New Polyelectrolyte Materials for High Temperature Fuel Cells

John B. Kerr

Lawrence Berkeley National Laboratory (LBNL)

Collaborators:

Los Alamos National Laboratory (LANL).

3M Company

June 10, 2008

Project ID #
FC 14

Overview

Timeline

- Project start – February 2007
- Project end – September 2010
- Percent complete – 25%

Budget

- Total project funding
  - DOE share $6,000k
  - Contractor share $1,000k in-kind
- Funding received in FY07 - $1150k
- Funding for FY08 - $1450k

Barriers

E. System Thermal and Water Management.

B. Stack Material and Manufacturing Cost.

A. Durability

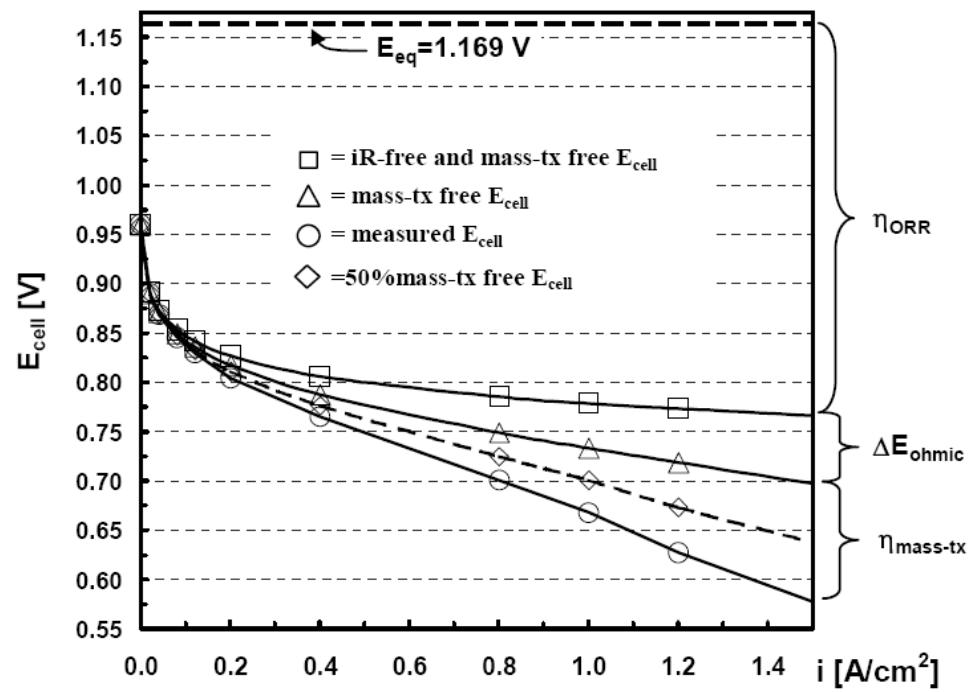
C. Electrode Performance.

Team/Partners

- Nitash Balsara, Rachel Segalman, Adam Weber (LBNL).
- Bryan Pivovar, James Boncella (LANL)
- Steve Hamrock (3M Company)

The need to replace water in PEM Fuel Cells

- Nafion PEM cells operate a 85^{o}C, >90% RH
  - complex water managemen 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

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, phosphates)
  - Prepare and test solid polyelectrolytes where only the proton moves. Both solvent and acid groups are tethered.
- Significant system simplifications for Fuel Cell Systems.
  - Heat and water management greatly simplified.
  - Water rejection reduces mechanical stress due to swelling
- Provide Car Manufacturers with knowledge on how to prepare Next Generation Materials.

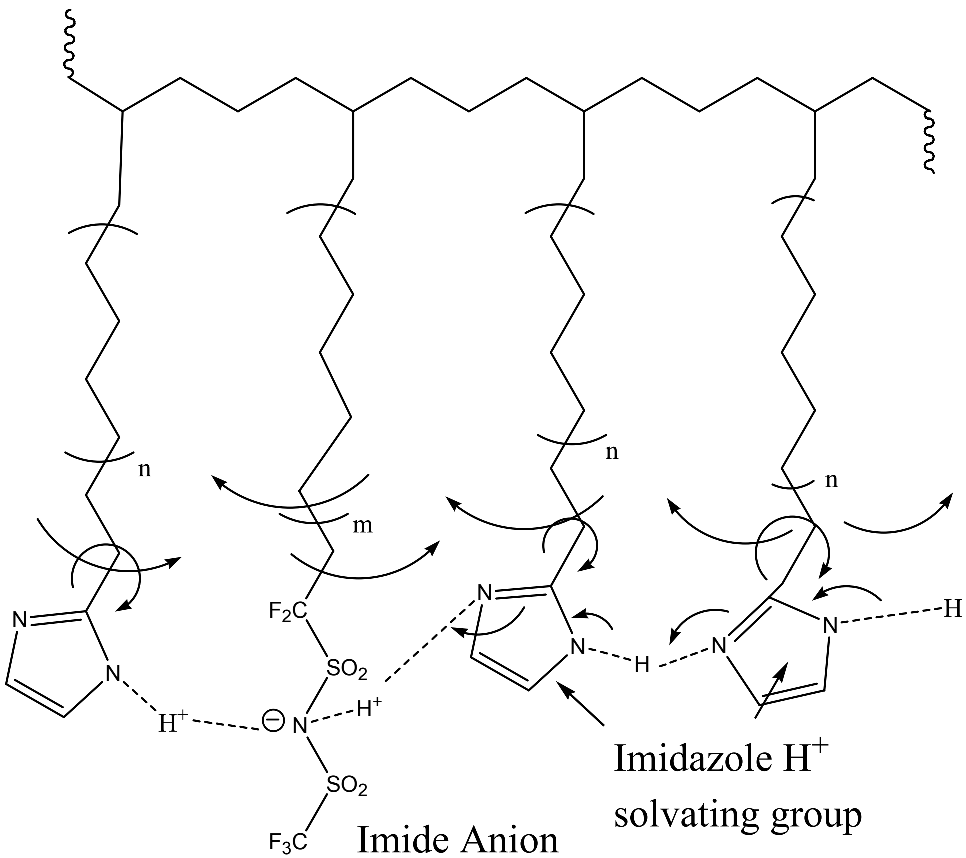
Milestones

Month/Year/Status	Milestone or Go/No-Go Decision
September -08 **On Track** **(ahead of original schedule).**	**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 . Determine conductivity in absence of free solvents. **Go/No-Go Decision:** How close to 0.1 S/cm at 0 to 25% RH and the full range of temperature (-40-120oC) is possible without free solvents?
September-08 **On Track**	**Milestone:** 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.
September-08 **On Track**	**Milestone:** 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.

Approach

- Measure properties of component mixtures to determine optimum polymer composition.
  - Conductivity of ionic liquids prepared from heterocyclic bases (e.g. imidazole) and acids (e.g. triflic acid)
  - conductivity, mechanical/thermal properties, SAXS/SANS, chemical stability of Nafion®, 3M PFSA, and other polymers doped with imidazoles and other heterocyclic bases. (FY07-08)
- Synthesize the Materials.
  - Covalently attach imidazoles to side chains of ionomers with appropriate polymer backbones and test for conductivity, mechanical/thermal/chemical behavior (FY07-08) and gas permeability (FY09)
- Prepare composite electrodes/membranes and operate MEAs without humidification (FY08-10).

APPROACH to making the materials.
Tether Imidazoles and Acid Groups to Polymers

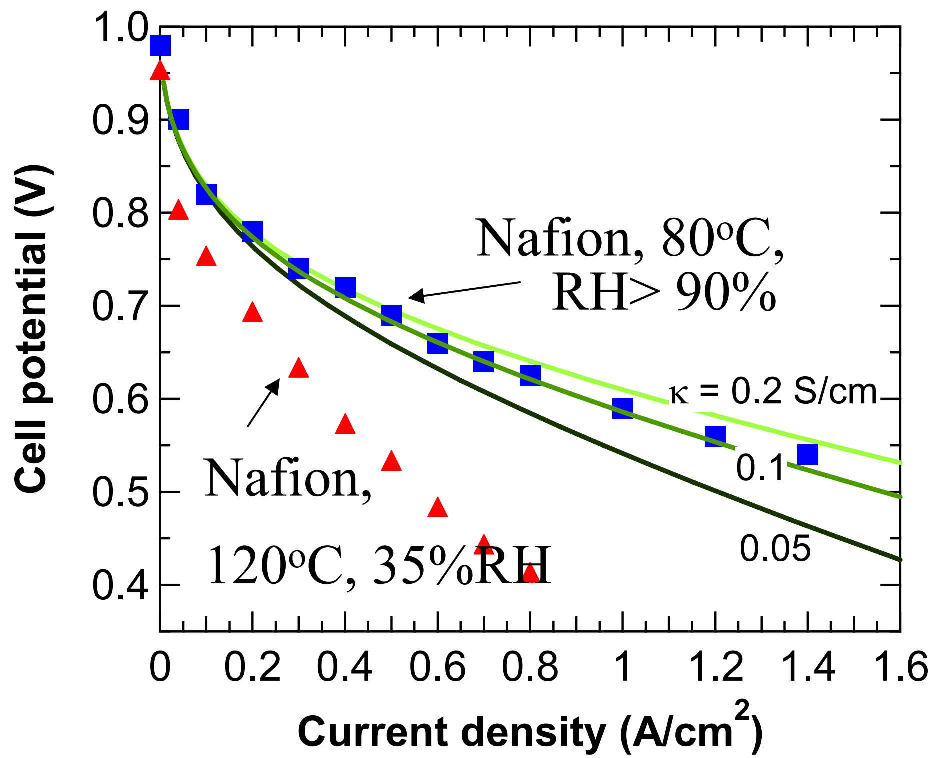


Side chains structures facilitate durability studies – small molecule fragments.

- Attach anions and solvating groups by grafting –control nature and concentration.
- Use nature and length of side chain to control mobility.
- Control mechanical & morphological properties by altering backbone and use of block co-polymers.
    - Polystyrene, Polynorbornene and Poly(arylene ether) backbones.
- **Promote Grotthuss Proton Transport → 10^{-1}S/cm**

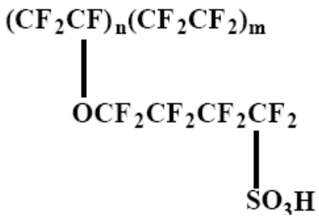
Technical Accomplishments
Check the Goals through Modeling

- **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**



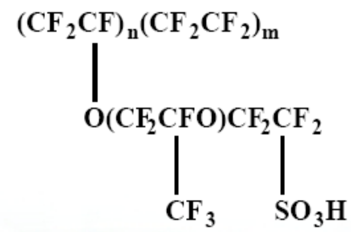
- **Diminishing returns for higher conductivity**
  - **Limited by kinetics**
- **System simplification could allow for a lower conductivity goal**

Conductivity of Imidazole-doped PFSA Materials

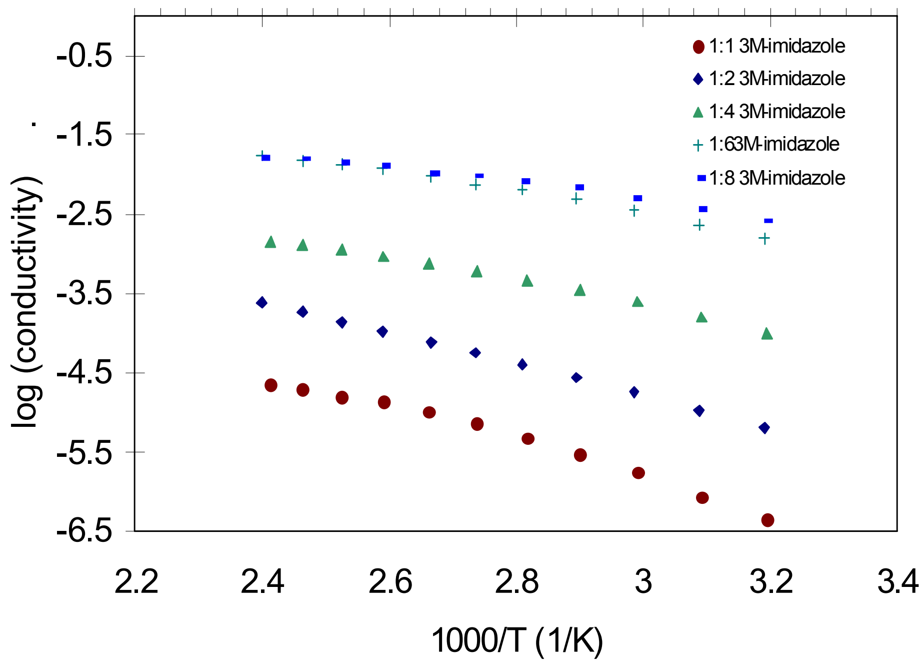


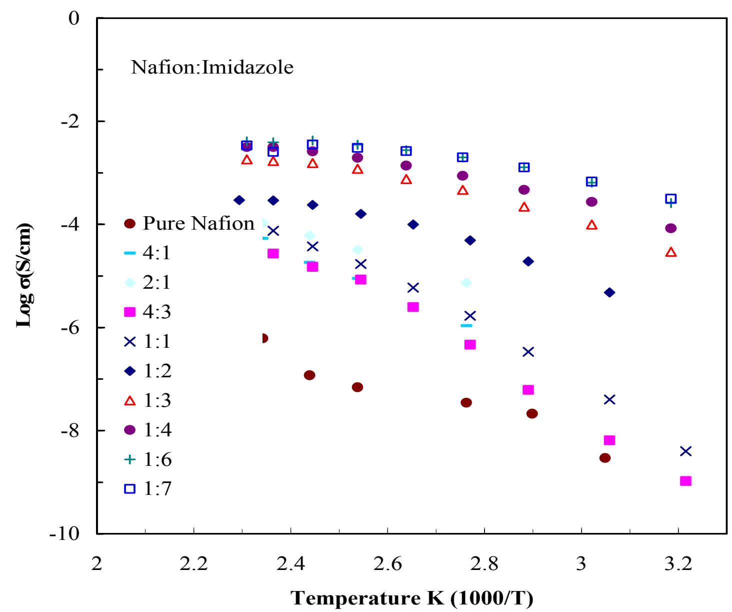
3M

EW 800



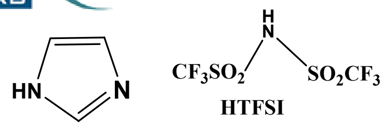
EW = 1100





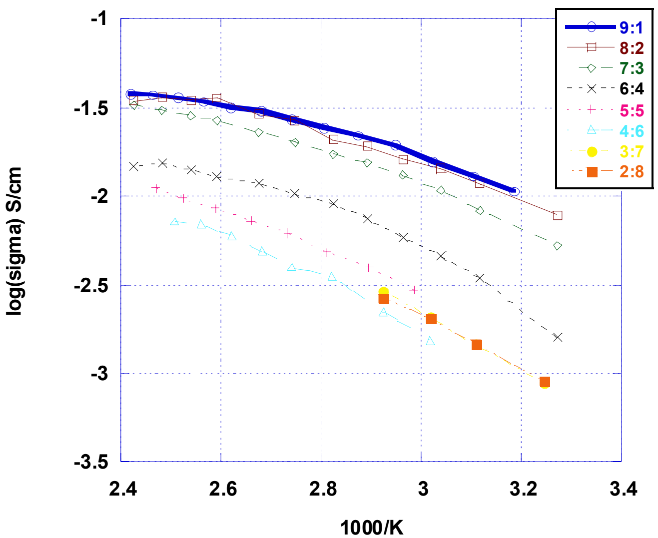
Lower EW provides higher charge carrier concentration – higher conductivity.

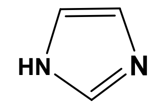
Conductivity of Proton Ionic Liquids



HTFSI

= ImTFSI

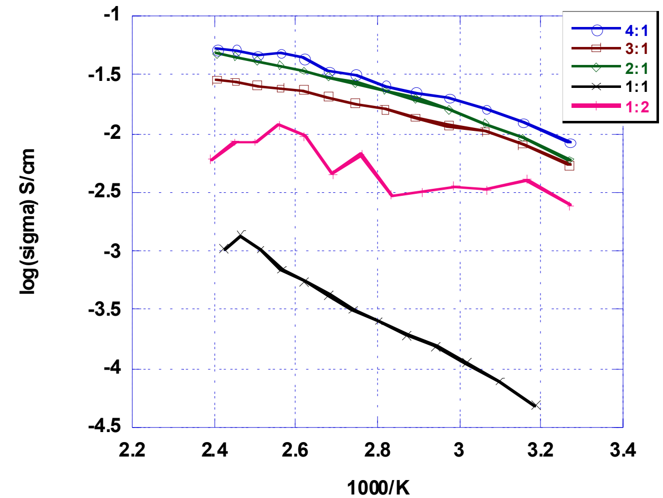


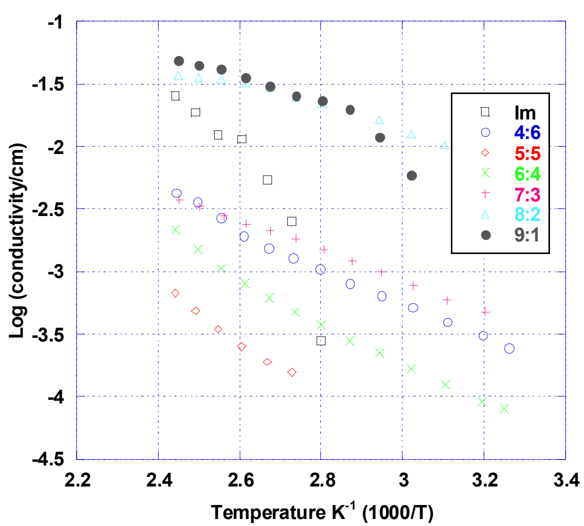


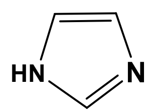
CF_3SO_3H

HTFA

=ImTFA







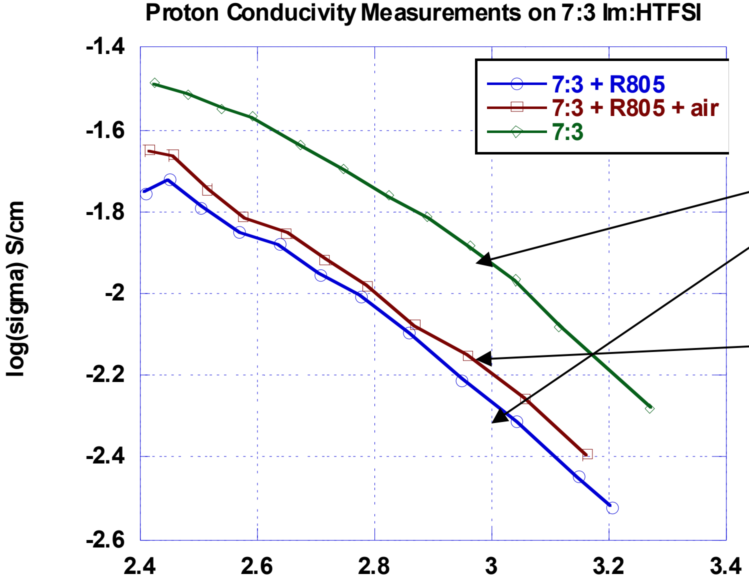
CH_3SO_3H

MSA

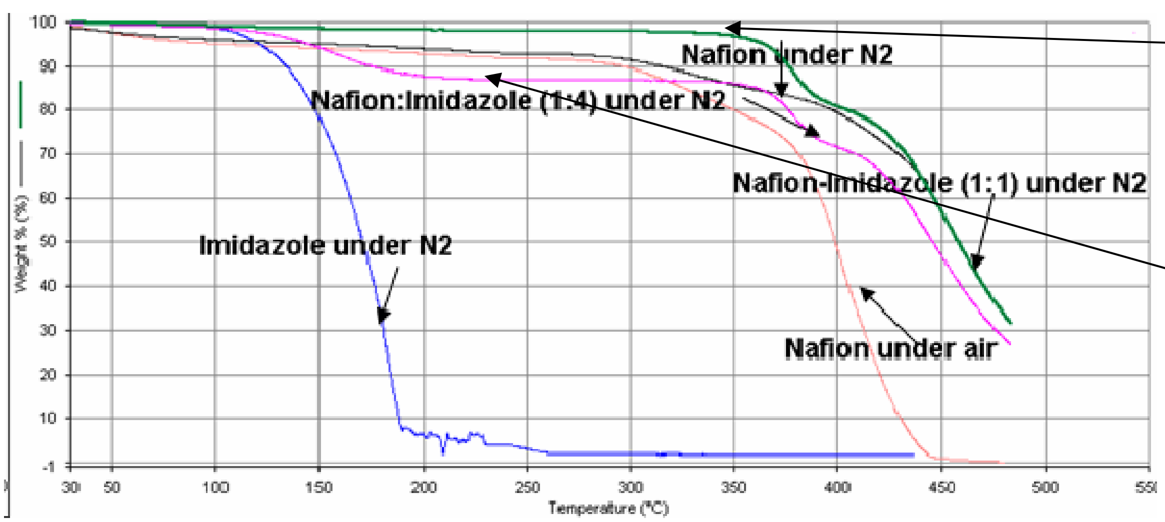
= ImMSA

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

Effects of Solid Matrices and Water on Conductivity

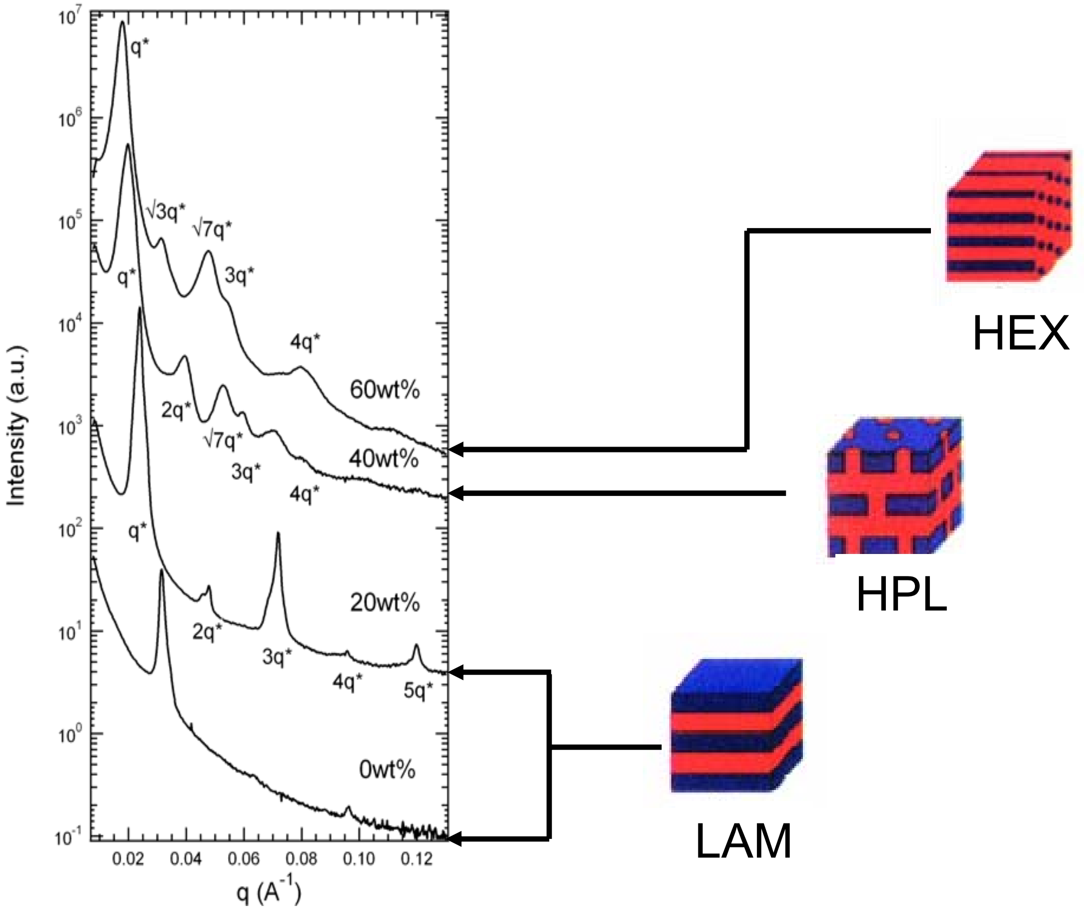


- Addition of Solid Matrix (R805 silica nanopartciles) to ionic liquid lowers conductivity.
- Exposure of ionic liquid to atmosphere (2hrs) results in little change in conductivity

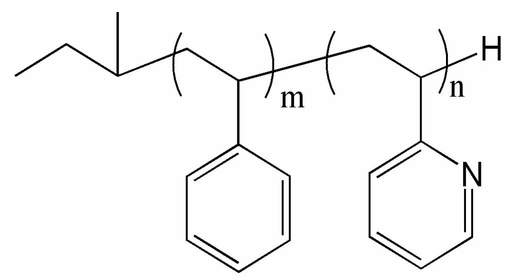


- TGA shows no water uptake for Nafion-Imidazole.
- Excess Imidazole Sublimes out
- Imidazole must be chemically bound.

Effect of Ionic Liquid Loading on Block Copolymer Nanostructure



Small Angle X-ray Scattering of Block Copolymer doped with ImTFSI ionic liquid



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

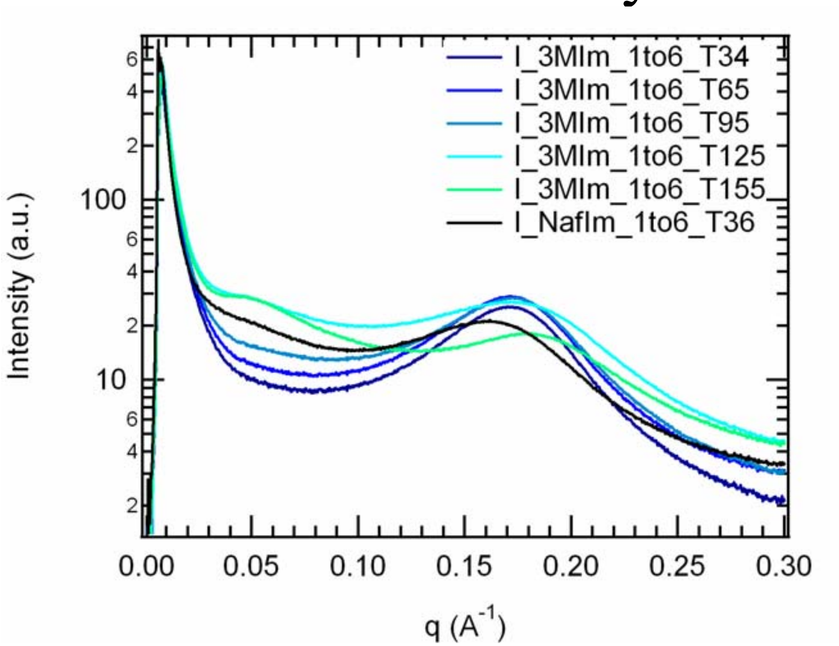
Polydispersity < 1.10

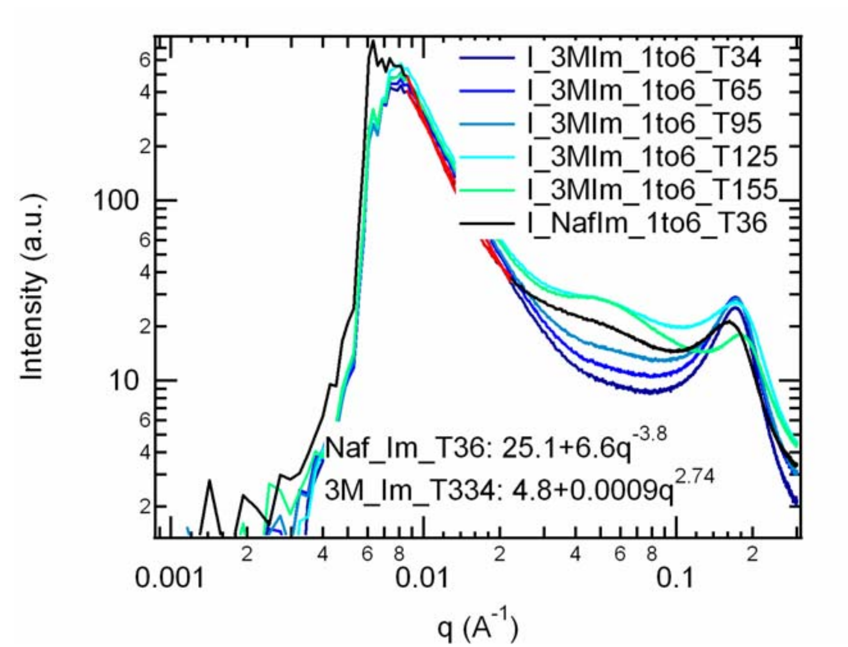
Lamellae forming: 47% PS

M_N = 28 kg/mole

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

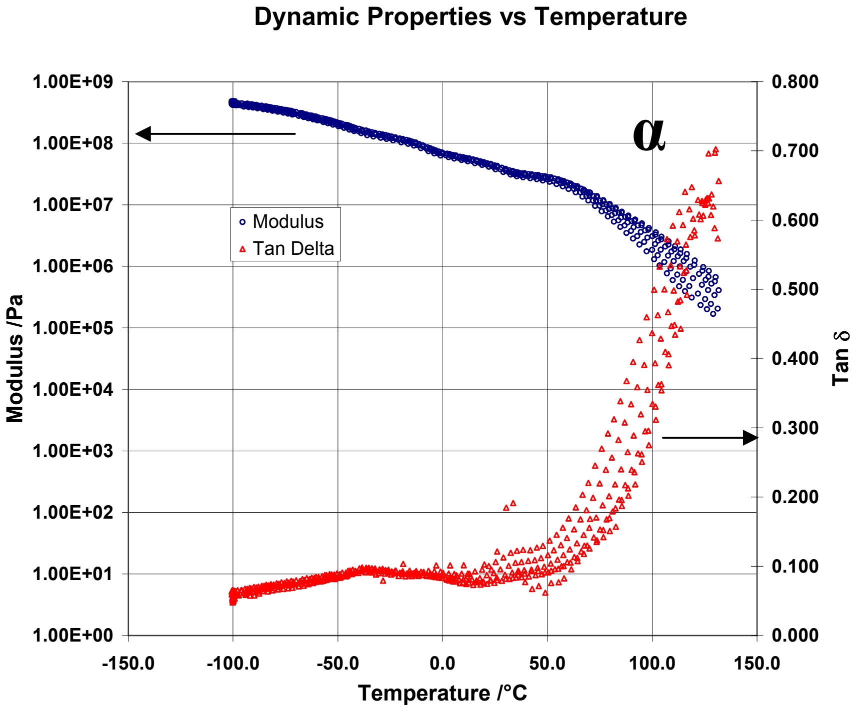
•3M+Imid 1 to 6 has a domain size of 3.7 nm at room temp.

• Nafion+Imid 1 to 6 has a domain size of 4.0 nm at room temp.

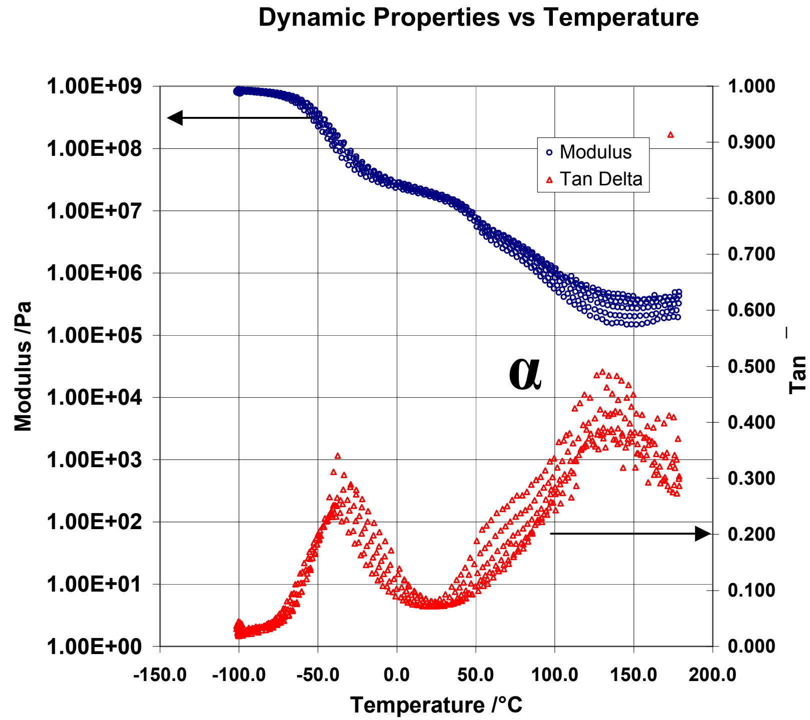
• Heating study was performed on 3M+Imid sample and the sample appears to undergo a transition at 125C<T<155C with an emerging domain size of 7.0 nm at T=155^{o}C

DMA of Nafion and Nafion-Imidazole

Dry Cast Nafion



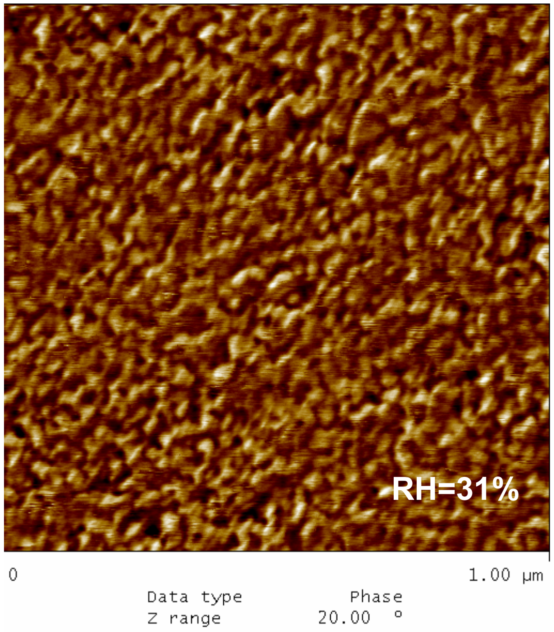
Dry Cast NAFION-Imidazole SO_3H:Im 1:4



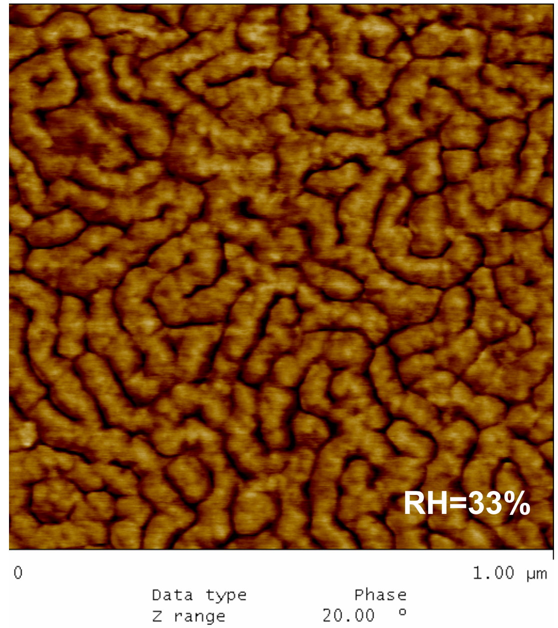
- Imidazole results in an increase in the α-transition of Nafion from 120°C to 140°C due to better dissociation of the protons and the formation of the imidazolium salt.
- Transition at -40°C indicates plasticization of perfluorinated matrix by imidazole, indicating mobile polymer backbones and less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

Morphology of Sulfonated PEMs at Low RH

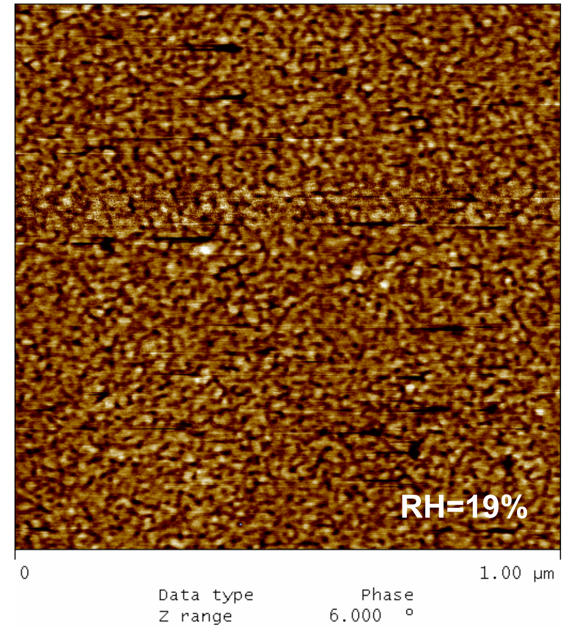
BPSH-35 Random



BPSH-PI Block

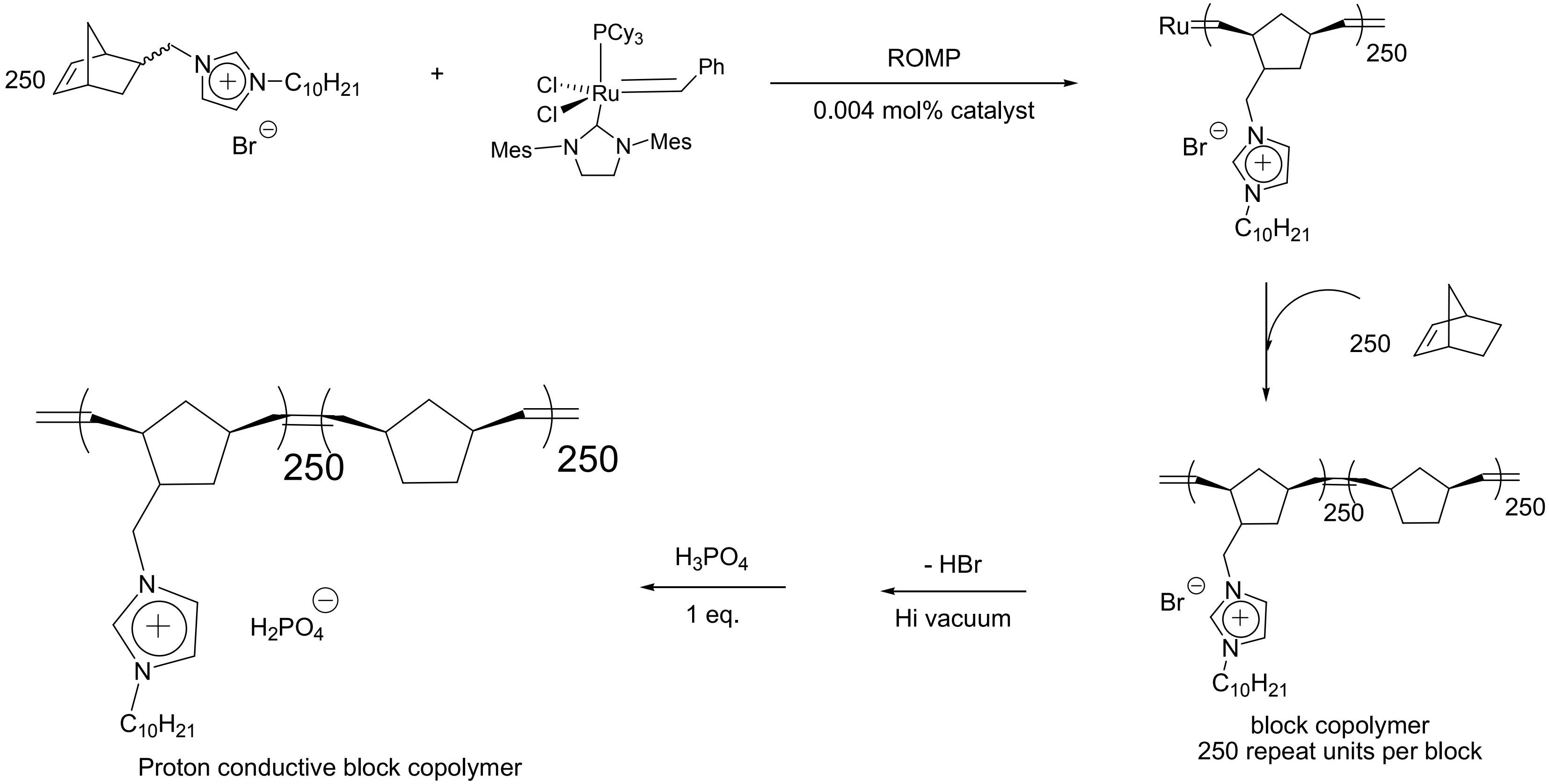


Nafion 212



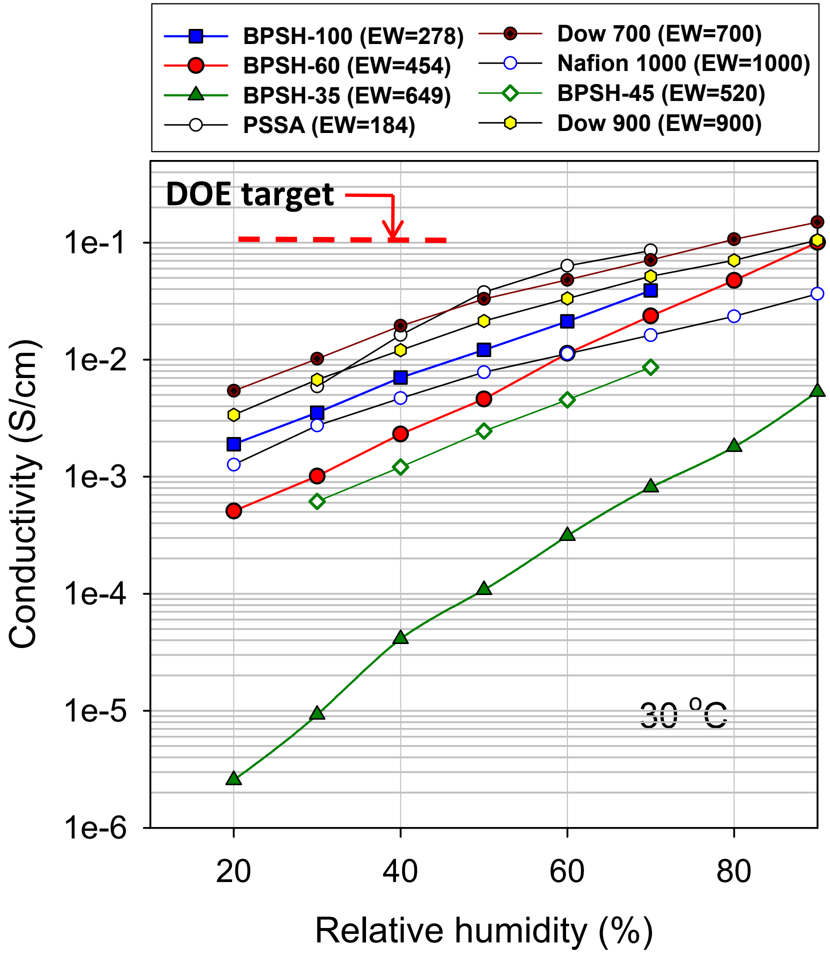
PEM	Hydrophilic Domain Size	Connectivity
Hydrocarbon (random)	Medium (13 nm)	Isolated
Hydrocarbon (multiblock)	Large (16 nm)	Well connected
Perfluorinated (Nafion)	Small (7 nm)	Somewhat isolated

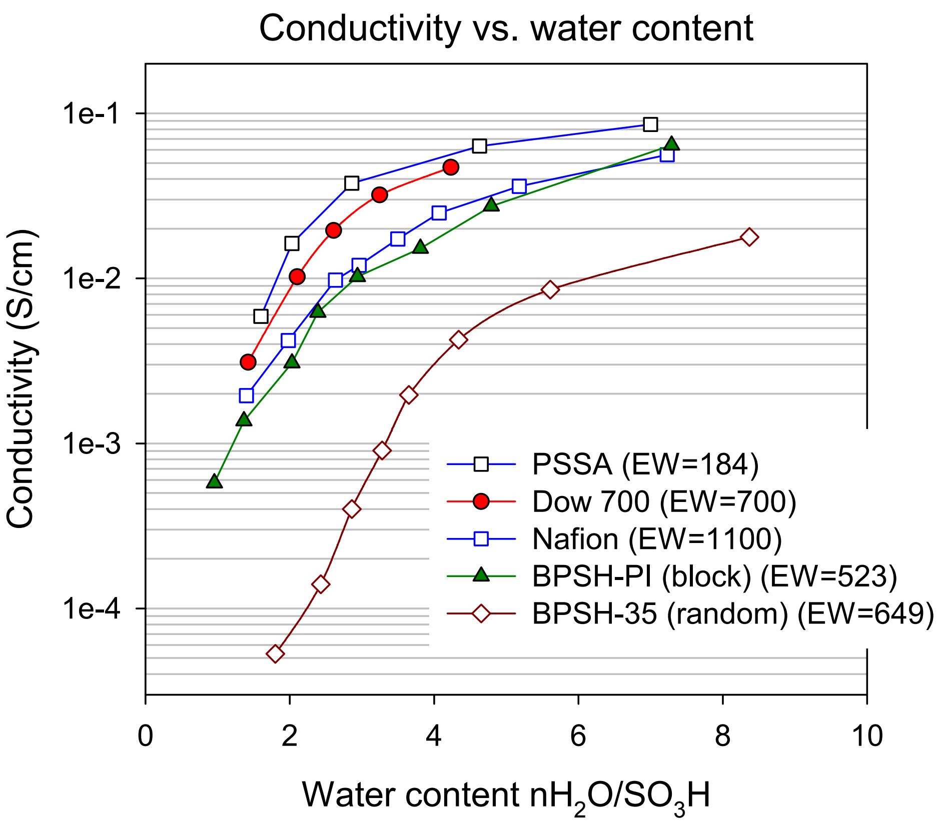
Norbornene(NBE)-Imidazole Copolymer



Replace NBE with Polysulfone backbones to benefit from knowledge developed with BPSH materials in collaboration with Prof McGrath

Conductivity of Various Sulfonated PEMs as a Function of Relative Humidity

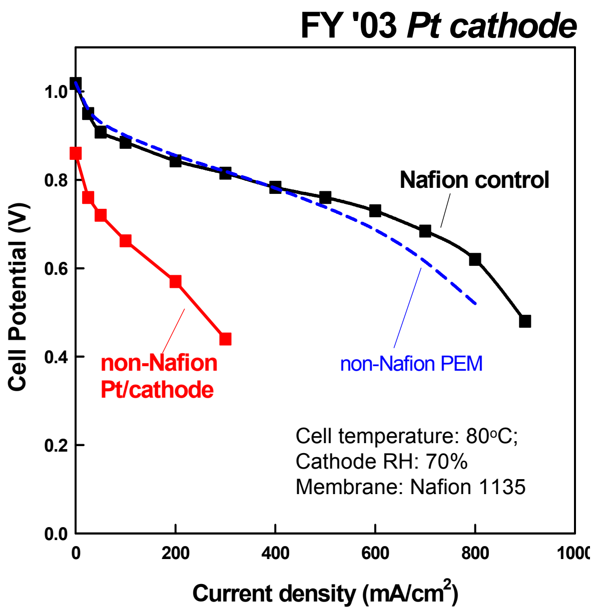


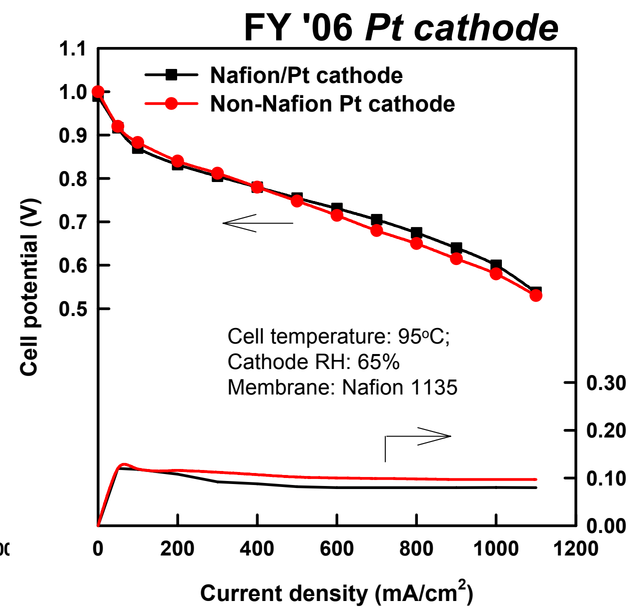


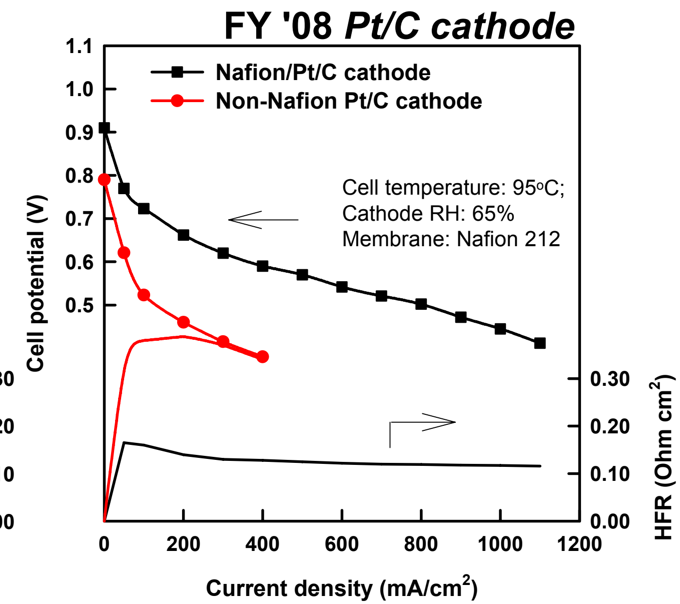
Los Alamos NATIONAL LABORATORY

Los Alamos
NATIONAL LABORATORY

Progress of Electrode Optimization using Non-Nafion Binder





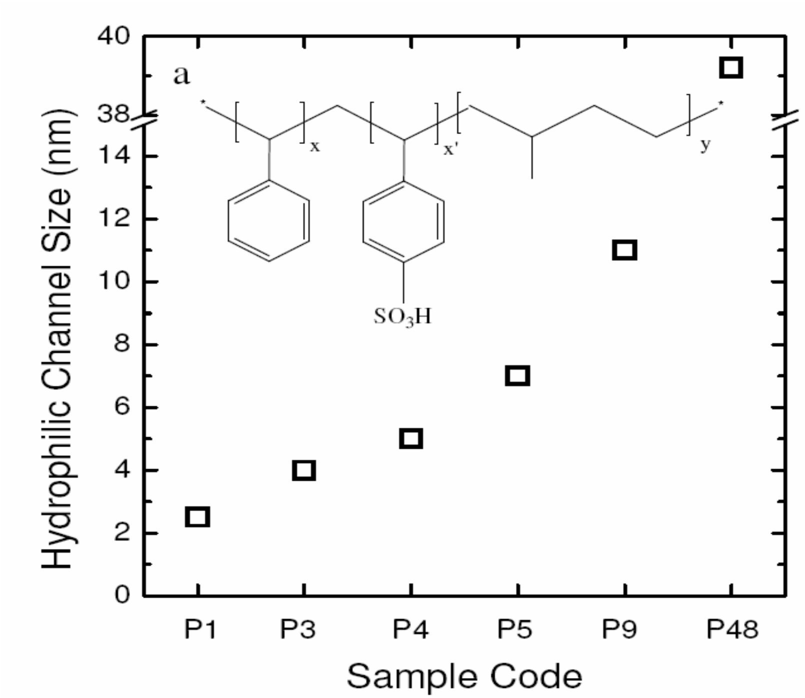


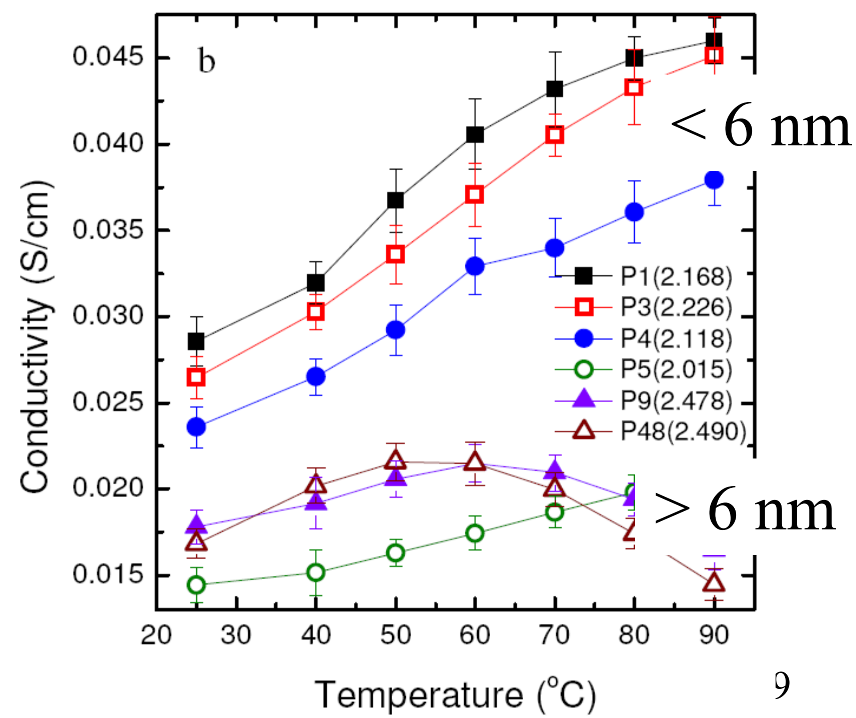
Variables	Fuel Cell Test	Optimization
Ionomer:catalyst ratio	1:2, 1:1, 1.5:1, and 2:1	1.5:1
Sulfonation (%)	20, 30, 35, 40, and 45	30 to 40
Hydrophobicity	Aromatic/Partially fluorinated	Partially fluorinated
Cat. loading (mg/cm^2)	2, 3, 4, 6, and 8	6

Conductivity of Water-based Conductors depends on Morphology

5-100 nm

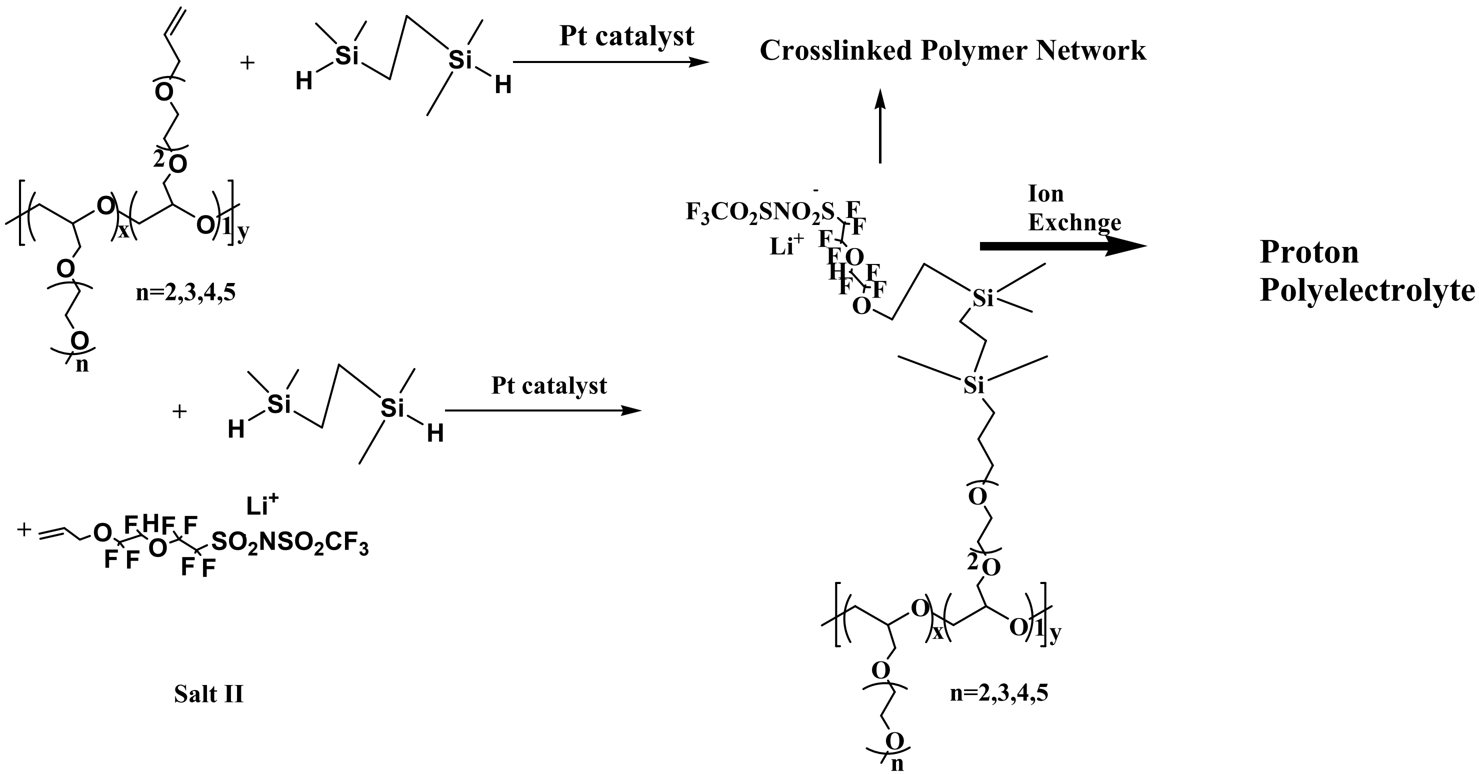
RH=50%





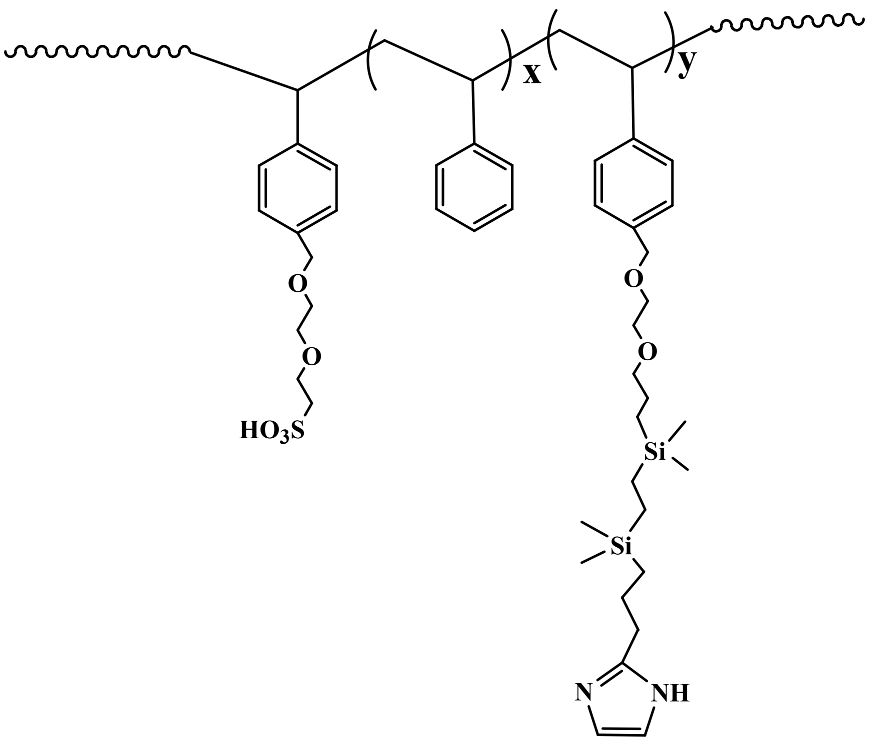
Synthesis

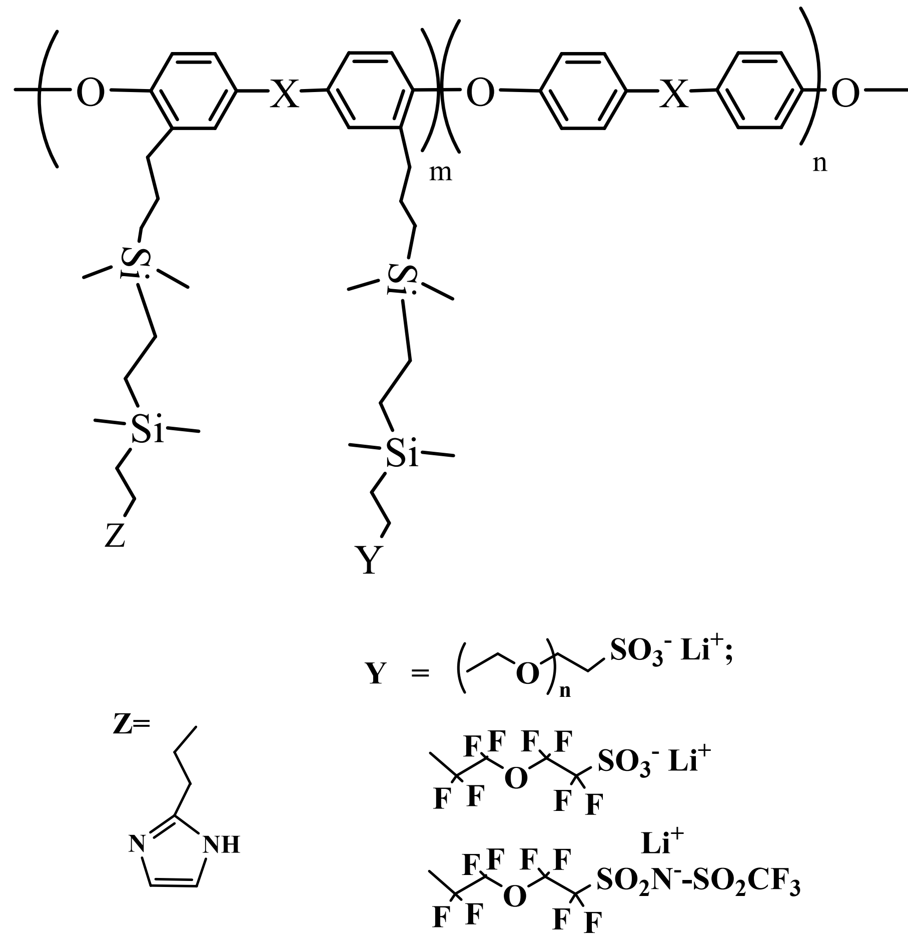
Grafting Strategy Allows any Combination of Acid groups and Heterocylic Bases



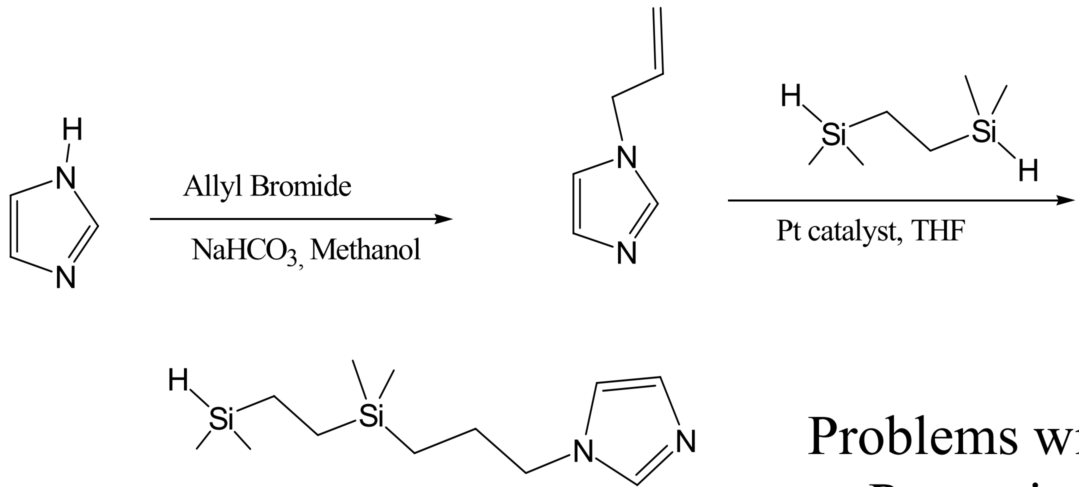
- USP 6,956,083,
- USP 7,101,643

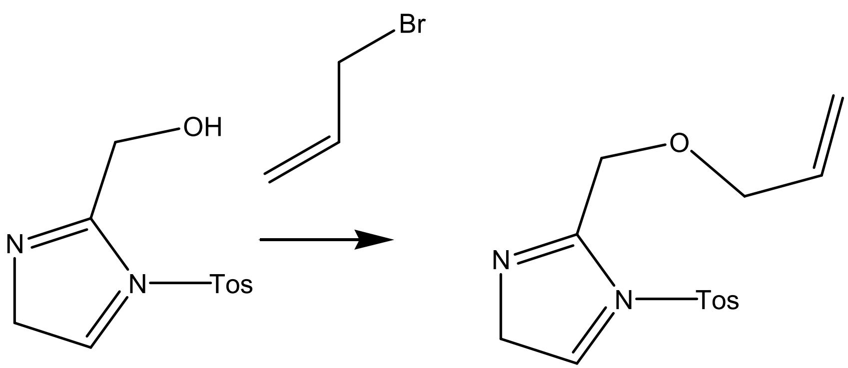
Change the Backbone for Morphology Control





Synthesis of allyl Imidazoles and intermediates for grafting

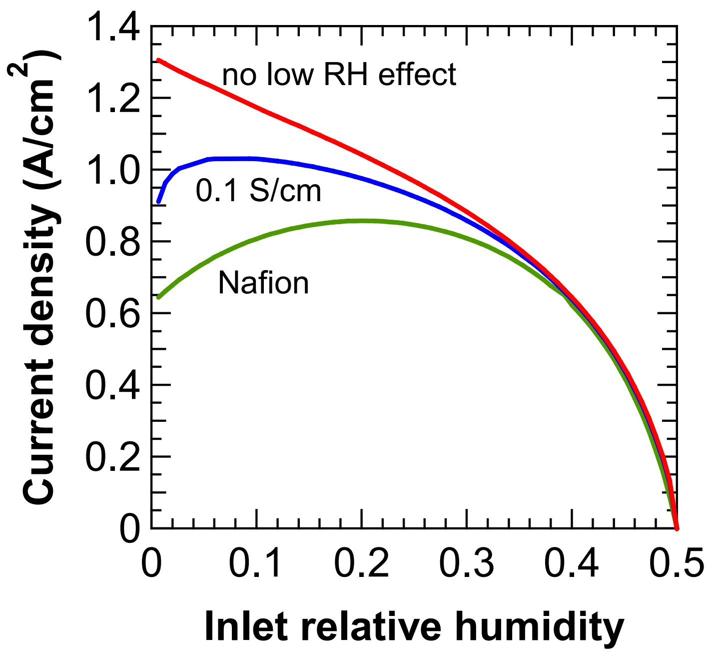


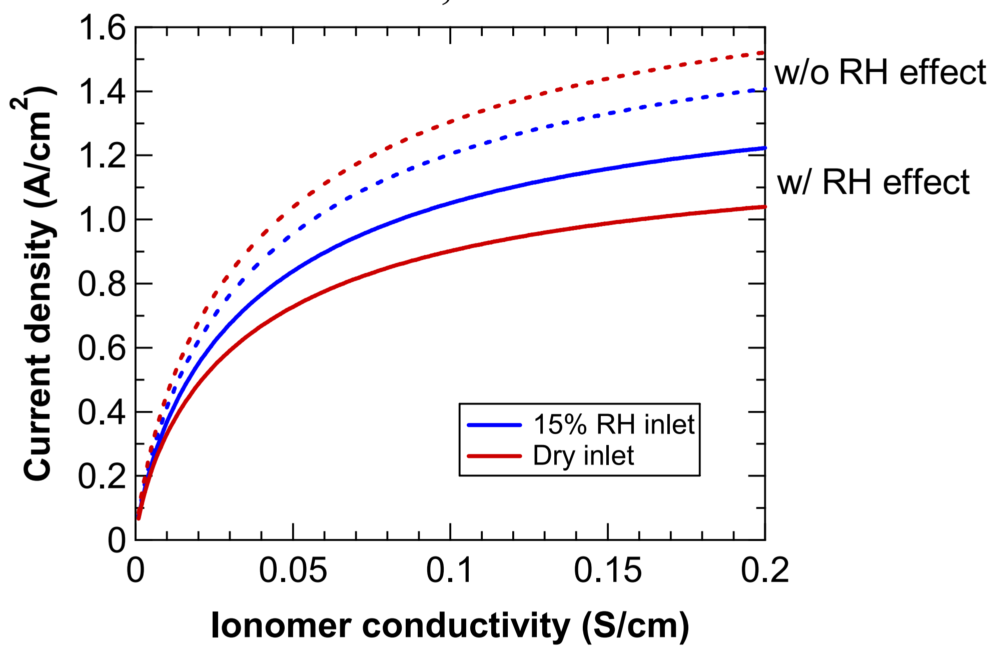


Problems with the use of Tosyl as Protecting group have delayed synthesis of tethered imidazole polymers.
New protecting groups are under test – benzyl, troc, etc.

Low RH Effect on ORR Kinetics

- Analyze the ORR humidity effect at 0.6 V with 800 EW, 25 mm membrane





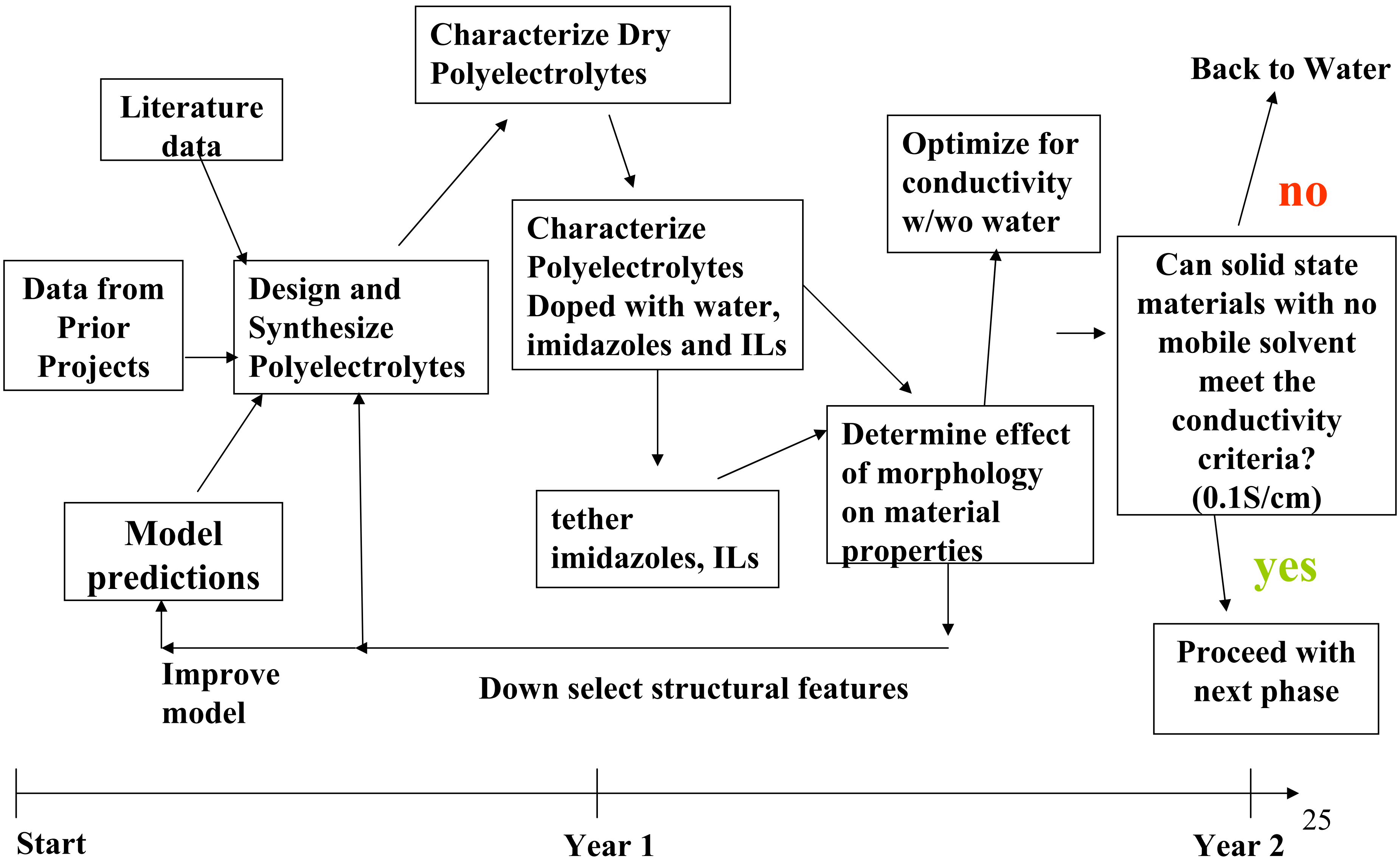
- Completely dry feeds is not practical unless remove low RH effect
  - Different solvation properties or better ionomer connectivity
  - For dry conditions, almost as much loss due to ORR RH effect as conductivity
  - Optimum RH is around 20 % for Nafion and 10 % for 0.1 S/cm ionomer

- Still require a minimum conductivity
- Currently quantifying and identifying the three effects of κ_{CL}, κ_m, low RH effect

Future Work -Who does What & When?

- **LBNL-Kerr/Balsara/Segalman/Weber**
  - Random and Block copolymer synthesis (FY07-10) – Kerr/Balsara
  - Tether acid and imidazole groups to polymers.(FY07-08) - Kerr/Balsara
  - Mechanical, morphological and electrochemical characterization of materials.(FY07-10) - Kerr/Balsara/Segalman
  - Chemical and mechanical stability.(FY07-10) - Kerr
  - System modeling (FY07-10) - Weber
- **LANL- Pivovar/Boncella**
  - Block copolymer synthesis of polynorbornene and poly(arylene ether) polymers.(FY07-08)- Boncella
  - Transport measurements (conductivity, gas crossover)(FY07-08), cell testing and MEA preparation/testing(FY08-10). Pivovar
- **3M - Hamrock**
  - Provide PFSA material for testing and explore attachment of imidazole (FY07-08).
  - Durability and chemical stability(FY07-10).
  - MEA preparation and testing (FY09-10).

Summary of Work Flow- Years 1 & 2



Summary - Modeling

- Teaming with ANL to analyze the overall system
  - Results depend on if need humidification at all
  - We provide insight and guidance into the cell model and they do the system model
- Gas permeation analysis and threshold value complete
  - Need a maximum value of 10^{-10} mol/cm-s-bar for hydrogen at 120°C for a 25 μm membrane
  - High values cause negative current densities due to mixed potentials, possible fuel starvation, and temperature spikes
- Conductivity threshold still ongoing and complicated by the observation of a low RH effect with the ORR
  - Need to consider conductor both in the catalyst layer and as a separator
  - Depends on system analysis as well
  - Work on this for next year
- Low-relative-humidity effect at cathode
  - Observed with PFSA based catalyst layers
  - Causes are ionomer tortuosity or kinetic proton accessibility or combination
  - Still being investigated (to be complete end of this FY)

Summary

- **Tests with mixtures of components indicate that 0.1 S/cm is a feasible conductivity for 120°C at 0% RH using the tethered imidazole and acids.**
- **Polymer morphology is critical for achievement of Grotthuss transport and hence high conductivity. The morphology will also be critical to reduce gas-crossover.**
- **Polymer composition will be different in the electrode layers than in the bulk. Conductivity and proton activity will be important for ORR kinetics.**
- **Synthesis activities need more resources to prepare more material.**
- **Chemical degradation studies have been initiated and are already showing results.**

Summary
- to be answered in the coming years.

- Is 0.1 S/cm conductivity necessary?
  - System simplifications allow lower conductivities?
- How does morphology affect gas crossover?
- What is the chemical and mechanical durability?
- What is the chemical stability of imidazole?
- What polymers lead to water rejection?
- Are PFSA polymers the most durable and do they reject water?