2004 DOE Hydrogen, Fuel Cell and Infrastructure Technologies Program Review

High Temperature Polymer Electrolytes Based on Ionic Liquids

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This presentation does not contain any proprietary or confidential information.

Project Objectives

Overall Objective: Contribute to DOE effort in developing high temperature polymer electrolytes for transportation applications.

Specific goals:

- Increase conductivity at high temperature (~120˚C) and low relative humidity (<50% RH)
- Improve fundamental understanding of conduction in 'free' proton containing ionic liquids
- Develop robust polymer systems
- Probe the dependence of properties on ion capacity, water content and temperature

- FY04 Budget: 300 K$

Technical Barriers and Targets

O. Stack Materials and Manufacturing Cost
P. Durability
R. Thermal and Water Management

While issues involving cost and durability exist, Thermal and Water Management is the primary driver for this task.

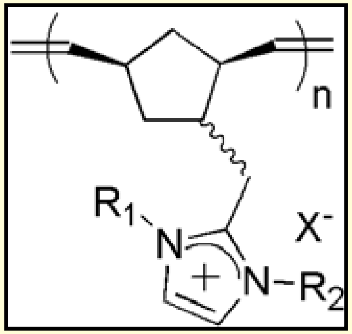
DOE High Temperature Membrane Working Group Technical Targets

		2000	2005	2010
Conductivity	S/cm	0.1	0.1	0.1
Cost	$/kW		50	5
Durability	hrs	1000	>4000	>5000
Operating Temp.	˚C	80	120	120

LANL Approach

- Investigate ionic liquids based on imidazole cations and dihydrogen phosphate ($H_2PO_4^-$) or bisulfate (HSO_4^-) anions capable of proton conduction in high temperature membranes

- 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.

Project Timeline

Investigation of proton containing ionic liquids began in February of 2003.

FY '04 Milestones and Progress:

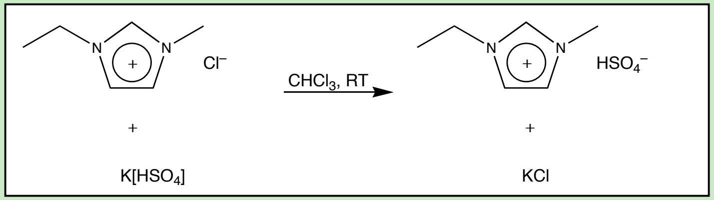
Nov 03: Screen functionalized imidazole-acid pairs for target materials
Status: Many (>10) imidazole-acid pairs have been synthesized and screened.

Feb 04: Characterize water and temperature dependence on conductivity.
Status: Characterization of 4 imidazole-acid pairs.

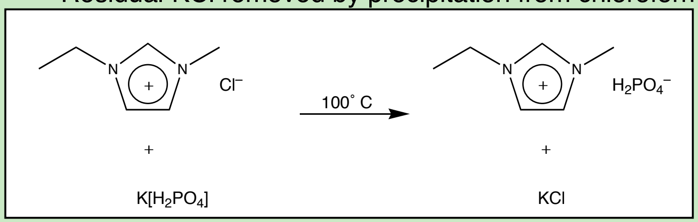
Sep 04: Synthesize and test polymers/oligomers based on target materials.
Status: First generation polymers already synthesized and tested, second generation block copolymers being synthesized.

Acid-Imidazole Pairs

Ionic Liquids



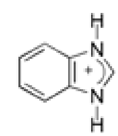
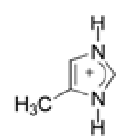
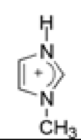
- Mixture is filtered to eliminate bulk of KCl
- Residual KCl removed by precipitation from chloroform



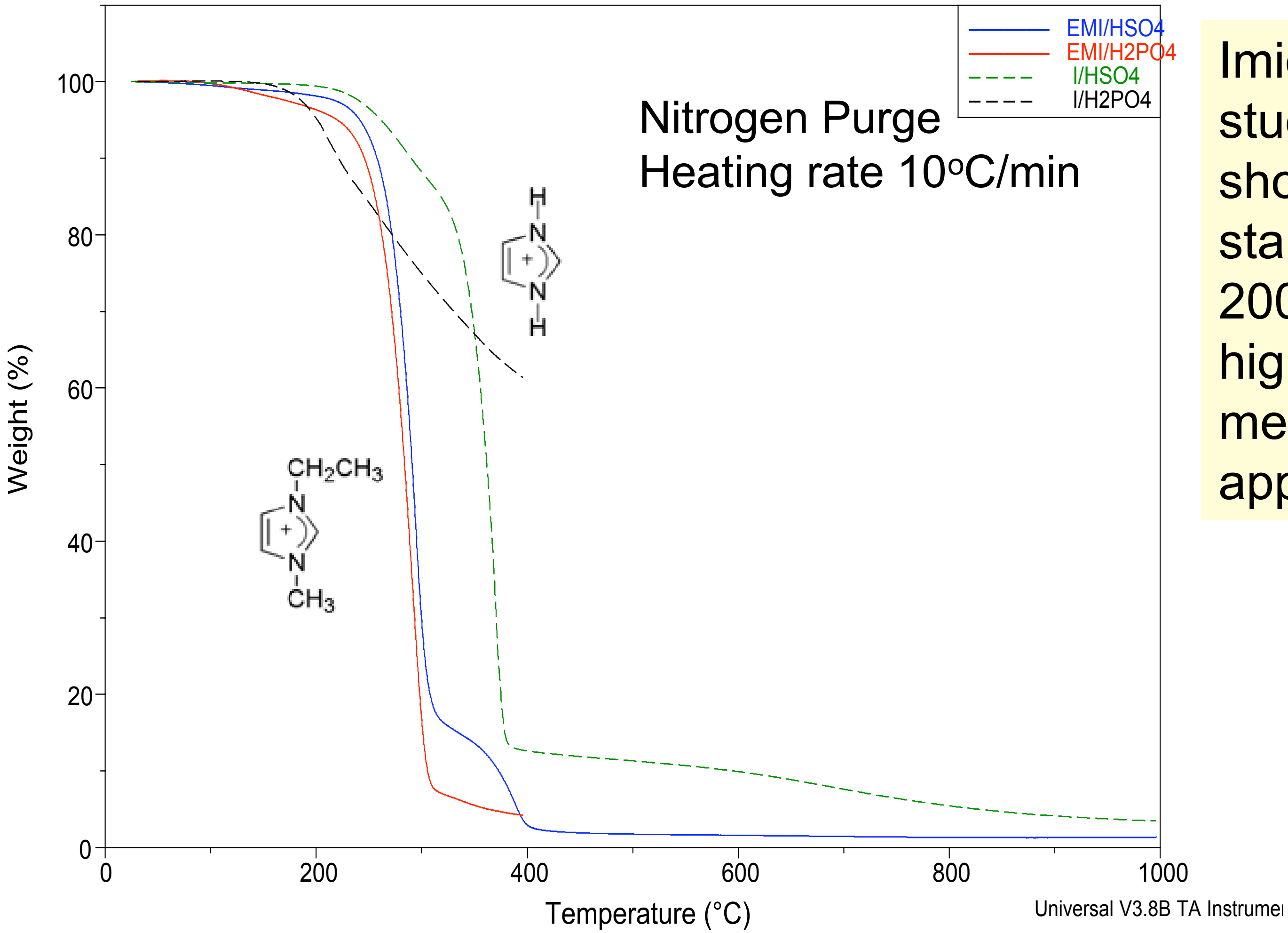
- Solid reaction product is extracted into methanol and filtered
- Methanol is removed under vacuum and residual KCl removed by precipitation from $CHCl_3$

Ethyl Methyl Imidazolium (EMI) Salts

- ‘Free’ proton containing acid-imidazole pairs synthesized
- Pairs characterized in terms of properties (melting point, conductivity, stability, etc.)

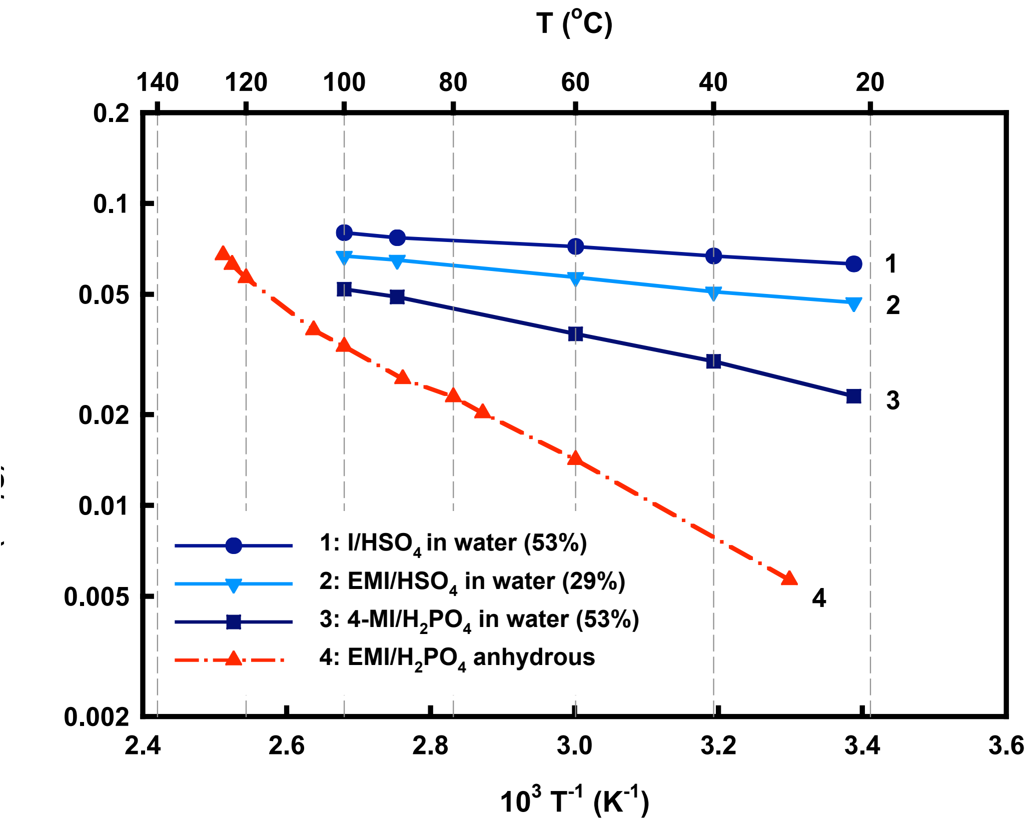
Imidazole Cation	Counterion	Melting Point (°C)
	$H_2PO_4^-$	124-126
	HSO_4^-	<100
	$B(OH)_3$ (1:1 mixture)	60 softening
	$H_2PO_4^-$	157-159
	$H_2PO_4^-$	134-136
	$H_2PO_4^-$	132-135

Thermal Stability



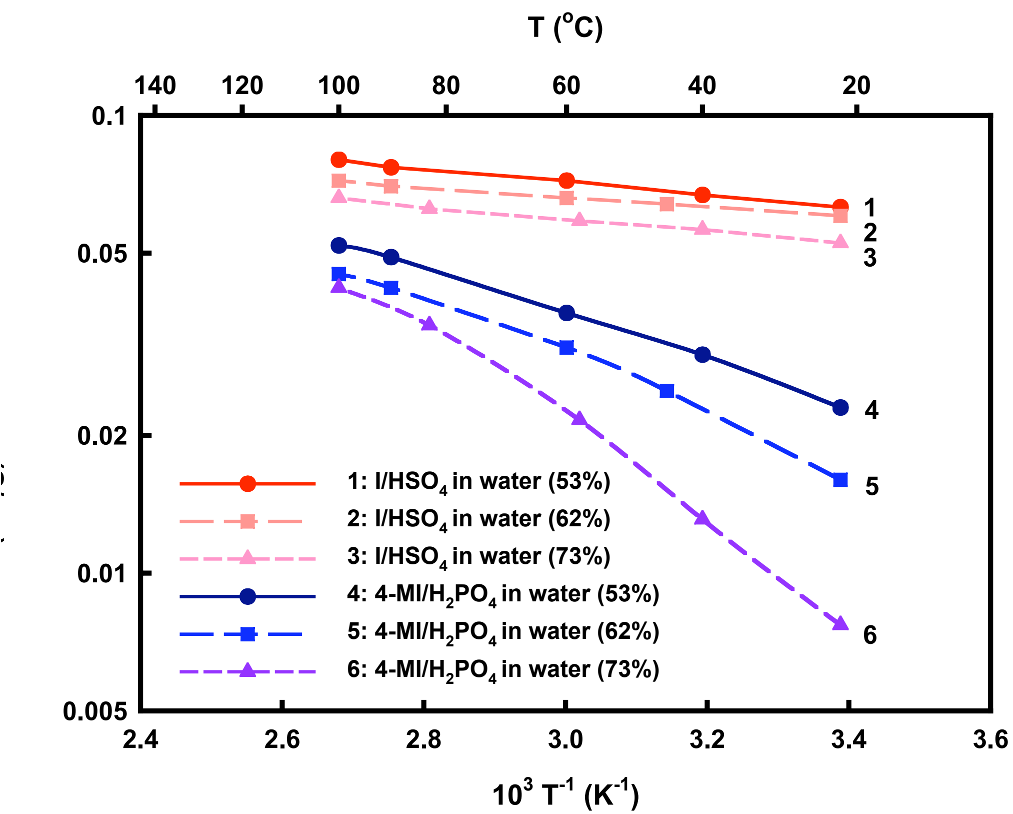
Imidazole-acid pairs studied by TGA showed thermal stability to at least 200C, adequate for high temperature membrane applications

Conductivity Dependence on Temperature



- Conductivity of acid-imidazole pairs (even water-free) was high and suggest further study is merited
- Pairs showed Arrhenius conductivity dependence
- Conductivities represent conductivity of all ionic species, NMR or other techniques needed to determine protonic contribution

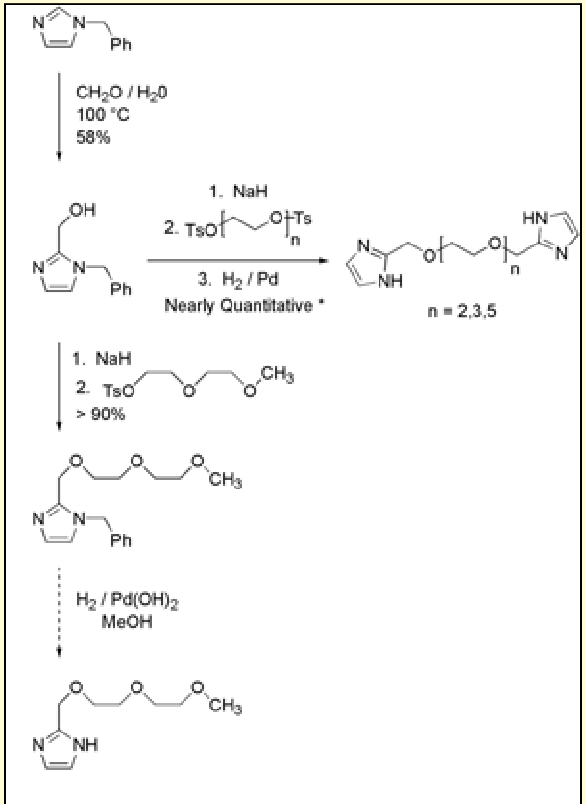
Influence of Water Content on Conductivity



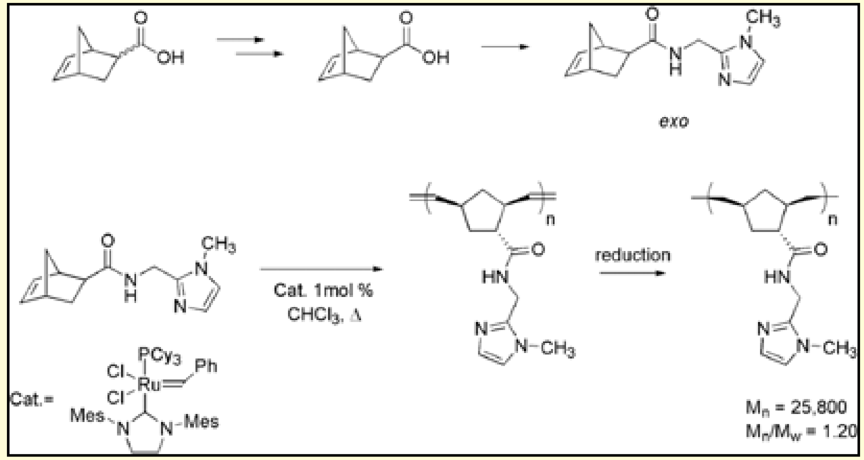
- Conductivity of acid-imidazole pairs was found to increase with water content and temperature within the range shown here
- Conductivities limited to 100C due to experimental apparatus
- Acid-imidazole pairs are very hygroscopic and retained water may prove critical in improving conductivity

Polymer Synthesis

Polymer Route



* Shuster, M.; Meyer, M. H.; et al *Solid State Ionics*, **2001**, *145*, 85-92.



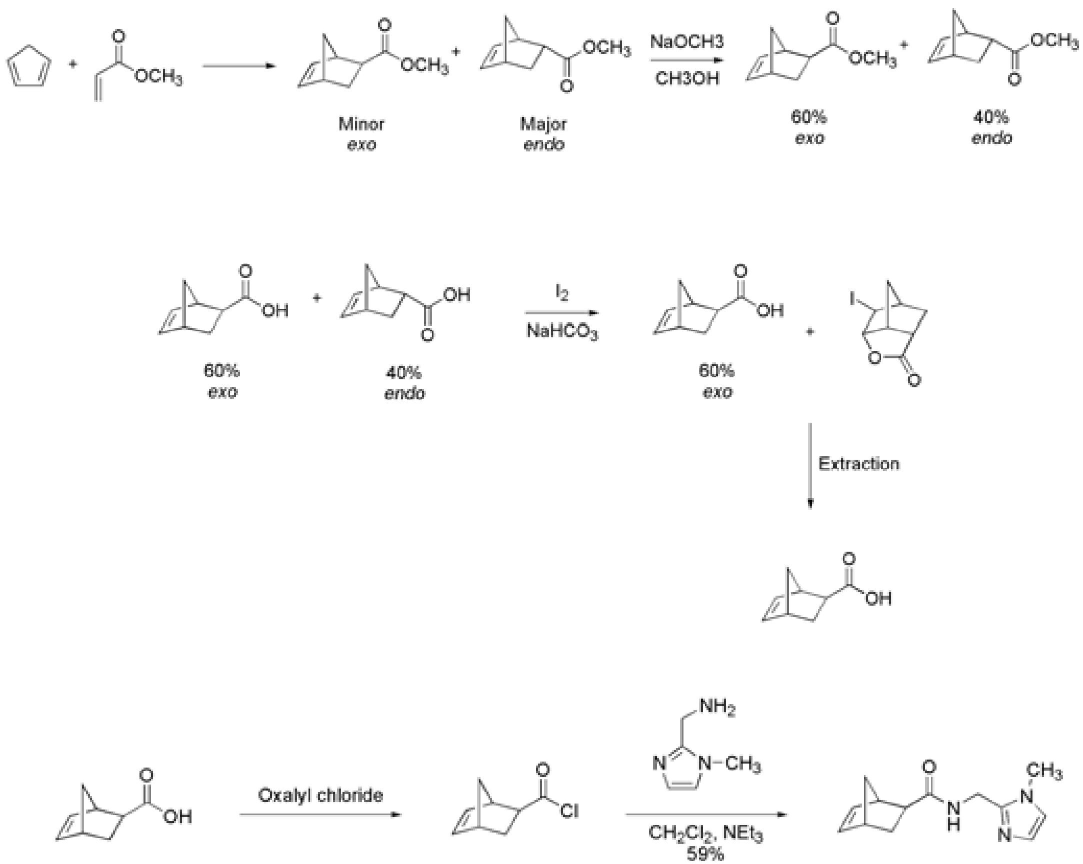
We have generated and first generation polymer films based on norbornene chemistry (above).
Other chemistry such as ether precursors can be easily incorporated into polymers using similar techniques (left).

Why use Polynorobornenes?

- Well defined polymers – low polydispersity
- Easy to make block copolymers
- Different types of polymerization mechanisms give materials with different properties
- Readily available monomers and catalysts
- Can be functionalized with little difficulty

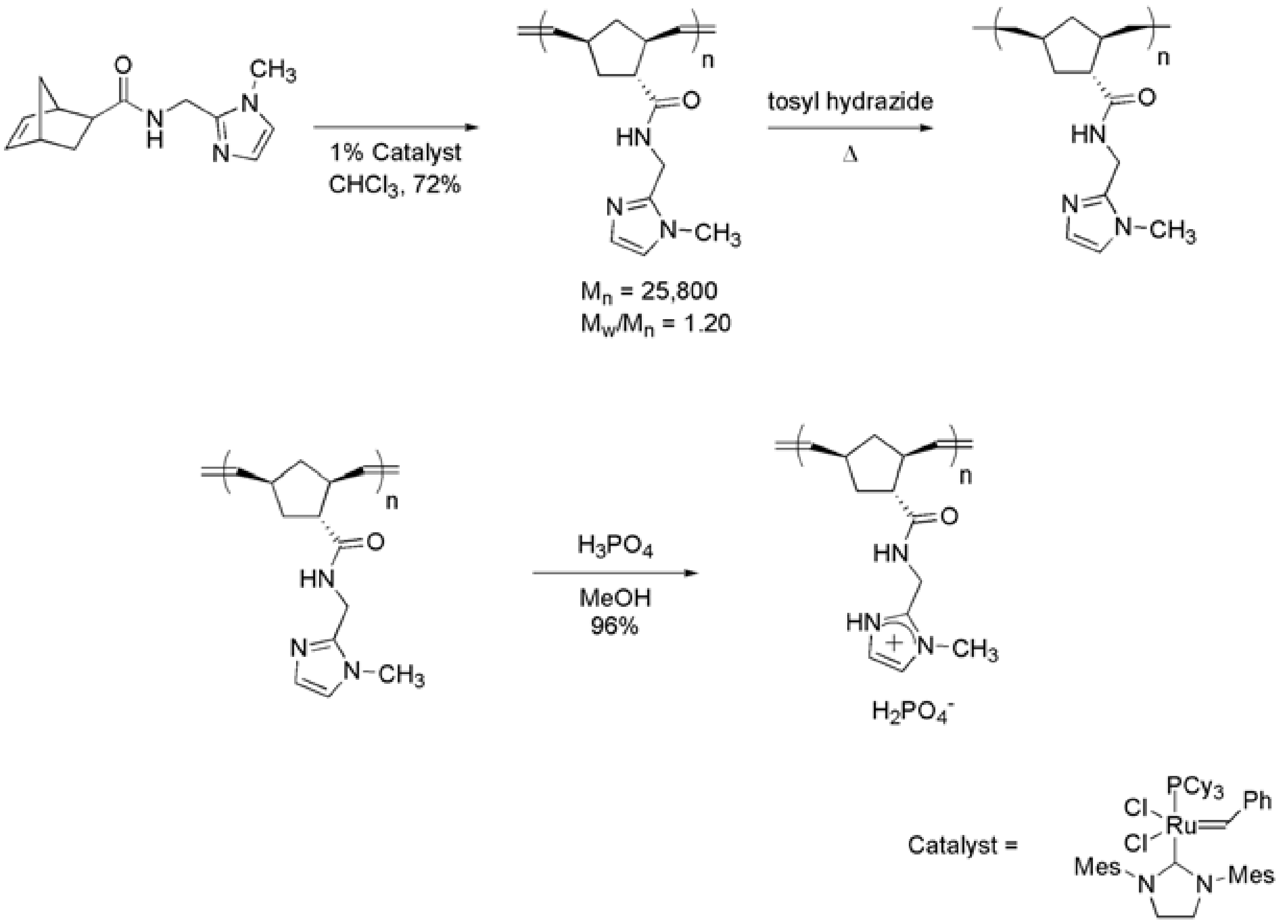
While chemical stability of backbone needs to be studied, this architecture allows us to study performance in well controlled morphologies with target functionality.

Synthesis of exo Monomers



- Synthesis of poly-norbornene was limited by the endo isomer
- The exo isomer was isolated
- The exo isomer can then be functionalized to give a monomer that yields reasonable molecular weight polymer
- Reaching this step took significant effort

Norbornene Polymerization

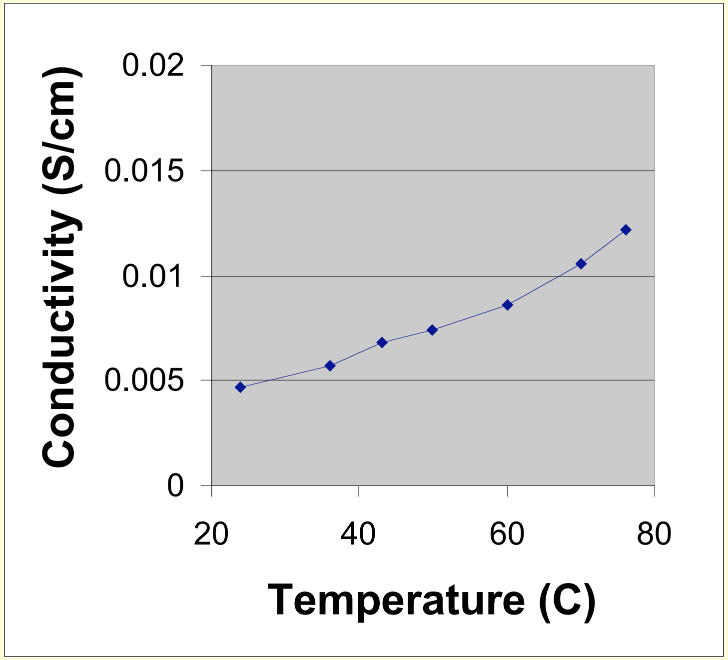


- We have synthesized polymers of reasonable molecular weight and film casting properties
- Very few polymer chemistries have been explored (copolymers, density or type of functional groups, etc.)

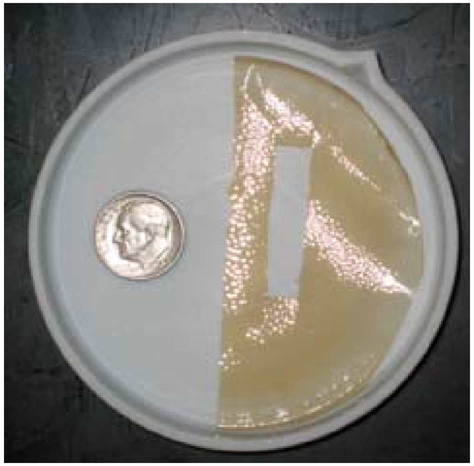
Hydrated Membrane Conductivity

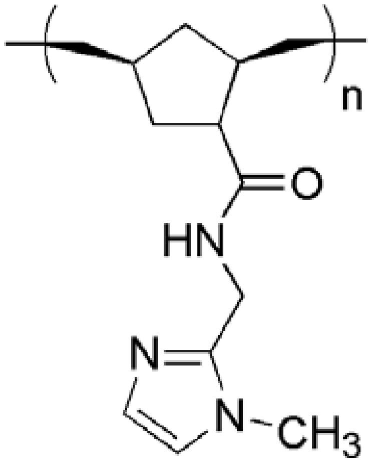
AC Impedance Spectroscopy

PNBA-2-MI in liquid water



- Initial tests showed surprisingly high conductivity, albeit far below Nafion. Further work needs to be done to verify these results.

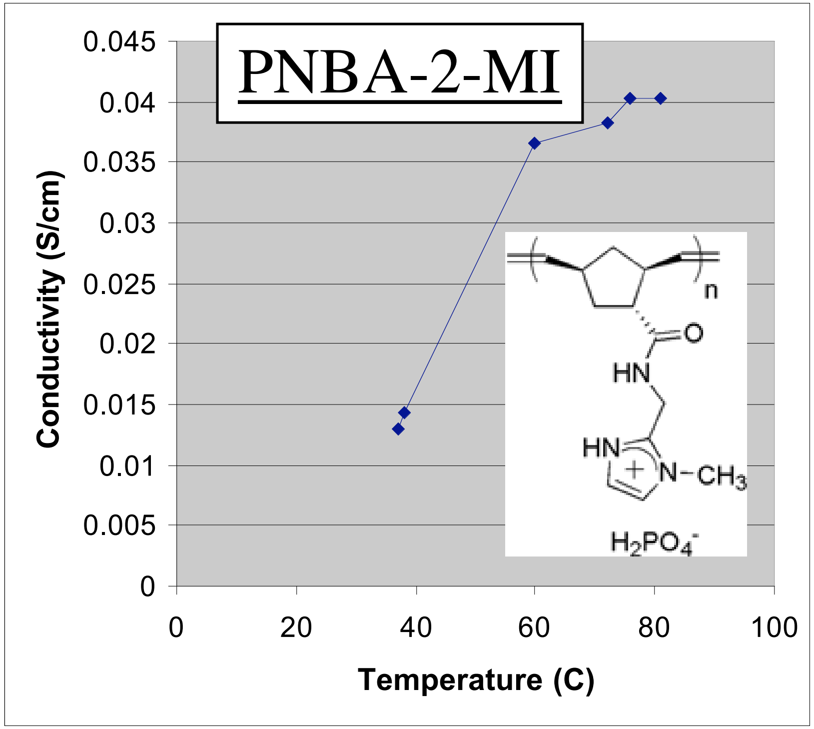


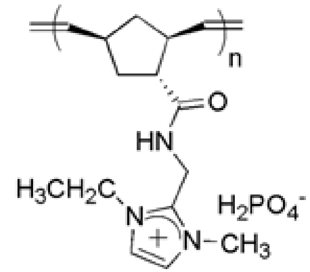


water uptake is high (45%) and this particular membrane is water soluble when doped with acid.

PNBA-2-MI poly-dihydro(norbornene-2-carboxy-N-(1-methyl-1H-imidazol-2-ylmethyl)-amide)

Membrane Conductivity Dependence on Water Content





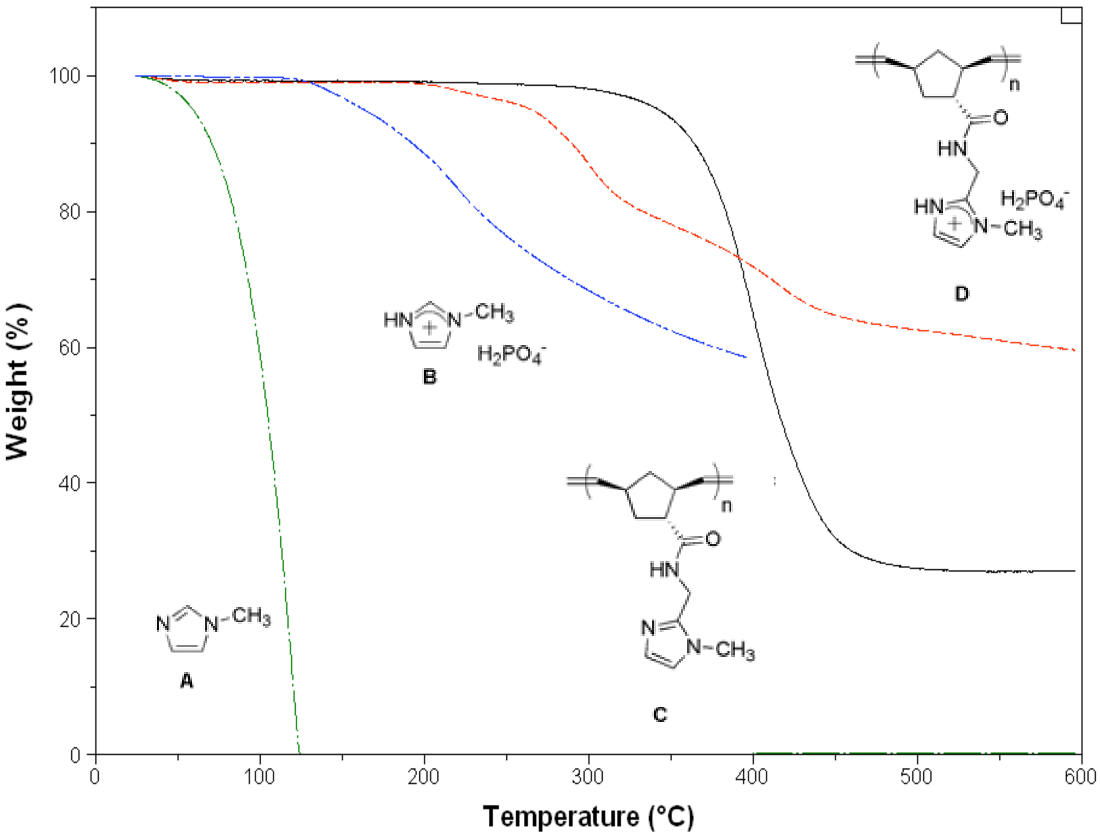
PNBA-2E5MI

Conductivity (90˚C)	Relative Humidity
0.035 S/cm	10%
0.047 S/cm	25%

- PNBA-2-MI phosphate is water soluble, but shows reasonable conductivity even in the dry state
- The role of the phosphate anion and proton in conduction needs to be clarified

- PNBA-2E5MI is the ethylated version of PNBA-2-MI and is also water soluble, but likewise shows reasonable conductivity at low RH

Thermal Analysis



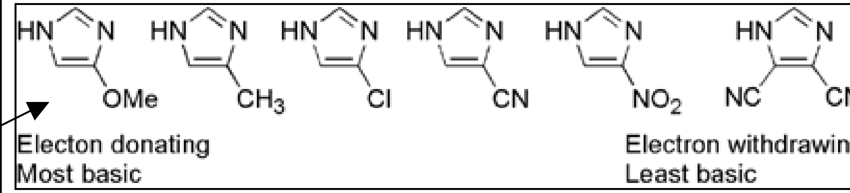
- Methyl imidazole evaporates at low T (30˚C)
- Methyl imidazole – dihydrogen phosphate shows mass loss at moderate T (150˚C)
- Polymer analogues show good temperature stability to at least 200˚C for the acid analogue, 300˚C for neutral polymer

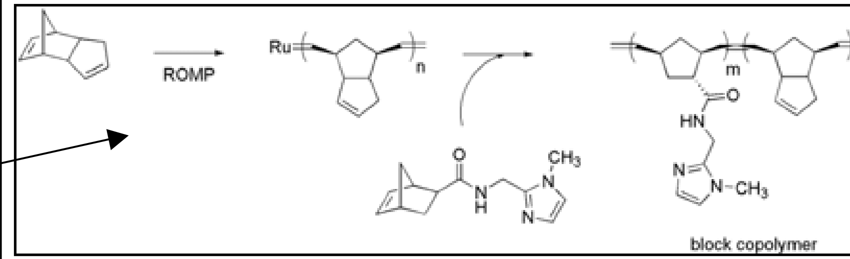
Conclusions

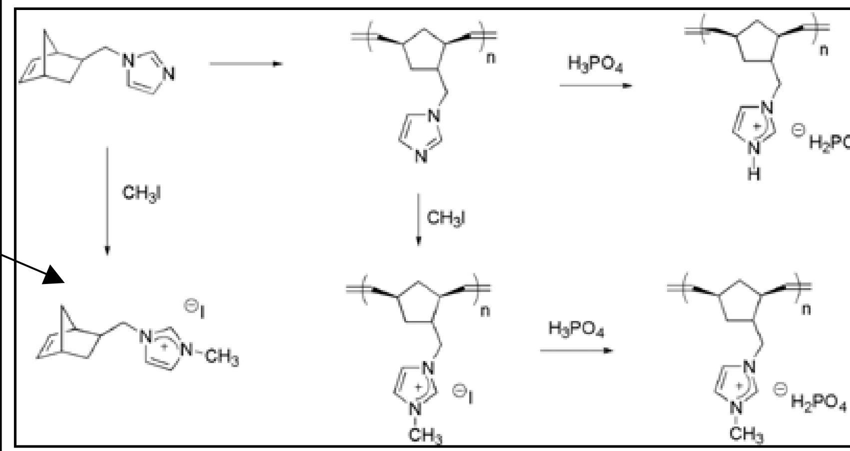
- Imidazole-acid pairs show reasonable conductivity at high temperatures even at low humidity, while still exhibiting good thermal stability
- We have successfully synthesized and characterized norbornene tethered ionic liquids
- The resulting polymers are thermally stable up to at least 200 ˚C
- While water solubility is a concern, conductivity data for the films is very promising
- The role of the anion versus the proton in ion conduction needs to be elucidated

Future Work

- Continued work on imidizole-acid pairs (further characterization of water and temperature effects)
- Copolymers (random and block) investigated for control of water uptake properties
- Investigation of tethered acidic moeities compared to free acids
- Incorporation of alternate imidazole functionality into the polymer
- Chemical stability in fuel cells







Collaborations and Interactions

1. **Lawrence Berkeley National Laboratory:** *John Kerr - developing high temperature ionic liquid based technology on battery electrolytes.*
2. **Virginia Polytechnic and State University:** *James McGrath – characterization and testing of MEAs for high temperature applications.*

Project Safety

Management Safety Controls

- Hazard Control Plan (HCP): *Hazard based safety review.*
- Integrated Work Document (IWD): Task *based safety review.*
- Relevant safety courses and OJT required for lab work.
- Integrated Safety Management (ISM).

Define work → Analyze hazards → Develop controls → Perform work → Ensure performance

Engineering Controls

- Hydrogen cylinders contain less than the LEL for full release into the room.
- Thermal barriers are commonly used to prevent burns.
- Two man rule employed for any 'energized' work.