknowledgement: K.D. Kreuer *et al*, Angewandte Chemie Int. Ed. Engl.(1983), No.3, 208.

Illustration from Macromolecules, 41 (2008), 3739

Learn from Nature –Proton Pumps



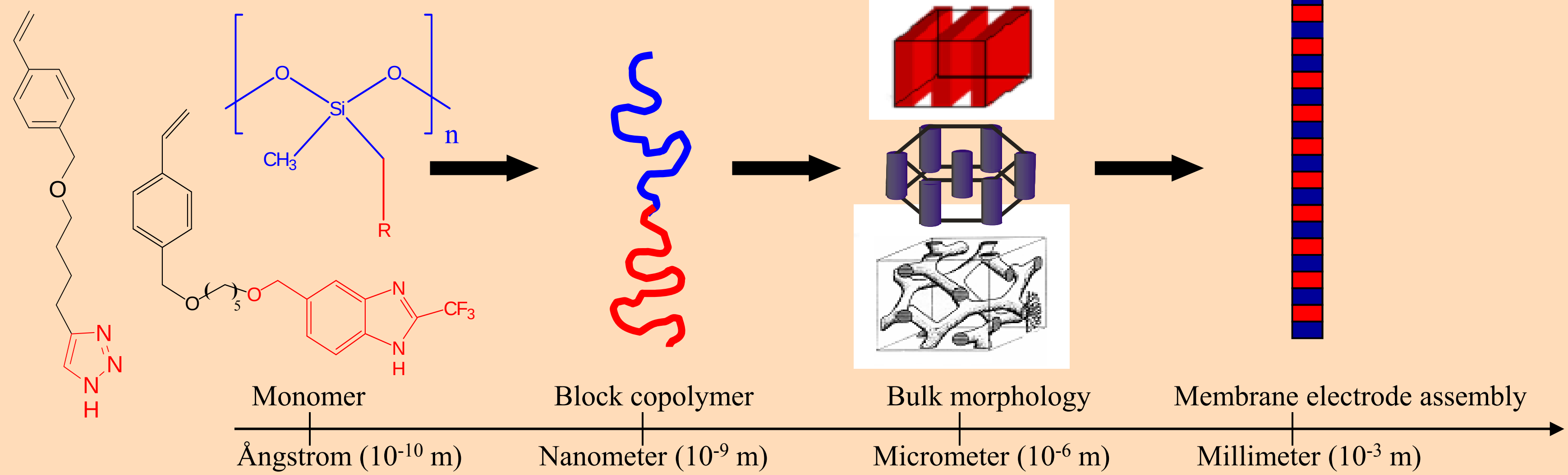
A model illustrating the opening of the M2 proton channel
Hu, Jun et al. (2006) Proc. Natl. Acad. Sci. USA 103, 6865-6870

Influenza A virus contains a protein that selectively transports protons across membranes using imidazole solvation groups arranged in a nanoscale pore.

We mimic this in our membranes

PNAS

Block Co-polymers for Morphology



Synthesize model protogenic monomers with heterocyclic groups

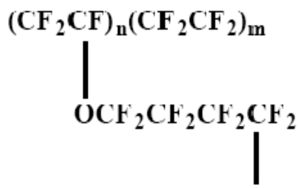
Well defined block copolymers through controlled polymerizations

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

Membranes and MEA’s that balance conductivity and structural integrity

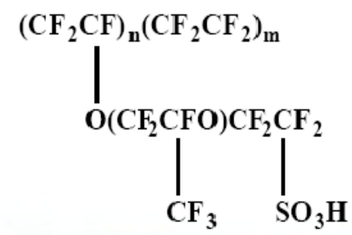
Acknowledgement: Brian Coughlin, U. Mass, Amherst

Conductivity of Imidazole-doped PFSA Materials

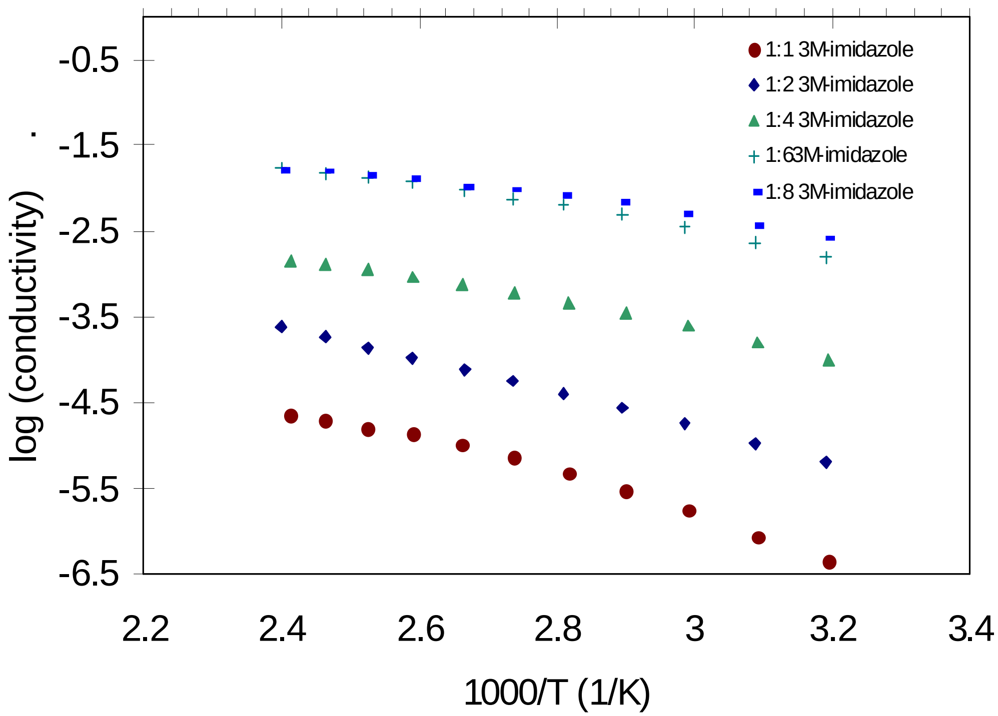


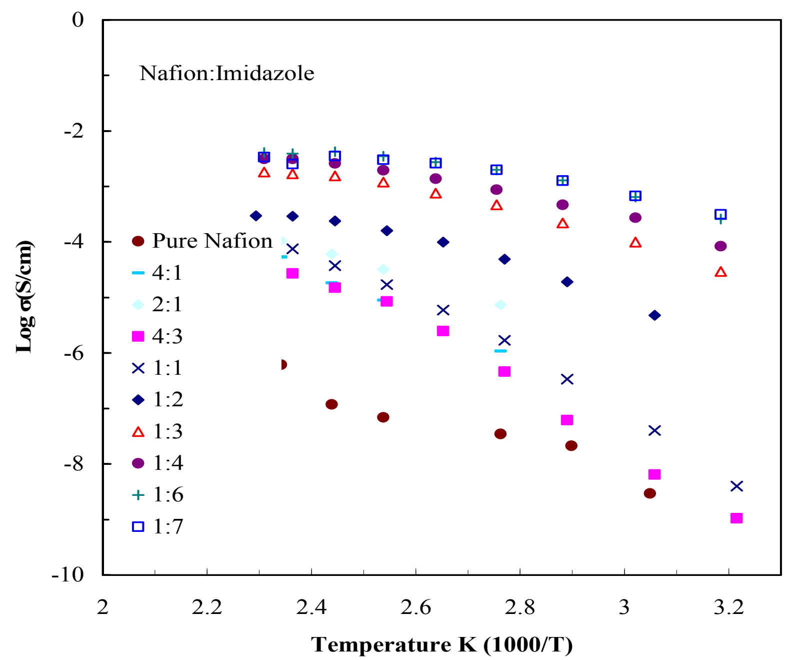
3M

EW 850



EW = 1100

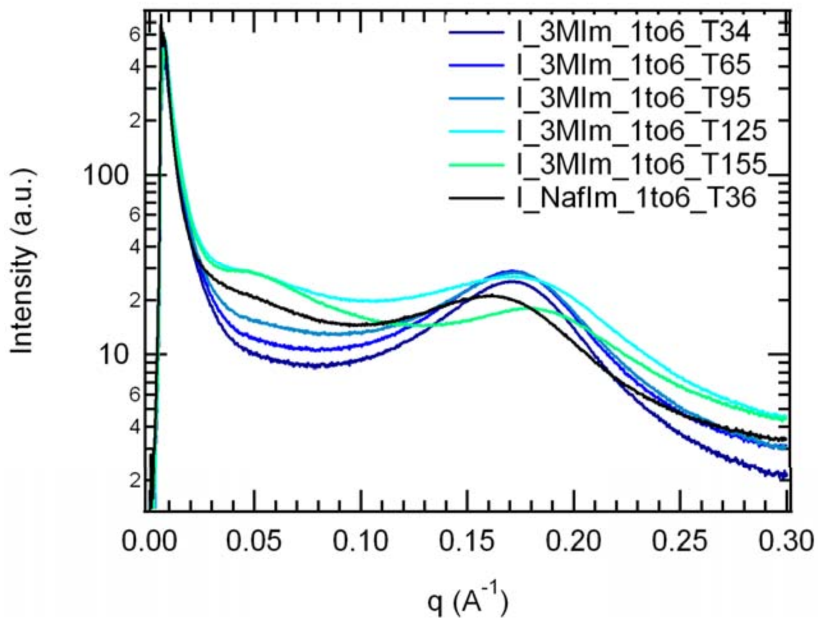


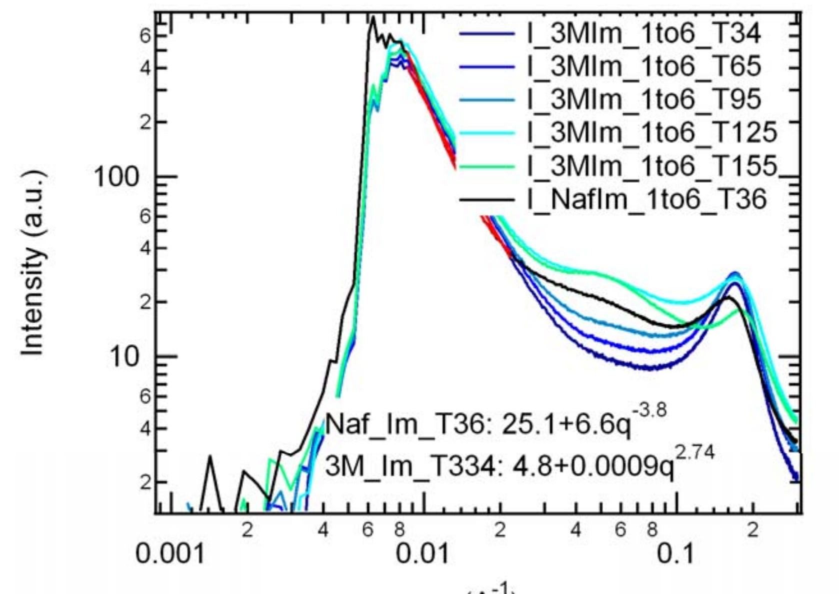


Lower EW provides higher charge carrier concentration – higher conductivity.

SAXS Measurements on Imidazole –doped PFSAs.

3M Polymer & Nafion with 1 to 6 Imidazole

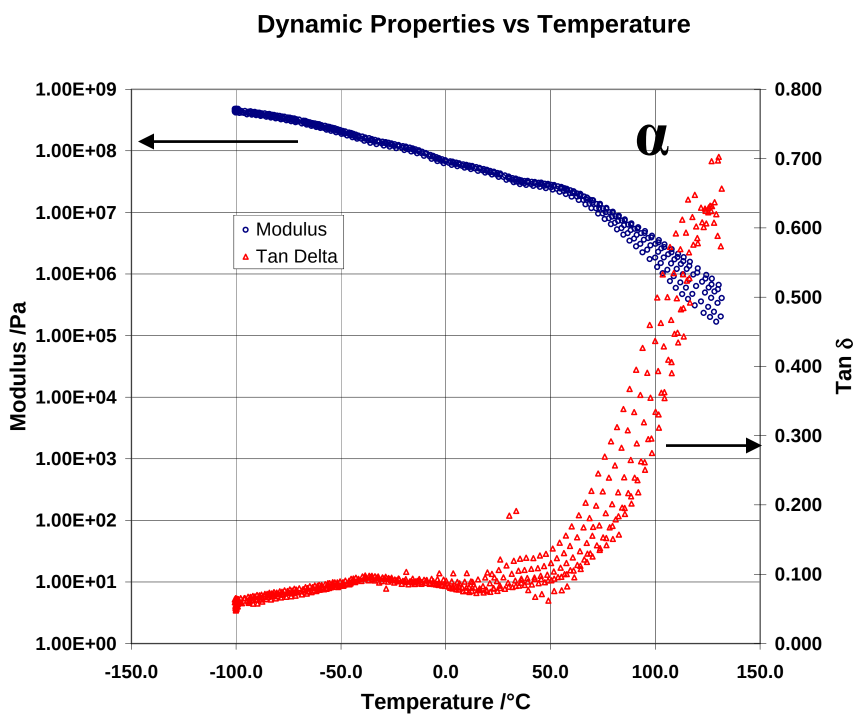




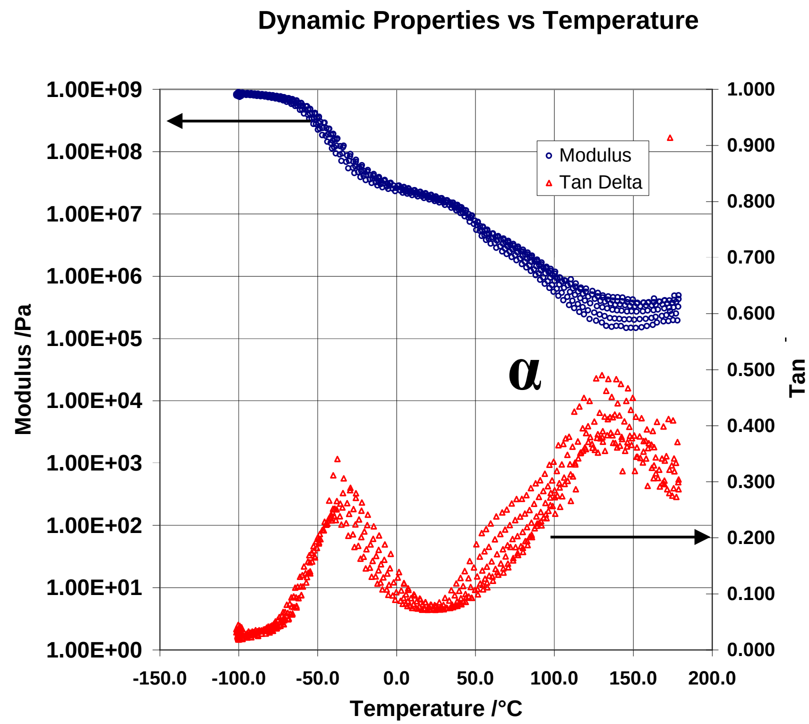
- Both samples (3M+Imid 1 to 6 and Nafion+Imid 1 to 6) show “ionomer” peak, which has been observed in literature
- 3M+Imid 1 to 6 has a domain size of 3.7 nm at room temp.
- Nafion+Imid 1 to 6 has a domain size of 4.0 nm at room temp.
- Heating study was performed on 3M+Imid sample and the sample appears to undergo a transition at 125C<T<155C with an emerging domain size of 7.0 nm at T=155^{o}C

DMA of Nafion and Nafion-Imidazole

Dry Cast Nafion

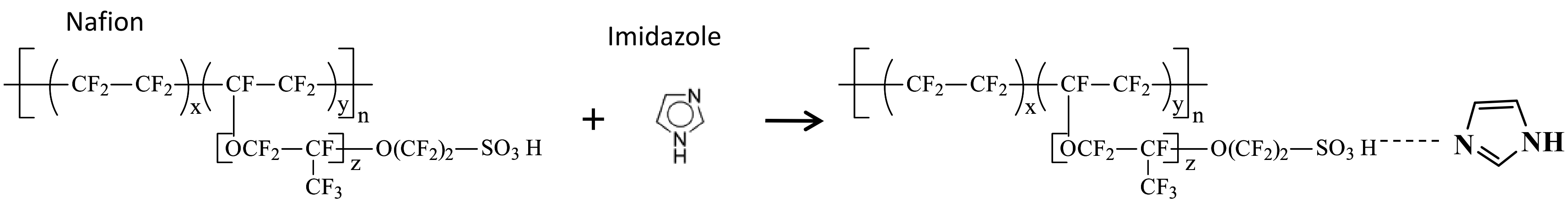


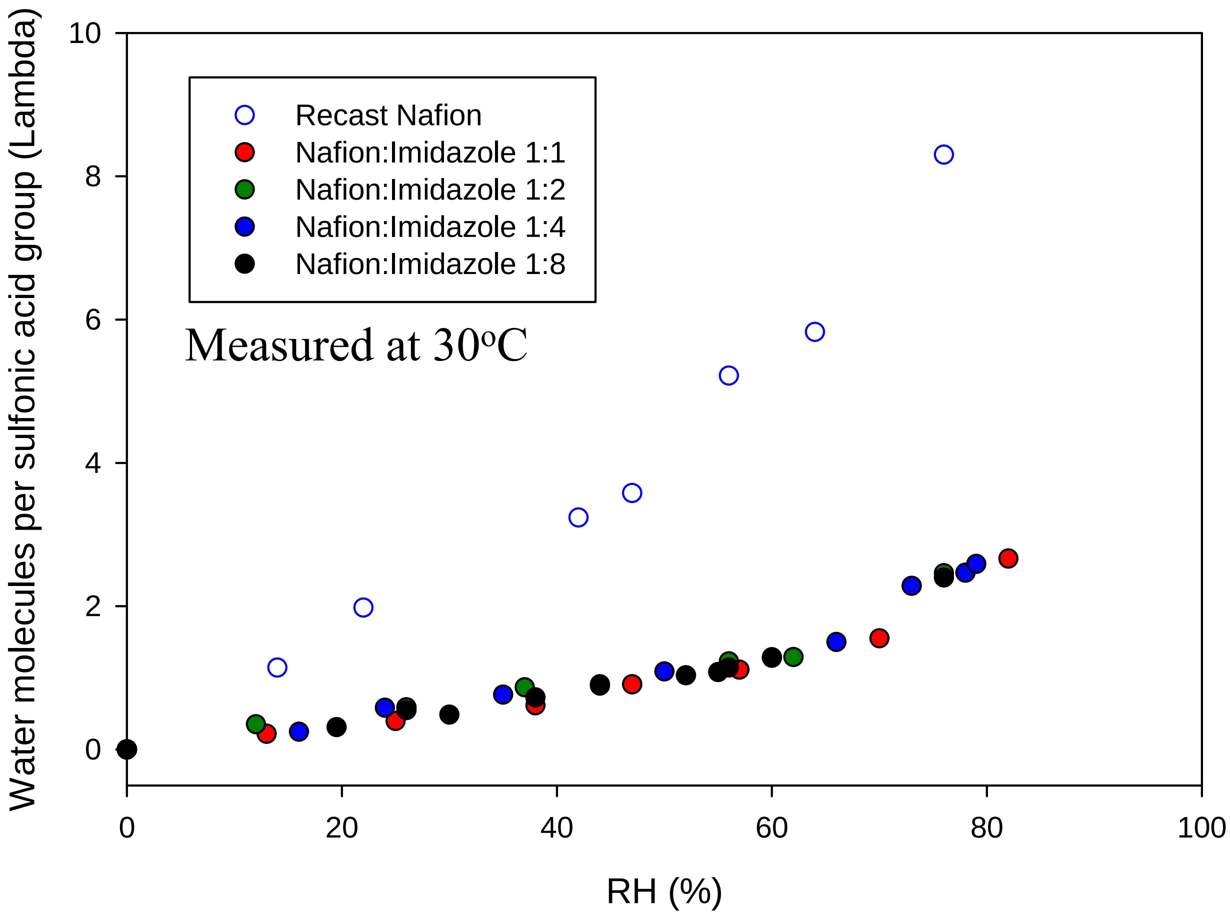
Dry Cast NAFION-Imidazole SO_3H:Im 1:4



- Imidazole results in an increase in the α-transition of Nafion from 120°C to 140°C due to better dissociation of the protons and the formation of the imidazolium salt.
- Glass Transition at -40°C indicates plasticization of perfluorinated matrix by imidazole, indicating mobile polymer backbones and less phase separation.

Effect of Imidazole on Water Uptake of Nafion

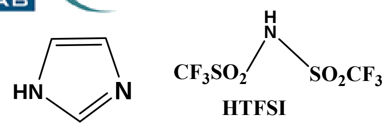




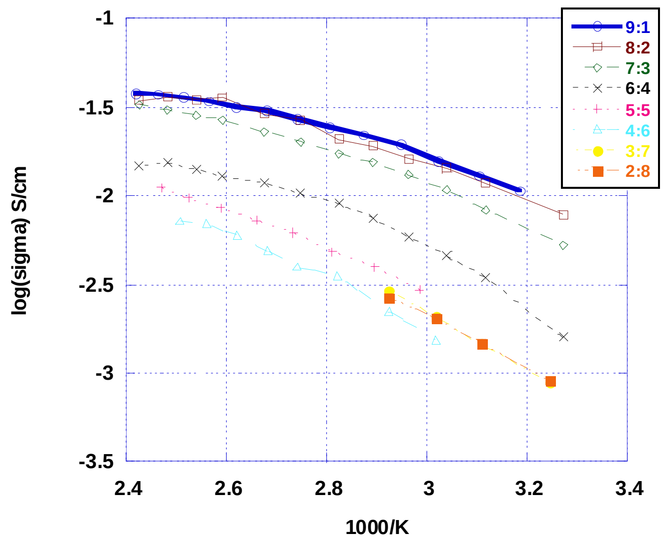
- **Water vapor uptake suppressed by presence of imidazole.**
- **pK_a & pK_b values of Imidazole nearly same as water.**
- **Can we produce membranes that reject water?**

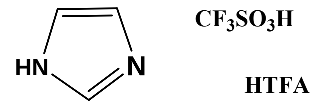
➢ **Reduce/eliminate stress due to swelling and freezing.**

Conductivity of Proton Ionic Liquids

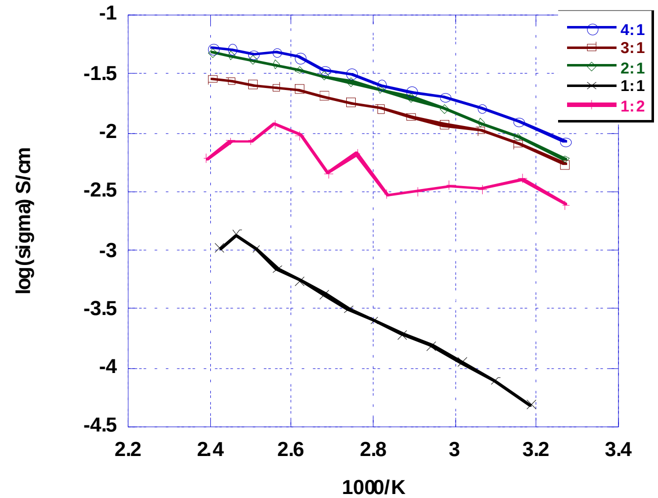


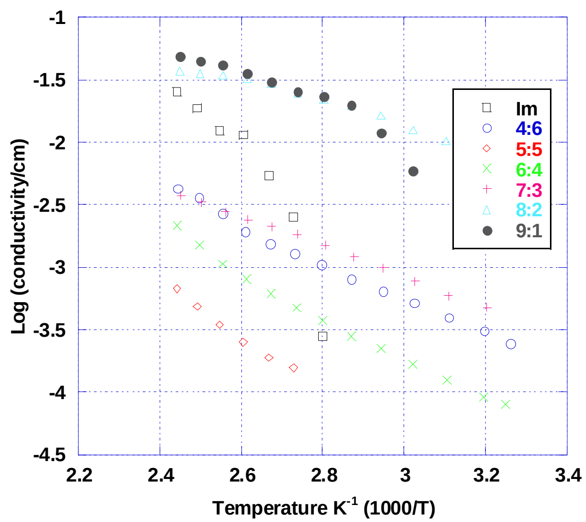
= ImTFSI

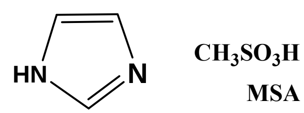




=ImTFA



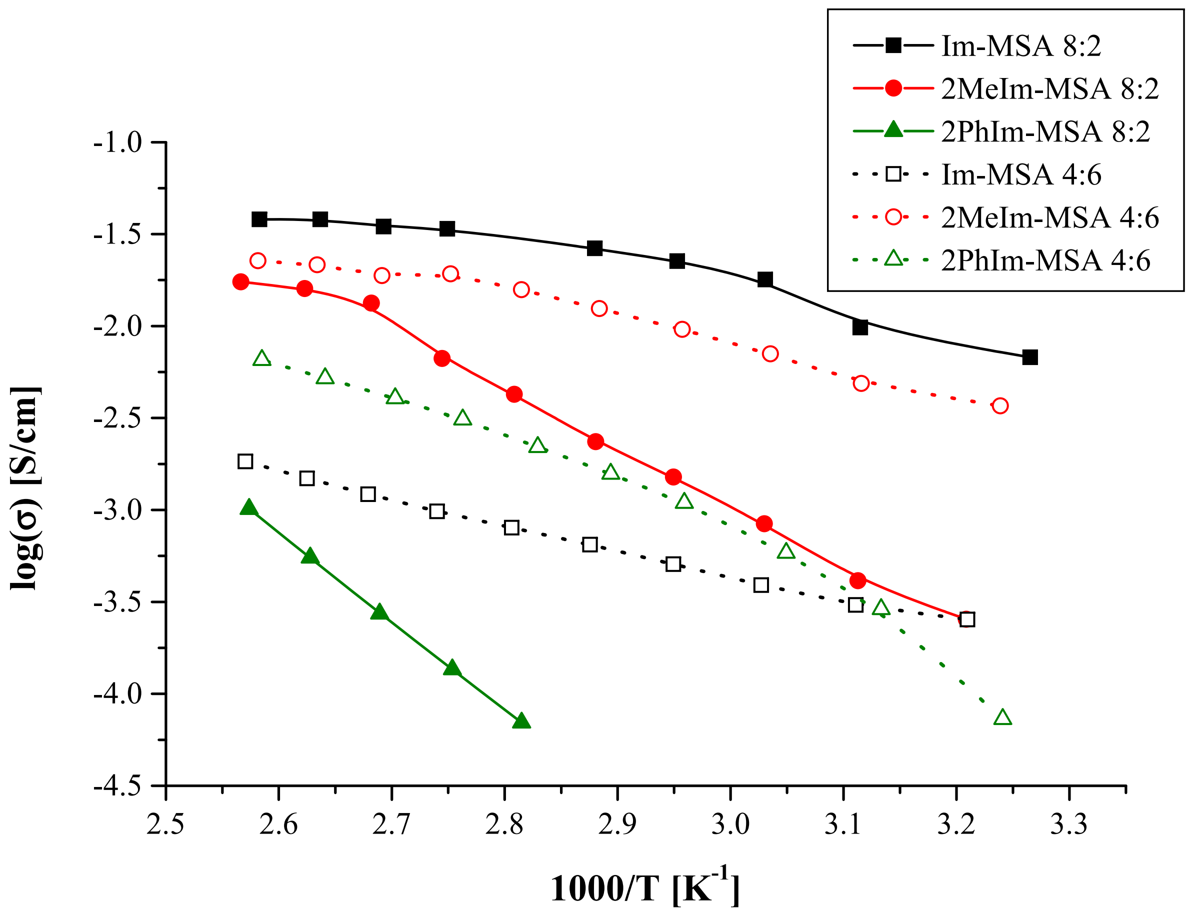




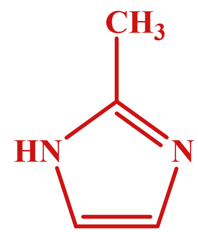
= ImMSA

- Conductivities unaffected by acid identity with excess imidazole.
- Conductivities dependent on imidazole excess.
- Temperature dependence greater than doped PFSA

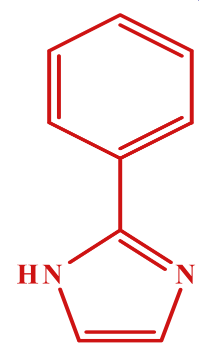
Comparative Ionic Conductivity of Substituted Imidazoles



Imidazole (Im)



2-Methyl-imidazole (2-MeIm)



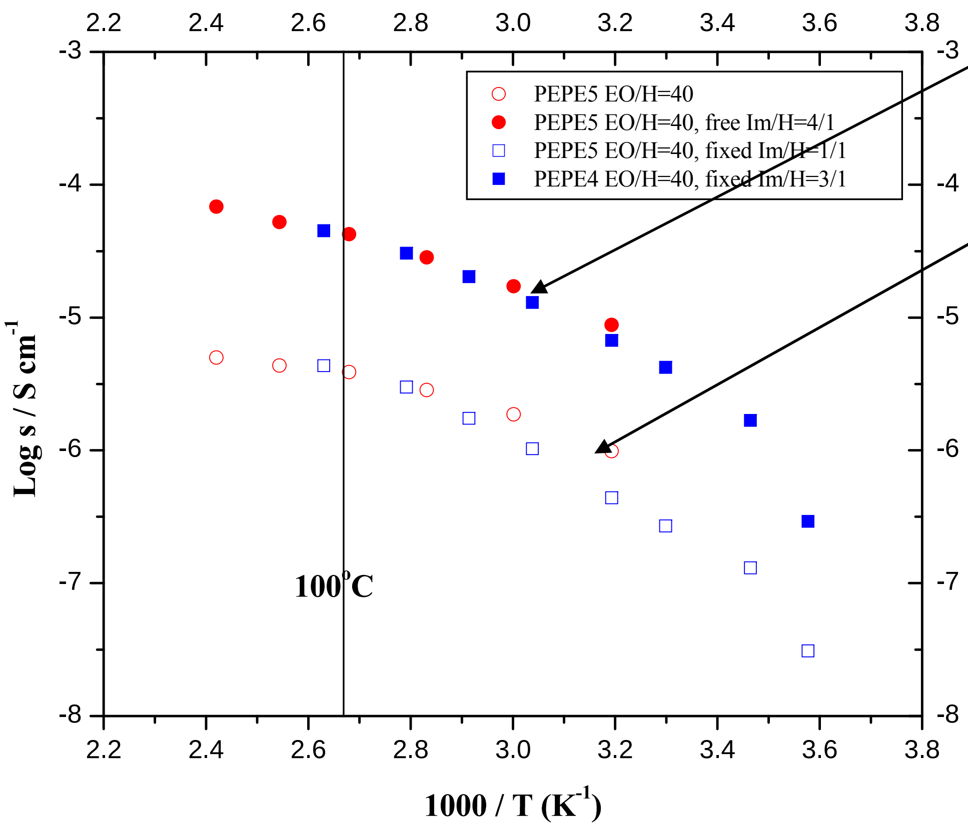
2-Phenyl-imidazole

(2PhIm)

Methanesulfonic Acid (MSA)

Conductivities of free imidazole and fixed imidazole based proton conductors.

Alkylsulfonic acid groups fixed to polyepoxide polyethers.



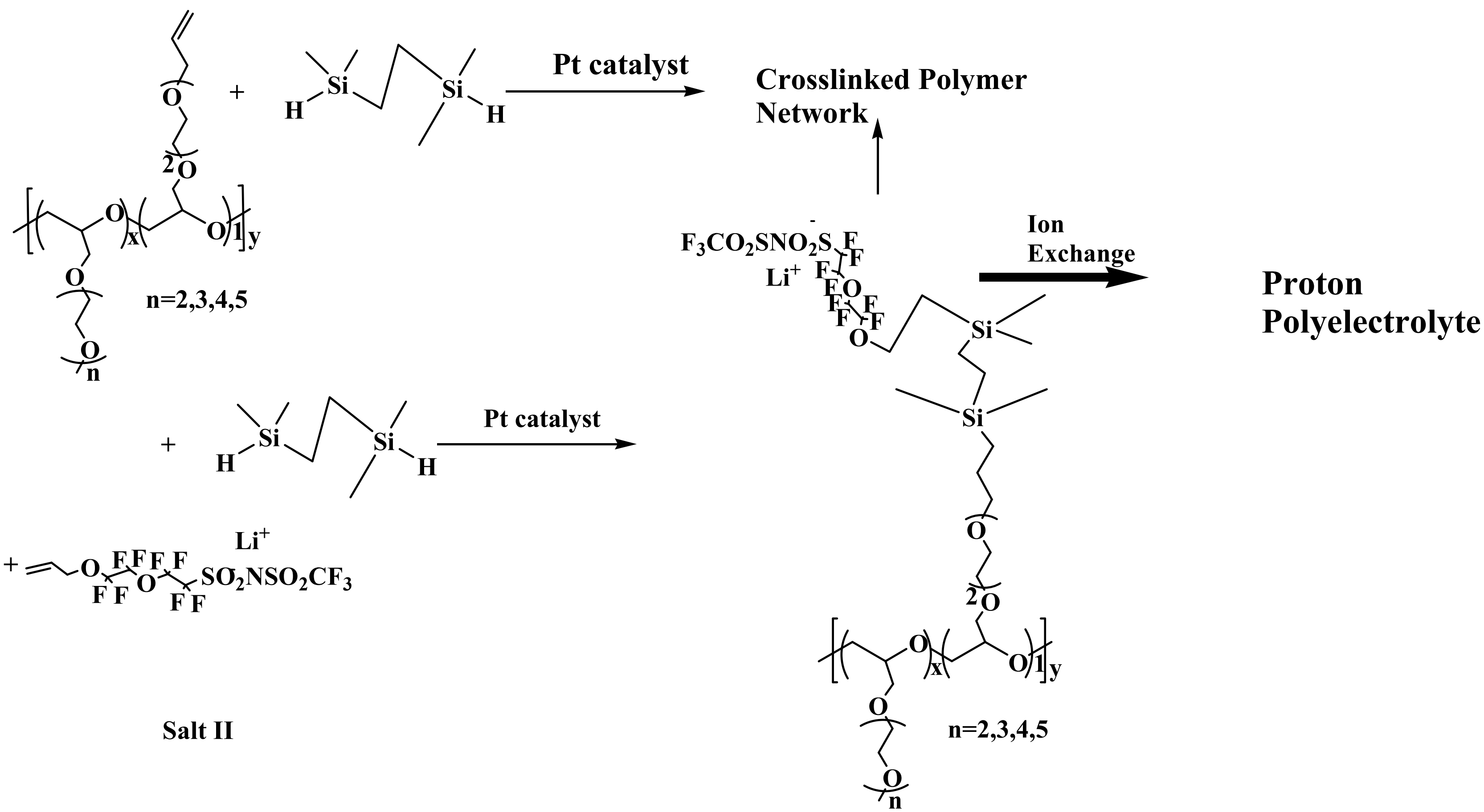
Tether done through Nitrogen on Imidazole. Grotthuss transport not possible

- **Conductivity of fixed Imidazole polymer equal to the conductivity of the polymer doped with free imidazole solvent.**
- 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.
- Polymer matrix and imidazole unable to particpate in Grotthuss transport.

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

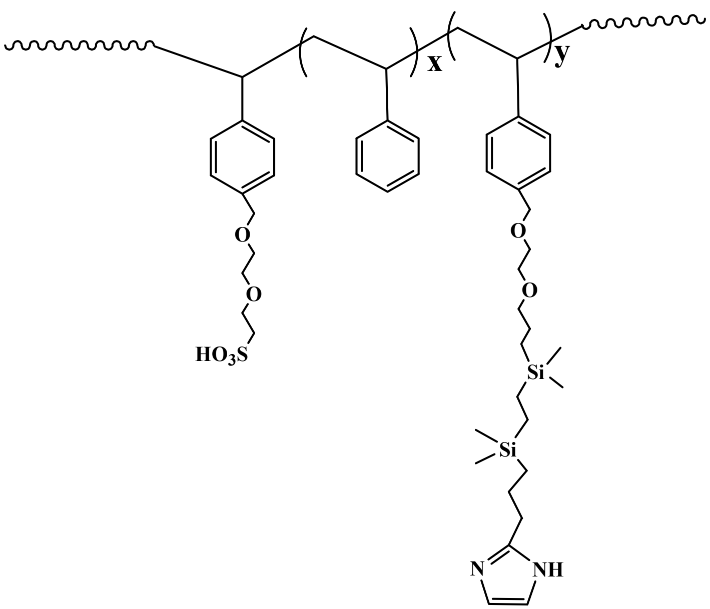
Synthesis

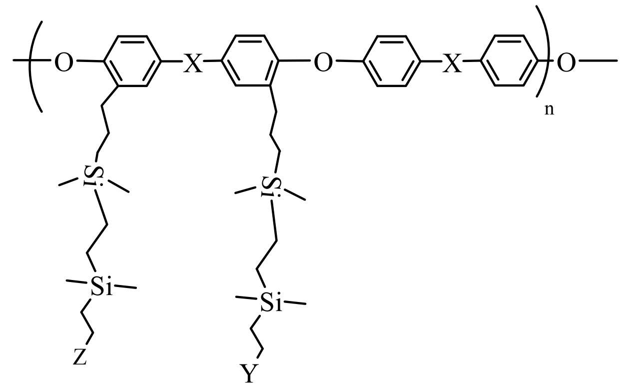
Grafting Strategy Allows any Combination of Acid groups and Heterocylic Bases

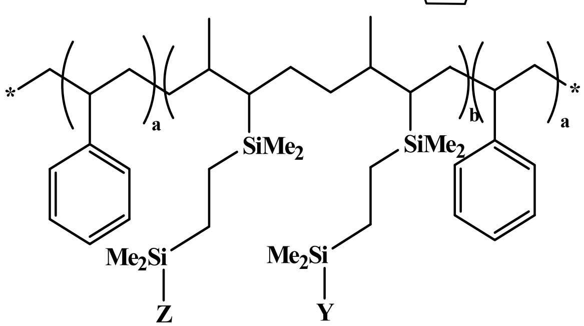


- USP 6,956,083,
- USP 7,101,643

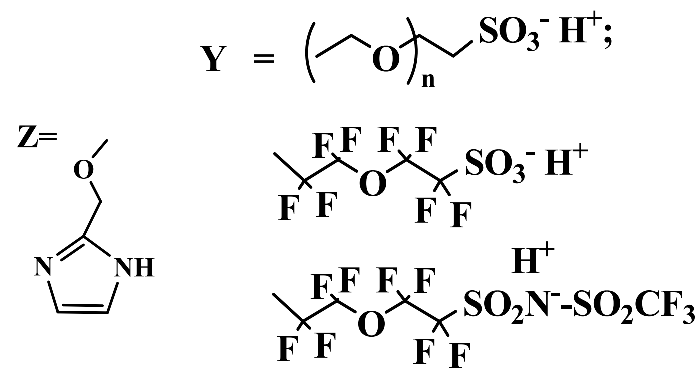
Change the Backbone





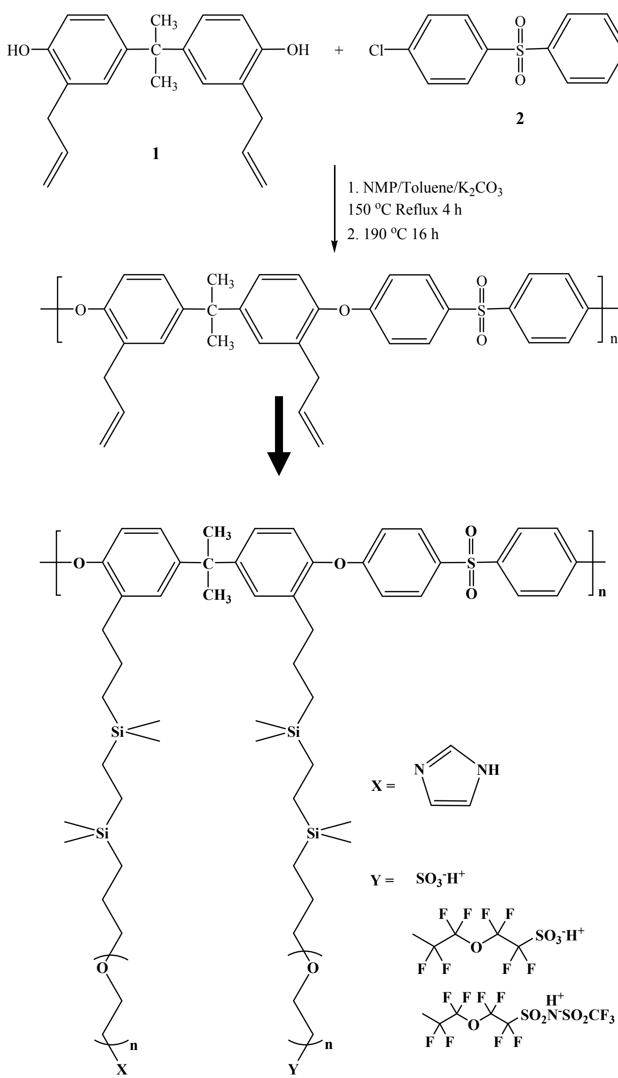


Block copolymer - Kraton



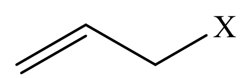
Technical Accomplishments.

PolySulphones with Imidazole and Acid Groups



Chemistry:

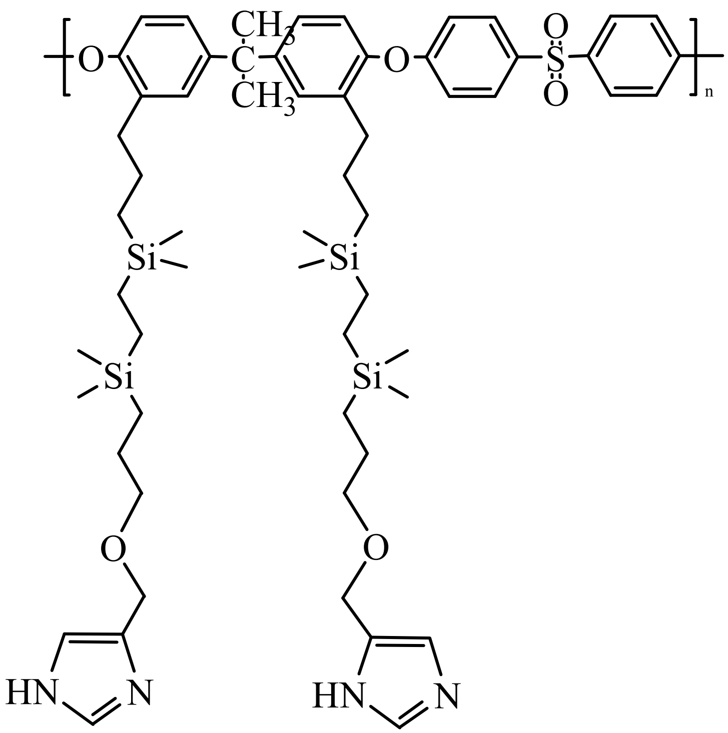
- Thermal rearrangement
- Chemical protection and de-protection
- Heterocyclic formation
- Hydrosilation
- Allylic chemistry



- Condensation polymerization
- etc…

Technical Accomplishments.

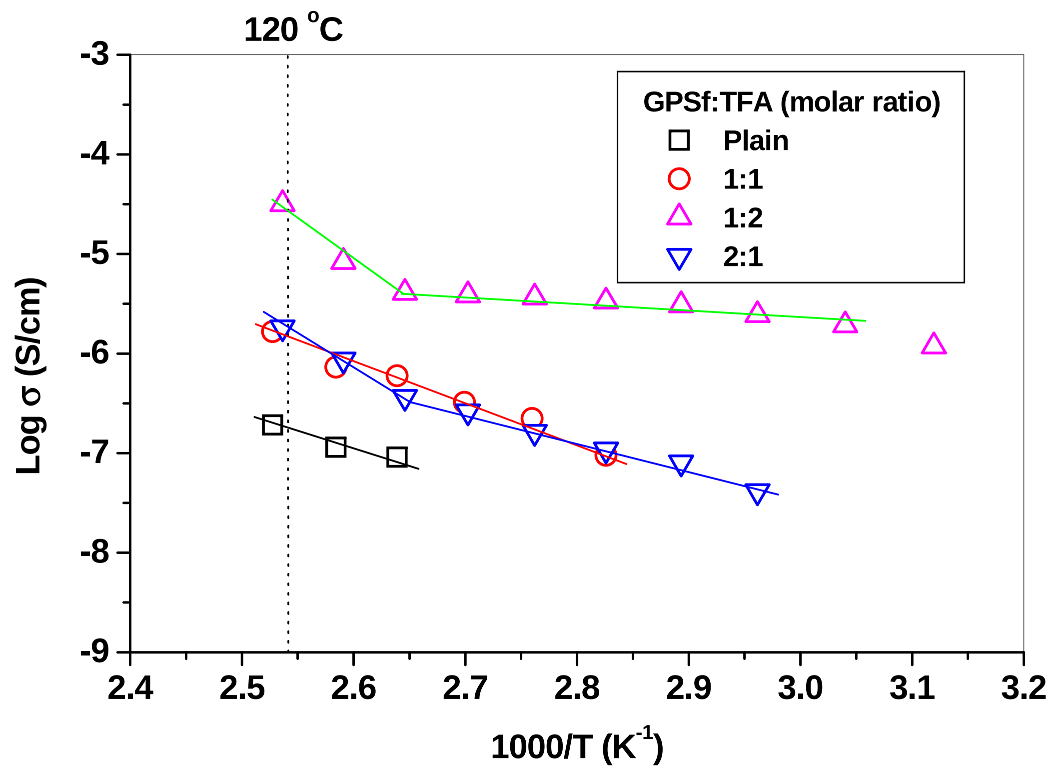
Imidazole Polymer (Graft 1st then Polymerize)



Degree of Graft: > 1.0

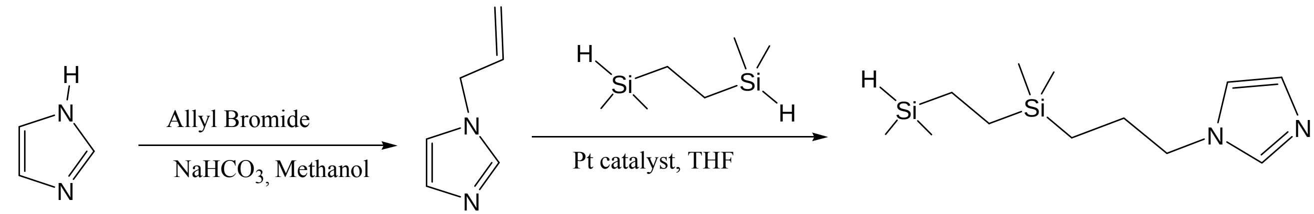
EW ~ 500

Conductivity when doped with Triflic Acid (TFA)

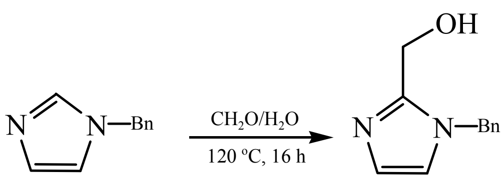


- Residual Pd/C catalyst, aggregation during cast was observed
- Random data, poor contact between electrode and polymer blend

Synthesis of allyl Imidazoles and intermediates for grafting



N-tethered imidazole cannot support Grotthuss transport.



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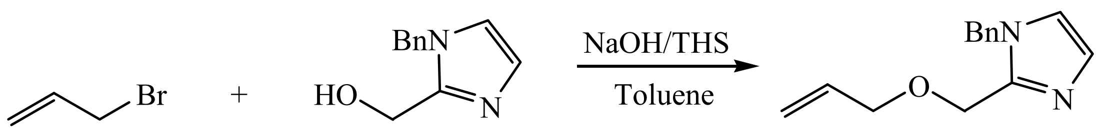

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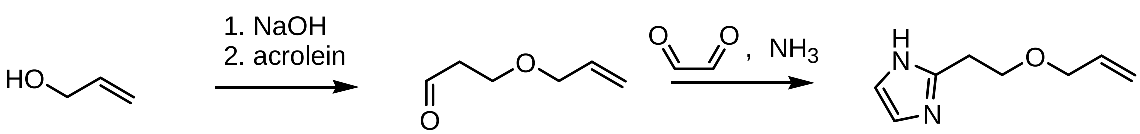


2 3

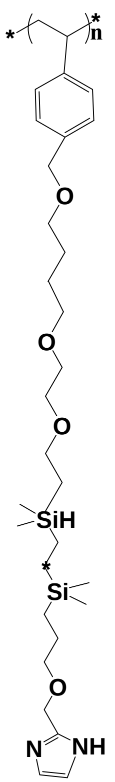
Problems with the use of Benzyl as Protecting group have delayed synthesis of tethered imidazole polymers.

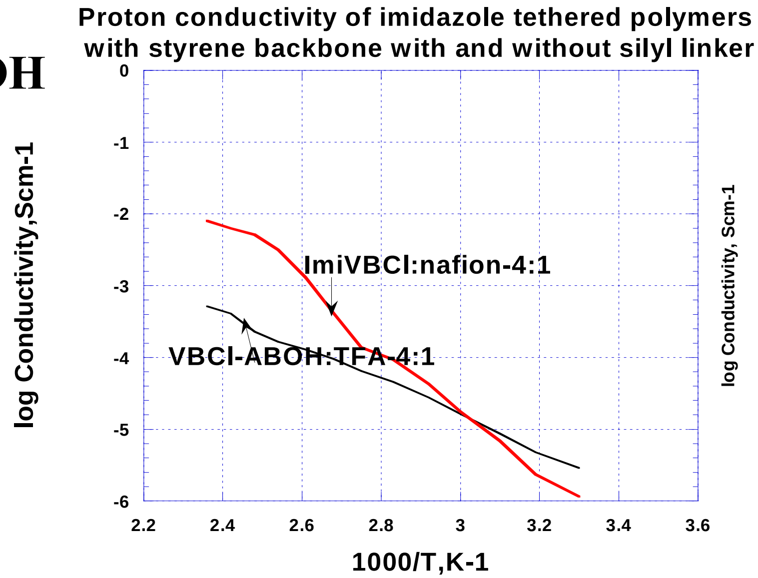
New protecting groups are under test – Trityl, Tosyl.

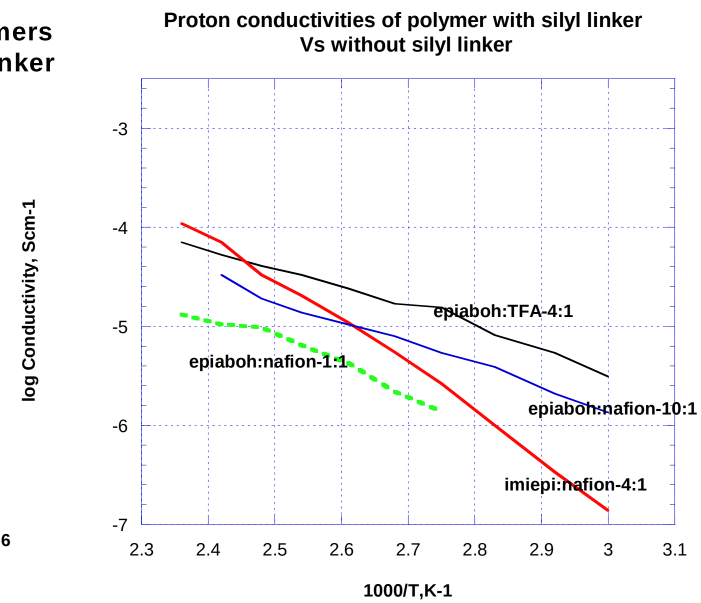
Technical Accomplishments.

Proton conductivities with different backbones

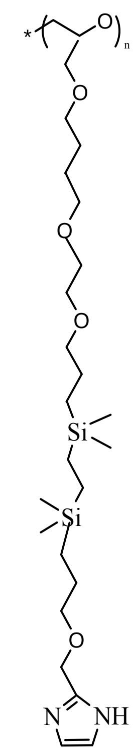
VBCl-ABOH

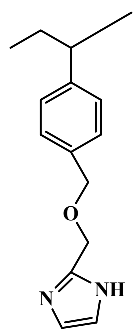




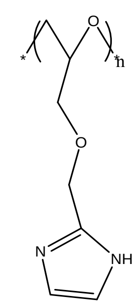


epiaboh





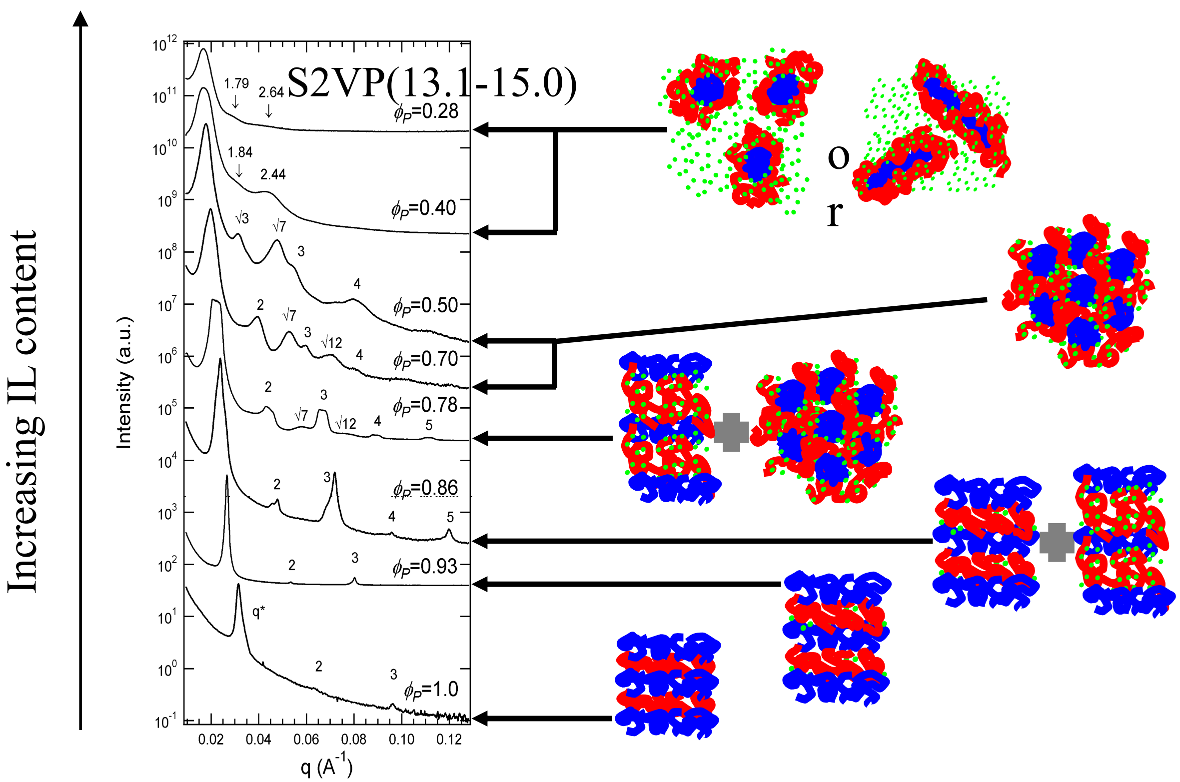
ImiVBCl

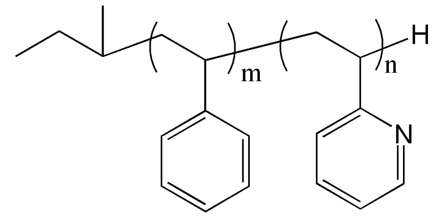


imiepi

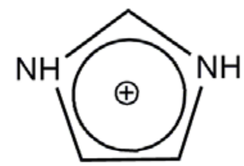
Short chain tether gives higher Ion Exchange Capacity and hence higher charge concentrations. Blends with Nafion seem stable. Phase separation behavior unknown here but styrene backbone more likely to phase separate.

Composition Dependence of Block Copolymer Nanostructure with Ionic Liquid(IL) Content.

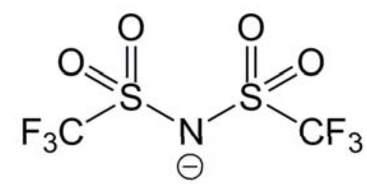




poly(styrene-*b*-2-vinylpyridine)
(S-2-PVP)



Imidazole

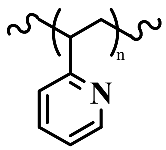


TFSI

SAXS patterns with increasing IL content.
Vinyl pyridine block selective for IL. Selectivity increases with temperature.
SANS measurements indicate IL segregating at interfaces.

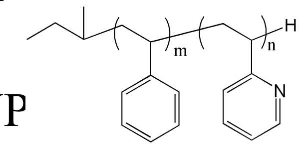
Technical Accomplishments and Progress

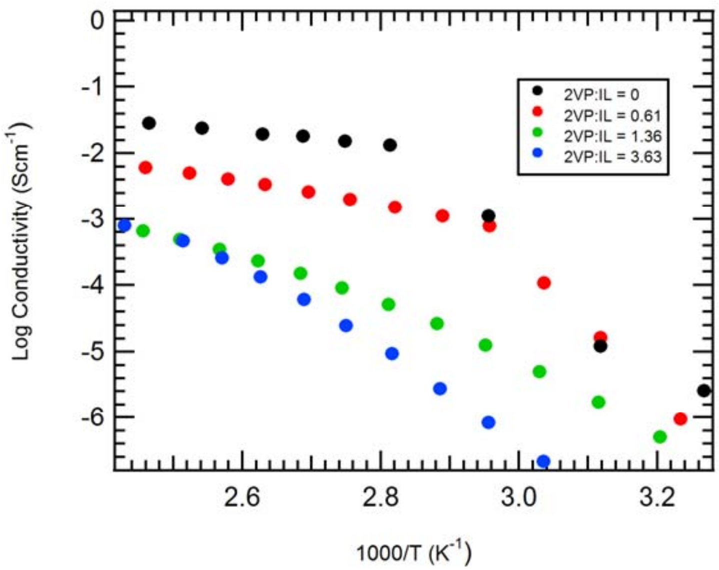
Conductivity of P2VP and S2VP in 5:5 Ionic Liquid

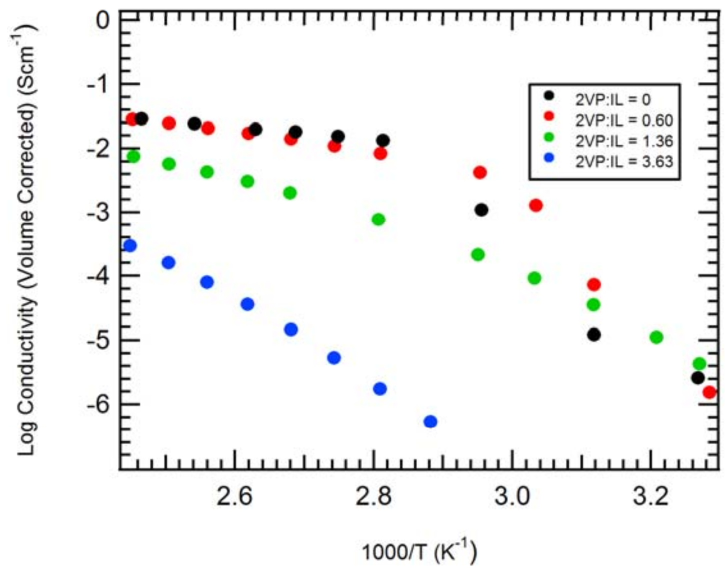


Homopolymer: P2VP
(13kg/mol) in 5:5 IL

Block Copolymer: S2VP
12.0kg/mol) in 5:5 IL





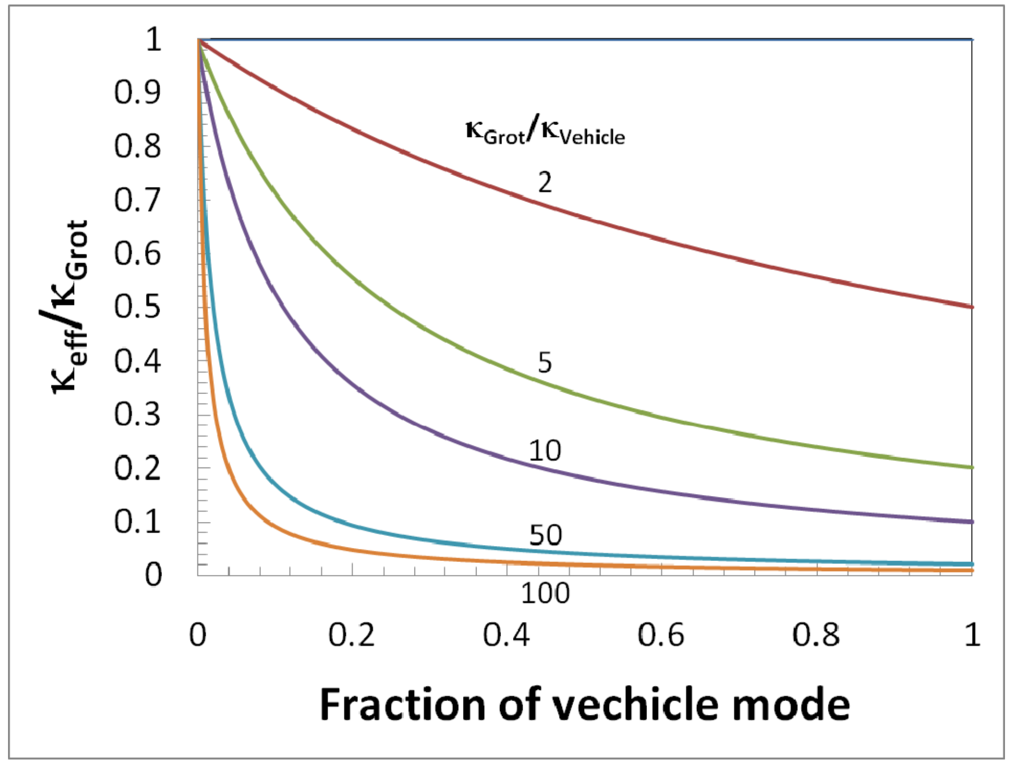


- Ionic conductivity decreases with increasing polymer content and temperature dependence increases, indicating interference of segmental motion
- A sharp decrease in conductivity occurs with a phase transition (to a solid)
- Block copolymer + IL system achieves higher conductivities than homopolymer + IL and Grotthuss-like temperature dependence extends to lower temperatures.
- Pulsed Field Gradient NMR measurements of self diffusion coefficients pending.

Conductivity Estimation

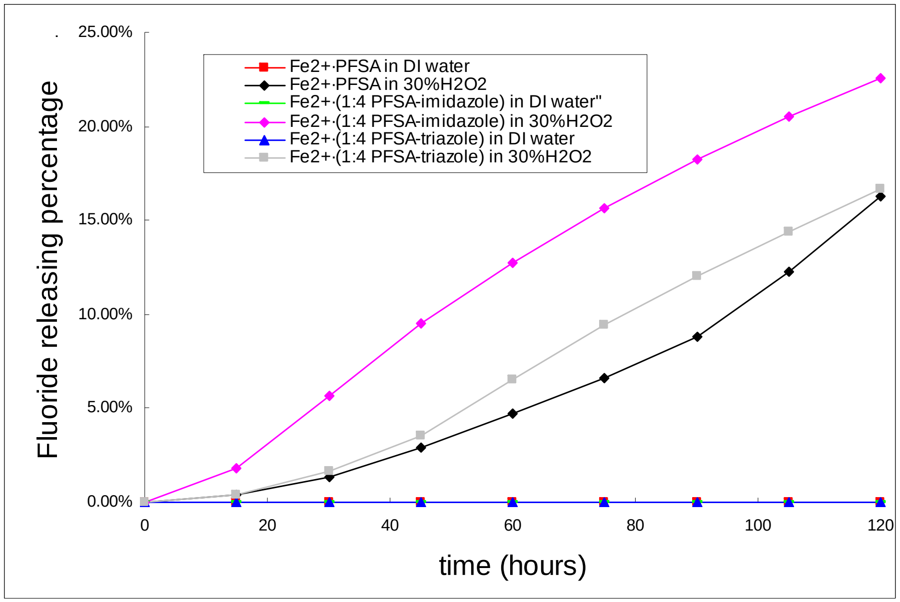
$$\frac{\kappa_{eff}}{\kappa_{Grot}} = \frac{1}{1-\left(1+\frac{\kappa_{Vehicle}}{\kappa_{Grot}}\right)\frac{\delta_{Vehicle}}{\delta_{Membrane}}}$$

- From Ohm's law, estimate how conductivity changes as a function of vehicle versus Grotthuss transport
  - Assume domains are connected in series
  - Only need very small amounts of vehicle mode connections to greatly reduce effective conductivity
  - Need to determine
    - Respective conductivities
    - Conditions that promote Grotthuss transport (e.g., excess imidazole, shorter side-chain length, etc.)
  - Need to model
    - Domains connected in a network
    - Movement within a domain (vehicle or segmental vs. Grotthuss)

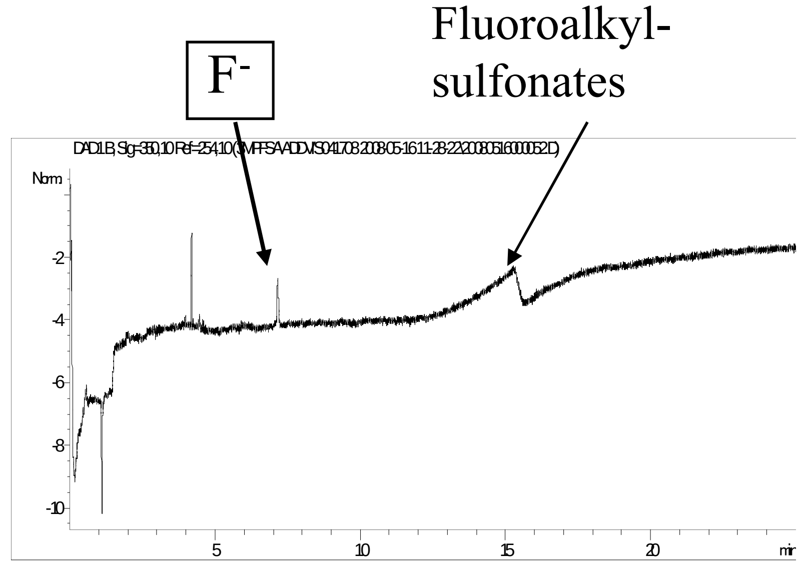


Need MD modeling for better understanding.
Explore collaboration with Smith,/Borodin/Voth (U.of Utah)

Oxidative and Acid Stability

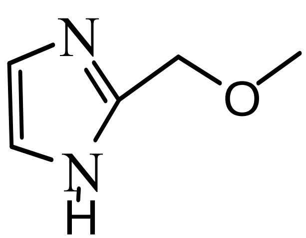


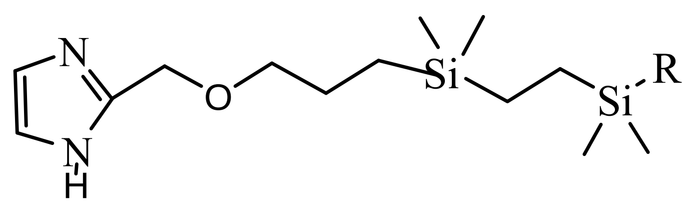
The fluoride release rates of Fe^{2+}•PFSA, Fe^{2+}•(1:4 PFSA -imidazole), Fe^{2+}•(1:4 PFSA -triazole) in DI water and 30% H_2O_2.



Capillary Electrophoresis analysis of water effluent from treatment of 3M PFSA-Triazole with Cu^{2+} and 30% H_2O_2

Fenton chemistry on imidazole leads to ring-opening. Initiated study of Fenton chemistry on substituted imidazoles with tether groups by means of model compounds, e.g.

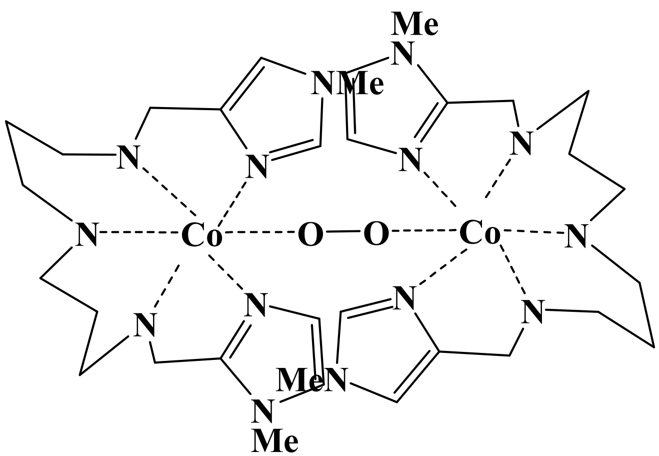




Imidazoles Stable?

Examples Known of great stability

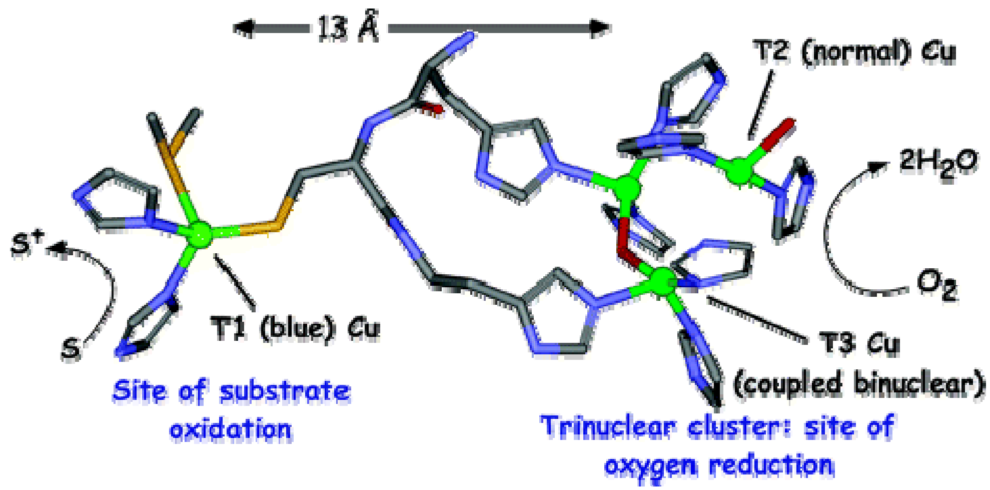
Oxygen separation systems use Imidazoles for stability.



E. De Castro, B. D. Zenner, J. P. Ciccone, L. A. Deardurff, and J. B. Kerr, USP 4,959,135 (1990).

Enzyme ORR catalysts.

Copper catalyst centers are held in place by IMIDAZOLE

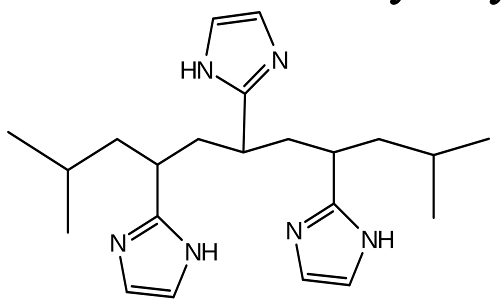


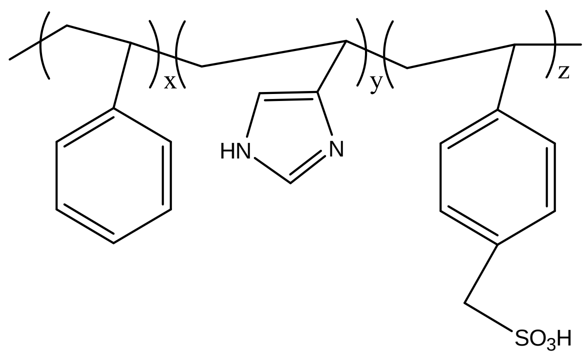
Nature chooses imidazole as a base in the presence of oxygen.

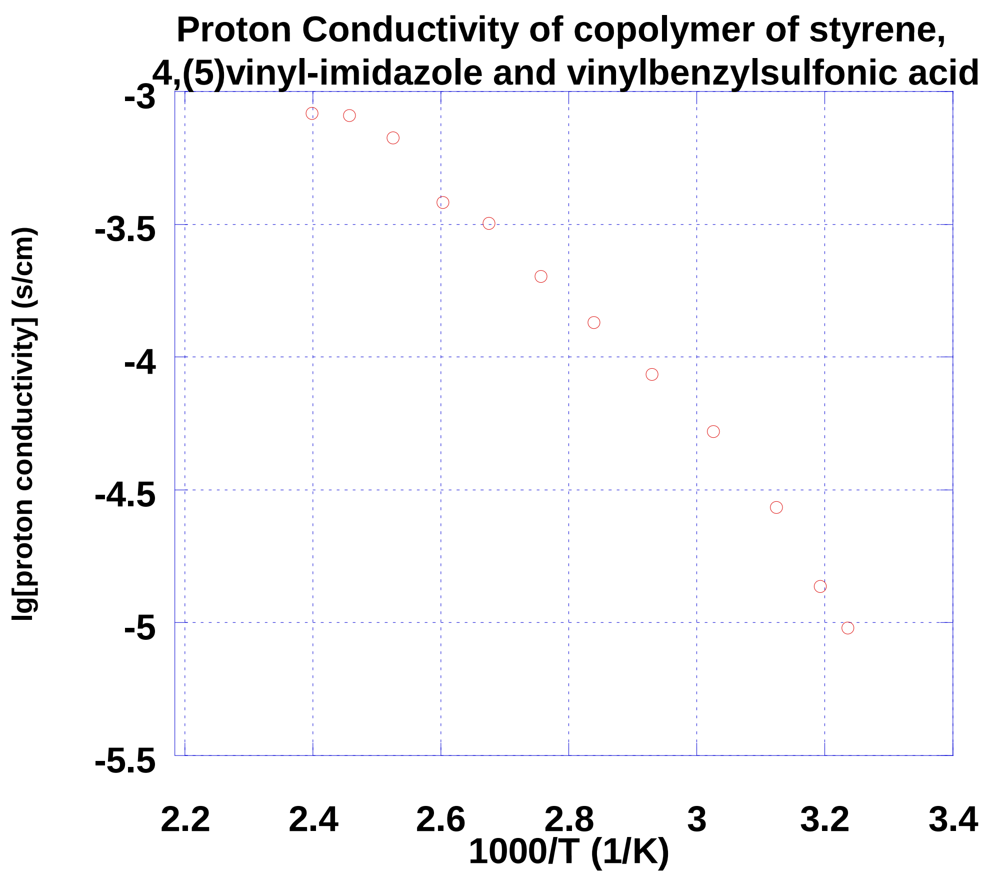
Copper catalysts better than platinum?

Imidazole Co-polymers

Polyvinylimidazole



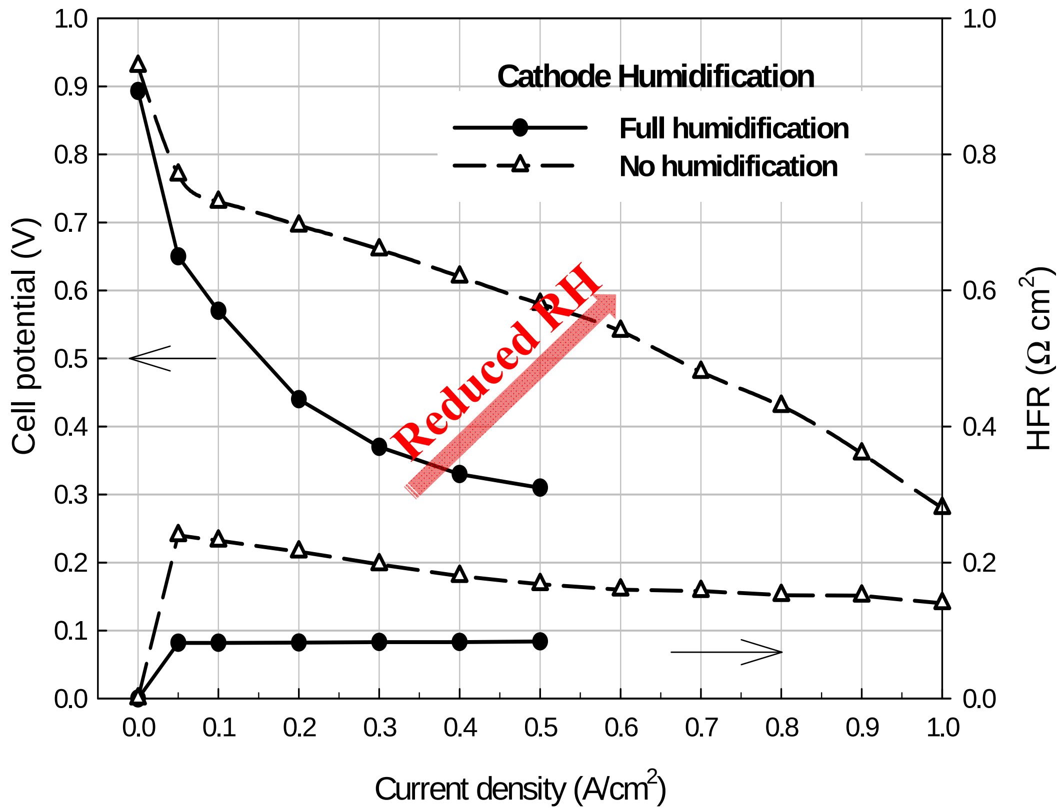




Non-Nafion Electrode Development For High Temperature Membranes

	FY '06-08	FY '08-09	FY '09-10	FY '10-
	Sulfonated Copolymers/Pt Black Catalyst	Sulfonated Copolymers/Pt/ Carbon Catalyst	Sulfonated/Imidazole tethered Copolymers/Pt/ Carbon Catalyst	Optimization of Electrode for High Temperature Membrane
Achievement Observation	***About 85% of Nafion-bonded Electrode at 95°C/ 60% RH***	***Ionomer chemical structure greatly impacts the electrode performance.*** ***Partial fluorination increases the electrode performance greatly***		
Major Issues	**Non-Nafion-bonded electrodes caused significant catalyst flooding**	**Ionomer morphology in dispersion and solid state**		

Hydrocarbon bonded Electrode – Better Performance at low RH



Hydrocarbon bonded electrode shows better performance under low RH conditions, due to better mass-transfer.

Good chance to replace PFSA-bonded electrode with thermally stable HC- bonded electrode for high temp. and less RH fuel cells.

Test temperature: 80°C
Catalyst: Pt/C (Pt loading=0.1 mg/cm^2)
Membrane: Nafion 212
MEA Fabrication: LANL method*

* Method of Making Membrane Electrode Assemblies
Y.S. Kim et al. US Patent Application 12/321,466 (2009).