New Polymeric Proton Conductors for High Temperature Applications

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Objectives

- Investigate the feasibility of use of solvent free solid polyelectrolytes for water-free and high temperature operation.
  - Measure conductivity, mechanical/thermal properties of Nafion® and Polyether polyelectrolytes doped with imidazoles.
  - Determine effect of imidazoles on Pt Catalysts.
  - Covalently attach imidazoles to appropriate polymer backbones and test for conductivity, mechanical/thermal behavior and gas permeability

Budget

- Total Budget - $200k
- No Cost-share
- FY04 Funding - $100k

Technical Barriers and Targets

- DOE Technical Barriers for Fuel Cell Components.
  - Phase 1(FY03-FY04):
    - Stack Material and Manufacturing Cost.
    - Thermal and Water Management.
    - Gas Permeation.
  - Phase 2 (FY04 onwards):
    - Durability
    - Electrode Performance.
- DOE Technical Target for Fuel Stack -2010
  - Cost $35/kw
  - Durability 5000Hours

Approach

1. Prepare polyelectrolyte gels from Nafion® and Imidazole or N-methylimidazole to replace water. Measure properties (conductivity, thermal/mechanical properties).
2. Examine effect of imidazole on electrocatalyst activity as a function of “pH” and nature of anions
3. 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.
4. Attach imidazoles covalently to modified polyether polyelectrolyte backbones using results from 3. 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).
5. Optimize structures for durability.

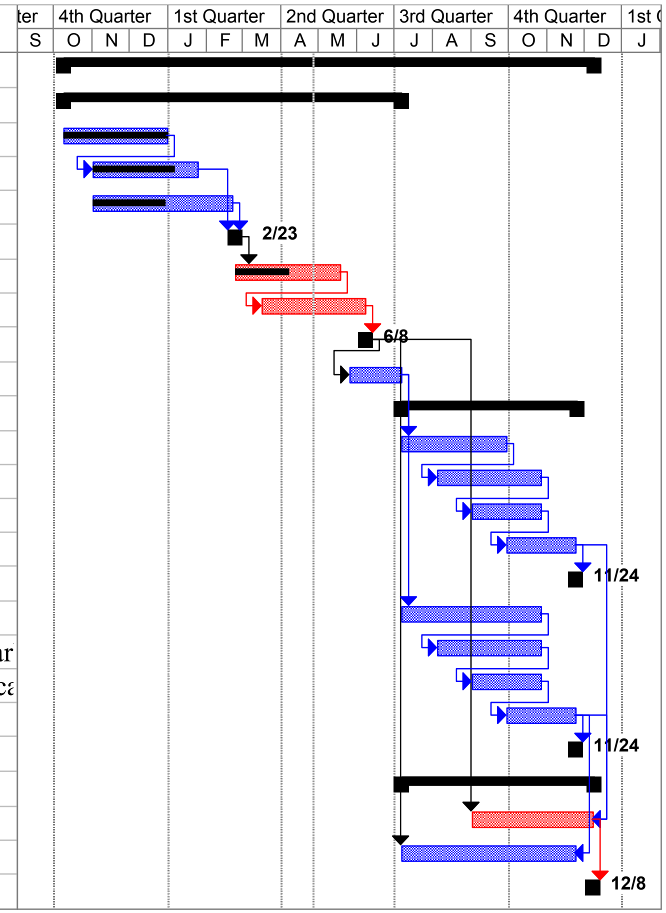
Project Safety

- Initial test materials prepared from materials available commercially or from other on-going programs. No testing with Hydrogen is performed at this stage due to component volatility.
- Covalent tethering of the solvent imidazoles removes the volatility danger.
- Mechanical and thermal testing (DMA/DSC) of membrane materials provides information needed to prevent gas permeation. Polymer architecture allows modification to minimize gas permeation
- Gas permeation tests for hydrogen to be carried out on small scale with diluent gas.

Project Schedule

(Milestone Tasks in Italics and Underlined)

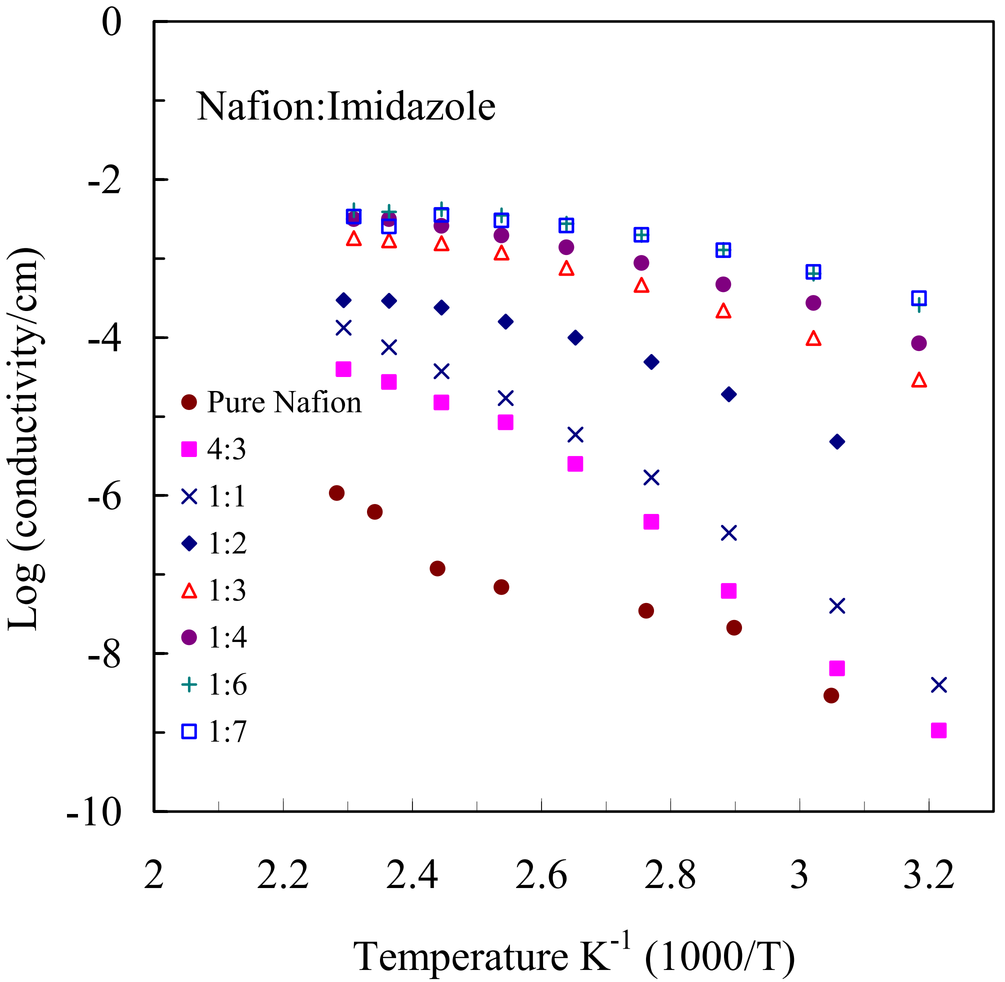
ID	Task Name
1	**Fuel Cell Membranes**
2	**High temperature Membranes - Phase 1**
3	Nafion-imidazole membrane formation and test
4	Polyether comb branch-imidazole membrane formation and test
5	Electroanalytical tests of imidazoles on platinum catalysts
6	***Feasibility of Imidazole solvation groups determined***
7	Attach imidazole to polyether polyelectrolytes
8	Prepare and test polyether membrane with tethered imidazole groups
9	***Feasibility of Imidazole-bound High Temperature membranes determined.***
10	Prepare Phase 2 plan to develop structure -function studies.
11	**High temperature Membranes - Phase 2**
12	Synthesize and optimize High Tg Membrane- Polystyrene backbone
13	Test conductivity and mechanical properties
14	Test gas permeability
15	Prepare membranes for full cell tests
16	***Water-free separator membrane prepared***
17	Synthesize and optimize Low Tg Membrane - polyoxetane ether backbone
18	Test conductivity and mechanical properties in presence of appropriate nanoparticles - car
19	Test gas permeability in presence of appropriate nanoparticles - carbon black, fumed silic
20	Prepare membranes for MEA fabrication and full cell tests
21	***Water-free MEA prepared***
22	**Set up Fuel Cell Test facilities**
23	Set up Fuel cell test fixtures - full fixture operation
24	Develop MEA fabrication capability in collaboration with LANL and CWRU
25	***Full Cell Testing initiated - no water***



Technical Accomplishments/Progress

- Nafion® doped with imidazole or N-methyl imidazole shows encouraging conductivities for high temperature operation.
- Conductivity difference between imidazole and N-methylimidazole is consistent with a Grotthus mechanism. Temperature dependence of conductivity is different.
- Vapor phase impregnation of Nafion® demonstrates a "Schroder's Paradox" similar to water. Thought to be related to morphology of the membrane.
- Conductivity of 1:1 Nafion®anion: Imidazole is much lower than the 1:4 membrane
- Voltammetry of Pt in aqueous H_2SO_4 in presence of imidazole is only affected when concentration of imidazole exceeds that of H^+. Can use imidazoles provided free imidazole is not able to contact catalysts.

Conductivities of Imidazole Doped Nafion Films



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.

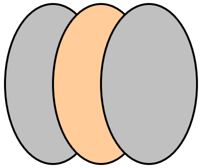
Film thickness: 100 µm ±20 µm

Testing conditions

Film between two parallel stainless steel plate.

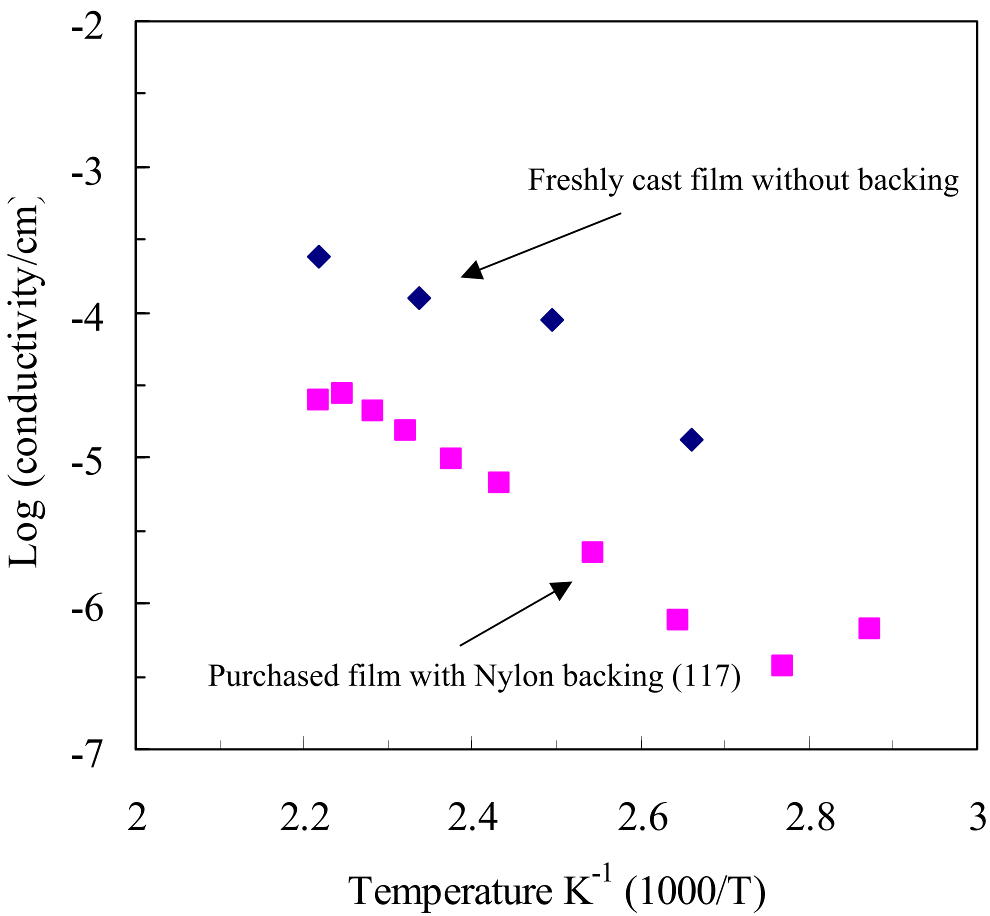
Impedance measurements.

Decreasing temperature from 170° C to 25° C.



Stainless steel disc-Membrane-Stainless steel disc

Conductivities of Imidazole Vapor Saturated Nafion Films



Details vapor saturation

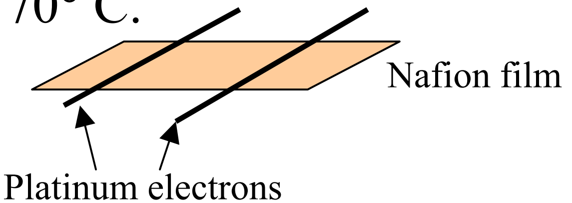
•Nafion films and imidazole are enclosed in oven together. However, Nafion and imidazole do not physically touch each other. Only imidazole vapors are allowed to diffuse into the Nafion films.

Testing conditions

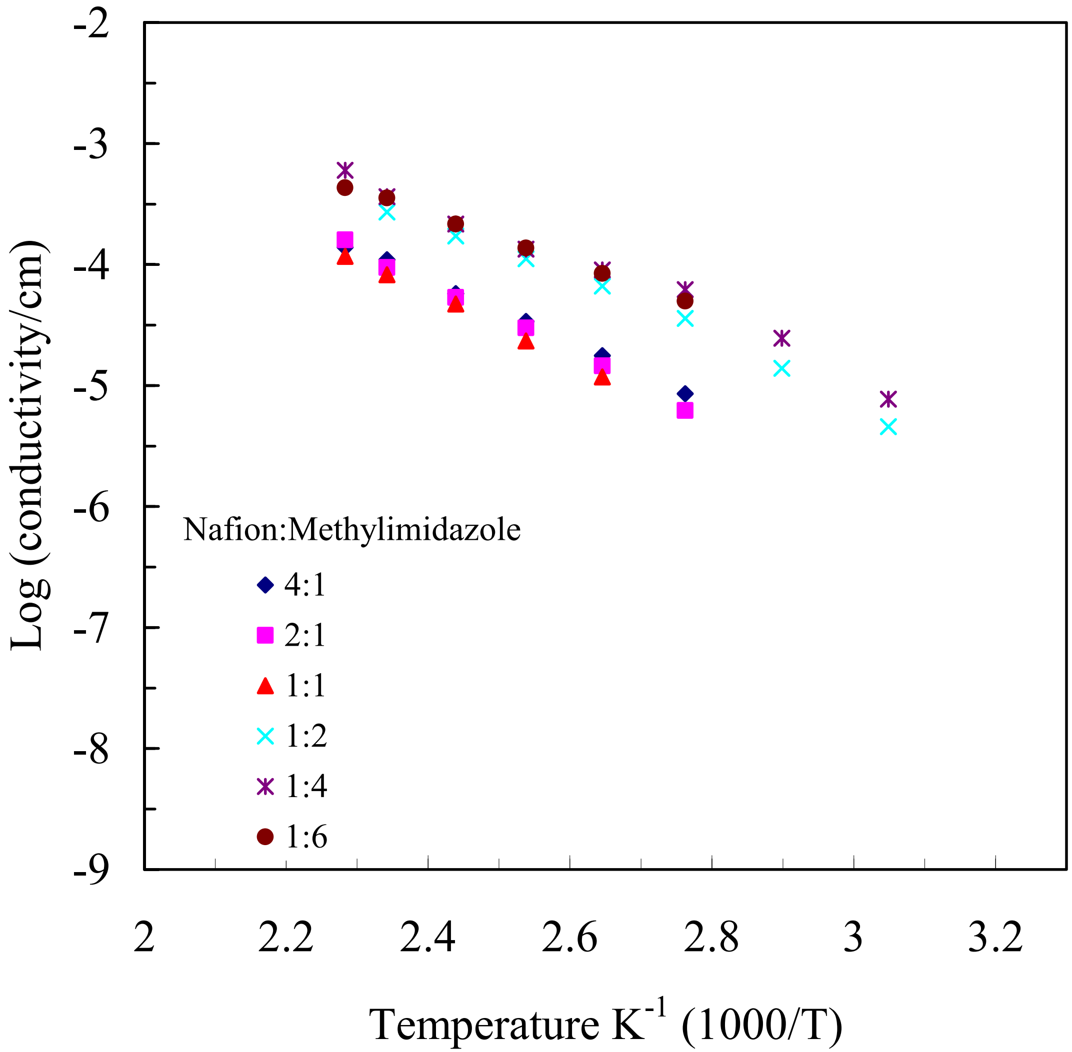
•Platinum wire electrodes.

•Impedance measurements.

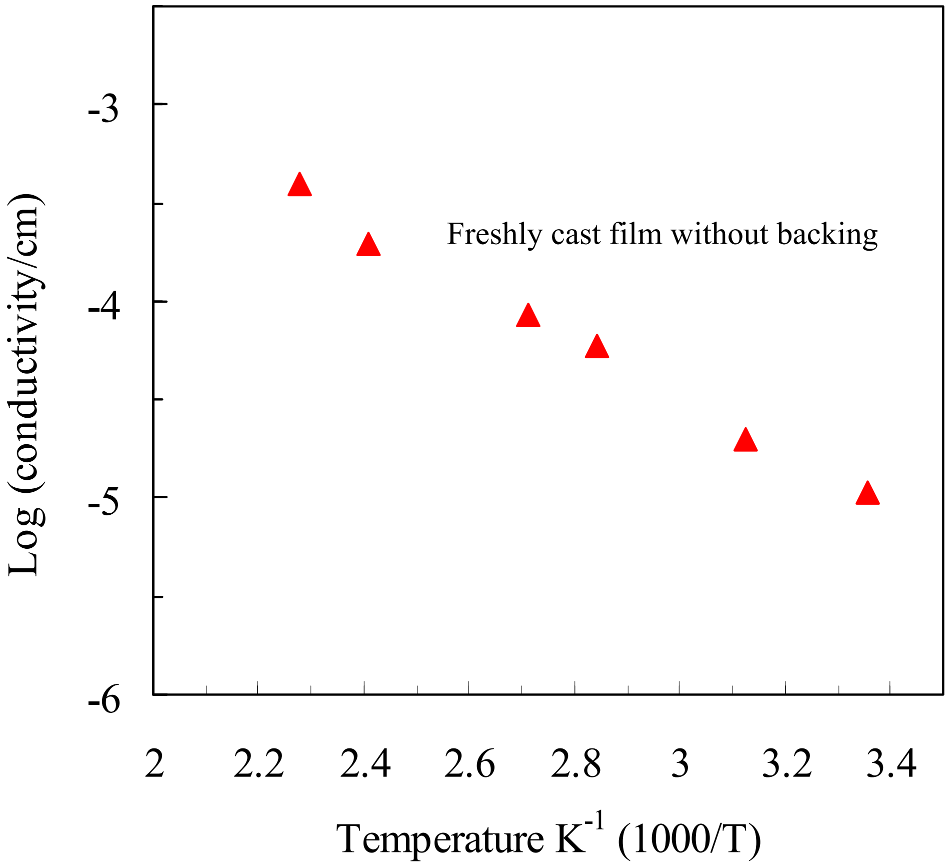
•The measurements were done at increasing temperature from 25° C to 170° C.



Conductivities of Methylimidazole Doped Nafion Films

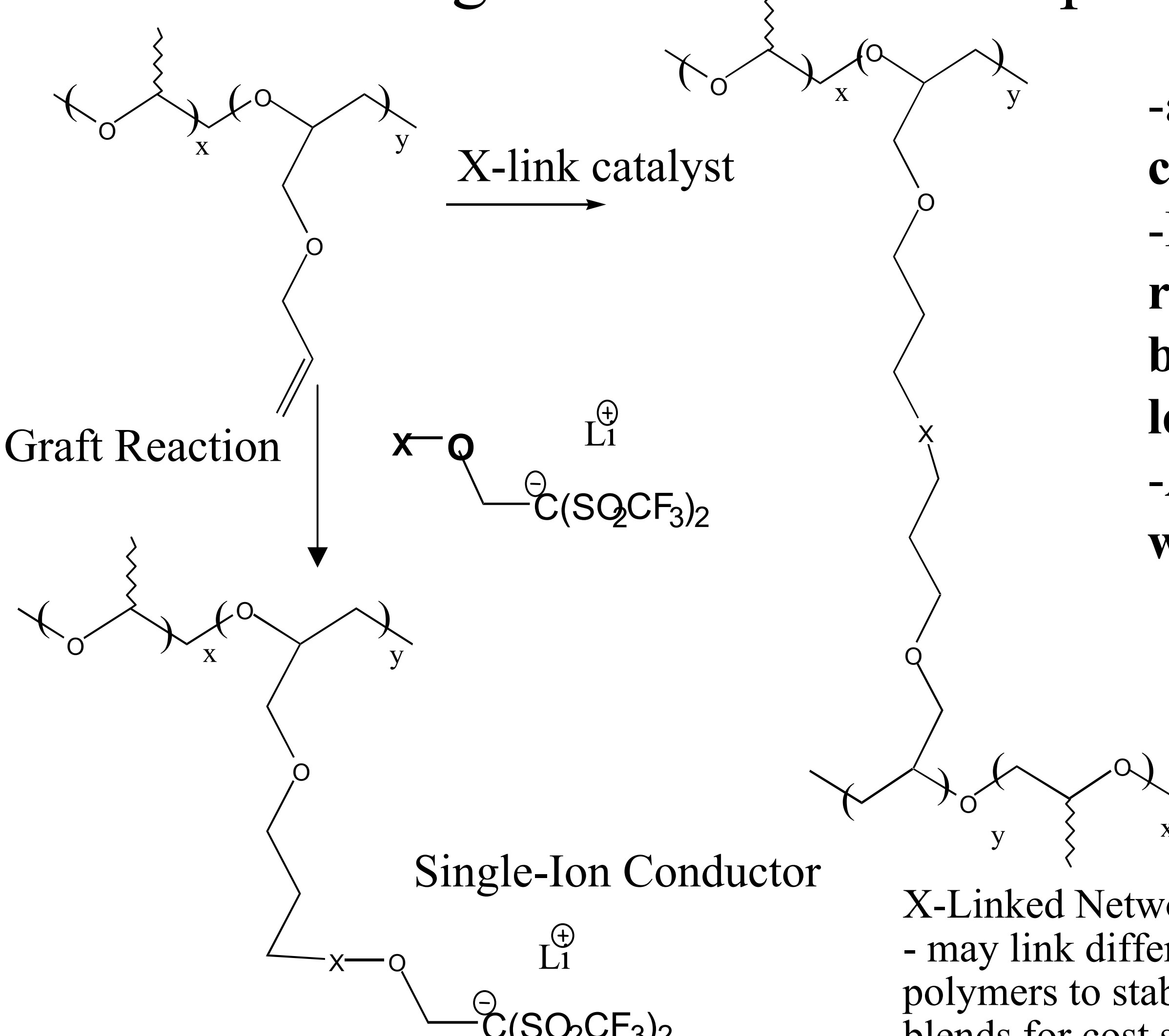


Conductivities of Methylimidazole Vapor Saturated Nafion Films



Polyether Polyelectrolytes under construction for Lithium Batteries - NASA

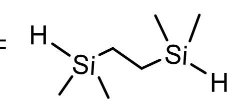
Exchange Li^{+} for H^{+} and dope with Imidazole



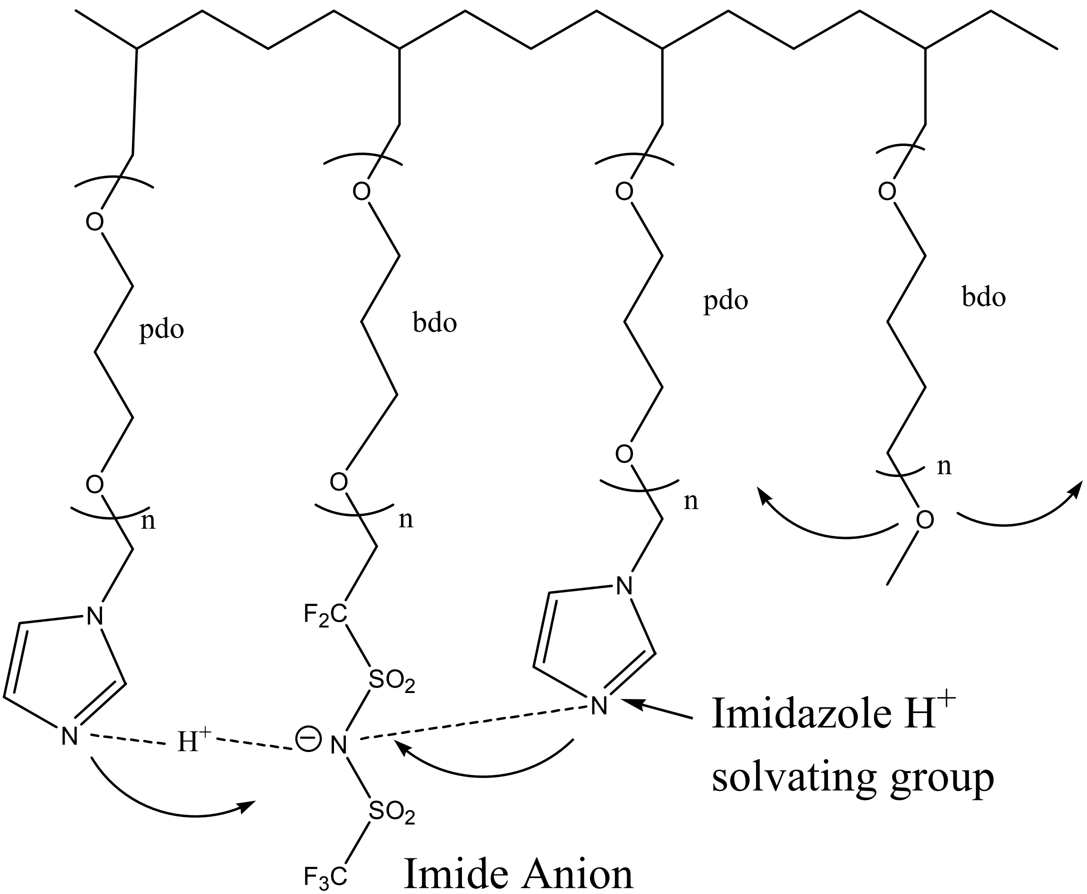
X-Linked Network
- may link different polymers to stabilize blends for cost savings

-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

X =

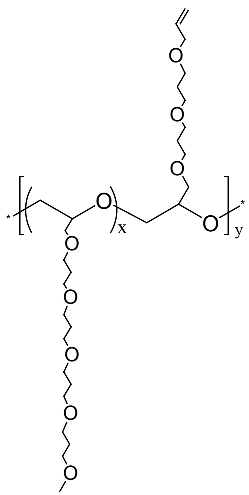


New Polymer Architectures currently under construction for Imidazole Solvating groups, Anion Mobility and Flexibility



•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.

Low T_g Prepolymers and Salts prepared for NASA and available for Testing as Proton Conductors

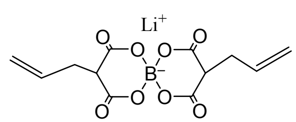


Prepolymer

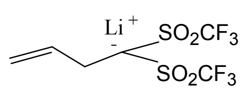
CH2=CH-CH2-O-CF2-CFH-O-CF2-CF2-SO2N(Li)SO2CF3

CH2=CH-CH2-O-CF2-CFH-O-CF2-CF2-SO3(Li)

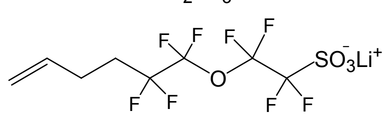
New salts arriving from DesMarteau Group (Clemson)



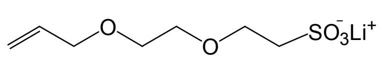
Salt I



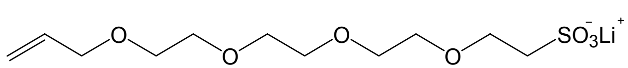
Salt II



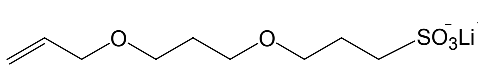
Salt III



Salt IV



Salt V



Salt VI

Conclusions

- Imidazole solvation groups are feasible for high temperature and water-free membranes.
- The imidazoles must be tethered to the polymer matrix. This results in a loss of conductivity.
- Imidazole groups in the MEA must be protonated to avoid catalyst poisoning. This results in a loss of conductivity.
- The morphology of the polymer matrix will be crucial for safe and effective operation. The matrix in the MEA will be different from the matrix in the separator

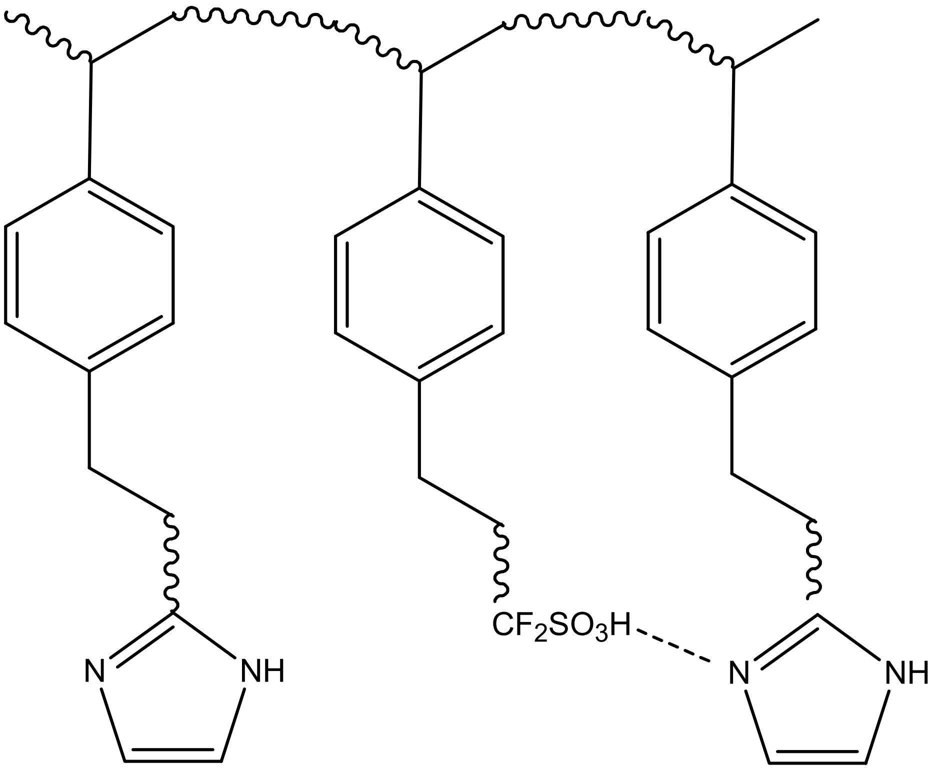
Interactions and Collaborations

- This work directly builds on work funded by NASA (PERS, Glenn Research Center) for lithium batteries.
- The work also builds on work funded by DOE-OAAT Freedom Car BATT programfor lithium batteries.
- Collaborations with LANL and CWRU are an integral part of the project plan.

Future Plans

- Synthesize polyelectrolyte-imidazole membranes with high T_g values- polystyrene backbones (see next slide)
  - Optimize for conductivity, mechanical properties.
  - Optimize for gas permeability
  - Prepare best structure for full cell test.
  - ***Milestone: Water-free separator membrane prepared***
- Synthesize polyelectrolyte-imidazole membranes with low T_g values – polyoxetane backbones for flexibility and oxidation resistance.
  - Optimize for conductivity, mechanical properties in presence of nano-particles such as carbon black or silica.
  - Optimize for gas permeability in presence of nano-particles such as carbon black or silica.
  - Prepare best structure for full cell test.
  - ***Milestone: Water-free MEA prepared***
- ***Perform Initial durability Tests.***

High T_g Prepolymer



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. This will control gas permeability.

Acknowledgements

- DOE-LANL
- NASA PERS program (Glenn Research Center).
- DOE Office of FreedomCAR and Vehicle Technologies