

## V.G.6 New Polyelectrolyte Materials for High Temperature Fuel Cells

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### Objectives

- Investigate the feasibility of solid polyelectrolyte proton conductors that do not require water to achieve practical conductivities (0.1 S/cm at 120°C).
- Provide significant simplifications for fuel cell systems.
  - Heat and water management greatly simplified.
  - Water rejection reduces mechanical stress due to swelling.
- Provide car manufacturers and their suppliers with knowledge on how to prepare next generation materials.

### Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section (3.4.4) of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

- (E) System Thermal and Water Management
- (B) Cost
- (A) Durability
- (C) Performance

### Technical Targets

(Numerical values of targets taken from RD&D Plan Tables 3.4.11 and 3.4.12)

This project is aimed at the development of membranes that do not require the presence of water to achieve adequate conductivity (0.1 S/cm [120°C], 0.07 S/cm [20°C] and 0.01 S/cm [-20°C]). Studies are conducted on proton solvent molecules and protogenic acid groups that can be tethered to polymer matrices to provide solid state membranes through which only the proton moves. Such membranes with no mobile solvents are expected to have lower gas permeabilities that lead to lower cross-over currents (target is <2 mA/cm<sup>2</sup>). Since swelling with solvent (e.g. water) is also much reduced, durability goals should be more easily attained (target is 5,000 hours) due to reduced mechanical stress. However, durability of the solvent molecules and their tethers to the polymer matrix is an issue of great concern. Finally, the materials must also be suitable for the preparation of electrode structures so that suitable membrane electrode assemblies (MEAs) may be prepared and tested. Not only do the materials have to be compatible with conventional catalysts but the electrode structure has to function adequately (target 1,000 mW/cm<sup>2</sup>) in a medium of low water content where catalyst activity may be quite different from a high water content (target 720 μA/cm<sup>2</sup> at 900 mV(Pt) or 300 A/cm<sup>3</sup> at 800 mv (non-precious group metal catalyst). The provision of membranes and MEAs that need no humidification provides significant system simplifications and large cost advantages over conventional materials

### Accomplishments

- Demonstrated the conductivity potential of possible solvent molecules and protogenic acid groups by preparation and study of proton conducting ionic liquids both in neat form (measured 0.05 S/cm at 120°C in absence of water) and incorporated into polymer matrices. The presence of the ionic liquid has been shown to significantly alter the polymer morphology.
- System modeling shows that a conductivity of 0.05 S/cm at 120°C is acceptable providing there is no loss of catalyst activity.
- Imidazole was found to have the best conductivity when compared to a wide range of heterocyclic bases tested.
- Demonstrated the advantages of an increase in acid concentration on conductivity of imidazole-doped polyfluorinated sulfonic acid (PFSA) membranes. An increase of nearly one order of magnitude was observed upon lowering the equivalent weight to

800 from 1,100. The temperature dependence of conductivity is consistent with the operation of the Grotthuss mechanism of proton transport and demonstrates the importance of polymer morphology for this property.

- Confirmed that imidazole-doped PFSA membranes take up much less water ( $\lambda = 2$ ) at high humidities than undoped membranes ( $\lambda = 8$ ). Non-fluorinated membranes (block polysulfone ether polymers, BPSH) doped with imidazole take up considerably more water showing the importance of polymer structure and morphology on this property.
- Partial success has been achieved in modification of polyarylether sulfone backbones with allyl side groups to allow easy attachment of imidazoles and acid groups. This process is still under optimization. Polystyrene and polynorbornene backbones (both random and block co-polymers) have been prepared with attached imidazole groups and with functionalities that allow attachment of the imidazoles and acid groups.



## Introduction

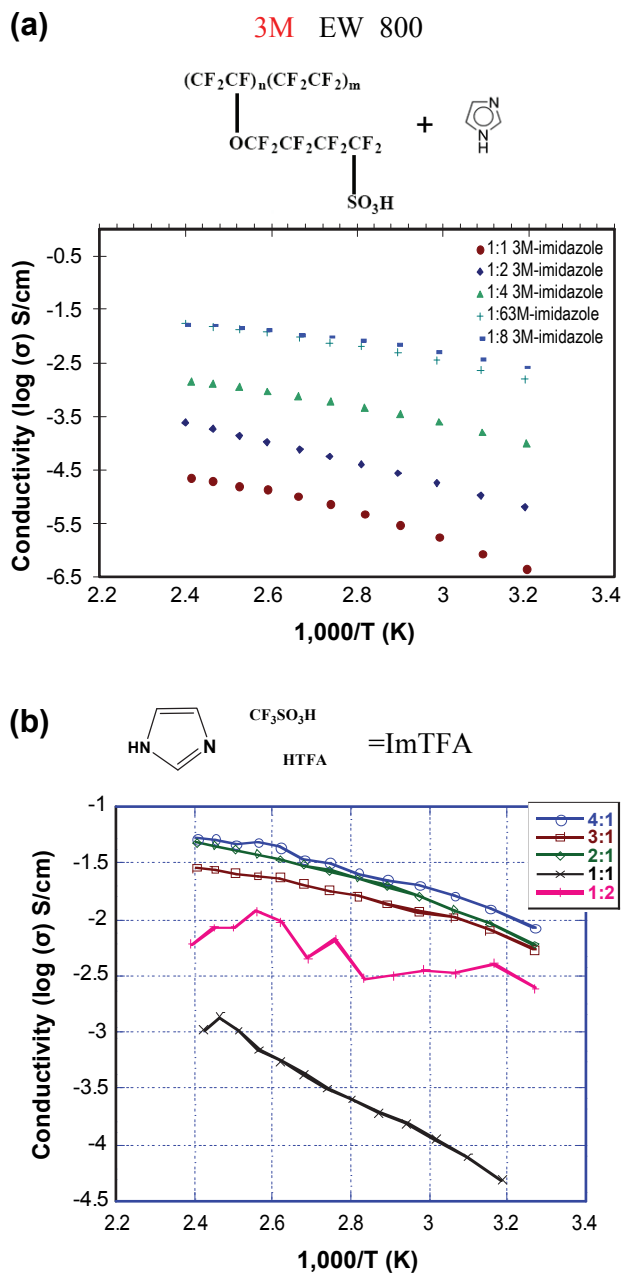
The need to remove water from the operation of fuel cell stacks is critical for their use in vehicles. Because of the poor performance of the electrocatalysts, nearly half of the fuel energy is converted to heat which requires a very complex and expensive heat and water management system that takes up an unacceptable volume in a light-duty vehicle. Changes in the water content of the membrane electrode assemblies results in large mechanical stresses on the membranes which are implicated in failure of the cells and the need for liquid water at low (-30°C) or high (120°C) temperatures is obviously a major problem. The case for developing membrane materials that do not require the presence of water to operate in fuel cells is now totally compelling. This is, however, a major undertaking and requires a considerable basic science effort in addition to technology development.

Kreuer has pioneered the investigation of alternative proton conducting solvents that could replace water and, in particular, reminded the research community of the ability of heterocyclic bases such as imidazole to support proton conduction [1]. It has also been recently discovered that nature uses imidazoles for the purpose of moving protons through membranes in living systems [2] and it has also been noted previously that imidazole bases appear to be resistant to oxidation [3] by oxygen species, an important property for a fuel cell solvent. This project was preceded by some preliminary work on the attachment of imidazoles to polyelectrolytes that showed that an all solid state proton conducting membrane was indeed possible [4]. Although the

conductivities achieved were low, many aspects of the polymer structure were not optimum and the purpose of this project is to optimize the polymer structures in order to achieve the desired properties.

## Approach

Since the project involves the manipulation of a large number of molecular features of the target polymers, the approach taken is to use mixtures of



**FIGURE 1.** Conductivity measurements versus temperature of a) 3M lonomer doped with different amounts of imidazole; b) ionic liquids prepared from imidazole and TFA. Numbers on legends refer to ratios of imidazole to acid equivalents.

easily obtained components to measure how the properties vary. Examples of this are shown in Figure 1 which shows conductivity measurements made upon a 3M PFSA material that is doped with imidazole (1a) and ionic liquids prepared from imidazole and trifluorosulfonic acid (1b). The preparation of mixtures allows rapid optimization of the relative ratio of imidazole base to acid group which is used to guide synthesis of the target polymer materials. The approach is to find out as much as possible about the properties of the components molecular fragments before expending the large effort to synthesize the polymers so that our synthesis efforts are properly focused. In addition to this material optimization process, we also use system modeling to try to foresee problems or shortcuts that would simplify the tasks required. For example, system modeling has shown that a conductivity of 0.05 S/cm at 120°C is acceptable provided system simplifications are achieved through the use of the material (e.g. no humidifier, small radiator). Collaboration with system modeling efforts at Argonne National Laboratory is helping this effort which will refine the targets.

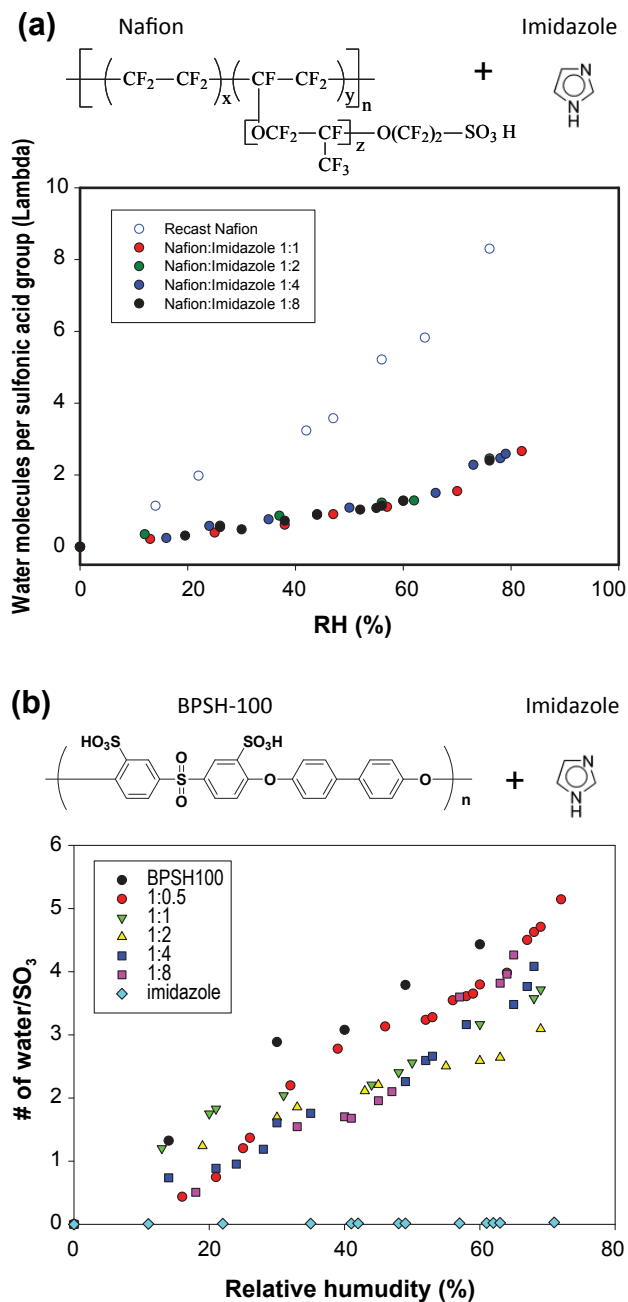
## Results

### Measurements on Easily Obtained Mixtures

Figure 1a shows the conductivity of the 3M PFSA material doped with imidazole. The structure of the PFSA material is shown in the figure. The results show the importance of an excess of imidazole with respect to the acid groups, as is the case with water in PFSA materials. The absolute values of the conductivity of the 1:8 mixture are nearly one order of magnitude higher than the corresponding mixture with Nafion® which has a higher equivalent weight and hence there is a lower concentration of acid groups. This simple experiment demonstrates the effect of variation of charge concentration. The variation of conductivity with temperature in Figure 1a is quite weak indicating low activation energy that is consistent with a Grotthuss mechanism. The value at 25°C is also encouragingly high. Figure 1b shows the conductivity of ionic liquids made from different ratios of imidazole and trifluoromethanesulfonic acid (TFA). Very similar results are obtained with methanesulfonic acid and bis(trifluoromethylsulfonyl)imide acid. These results are consistent with the fact that the medium is dominated by the presence of the imidazole and the polarity of this is sufficient to fully dissociate all of the acid groups. It is expected that in the presence of polymer matrices where the dielectric constant will be lower than the self ionization of the acid group will be more important. A further observation on these results is that the slopes of the temperature dependence do not appear to be completely flat, indicating that the Grotthuss charge transport may be weak. This might well be expected

since there is no morphology structure in the liquid to keep the solvent molecules aligned.

In previous work it had been remarked that it appeared that Nafion® doped with imidazole took up very little water when humidified. Figure 2a shows some more careful measurements carried out at Los Alamos that confirms this observation where the water uptake of Nafion® doped with imidazole was measure as a function of humidity. Imidazole possesses  $pK_a$  and  $pK_b$  values which are very similar to water and hence there

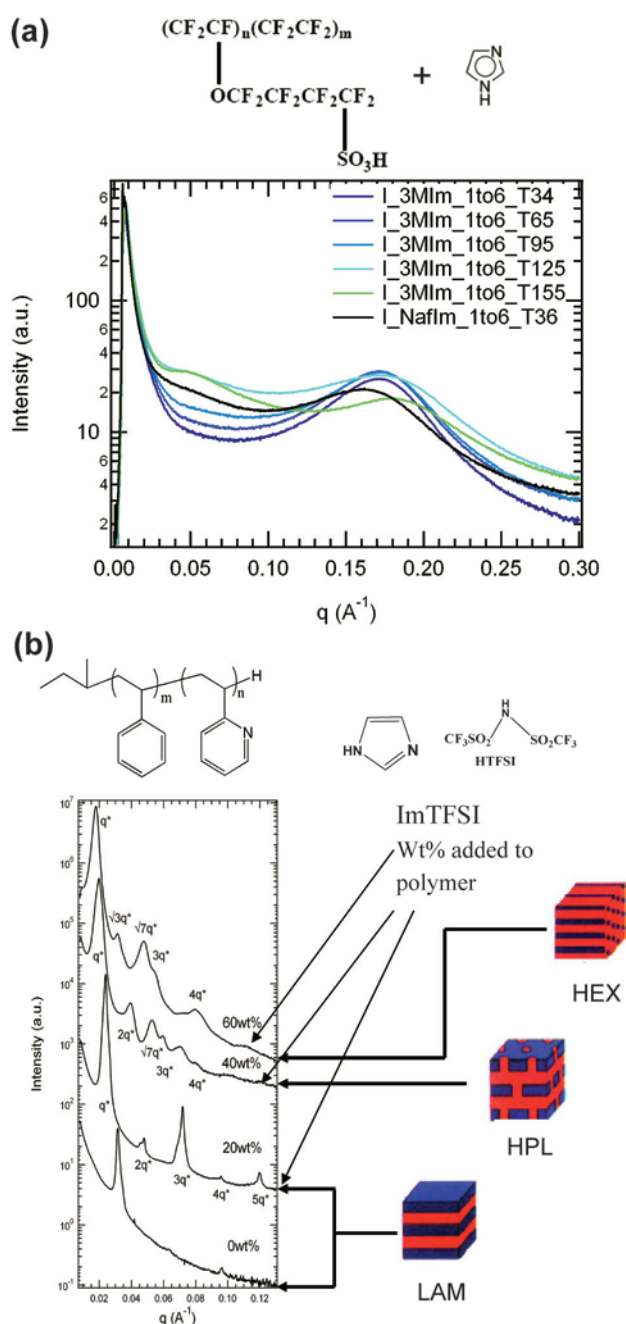


**FIGURE 2.** Water uptake as a function of relative humidity for a) Nafion® doped with imidazole; b) BPSH-100 doped with imidazole.

is no strong thermodynamic force for water to displace imidazole. However, in Figure 2b is shown the water uptake of a different backbone which is more polar (due to the sulfone) and in this case the water uptake is somewhat higher although still less than the neat polymer. This indicates again the possible importance of the polymer backbone structure and the resulting morphology.

Figure 3a shows small angle X-ray scattering (SAXS) experiments on the imidazole-doped PFSA whose conductivity is shown in Figure 1a. The SAXS measurements show an ionomer peak which indicates a domain size of about 3.7-4 nm. A temperature study on this shows the size of the domain increasing above 125°C, which is consistent with dynamic mechanical analysis (DMA) measurements made on the same material. The DMA results showed a large amount of backbone plasticization by the imidazole which may indicate that the morphology is affected by the presence of the imidazole. To investigate this effect, a SAXS study has been carried out on a block co-polymer prepared from styrene and vinyl pyridine. This block co-polymer can be prepared with very well defined blocks (both molecular weight and polydispersity) so that a well controlled morphology is produced. This polymer is then cast with an imidazole-based ionic liquid to observe the effects of the presence of the ionic liquid on the morphology. Figure 3b shows how an increase in the ionic liquid component causes the morphology to change from lamellar pattern to tubular with an intermediate pattern during the transition. Conductivity measurements are being taken to observe how these changes affect transport.

Synthetic work has focused upon methods of synthesizing various polymer backbones that can be made as random or block co-polymers in order to attempt to control the morphology. The main strategy involves the attachment of allyl side groups on the polymers which then may be functionalized by hydrosilylation chemistry as shown in Figure 4. This strategy permits us to take the results from our experiments with mixtures and directly translate them into a solid state membrane. As is usual for an attractive strategy there are always difficulties in the details. In order to allow the Grotthuss mechanism to occur the imidazole must be tethered through the 2-, 4- or 5- positions and must have a protecting group on the nitrogen to allow the attachment chemistry to be carried out. Our first choices of protecting groups unexpectedly gave difficulties and we have settled upon benzyl as a protecting group. However, much effort continues on testing new protecting groups. The preparation of random and block co-polymers of polystyrene is proceeding slowly due to the sensitivity of these materials. The polyarylpoly sulfone structures (Figure 4a) are most interesting because of the stability that this class of materials has shown in fuel cell testing



**FIGURE 3.** SAXS measurements on a) 3M Ionomer and Nafion® doped with imidazole; b) polystyrene-polyvinylpyridine block copolymer doped with different levels of imidazole ionic liquid.

and because of the large amount of work carried out with these materials at LANL not only in the form of membranes but also in MEAs where the electrodes use the material as ink. The structure shown in Figure 4 allows us to prepare materials that can build upon the LANL experience. So far we have been able to prepare monomers with graftable allyl side chains but these do not survive the polymerization well due to the high temperatures used. Some optimization of





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