



New Polyelectrolyte Materials for High Temperature Fuel Cells

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This presentation does not contain any proprietary or confidential information

Project ID#
FCP 8

Overview

Timeline

- Project start:
April 30, 2003
Interrupted Jan 2004-July 2005
- Project end:
September 30, 2006

Budget

Total - \$500k

DOE Share - \$500k

- Funding received in FY05 - \$200k
- Funding for FY06 – \$200k

Barriers addressed

- Phase 1(FY03-FY06):
 - B. Stack Material and Manufacturing Cost.
 - D. Thermal and Water Management.
- Phase 2 (FY06 onwards):
 - A. Durability
 - C. Electrode Performance.
- DOE Technical Target for Fuel Stack -2010
 - Cost \$35/kw
 - Durability 5000 Hours

Partners

High temperature Membrane
Working Group.

NASA

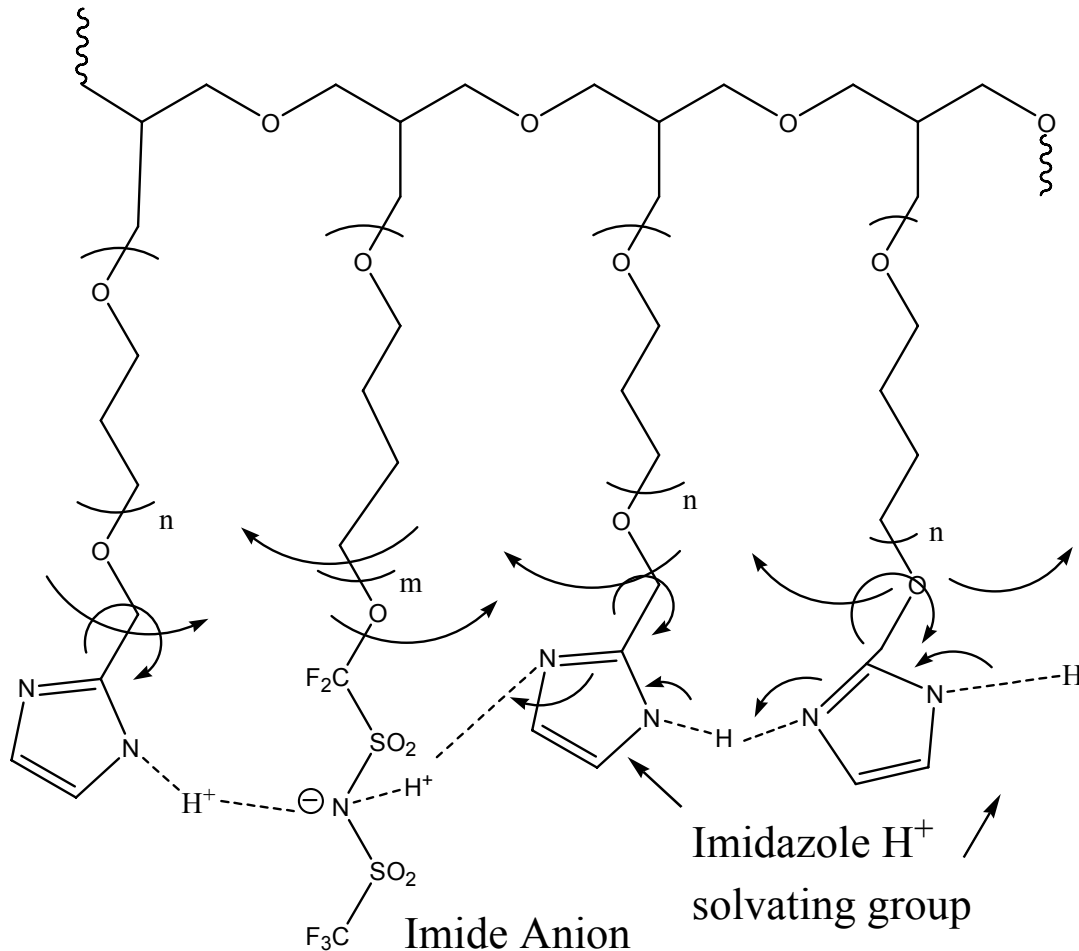
Objectives

- Investigate the feasibility of use of solid polyelectrolytes for high temperature operation that do not require the presence of water.
- Prepare solid electrolytes where only the proton moves.
 - Measure conductivity, mechanical/thermal properties of Nafion® and Polyether polyelectrolytes doped with imidazoles.
 - Covalently attach imidazoles to side chains of ionomers with appropriate polymer backbones and test for conductivity, mechanical/thermal behavior and gas permeability.
- Significant system simplifications for Fuel Cells.
 - Heat and water management greatly simplified.

Approach

1. Prepare polyelectrolyte gels from Nafion® and Imidazole or N-methylimidazole to replace water. Measure properties (conductivity, thermal/mechanical properties)
2. Prepare polyelectrolyte gels with imidazoles and polyether polyelectrolytes prepared under NASA PERS program for lithium batteries. Measure properties for variety of polyelectrolytes with different structures and pendant anions.
3. Attach imidazoles covalently to modified polyether polyelectrolyte backbones using results from 2. as guidance. Measure properties and optimize for use in separator membrane (high T_g , low gas permeability, high conductivity) or MEA (low T_g , high gas permeability, high conductivity).
4. Optimize structures for durability.

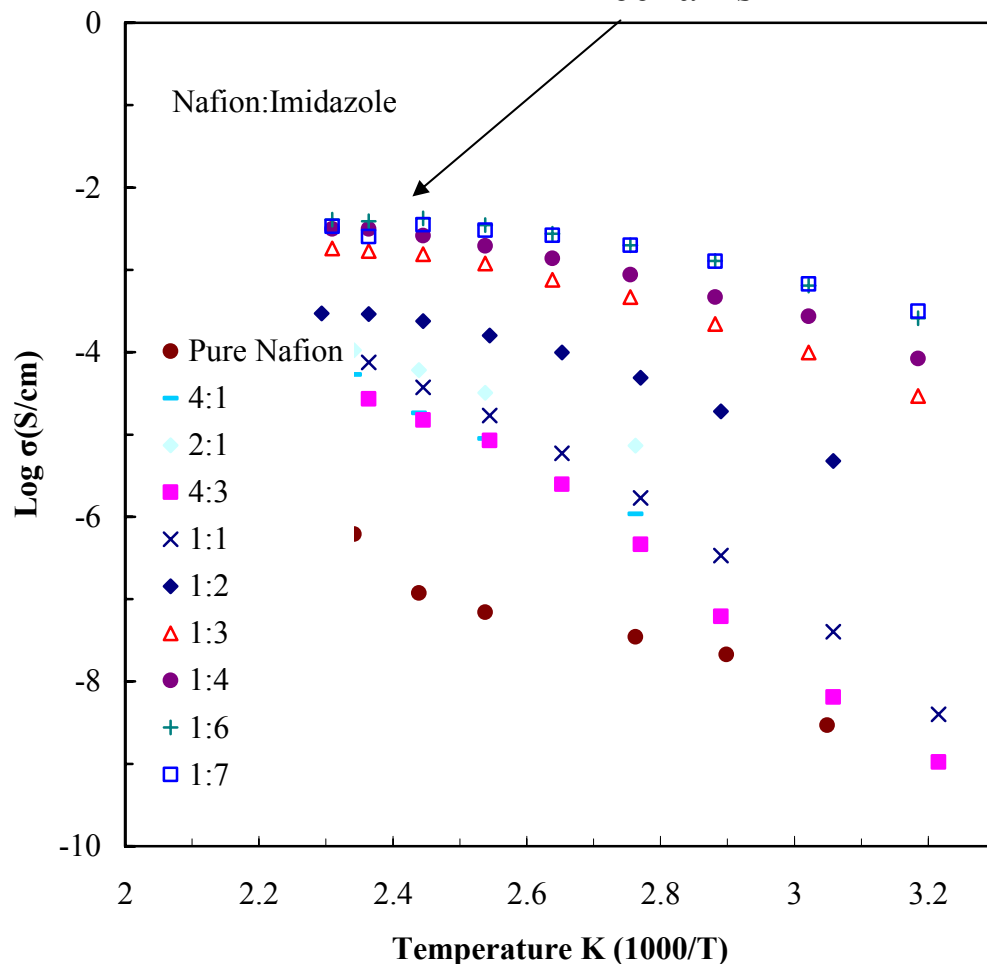
New Polymer Architectures for Imidazole Solvating groups (Kreuer), Anion Mobility and Flexibility



- 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.
- Degradation results in Release of small fragments - facilitates failure analysis.

Conductivities of Imidazole Doped Nafion Films

Flat temperature dependence
Consistent with Grotthuss
Mechanism



Details of film casting

Nafion: acid form

Equivalent MW: 1,100

Solvent used: aliphatic alcohol
and water mixed solvent.

Drying condition: 65° C for 2
hours.

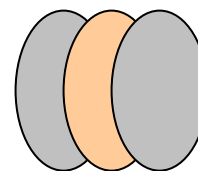
Film thickness: 100 $\mu\text{m} \pm 20 \mu\text{m}$

Testing conditions

Film between two parallel
stainless steel plate.

Impedance measurements.

Decreasing temperature from
170° C to 25° C.

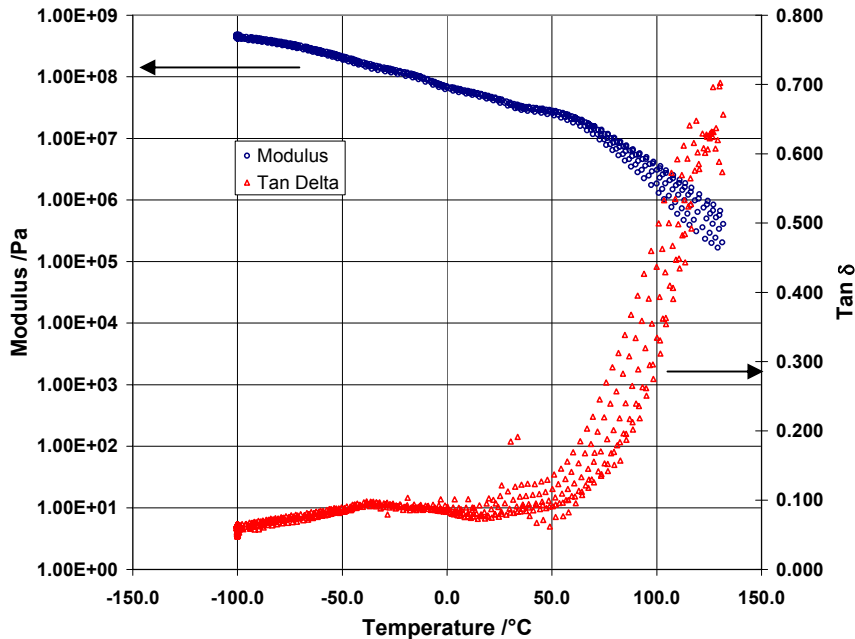


Stainless steel disc-Membrane-Stainless steel disc

DMA of Nafion and Nafion-Imidazole

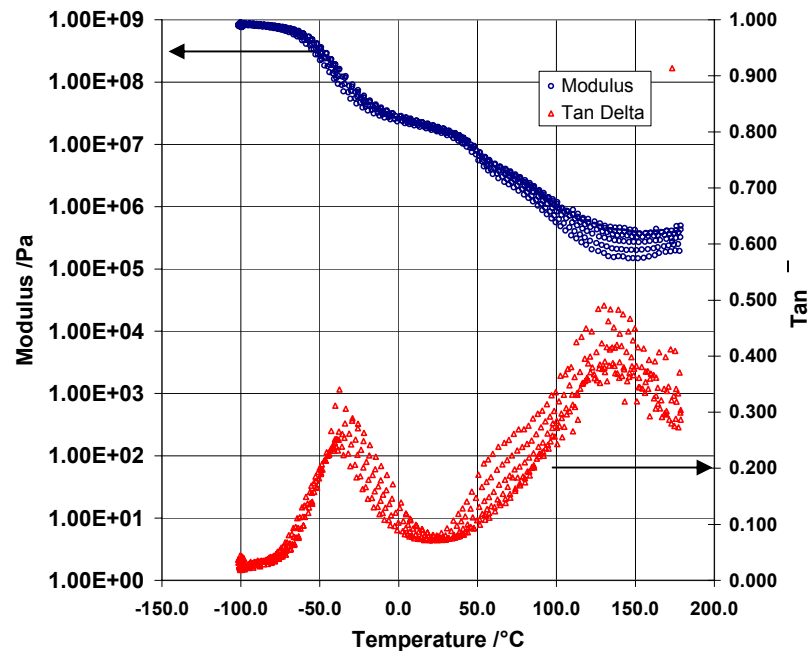
Dry Cast Nafion

Dynamic Properties vs Temperature



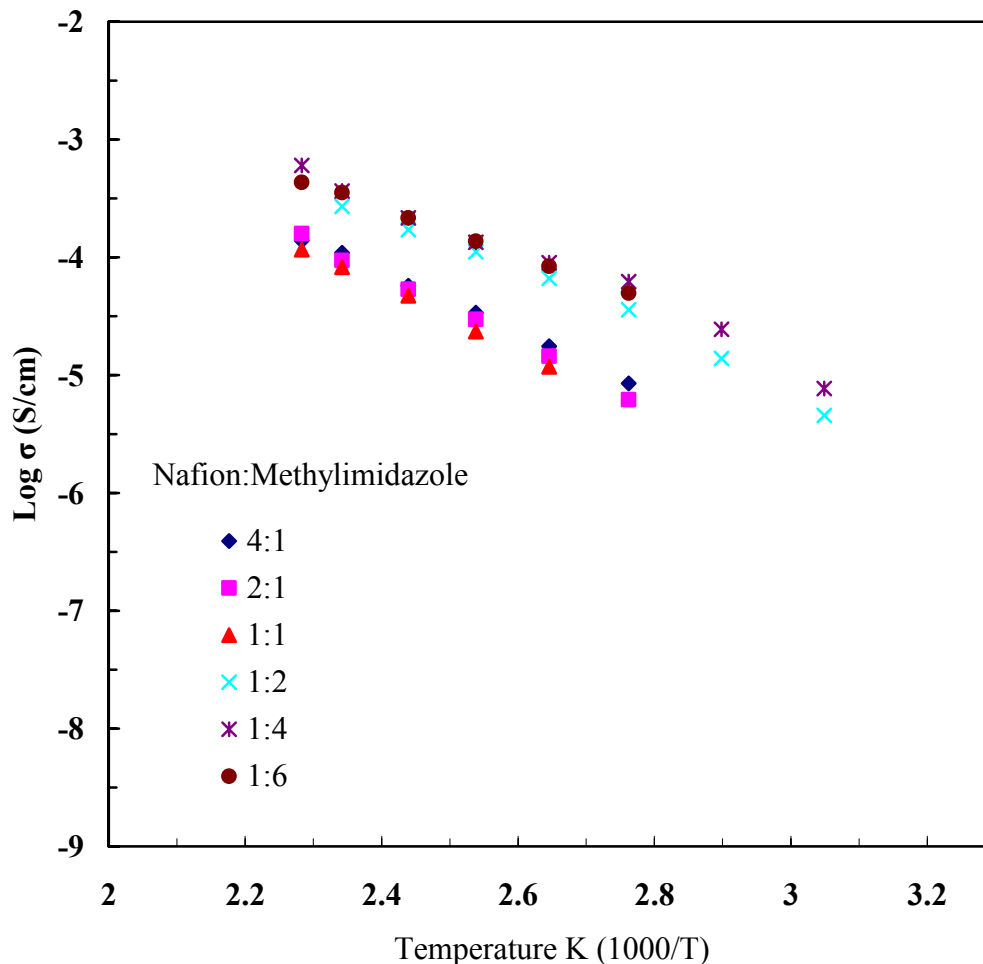
Dry Cast NAFION-Imidazole SO₃H:Im 1:4

Dynamic Properties vs Temperature



- Imidazole results in an increase in the T_g 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.

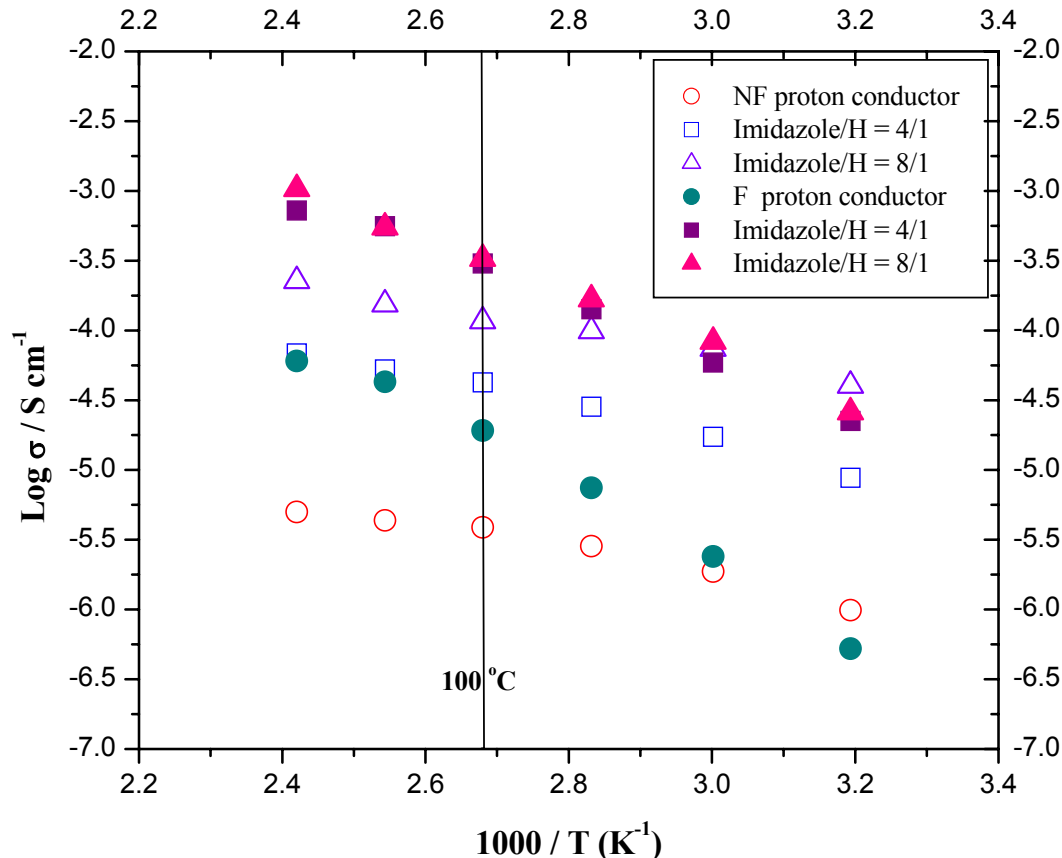
Conductivities of Methylimidazole Doped Nafion Films



N-methyl Imidazole unable to participate in Grotthuss mechanism of proton transport. Only segmental motion responsible for proton mobility, hence larger activation energy and steeper slope. Compare with Imidazole doped Nafion where Grotthuss mechanism is possible.

Polyether Polyelectrolytes doped with Imidazole

- Acid Strength increases Conductivity.



Polyether polyelectrolytes prepared from:

PE(EO)₅co-Allyl(EO)₂

and

CH₂=CHCH₂OC₂H₄OC₂H₄SO₃Li
(NF conductor)

and

CH₂=CHCH₂C₂F₄OC₂F₄SO₃Li
(F proton conductor).

Exchange Li⁺ for H⁺ with Dowex®
-HCR-W2 ion exchange resin.

Vacuum dried over P₂O₅

Co-cast polyelectrolyte with
Imidazole from EtOH soln.

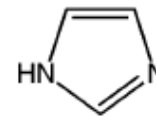
Dry over P₂O₅.

**Temperature dependence indicates no Grotthuss mobility of the protons.
Phase separation not strong in the polyethers which interfere with structure
diffusion mechanisms needed for Grotthuss mechanism and high conductivity.**

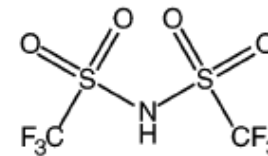
Ionic Liquids made from

Watanabe et al.

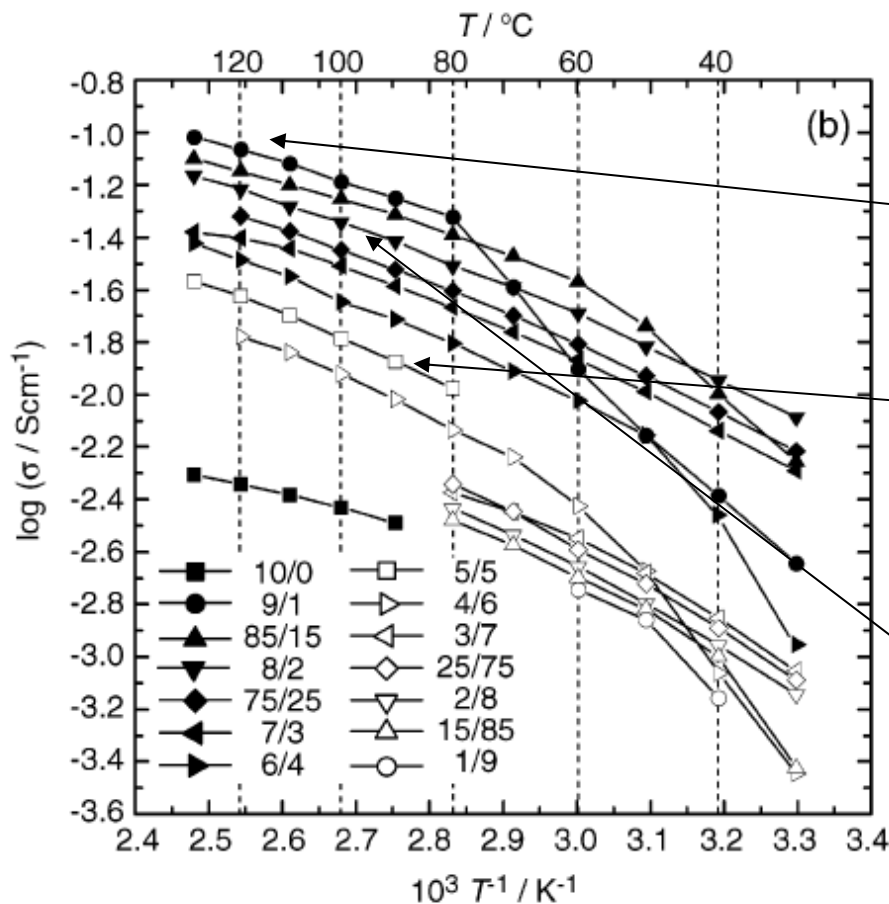
J.Phys Chem B, 2003, 017, 4024.



Im



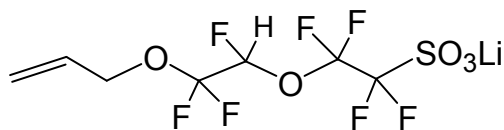
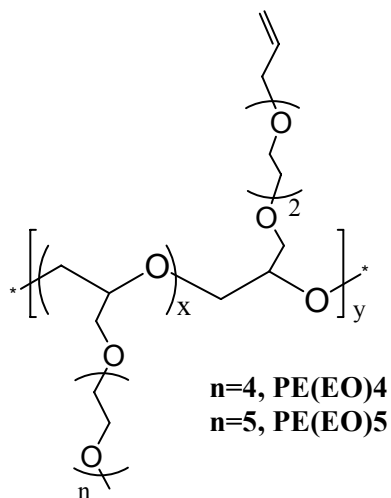
HTFSI



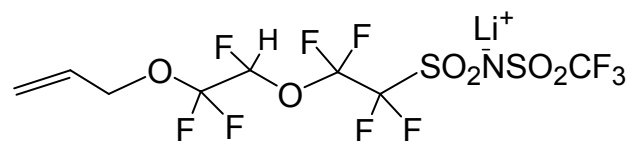
- Highest conductivities close to 10^{-1} S/cm (9:1).
- Even 5/5 has acceptable conductivity at all temperatures for an electrode binder
- E_{act} (slope) high for Grotthuss proton transfer.
- Indicates fluoroalkyl-sulfonylimides provide best H^+ mobility.

Ionic conductivities as function of temperature and Imidazole:HTFSI ratio

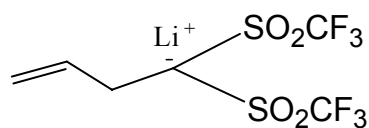
Low T_g Pre-polymers and Salts for Testing as Proton Conductors



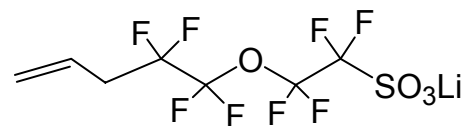
Salt I



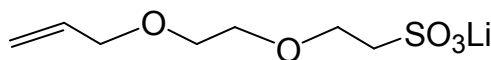
Salt II



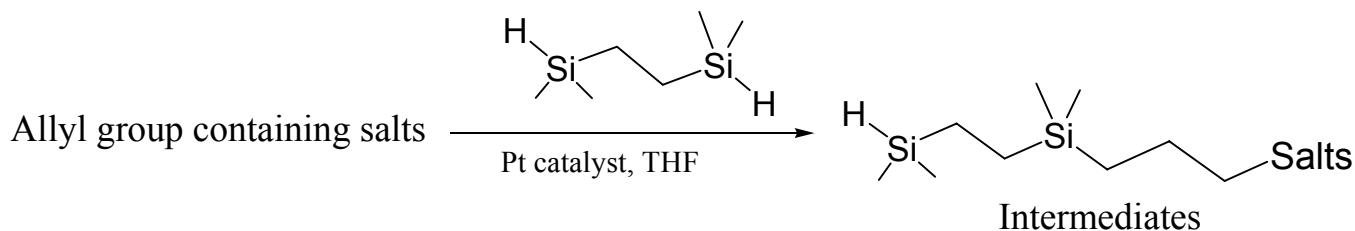
Salt III



Salt IV

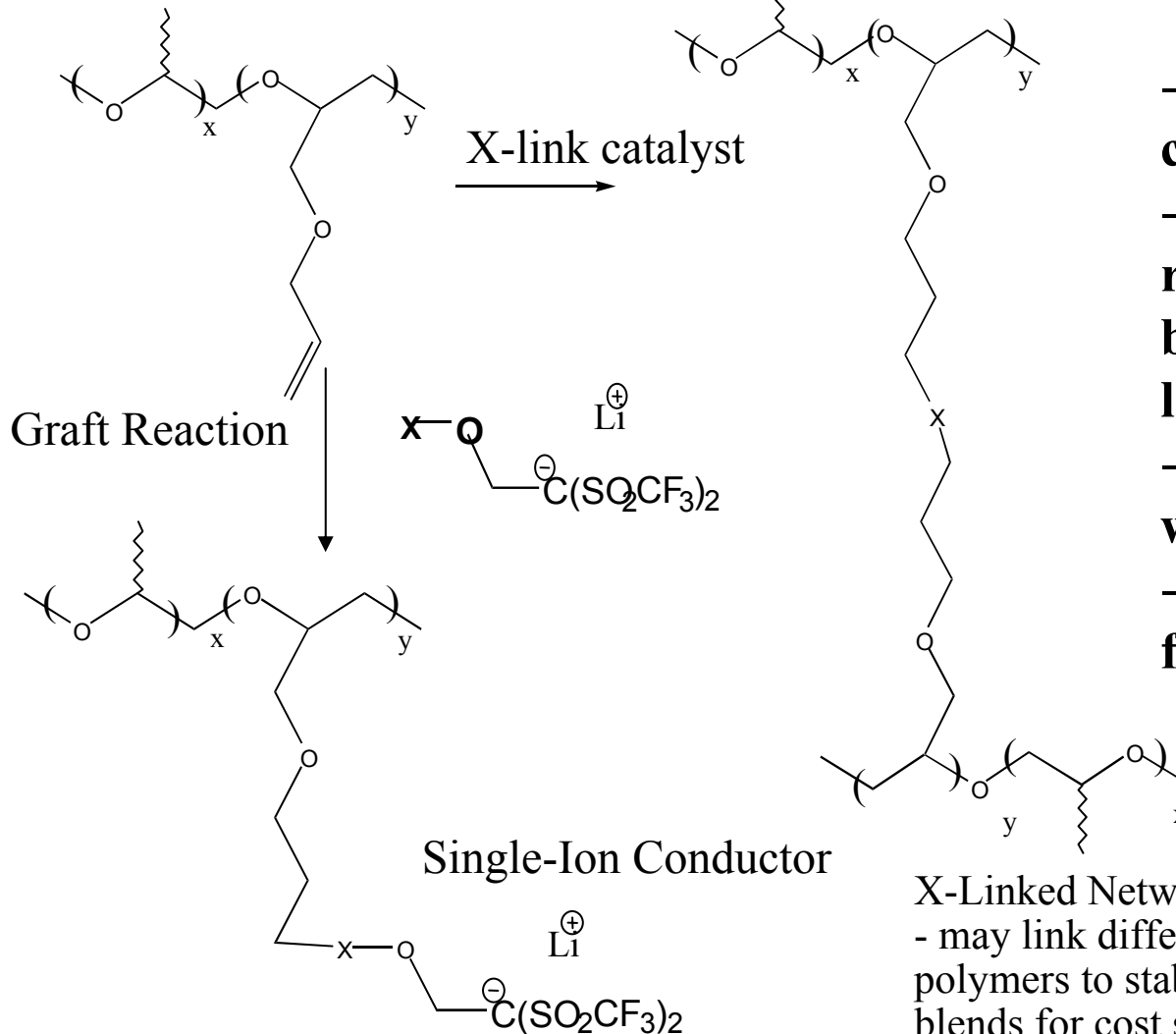


Salt V

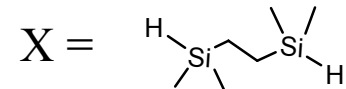


Polyether Polyelectrolytes under construction for Lithium Batteries - NASA

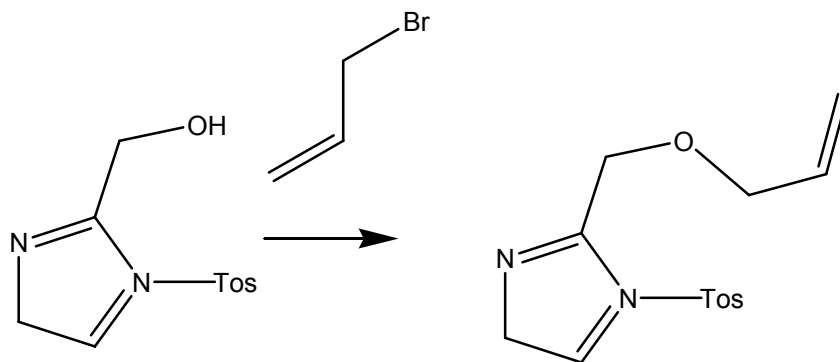
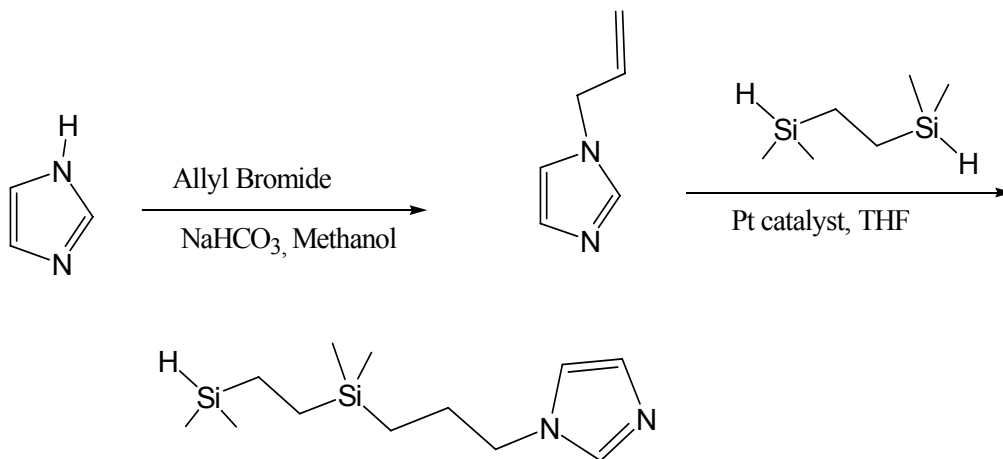
Exchange Li^+ for H^+ and dope with Imidazole



- allyl groups are reactive centers in this chemistry.
- Hydrosilation is reproducible, provides better uniformity and leaves no residues.
- Allyl groups do not react with radical initiators.
- Excess allyl groups used for cross-linking

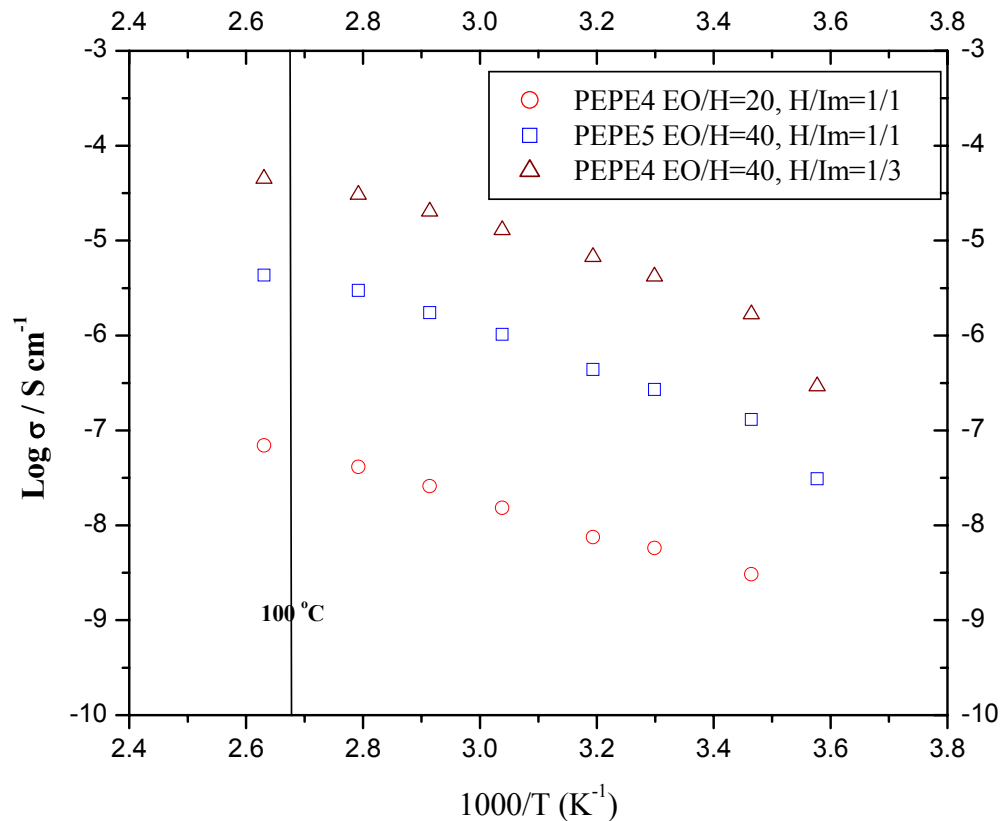


Synthesis of allyl Imidazoles and intermediates for grafting



Conductivity of grafted imidazole-based proton conductors – alkylsulfonic acid.

All solid state – only the proton moves

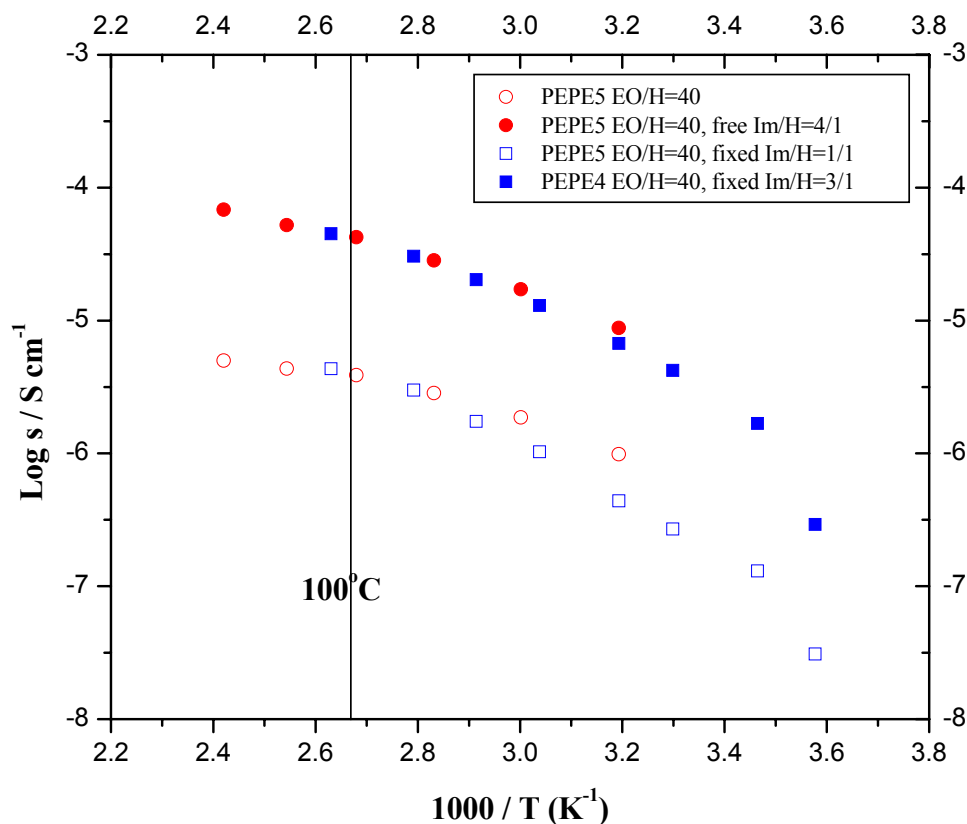


Physical Properties of Polyepoxide Ether Polyelectrolytes.

Polyme r	EO/H	Im/H	T _g /°C
PEPE ₄	20:1	1/1	-69.7
PEPE ₅	40:1	1/1	-75.1
PEPE ₄	40:1	3/1	-75.2

Comparison of conductivities of free imidazole and fixed imidazole based proton conductors.

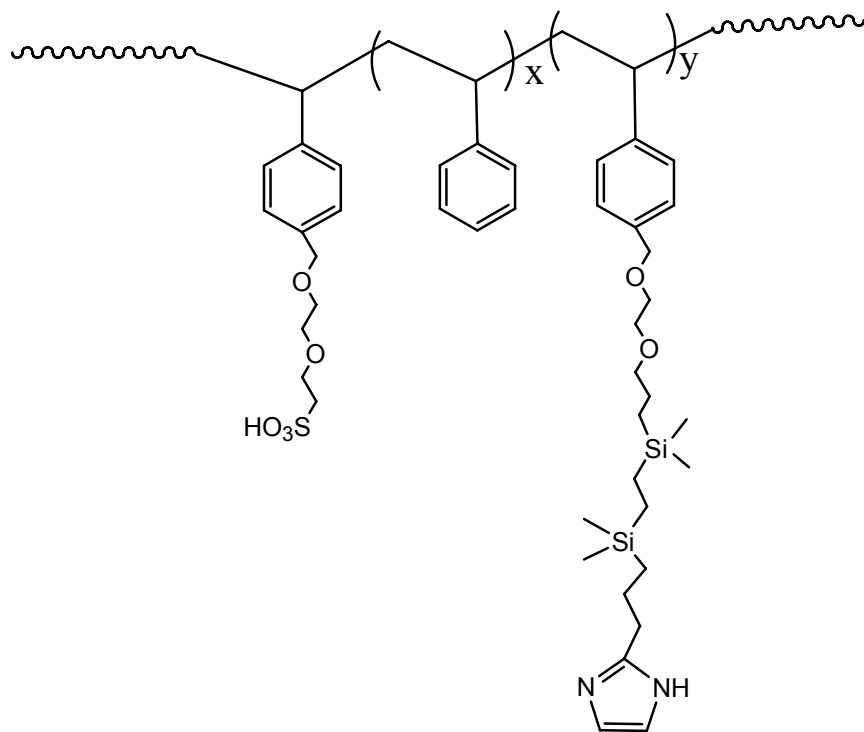
Fixed alkylsulfonic acid groups.



- 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 optimization of tether length, acid/base concentration, nature of the acid group (Fluoroalkylsulfonylimides vs. Alkylsulfonate).
- Road Map to solvent-free conductivity above 10^{-2} S/cm exists.**

High T_g polymer

Better for Bulk Membrane – glassy phase impermeable to gases, phase separation favors Grotthuss Transport.



- Styrene Backbone provides matrix stiffness, hydrophobicity, phase separation and low gas permeability.
- Side chain length provides solvent and ion mobility.
- Side chains also used to cross-link structure and lock in morphology.
- Multiplet cluster size dependent on relative concentration of solvent imidazole and anions in addition to side chain length.

Initial polymer prepared but T_g too low – need more hydrophobic styrene in backbone or block copolymers to raise T_g .

Conclusions

- Imidazole solvation groups are feasible for high temperature and water-free membranes.
- Temperature dependence of conductivity of free imidazole is consistent with the Grotthuss mechanism of proton transfer.
- The morphology of the polymer matrix plays a role on the promotion of the Grotthuss mechanism.
- The imidazoles must be tethered to the polymer matrix due to volatility. This results in a loss of conductivity.
- The conductivity loss due to tethering of imidazoles is small.
- Stronger acid groups such as fluoroalkylsulfonylimides promote higher conductivities.
- Longer tethers for the acid groups promote conductivity.
- Imidazole groups in the MEA must be protonated to avoid poisoning of platinum catalysts. This results in a loss of conductivity since conductivity is favored by excess imidazole.

Future Work

- Complete synthesis and characterization of polyether polyelectrolyte with imide acid groups and imidazole solvating groups.
- Modify polymer backbone with more hydrophobic styrene groups to promote phase separation and promotion of Grotthuss mechanism of proton transfer.
- Modify side chains to provide optimum mobility, phase separation and chemical stability towards active oxygen species.
- Develop degradation analysis methods.
- Prepare membranes for testing with MEAs.

Upcoming Milestones and Decision Points.

- Preparation and testing of imidazole/imide system provides indication on feasibility of solvent-free electrolytes (conductivities close to 10^{-1} S/cm).
- Preparation of High T_g , phase separated polymers demonstrate the importance of morphology.
- Initial stability tests indicate durability requirements.
- Preparation and testing of water-free membrane.

Achievement of these milestones will allow the design of the ideal electrolyte to be prepared and recommendations may be made on whether they should be pursued.

Summary

- Proton Conductivities of completely solid state polyelectrolytes with a tethered solvation group show little loss of conductivity compared to polyelectrolytes doped with free solvent.
- Phase separation and polymer morphology are important for promotion of fast proton mobility (Grotthuss mechanism) and selectivity in gas transport.
- A road map exists for how to attain solvent-free membranes with attractive proton conductivities (close to 0.1 S/cm).

Publications and Presentations

“New polymeric proton conductors for water-free and high temperature fuel cells”. Liu, G., Kerr, J. B., Reeder, C. & Sun, X. G. Abstracts of Papers of the American Chemical Society 228, U661-U661 (2004).

“Single-ion conductors for Batteries and Fuel Cells,” John B. Kerr, Polymer Batteries and Fuel Cell Conference-2, Las Vegas, Nevada, June 2005.

“Cross-fertilization between Polymers for Batteries and Fuel Cells”, John B. Kerr, Pacific Polymer Conference-9, Maui, Hawaii, December 2005.