A Discussion of Conductivity Testing in High Temperature Membranes (lessons learned in assessing transport)

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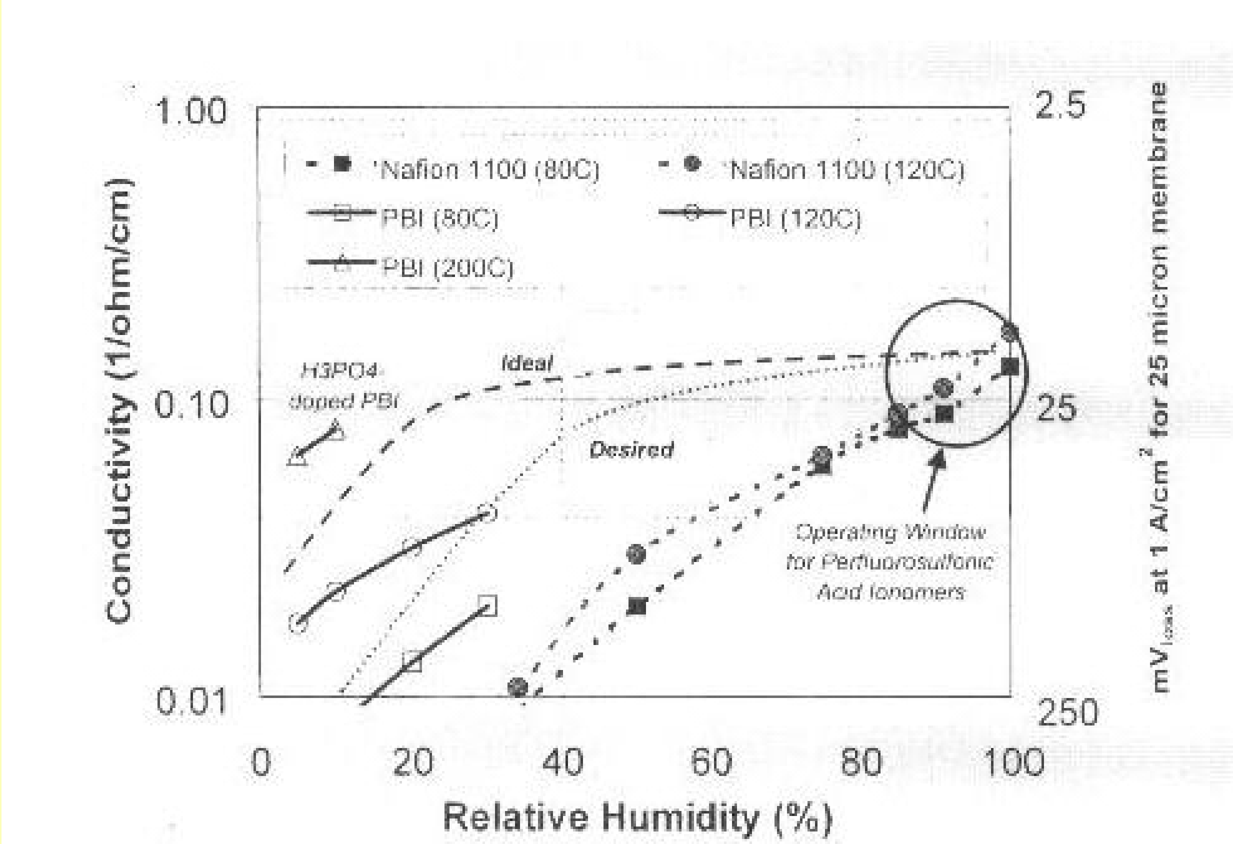
What are shortcomings of current materials?

- While thermal and chemical stability are required, unless the materials demonstrate conductivity at low humidity, it doesn’t matter.
- <u>The ability to conduct protons with low relative humidity is the currently missing piece.</u>
- Phosphoric acid comes close to meeting requirements (unfortunately, anion adsorption and water soluble liquid electrolyte limit application)

Conductivity of Various Samples

- Different materials have different experimental difficulties (polymers vs ‘free’ liquids)
- Common ground is difficulty associated with high T
  - Temperature control
  - Pressurized cells when water is involved
- Primary experiment is AC impedance spectroscopy (EIS or current interrupt)
  - These give conductivity not proton conductivity, unless protons are the only charge carrier.
- For multiple species (acid doped or ILs) ionic conductivity is obtained (need NMR or H pump)

Conductivity Goals



Even phos acid/PBI falls short at DOE T target (120C).

"Desired Characteristics of a High Temperature Membrane for Automotive Fuel Cells," Angelopoulos et. al., Abstracts from Advances in Materials for Proton Exchange Membrane Fuel Cell Systems, Pacific Grove, CA, February 23-26, 2003.

Phosphoric Acid System (single molecule)

Self Ionization

$3\ H_3PO_4 <\!\!\!=\!\!\!> H_7P_2O_8^+ + H_2PO_4^-$ (anhydrous)

$H_2O + H_7P_2O_8^+ <\!\!\!=\!\!\!> H_3O^+ + 2\ H3PO4$ (wet)

Numerous hopping mechanisms possible

$H_7P_2O_8^+ <\!\!\!=\!\!\!> H_3PO_4 <\!\!\!=\!\!\!> H_2PO_4^-$ (anhydrous)

H_3O^+ or $H_7P_2O_8^+ <\!\!\!=\!\!\!> H_3PO_4$ or $H_2O <\!\!\!=\!\!\!> H_2PO_4^-$ (wet)

All ions capable of vehicle transport (diffusion-like)

All mechanisms responsible for net proton transport.

Ionic Liquids (two molecules)

Ions

EMI^+, Im-H^+, H_3O^+, $H_2PO_4^-$, PF_6^-

Hopping mechanisms possible

H_3O^+ or Im-H^+ $\Leftrightarrow$ Im or H_2O

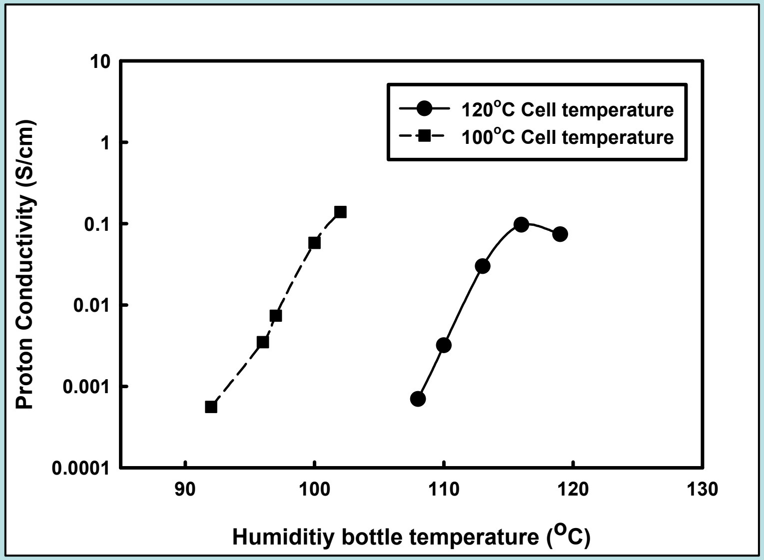
H_3PO_4 or H_2O $\Leftrightarrow$ $H_2PO_4^-$

All ions capable of vehicle transport (diffusion-like)

Not all mechanisms responsible for net proton transport.

Controlled Humidity Conductivity

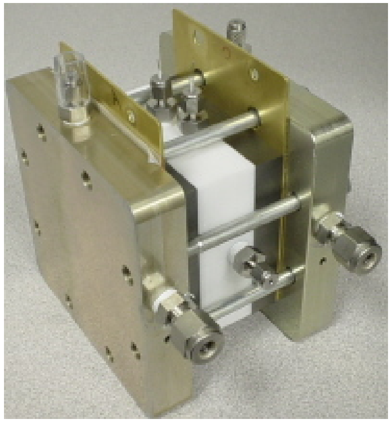
AC Impedance Spectroscopy
Nafion 1135 Data



➡ We have been able to establish high temperature conductivity testing under controlled humidity.

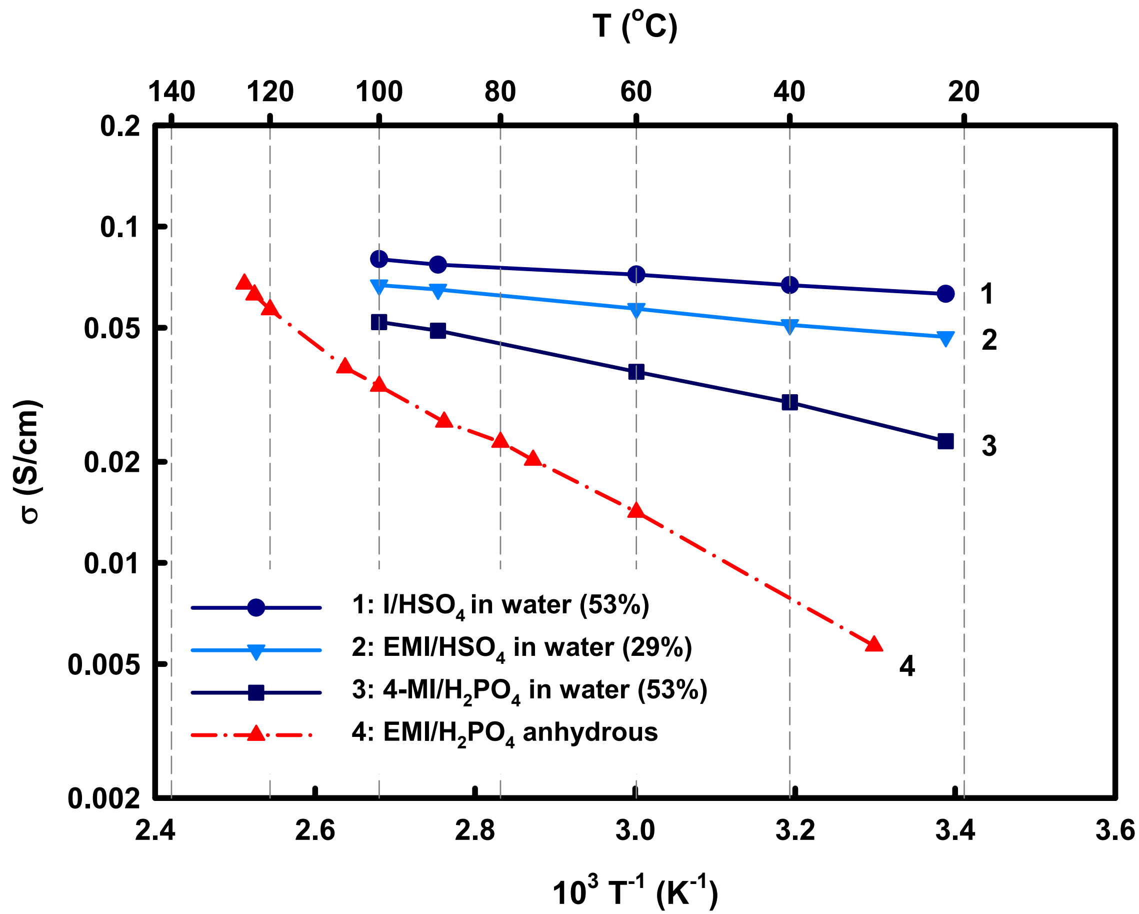
Control Humidity

- By salt mixtures (LiCl, etc)
- By humidifier bottles

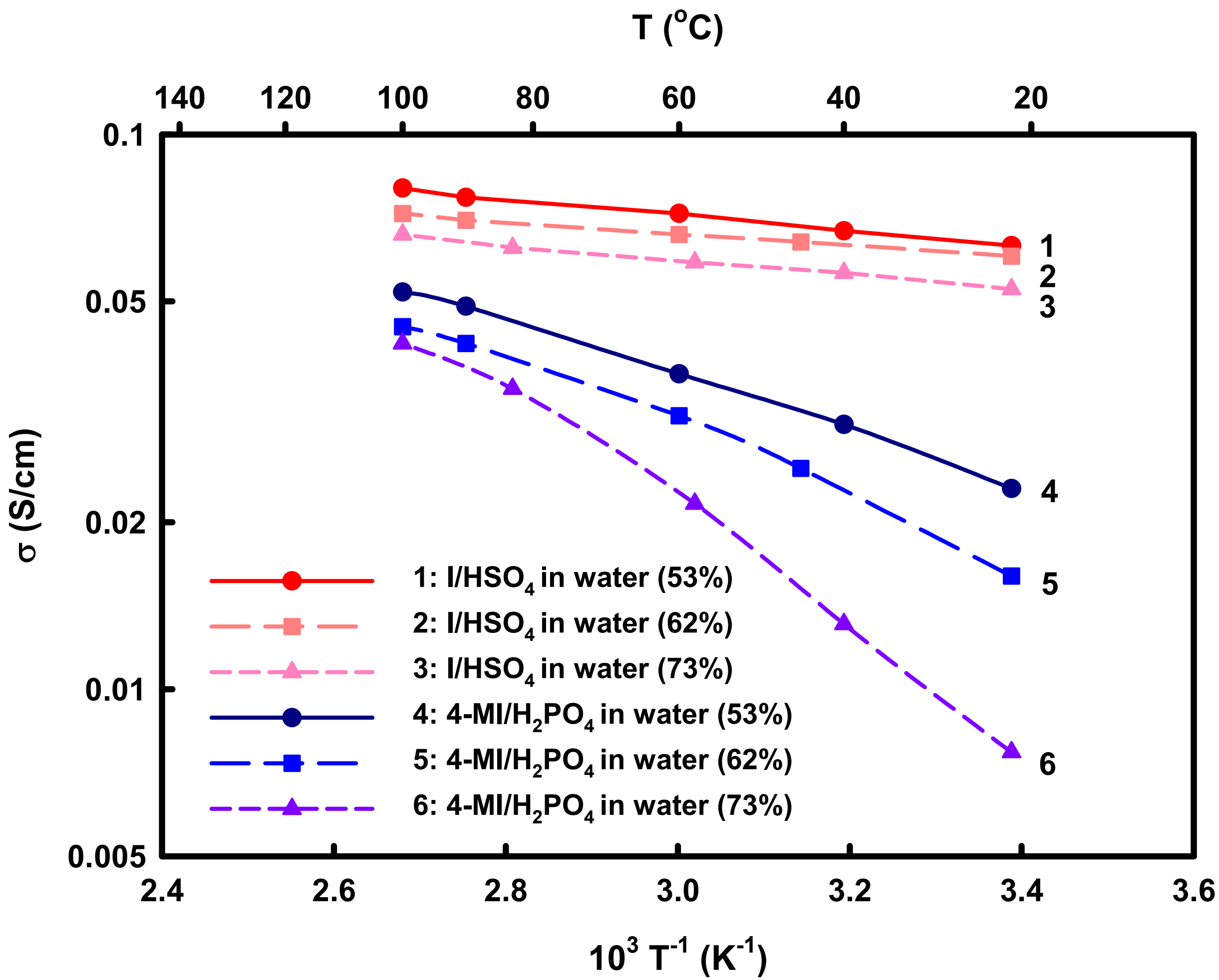


Conductivity experiments have been performed in modified fuel cell hardware with a Teflon insert from Bekktech, LLD. Test cells like this allow operation at elevated temperature.

Conductivity of 4 test materials

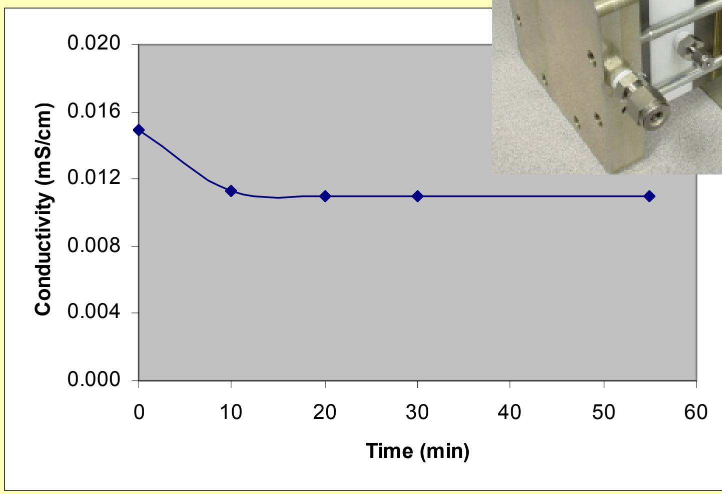


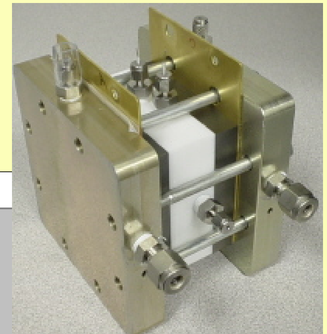
Influence of water content on conductivity



Special test cells may be necessary, we were limited here to 100C.

Hydrogen Pump





Conductivity of EMI/H2PO4 under hydrogen pump

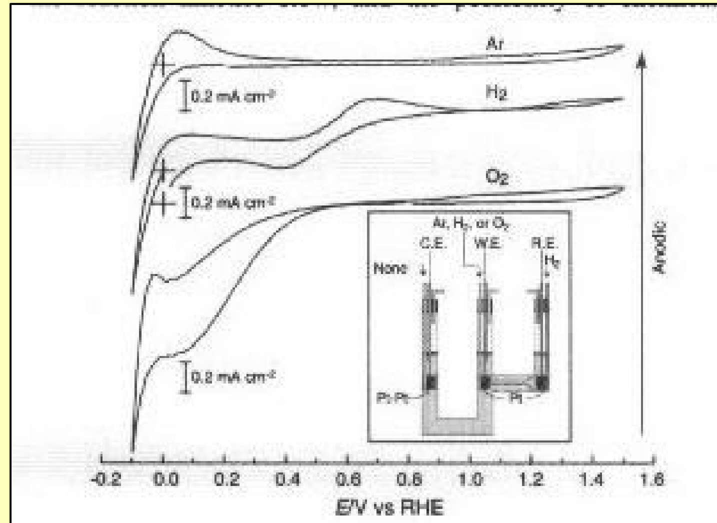


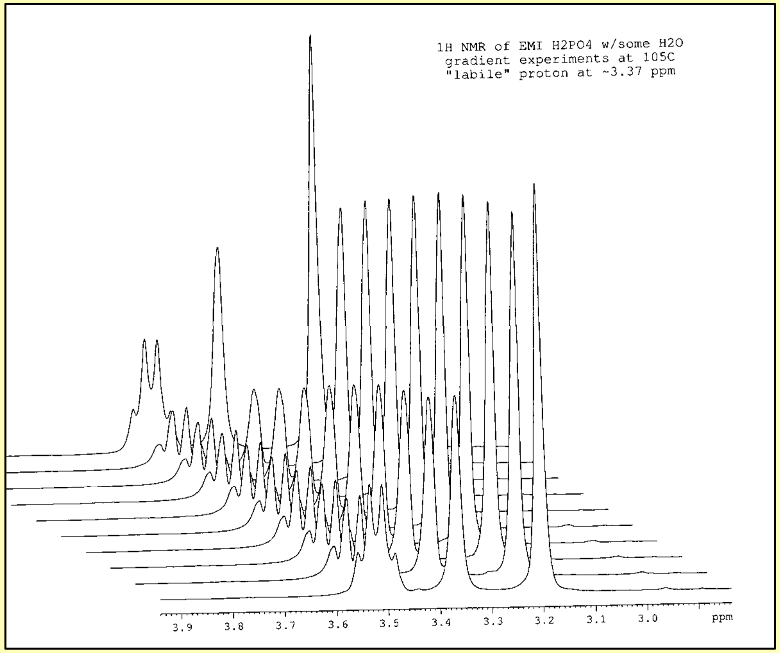
Fig. 1 Cyclic voltammograms for Im/HTFSI neutral salt at 130 °C. The crosses correspond to 'zero' current at the potential of 0 V. Scan rate is 50 mV s^{-1}. W.E. is a Pt-wire in Ar, H_2 or O_2 atmosphere, C.E. is a Pt-black wire in H_2 atmosphere and R.E. is a Pt-wire in H_2 atmosphere. Inset shows the schematic diagram of the two-compartment cell used.

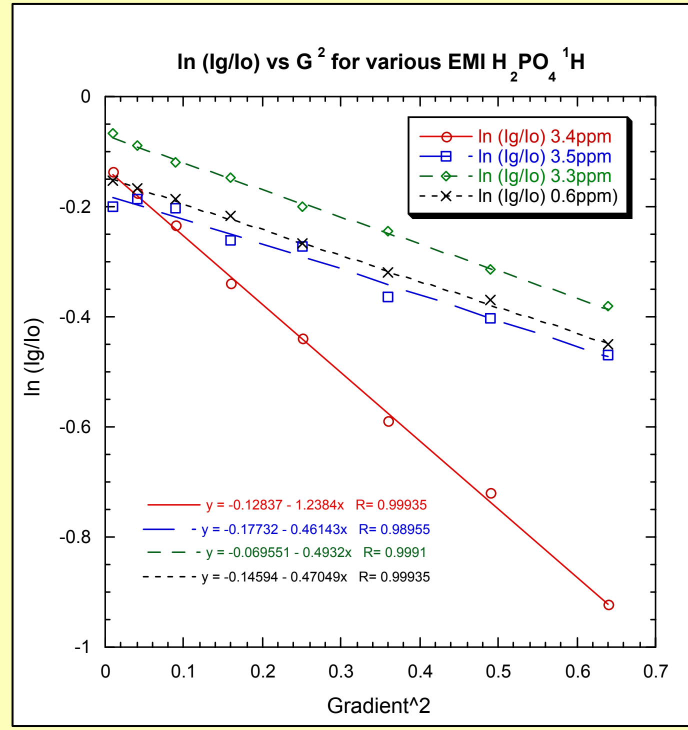
Chem. Commun., 2003, 938-939.

ac conductivity -> 5 mS/cm (400x)

Can't be certain of reliability of data, but ionic conductivity doesn't equate to proton conductivity.

^{1}H PFG SE NMR for Diffusion





$\ln(Ig/Io) = -[\gamma 2\ \delta 2\ G2\ (\Delta - \delta/3)]\ D$

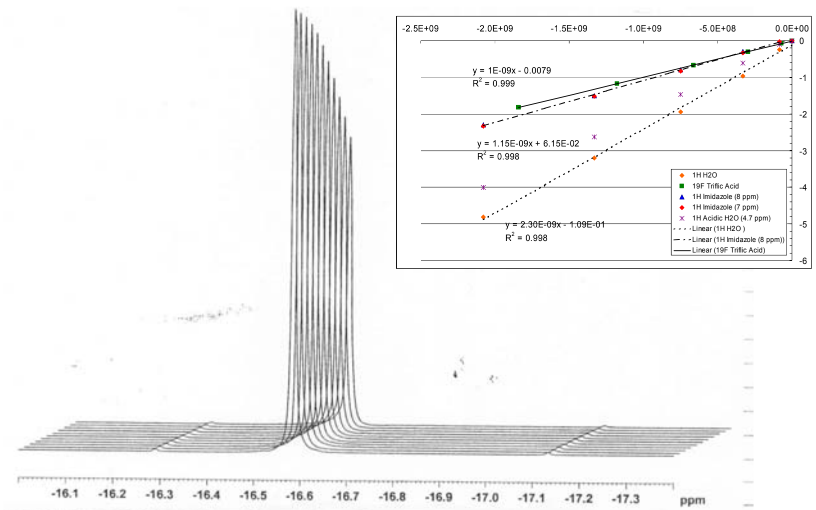
$D_{acid} = 1.4 \times 10^{-5}\ cm^2/s$ **$D_{EMI} = 5.2\text{-}5.6 \times 10^{-6}\ cm^2/s$**

Acid proton ~2.6x faster than EMI proton

next step phosphate diffusion

Conductivity of Imidazole Containing Solutions

^{19}F PFGSE Results (inset 19F and 1H data)



Sample	pH	Conductivity (mS/cm)
2 M imidazole 1 M CF_3SO_3H in D_2O [estimated from NMR]	8	58 (at 22°C) 65 (at 30°C) [80 (at 30°C)]
2 M imidazole 1 M CF_3SO_3H in H_2O	8	68 (at 22°C) 79 (at 30°C)

$$D_{\text{Trifilic Acid from F-19}} = 1.00 \times 10^{-5}\ \text{cm}^2/\text{s}$$

$$D_{\text{Imidazole from H-1}} = 1.15 \times 10^{-5}\ \text{cm}^2/\text{s}$$

We have prepared and characterized ‘buffered’ solutions of triflic acid and excess imidazole. The high pH of the solution suggests ‘free’ protons play little role in the observed conductivity, while differences in conduction between D_2O and H_2O suggest proton hopping may be important. However, conductivity values estimated from pulsed field gradient NMR based only on vehicle mechanism conduction are higher than those found by conductivity measurements and more work needs to be done to understand these phenomenon.

Work investigating higher pH electrolytes is very preliminary. Areas of future investigation include: effects of D_2O versus H_2O, higher concentration imidazole solutions, strongly basic buffered solutions, and substituted imidazoles.

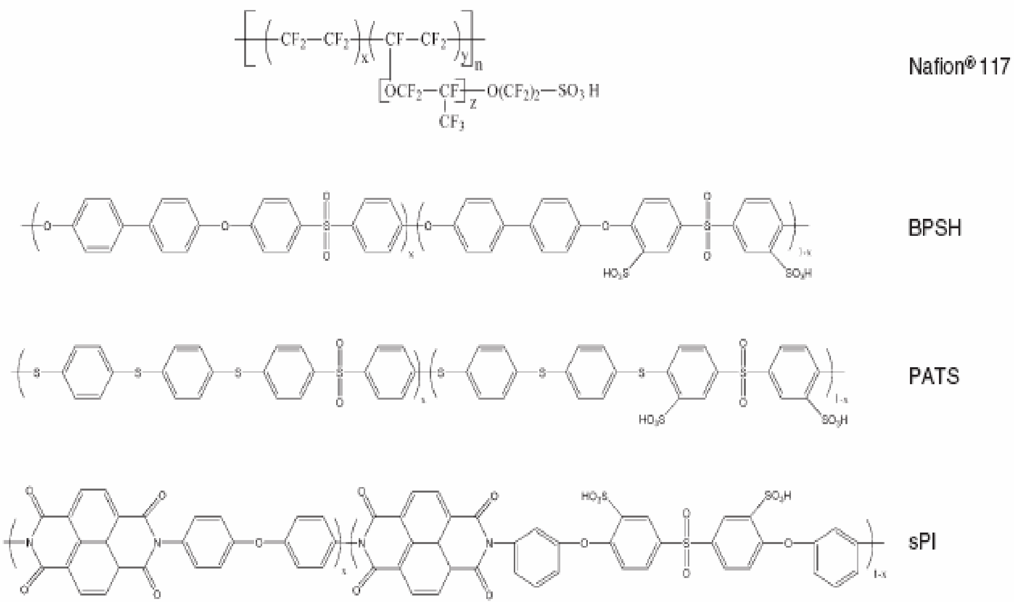
Tunable Parameters
What we control

Table 1 Transport properties and primary influencing factors (broken into tunable parameters and structural feature) for polymer electrolytes.

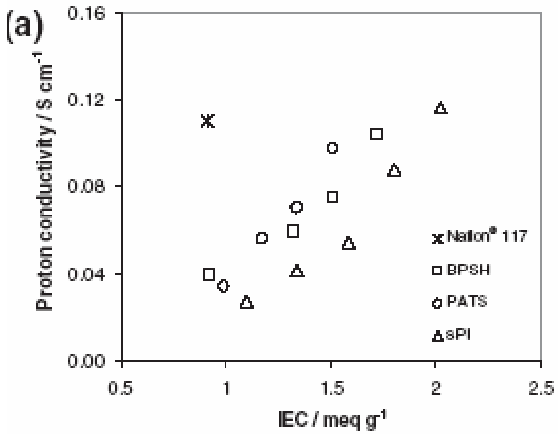
Transport Properties	Tunable Parameters	Structural Features
Proton conductivity Water transport properties (D_{H2O}, E_D) Reactant permeability	Backbone characteristics Acid group characteristics Ion exchange capacity Processing/History	Water domain size, shape and interface Interanionic distances Water uptake Tortuosity

M. Hickner, B. S. Pivovar, *Fuel Cells* **5, 213 (2005).**

Backbone Stiffness

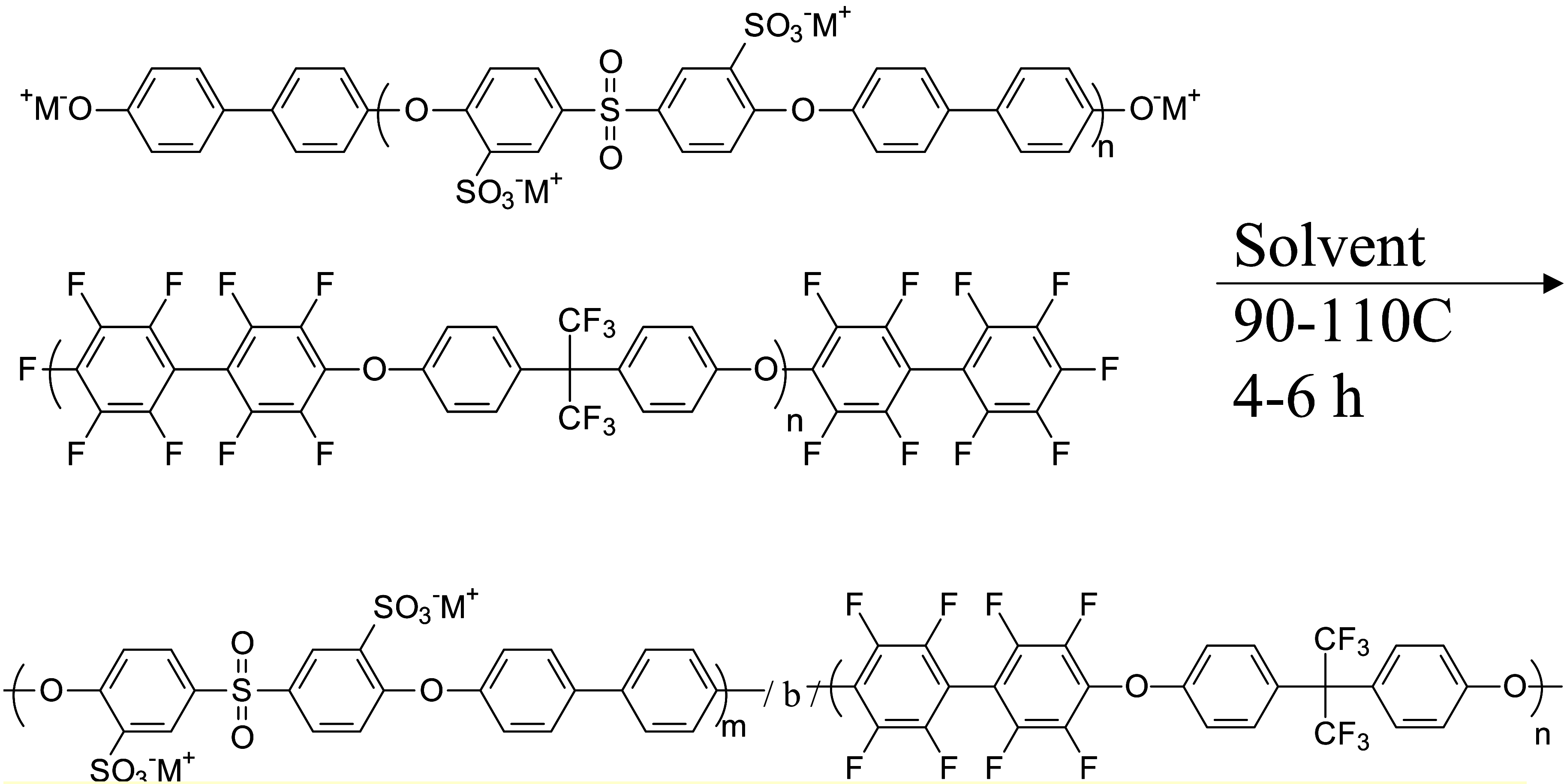


Trends in transport properties related to phase separation.



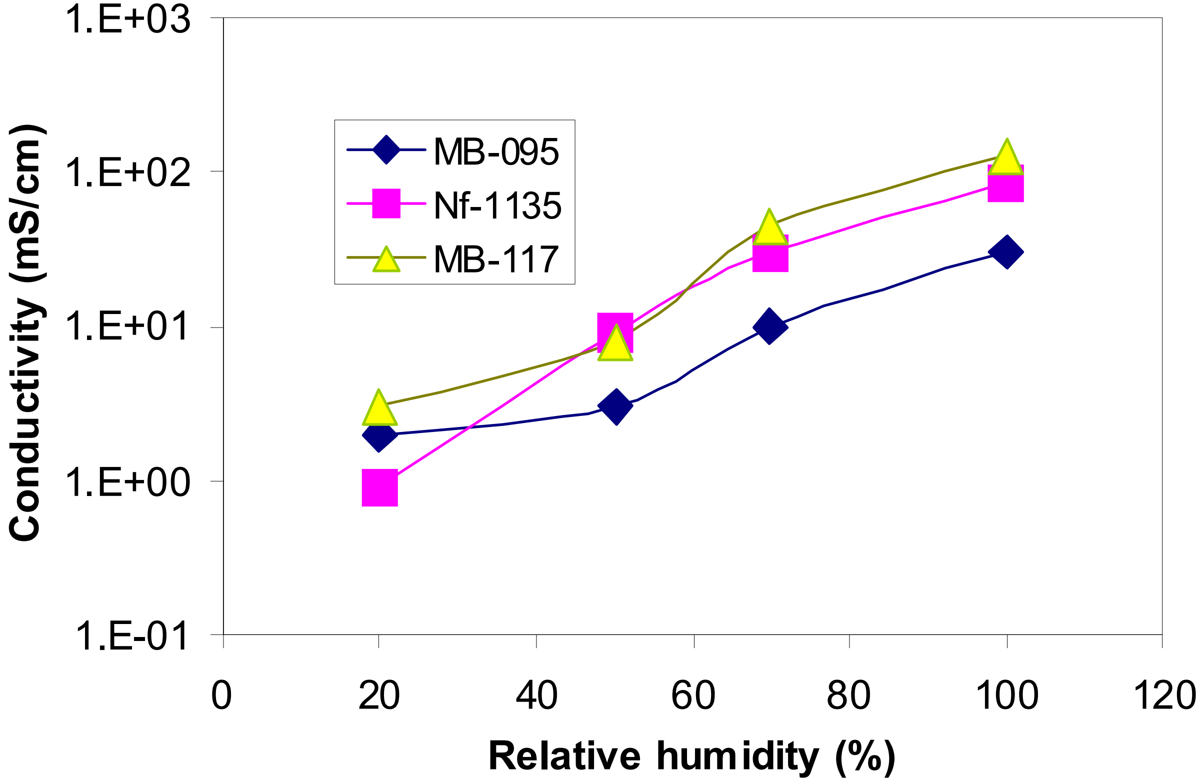
M. Hickner, B. S. Pivovar, *Fuel Cells* **5, 213 (2005).**

Multiblock Copolymers



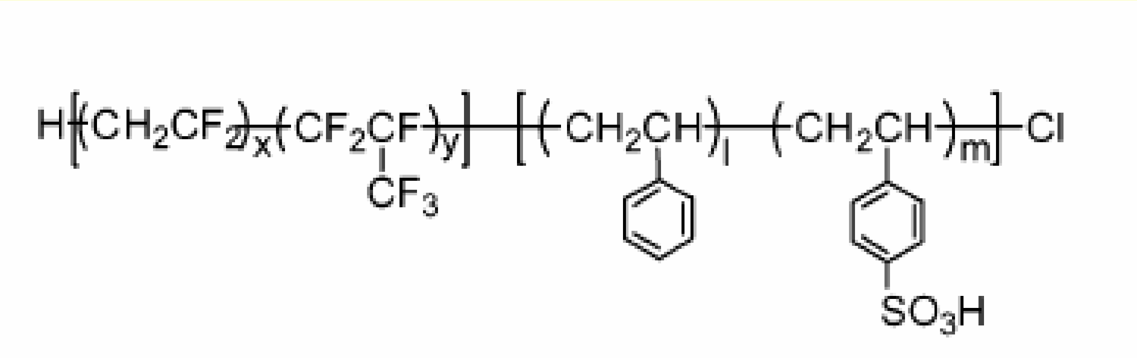
Hossein Ghassemi, William Harrison, Tom A. Zawodzinski, Jr., and James E. McGrath, "New Multiblock Copolymers Containing Hydrophilic-Hydrophobic Segments For Proton Exchange Membrane," *Polymer Preprints* (American Chemical Society, Division of Polymer Chemistry) (2004), 45(1),68-69.

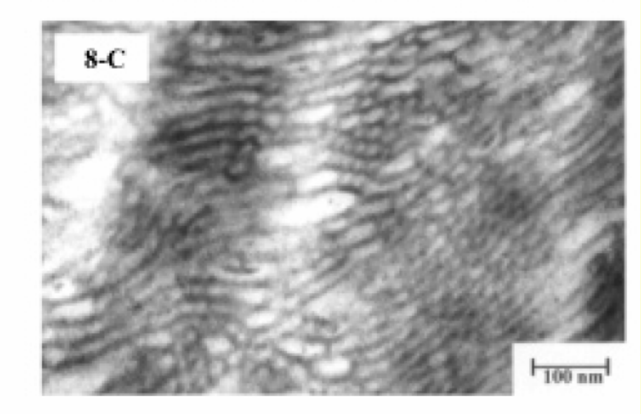
Influence of relative humidity on proton conductivity

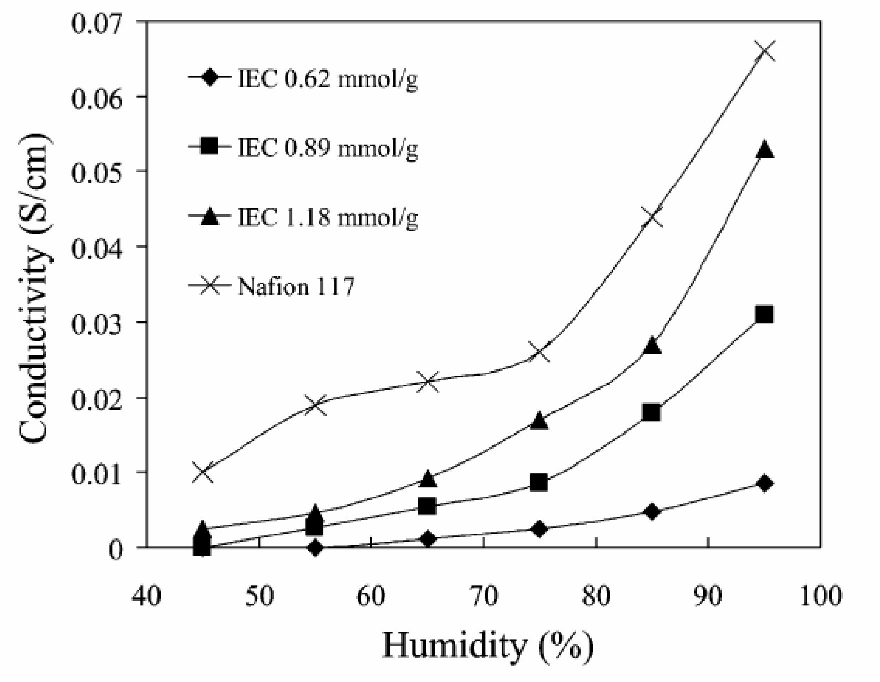


H. Ghassemi and T. Zawodzinski, ECS Abstracts, October 2004.

Block Polymers



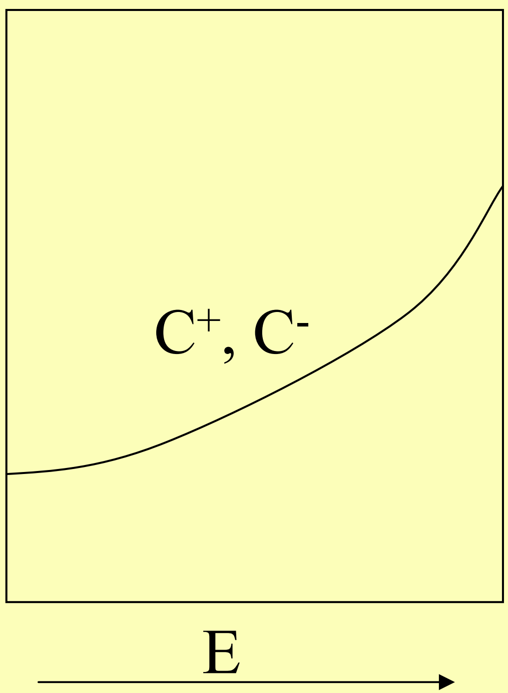




Show phase separation, but not performance of polyarylenes.

Concentration Polarization

If cation/anion do not have same mobility, concentration polarization will result in higher resistance.



Ac impedance measurements not reflective of proton conductivity at steady state.

Presumably not important in phos acid due to fast diffusion.