A Discussion of Testing Protocols and LANL's Contribution to High Temperature Membranes (lessons learned in assessing transport in new electrolytes)

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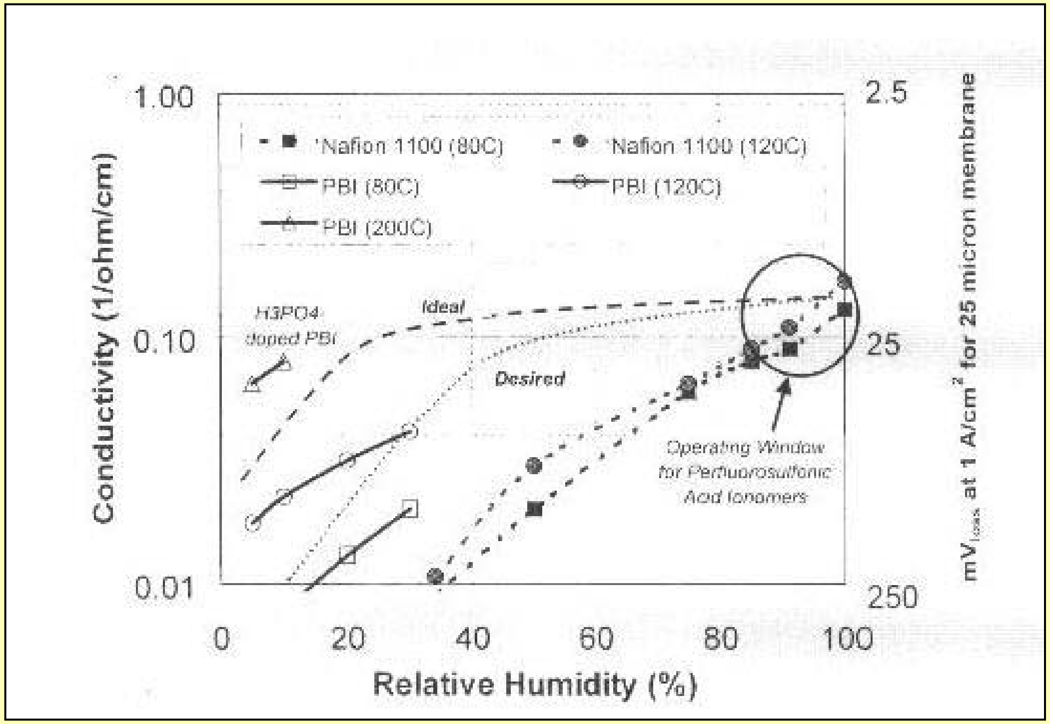
What's Needed/Desired?



*taken from GM abstract

Automotive

- 120°C
- Low humidity

Stationary

- >150°C
- Very low humidity

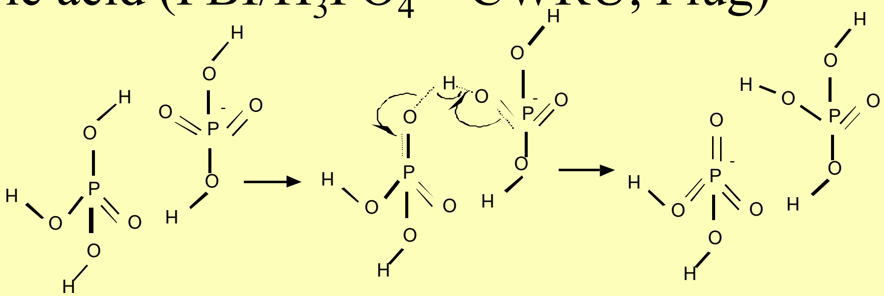
Increased catalytic activity and increased heat rejection
Even phosphoric acid doped PBI has below target conductivity at very low (<10%RH) humidity

~120 C Approach

- Water based conduction improved by incorporation of additives
  - Dispersed solid acids (UConn, VT, NREL, Alberti, etc.)
    - → HPA - Heteropolyacids ($H_3PO_4 \cdot 12WO_3$ or $H_3PO_4 \cdot 12MoO_3$)
    - → ZrP - $Zr(HPO_4)_2$
    - → variants on above (triflower, layered zirconiums)
  - Silica particles (SiO_2 in Nafion – Nuvera)
  - Other water retaining or highly conducting additives?
  - Higher free volume polymers (CWRU)

>150 C Approach

- Water free conduction based on water replacement (possible polymer incorporation)
  - Phosphoric acid (PBI/H_3PO_4 – CWRU, Plug)



  - Imidazole, pyrazole (Kreuer, JPL, etc.)
- Water free conduction based on solids
  - Solid acids ($CsHSO_4$ - JPL/Cal Tech)
  - Oxides
  - Proton conducting glasses

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.
- The ability to conduct protons with low relative humidity is the barrier
- Phosphoric acid is the only material that meets requirements (unfortunately, anion adsorption lowers performance and it is liquid water intolerant)

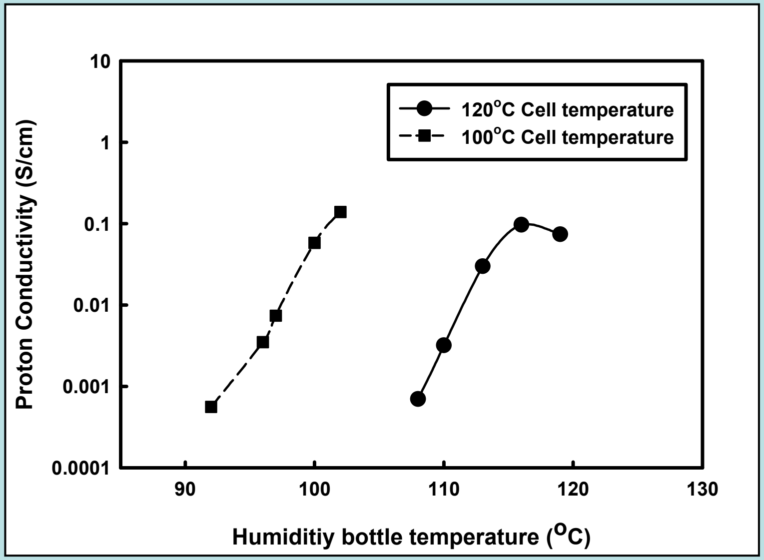
What experimental conditions are valid?

- Different materials will 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 H^+ conductivity at known RH
- For multiple species (acid doped or ILs) ionic conductivity is obtained need (NMR or H pump)
- Exp'ts such as DSC, TGA, others are secondary

Controlled Humidity Conductivity

AC Impedance Spectroscopy

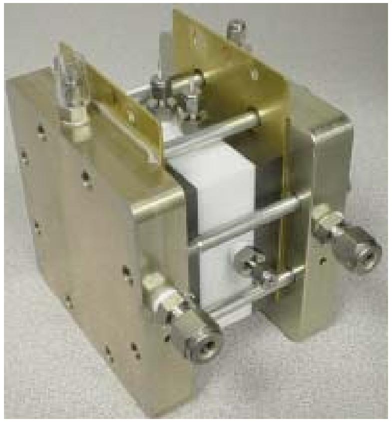
Nafion 1135 Data



➡ 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.

Water Uptake

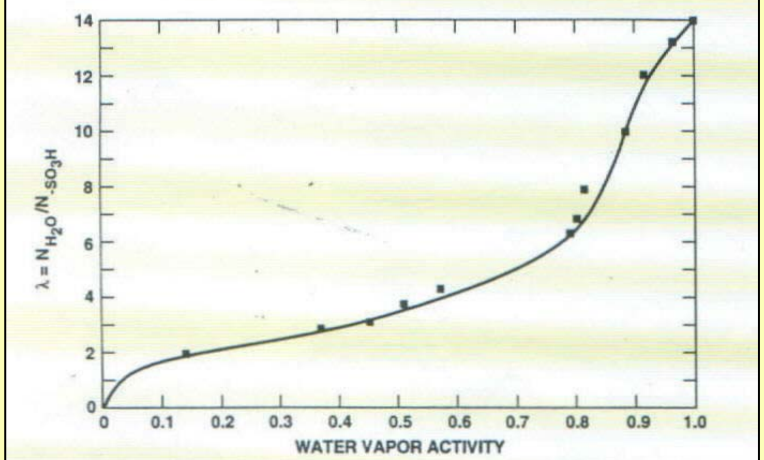


Fig. 4. Equilibrium sorption of water vapor as a function of water vapor activity.

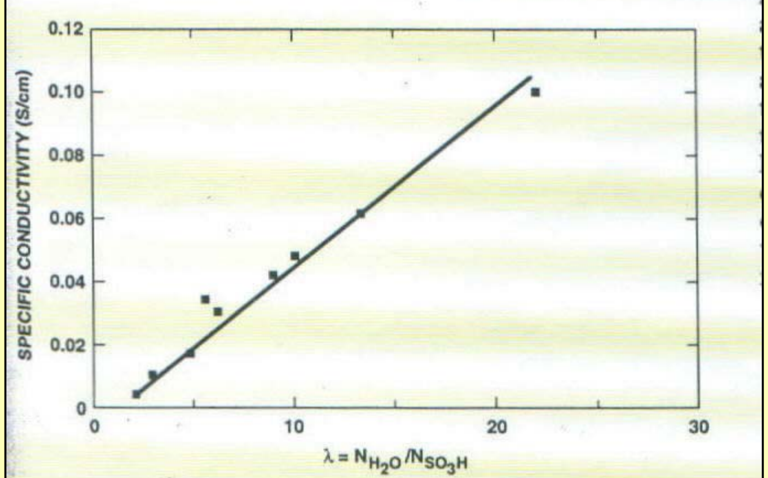
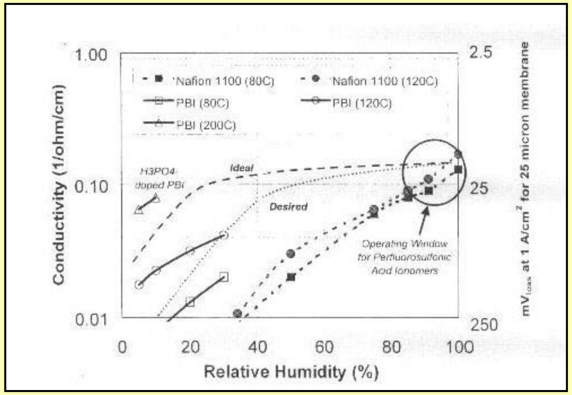


Fig. 7. Membrane conductivity as a function of water content.

Zawodzinski et al., JECS, 1993.



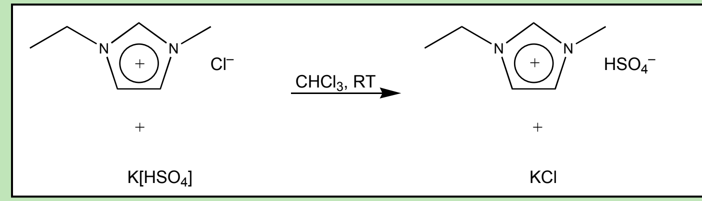
For polymer based systems room temperature measurements may be more than adequate. Liquid systems will be more difficult.

LANL HTMWG Synthesis

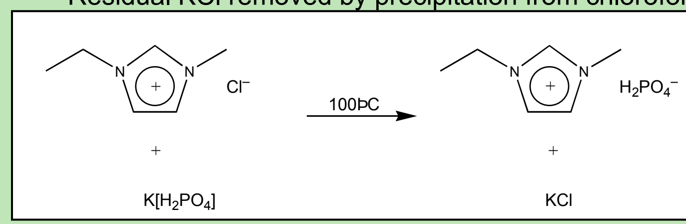
Imidazolium salts have high conductivities, however little has been done in this area with proton conductors. Our approach is to find materials with needed conduction properties and then incorporate into membranes.

Advantages:
Stable (temperature, oxidation)
No vapor pressure
High ionic conductivity

Ionic Liquids



- Mixture is filtered to eliminate bulk of KCl
- Residual KCl removed by precipitation from chloroform

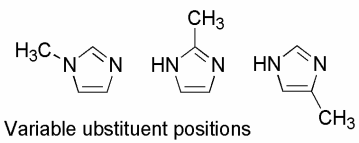


- Solid reaction product is extracted into methanol and filtered
- Methanol is removed under vacuum and residual KCl removed by precipitation from $CHCl_3$

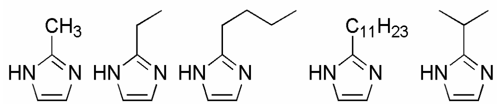
Ethyl Methyl Imidazolium (EMI) Salts

LANL Chemistry Directions

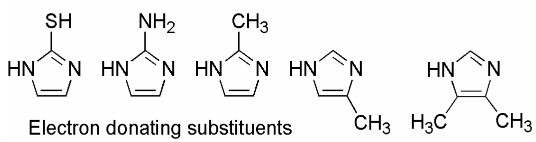
A sample of commerically available imidazoles



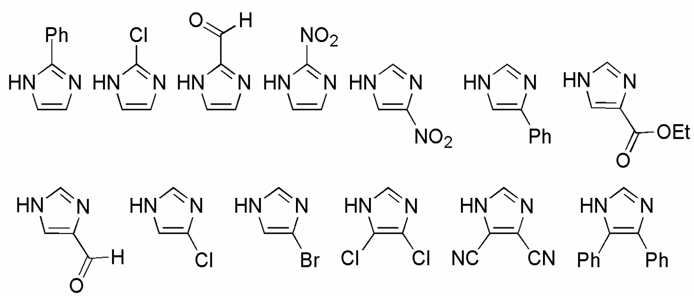
Variable ubstituent positions



Steric effect of alkyl substituent and position 2

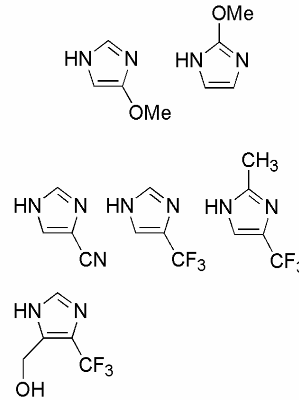


Electron donating substituents

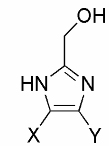


Electron withdrawing substituents

Simple known synthesis

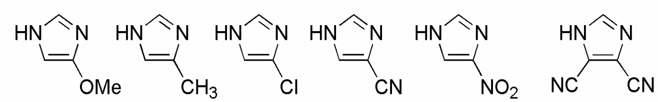


New synthetic targets



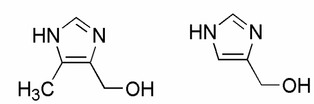
X and Y could be donating or withdrawing groups or a combination of both.

Imidazole series designed to probe substituent effects

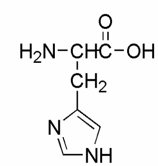


Electon donating
Most basic

Electron withdrawing
Least basic



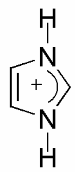
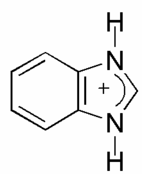
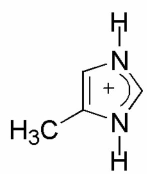
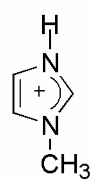
Other interesting imidazoles



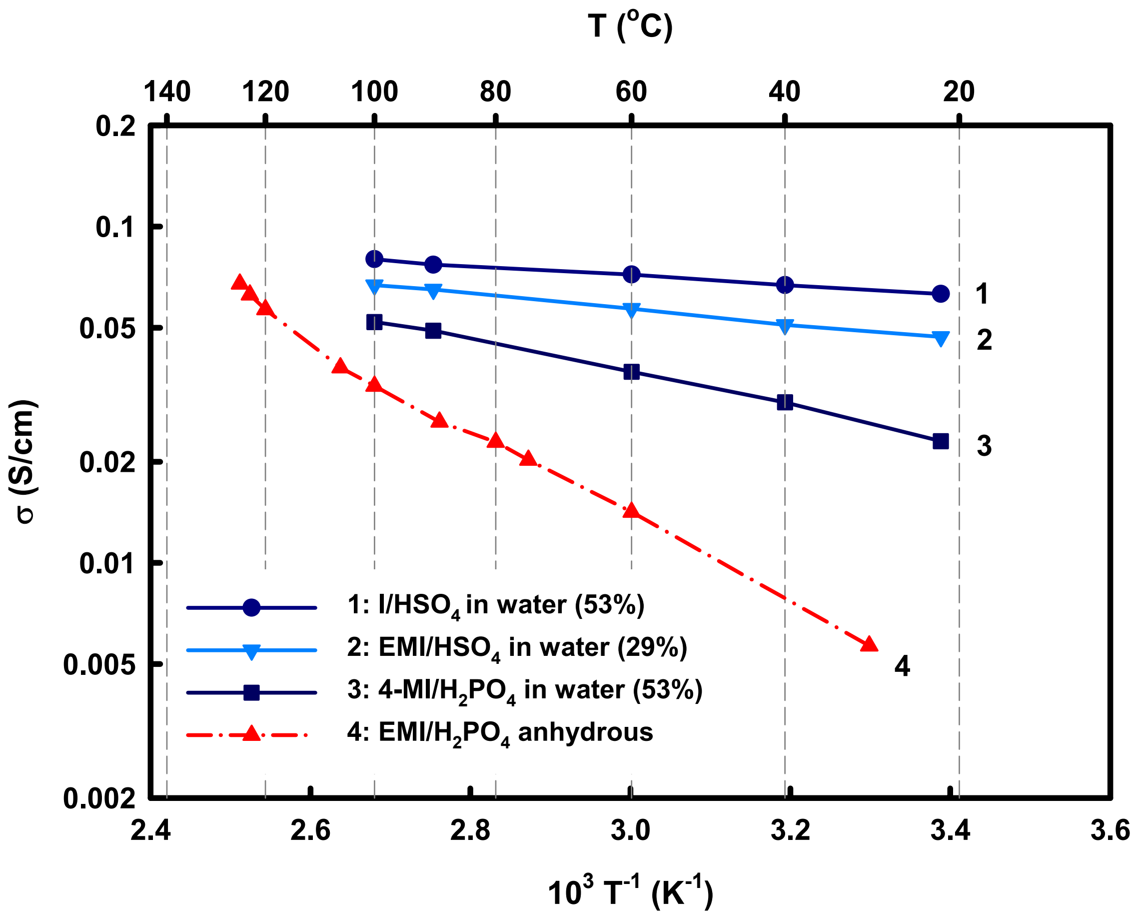
histidine

Further investigation into role of imidazole in proton transport. Comparing N substituted imidazoles with unsubstituted imidazoles and substituent effects.

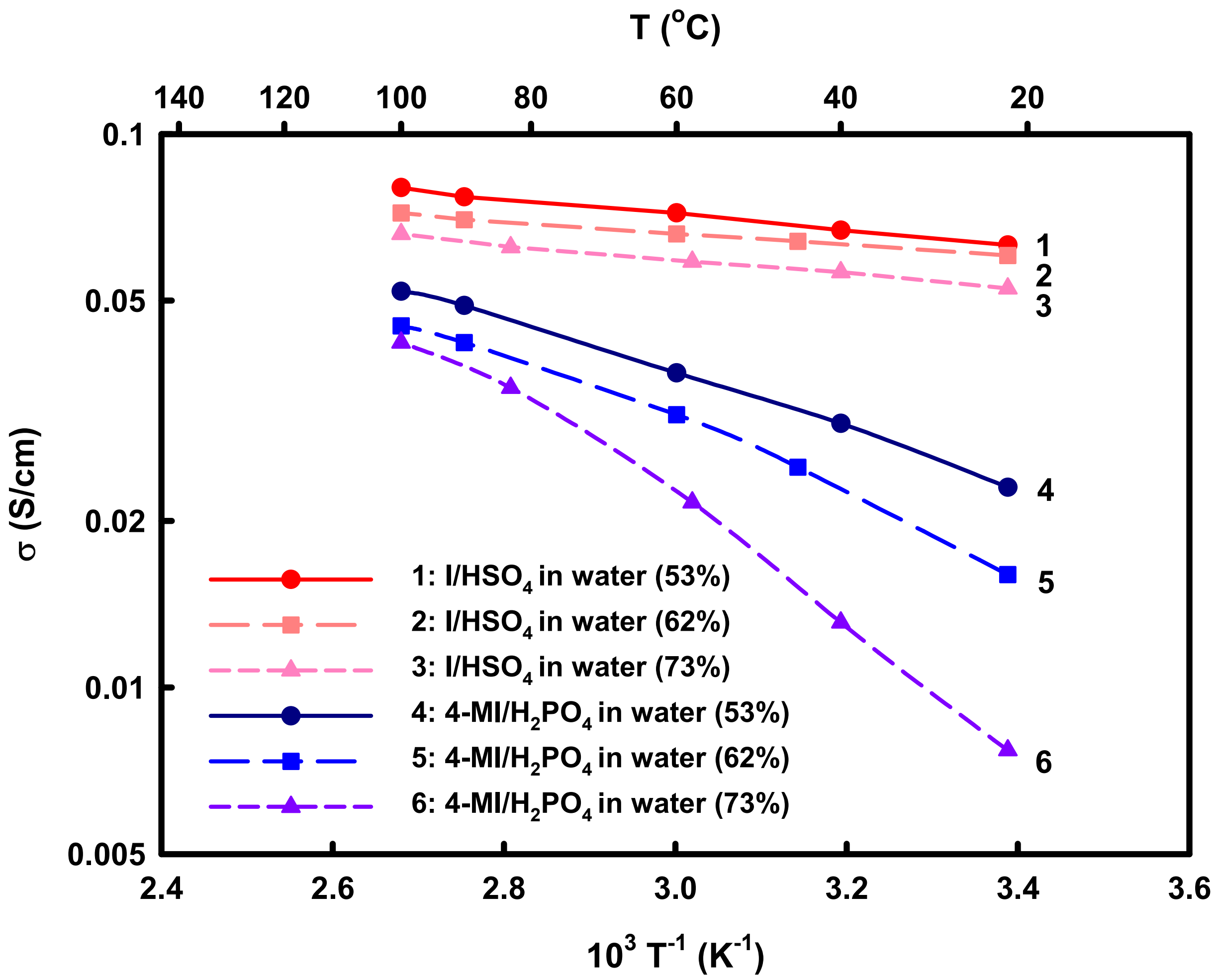
Melting Point

Imidazole Cation	Counterion	Melting Point (°C)
	$H_2PO_4^-$	124-126
	HSO_4^-	<100
	$B(OH)_3$ (1:1 mixture)	60 softening
	$H_2PO_4^-$	157-159
	$H_2PO_4^-$	134-136
	$H_2PO_4^-$	132-135

Conductivity of 4 test materials

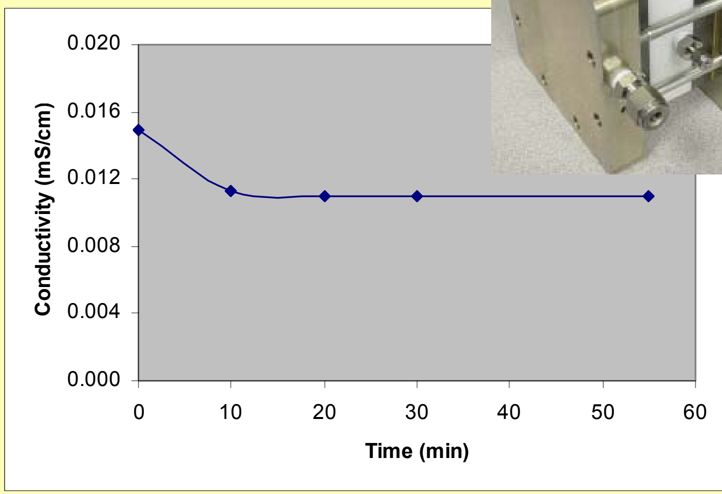


Influence of water content on conductivity



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

Hydrogen Pump



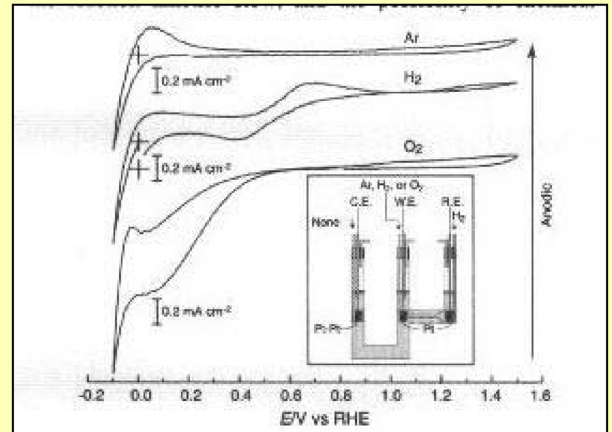


Fig. 1 Cyclic voltammograms for Im/HTFSI neutral salt at 130 °C. The crosses correspond to 'zero' current at the potential of 0 V. Scan rate is 50 mV s^{-1}. W.E. is a Pt-wire in Ar, H_2 or O_2 atmosphere, C.E. is a Pt-black wire in H_2 atmosphere and R.E. is a Pt-wire in H_2 atmosphere. Inset shows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

Chem. Commun., 2003, 938-939.

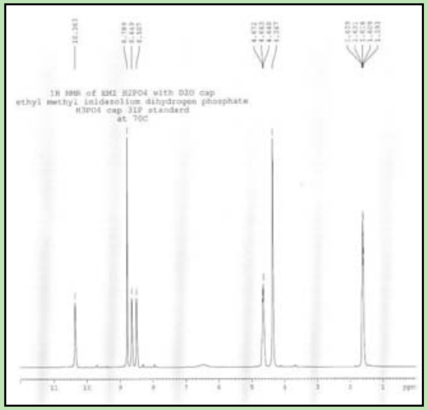
Conductivity of EMI/H2PO4 under hydrogen pump

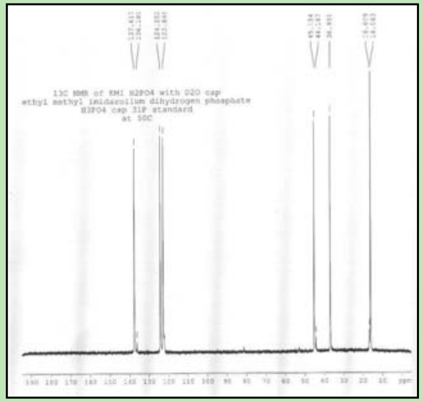
ac conductivity -> 5 mS/cm (400x)

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

NMR Data

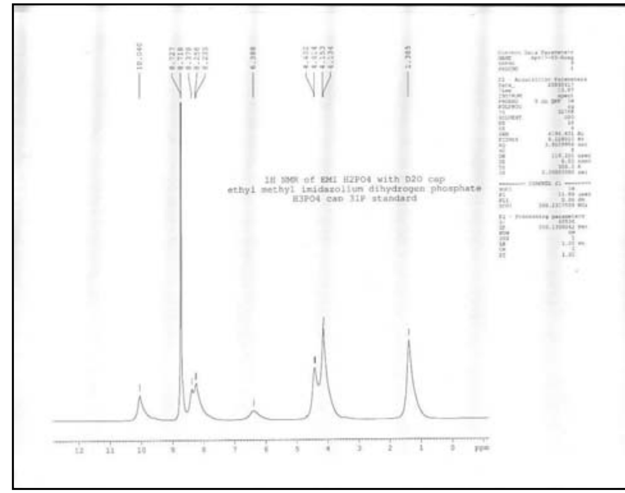
^{1}H and ^{13}C NMR

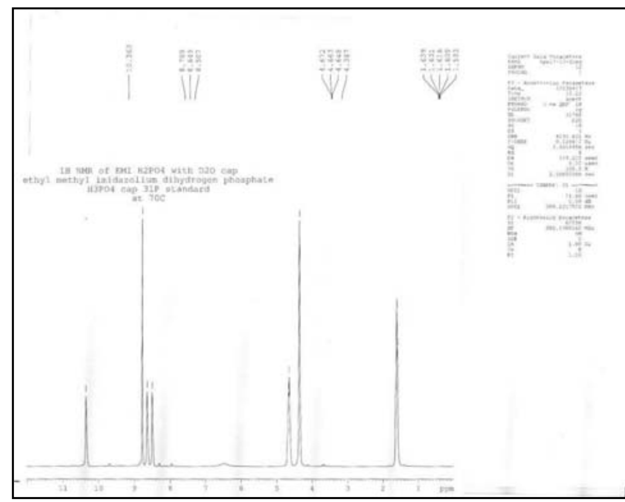




- We have used ^{31}P, ^{13}C and ^{1}H NMR to look at to characterize the ionic liquids we have synthesized (EMI/H_2PO_4 and EMI/HSO_4). We have confirmed purity by comparing to literature spectra*.

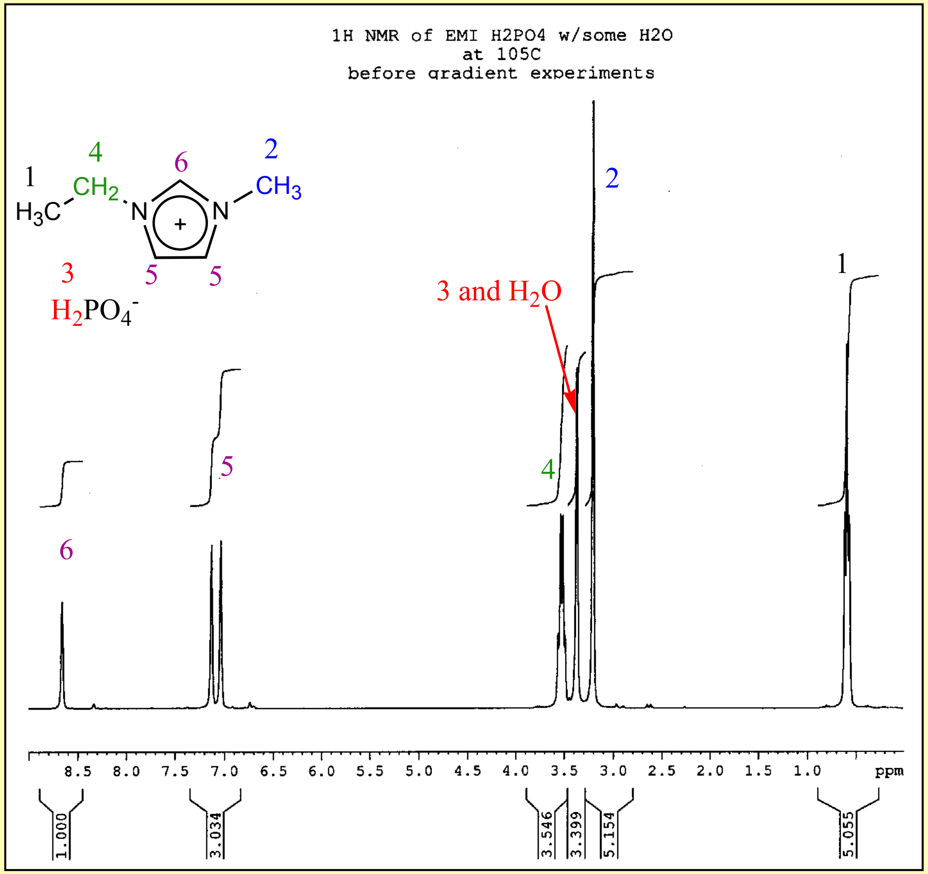
*W. Keim et. al., 2000; International Patent # WO 00/16902





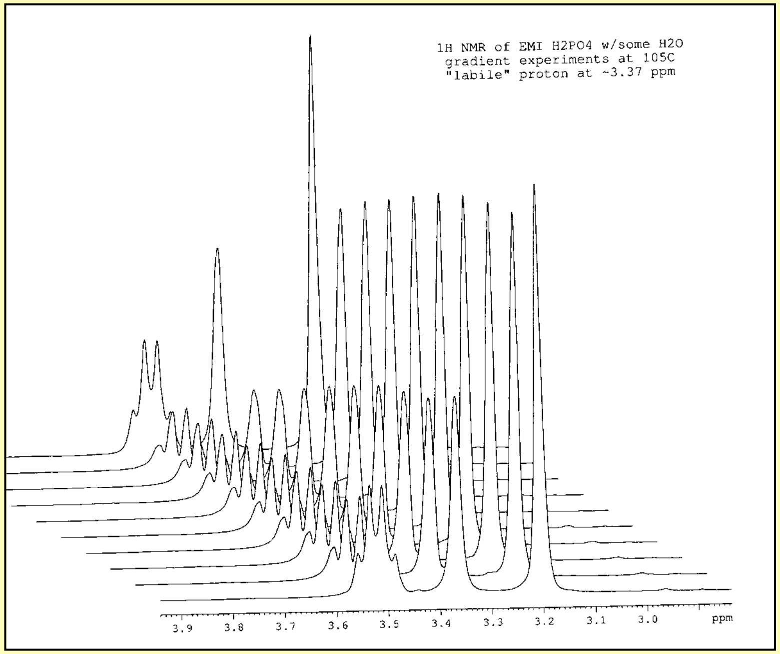
^{1}H NMR shows significant differences in spectra at 50C and 70C for EMI/H_2PO_4 related to the mobility of species.

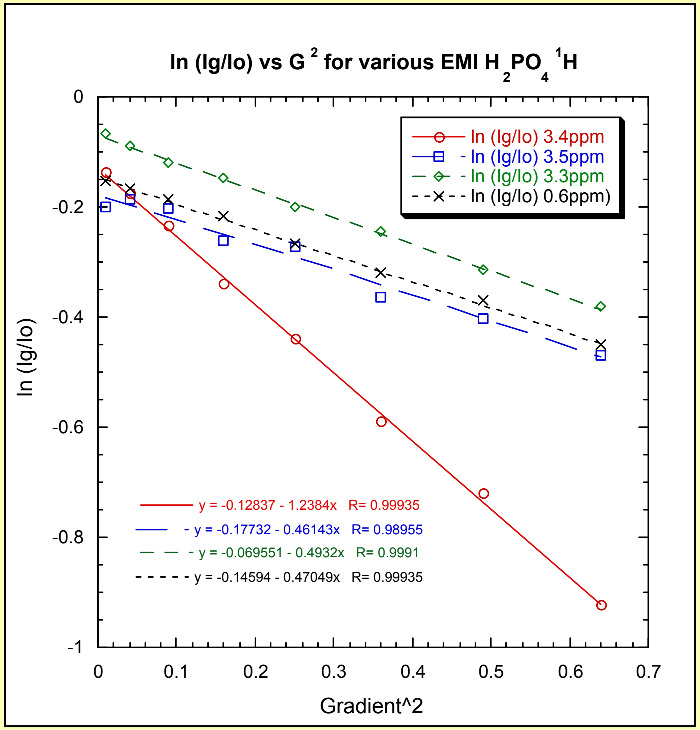
EMI-H_2PO_4 ^1H NMR Spectra



Sample contained traces of water (few mol%) from contact with air

^{1}H PFG SE NMR for Diffusion



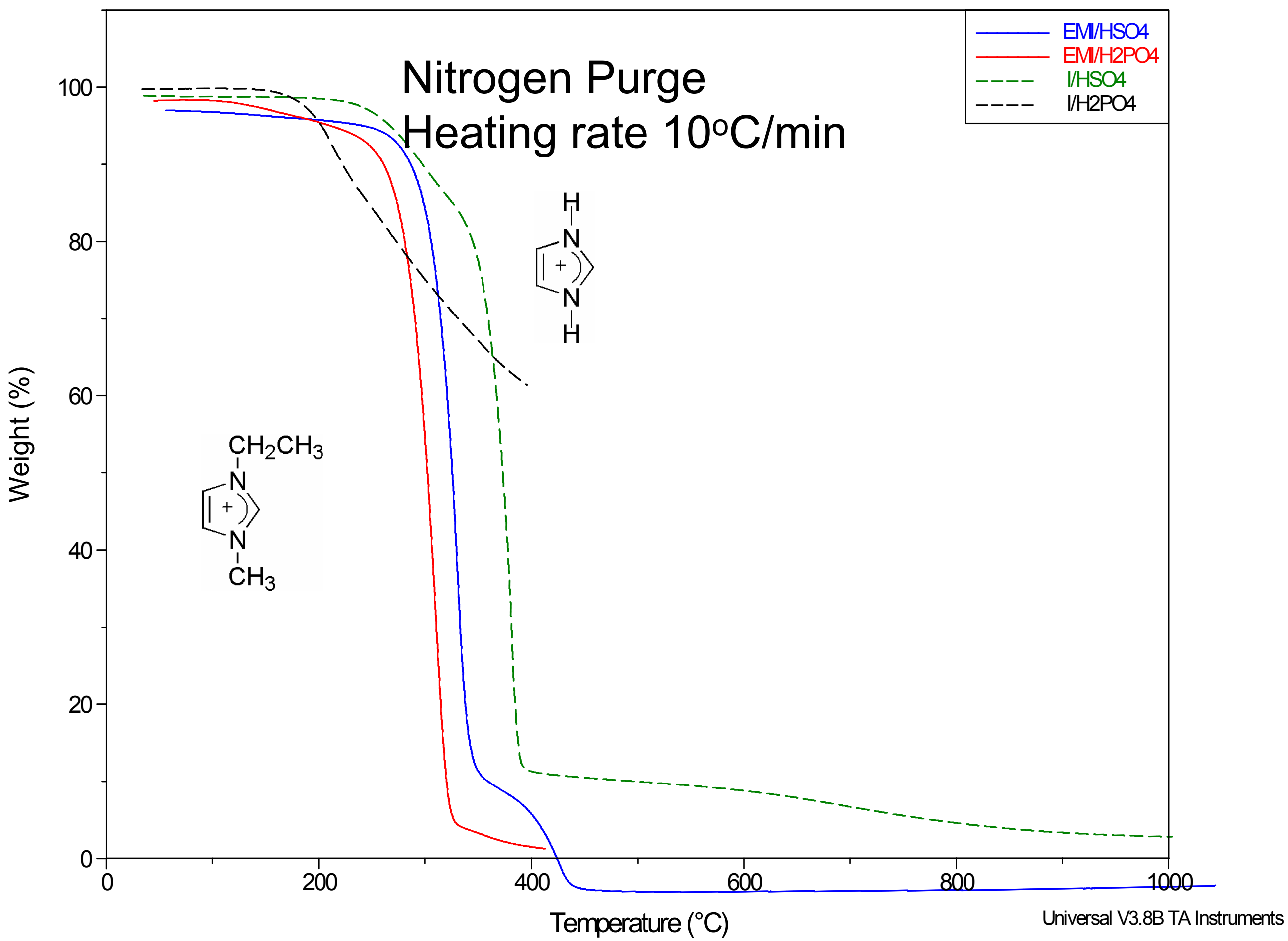


ln(Ig/Io) = -[γ2 δ2 G2 (Δ - δ/3)] D

$D_{acid} = 1.4 \times 10^{-5}$ 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

Effect of Acid Counterion on Thermal Stability of Imidazolium Salts



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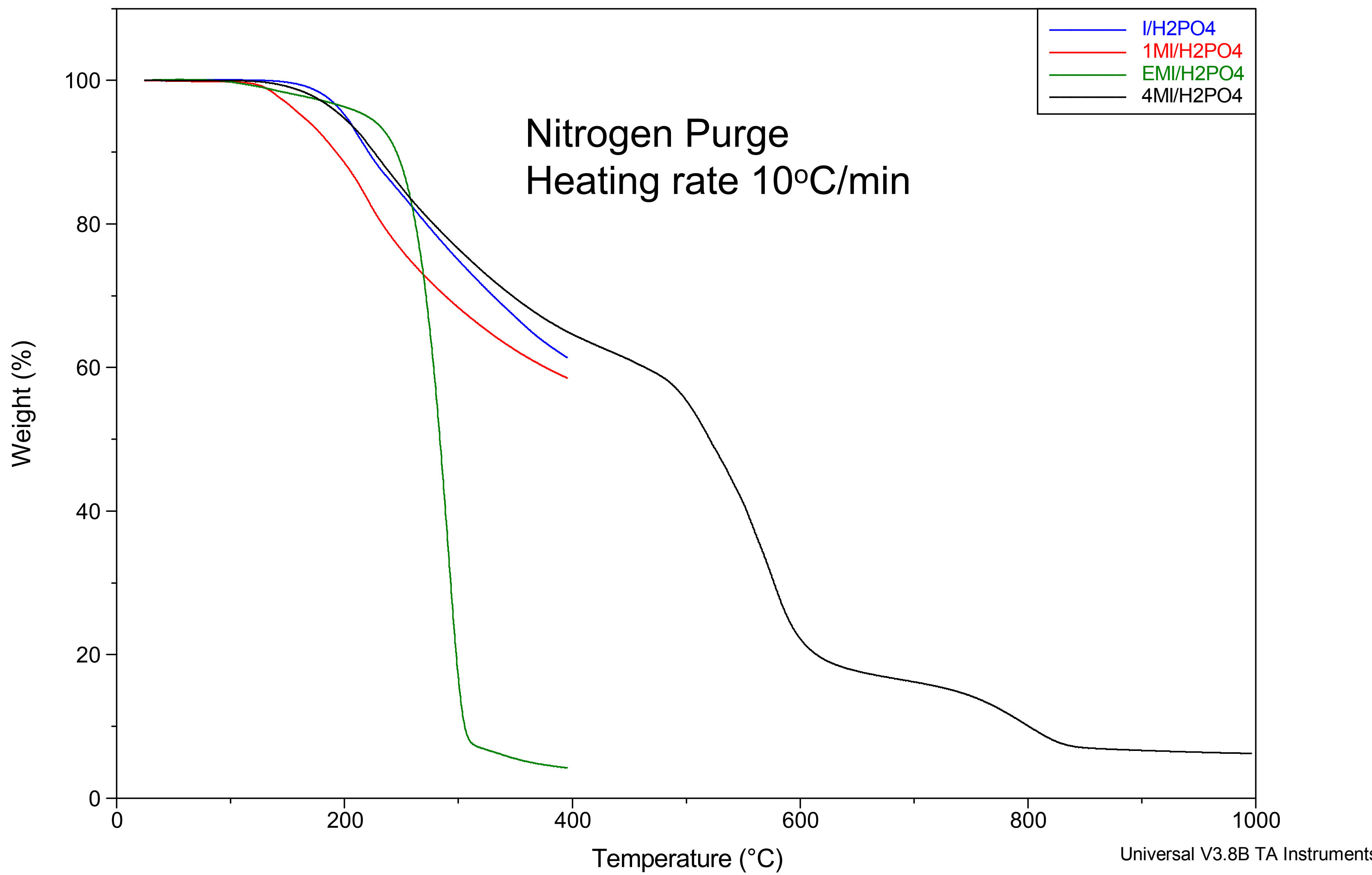
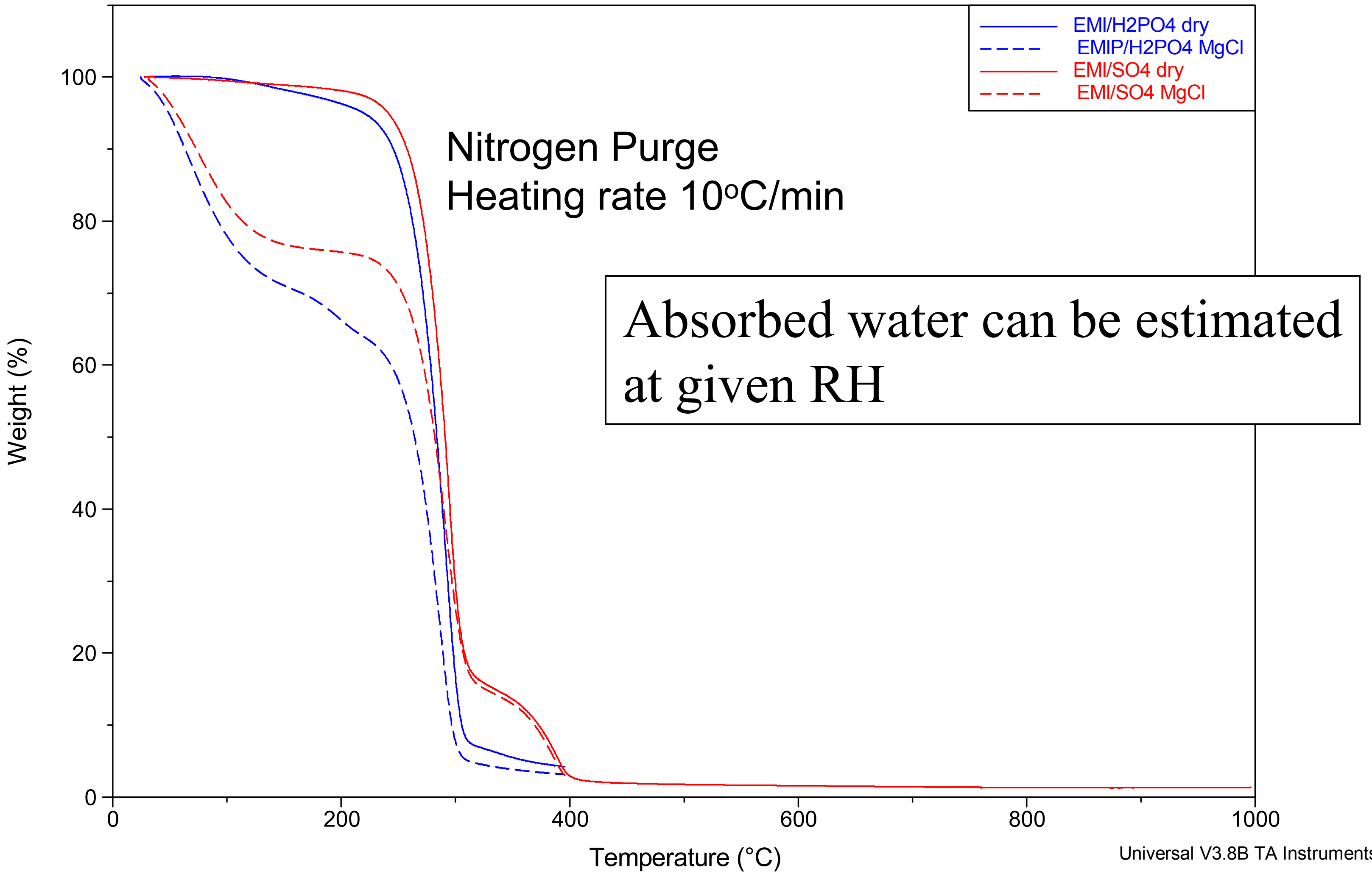
Effect of Imadozole Substituents on Thermal Stability of Phosphonium Salts or TGA of Phosphonium Salts

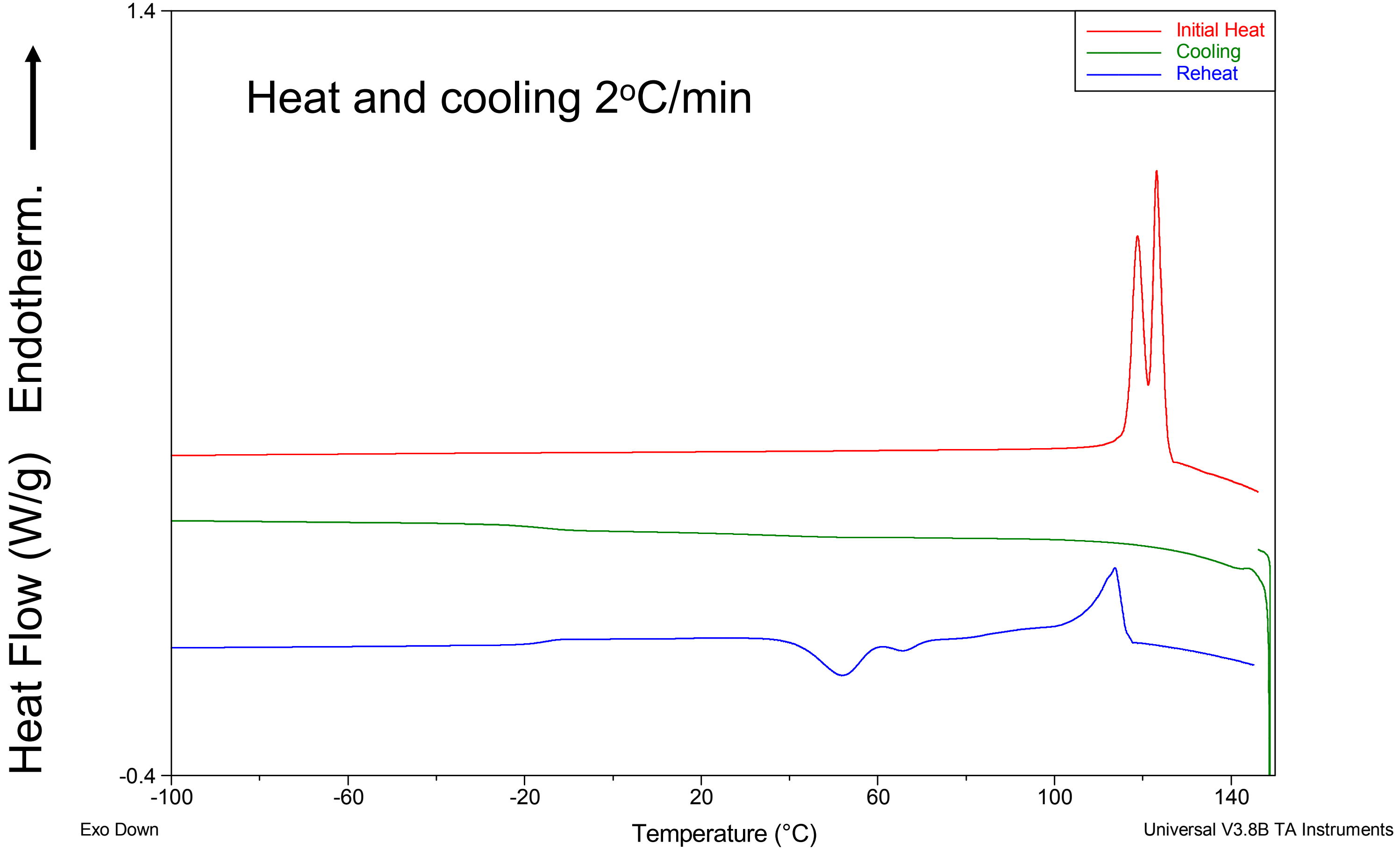


Effect of Water on Thermal Stability of EMI Salts



Absorbed water can be estimated at given RH

Effect of Thermal History on I/H_2PO_4 (3BO31I)

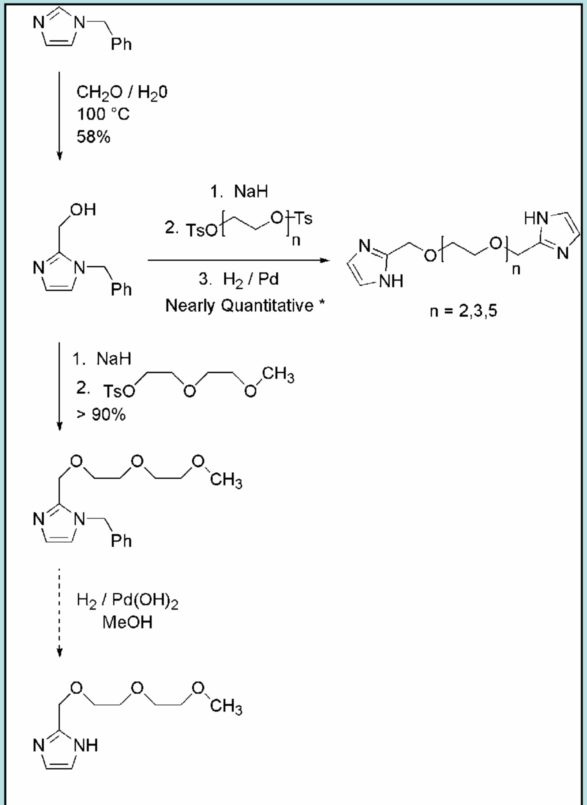


Summary of DSC Results

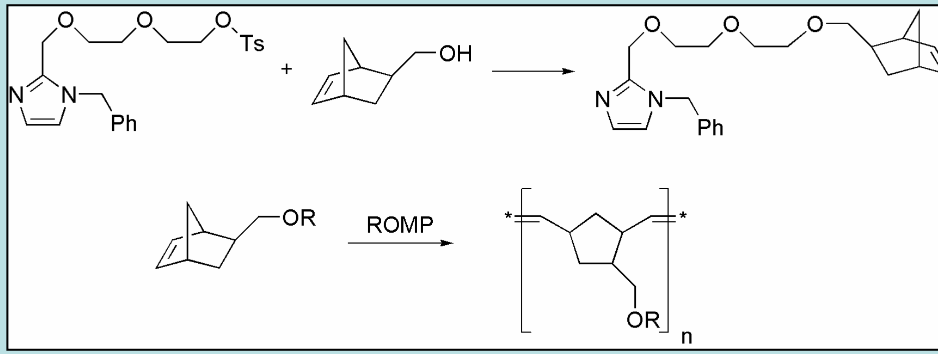
Sample	Texture	Tg (^{o}C)	Tm (^{o}C)	Rate of Xtal	Heat of Fusion (J/g)
I/HSO_4	Semisolid	-70	32	Slow	13
I/H_2PO_4	Xtals	-16	114	Slow	53
EMI/HSO_4	Semisolid	-60	66	Moderate	42
EMI/H_2PO_4	Waxy	-58	68	Moderate	45
1MI/H_2PO_4	Powder	N/A	134	Fast	140
4MI/H_2PO_4	Semisolid	-22	113	Moderate	59

LANL HTMWG Synthesis

Polymer Route



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



Ether precursor can be easily incorporated into polymers like pnb for example

Summary and Conclusions

- Proton conductivity at low humidity is the problem.
- Future work includes using AC impedance and NMR to measure proton mobility/ conductivity as a function of temperature, water content, the presence of additional ‘free’ acid or imidazole and varying imidazole chemistry.
- An improved understanding of proton conduction is necessary for engineering materials with the required properties.