

IV.B.13 New Polyelectrolyte Materials for High-Temperature Fuel Cells, Membrane Electrode Assemblies and Enhanced Selectivity

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Objectives

- Investigate the feasibility of use of solvent-free solid polyelectrolytes for water-free and high-temperature operation.
 - Measure conductivity and mechanical/thermal properties of Nafion[®] and polyether polyelectrolytes doped with imidazoles.
 - Determine effect of imidazoles on platinum catalysts.
 - Covalently attach imidazoles to appropriate polymer backbones and test for conductivity, mechanical/thermal behavior and gas permeability.

Technical Barriers

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

- Phase 1 (FY 2003-FY 2004 and onwards):
 - O. Stack Material and Manufacturing Cost
 - R. Thermal and Water Management
- Phase 2 (FY 2004 onwards):
 - P. Durability
 - Q. Electrode Performance

Approach

1. Prepare polyelectrolyte gels from Nafion[®] and imidazole or N-methylimidazole to replace water. Measure properties (conductivity, thermal/mechanical properties).
2. Examine effect of imidazole on electrocatalyst activity as a function of “pH” and nature of anions.
3. Prepare polyelectrolyte gels with imidazoles and polyether polyelectrolytes prepared under NASA Polymer Energy Rechargeable System (PERS) program for lithium batteries. Measure properties for variety of polyelectrolytes with different structures and pendant anions.
4. Attach imidazoles covalently to modified polyether polyelectrolyte backbones using results from the polyelectrolyte measurements as guidance. Measure properties and optimize for use in separator membrane (high T_g , low gas permeability, high conductivity) or membrane electrode assembly (MEA) (low T_g , high gas permeability, high conductivity).
5. Optimize structures for durability.

Accomplishments

- Nafion[®] doped with imidazole or N-methylimidazole shows encouraging conductivity for high-temperature operation.
- Conductivity difference between imidazole and N-methylimidazole is consistent with a Grotthuss mechanism. Temperature dependence of conductivity is different.
- Vapor-phase impregnation of Nafion[®] demonstrates a “Schroder’s Paradox” similar to water. Thought to be related to morphology of the membrane.
- Conductivity of 1:1 Nafion[®] anion: Imidazole is much lower than the 1:4 membrane.
- T_g of Nafion[®] doped with imidazole is 20°C higher than Nafion[®] alone.
- Voltammetry of Pt in aqueous H₂SO₄ in presence of imidazole is only affected when concentration of imidazole exceeds that of H⁺. Can use imidazoles in fuel cells provided free imidazole is not able to contact catalysts.
- Polyether polyelectrolyte doped with imidazole shows similar conductivity as Nafion[®]. Fluoroalkylsulfonate acid groups show higher conductivity than alkylsulfonate.

Future Directions

- Synthesize polyelectrolyte-imidazole membranes with high T_g values—e.g., polystyrene backbones.
 - Optimize for conductivity, mechanical properties.
 - Optimize for gas permeability.
 - Prepare best structure for full cell test.
 - Milestone: Water-free separator membrane prepared.
- Synthesize polyelectrolyte-imidazole membranes with low T_g values—e.g., polyoxetane backbones—for flexibility and oxidation resistance.
 - Optimize for conductivity, mechanical properties in presence of nano-particles such as carbon black or silica.
 - Optimize for gas permeability in presence of nano-particles such as carbon black or silica.
 - Prepare best structure for full cell test.
 - Milestone: Water-free MEA prepared.
- Perform initial durability tests.

Introduction

Polymer electrolyte membrane fuel cells (PEMFCs) are of interest for transportation power systems that use hydrogen as fuel due to their inherent portability and low operating temperatures¹. These fuel cells have typically used perfluorosulfonic acid (PFSA) copolymers such as Nafion[®] as the membrane to separate the electrodes and the oxygen and hydrogen gas streams². These materials are remarkably selective. In fuel cells, the membrane permits the transport of cations (hydrogen ions) at rates sufficient to support high current densities (1-2 A/cm²) and yet prevents the transport of gases (hydrogen and oxygen) through the membrane which

would result in undesirable and inefficient reactions. The source of the selectivity apparently lies in the morphology of the membrane, which forms ion-rich domains among the glassy backbone structure which can swell with water to allow passage of the ions. The glassy backbone domains do not permit transport of either water or gases, thereby providing the observed selectivity. In fuel cells, the PFSA polymers prevent gas transport in the bulk membrane yet allow gas transport to the electrode surfaces. This good fortune occurs due to the extra free volume created in the glassy polymers by the electrode particles that allows increased gas permeation in the MEA. Thus, the morphology of the polymer membrane plays a critical role.

The recently recognized need to operate fuel cells at higher temperatures (120-150°C) has moved the operating conditions to a range where the remarkable properties of the PFSA's no longer hold. Nafion[®] has a glass transition temperature (T_g) of about 110-115°C, so operation at 120°C and above results in loss of mechanical strength, increased gas permeability and less phase separation between ionic and non-ionic portions of the polymer. Obviously, at these temperatures, retention of water in the membrane is difficult, but even if it were possible, due to use of high pressure, the change in phase of the polymer would still lead to failure. It is therefore necessary to prepare polymer structures that have higher T_g values and which can solvate the mobile cations in a polar phase that contains the anions and solvation groups. The solvation groups that are chosen to replace water include imidazoles among other possibilities³⁻⁵. Figure 1 shows a schematic of the kinds of polymers that could be prepared, with imidazole as the proton solvating groups that are tethered to the polymer matrix. The anion, in this case the fluoroalkylsulfonimide, is also tethered to the polymer matrix to provide a totally solid-state membrane with no leachable components. Such a membrane would result in considerable simplification of fuel cell systems and allow operation at elevated temperatures with no added water provided the conductivity is adequate and the membrane permeability to gases is acceptable.

Approach

During the last several years, work has been carried out at Lawrence Livermore National Laboratory (LLNL) to prepare and characterize polyelectrolyte membranes for use in lithium batteries. This work was originally funded by 3M/ U.S. Advanced Battery Consortium and more recently by the NASA Glenn PERS Program and involved the design, synthesis and testing of polyelectrolytes designed to facilitate the motion of lithium cations. The polymer structures are based on polyether comb-branch architectures to which the anion is attached. LLNL has developed methods for attaching virtually any desired group to the polymer in any desired concentration and in a wide variety of configurations^{6,7}. Thus, it's an easy step to attach imidazole groups to the polymer skeleton as well as the anions and to convert the polyelectrolyte from the

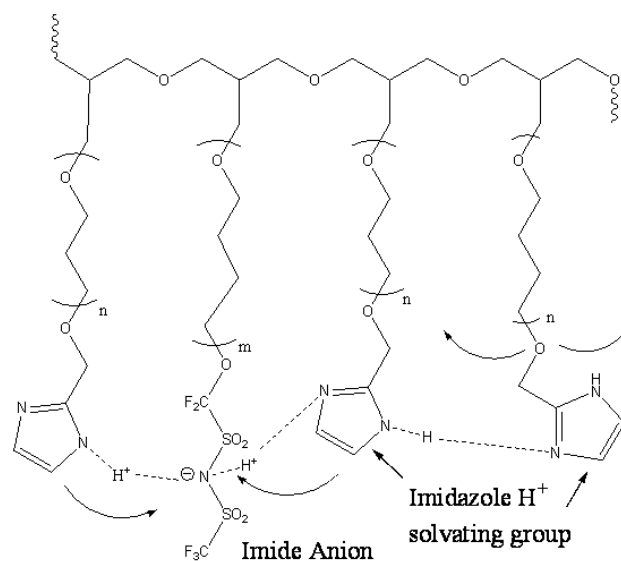


Figure 1. Schematic Structure of the Target Polyelectrolyte Membrane Containing Tethered Fluoroalkylsulfonimide Anions and C-Linked Imidazoles to Solvate the Protons

lithium form to the acid form. Figure 1 is a schematic illustration of the kind of polymer structure that is of interest. The basic backbone and side chains are formed with reactive allyl groups on the ends of the side chains. The groups to be attached—the anions and imidazoles, for example—are prepared with reactive silyl groups, which are then attached to the polymer side chains in the desired concentrations. The reactive allyl groups can also be used to form cross-links between chains in order to modify the mechanical properties. This synthetic strategy allows numerous features of the polymer structure to be easily modified to see how various properties of the polymer membrane are affected. For example, the backbone can be changed from a flexible chain, as shown in Figure 1, to a stiff (polystyrene) or inflexible (polyetherketone) one. The length of the side chains to which the anions and imidazoles are attached can be easily changed, as can the density of polar groups which affect the flexibility and motion of the side chains. The relative concentrations of anions to imidazoles can also be altered at will. In this way, the properties of the membrane can be tuned to provide optimum proton mobility and appropriate gas permeability. At the early stages, the stability of the structure to the fuel cell conditions is of secondary importance, but it may

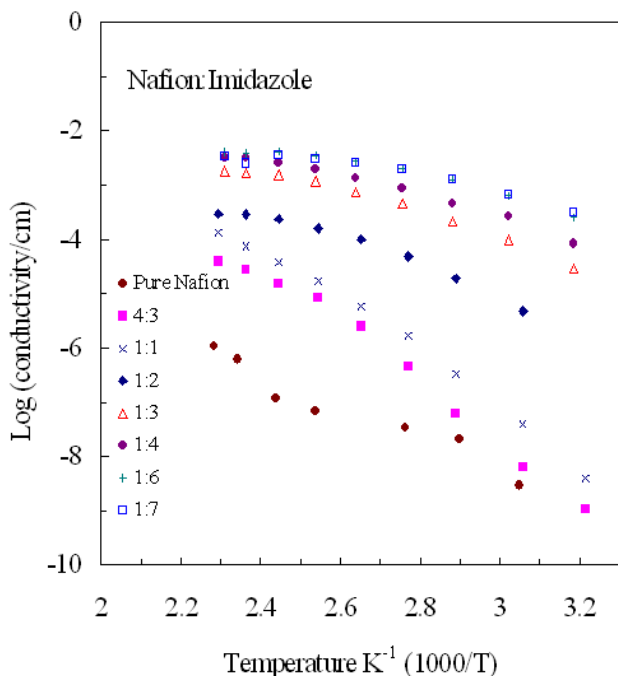


Figure 2. AC Conductivity Measurements as a Function of Temperature of Nafion[®] (Equiv. Wt. 1100) Doped with Imidazole (The imidazole is dissolved in the Nafion[®] solution and the doped film is cast from this solution. The concentration ratios refer to the molar concentration of imidazole to acid group in the polymer.)

be noted that reactions on the side chains of the comb structure will lead to the release of small fragments that can be readily analyzed by classical chemical analysis techniques, thereby providing unique insight into the modes of chemical failure that may occur.

With this versatile and powerful synthetic capability available, structure-function relationships can be rapidly established. Of great importance is how the structures affect the morphology of the polymer membrane, as this will have considerable impact on the ionic mobility and the gas permeability, the two properties that are most important to understand. For this reason, the phase behavior and different glass transition temperatures must be measured by thermal/mechanical analysis and various types of microscopy (atomic force microscopy, transmission electron microscopy). The proton mobility is measured by classical electrochemical techniques and correlated as a function of the polymer structure. The possible

operation of the Grotthuss-type mechanism of proton conduction⁸ through the membrane is of particular interest, as it is likely that only through this mechanism will a solvent-free membrane be able to achieve acceptable conductivities. Similarly, the effect of the phase behavior on gas permeability will be measured, as the membrane must function as a gas barrier in the bulk. Finally, all of these properties must also be measured in the presence of solid filler materials such as fumed silica, carbon black, etc., to determine how the polymer properties change in the presence of solid surfaces, which, of course, represent the electrode-polymer interfaces in the MEA.

Results

The experimental work for this project was delayed due to the unavailability of a crucial chemical used to graft groups (e.g., imidazoles, anions) onto the polymer matrix. The material (tetramethyldisilyl ethane) became available from the manufacturer in January of 2004. The status of the milestones is as follows:

1. Determine feasibility of imidazole use as solvation groups by measurement of conductivity of Nafion[®] and comb branch polyether polyelectrolytes doped with imidazole, N-alkyl imidazole and C-alkyl imidazole solvents.

Status: Completed. Measurements on both Nafion[®] and polyether polyelectrolytes doped with imidazole and N-methyl imidazole have been carried out.

Figure 2 shows the conductivities measured by AC impedance of Nafion[®] (equivalent weight 1,100) doped with various levels of imidazole, while Figure 3 shows the same measurements for Nafion[®] doped with N-methylimidazole. Highest conductivities have been measured at 3.3 mS/cm at 120-160°C under dry conditions for Nafion[®] doped with greater than a four-fold excess of imidazole over the acid function in the Nafion[®]. The temperature dependence of conductivity is clearly different between imidazole and N-methylimidazole, indicating that a Grotthuss-type mechanism may be occurring. The conductivity declines with lower concentrations of imidazole, and the temperature dependence is the same as with the N-

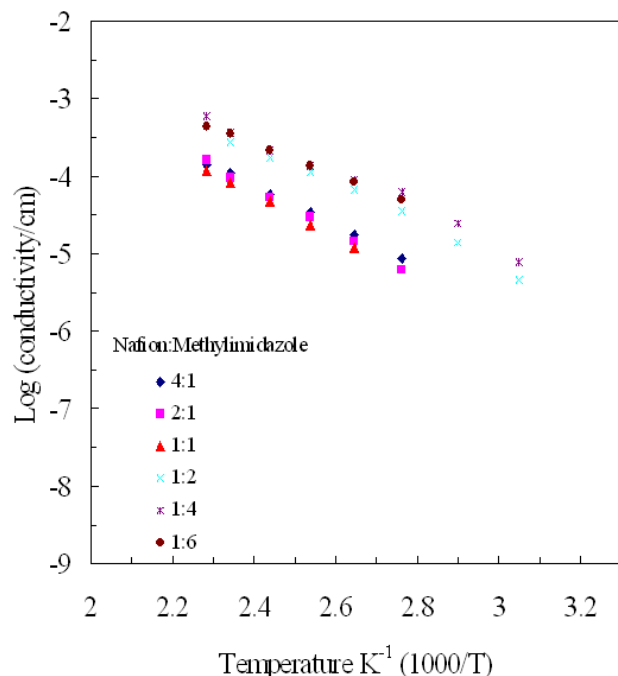


Figure 3. AC Conductivity Measurements as a Function of Temperature of Nafion[®] (Equiv. Wt. 1100) Doped with N-methylimidazole (Preparation and concentration ratios same as in Figure 2.)

methylimidazole-doped polymers. This indicates that a critical excess of imidazole over protons may be necessary to facilitate the Grotthuss mechanism.

The greater temperature dependence of the N-methylimidazole and lower-concentration imidazole doped Nafion[®] indicates that a similar mechanism of proton transport is occurring under these conditions. Since the Grotthuss mechanism cannot occur with N-methylimidazole, the only mechanism that can operate involves the segmental motion of the polymer side chains. This is a similar mechanism to the mode of transport of lithium ions in lithium polyelectrolytes, which is completely dependent on polymer chain mobility. Dynamic mechanical measurements were carried out on the imidazole- and N-methylimidazole-doped Nafion[®] films in the compression mode. These measurements showed that the presence of the imidazole leads to an increase of the T_g by about 20°C. Since the imidazoles are quite volatile, it is probable that the actual measured membrane contained a 1:1 ratio of imidazole:acid groups since the sample had to be heated to temperatures above

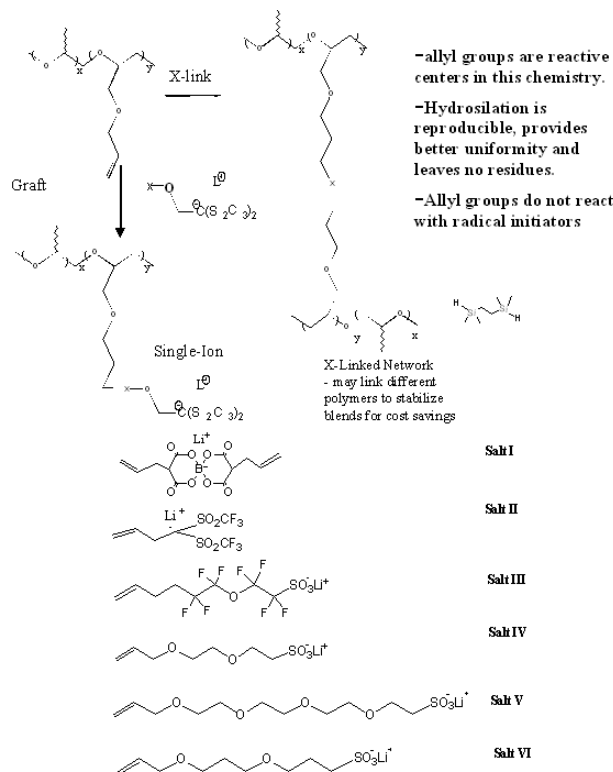


Figure 4. Schematic of Grafting Chemistry used to Attach Anions and Imidazole Functions to Comb-Branch Polymer Framework (Polyether polymers and lithium salts are designed for lithium battery work funded by NASA PERS Program. This DOE project uses the same chemistry to attach imidazoles and convert to the acid form for fuel cell operation. List of salts illustrates the versatility of the method and the variety of anions that have been successfully attached.)

the T_g in order to obtain satisfactory contact with the fixtures. The increase in T_g is likely due to the formation of a salt complex between the protonated imidazolium cation and the anions.

Similar experiments were carried out with the polyether polyelectrolytes. The synthesis of these materials was initially carried out to prepare polyelectrolytes for lithium batteries, and the procedures are shown in Figure 4 as well as being available in the literature^{6,7}. The lithium salt polyelectrolytes were converted to the acid form by treatment with Dowex ion exchange resin followed by doping with imidazole. The AC conductivity

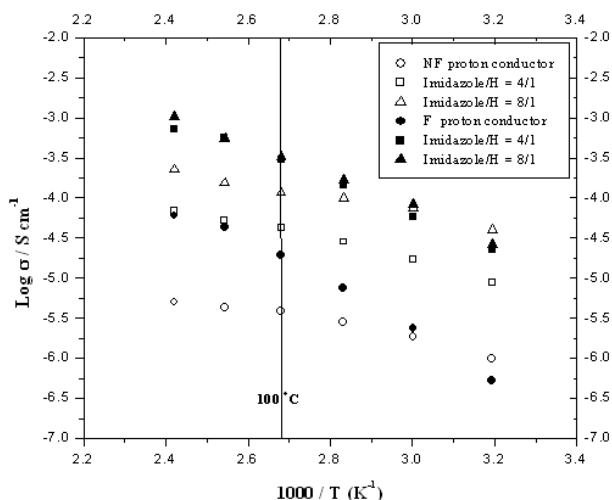


Figure 5. AC Conductivity Measurements as a Function of Temperature for Imidazole-Doped Polymers Prepared According to Figure 4 Using Salts III (fluorinated (F) sulfonate) and IV (non-fluorinated (NF) sulfonate) (The polyelectrolytes are converted to the acid form by ion exchange with Dowex ion exchange resin and cast from solution that also contains the imidazole.)

measurements are shown in Figure 5 for a polyelectrolyte containing a sulfonate attached to an alkyl group and a sulfonate attached to a fluoroalkyl group. The results show that the strength of the acid is important to the conductivity, and this indicates that attachment of the sulfonylimide anion will lead to better performance. An interesting observation is that the flat dependence of the conductivity on temperature does not appear for these doped polymers. This may be due to the lack of a distinct phase separation with the rubbery polyether polyelectrolytes, which may result in more mixing of the imidazoles with the polyether chains, thereby leading to disruption of ordering of the imidazole groups necessary to support a Grotthuss mechanism of proton transfer. This may be another indication of the importance of the morphology of the polymer membrane. Another indication of the role of morphology is the very different conductivity observed for Nafion[®] doped with imidazole in the gas phase. In this experiment, the membrane is cast with only polymer present and then is exposed to imidazole vapor until saturated. The resulting membrane has a lower conductivity than the membranes shown in Figure 1 and a temperature

dependence similar to that of the lower-concentration imidazole- and the N-methylimidazole-doped Nafion[®]. In this case, the morphology of the polymer is formed in the absence of imidazole, which has to penetrate the polar channels after they have formed.

Cyclic voltammetry experiments with platinum in acid solutions demonstrate that the reported poisoning of the platinum catalyst by imidazole⁹ can be prevented by protonation of the imidazole. This implies that the concentration of imidazole in the MEA should be less than in the bulk membrane in order to avoid poisoning of the electrocatalyst. The imidazole concentration in the bulk can be considerably higher provided the imidazoles are tethered to the polymer, and this will promote the operation of the Grotthuss mechanism through the bulk membrane. The polymer in the MEA will need to have lower concentrations of imidazoles in order to avoid poisoning the catalyst. Thus, different materials will be necessary for the bulk membrane versus the MEA. Similar considerations will also hold for the gas permeability properties. It is desired to prevent gas transport through the bulk membrane while promoting gas transport to the electrodes. This may be accomplished by altering the polymer structure in the MEA to provide more permeability, usually by lowering the T_g or by increasing free volume around the electrode surfaces.

2. Attach appropriate imidazole to polyether polyelectrolyte for solvent-free operation and measure electrochemical and mechanical properties.

Status: In progress. The late arrival of the grafting reagent delayed this milestone, but completion is expected by August 2004.

Conclusions

- Imidazole can replace water as the solvation group for proton conduction.
- Under certain conditions, the Grotthuss mechanism appears to operate with imidazoles.
- In order to operate at elevated temperatures, the imidazole must be tethered to the polymer.
- The polymer in the bulk membrane must have a different structure from the polymer in the MEA due to the gas permeability needs and the requirements of the electrocatalyst.

References

1. DOE/ONR. (Baltimore, MD. <http://www.lanl.gov/energy/est/transportation/trans/workshop.html>, 1999).
2. Eisenberg, A. & Kim, J.-S. *Introduction to Ionomers* (Wiley, New York, NY, 1998).
3. Kreuer, K. D., Fuchs, A., Ise, M., Spaeth, M. & Maier, J. Imidazole and pyrazole-based proton conducting polymers and liquids. *Electrochimica Acta* 43, 1281-1288 (1998).
4. Schuster, M. et al. Proton mobility in oligomer-bound proton solvents: imidazole immobilization via flexible spacers. *Solid State Ionics* 145, 85-92 (2001).
5. Schuster, M. F. H., Meyer, W. H., Schuster, M. & Kreuer, K. D. Toward a new type of anhydrous organic proton conductor based on immobilized imidazole. *Chemistry of Materials* 16, 329-337 (2004).
6. Sun, X. G., Reeder, C. L. & Kerr, J. B. Synthesis and characterization of network type single ion conductors. *Macromolecules* 37, 2219-2227 (2004).
7. Sun, X. G., Reeder, C. L., Kerr, J. B. & DesMarteau, D. D. in *Polymer Preprints* (2004).
8. Agmon, N. The Grotthuss Mechanism. *Chemical Physics Letters* 244, 456-462 (1995).
9. Yang, C., Costamagna, P., Srinivasan, S., Benziger, J. & Bocarsly, A. B. Approaches and technical challenges to high temperature operation of proton exchange membrane fuel cells. *Journal of Power Sources* 103, 1-9 (2001).

FY 2004 Publications/Presentations

- 1) "New Polymeric Proton Conductors for High Temperature Applications", Presentation to the DOE High Temperature Membrane Working Group, Orlando, FL, October 16, 2003.
- 2) "New Polymeric Proton Conductors for High Temperature Applications", Presentation to the DOE High Temperature Membrane Working Group, Philadelphia, PA, May 27, 2004.