High Temperature Polymer Membranes for Fuel Cells

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DOE Technical Barriers for Components

O. Stack Material and Manufacturing Cost

P. Durability

Q. Electrode Performance

R. Thermal and Water Management

DOE Technical Target for Fuel Cell Stack System for 2010

Cost $35/kW

Durability 5000 hours

High Temperature Membranes Participating Partners

- ⇩CWRU
- ⇩UT/Dallas
- ⇩Arizona State
- ⇩JPL
- ⇩Virginia Commonwealth
- ⇩Northeastern
- ⇩UConn
- ⇩LANL
- ⇩LBNL
- ⇩Foster-Miller

Rationale

Operation at Elevated Temperature: substantial system benefits for both automotive and stationary applications

- Auto: smaller radiator size
- Stationary: simpler reformate clean-up

- A High Temperature membrane is an enabling technology for hydrogen-based fuel cells in automotive applications!

This Effort

- Calls for development of systems for both:
  - 120^{o}C: maybe we can use hydrated polymers
    - Focus on new polymers and other scaffolds carrying sulfonic acids or other superacids
    - 25% RH at operating temperature suggested by GM, based on system requirements
    - Need improved durability

  - >150^{o}C: need to replace water with ‘proton mobility facilitator’
    - Focus on different conduction modes, non-volatile molecules to effect proton transfer
    - Durability of any polymeric components also a must

Barriers to Overcome

1. Adequate conductivity from start-up to $T > 100^{o}$C
2. Adequate polymer stability
3. Ability to fabricate MEAs with new polymers
4. Electrode performance at high T

High T Membrane/MEA Development: Organizational Approach

- ⇩ Develop team of innovative researchers in polymer synthesis, physical chemistry of electrolytes, MEA development, fuel cell testing; team assembled through proposal process
- ⇩ Work the problem from fundamentals to implementation in fuel cells
- ⇩ Seed funding provided (administered by LANL); after ~2 years, we hope to see transitions to other funding sources based on promising results

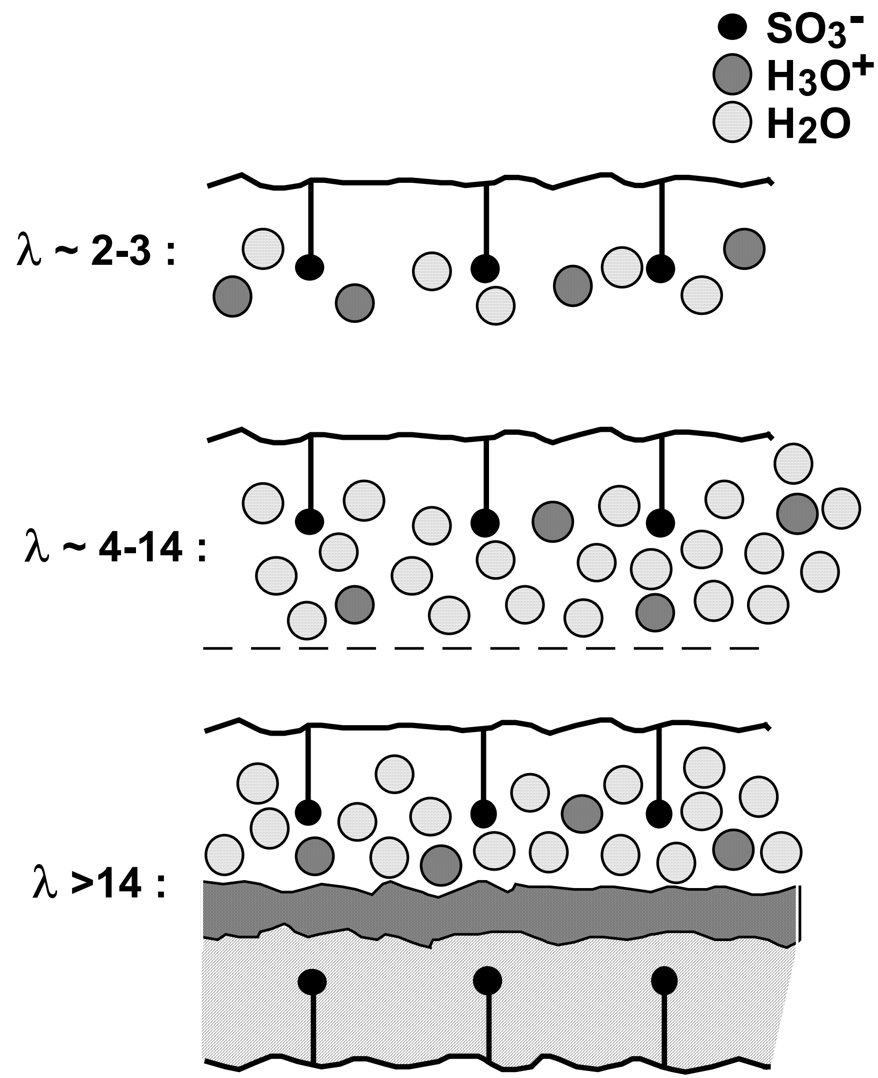
High T Membrane/MEA Development: Technical Approach

- Synthesis based on new 'scaffolds': (different polymers, inorganic hosts etc.)
- Using 'additives' to enhance conductivity
- Physical chemistry and computational Studies: guiding synthetic approach
- MEAs/Electrodes:
  - ORR at higher temperature
  - Electrode structure: buried interfaces within electrodes
  - MEA fabrication for new membranes
- Scale-up: polymers, film-making and MEA production

Proton Conduction in PEMs: A Qualitative Picture

Steps in the Process

- Dissociate
- Escape and ‘Bridge the Gap’
- Plasticize



A General Approach

- Acid moieties on polymer or other support (‘scaffold’) must be connected to some type of structure

- Transport of protons require ‘extended structures’---> water or additives (ProMoFacs)

‘Scaffolds’, ProMoFacs, Acids Under Investigation in this Project

- Polymeric scaffolds
  - Poly(phosphazene), Poly(benzimidazole), Poly(phenylenes), Poly(sulfone), Poly(imide), Functionalized poly(arylene ether)
- Inorganic scaffolds
  - Silica, Alumina, Alumino-silicates
- ProMoFacs
  - Water!!
  - Imidazole, Phosphoric Acid
  - Molten Salts/Ionic Liquids
  - Solid acids
- Strong acids
  - Fluorosulfonates attached to phenyl
  - Bis(sulfonimides)

High Temperature Membranes Approaches by research group

⇩CWRU: inorganic/organic hybrid systems; new polymers; strong acid groups; electrode studies at high T; MEA making; polymer scale-up and film processing; computational studies; FC testing. (working on both temperature ranges)

⇩UT/Dallas: inorganic scaffolds with added conducting polymers (primarily high temperature range)

⇩Arizona State: molten salts (primarily high temperature range)

⇩JPL: proton conducting salts (primarily high temperature range)

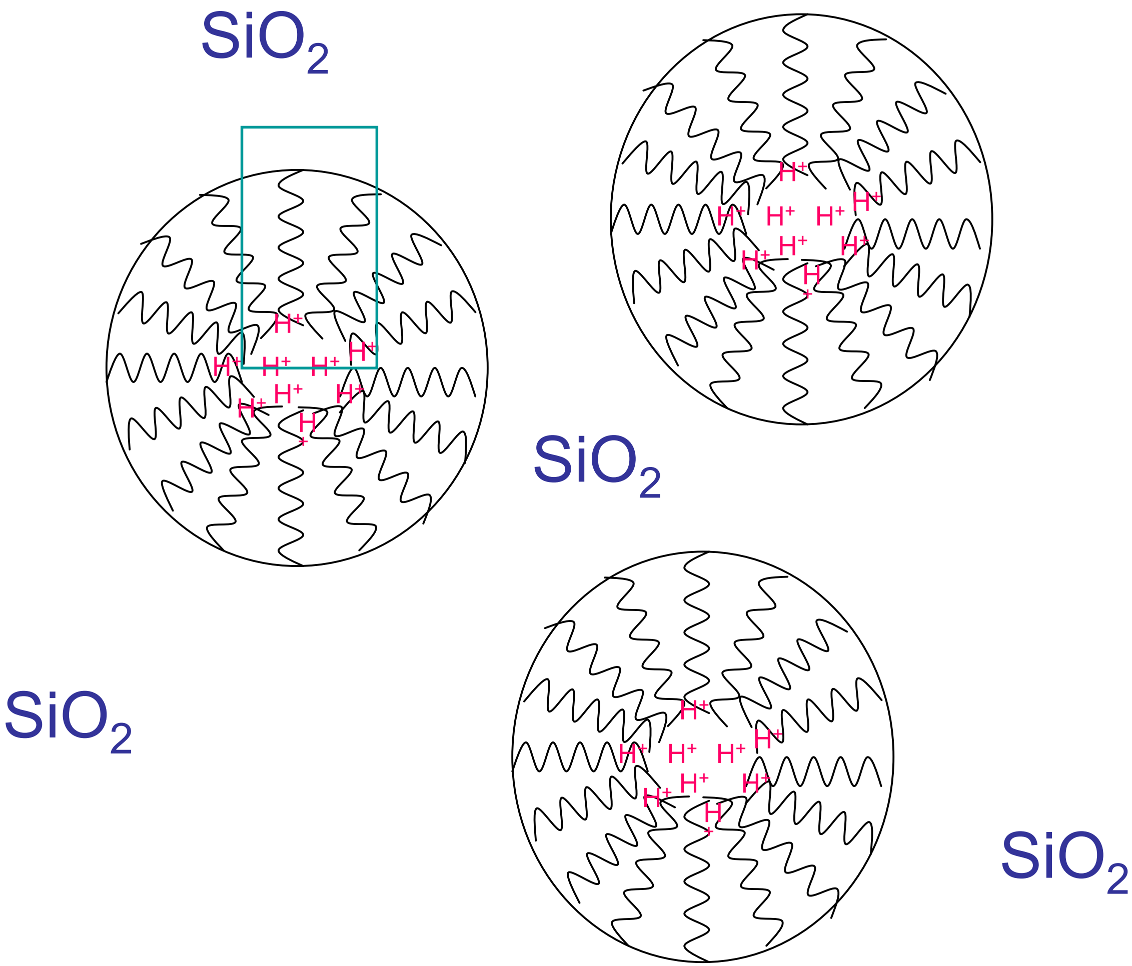
⇩Virginia Commonwealth: strong acid groups; * advanced MEA processing method (primarily low temperature range)

High Temperature Membranes Approaches by research group

- ⇩Northeastern: electrode studies
- ⇩UConn: polymer blends
- ⇩LANL: imidazoles, molten salts
- ⇩LBNL: imidazoles immobilized on polymers; composite electrode studies
- ⇩Foster-Miller: novel matrix loaded with imbibed ionomer

Progress and Results to Date

Attach acid moieties to nanoporous materials, Al_2O_3 or SiO_2 membranes



Concept: very close spacing of sulfonates leads to extended network of tightly bonded water leading to conducting pathway in insoluble matrix

Result:
RT conductivity ~10^{-2} S/cm;
Membrane too brittle

Next steps: hybrid membranes with better physical properties

Computational Studies
A guide to development

- ⇩ Target 1: Understand proton transfer in polymer systems: studies of solvation of different types of acids extended

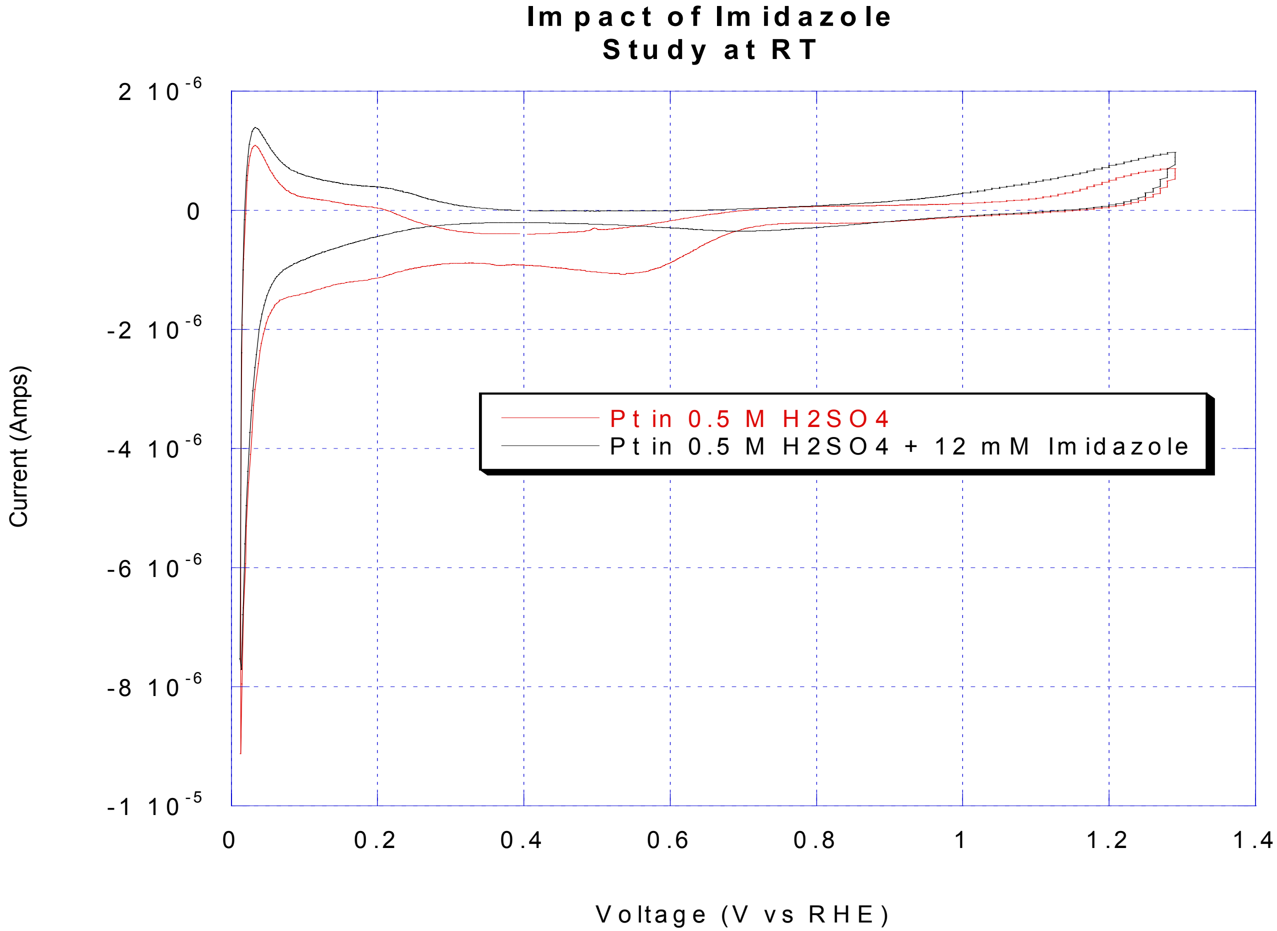
- ⇩ Target 2: Tailor bases to mimic water: electronic structure calculations to estimate pK's of appropriate bases (esp. substituted imidazoles)

Imidazole – Electrode Interaction

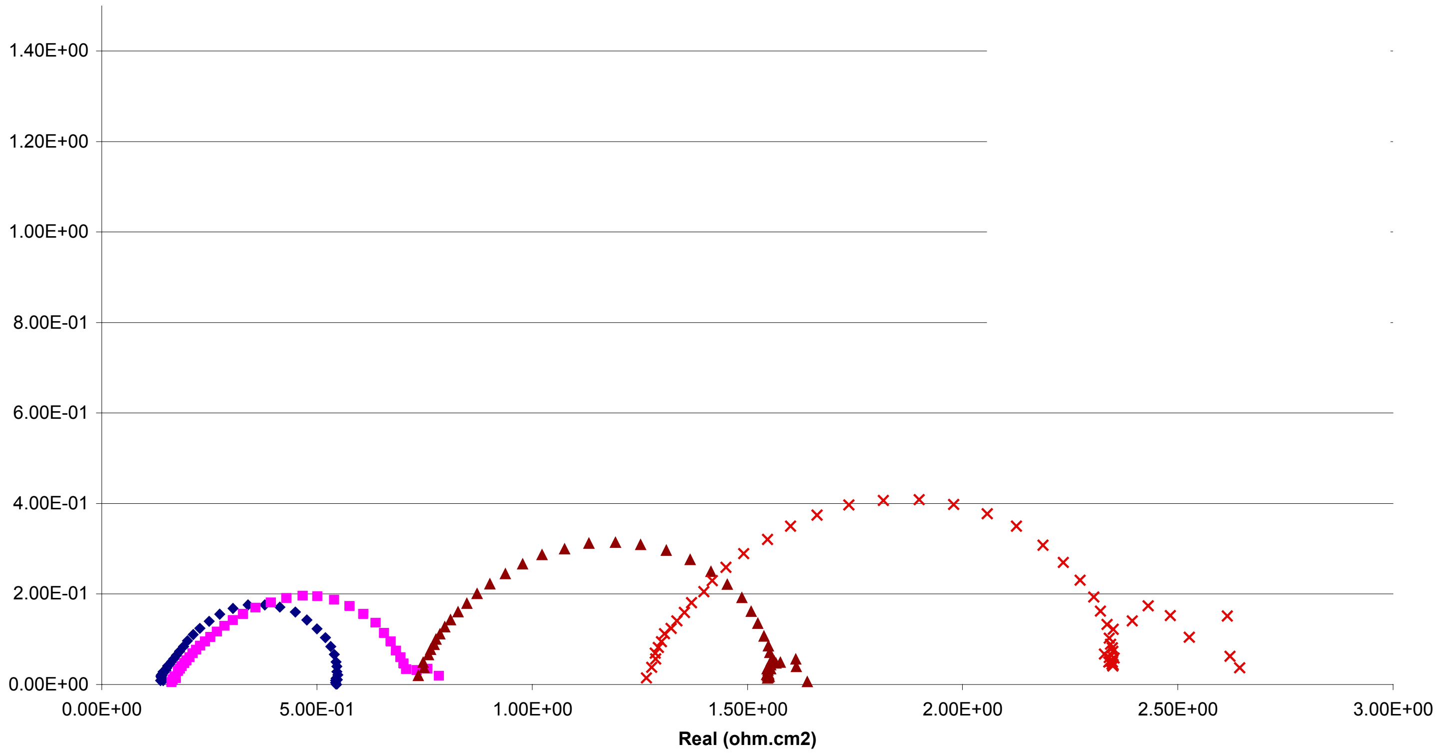
What impact does Imidazole and its derivatives have on the hydrogen oxidation and oxygen reduction ?

- Cyclic Voltammetry – adsorption – qualitative
- RDE studies – Hydrogen Oxidation, Oxygen Reduction
- Computational – looking at charge distribution

Imidazole – Electrode Interaction



Impedance Studies of Cathode under sub saturated conditions

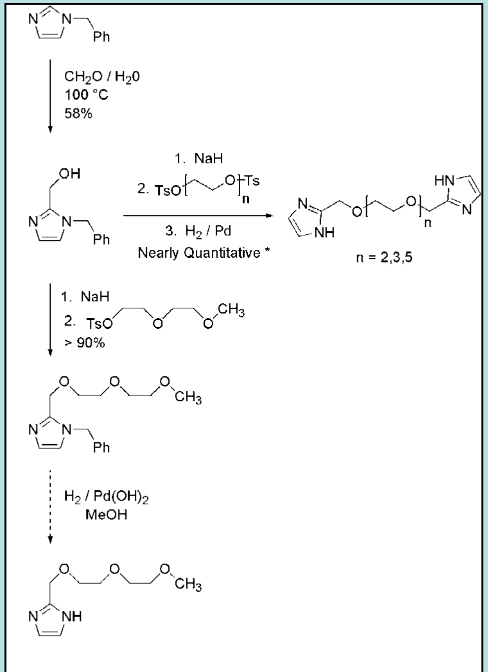


<u>Operating conditions:</u> Current density : 0.1 A/cm^2 Pressure: Ambient; Fuel: H_2; Oxidant: Oxygen; Gas utilization: 10% Cell tempr. 70 C to 100 C; Dew Point : 70 C;

LANL HTMWG Synthesis

Synthesis and characterization of imidazole based materials has already yielded some initial results.
Our approach is to find materials with needed conduction properties and then incorporate into membranes.

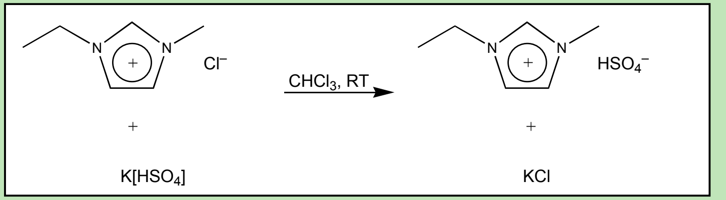
Functionalized Imidazoles



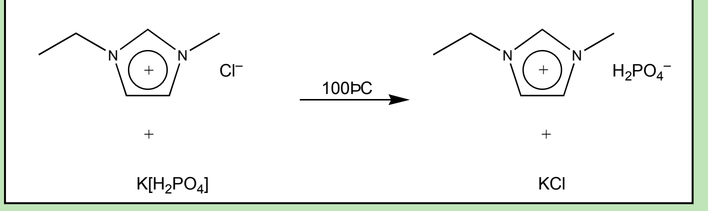
* Shuster, M.; Meyer, M. H.; et al *Solid State Ionics*, **2001**, *145*, 85-92.

We have synthesized functionalized imidazole groups with a chemistry that could be used to tether them to polymer backbones or other porous substrates.

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

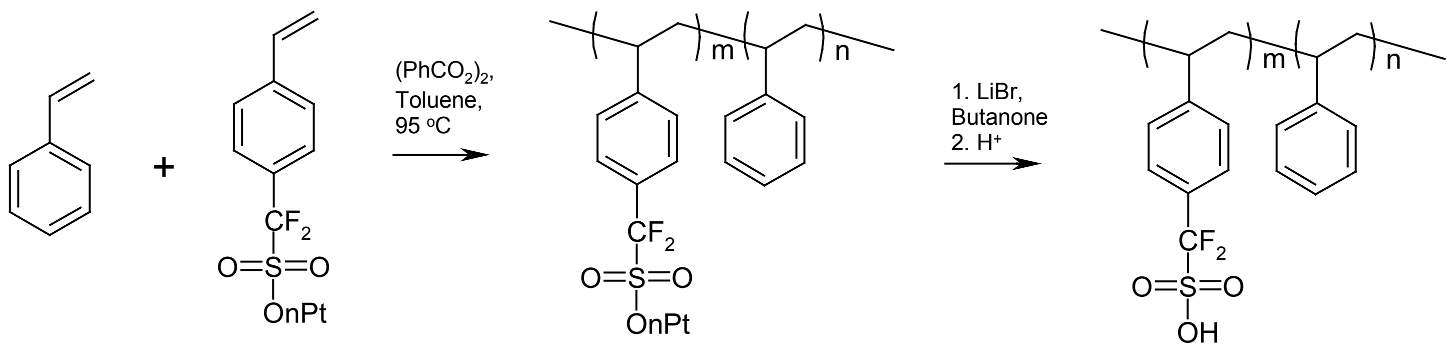
We have successfully synthesized these two proton containing imidazolium molten salts.

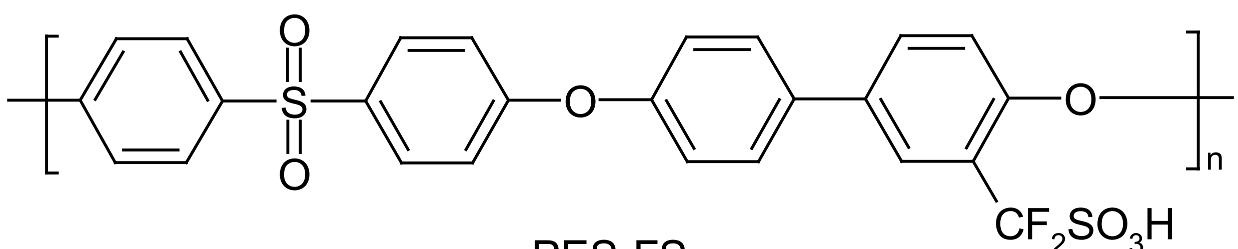
DOE High-T Membrane Program

Gary Wnek
Department of Chemical Engineering
Virginia Commonwealth University

1. Toward Routes to Functionalize Monomers and Polymers with –CF_2SO_3H Units

Motivation: lower pK_a ('Nafion-like'); higher conductivity at lower water content due to lower basicity of difluorosulfonate anion; desulfonation reactions at high-T minimized.





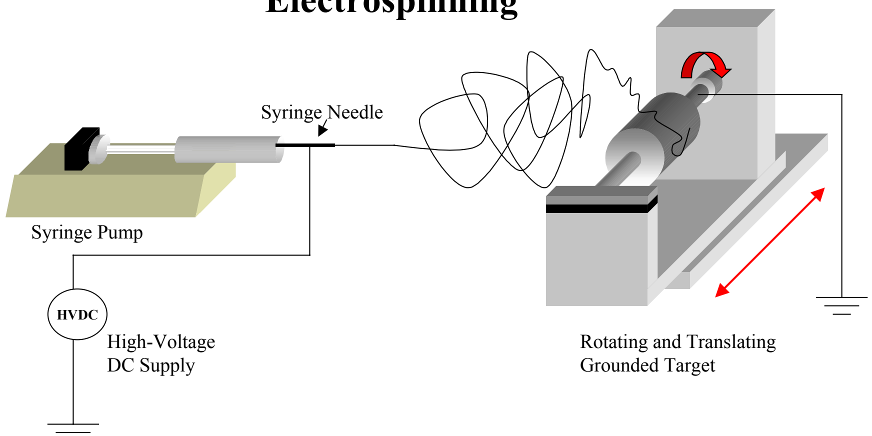
PES-FS

Optimization of reaction conditions and characterization of polymers are in progress

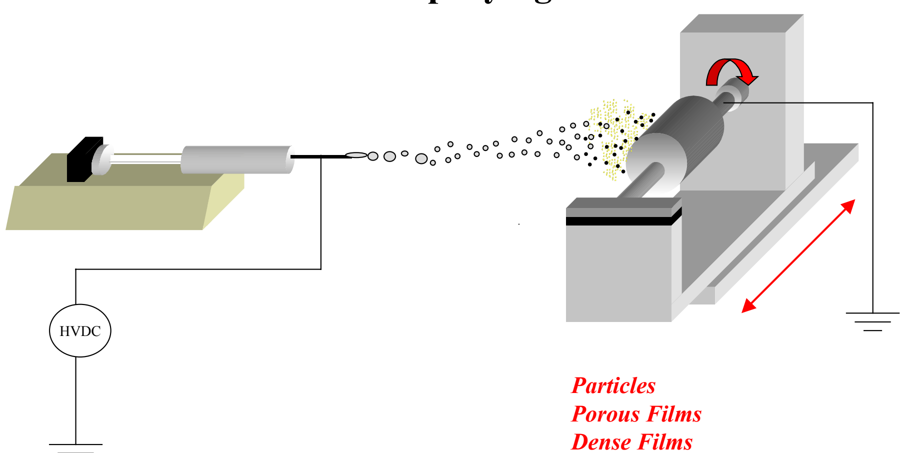
2. Electrostatic Processing (Electrospraying, Electrospinning) of PEM Components

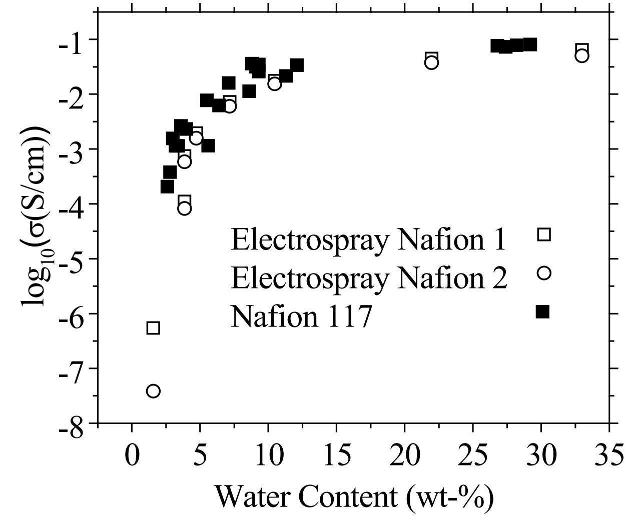
Motivation: potentially general and broad approach to tailoring PEM, electrocatalyst, and gas diffusion layer properties.

Electrospinning

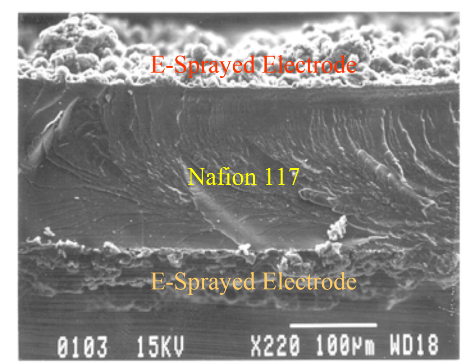


Electrospraying





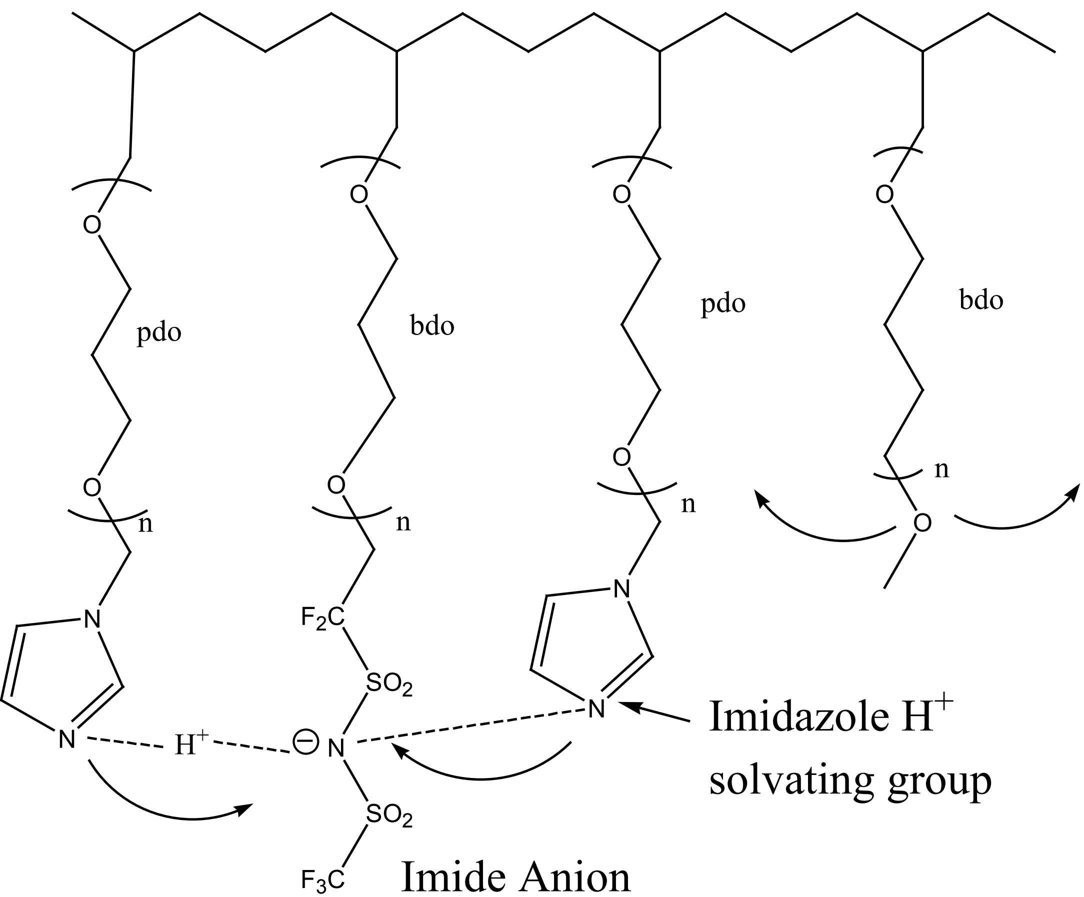
Conductivity vs. water content for 2 electrosprayed Nafion films compared w/ Nafion 117. Data from John Fontanella and Charles Edmonson, USNA



SEM of fracture surface of electrosprayed electrodes (Nafion + Pt/C) on Nafion 117 showing good adhesion between electrode and PEM

Sanders et al., in "*Advances in Materials for Proton Exchange Membrane Fuel Cell Systems,*" poster presentation abstract, Asilomar, CA, Feb. 2003.

LBNL: New Polymer Architectures 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.

ARIZONA STATE UNIVERSITY

1. Liquids for ambient-to-high-temperature applications are provided by **ATMS** (Ambient Temperature Molten Salts). These are vapor-free.
2. ATMS with exchangeable protons can be prepared by using anhydrous Brönsted acid-base reactions

*C*HARACTERIZATION DATA:

1**. Vapor pressure**

We can correlate the depression of vapor pressure over these liquids with the difference in pKa values of the reacting pair, using aqueous solution data and plotting against excess boiling point (see Fig. 1). Some liquids are stable against boiling to >300ºC (Tb estimated for propylammonium triflate is ≈700ºC, far exceeding the decomposition temperature)

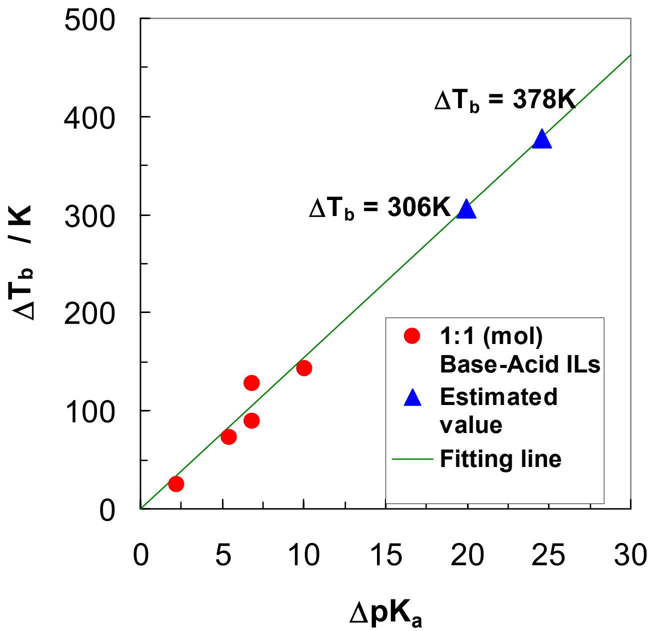


Figure 1. Relationship of ΔT_b and ΔpK_a

2. **Conductivity.**

Some of these proton transfer ionic liquids in their neutral state can have extremely high ionic conductivities, rivaling aqueous solutions. They also support formation of dianion complexes, which have even higher conductances.

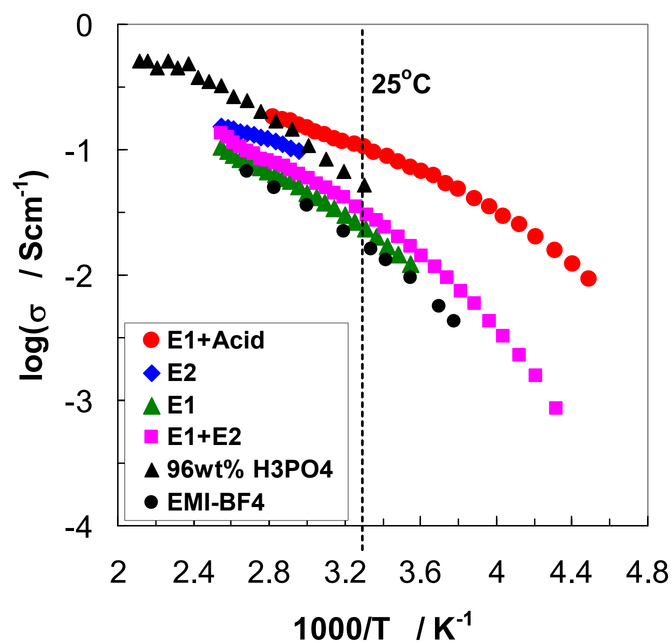


Figure 2. Temperature Dependence of the Conductivity

Nanostructured Hybrid Membranes for High Temperature Fuel Cells

Performer: Dr. John P. Ferraris and Dr. Kenneth J. Balkus, Jr.
Department of Chemistry
The University of Texas at Dallas

Objective:

- The design and experimental demonstration of polymer/molecular sieve composite membranes with high proton conductivity.

Payoffs:

- Mesoporous molecular sieves
  - Thermal stability
  - Chemical stability
  - Proton conductivity
  - Water-retention
- Organic/polymer
  - Proton conducting
  - Flexible
  - Less fuel crossover
- Polymer/molecular sieve composites:
  - Proton conducting
  - Thermal/chemical stability

Approach:

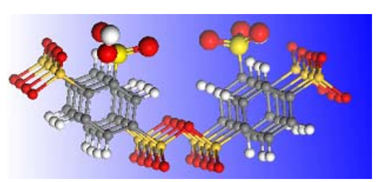
- Proton conducting mesoporous molecular sieves.
  - Sulfonic acid functionalized mesoporous silica
  - Sulfonated mesoporous benzene silica (MBS)
  - Tungsten silicates and tungsten phosphate molecular sieves
  - Mesoporous silica filled with polyaniline (PANI)
  - Free standing molecular sieve films
- Prepare and investigate proton conductivity of acid doped free standing *meta*-PANI films.
- Prepare and investigate proton conductivity of sol-gel hybrid acid doped polyethyleneimine (PEI).
- Prepare and investigate sulfonated PEI.
- Investigate proton conductivity of acid doped polymer/molecular sieve composite.

Nanostructured Hybrid Membranes for High Temperature Fuel Cells

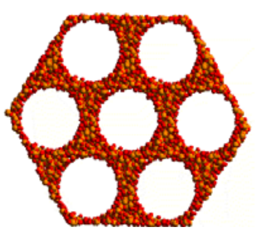
Accomplishments:

- Functionalized mesoporous molecular sieves:
  - PANI filled SBA-15 was prepared
  - MBS was prepared, and ~15% of phenyl rings were sulfonated.
  - Sulfonic acid functionalized SBA-15 was prepared
  - Tungsten silicates and tungsten phosphate molecular sieves are under development.
- Proton conductivity of H_3PO_4-doped *meta*-PANI was investigated.
- Sol-gel/PEI hybrid membrane doped using different acids and proton conductivity are under investigation.
- Polymer/molecular sieve composites are under development.

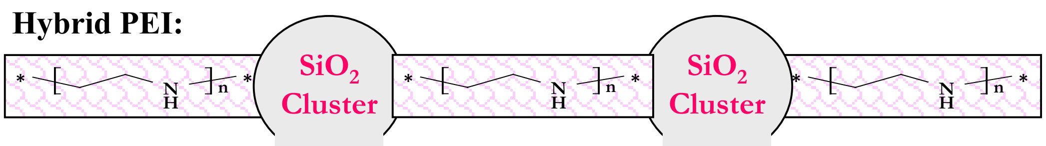
Sulfonated MBS



SBA-15



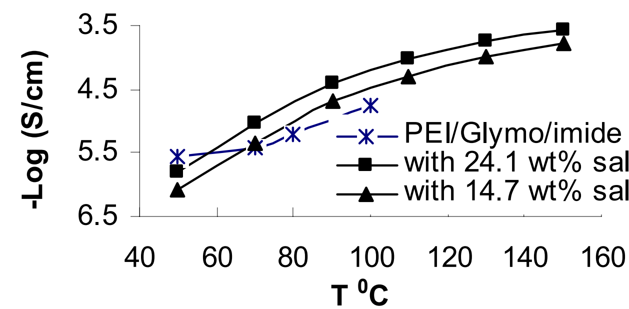
Hybrid PEI:



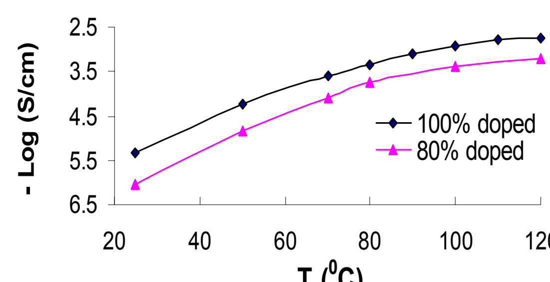
(a) σ of molecular sieves

Materials	Water content (wt%)	- Log σ (S/cm)
Sulfonated MBS	64.9	1.61
Sulfonated SBA-15	55.5	1.85
W-MCM-41 (W/Si=0.025)	42.4	1.75
W-MCM-41 (W/Si=15)	20.6	1.48
Si-MCM-41	21.5	1.30

(b) σ of PEI films under dry conditions, with or without Trifluoromethyl sulfonimide-dipropylamine salt



(c) σ of H_3PO_4-doped *m*-PANI



High Temperature Membrane Working Group

- Meeting bi-annually (typically associated with ECS meetings)
- Representatives from a variety of industry, academic and national lab groups
- Recent briefings and guidance from GM, 3M, UTC, WL Gore, DuPont etc.

Roadmap: Research Topics

Priority	Approach/Research Topic	Approx. Timeframe
High	New polymers with improved thermal stability (non-Nafion systems)	To 2008
Medium	Polymers with hydrophilic additives or improved hydrophilicity	To 2004
Medium	Polymers with added acids	To 2004
Low	Water-dependent inorganic conductors	To 2003
Medium	Phosphoric acid-based systems	To 2006
High	Non-aqueous proton conducting phases as additives	To 2008
Medium	Inorganic conductors	To 2008
High	Adhesion between polymer membrane and catalyst layer	To 2008
Medium	Materials properties of catalyst layers	To 2008
High	Understanding of proton dissociation, conduction in non-aqueous systems	To 2008
High	Non-adsorbing ionic conducting phases	To 2008
High	Understanding, Improving local structure in catalyst layers and its relation to function	To 2008

Roadmap dates in process of updating!

Summary/Future Directions

- We feel that this program is finally 'launched'; mix of funded players emphasizes synthesis

- Continue directions described above
  - Start developing MEAs from new materials (CWRU)
  - Begin to distribute 'lessons learned' info via website

- Next round of new start funding: increased emphasis on 120^{o}C solutions

- Continue to streamline funding process