Polyelectrolyte Materials for High Temperature Fuel Cells

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Objectives

- Investigate the use of solid polyelectrolyte proton conductors that do not require the presence of water.
- Prepare solid electrolytes where only the proton moves.
  - Measure conductivity, mechanical/thermal properties of Nafion® and other polyelectrolytes doped with imidazoles. Compare with water doped materials.
  - Covalently attach imidazoles to side chains of ionomers with appropriate polymer backbones and test for conductivity, mechanical/thermal behavior and gas permeability.
  - Prepare composite electrodes and operate MEAs without humidification.
- Significant system simplifications for Fuel Cells.
  - Heat and water management greatly simplified.

Technical Barriers & Targets

- DOE Technical Barriers addressed

E. System Thermal and Water Management.

C. Electrode Performance.

A. Durability

B. Stack Material and Manufacturing Cost.

D. Water Transport Within the Stack.

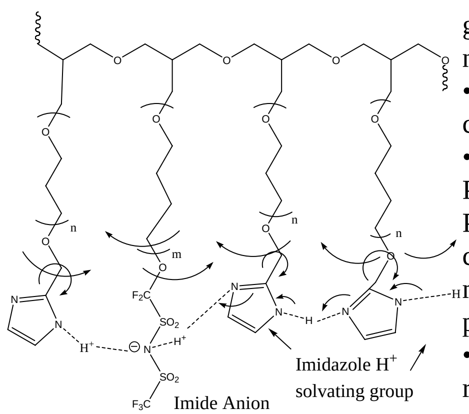
- DOE Technical Targets
  - Conductivity 0.1S/cm at up to 120^{o}C & inlet water vapor pressure < 1.5kPa.
  - Acceptable gas crossover (O_2 & H_2 < 2mA/cm^2)
  - Cost < $20/m^2
  - Durability > 5000 hours

Summary of Prior Work

(2003 –present)

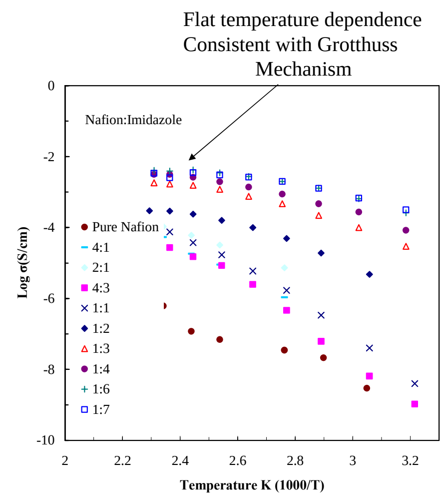
- Proton Conductivities of completely solid state polyelectrolytes with a tethered imidazole solvation group show little loss of conductivity compared to polyelectrolytes doped with free solvent imidazole.
- Phase separation and polymer morphology are critical for promotion of fast proton mobility (Grotthuss 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):
  - Nature and concentration of acid group, polymer morphology, C-tethered imidazole present in large excess for Grotthuss proton transport.
- Keep imidazole protonated in electrode to prevent catalyst poisoning – non-Pt catalysts.
- Imidazole doped PFSA appears to reject water.
  - PFSA with tethered imidazole may be most durable membrane.

New Polymer Architectures for Imidazole Solvating groups and Anion Mobility



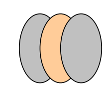
- Attach anions and solvating groups by grafting –control nature and concentration.
- Use nature and length of side chain to control mobility.
- Backbone (PE, polystyrene, Polynorbornene and Poly(arylene ether)) and cross-link density to control mechanical & morphological properties.
- Degradation results in release of small fragments - facilitates failure analysis.

Conductivities of Imidazole Doped Nafion Films



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

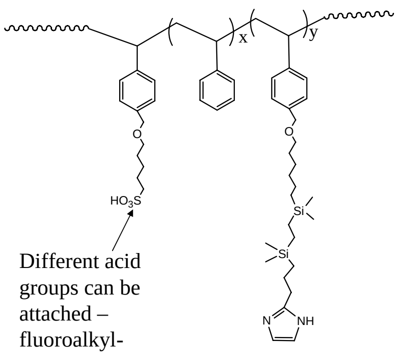
Testing conditions
Film between two parallel stainless steel plate.
Impedance measurements.
Decreasing temperature from 170° C to 25° C.



Stainless steel disc-Membrane-Stainless steel disc

High T_g polymers

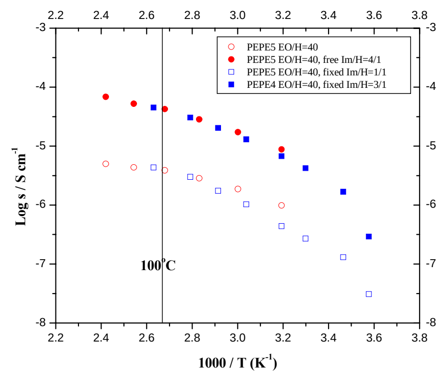
Better for Bulk Membrane – glassy phase impermeable to gases, phase separation favors Grotthuss Transport.



Different acid groups can be attached – fluoroalkyl-sulfonate and sulfonyl imide.

- 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.
- Block co-polymers provide control of morphology.

Comparison of conductivities of free imidazole and fixed imidazole based proton conductors. Fixed alkylsulfonic acid groups.

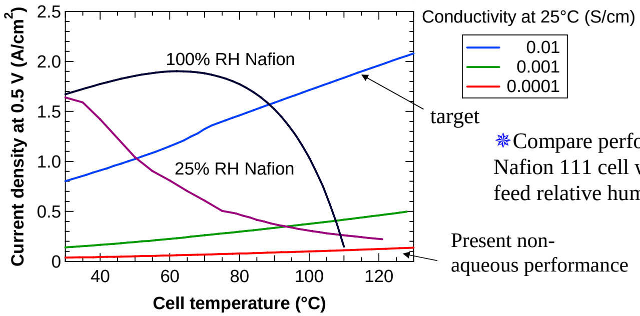


- Conductivity of fixed Imidazole polymer equal to the conductivity of the polymer doped with free imidazole solvent.
- Relative concentration of Imidazole to acid group is critical.
- Increase conductivity by optimiz-ation of tether length, acid/base concentration, nature of the acid group (Fluoroalkylsulfonylimides vs. Alkylsulfonate) and by control of the morphology to promote Grotthuss proton transfer.

➔**Road Map to solvent-free conductivity above 10^{-2}S/cm exists.**

Use Modeling to Develop Decision Citeria

- Estimate suitability of membrane properties
  - Establish design targets and goals
- Analyze property and system tradeoffs
  - Examine distributions and limiting phenomena
- Ask and analyze “what if” questions
  - What conductivity do we really need?
  - **What if we have a membrane that rejects water?**

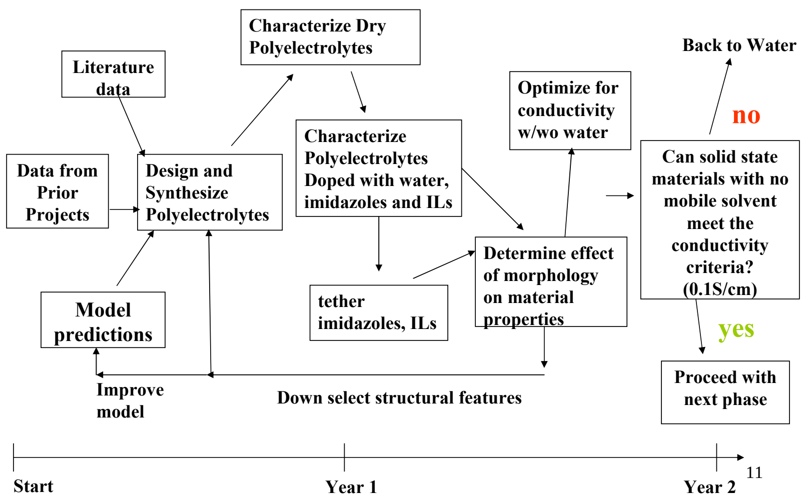


❋Compare performance to Nafion 111 cell with different feed relative humidities

Who does What?

- LBNL
  - Random and Block copolymer synthesis
  - Tether acid and imidazole groups to polymers.
  - Mechanical, morphological and electrochemical characterization of materials.
  - Chemical stability.
  - System modeling
- LANL
  - Block copolymer synthesis of polynorbornene and poly(arylene ether) polymers.
  - Transport measurements (conductivity, gas crossover), cell testing and MEA preparation/testing.
- 3M
  - Provide PFSA material for testing and explore attachment of imidazole.
  - Durability and chemical stability.
  - MEA preparation and testing.

Work Flow- Years 1 & 2



Project Schedule