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14. ABSTRACT This report contains three sections (a)-(c) in which we report progress of the last year as follows. (a) The characterization of protic ionic liquids involving nitrogenous bases, by the state of the proton, as revealed by the N-H proton chemical shift, has been carried out and we show how this measure can be used to classify strong and superacids in a clear-cut manner. (b) The assembly and testing of fuel cells using derivatized siloxane membranes. Here we (i) take the polyanionic and polycationic siloxane membranes that we developed in the previous phase,					
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Report Title

Period of Performance: 04/01/2007 – present (07/15/08)

ABSTRACT

This report contains three sections (a)-(c) in which we report progress of the last year as follows. (a) The characterization of protic ionic liquids involving nitrogenous bases, by the state of the proton, as revealed by the N-H proton chemical shift, has been carried out and we show how this measure can be used to classify strong and superacids in a clear-cut manner. (b) The assembly and testing of fuel cells using derivatized siloxane membranes. Here we (i) take the polyanionic and polycationic siloxane membranes that we developed in the previous phase, and now use them in sandwich –type cells to obtain working fuel cells, one class of which has no mobile proton carriers hence must serve as a “dry” proton membrane fuel cell. We then (ii) assemble and test these same membranes in states that are plasticized with protic ionic liquids. This class of fuel cell has much lower internal resistance so has higher power output, at the expense of containing a “leachable” component. Finally (iii) we test membranes in which the siloxane backbones replaced by polyhydroxy cellulose membranes and loaded with ionic liquids. Polyhydroxycellulose membranes have been tested as hosts for imbibed ionic liquid electrolytes and found to provide quite good fuel cell performance. Finally (c) we have studied fluorinated ionic electrolytes, and fuel cells based on them, obtaining a striking result, in which the new system significantly outperforming phosphoric acid in the same cell configuration. Based on the results from part (b) of this study we now know how to proceed further in this direction. The challenge will be to provide the appropriate host for the ionic liquid.

List of papers submitted or published that acknowledge ARO support during this reporting period. List the papers, including journal references, in the following categories:

(a) Papers published in peer-reviewed journals (N/A for none)

[1] Thompson J, Dunn P, Holmes L, Belieres J-P, Angell CA, Gervasio D.
A Fluorinated Ionic Liquid as a High-Performance Fuel Cell Electrolyte
Electrochemical Transactions 13, 21, (2008)

[2] C. A. Angell Electron free energy levels in oxidic solutions: relating oxidation potentials in aqueous and non-aqueous systems. J. Solid State Electrochemistry, (Bockris Festschrift) , 13 981 (2009). (early 2009 but not listed in 2009 report).

Number of Papers published in peer-reviewed journals: 2.00

(b) Papers published in non-peer-reviewed journals or in conference proceedings (N/A for none)

Number of Papers published in non peer-reviewed journals: 0.00

(c) Presentations

1. Ionic liquid and polyionic electrolytes for fuel cells and lithium batteries. C. Austen Angell, Spring meeting, Electrochem. Soc., Phoenix, AZ April 2008.

2. High Temperature Fuel Cells Based On Polyvinyl Pyridine Dihydrogen Phosphate. Xiao-Guang Sun¹, Don Gervasio², C. Austen Angell¹ Spring meeting, Electrochem. Soc., Phoenix, AZ April 2008.

3. On the state of the proton in protic ionic liquids. Jean-Philippe Belieres¹), Nolene Byrne¹), Don Gervasio²) and C. Austen Angell¹) Fall meeting of the American Chemical Society (Symposium on Ionic Liquids)

4. Ionic liquid and polyionic electrolytes for fuel cells and lithium batteries. C. A. Angell, Arizona State University, Keynote lecture for session on “Power and energy from molten salts”. Electrochemical Society Winter meeting, Honolulu

Number of Presentations: 4.00

Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

Number of Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

0

Peer-Reviewed Conference Proceeding publications (other than abstracts):

Number of Peer-Reviewed Conference Proceeding publications (other than abstracts):

0

(d) Manuscripts

Number of Manuscripts:

0.00

Number of Inventions:

Graduate Students

<u>NAME</u>	<u>PERCENT SUPPORTED</u>
FTE Equivalent:	
Total Number:	

Names of Post Doctorates

<u>NAME</u>	<u>PERCENT SUPPORTED</u>
Jean-Philippe Belieres	0.50
Xiaoguang Sun	0.50
FTE Equivalent:	1.00
Total Number:	2

Names of Faculty Supported

<u>NAME</u>	<u>PERCENT SUPPORTED</u>
FTE Equivalent:	
Total Number:	

Names of Under Graduate students supported

<u>NAME</u>	<u>PERCENT SUPPORTED</u>
FTE Equivalent:	
Total Number:	

Student Metrics

This section only applies to graduating undergraduates supported by this agreement in this reporting period

The number of undergraduates funded by this agreement who graduated during this period: 0.00

The number of undergraduates funded by this agreement who graduated during this period with a degree in science, mathematics, engineering, or technology fields:..... 0.00

The number of undergraduates funded by your agreement who graduated during this period and will continue to pursue a graduate or Ph.D. degree in science, mathematics, engineering, or technology fields:..... 0.00

Number of graduating undergraduates who achieved a 3.5 GPA to 4.0 (4.0 max scale): 0.00

Number of graduating undergraduates funded by a DoD funded Center of Excellence grant for Education, Research and Engineering:..... 0.00

The number of undergraduates funded by your agreement who graduated during this period and intend to work for the Department of Defense 0.00

The number of undergraduates funded by your agreement who graduated during this period and will receive scholarships or fellowships for further studies in science, mathematics, engineering or technology fields: 0.00

Names of Personnel receiving masters degrees

NAME

Total Number:

Names of personnel receiving PhDs

NAME

Total Number:

Names of other research staff

NAME

PERCENT SUPPORTED

FTE Equivalent:

Total Number:

Sub Contractors (DD882)

Inventions (DD882)

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Period of Performance: 04/01/2007 – present (07/15/08)

Type of Award: x **Research** **Instrumentation**

OBJECTIVE(S): The goals of this work are 1) to characterize new types of proton conducting electrolytes, the protic ionic liquids, that perform fuel cell functions at high temperatures and 2) to identify polyanionic versions of these salts that can (a) serve as “dry” proton conducting fuel cell membranes and can also imbibe the unpolymerized ionic liquids (ILs) to yield proton-conducting membranes with high mechanical strength, ionic conductivity and appropriate electrochemical windows, for use in a new generation of fuel cells.

APPROACH:

- (i) By understanding the basis of electrolyte formation, we create anhydrous solvent-free proton conducting electrolytes, of controlled acidity or basicity.
- (ii). By understanding compatibility rules, we design polymer hosts that will imbibe large loadings of ionic liquids so as to yield tough, flexible, high temperature polymers with high proton conductivities (high T PEM's)
 - (a) To this end, we target polymers that have pendant amine, imine, or hydroxyl groups.
 - (b). To increase the mechanical strength, we develop effective cross-linking procedures.
- (iii). To increase mechanical strength, without decrease of conductivity, we explore the effect of nano particle incorporation in the membrane on conductivity and polymer strength.

SUMMARY:

This report contains sections on:

(a) The characterization of protic ionic liquids involving nitrogenous bases, by the state of the proton, as revealed by the N-H proton chemical shift.

In our previous research program we described the preparation, and characterization with respect to physical properties (phase transitions, conductivity and viscosity), of some 100 ionic liquids of the proton transfer type[1]. In the first phase of the present program we have extended the characterization to the *chemical* properties, in particular to the state of the proton.

(b) Assembly and testing of fuel cells using derivatized siloxane membranes
(i) polycation and polyanion membranes with no leachable components.

In our previous research program, we developed polyanionic and polycationic siloxanes, by synthesizing siloxane polymers with, alternatively, propylamine side chains, or propylsulfonic acid sidechains, and then carrying out the appropriate neutralizations. In the first phase of the present program we have used these

membranes in sandwich –type cells to obtain working fuel cells, one class of which has no mobile proton carriers hence must serve as a “dry” proton membrane fuel cell

(ii) Assembly and testing of fuel cell using polyionic siloxane membranes plasticized with protic ionic liquids. This class of fuel cell has much lower internal resistance so has higher power output, at the expense of containing a “leachable” component.

(iii) membranes with siloxane backbones replaced by polyhydroxy cellulose membranes and loaded with ionic liquids.

Polydroxycellulose membranes have been tested as hosts for imbibed ionic liquid electrolytes and found to provide quite good fuel cell performance

(c) Fluorinated ionic electrolytes, and fuel cells based on them

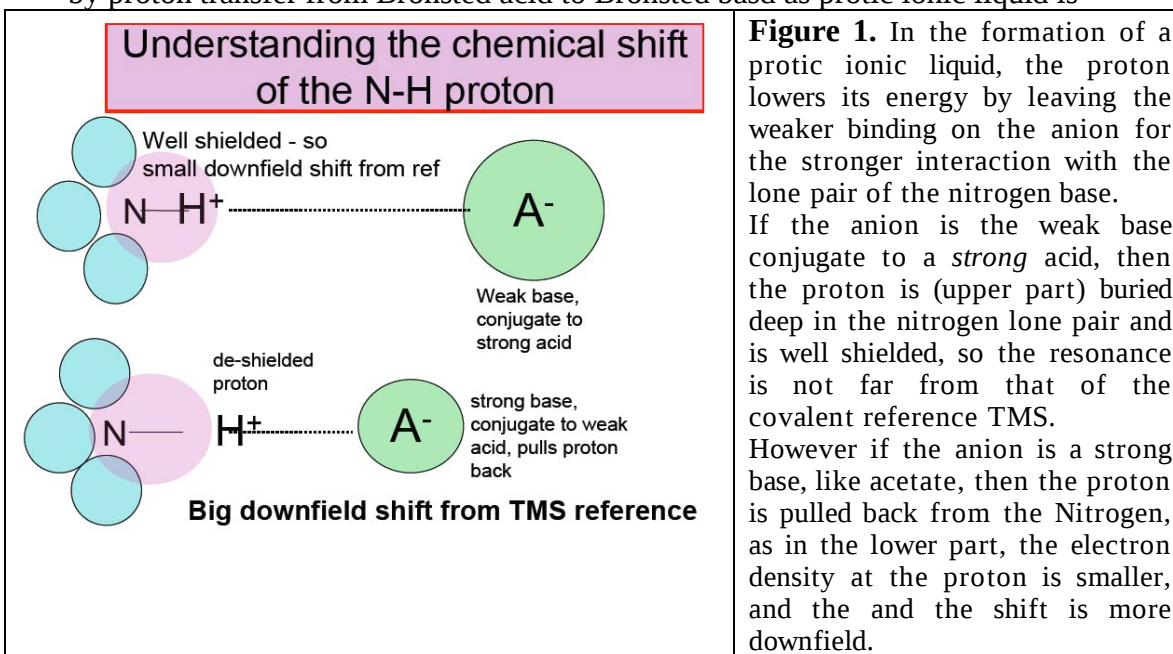
A new fluorinated base ionic liquid has been synthesized and tested in a Teflon sandwich fuel cell with striking results, significantly outperforming phosphoric acid in the same cell configuration. Based on the results from part (b) of this study we now know how to proceed further in this direction. The challenge will be to provide the appropriate host for the ionic liquid.

DETAILS OF WORK PERFORMED

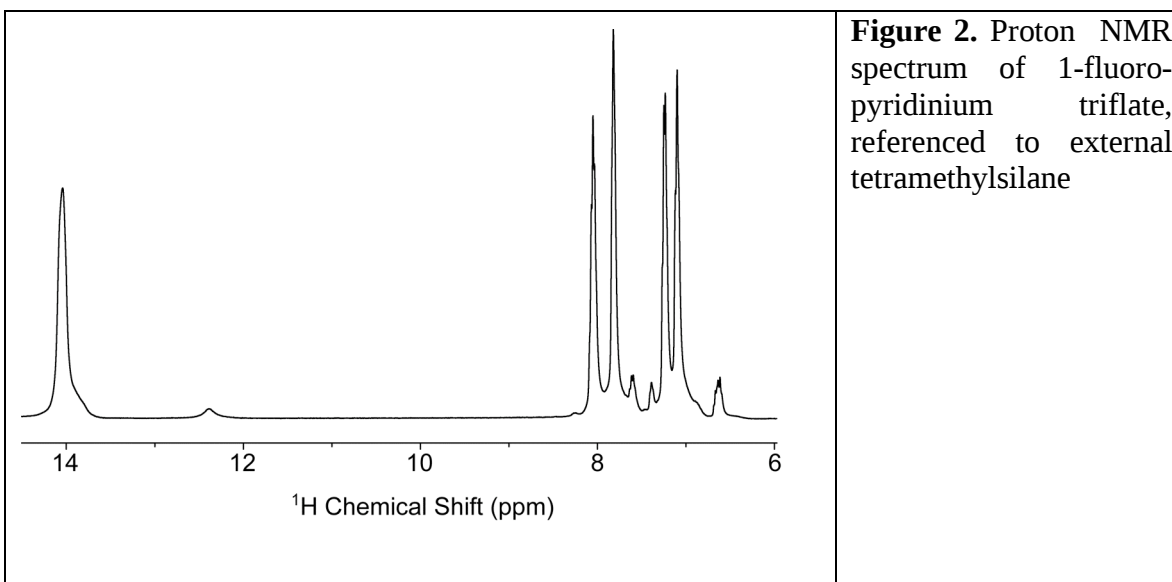
Many details of the work performed in the past year are contained in four journal articles that are either in press (Electrochemical Transactions[2], or are shortly to be submitted (J. Am. Chem. Soc.[3, 4]) and J. Electrochemical Society[5, 6]. The important developments are given briefly in the following paragraphs.

(a) NMR characterization of the proton chemical shift for transferred protons (co-worker Jean-Philippe Belieres)

This is a fundamental study of the chemical state of the proton on the cation formed by proton transfer from Bronsted acid to Bronsted base as protic ionic liquid is



synthesized. The behavior of the protic ionic liquid as a solvent depends on the state of the transferred proton, determining whether the PIL will have acid, neutral or basic character. This can be understood from Figure 1, illustrating the case of a single strong base. If the base is not as strong then, for same acid, the proton will be less firmly transferred and the PIL will be more acid in character. This is the case for the transfer of the proton from triflic acid to 1-fluoropyridine, for which the spectrum is shown in Figure 2. Where the pIL trimethylammonium triflate is neutral in character, fluoropyridinium triflate is quite acid. It is found that a fuel cell based on the use of fluoropyridinium triflate as electrolyte outperforms phosphoric acid fuel cell at all current densities, and is the first non-aqueous fuel cell to do so[2] (see later figure.).



We have used the N-H proton transfer to a given base as a new method of characterizing strong and superacids, and have obtained some striking results. We have been able to illustrate unambiguously that triflic acid, long considered a superacid, but the subject of much controversy amongst theorists, is much less strong an acid than perchloric acid, and also less strong than iodic acid, HI. On the other hand, according to chemical shift measurements, HBF_4 is stronger than HClO_4 , and considerably stronger than triflic acid. This is consistent with reports in the inorganic chemistry literature[7] helps us understand why ionic liquids with BF_4^- anions are better conductors than those with triflate anions, for the same cation.

A table of chemical shifts for the N-H proton after transfer to the tertiary amine base, diethylmethylaniline (DEMA), from various Bronsted acids, ranging from acetic acid up to HTSFI, amongst the acids that exist free, and including the acids HBF_4 and HAlCl_4 , which don't exist free but can nevertheless be tested for their strength by forming the proton transfer salt by metathetical reactions, such as



This is rather novel way of obtaining a quantitative comparison of the strengths of strong acids.

With very minor differences, the same shifts are obtained when the base is triethylamine, the pK_a of which is nearly the same. This is shown in the extended table, Table 2.

Table 2. Values of proton chemical shifts for the N-H proton in anhydrous ionic liquids sharing the cation diethylmethyammonium

Acid	ppm water in PIL	$\delta(\text{NH})/\text{ppm}$
HFeCl ₄	Very low	No NMR
HFeI ₄		
HAICl ₄	Very low	4.618
HBF ₄		5.0
HTFSI	101	6.697
HBETI	183	6.65
HI		
HClO ₄	31	7.010
HTf	24	7.771
HSbF ₆	469	8.56 ??
H ₂ Cl ₂ ^{**}		
HBr		
HCl		
HCH ₃ SO ₃	910	9.5
HN(CN) ₂	1603**	9.5
HNO ₃	36	9.730
HCl ₂ CHAc	1476 **	10.245
HTfAc	230	11.268
HAc	1306**	14.0

When the base is changed to one that is weaker, but the proton is transferred from the same acid, the proton chemical shifts move downfield. Again a correlation with the base pK_a values determined in aqueous solutions can be observed. The reasons that these relations hold up, as well as they do, must be that the free energies of solution of the ionic species must all be comparable or the differences must be compensating.

When the base is chosen to be weak, like 1-fluoropyridine, and it is protonated by a strong acid like triflic acid, the resulting ionic liquid will be an acid electrolyte, but one

that has no aqueous component. It should be a potential fuel cell electrolyte. Indeed, as mentioned already we have had some success with this electrolyte.

The relation of the chemical shift to the best estimates available for the pK_a values of the strong acids, is shown in Figure. 3. The curve is shown asymptotic to the value 6.0. A

Table 2. N-H PMR chemical shifts for PILs formed from acids of differing acid strength.

A. for base diethylmethylaniline (DEMA), pK_a (aqueous) = 10.55	B. for base triethylamine, (TEA) pK_a (aqueous) = 10.62
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Acid	ppm water in PIL	$\delta(NH)/ppm$	Acid	ppm water in PIL	$\delta(N-H)/ppm$
HFeCl ₄	Very low	No NMR	HFeCl ₄	Very low	No NMR
HFeI ₄					
HAICl ₄	Very low	4.618			
HBFe ₄		5.0			
HTFSI	101	6.697	HTFSI	138	6.505
HBETI	183	6.65		219	6.437
HI					
HClO ₄	31	7.010			
HTf	24	7.771		22	7.732
HSbF ₆	469	8.56 ??			
H ₂ Cl ₂ ^{**}					
HBr					
HCl					
HCH ₃ SO ₃	910	9.5		1291	9.374
HN(CN) ₂	1603**	9.5			
HNO ₃	36	9.730			
HCl ₂ CHAc	1476 **	10.245			
HTfAc	230	11.268			
HAc	1306**	14.0			
Citric acid					

theoretical gas phase value is not yet available for this base, but values have been published for a number of others, for instance pyridine ($\delta(N-H) = 8.8$)[8]

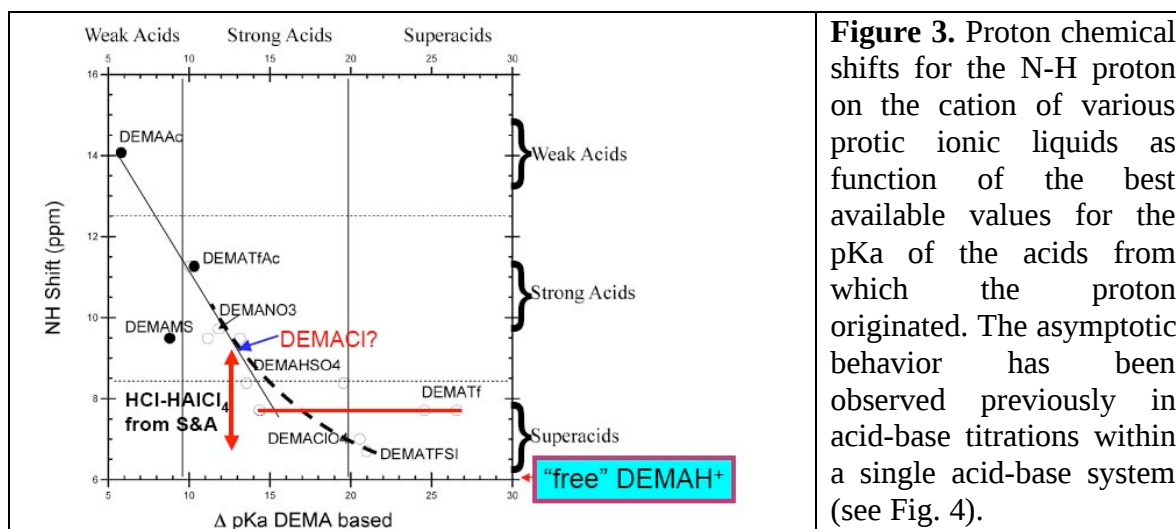


Figure 3. Proton chemical shifts for the N-H proton on the cation of various protic ionic liquids as function of the best available values for the pK_a of the acids from which the proton originated. The asymptotic behavior has been observed previously in acid-base titrations within a single acid-base system (see Fig. 4).

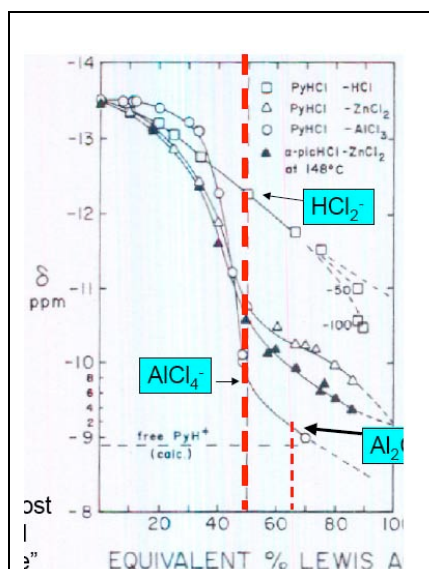


Figure 4. Effect of increasing acidity on the $\delta(N-H)$ of the pyridinium cation (from ref. X)

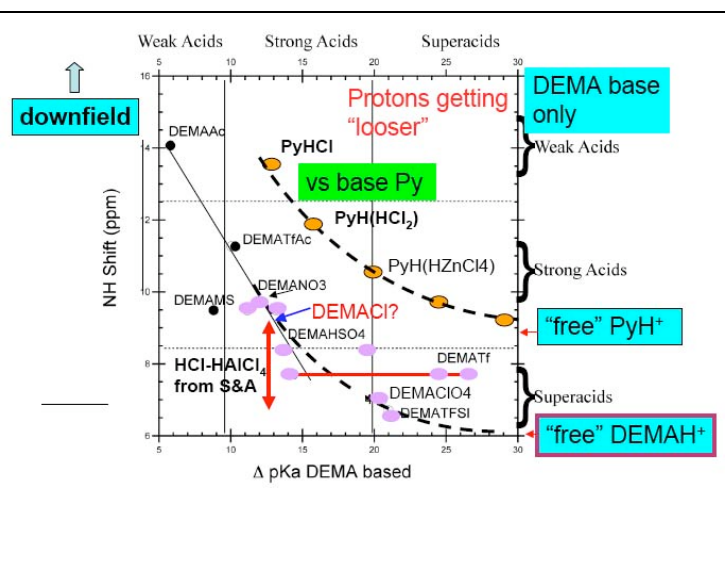


Figure 5. Effect of increasing acidity (by difference of acid and DEMA pK_a values) on the N-H chemical shift approximate values for base pyridine also included

Superacidic ionic liquids

When the base is chosen to be very weak, like pentafluoropyridine PFPy, and it is protonated by a superacid, the resulting ionic liquid must be superacidic. PFPy is not protonated by triflic acid, so a protonated PFPy must be a stronger acid than triflic acid – which is considered a superacid. An ionic liquid superacid is, to the best of our knowledge, a new concept and is potentially a new invention, since all previous superacids have been molecular in nature. We are currently evaluating the superacid characteristics of PFPyH⁺ TFSI⁻ (where TFSI⁻ is the much-studied bis-trifluoromethanesulfonyl imide anion). The $\delta(N-H)$ value has been measured and is the most downfield we have yet measured for any base protonated by HTFSI. A Table of chemical shifts for bases protonated by HTFSI is given as Table 3.

Table 3. N-H proton chemical shifts for bases being protonated by HTFSI and HTf

For acid HTFSI			For acid HTf		
Base	$\delta(\text{N-H})$	Base pKa	Base	$\delta(\text{N-H})$	Base pKa
pentaFPy	13.92	-12	pentaFPy	Doesn't form, so >17	
1-FPy		-2	1-FPy	12.4	-2
1-CH ₃ Py (α -pic)					
			α -pic	12.8	5.97
EA (prim)	5.524	9.			
DEA (sec)	5.904				
TEA (tert)	6.505	10.55			
DEMA	6.697	10.62			
guanine		12?			

(b) Assembly and testing of fuel cells using derivatized siloxane membranes of both polycation and polyanion character

(i) no leachable components.

The primary objective has been to make a highly stable protic salt electrolyte electrolyte, to promote high efficiency operation of a hydrogen – air fuel cell from low (-20°C) to high (120°C) temperatures.

We have earlier reported the synthesis and characterization of siloxane membranes with moderate conductivities in the case of “dry” ionic conductivity (no leachable components) and high conductivities (approaching 10mS.cm when the polyionic siloxanes were plasticized with ionic liquids of different types).

In the literature it is quite common to see the results of conductivity studies of proposed membrane materials but quite unusual to see actual results for fuel cells utilizing such membranes. Here we show evidence that the membranes produced in our synthetic studies to date can actually be incorporated into fuel cells that deliver power output. We first present results for the membrane made by neutralization of pendant sulfonic acid groups neutralized by methylamine, as represented in Figure 6.

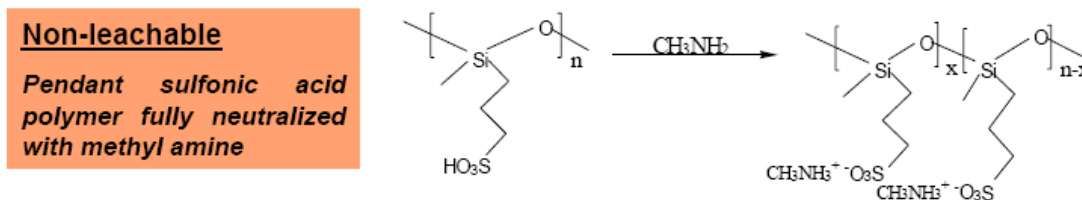


Figure 6. Anionic siloxane polymer, based on neutralization of pendant sulfonic acid groups.

For the “dry” ionic membranes, it has been found that, although the membranes are self-supporting, in the assembled fuel cell deformation of the membranes was occurring, leading to failure. Evidently the degree of polymerization and/or crosslinking that we were obtaining, was not enough to resist mechanical shearing stresses at the high operating temperatures. To deal with this problem sufficiently to test the fuel cell assembly in action we fused the polymer into a rigid anodisc Whatman porous alumina disc support. This was sufficient to permit polarization curves to be obtained, and the findings are presented in Figure 7 below. Figure 7a shows Nyquist plots for the assembled cell resistivity, while Figure 7b shows the polarization curve and the power curve for the cell.

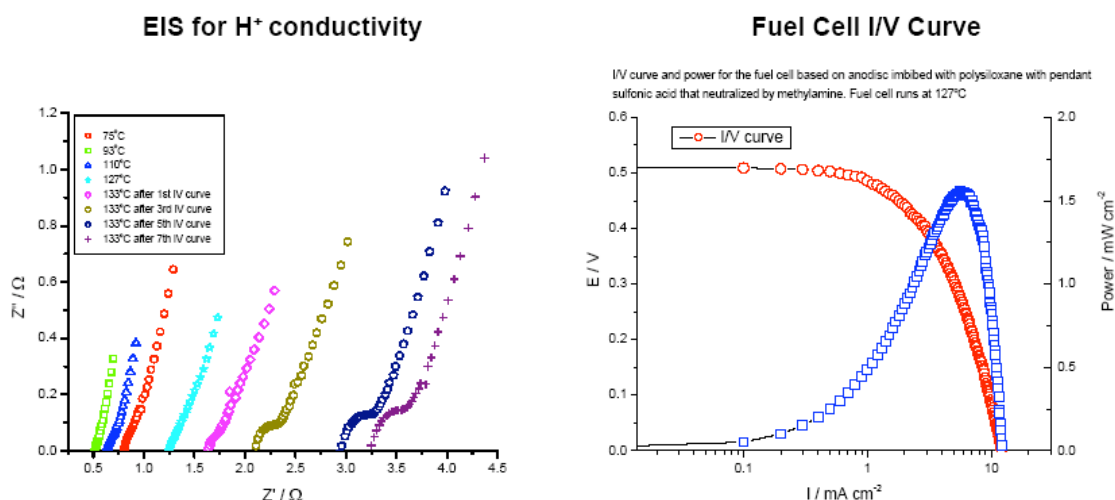


Figure 7 (a) Nyquist plots for fuel cell with “dry” single ion conductor polymer membrane (CH_3NH_3^+ mobile species) showing the dc resistivity of the membrane, in situ, before and after determination of the IV curve. Irreversible increases in resistance, the origin of which is not clear, occur during temperature increase and also during the IV curve determination, diminishing performance.

(b) Tafel plots at 127°C, showing a severely reduced open circuit voltage, and low maximum power output

From the Tafel plot of Fig. 7b, which shows an open circuit voltage of only 0.5 V, it seems likely that the siloxane membrane is permitting serious gas crossover. This would be less serious if the conductivity of the membrane permitted a greater power output, but generally it appears difficult to improve the conductivity of the membrane, without additional mobility provided by plasticization.

Figures 8 and 9 show the related results for the inverse case of Figure 6, in which the pendant group is an amine, and it is neutralized with methane sulfonic acid. As before the polymer structure is shown first, in Figure 8, and the Tafel plots for the fuel cell are shown in Figure 9. It is interesting to note that in this case the proton is located on an immobilized species, and yet the fuel cell performance is comparable.

Non-leachable

**Pendant propyl amine
polymer fully neutralized
with methyl sulfonic acid**

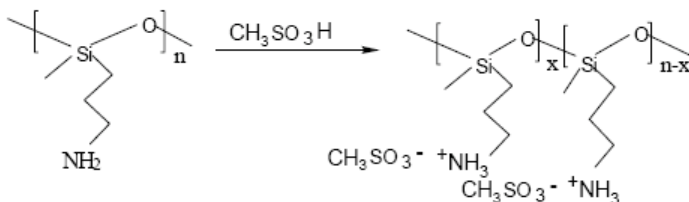


Figure 8. The structure of the polycationic membrane tested in Figure 9.

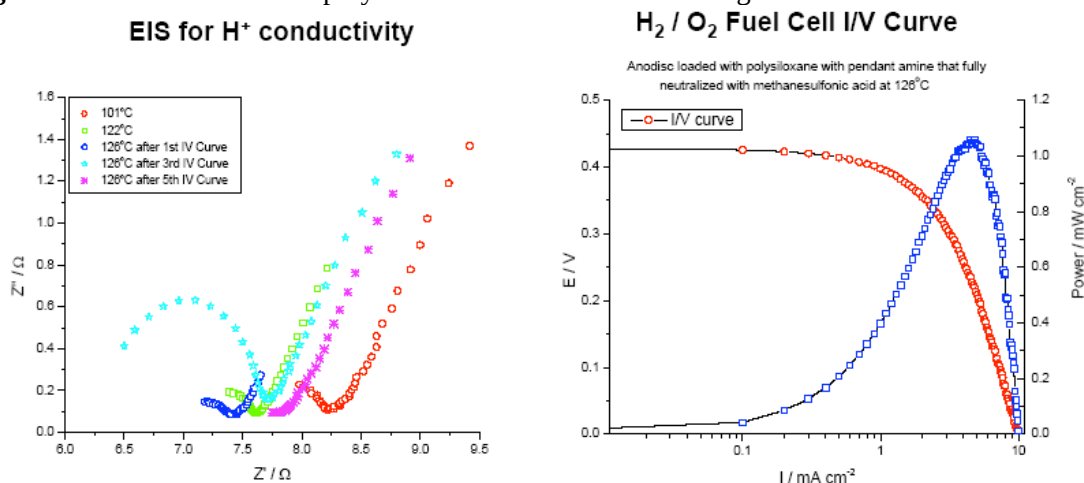


Figure 9. Cell resistivity Nyquist plots, and cell polarization and power output curves for the case of dry proton conducting, non-leachable polycationic siloxane membrane

The cell resistivity is higher for this less conductive polycation case, and concomitantly, the open circuit voltage is a little lower than where the proton is on the mobile species (methylammonium cation, Figs 6 and 7), but it is not much lower. This is interesting because there is a significance physical difference between the two cases. Since the protons are located on a tethered group, it is clear that the protons passing through the cell must be moving by a “dry” mechanism. They must be passing either directly between protonated and non-protonated pendant amines or be rejoining the anions in a transitory acid state (though this would require a high energy fluctuation).

(ii) cells with ionic siloxane membranes plasticized with ionic liquids.

When the membrane is plasticized by ionic liquids, as originally proposed, the performance becomes much better. Figure 10 shows the cell impedance at different temperatures, and after a polarization curve determinations, for a cell based on the pendant amine neutralized with methanesulfonic acid, which has been plasticized with 50 wt % of the eutectic mixture of ammonium nitrate and ammonium triflate, a highly-conducting stable mixture of salts utilized in our demonstration of inorganic ionic liquid fuel cell performance, published in Chemical Communications in 2005[9]. Figure 11 shows the Tafel plot and power curve for this fuel cell. The effect of the lowered impedance on both the open circuit voltage and the maximum power is clear. However, the open circuit voltage is still far below the theoretical value of 1.18 V at the running temperature of 130°C, and it seems that fuel crossover remains a

problem. Better performance will be seen in the next section where further decreases in cell impedance have been shown possible with a different base polymer in the membrane.

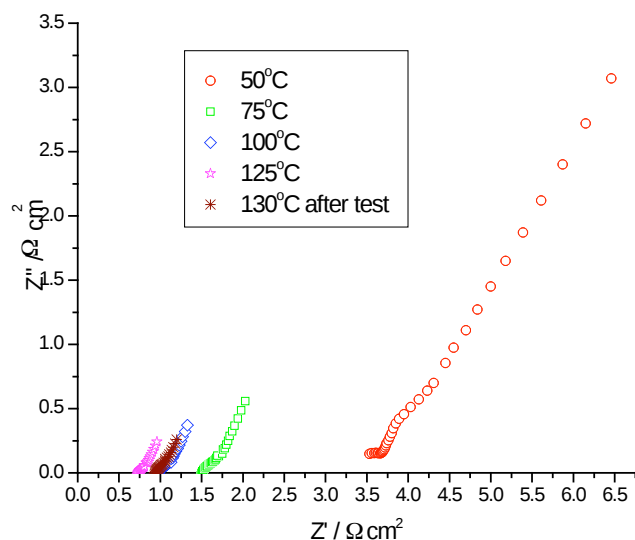


Figure 10. Nyquist plot for fuel cell membrane of pendant amine siloxane neutralized with methanesulfonic acid and plasticized with 50 wt % $\text{NH}_4\text{NO}_3\text{-NH}_4\text{CF}_3\text{SO}_3$ eutectic

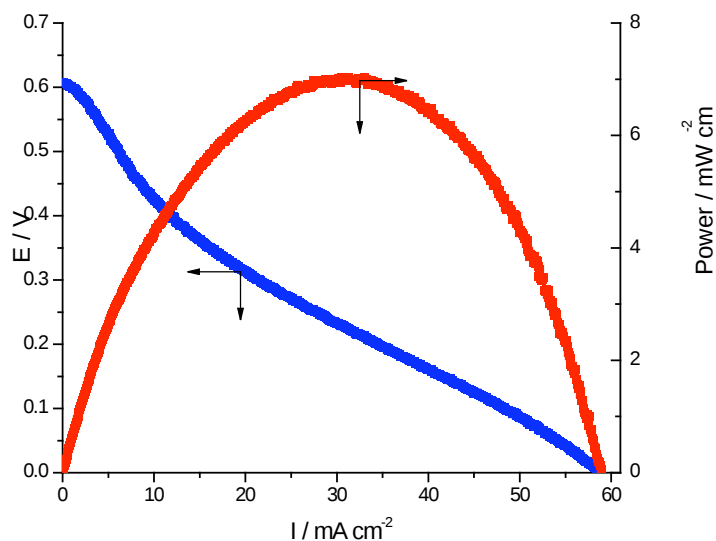


Figure 11. Tafel plot and power curve for the cell with membrane of Fig.10

(ii) cells with hydroxycellulose-based polyionic membranes, plasticized with ionic liquids.

In an attempt to avoid loss of performance by gas crossover, we have recently abandoned the siloxane polymers in which much effort has been invested and turned to derivatized hydroxycellulose polymers, again plasticized with inorganic ionic liquids. Some test results are shown in Figures 12-14. Some improvement in cell voltage has been obtained but it remains far below expectations. Efforts to understand these sources of efficiency loss, which may be more complex than simple fuel crossover, are in progress. Meanwhile studies with *liquid* electrolytes of a more acid character than those reported on to date, have yielded results of impressive character. (see section (c) below).

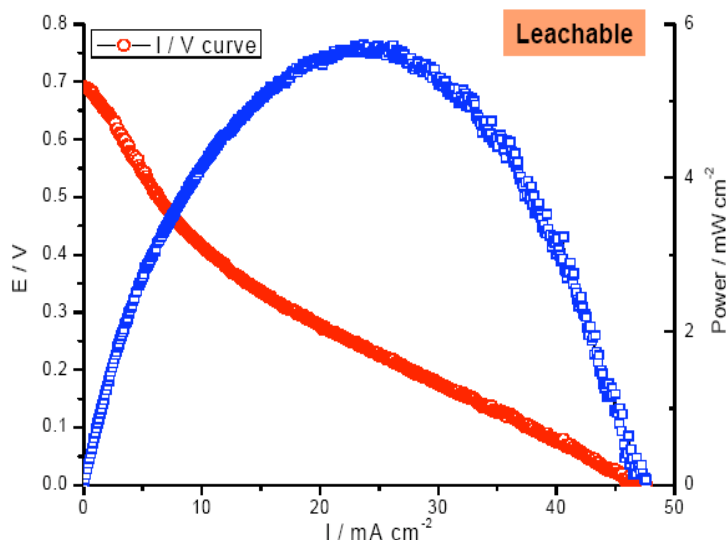


Figure 12. Polarization Curve for Hydrogen/Oxygen Fuel Cell with crosslinked hydroxyethyl cellulose membrane containing 60wt% ionic mixture of 6 moles NH_4NO_3 and 4 moles $\text{NH}_4\text{CF}_3\text{SO}_3$.

Cell was tested at 138°C with $P(\text{H}_2\text{O}) = 24$ torr in H_2 and O_2 feeds.

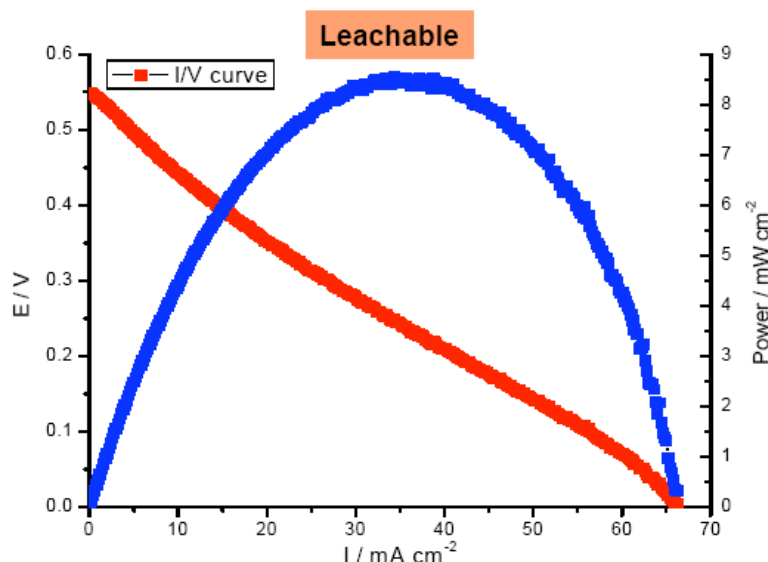


Figure 13. Polarization Curve for Hydrogen/ Oxygen Fuel Cell with a crosslinked hydroxyethyl cellulose membrane containing 20wt% polyammonium

styrenesulfonic acid and 60wt% ionic mixture of 6 NH_4NO_3 and 4 $\text{NH}_4\text{CF}_3\text{SO}_3$. $T = 125^\circ\text{C}$; $P_{\text{total}} = 1 \text{ atm}$. $P(\text{H}_2\text{O}) = 24 \text{ torr}$ in H_2 and O_2 feeds.

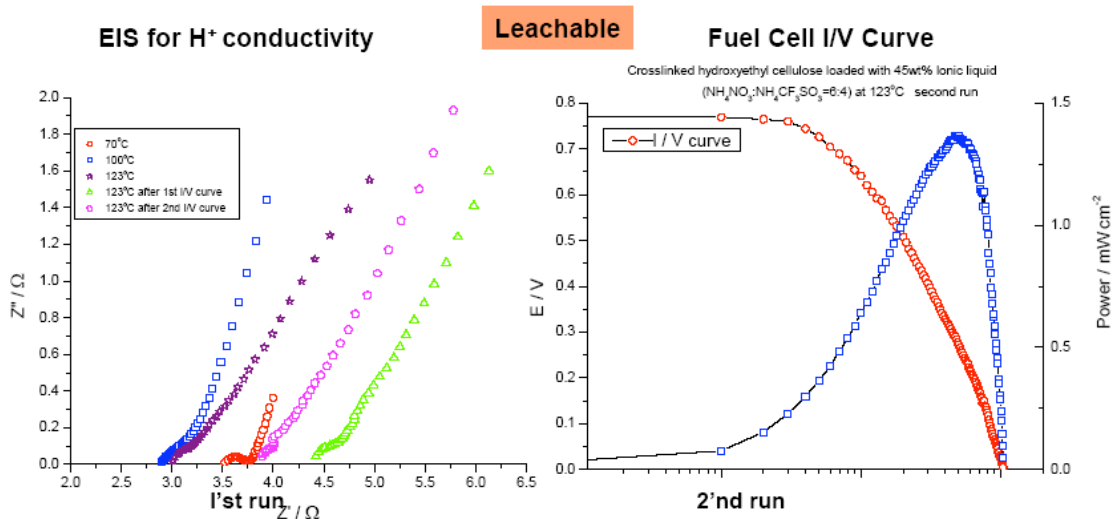
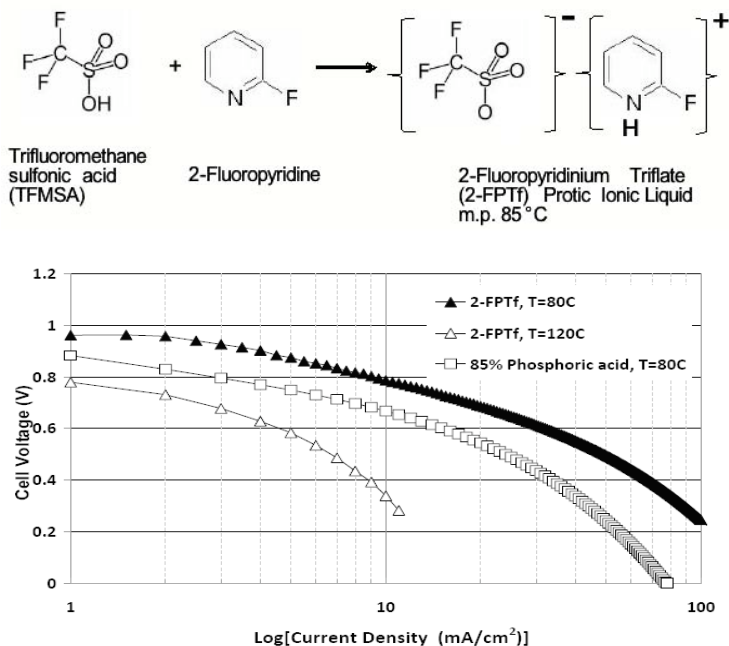


Figure 14 (a) Impedance and (b) Fuel cell Polarization, with a crosslinked hydroxycellulose membrane filled with 45wt% of ionic liquid consisting of $\text{NH}_4\text{NO}_3:\text{NH}_4\text{CF}_3\text{SO}_3$ at 123°C . ETEK electrodes with 0.5 mg-Pt/cm^2 and ambient pressure. NO HYDRATION.

(c) Fluorinated ionic electrolytes, and fuel cells based on them



According to the foregoing results, the membranes based on polymerized versions of the neutral ionic liquid electrolytes, both with and without ionic liquid plasticization, have not so far proven capable of yielding high efficiency fuel cells, we have taken the first steps on a new approach which develops the ionic liquid concept in the direction of more acid ionic liquids. This is achieved by transferring protons from Bronsted acids to fluorinated bases. The fluorinated electrolytes are thus another approach to achieving a highly

efficient fuel-cell with an electrolyte that has high proton-conductivity, that is stable under fuel-cell operating conditions and that allows hydrogen and oxygen to adsorb on

electrocatalysts. By judicious selection of acid and base moieties, guided by the proton energy level diagram developed in our initial ARO grant period, a salt can be formed to give all of the properties needed for good fuel-cell performance.

These liquid salts are being made to accelerate protic salt chemistry discoveries and to model solid membranes. Recently, a stable high-performance fuel-cell was made using a fluorinated pIL, 2-fluoropyridinium triflate (2-FPTf). The 2-FPTf is formed by mixing 1 mole of 2-fluoropyridine and 1 mole of triflic acid. The proton conductivity of 2-fluoropyridinium triflate, $\sigma(2-FPTf)$, is $4 \times 10^{-3} \text{ Scm}^{-1}$ at 80°C . Figure 1 shows the steady state

Fig. 1. I/V curves for H_2 and O_2 fed to Pt-catalyzed porous electrodes with 2-FPTf at 80°C and 120°C and 85% phosphoric acid at 80°C . $A = 0.5 \text{ cm}^2$, $t^{\text{electrolyte}} = 0.3 \text{ cm}$.

curves, not corrected for resistive losses.

The improved fuel-cell performance with 2-fluoro pyridinium triflate electrolyte is notable in two important ways. *First*, there is NO NITRATE in 2-FPTf electrolyte. Up until 2-FPTf, all high performance pILs had nitrate, which implied the possibility of radical chemistry. *Second*, the 2-FPTf is stable under fuel-cell operating conditions over

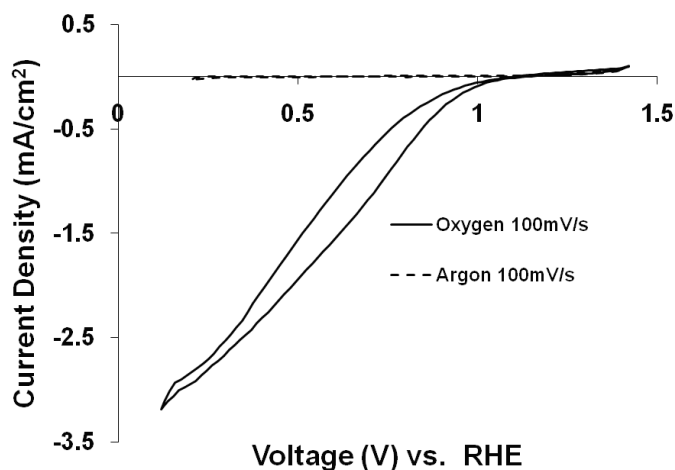


Figure. 2 Voltammetry of Pt in neat 2-fluoropyridinium triflate (2-FPTf) at 80°C under dry oxygen and Argon at a total gas pressure of 1 atm. Scan Rate = 100 mV/s Electrode area = 0.1 cm^2

potential of 1.2 V versus RHE. The oxidation current above 1.2 V is not for Pt-oxide formation or electrolyte oxidation, but is for oxidation of water in the diffusion layer. This is another sign that oxygen reduction is reversible in the 2-FPTf.

all current densities for many hours from low temperatures up to 80°C . The stability with 2-FPTf is attributed to two factors: i) fluorine being substituted for H in reactive CH bonds and ii) that it does NOT wet Teflon. The enhanced fuel-cell performance is attributed to lower polarization for oxygen reduction, because the salt has little water, resulting in Pt staying metallic and being catalytically active even at potentials as high as 1.2V vs. RHE.

The lower oxygen reduction polarization was confirmed by the voltammetry of Pt in 2-fluoropyridinium triflate at 80°C (Figure 2). The onset for oxygen reduction is near the reversible

Summary

A major fundamental study of the state of the proton in protic ionic liquids, by application of proton magnetic resonance focused on the proton attached to the nitrogen of various bases, has been carried out. The upfield shift of this resonance has been used as a means of classifying the proton donating ability of the acid, with the finding that the proton from HAlCl_4 is the most powerfully transferred of any available acid, though the acid itself only exists at very low temperatures. Of the readily available ambient temperature stable acids HTFSI (often written HNTf_2 , standing for bis- trifluoromethylsulfonyl imide, is the strongest, and some novel powerfully acid ionic liquids have been made by transferring protons from this acid to weak bases. By such proton transfers we have formed polyanionic substances with tethered acids as well as tethered bases, and shown that they can serve as membranes in fuel cells though the performance has not been good, apparently due to excessive fuel crossover or interface impedance. Better performance has been obtained with such membranes plasticized with ionic liquids and ionic liquid mixtures. Finally performance exceeding that of the liquid phosphoric acid cell has been obtained using a new acid ionic liquid electrolyte formed by transfer of a proton from triflic acid to fluoropyridinium triflate.

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