Protic Salt Polymer Membranes

High-Temperature Water-Free Proton-Conducting Membranes

GERVASIO et al.

Arizona State University

Tempe, AZ 85287

University of Akron

Akron, OH

DOE HTMWG DIVISION REVIEW

Friday, May 19, 2006, Arlington, VA

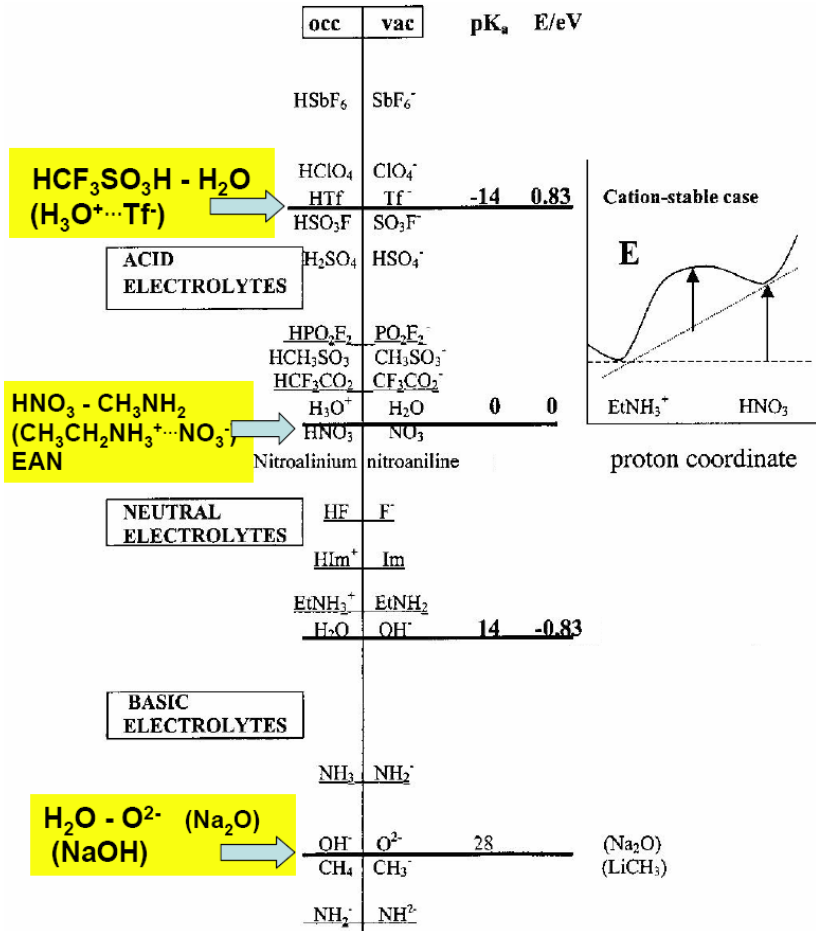
Project ID# FCP 6

What is a neutral protic ionic liquid (PIL) electrolyte?

- An acid electrolyte is obtained by transfer of a proton to the water molecule (e. g. HCl and water, or CF_3SO_3H and water). When the CF_3SO_3H acid is pendant to a polymer this gives the Nafion PEM.

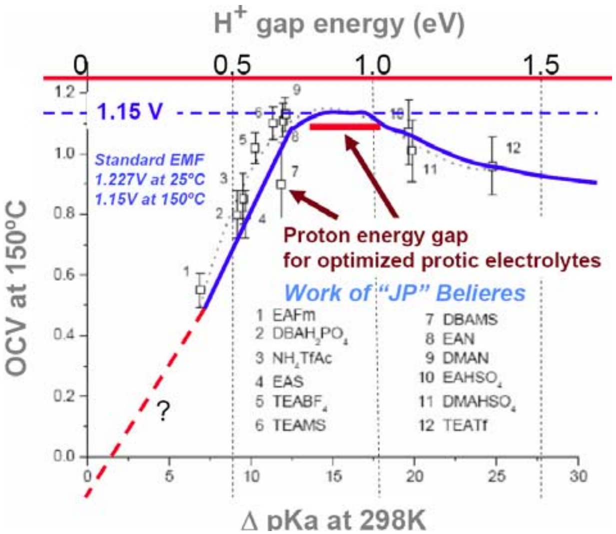
- A basic electrolyte is obtained by adding water to a strong base like potassium oxide, to give KOH which is used, as an aqueous solution, in the Bacon fuel cell.
  - In each case the proton transfers across an energy gap, which depends on the "strength" of the acid or base.

- To make a neutral PIL electrolyte we transfer a proton from a moderately strong acid to a base stronger than water, e.g., ethylamine. The product is often liquid at 25ºC - a protic ionic liquid (IL) - which is highly conductive without any solvent.
  - These ideas can be presented using a proton energy diagram, (after Gurney) which is like a table of redox potentials.

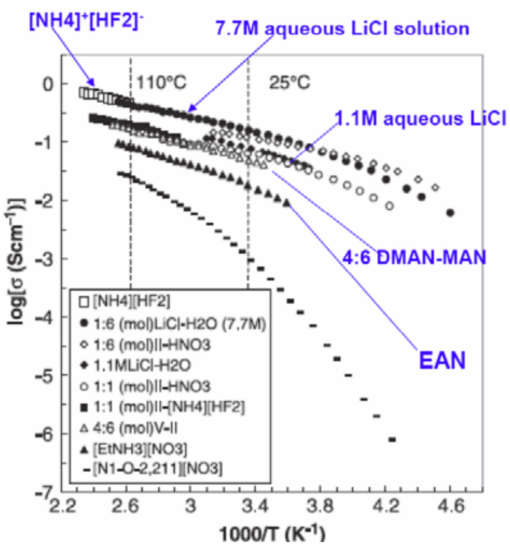


Observations with protic IL electrolytes

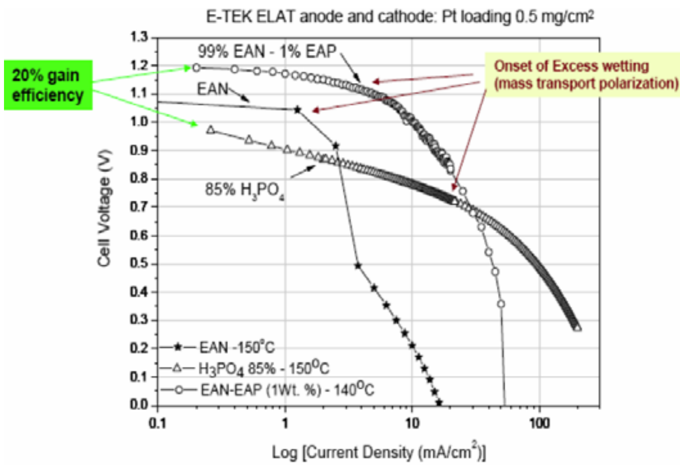
- can have high ionic conductivities, rivaling aqueous solutions
- PIL electrolytes function well as electrolytes in fuel cells



Discovered relation between OCV & proton transfer E gap



IL Conductivities

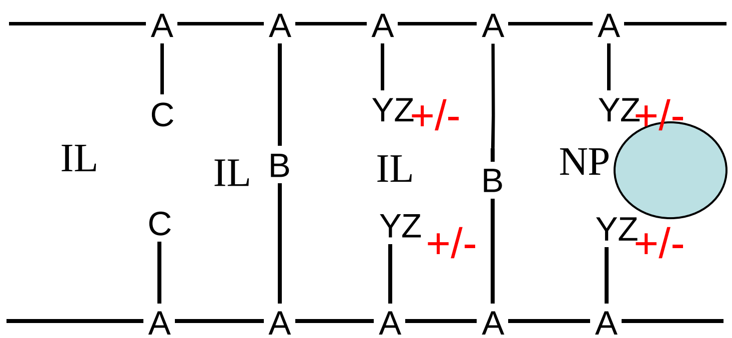


H2/O2 Polarization Curves with 3 Liquid Electrolytes

To create an protic ionic membrane:

OPTIONS: **1. Pendant acid protonating free base (polyanion)**
2. Pendant base protonated by free acid (polycation)
3. Polyanion plasticized by excess base
4. Polycation plasticized by excess acid
5. Polyanion plasticized by protic ionic liquid
6. Polycation plasticized by protic ionic liquid

GENERAL SCHEME



A, Repeating unit in the main chain
B, Crosslinker chain
C, End group(hydroxy, amine, imine etc.)
YZ, Neutralized couple at chain end
IL, Ionic liquids
NP, Nano particles

Specific examples and planned examples

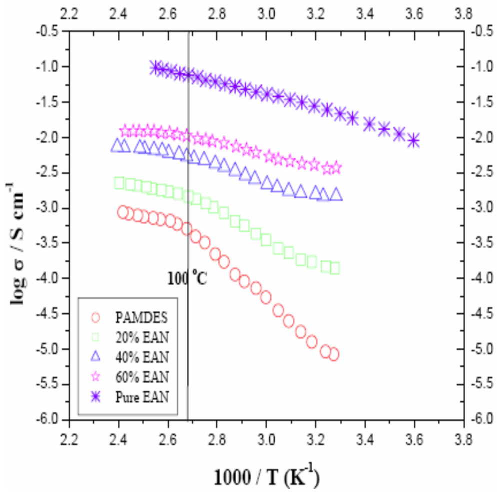
Linear polysiloxanes
with pendant amines, doped with TFMSA
or acidified 1:1 and plasticized with EAN

Neutral hydroxylated polymers, such as:
hydroxylated polymethylmethacylate plasticized with EAN, TEAMS

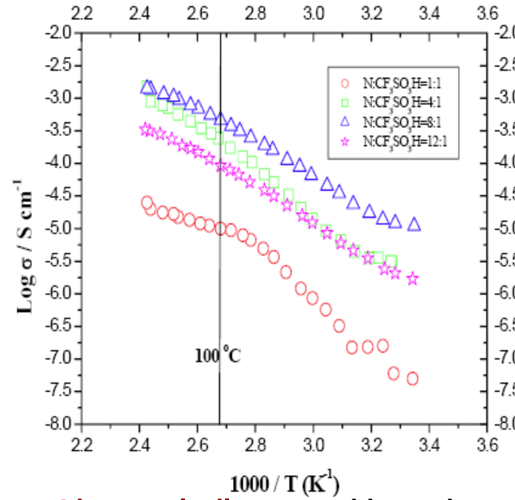
N heterocycles such as:
Poly (4-vinylimidazole), Poly (N-vinyltriazole) and Mixed Polymers
by Atom Transfer Radical Polymerization (ATRP)
e.g., Poly (N-vinyltriazole-co-N-vinylimidazole-co-4-vinylimidazole)
reacted with acids like: HNO3 , HF , TFMSA , H3PO4 , etc.

Planned :
Alkylated acid heterocycles such as:
e.g., poly [4-vinylimidazole-N-(4-butasulfonic acid)]
React with base such as ammine, azoles, etc.
to make a PSM

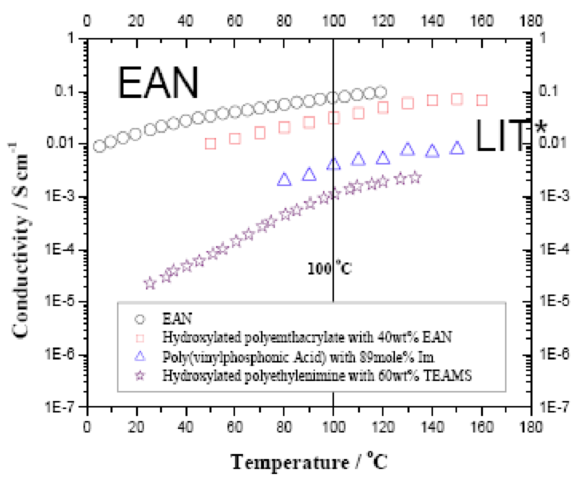
PSM conductivities

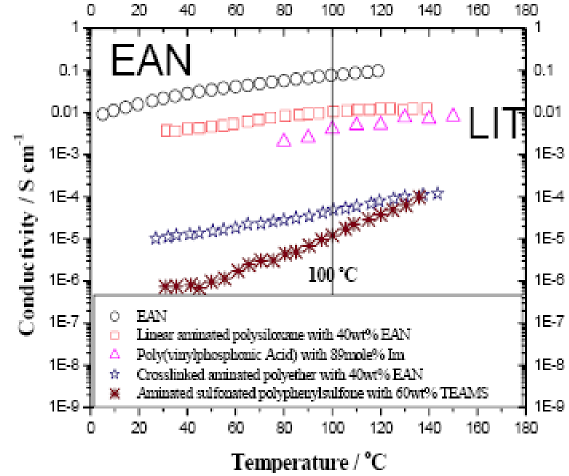


Polysiloxane with pendant amine, acidified 1:1 and plasticized with EAN



Linear polysiloxanes with pendant amines, doped with TFMSA



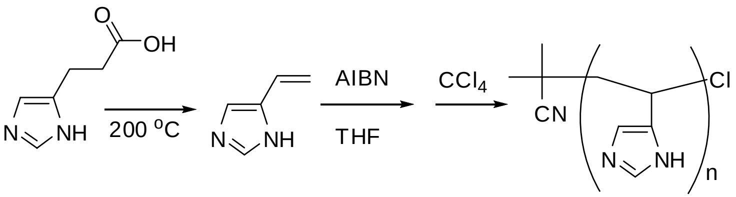


Neutral hydroxylated polymers plasticized with ILs. 100ºC conductivity as high as $10^{-1.5}$ S/cm with EAN. LIT = *Yamada and Honma, Polymer, 46, 2986 (2005)

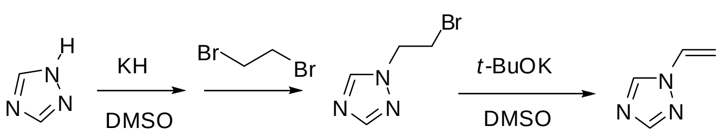
Planned Syntheses

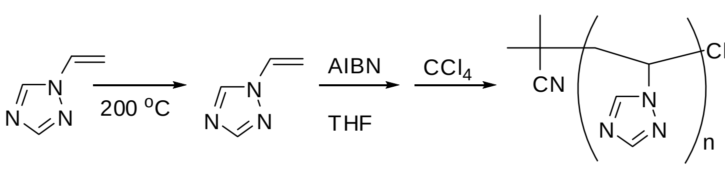
Arizona State University

Poly (4-vinylimidazole)



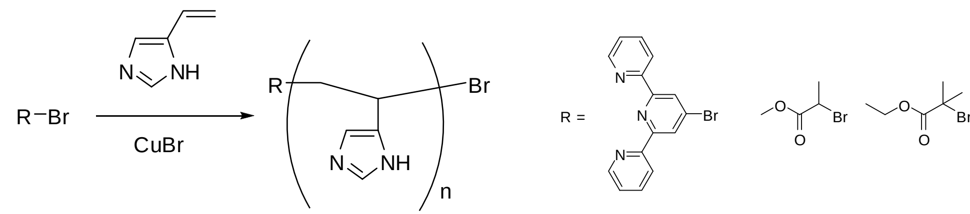
Poly (N-vinyltriazole)

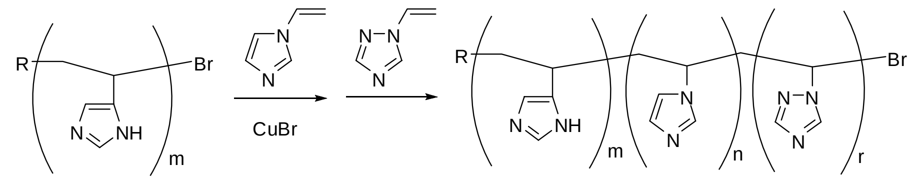




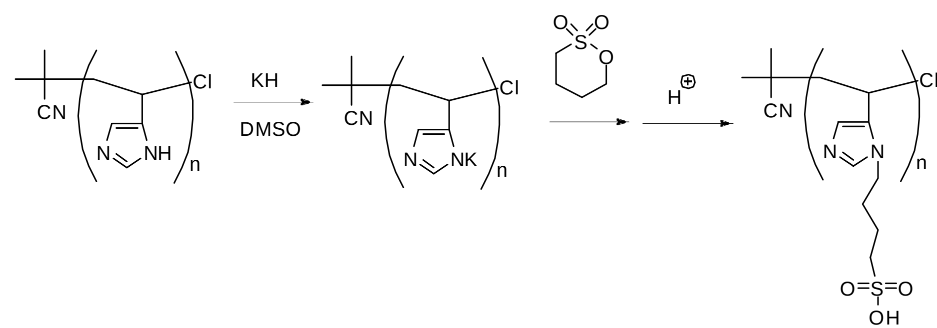
Poly (N-vinyltriazole-co-N-vinylimidazole-co-4-vinylimidazole)

A Mixed Polymers by Atom Transfer Radical Polymerization (ATRP)





Poly [4-vinylimidazole-N-(4-butasulfonic acid)]



React these basic moieties with acids like: HNO_3, HF, TFMSA, H_3PO_4, etc. to make a PSM.

React acidic moieties with base such as ammine, azoles, etc., to make a PSM

The University of Akron

Project ID# FCP 6

Objectives for Future Work

- seek further protic ILs with optimized proton gaps, and high stabilities with respect to Pt
- develop optimized PIL-swollen polymer with conductivity of 100 mS/cm at 100ºC
- develop theoretical understanding of OCV vs proton gap correlation using EIS and eNMR techniques
- Improve stability with deactivated alkyl and fluoro moieties
- Expand temperature of operation to lower (-20ºC) as well as higher (> +120ºC) temperatures
- Explore membranes that are non-wetting to fuel cell electrodes for testing in fuel cells.