High Temperature/Low Humidity Polymer Electrolytes Derived from Ionic Liquids

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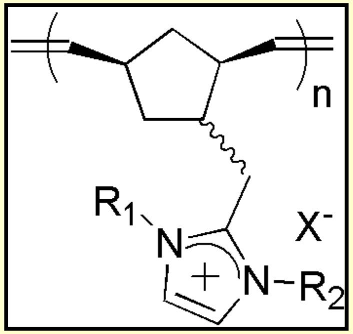
LANL Approach

- Investigate polymer immobilized exchangeable proton containing ionic liquids with imidazolium cations and dihydrogen phosphate ($H_2PO_4^-$) or bisulfate (HSO_4^-) anions capable of proton conduction (hopping candidates).

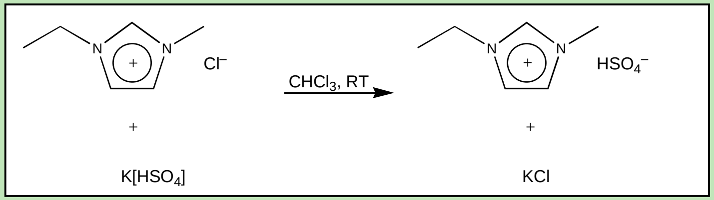
- Advantages of ionic liquids are
  - Thermally stable (up to 300 ˚C)
  - Stable to oxidation and reduction
  - Essentially no vapor pressure
  - High intrinsic ionic conductivity



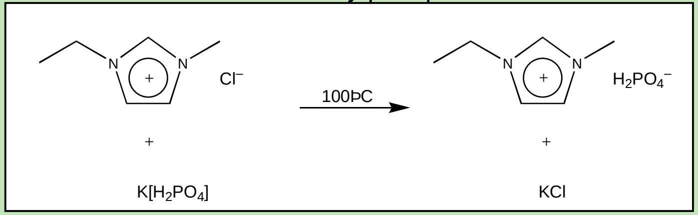
- Investigate conduction limits of these materials, incorporate the most promising candidates into polymeric materials.

Acid-Imidazole Pairs

Ionic Liquids



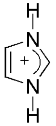
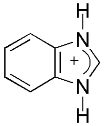
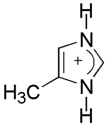
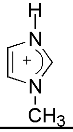
- Mixture is filtered to eliminate bulk of KCl
- Residual KCl removed by precipitation from chloroform



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

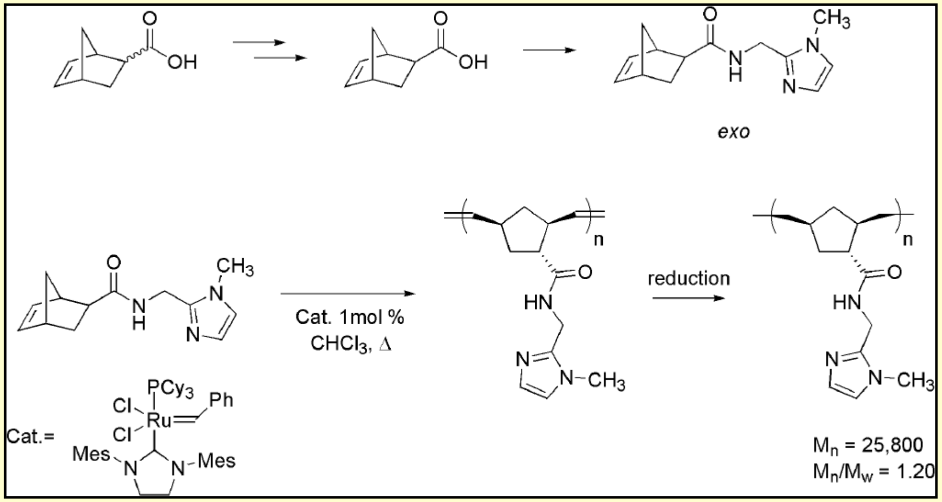
Ethyl Methyl Imidazolium (EMI) Salts

- ‘Free’ proton containing acid-imidazole pairs synthesized
- Pairs characterized in terms of properties (melting point, conductivity, stability, etc.)

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

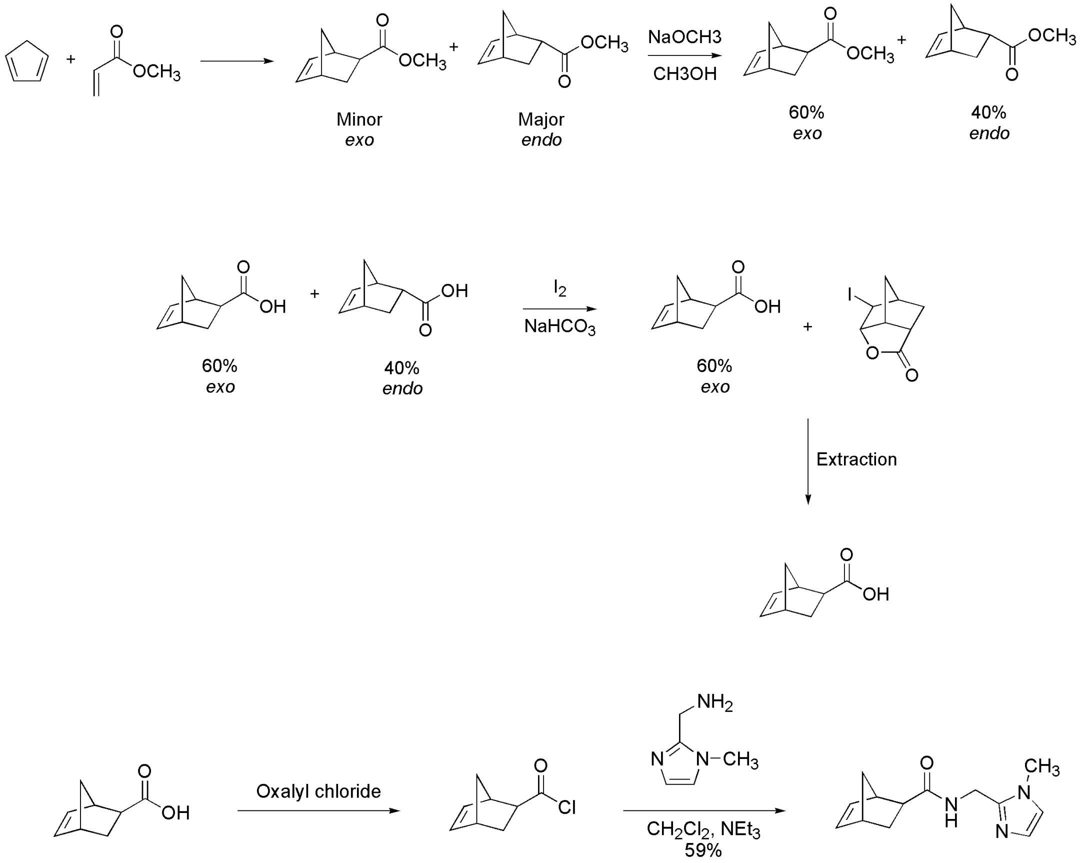
Why use Polynorbornenes?

- Well defined polymers – low polydispersity
- Easy to make block copolymers by ROMP mechanism
- Readily available catalysts
- Monomers can be functionalized with little difficulty



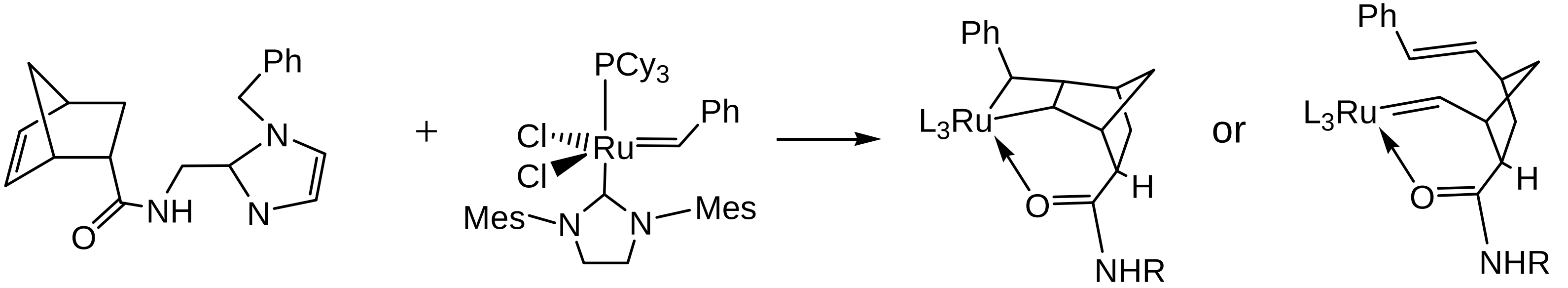
While chemical stability of backbone needs to be studied, this architecture allows us to study performance in well controlled morphologies with target functionality.

Synthesis of exo Monomers

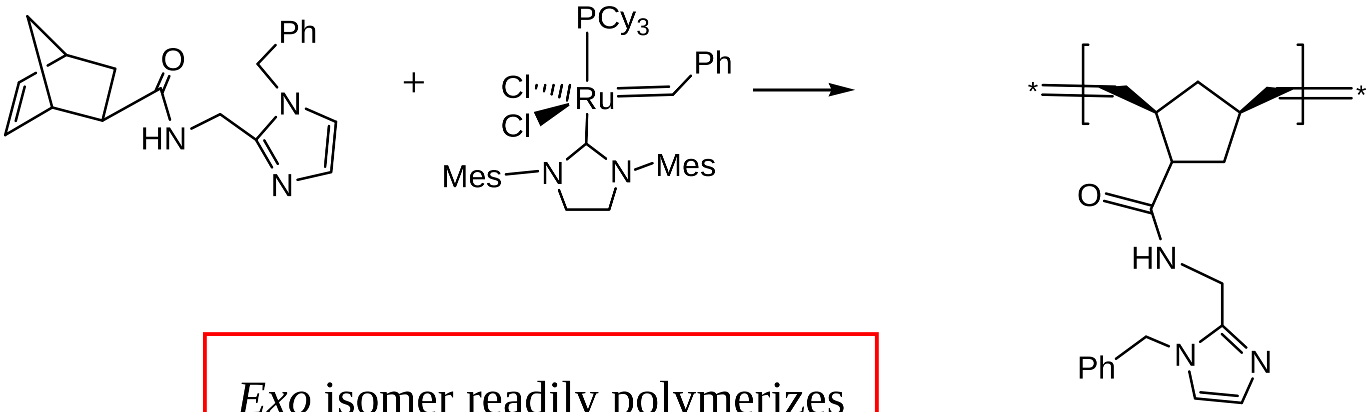


- Synthesis of poly-norbornene was limited by the endo isomer
- The exo isomer was isolated
- The exo isomer can then be functionalized to give a monomer that yields reasonable molecular weight polymer
- Reaching this step took significant effort

Amide Complexation of Ruthenium

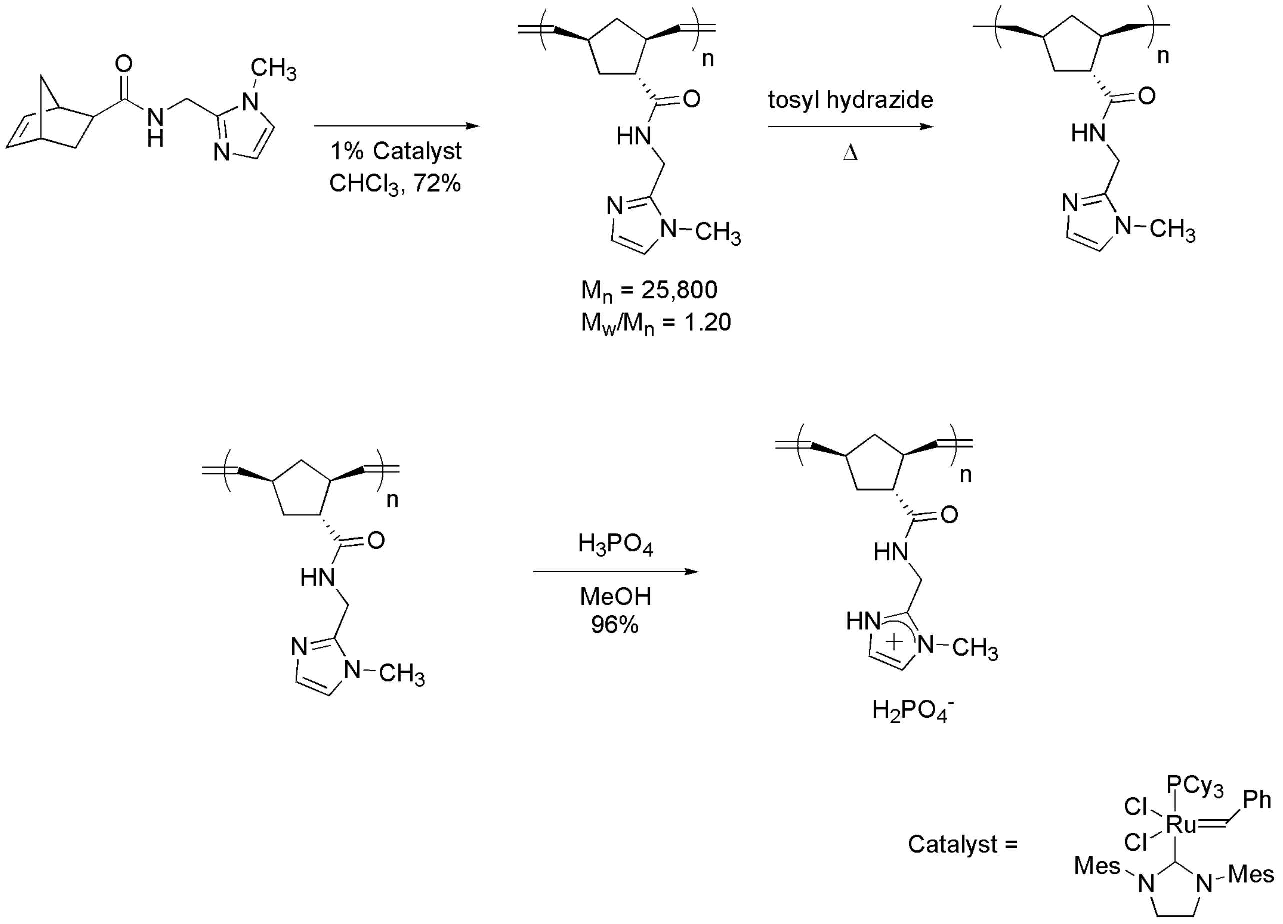


Chelation by *endo* isomer prevents polymerization



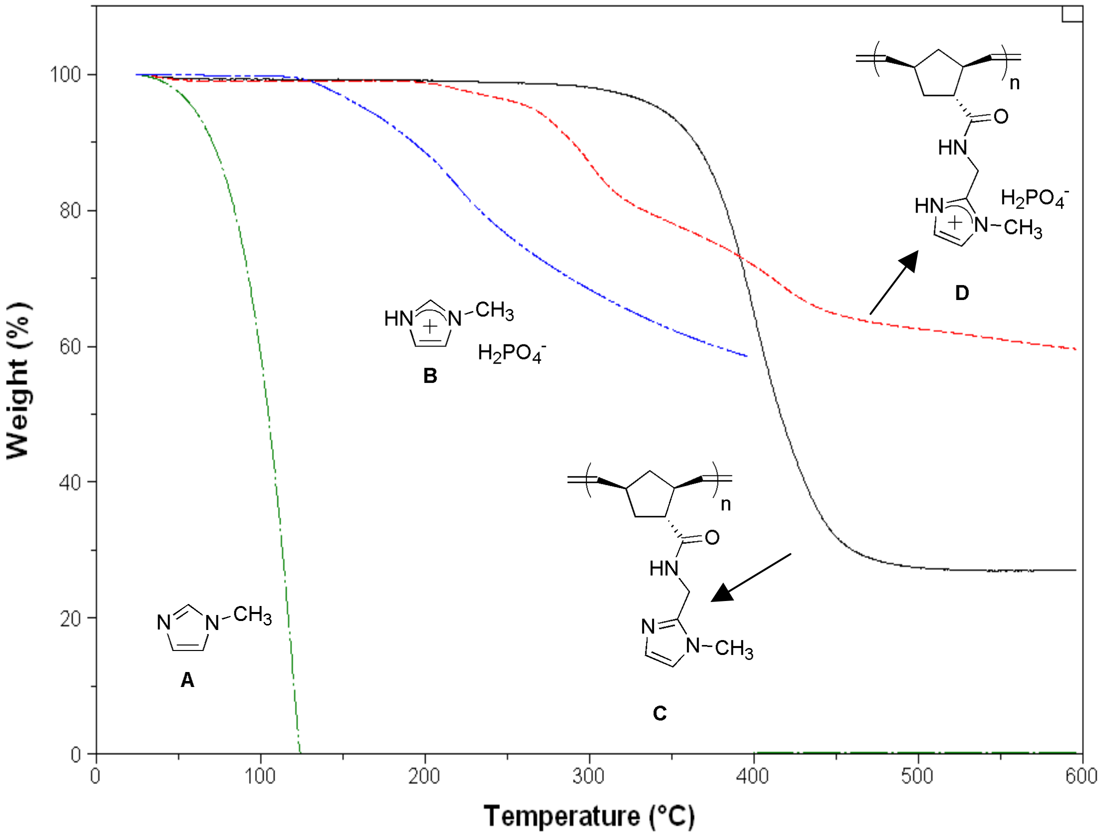
Exo isomer readily polymerizes

Norbornene Polymerization



- We have synthesized polymers of reasonable molecular weight and film casting properties
- Very few polymer chemistries have been explored (copolymers, density or type of functional groups, etc.)

Thermal Analysis



- Methyl imidazole evaporates at low T (30˚C)
- Methyl imidazole – dihydrogen phosphate shows mass loss at moderate T (150˚C)
- Polymer analogues show good temperature stability to at least 200˚C for the acid analogue, 300˚C for neutral polymer

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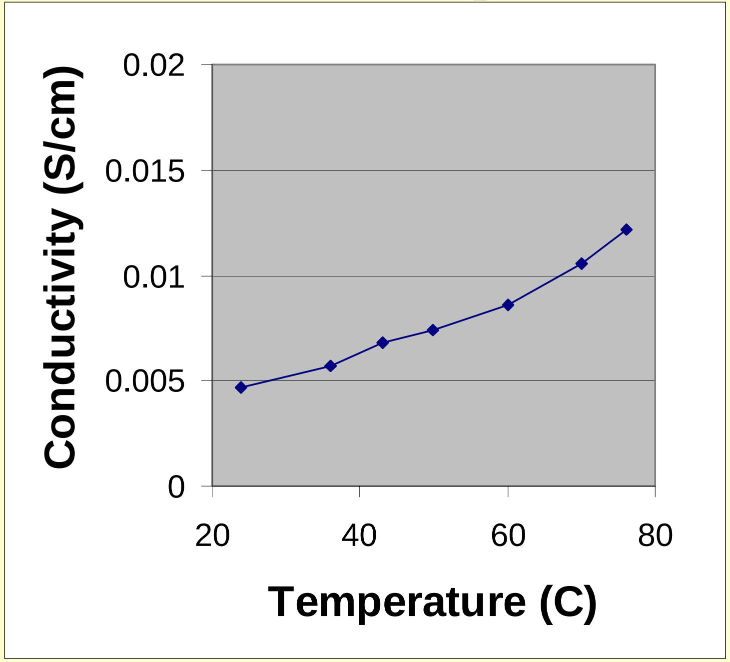
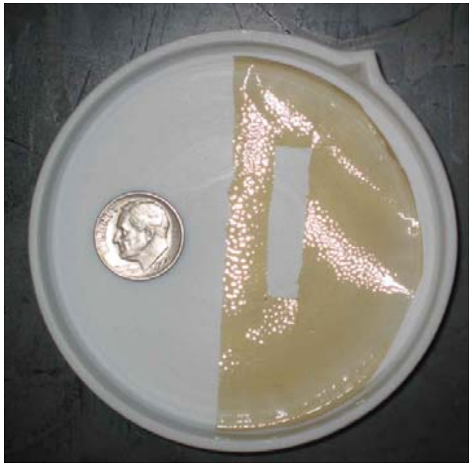
Hydrated Membrane Conductivity

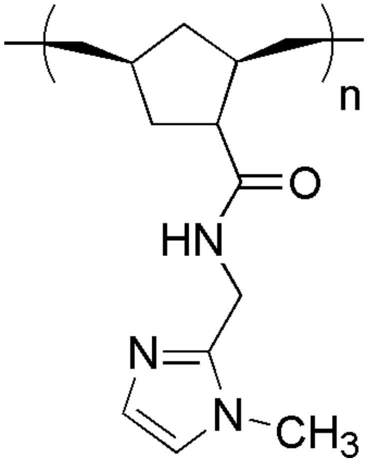
<u>AC Impedance Spectroscopy</u>

PNBA-2-MI in liquid water



- Initial tests showed surprisingly high conductivity, albeit far below Nafion. Further work needs to be done to verify these results.

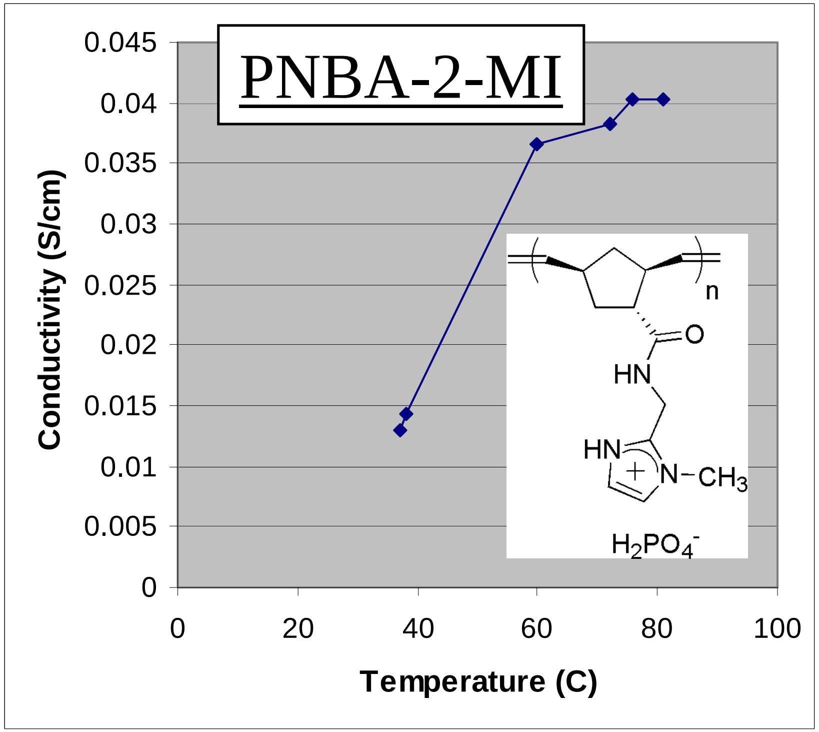


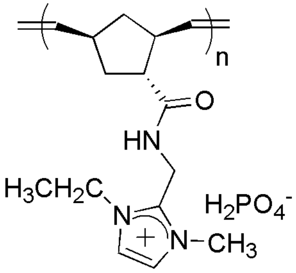


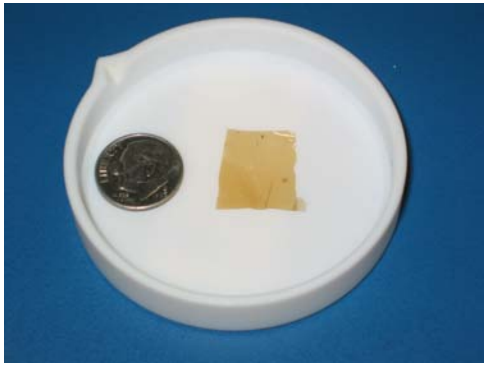
water uptake is high (45%) and this particular membrane is water soluble when doped with acid.

PNBA-2-MI poly-dihydro(norbornene-2-carboxy-N-(1-methyl-1H-imidazol-2-ylmethyl)-amide)

Membrane Conductivity Dependence on Water Content







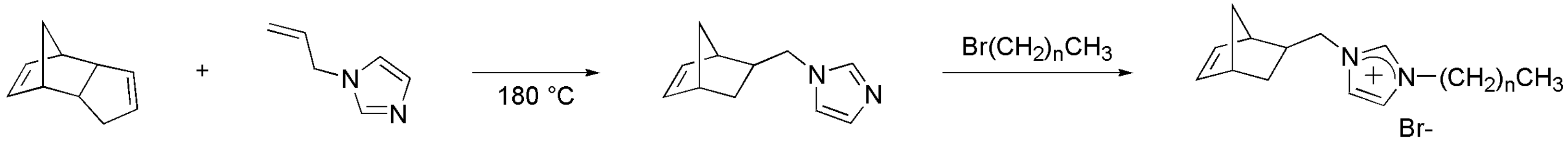
PNBA-2E5MI

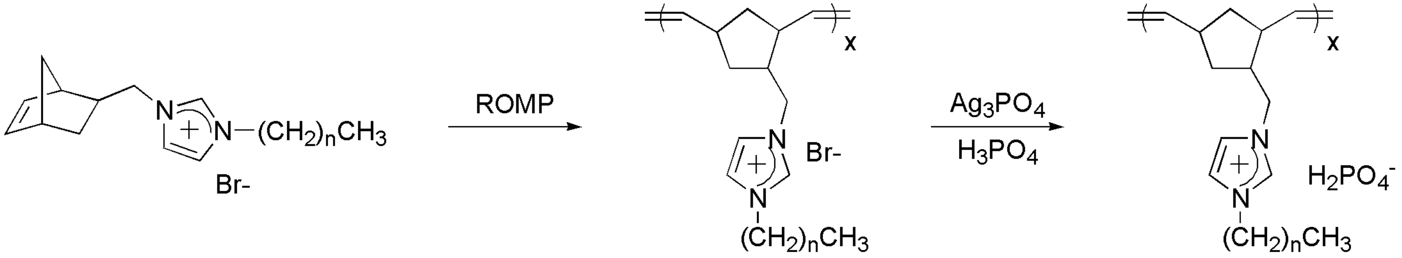
Conductivity (90˚C)	Relative Humidity
0.035 S/cm	10%
0.047 S/cm	25%

- PNBA-2-MI phosphate is water soluble, but shows reasonable conductivity even in the dry state
- The role of the phosphate anion and proton in conduction needs to be clarified

- PNBA-2E5MI is the ethylated version of PNBA-2-MI and is also water soluble, but likewise shows reasonable conductivity at low RH

Next Generation Norbornene Polymers

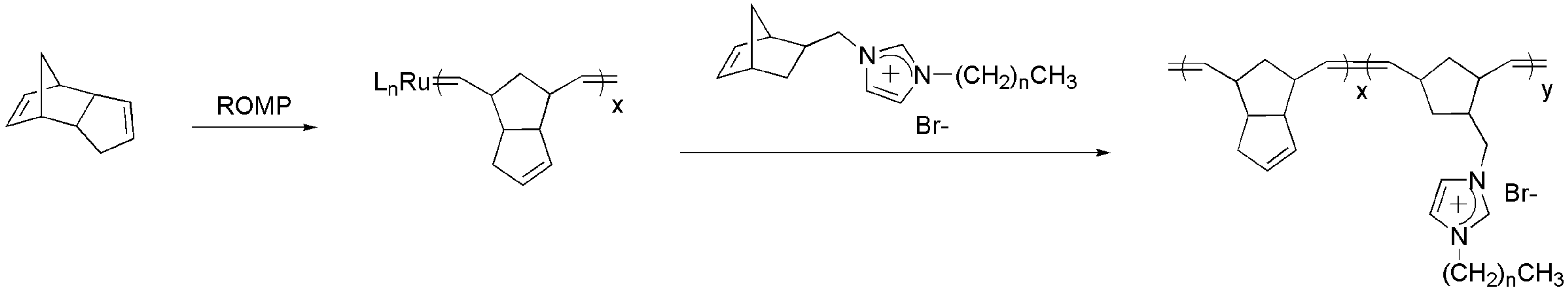


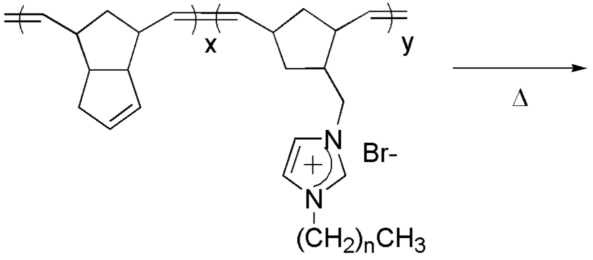


Insouluble in water

Soluble in water

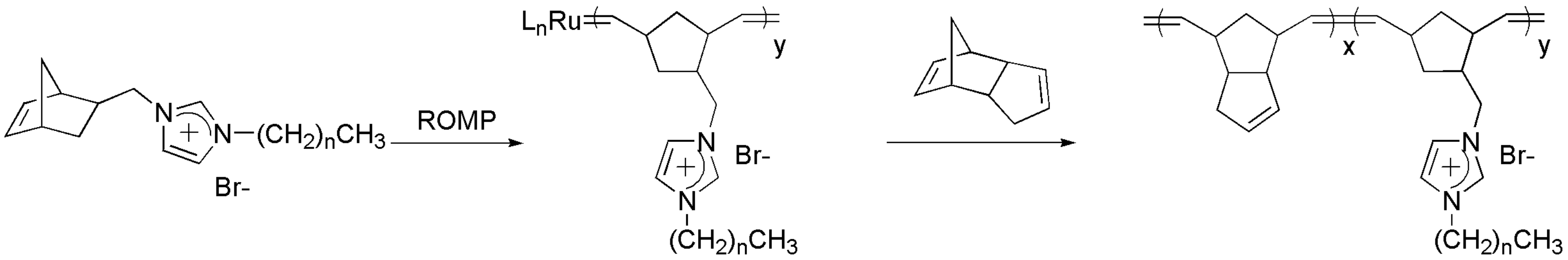
Block Copolymers



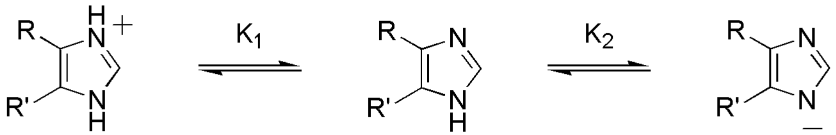


Extensive Crosslinking

"Brick Dust"



pKa's of Substituted Imidazoles

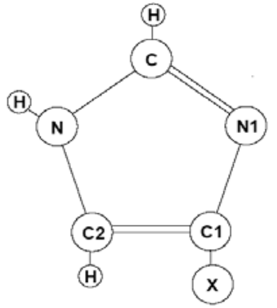


R	R'	pK_{a1}	pK_{a2}
CH_3	H	7.45	>15**
H	H	6.95	15
Br	H	3.7	11*
Cl	H	2.9*	11*
NO_2	H	1.5	9.1
Cl	Cl	<1** <1**	8*
CN	CN		6*

* Values are calculated using Advanced Chemistry Development (ACD/Labs) Software Solaris V4.67 (© 1994-2005 ACD/Labs)

** Estimated values.

Ab-initio pK_{a1} calculations



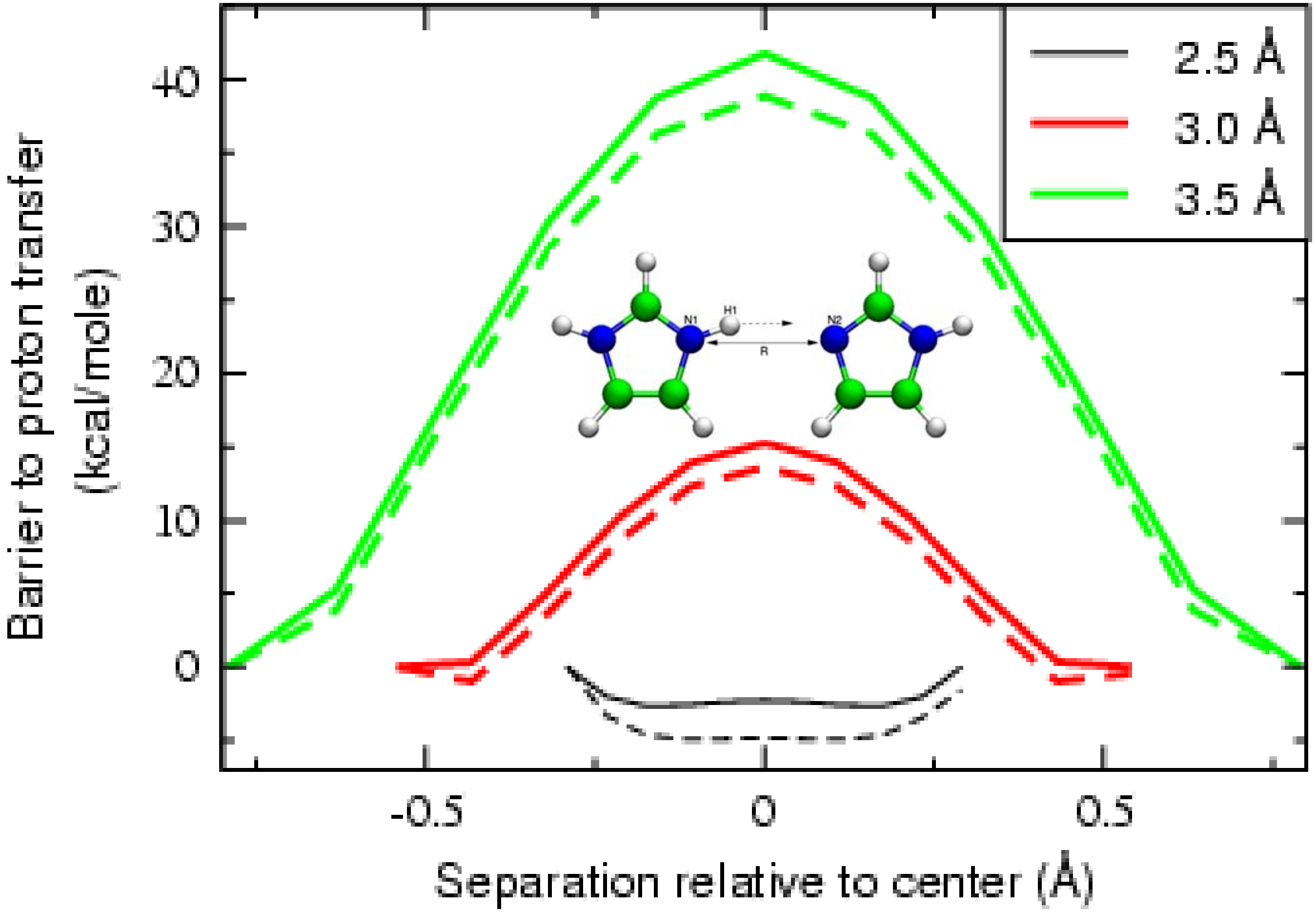
Mono-substituted

X	ΔG_{gas}	$\Delta\mu$	ΔpK_a
H	0.0	0.0	0.0
$-OCH_3$	-2.2	-4.3	-4.8
$-F$	-11.2	0.8	-7.6
$-CN$	-15.6	1.4	-10.4
$-NO_2$	-18.6	0.7	-13.2

Depending on chemical substitution and contacting solution imidazoles can be used to span pH ranges from very acidic to very basic.

Model calculations show expected trends with substitution; however, pKa values are notoriously difficult to predict using quantum mechanics.

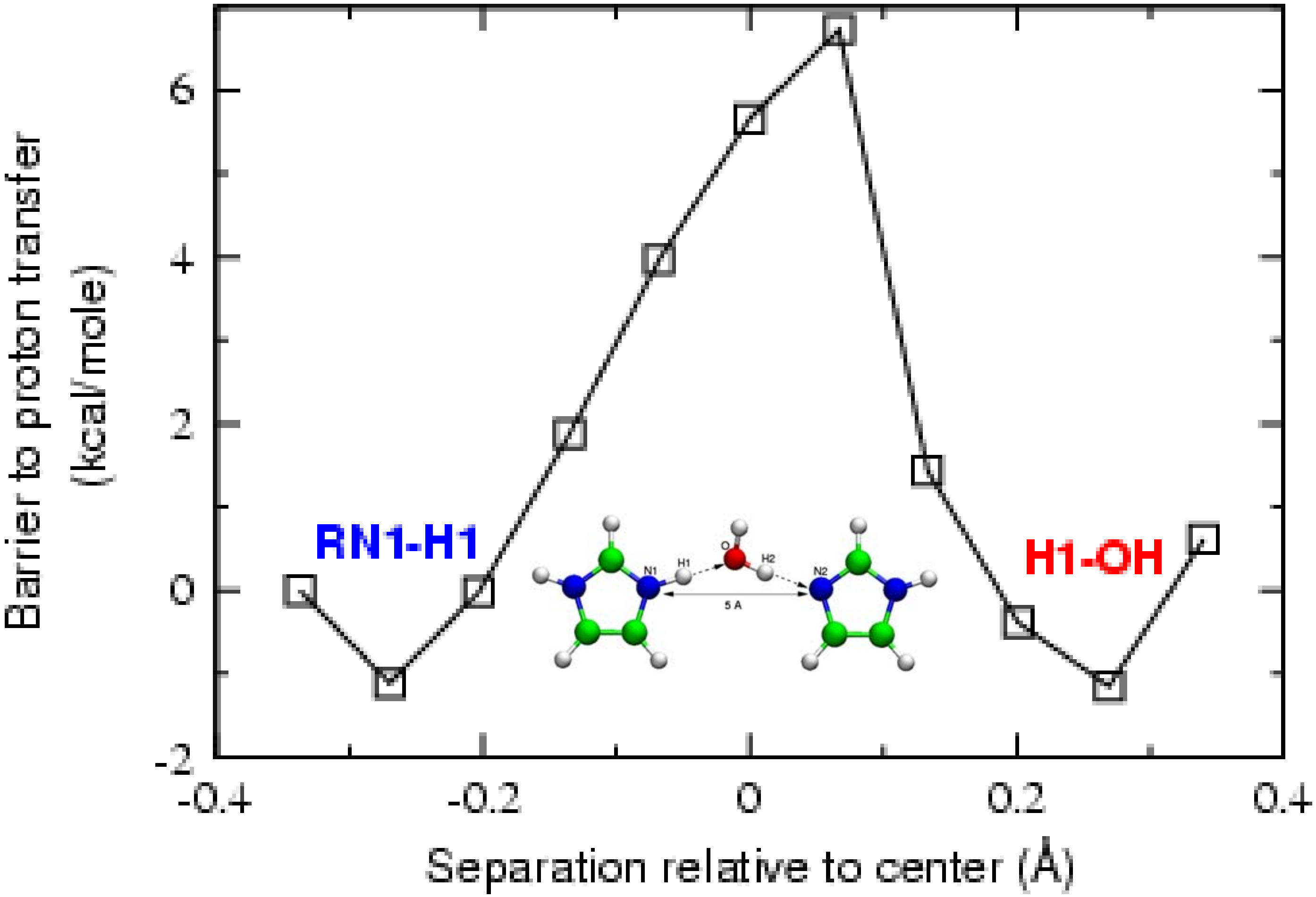
Proton Transport in Imidazoles



Dashed lines indicate barrier To proton transfer in water

E

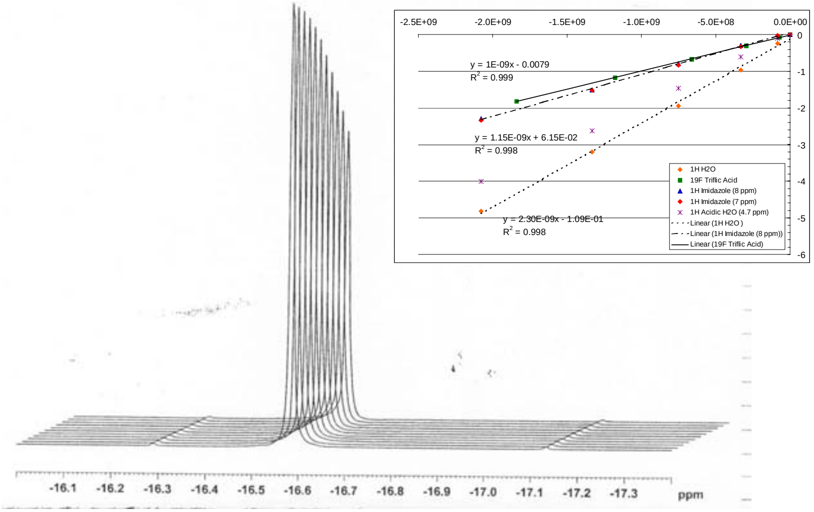
Proton Transport in Imidazoles



Including one H_2O molecule lowers the barrier to *ca.* 6.4 kcal/mol at an N-N distance of 5Å.

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^{o}C) 65 (at 30^{o}C) [80 (at 30^{o}C)]
2 M imidazole imidazole 1 M CF_3SO_3H in H_2O	~ 8	68 (at 22^{o}C) 79 (at 30^{o}C)

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

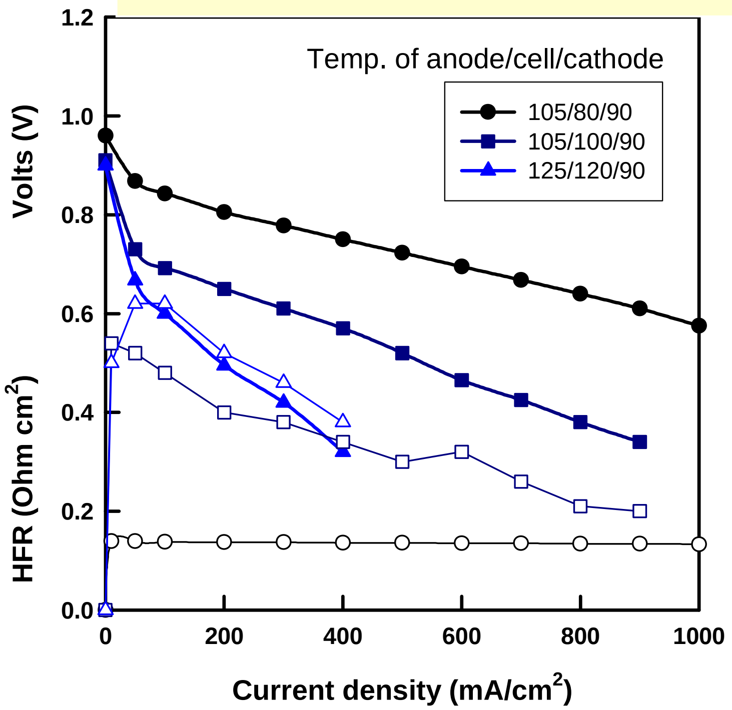
$D_{\text{Imidazole from H-1}} = 1.15 \times 10^{-5}\ cm^2/s$

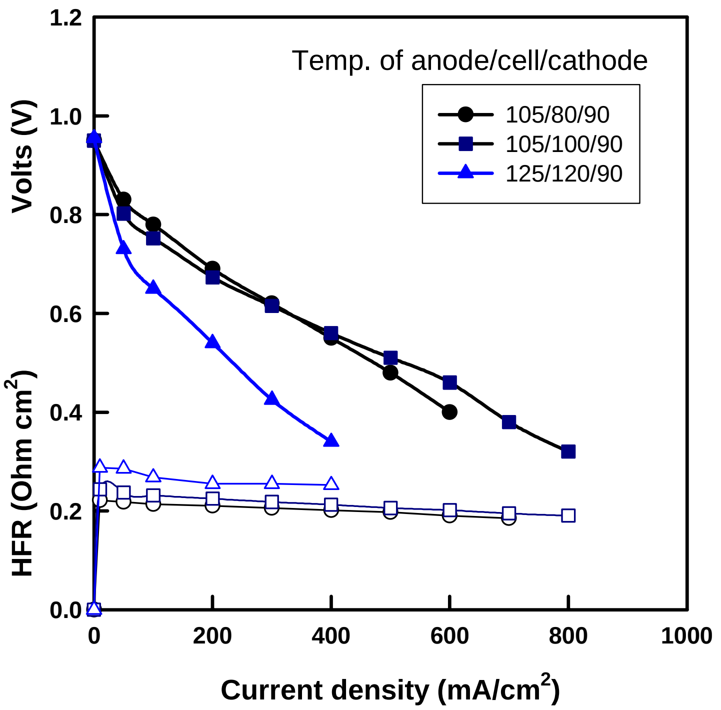
Work investigating higher pH electrolytes is very preliminary. Areas of future investigation include: effects of D_2O versus H_2O, higher concentration imidazole solutions, strongly basic buffered solutions, and substituted imidazoles.

Summary and Conclusions

- Imidazole-acid pairs show reasonable conductivity and stability at high temperatures and low humidity.
- We have successfully synthesized and characterized norbornene tethered ionic liquid analogs.
- The conductivity of the ionomers is encouraging.
- While water solubility is a concern, this can be mitigated by block co-polymer synthesis.
- The role of the anion versus the proton in ion conduction needs to be elucidated.

Novel MEAs for High T





Novel MEA
slightly better performance at 120ºC with stable HFR

Catalyst: carbon supported
Pt 0.2 mg/cm^2 on both electrodes
Back pressure: 20 psig on both electrodes
High H_2/air stoic.

Use of Microelectrodes to Study Effects of Humidification on Oxygen Reduction

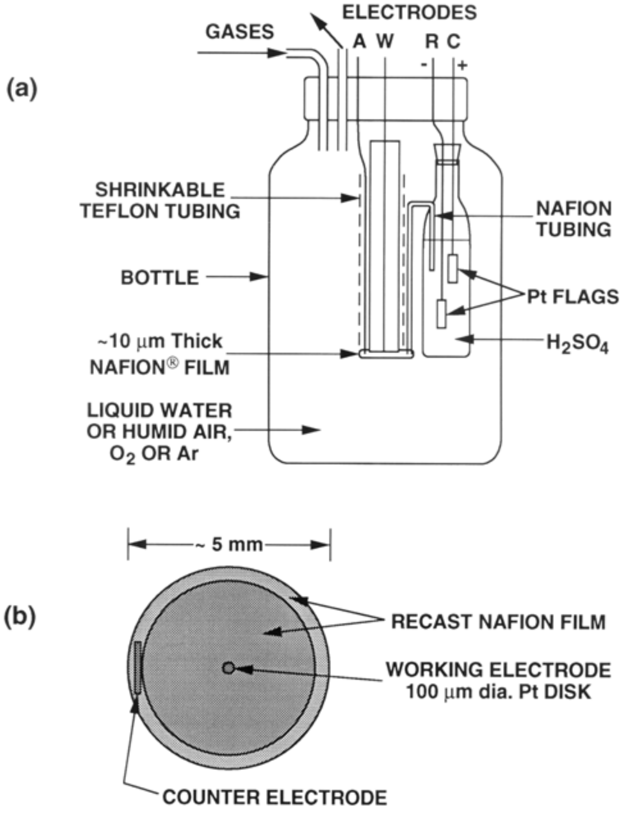
During our earlier study we demonstrated a difference in oxygen reduction between liquid and saturated vapor water (F.A.Uribe et al, J. Electrochem. Soc, 139 (1992) 765).

Here we extend this work to include humidity levels lower than 100%

Modifications of the experimental setup and conditions:

- Oxygen delivered to the minicell through two bubblers containing inert salt solutions or water and through the layer of the respective solution on the bottom of the minicell chamber
- Conventional hydrogen electrode utilizing “forming” gas (6% H_2, 94% Ar) and 0.5 M H_2SO_4 used as a reference
- Long equilibration times of the film with the gas phase water as opposed to direct film hydration (liquid water) followed by short equilibration times in the previous study
- Voltammograms recorded until a steady state electrochemical behavior was attained

Electrochemical minicell used in the previous study (minor alterations for current study)

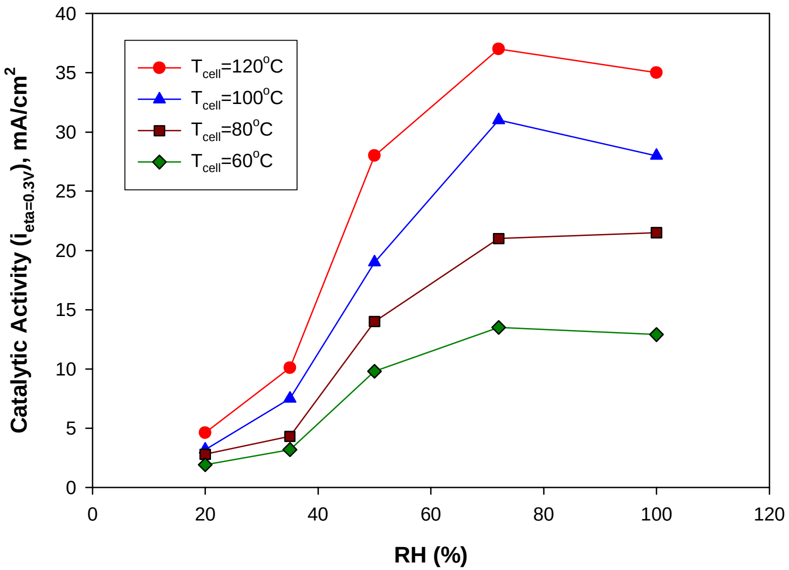


F.A.Uribe et al, J.Electrochem.Soc. 139(1992)765.

Water Influence on Oxygen Reduction (Thrust 3)

(Chlistunoff, Uribe, Pivovar)

- Our and other researchers recent and historic evidence suggest ORR might be influenced by water availability and/or activity.
- This has significant implications when it comes to low humidity operation of fuel cells and the development of higher conductivity low RH membranes.



“The Effect of Ionomer Properties on Oxygen Reduction Kinetics on

- Work by Yeager and coworkers and

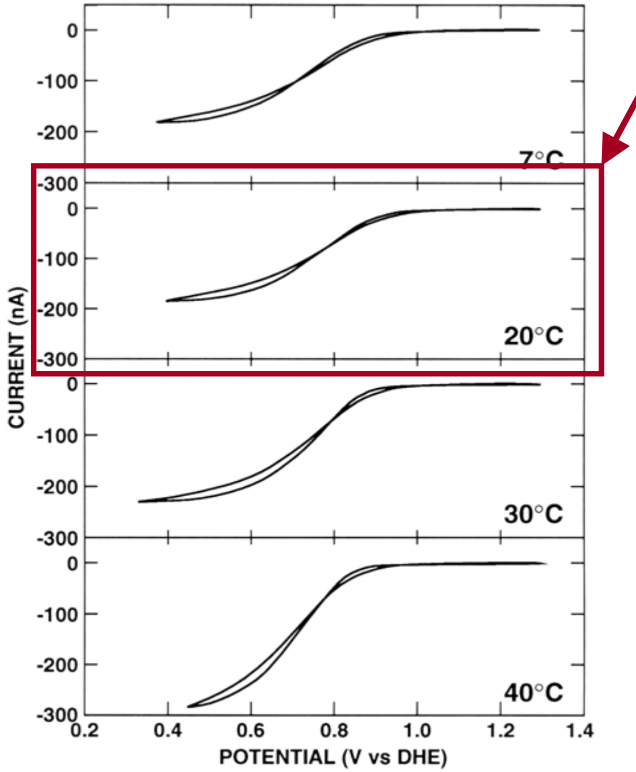
  adsorption effects (although the role of water activity on oxygen reduction was not dismissed).

H. Saffarian et al., J. Electrochem. Soc, 139 (1992) 2391.
M. Enayetullah et al., J. Appl Electrochem, 18 (1988) 763.

The Effect of Relative Humidity on Oxygen Reduction

Previous study

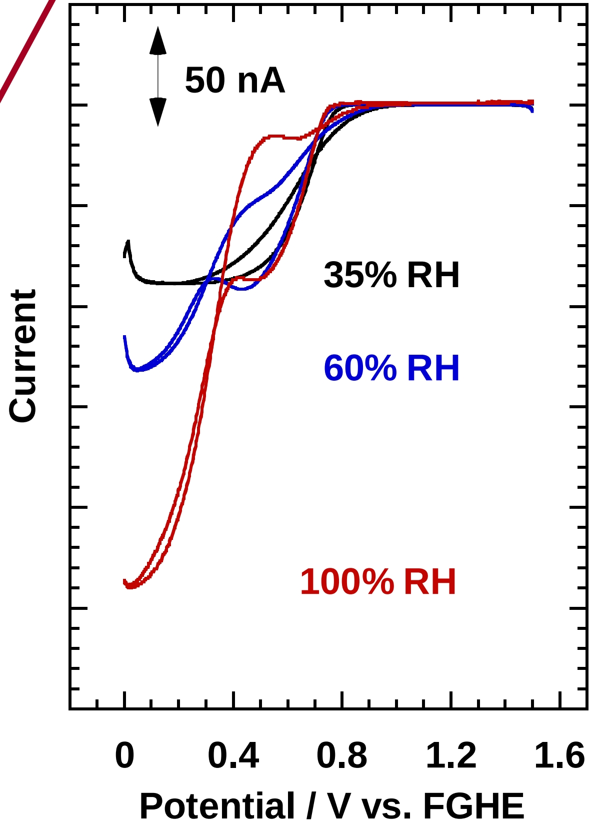
100% RH, direct film hydration



F.A.Uribe et al, J.Electrochem.Soc. 139(1992)765.

Current study

20ºC, long equilibration time



Complex mechanism of oxygen reduction

- Significantly different voltammetry at different relative humidity
- Oxygen reduction on platinum can occur at a high rate even when the Nafion film is strongly dehydrated
- Two mechanisms of ORR may be operating depending on the local Nafion hydration at its interface with platinum
- Stronger Nafion hydration seems to increase the contribution from the mechanism occurring at higher overvoltages