New Polyelectrolyte Materials for High Temperature Fuel Cells

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

May 19, 2009

Project ID #
fc_14_kerr

Overview

Timeline

- Project start – February 2007
- Project end – September 2010
- Percent complete – 50%

Budget

- Total project funding
  - DOE share $6,000k
  - Contractor share - in-kind (up to $1,000k) plus NSF studentships (UCB)
- Funding received in FY08
  - $1450k
- Funding for FY09 - $1550k

Barriers

E. System Thermal and Water Management.

A. Durability.

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 - Objectives

- Develop knowledge that leads to materials that can meet the performance needs at acceptable cost.
- Fuel Cells that operate efficiently without external humidification at operating temperatures between -40^oC and 120^oC - significant system simplifications.
  - 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 (≤ 120^oC) and inlet water vapor partial pressures <1.5 kPa.
    - Durability with cycling > 5000 hours at > 80^oC.
    - Oxygen and Hydrogen cross-over currents ≤ 2mA/cm^2.
  - Durable MEAs with rated power at 1,000 mW/cm^2 and less than 5% performance degradation over lifetime.

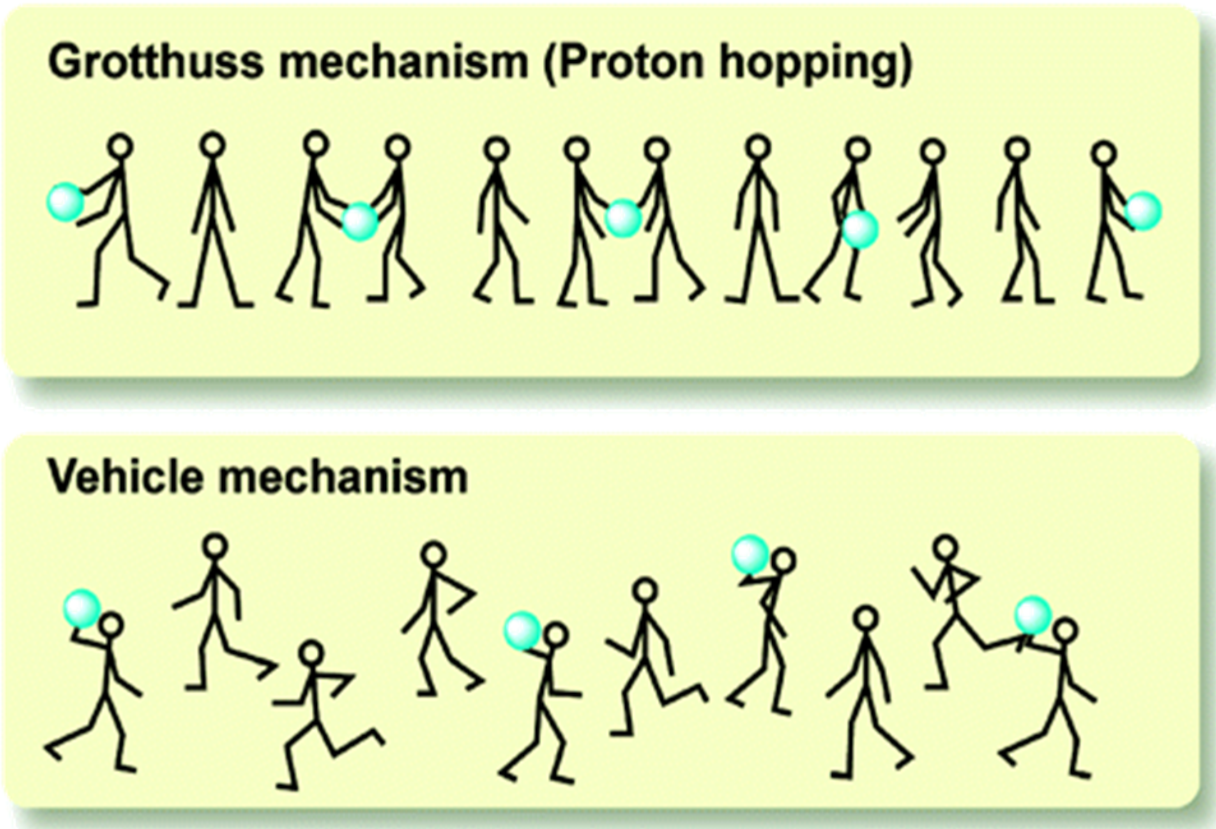
Approach - Objectives

- 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

Approach – Go/No-go Decisions

Month/Year/Status	Milestone or Go/No-Go Decision
March/09/ Estimated complete by June 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^{o}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^{o}C) is possible without free solvents?
September/09/ 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.
September/10/ 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^{o}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



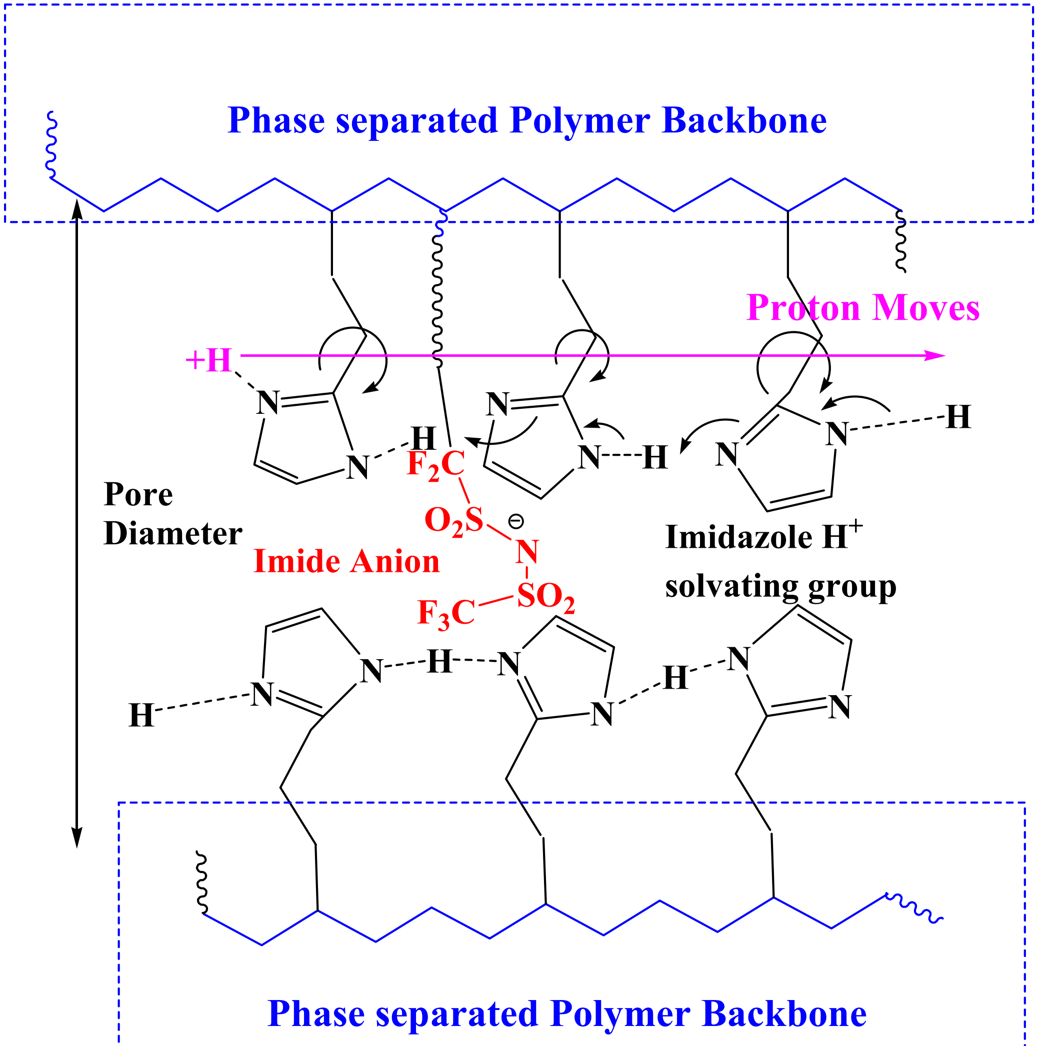
Acknowledgement: K.D. Kreuer *et al*, Angewandte Chemie Int. Ed. Engl.(1983), No.3, 208.
Illustration from Macromolecules, 41 (2008), 3739

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.

APPROACH to Material Design of Polymers to support Grotthuss Transport.



Tether imidazoles and acid groups to polymers

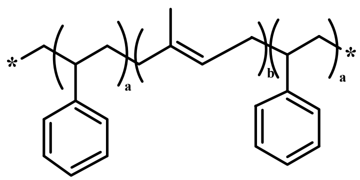
Determine acid/base ratio from ionic liquid studies.

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

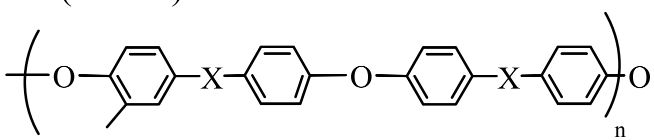
Keep imidazole tether short to increase organization, prevent tether disrupting proton transport and maximize concentration.

Approach – Synthesis of the Membrane Materials. Two routes, equally under study

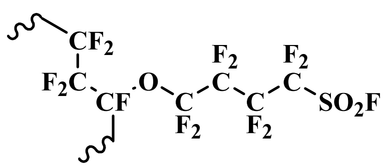
- Modify available polymer backbones to tether base and acid groups:
  - Kraton block co-polymers (LBNL)



  - Polysulphones (Udel, BPSH from Prof McGrath. Random and block co-polymers (LANL).

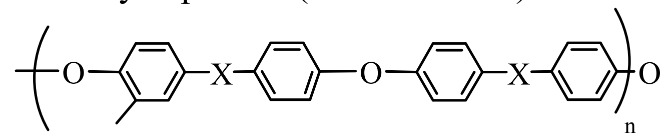


  - PFSA precursor (3M). Random copolymer (LBNL/3M

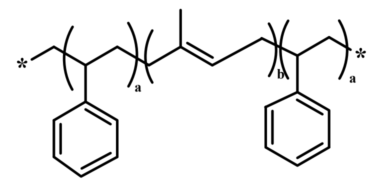


- **Pros:** Lots of material can be made quickly which can be rapidly
- **Cons:** Material may be hard to characterize; modification chemistry may be variable. Lots of unknowns which are bad for fundamental understanding.

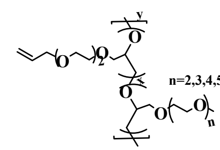
- Prepare functionalized monomers and polymerize followed by chemistry to attach base and acid groups.
  - Polysulphones (LBNL/LANL)



  - Polystyrenes, Kraton-like block copolymers (LBNL)



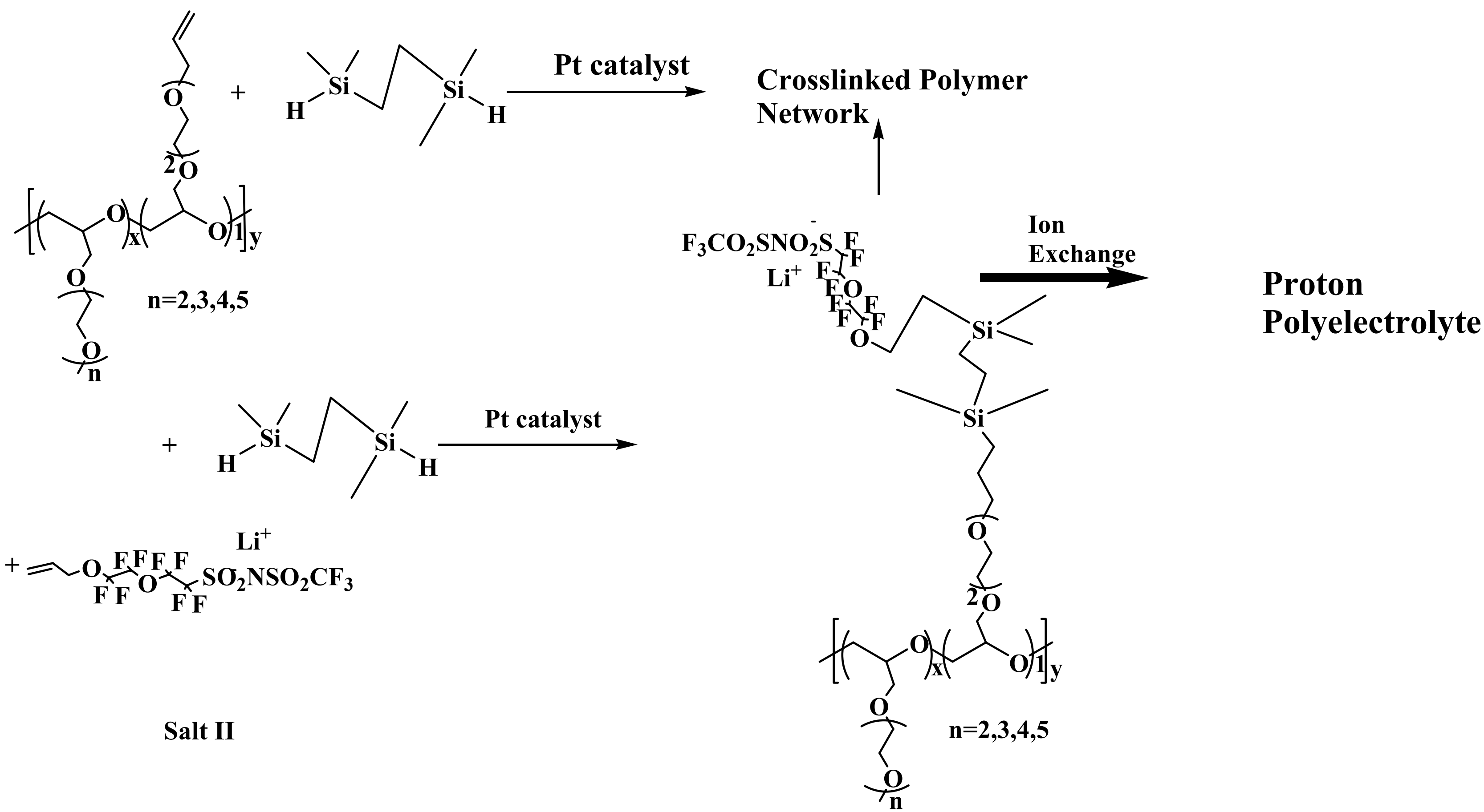
  - Flexible hydrocarbon or polyether backbones (LBNL).



- **Pros:** material composition can be controlled and material can be well characterized – good for fundamental understanding
- **Cons:** difficult synthetic problems that lead to materials with poor mechanical properties – leads to slow progress

Approach - Synthesis

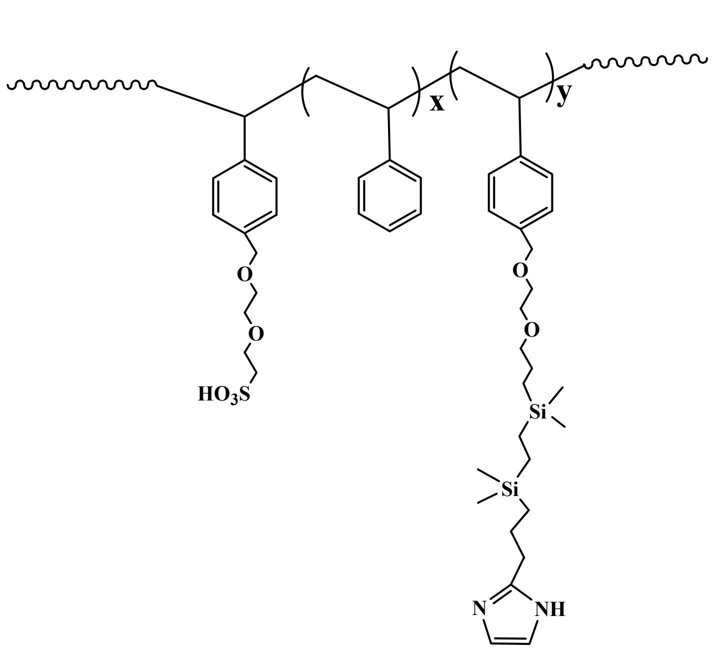
Grafting Strategy Allows any Combination of Acid groups and Heterocylic Bases

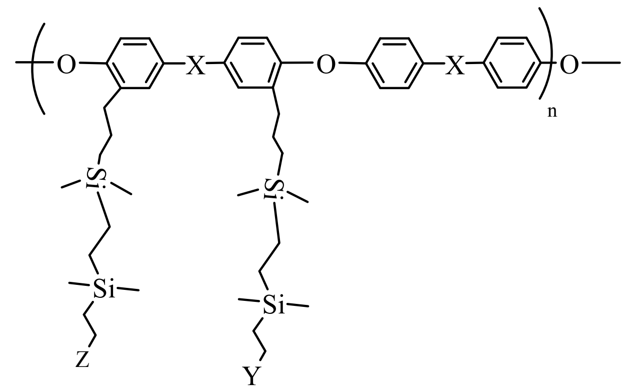


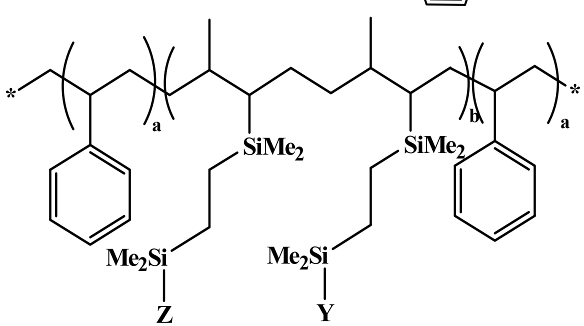
- USP 6,956,083,
- USP 7,101,643

Technical Accomplishments.

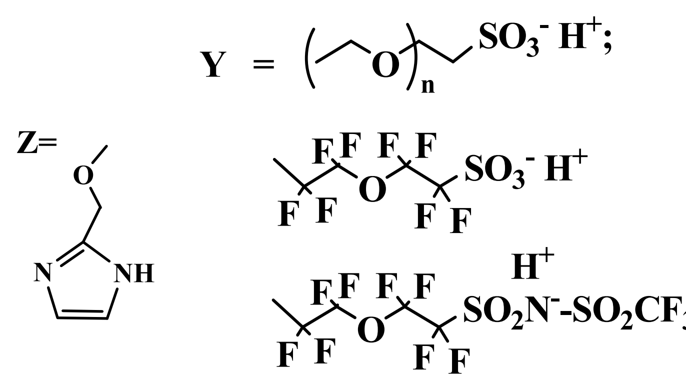
Change the Backbone



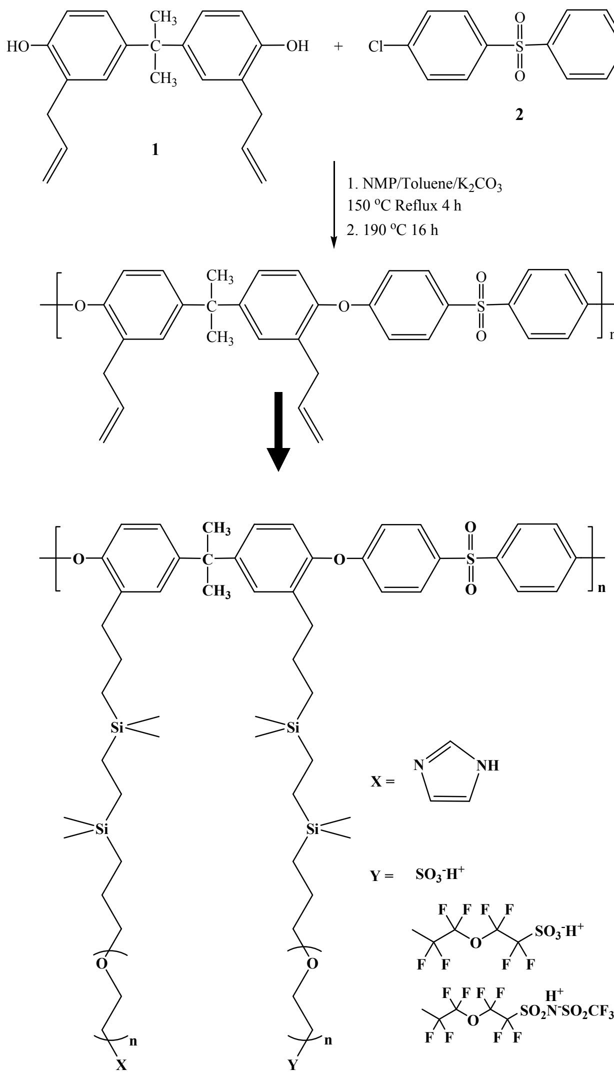




Block copolymer - Kraton

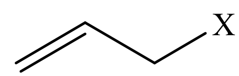


Technical Accomplishments.
PolySulphones with Imidazole and Acid Groups



Chemistry:

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

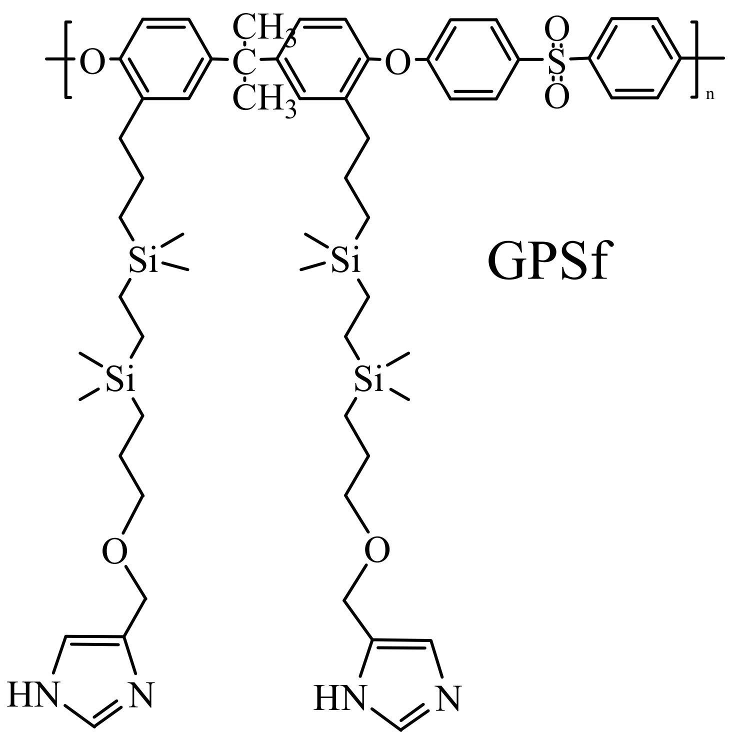


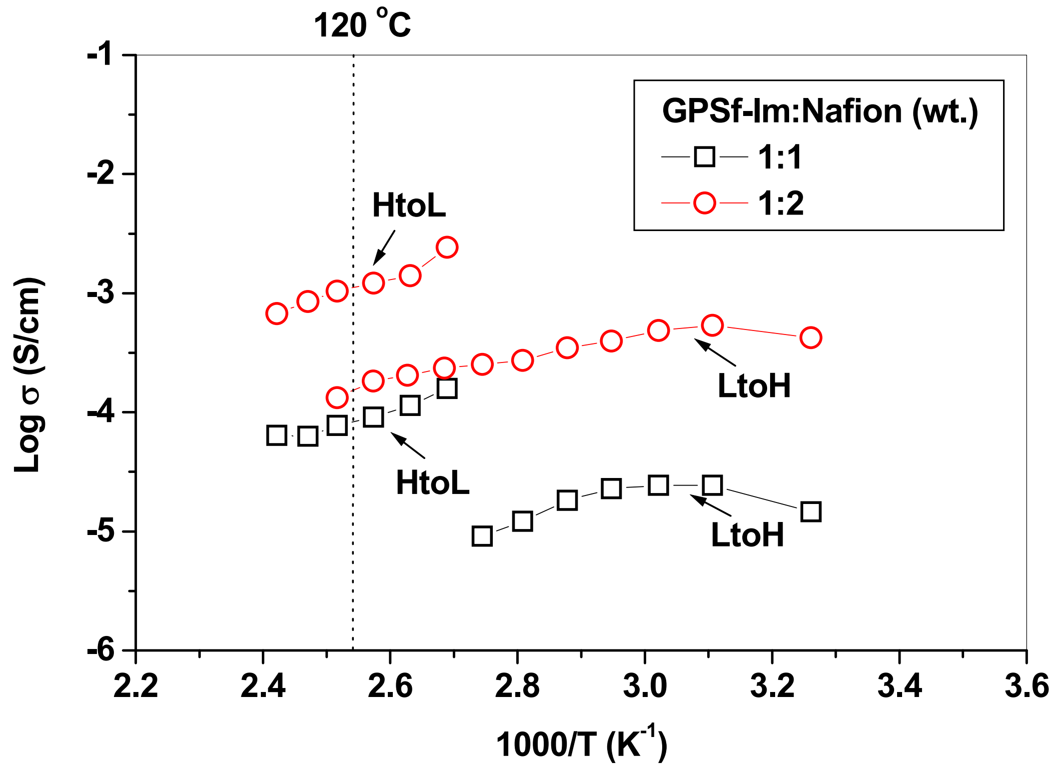
- Condensation polymerization
- etc…

Technical Accomplishments.

Imidazole Polymer (Polymerize then Graft)

Blend with Nafion®





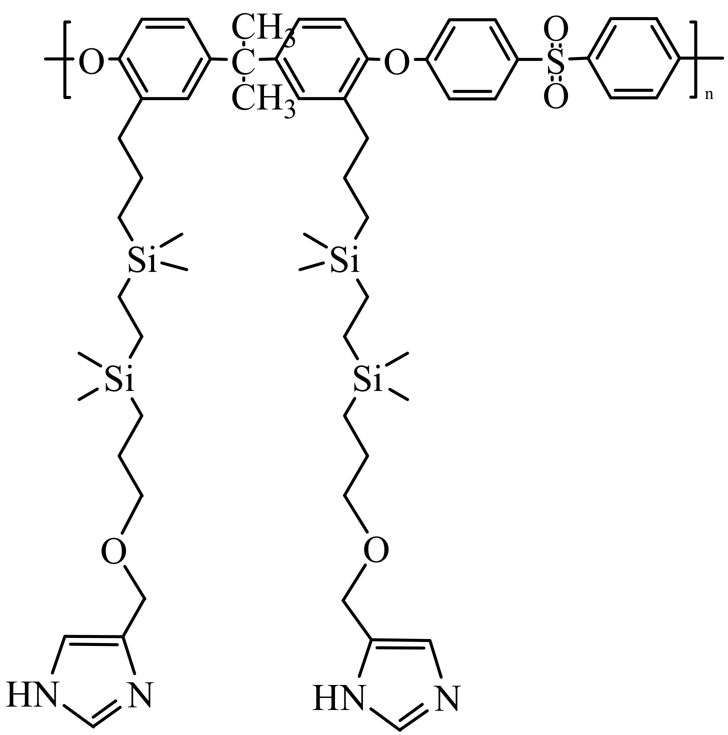
Degree of Graft: ～ 0.2

EW ~ 3000

- Normal Nyquist plot; the reason could be the plasticization by Nafion® (soft polymer) between electrode and polymer blend
- Abnormal conductivity (phase separation?)

Technical Accomplishments.

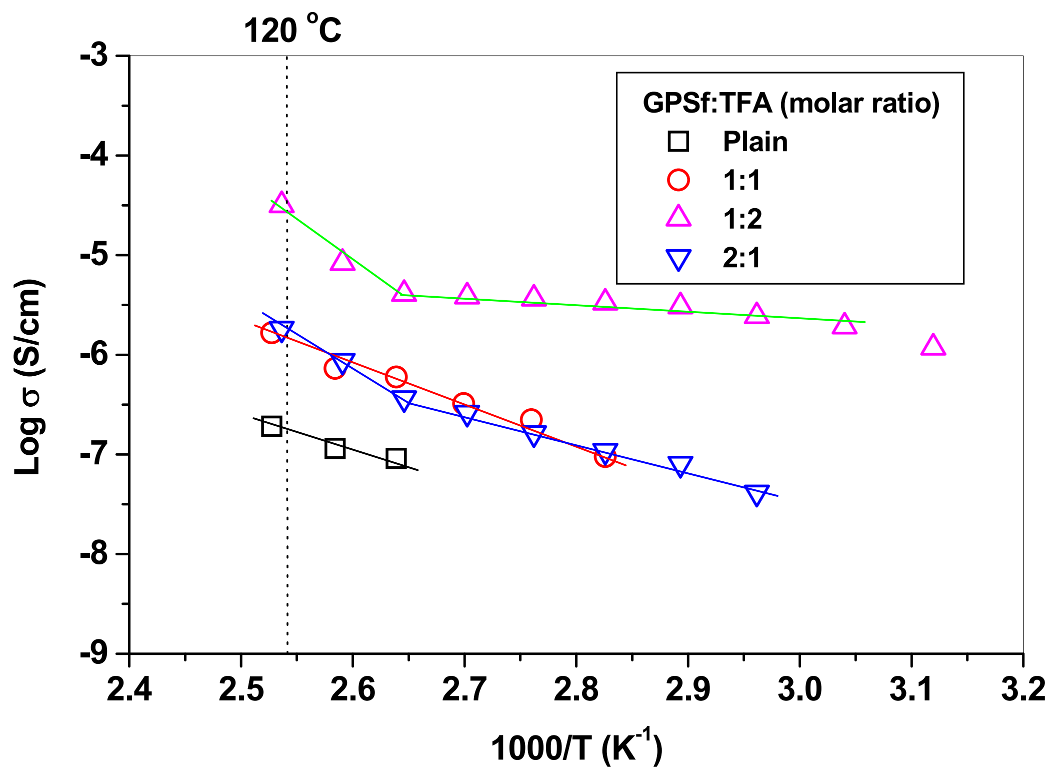
Imidazole Polymer (Graft 1st then Polymerize)



Degree of Graft: > 1.0

EW ~ 500

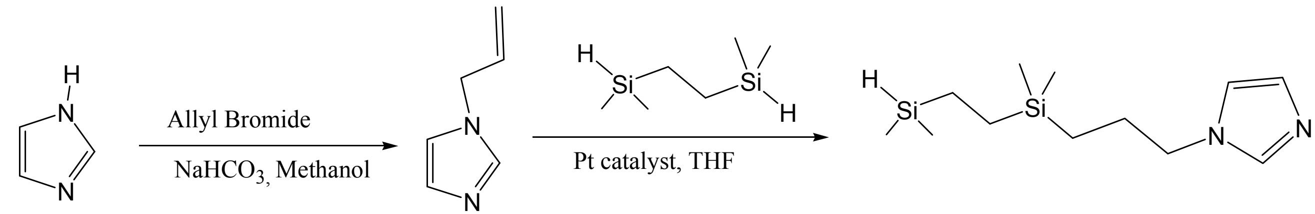
Conductivity when doped with Triflic Acid (TFA)



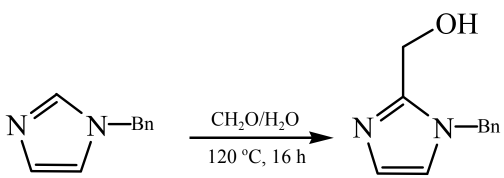
- Residual Pd/C catalyst, aggregation during cast was observed
- Random data, poor contact between electrode and polymer blend

Technical Accomplishments and Progress.

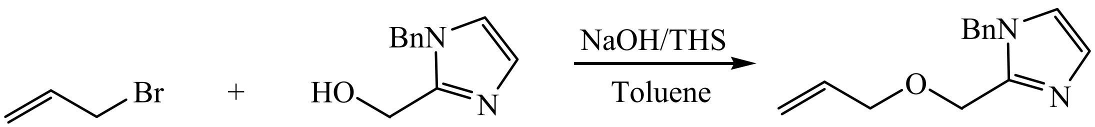
Synthesis of allyl Imidazoles and intermediates for grafting



N-tethered imidazole cannot support Grotthuss transport.



1 2



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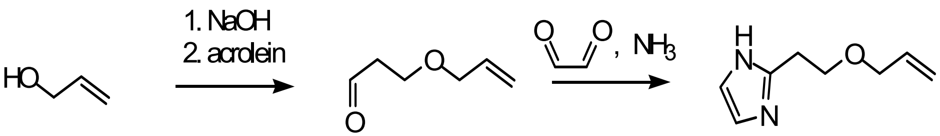


2 3

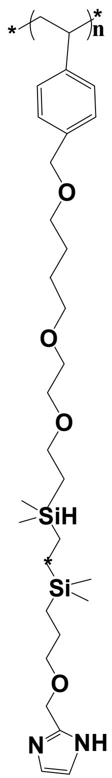
Problems with the use of Tosyl as Protecting group have delayed synthesis of tethered imidazole polymers.

New protecting groups are under test – benzyl, trityl, etc. Benzyl works but has drawbacks with polymers.

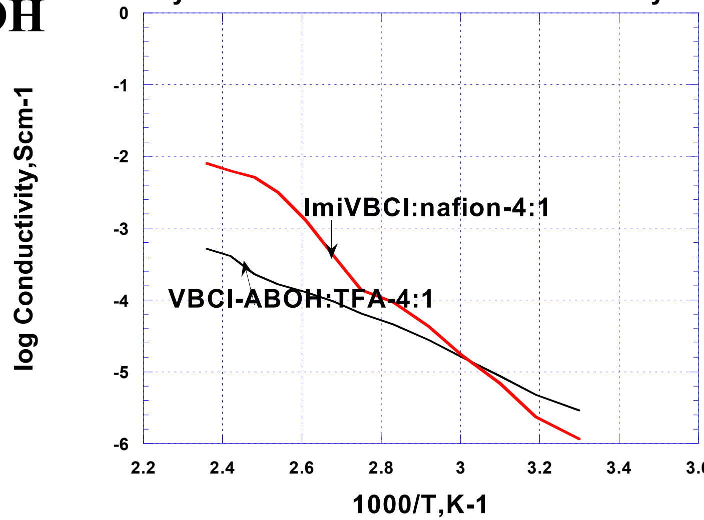
Technical Accomplishments.

Proton conductivities with different backbones

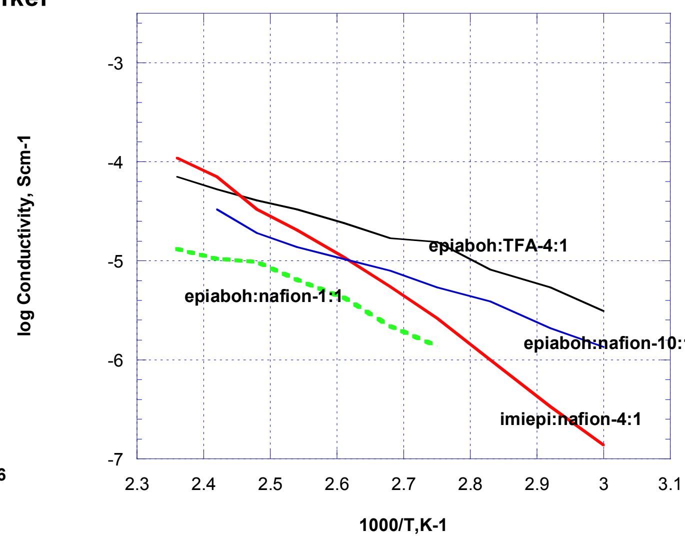
VBCl-ABOH



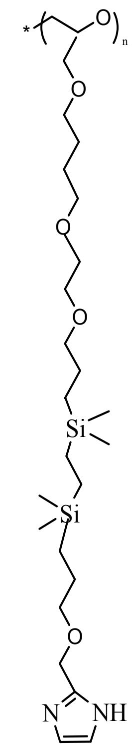
Proton conductivity of imidazole tethered polymers with styrene backbone with and without silyl linker

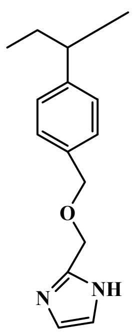


Proton conductivities of polymer with silyl linker Vs without silyl linker

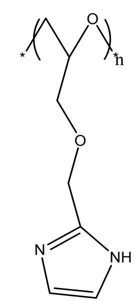


epiaboh





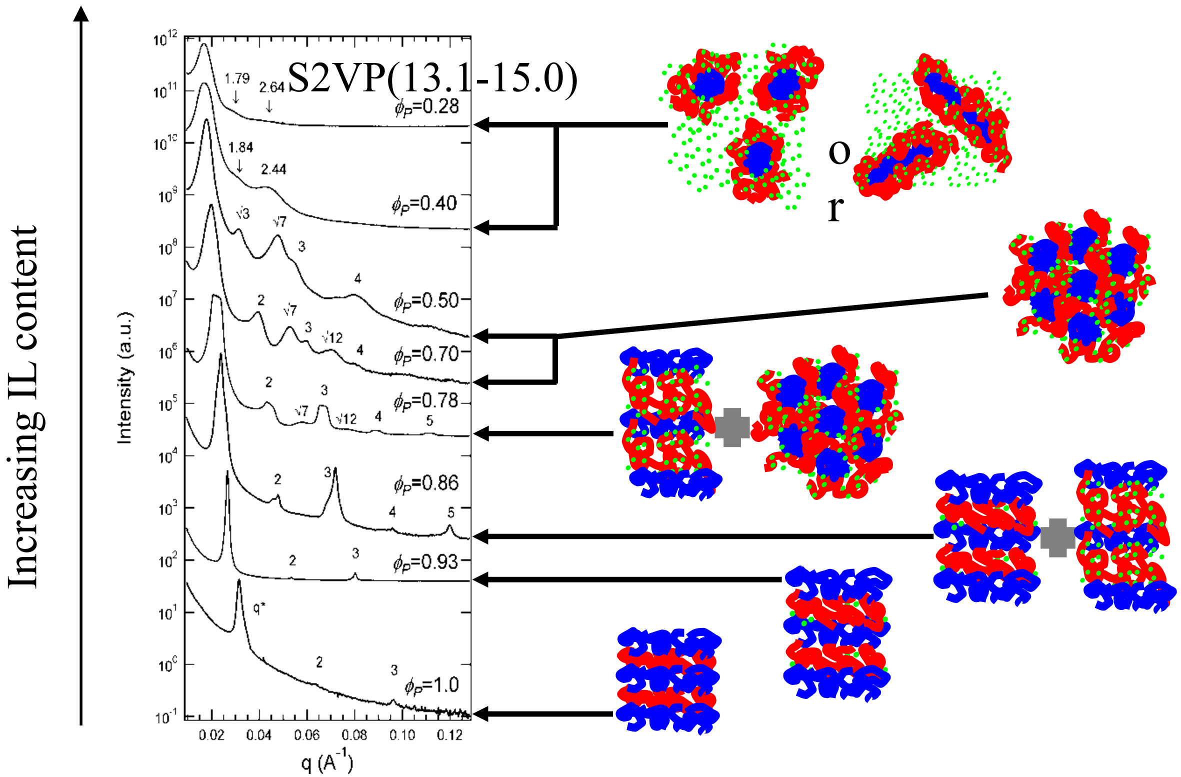
ImiVBCl

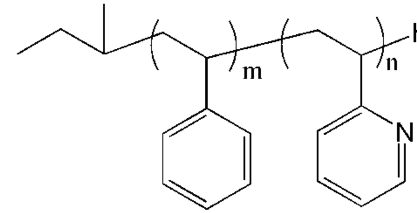


imiepi

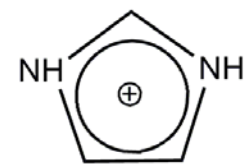
Short chain tether gives higher Ion Exchange Capacity and hence higher charge concentrations. Blends with Nafion® seem stable. Phase separation behavior unknown here but styrene backbone more likely to phase separate.

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

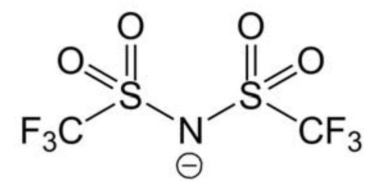




poly(styrene-*b*-2-vinylpyridine)
(S-2-PVP)



Imidazole



TFSI

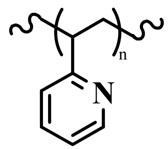
SAXS patterns with increasing IL content.

Vinyl pyridine block selective for IL. Selectivity increases with temperature.

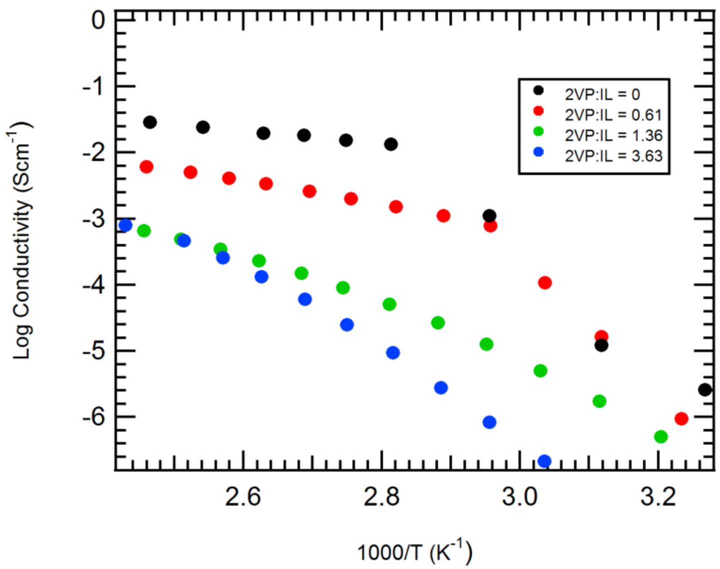
SANS measurements indicate IL segregating at interfaces.

Technical Accomplishments and Progress

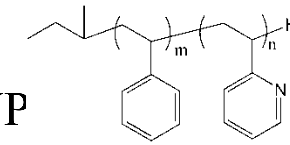
Conductivity of P2VP and S2VP in 5:5 Ionic Liquid

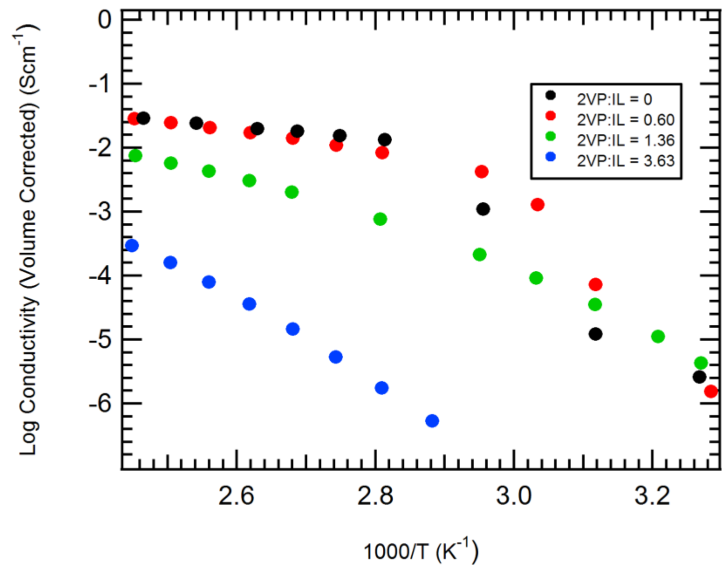


Homopolymer: P2VP (13kg/mol) in 5:5 IL



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



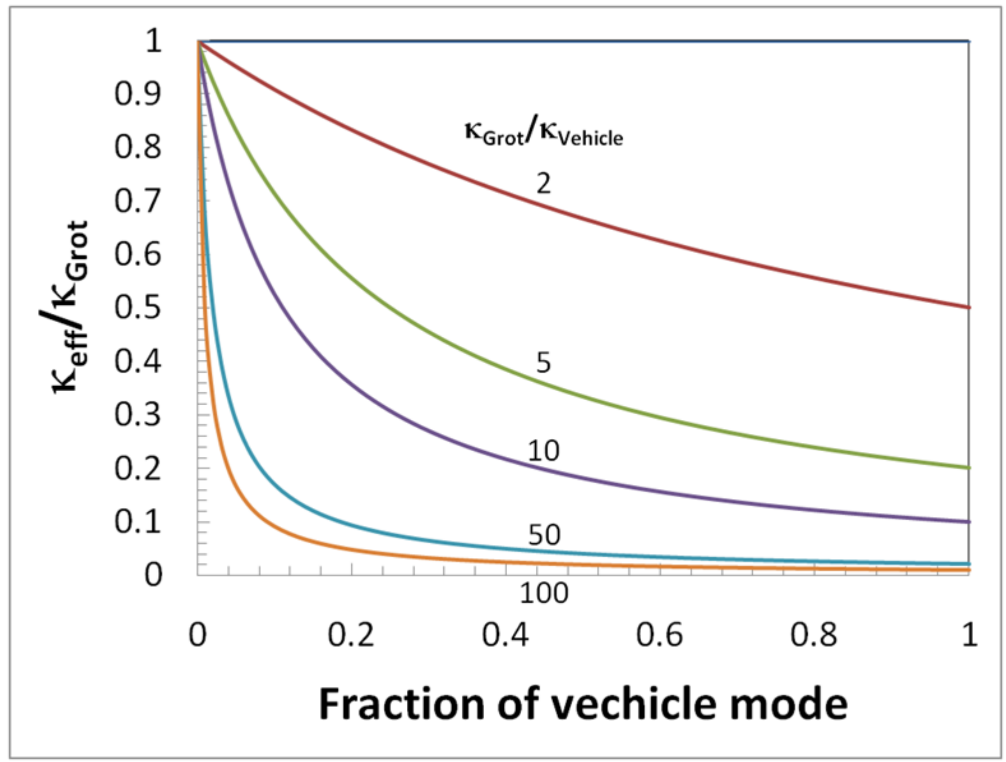


- Ionic conductivity decreases with increasing polymer content and temperature dependence increases, indicating interference of segmental motion
- A sharp decrease in conductivity occurs with a phase transition (to a solid)
- Block copolymer + IL system achieves higher conductivities than homopolymer + 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)

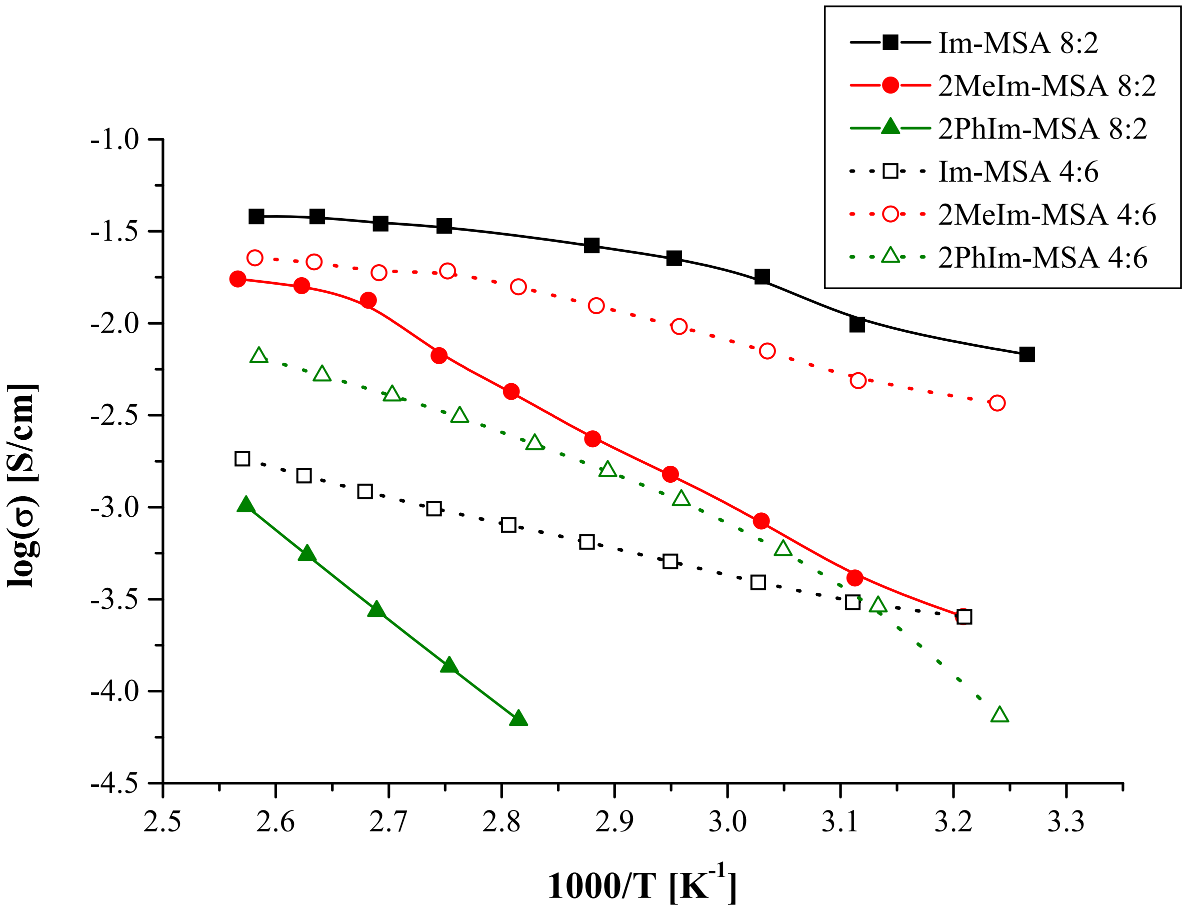


Need MD modeling for better understanding. Explore collaboration with Smith,/Borodin/Voth (U.of Utah)

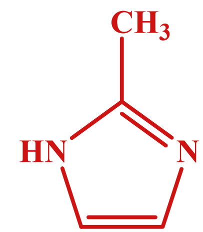
Comparative Ionic Conductivity of Substituted Imidazoles

Eliot Chang

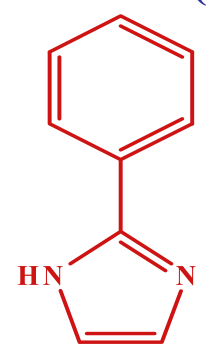
DOE Science Undergraduate Laboratory Intern



Imidazole (Im)



2-Methyl-imidazole (2-MeIm)

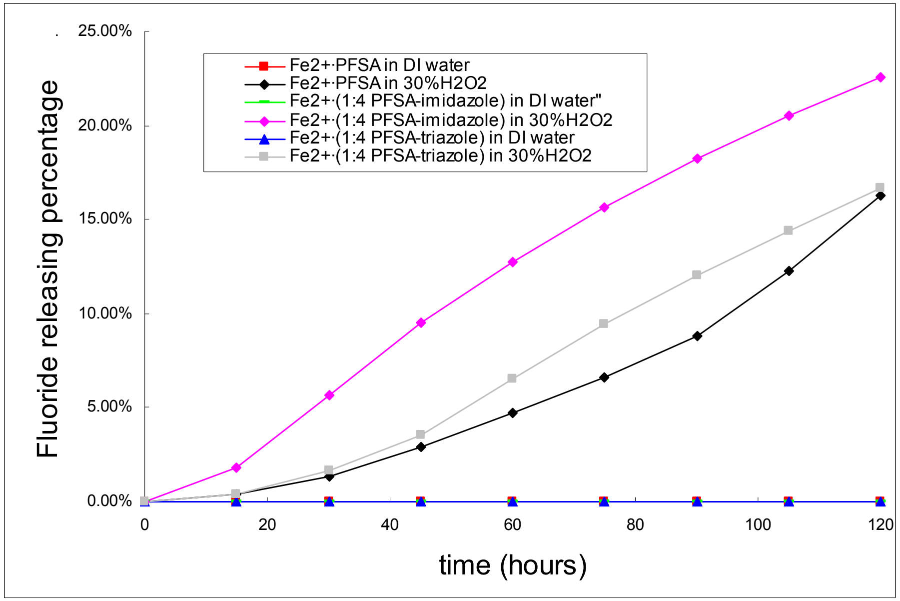


2-Phenyl-imidazole

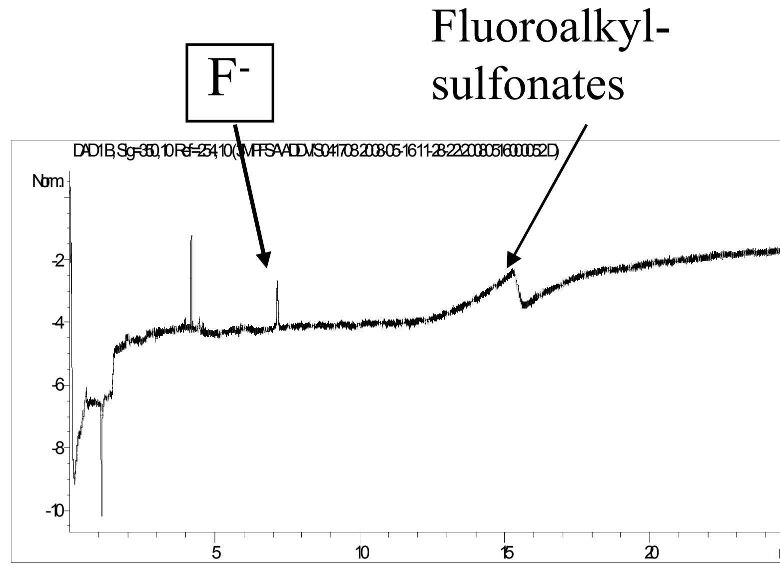
(2PhIm)

Methanesulfonic Acid (MSA)

Oxidative and Acid Stability

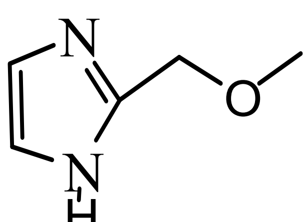


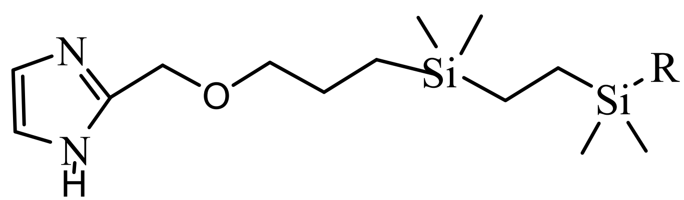
The fluoride release rates of Fe^{2+}•PFSA, Fe^{2+}•(1:4 PFSA -imidazole), Fe^{2+}•(1:4 PFSA -triazole) in DI water and 30% H_2O_2.



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.

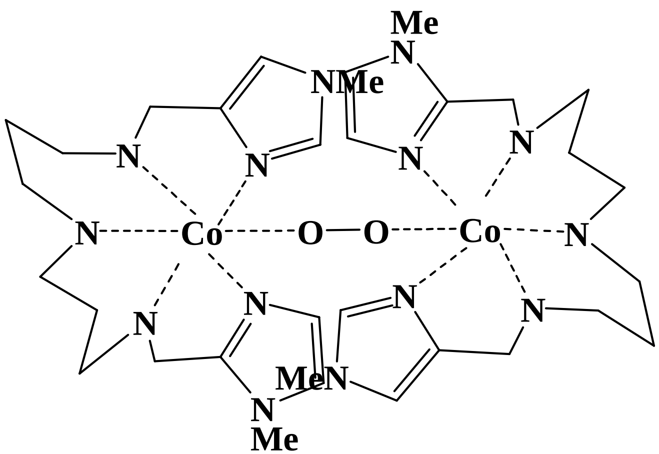




Imidazoles Stable?

Examples Known of great stability

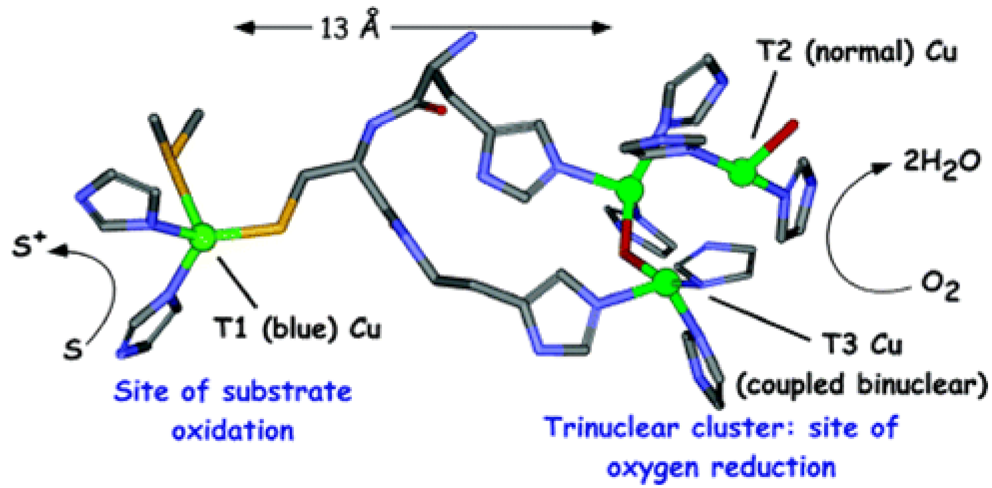
Oxygen separation systems use Imidazoles for stability.



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?

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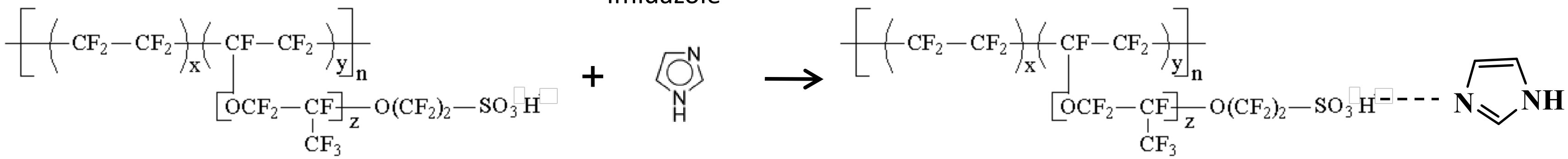
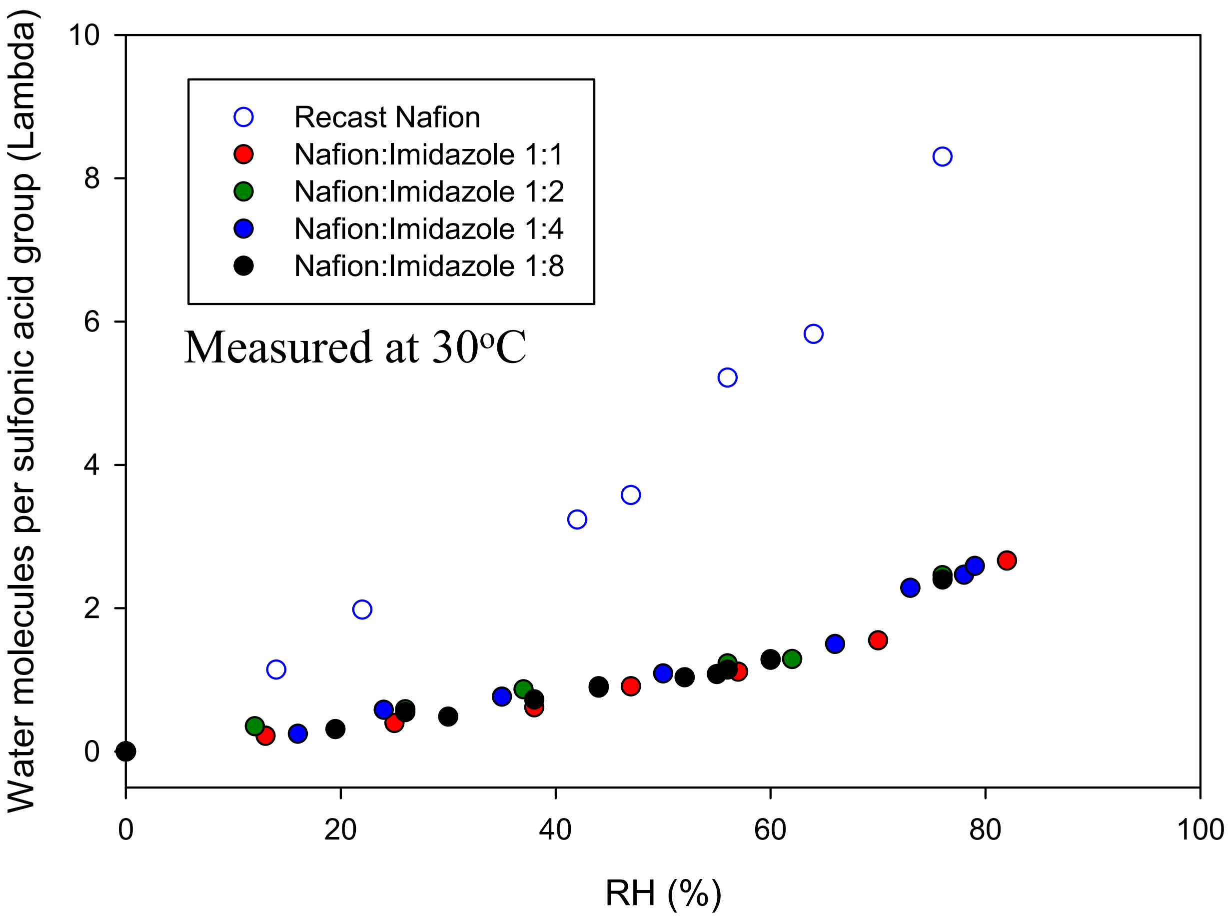
Effect of Imidazole on Water Uptake of Nafion®

Nafion

Imidazole





- **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.**

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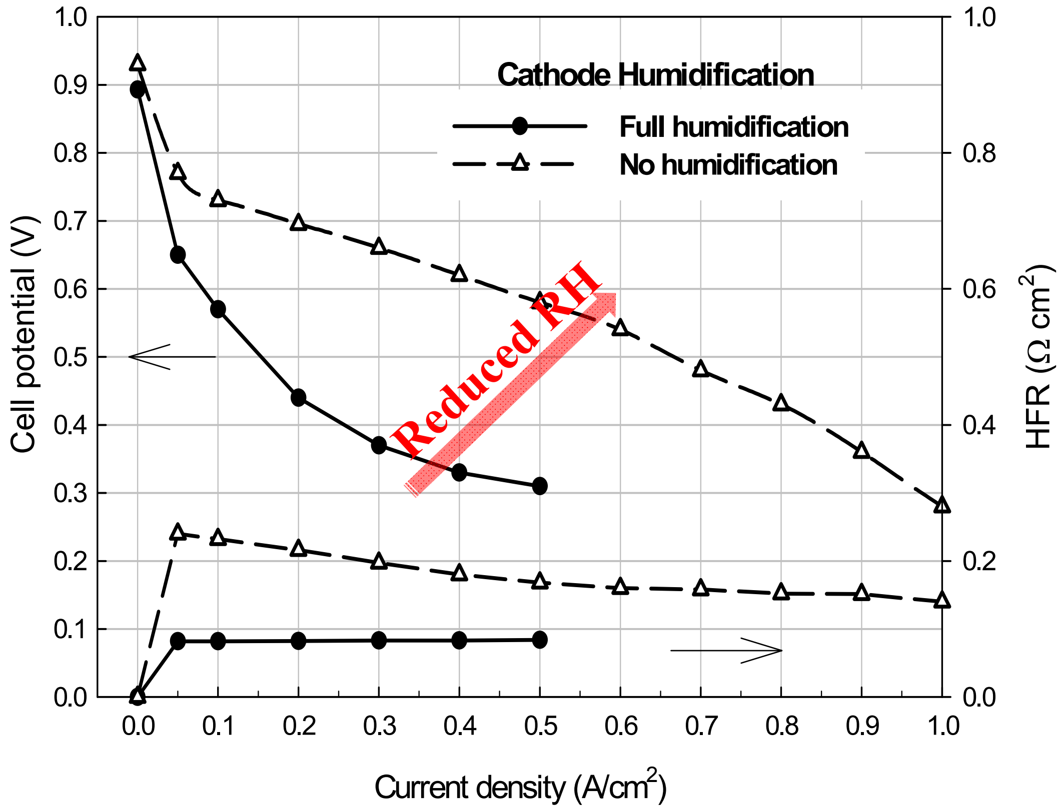
Non-Nafion® Electrode Development For High Temperature Membranes

	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
Observation Achievement	*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/cm²)
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).

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 will increase as production of 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) – use initiated.
  - 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

Proposed Future Work

- Synthesis to provide material for testing (LBNL/LANL)
  - Attach imidazoles to commercially available materials – Kraton and polysulfones – prepare blends with PFSA materials (with 3M) to give fully tethered materials that can be fabricated as membranes.
  - Continue to improve imidazole protection/deprotection chemistry to allow more efficient attachment to polymer chains or monomers. Attach imidazoles to 3M PFSA precursor (with 3M)
  - Prepare block copolymers that can be functionalized with imidazoles and acid groups and whose morphology can be tuned to help achieve the conductivity goals of 0.1S/cm at 120^{o}C at < 25% RH.
- Oxidative stability studies (LBNL/3M)
  - Model compound studies to test the stability of substituted imidazoles, acid groups (fluoroalkylsulfonate, fluoroalkylsulfonylimide) and molecular tethers under Fenton conditions and to identify degradation products.
  - Test oxidative stability of synthesized polymers with Fenton chemistry, use model studies to help identify released fragments and measure rates of polymer fragmentation to meet requirements of the stability Go/No-Go decision.

Proposed Future Work (Continued)

- Continue fundamental studies on Ionic Liquids in Polymers (LBNL/LANL).
  - Study imidazoles and acid groups substituted with tether.
  - Study block coploymers that are closer to the target materials.
  - NMR and neutron scattering studies for polymer and solvent dynamics.
  - Investigate effects of solid particles on behavior to mimic electrodes.
  - Investigate effect of water.
- Model Conductivity – investigate MD modeling. (LBNL)
  - Measure conductivity (with LANL), diffusion and polymer dynamics (NMR), solvent dynamics (NIST Neutron scattering).
  - **Provide definitive answer to conductivity Go/No-go decision.**
- Fabricate & test composite electrodes and MEA's if practical conductivities(>0.01S/cm at 30^{o}C) are achieved (LANL). Meets third Go/No-Go decision (FY10)

Summary

- Synthesis of polymers with tethered imidazoles has been achieved with several different polymer backbones – polystyrene, polysulfone, polypropylene oxide and with different side chain lengths. The imidazole protection/deprotection needs further improvements.
- Conductivity tests have been achieved by blending the imidazole polymers with PFSA materials and with free acids such as triflic acid. Conductivities are found to be low due to low concentrations of acid. Almost 0.01S/cm at 120^{o}C has been observed in bone-dry immobilized blends but the temperature dependence is too great, indicating that these materials do not support Grotthuss transport.
- Studies of proton conducting ionic liquids in block copolymers show that morphological control can promote Grotthuss transport and maintain high conductivities at lower temperatures.
- Fenton chemistry has been used to study the oxidative stability of imidazoles alone and doped in polymers. The presence of the imidazole does not prevent fluoride release. Ring opening is observed for the imidazoles. Quantitative measures of oxidative degradation are under way.
- Composite electrode and MEA fabrication methods have been developed for hydrocarbon polyelectrolytes.

Supplemental Slides

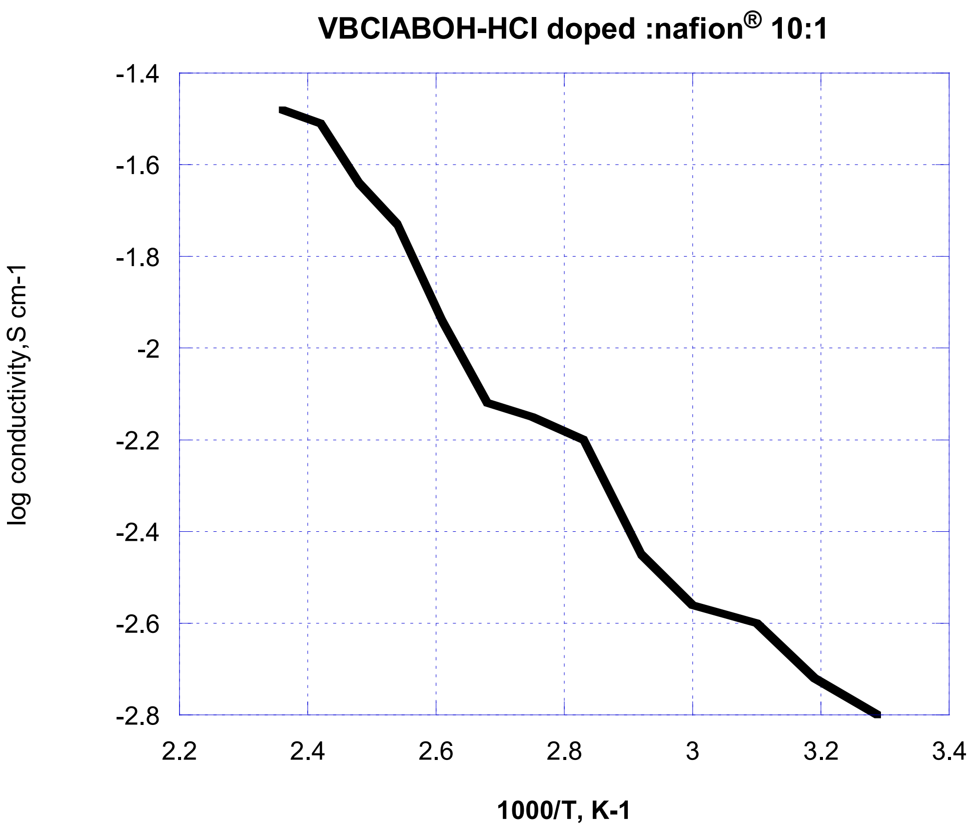
Approach - Milestones

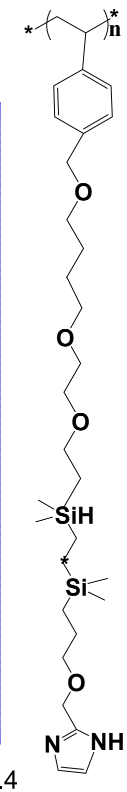
Month/Year/Status	Milestone
September/08/ Completed	Complete initial round of MEA fabrication and testing with selected new polymers (1 minimum) completed and preliminary polymer composite characterization. This provides information on the catalyst behavior under low RH conditions. (LANL)
September/08/ Completed for gas permeability, conductivity on-going	Design targets defined and measured for conductivity (0.05-0.2S/cm) and gas permeability for high-temperature, low RH operation without external humidification through the combined cell- and system-level mathematical simulation. (LBNL)
September/09/ Pending	Prepare samples (minimum of 5 different samples of fully tethered solid state proton conducting materials including blends) in sufficient quantity (10g each) for characterization and fabrication into membranes ($5cm^2$) and MEA's ($5cm^2$). (LBNL/LANL)
September/09/ Pending	Optimization of conductivity with polymer structure and morphology will be completed. Conductivity limit of tethered base materials established over the full operating temperature range. (-20^oC to 120^oC) (LBNL/LANL)

Approach - Milestones

Month/Year/Status	Milestone
September/09/ Pending	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/cm2 at 120^{o}C, <25%RH (LANL/LBNL/3M).
September/09/ Pending	Design targets defined for conductivity in both the bulk membrane and the electrode layers at low RH operation without external humidification through the combined cell- and system-level mathematical simulation. The simulations will account for low humidity or low solvent concentration effects upon the catalyst activity *(LBNL)*.

Technical Accomplishments?
VBCl-ABOH : nafion® 10:1





- High conductivities apparently due to some contamination with HCl.
- Large excess of imidazoles present. over Nafion® acid groups.
- Result is confusing but included for background information.

Clean material is being prepared.