V.B.16 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 solid polyelectrolytes for high temperature operation that do not require the presence of water.
- Prepare solid polymer electrolytes where only the proton moves across the membrane during operation (no mobile solvent such as water).

Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section (3.4.4.2) of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

(A) Durability
(B) Cost.
(C) Electrode Performance
(D) Thermal, Air and Water Management

Technical Targets

1. Dry membrane conductivity (no humidification) = 0.1 S/cm at 120°C, 0.07 S/cm at ambient temperature, 0.01 S/Cm at -20°C
2. Hydrogen and oxygen cross-over <2 mA/cm^2 equivalent
3. Area specific impedance in practical MEAs <0.02 ohm-cm^2
4. Cost $35/kw
5. Durability: 5,000 hours

Accomplishments

- Demonstrated the feasibility of a polymeric solid-state proton conducting membrane with no mobile solvent.
- Demonstrated that the proton conductivity loss due to immobilization of the solvent molecule is negligible.
- Demonstrated that the structure-diffusion (Grotthuss) mechanism is necessary to achieve the conductivity goals.
- Completed initial determination of structural features of the polymer that are important for achievement of the conductivity, gas permeability and mechanical property goals for membrane materials.
- Initial water-uptake measurements indicate that perfluorinated sulfonic acids when combined with imidazole solvents may reject water. This could be very attractive for sub-zero temperature operation and start-up.

Introduction

Polymer Electrolyte Membrane (PEM) fuel cells are the main focus of the DOE effort for alternatives to the internal combustion engine. The demands made by electrochemical engineers upon the PEM material that separates the electrodes are severe. The membrane separator has to facilitate rapid transport of protons from one electrode to the other yet simultaneously prevent transport of the gaseous reactants (oxygen and hydrogen), a remarkable feat of selectivity. Even more remarkably, the membrane material must change its selectivity when it is incorporated into the composite electrode structures as rapid transport of both protons and gases to the electrode surfaces is required. The material must possess sufficient mechanical strength as a membrane to stand up to the pressures generated in a cell stack and yet be sufficiently adhesive and processable to form good composite electrodes which adhere well to the membrane separator in the membrane electrode assembly (MEA). The membrane material must also resist chemical degradation in the presence of oxygen and reactive oxygen species so that these remarkable properties persist for the operating life of the fuel cell.

Fortunately, and somewhat improbably, materials exist which possess such properties. Perfluorinated sulfonic acid (PFSA) polymers such as Nafion® have been used as the membrane material for PEM fuel cells for many years where they have provided many of the desired properties. However, in order to provide the required conductivity the PFSA must be swollen with liquid water which solvates the protons and allows dissociation of the sulfonic acid groups. The remarkable selectivity with respect to gas permeability derives from the morphological properties of the polymer which is also largely responsible for the mechanical properties. However, the need to control the water content of the membrane requires a complicated water management system which is undesirable in a vehicular application where space and weight are at a premium. It has also been recently found that operation at 120°C is desirable in order to simplify the heat management of the fuel cell. At such temperatures, retention of liquid water is difficult as pressurization is not feasible due to the energy losses involved. Therefore, there is a compelling need to develop new membrane materials that do not require water in order to conduct protons.

Approach

Solid-state conductive polymer electrolytes that require no mobile solvent for ion conduction have been known for thirty years and have been extensively studied for lithium batteries. These polymers solvate the mobile cation thereby promoting dissociation of salts dissolved in the polymer which carries the current. Just as in PFSA membranes the anion or the cation group may be tethered to the polymer to produce a polyelectrolyte single ion conductor. Heterocyclic bases such as imidazole have been known for many years to be capable of proton solvation and to support proton conduction. These bases can be used as a mobile solvent to replace water or they may be covalently tethered to the polymer structure to prevent losses due to evaporation, electro-osmosis or dissolution in water formed at the fuel cell cathode. In the latter case, a completely solid-state membrane would result in which only the proton moves. Figure 1 shows the molecular structure of a polymer material that should act in this manner. Both the acid group and the imidazole are tethered to the polymer by means of side chains which may be mobile. The proton is solvated by the imidazole which can move though segmental motion of the tethered imidazole or through structure diffusion of the imidazoles. The arrows represent these kinds of motion. It is important that structure diffusion occurs in order to support the conductivities required by the fuel cell as segmental motion is generally too slow and the resulting lower conductivity would require a much larger electrode area which would be prohibitively expensive.

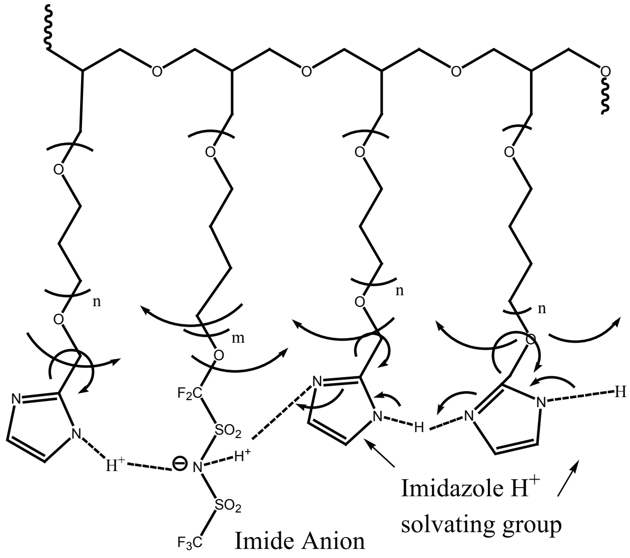

FIGURE 1. Schematic of polymer structure designed to facilitate proton conduction without the need for mobile solvents such as water.

The ideal structure of the polymer that the acid and base groups would be tethered to needs to be elucidated. A large number of parameters are variable, such as the nature of the backbone, the length and flexibility of the side chains that tether the acids and bases, the concentrations of the acids and bases both absolutely and relative to each other and how the bases are tethered in order to promote structure diffusion. These are parameters that are considered to influence the proton conductivity which is the primary property of interest. They also influence the other properties such as gas permeability, morphology, mechanical strength and interfacial behavior. In order to vary these structural parameters, use has been made of a synthetic technique developed previously for lithium batteries which allows functionalities such as acid and basic groups to be clipped on to a polymer backbone with appropriate side chains. In order to simplify the optimization process, polyelectrolyte materials including PFSAs such as Nafion® have been doped with free imidazole and substituted imidazole to determine the best ratios of base to acid for conductivity. The nature and concentration of the acid groups are also varied in order to zero in on the best structures before the more difficult synthesis of the fully tethered materials is attempted. The doped polymers and the fully tethered materials are characterized for the properties of interest to generate structure-function relationships that may be used to design and build the most desired membrane materials.

Results

Initial conductivity measurements over a temperature range from ambient to 160°C of Nafion® doped with imidazole and with N-methyl imidazole showed that the best conductivities were obtained at molar ratios of 8:1 for the base to acid (0.01 S/cm at 120-150°C). The imidazole doped membranes showed a very low temperature dependence of conductivity for the higher base concentrations which is consistent with the structure-diffusion (Grotthuss) mechanism. With N-methyl imidazole which cannot participate in the structure diffusion mechanism, the temperature dependence of conductivity was much higher, consistent with a conduction mechanism based on the segmental motion of the polymer or translational motion of the solvent. Polyether polyelectrolytes originally prepared for lithium battery use showed a conductivity behavior inconsistent with Grotthuss mechanism when doped with imidazole. This appears to be due to the lack of phase separation between the polymer and imidazole. The polyether groups are miscible with the imidazole so that channels of imidazoles do not form that could support the structure diffusion mechanism. This indicates that phase separation and the morphological behavior of the polyelectrolytes are critical for achievement of high conductivities. These properties are also required to obtain selectivity with respect to gas permeability.

Dynamic mechanical analysis (DMA) of dry Nafion® and doped with imidazole shows that the presence of the imidazole leads to an increase in the glass transition temperature (T_g) due to the formation of an imidazole salt with the sulfonic acid (Figure 2). The appearance of transitions at low temperatures (-40°C and 65°C) indicates some degree of plasticization of the Nafion® backbone by the imidazole which indicates a less distinct phase separation than with water. However, the mobility at very low temperatures is encouraging for operation at sub-zero temperatures. Differential scanning calorimetry measurements shows that the imidazole in the Nafion® does not crystallize. Themogravimetric analysis (TGA) of the Nafion®-imidazole blends (Figure 3) shows that the excess imidazole easily sublimes while the 1:1 mixture is stable to 300°C. The same figure also shows the moisture uptake of the Nafion® to be around 5% while the imidazole-doped Nafion® shows almost no moisture uptake from atmosphere, indicating that the imidazole-Nafion® mixtures reject water. This is reasonable since the acid dissociation constant (pK_a) of imidazole is similar to that of water. This observation is also significant for sub-zero operation as it implies that PFSA-imidazole membranes reject water which will avoid problems with water freezing in the membrane. More extensive water up take measurements are currently ongoing.

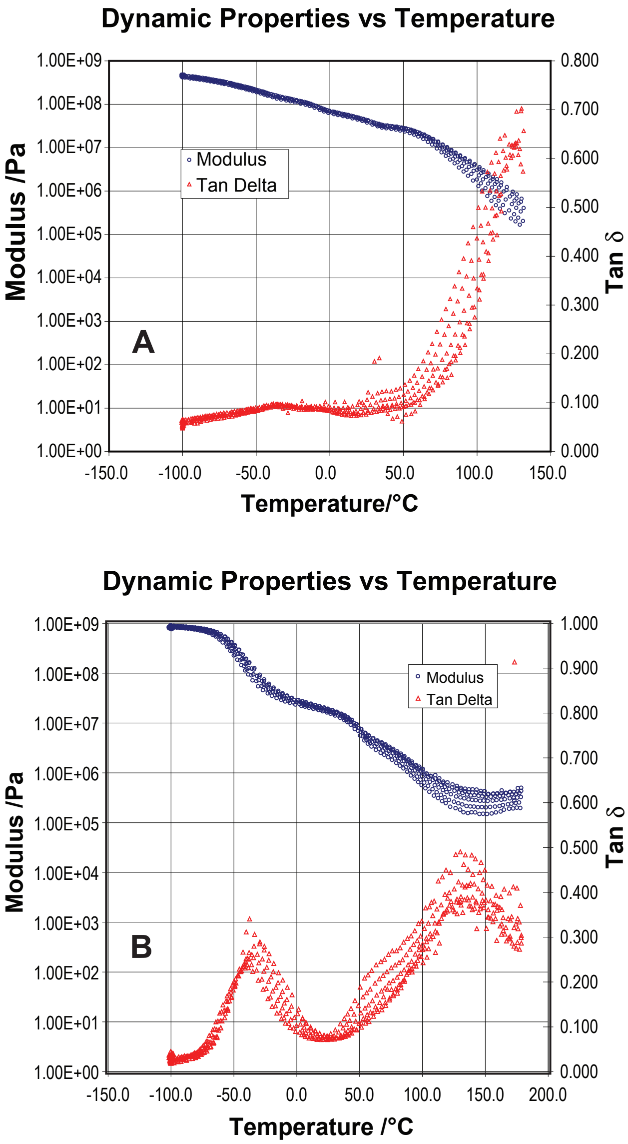

FIGURE 2. DMA of Nafion® and Nafion®-Imidazole: a) Dry-cast Nafion®; b) Dry-Cast Nafion®-Imidazole SO_3H:Im 1:4

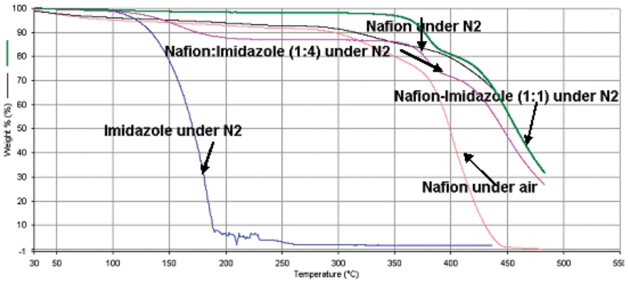

FIGURE 3. Thermal Gravimetric Analysis of Nafion®, Imidazole and Blends

Membranes were prepared with polyetheralkylsulfonate polyelectrolytes doped with imidazole and with imidazole tethered to the polymer through the N-position. In both cases structure diffusion conduction of protons is not possible. The proton conductivities of the doped polyelectrolyte and the tethered imidazole polyelectrolyte are shown in Figure 4. At a base/acid ratio of 1/1 the conductivity of the tethered material is the same as the undoped polyelectrolyte indicating a strong salt formation between the imidazole and the acid group. Most encouragingly, the conductivity of the 3/1 imidazole/acid tethered material is the same as

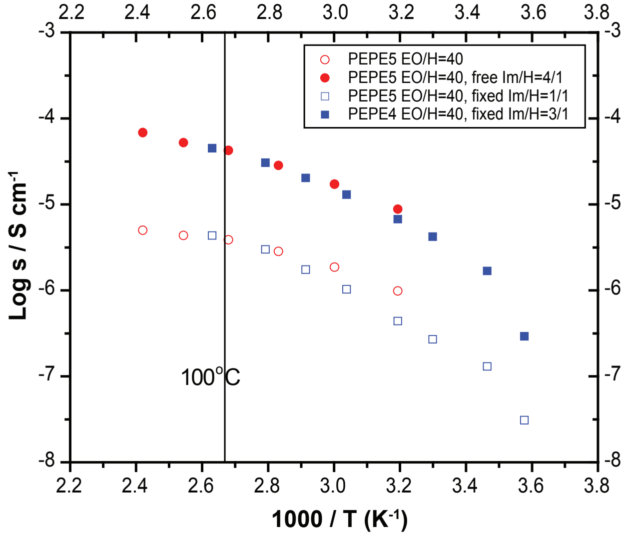

FIGURE 4. Conductivities of polyetheralkylsufonate doped with free imidazole and with tethered imidazole (N-tethered) with different Im/H$^+$ ratios (1/1 and 3/1).

that of the polyelectrolyte doped with free imidazole. This indicates that the tethering of the imidazole does not necessarily mean a low conductivity. When the Grotthus mechanism is operating one can expect that the tethering will have an even smaller impact.

These results indicate that a solid state polymer electrolyte with a high conductivity is possible. It is known that the fluoroalkylsulfonylimide acid promotes very high conductivities when combined with imidazole. Tethering via the C-position and attachment to a polymer backbone that promotes better phase separation seems likely to produce membranes with conductivities approaching the DOE targets.

Conclusions and Future Directions

Conclusions

- Imidazole solvation groups are feasible for high temperature and water-free membranes.
- Temperature dependence of conductivity of free imidazole is consistent with the Grotthuss mechanism of proton transfer.
- The morphology of the polymer matrix plays a role on the promotion of the Grotthuss mechanism.
- The imidazoles must be tethered to the polymer matrix due to volatility. This results in a loss of conductivity.
- The conductivity loss due to tethering of imidazoles is small.
- Stronger acid groups such as fluoroalkylsulfonylimides promote higher conductivities.
- Longer tethers for the acid groups promote conductivity.
- Imidazole groups in the MEA must be protonated to avoid poisoning of platinum catalysts. This results in a loss of conductivity since conductivity is favored by excess imidazole.
- Imidazole-doped Nafion® exhibits a higher T_g due to the salt formation between the imidazole and acid, and two transitions at low temperatures that indicate mobility of side chains and backbone enhanced by plasticization with the imidazole.
- Imidazole-doped Nafion® appears to have much lower water uptake than Nafion® indicating that PFSA-imidazole membranes may reject water leading to better sub-zero temperature performance and durability.

Future Directions

- Preparation and characterization of polyelectrolytes with C-tethered imidazole.
- Preparation and characterization of fluoroalkylimide acid polyelectrolyte.
- Preparation and characterization of phase separated polyelectrolyte with C-tethered imidazole.
- Studies of chemical stability of imidazoles with oxygen species.
- Further studies of water uptake and low temperature behavior.

Special Recognitions & Awards/Patents Issued

1. U.S. Patent 6,956,083. Single ion conductor cross-linked polymeric networks (issued October 18, 2005).

FY 2006 Publications/Presentations

1. "Cross-fertilization between Polymers for Batteries and Fuel Cells", John B. Kerr, Pacific Polymer Conference 9 (PPC-9), December 12, 2005, Mauii, Hawaii.

2. "Single Ion Conductor Polymer Electrolytes for Lithium Batteries and Fuel Cells", John B. Kerr, Invited speaker, Karl Weiss Graduate Student Symposium, Northeastern University, April 13, 2006.

3. "Single Ion Conductor Polymer Electrolytes for Lithium Batteries and Fuel Cells", John B. Kerr, Invited Speaker, University of Massachusetts Amherst, MRSEC on Polymers Symposium, May 17, 2006.

4. "New Polyelectrolyte Materials for High Temperature Fuel Cells", John B. Kerr, Poster Presentation FCP-8, DOE Office of Hydrogen, Fuel Cells and Infrastructure Technologies Review Meeting, Washington, D.C., May 17, 2006.