

V.D.14 New Polyelectrolyte Materials for High Temperature Fuel Cells

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Technical Targets

This project is aimed at the development of membranes that do not require the presence of added water to achieve adequate conductivity (0.1 S/cm at 120°C, 0.07 S/cm at 20°C and 0.01 S/cm at -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/cm²). 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 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/cm²) in a medium of low water content where catalyst activity may be quite different from a high water content condition (target 720 μ A/cm² at 900 mV(Pt) or 300 A/cm² 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 that phase-separated polymer structures are essential in order to achieve practical conductivities (0.1 S/cm) with tethered heterocyclic bases such as imidazole to solvate the protons in place of water. These structures are best controlled through the use of block copolymers to control the backbone morphology.
- Demonstrated that short side chain tethers for the heterocyclic bases are necessary to facilitate fast proton transport by the Grotthuss mechanism.
- System modeling of the relative effects of Grotthuss versus segmental motion transport of the protons through the membrane shows that the overall conductivity is rapidly diminished by relatively small amounts of segmental motion bottlenecks.
- Degradation studies of imidazole-containing materials using metal ion initiated Fenton chemistry shows that the degradation is accelerated by the presence of the heterocyclic bases which act as ligands to the metal ions that decompose the peroxide to hydroxyl. It is concluded that

Objectives

Develop durable water-free membrane materials with properties that meet the 2015 DOE targets:

- Conductivity: 0.1 S/cm at operating temperatures ($\leq 120^\circ\text{C}$) and inlet water vapor partial pressures < 1.5 kPa.
- Durability with cycling $> 5,000$ hours at $> 80^\circ\text{C}$.
- Oxygen and hydrogen cross-over currents ≤ 2 mA/cm².
- Durable membrane electrode assemblies (MEAs) with rated power at 1,000 mW/cm² and less than 5% performance degradation over lifetime.

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
- (C) Performance
- (A) Durability
- (B) Cost

ultraviolet/visible light or thermal initiation of peroxide decomposition will provide a more appropriate test.

- Studies of the behavior of imidazolium bis(trifluoromethylsulfonyl)imide (TFSI) ionic liquids in block copolymer matrices have demonstrated the effect of the proton-conducting medium on polymer morphology. The presence of the polymers structures appears to impose order on the conducting medium that promotes Grotthuss transport over longer distances and at lower temperatures by concentrating the ions in the channel structures. This results in conductivities >0.02 S/cm at 120°C and >0.01 S/cm at 85°C in the absence of any water.
- Composite electrodes and MEAs have been successfully prepared with non-Nafion[®] binder ionomers which perform almost as well as Nafion[®] MEAs in the absence of humidification. The best performing materials are fluorinated and the performance appears to be related to mass transport and flooding issues due to product water. This success is attributable to careful preparation of binder inks and appropriate formulations and demonstrates the capability to prepared MEAs with imidazole-containing materials in the coming year.



Introduction

Presently available fuel cell membranes require the presence of liquid water in order to transport protons and support the current demands. Because of the poor performance of fuel cell electrocatalysts, nearly half of the fuel energy is converted to heat which requires a very complex and expensive heat and water management system in order to maintain the water content of the membranes. Kreuer 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 also uses imidazole groups to bind metal ions in oxygen reduction enzyme catalysts such as copper laccase [3]. It has also been noted previously that imidazole bases appear to be resistant to oxidation [4] by oxygen species, an important property for a fuel cell solvent. Previous work on the attachment of imidazoles to polyelectrolytes that showed that an all solid state proton conducting membrane was indeed possible [5]. While the conductivities achieved were low the polymer structures were not ideal and the purpose of this project is to understand how to optimize the polymer structures 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 easily obtained components to measure how the properties vary and to use these results to formulate the composition of the final polymer materials which are difficult to make. In the Fiscal Year 2008 annual report, measurements on proton conducting ionic liquids, both neat and dispersed in polymer matrices were described, as were measurements on polyelectrolyte materials doped with heterocyclic bases. Similar measurements have been continued on models that more closely resemble the tethered groups in the final target polymers and neutron scattering, and nuclear magnetic resonance (NMR) relaxation measurements have been added to study the mechanisms of proton transport. Models of the proton transport through the membrane have been constructed to isolate the consequences of bottlenecks due to slow proton transport and this knowledge helps guide the polymer synthesis and morphology control, which is critical to achievement of the conductivity goals, adequate mechanical properties and control of gas cross-over. Synthesis of polymer materials with imidazole attached to side chains has been carried out and these polymers have been blended with polymer bound acids to give fully tethered materials using the results with the model ionic liquids to formulate the relative concentrations of imidazole and acid. Conductivity, water uptake and degradation studies are carried out on both the models and the completed fully-tethered polymers. Since the synthesized membrane materials must be used with electrodes to be useful, methods of preparing composite electrodes with novel, non-Nafion[®] binders are investigated to determine the polymer properties that lead to good electrode performance. Less expensive ionomer materials are used first to develop the methodology to be applied with the target imidazole-containing ionomer materials..

Results

Figure 1 shows a schematic of the type of polymer structure that appears to be desired in order to achieve fast proton transport through the membrane. The results obtained in the past year on ionic liquid models and on synthesized polymers with tethered imidazoles indicate that the morphology shown is necessary to promote the Grotthuss mechanism of proton transport. For this it is necessary to develop phase separation so that a pore-like structure is formed to provide some order for the imidazole structures to rapidly transport protons via a hopping mechanism. The phase separation is best controlled by use of block copolymers and by use of appropriate backbones. Figure 1(b) shows examples of

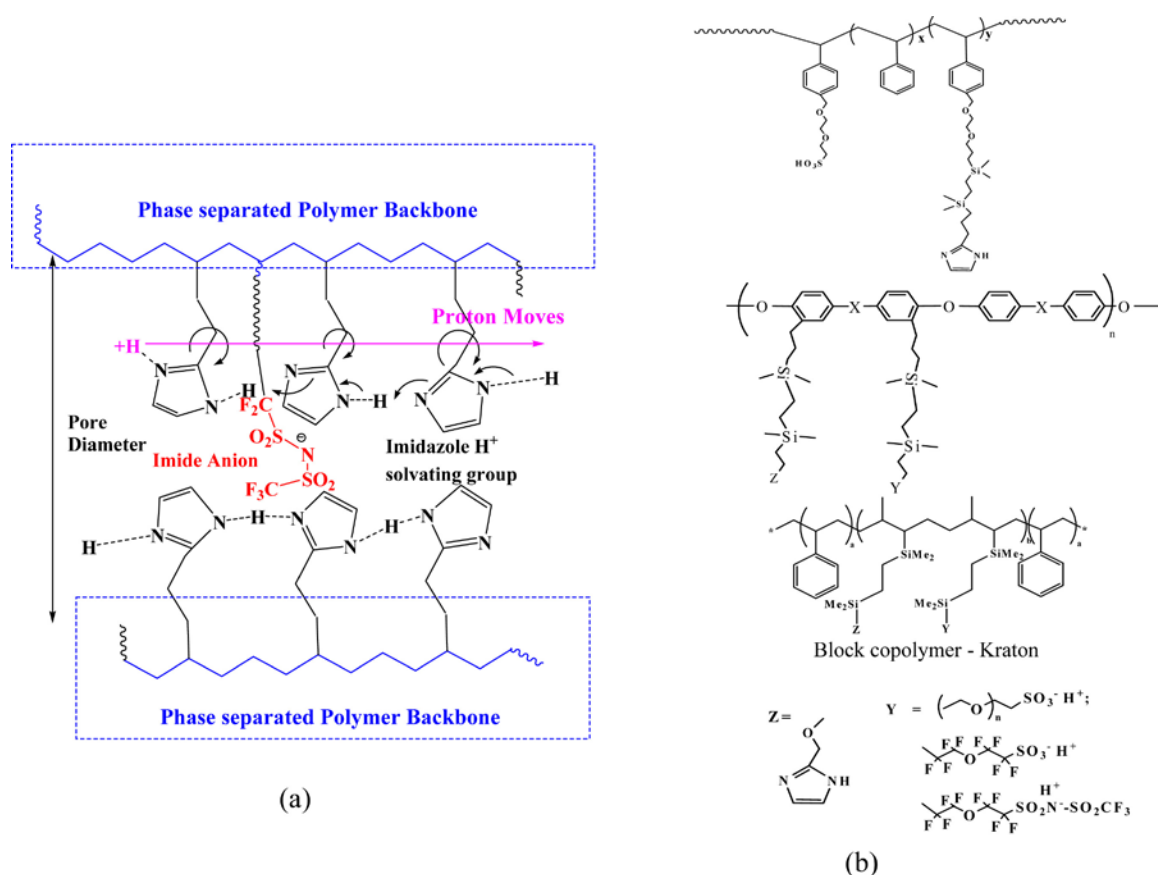


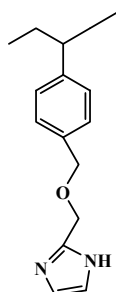
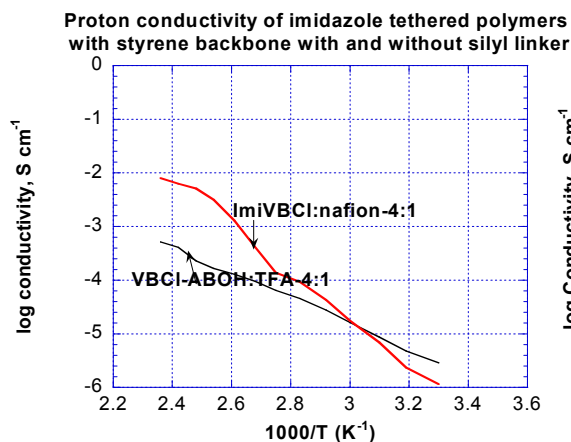
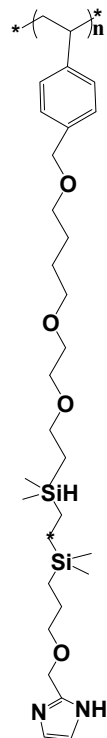
FIGURE 1. (a) Schematic representation of desired polymer morphology to promote high conductivity based on results obtained in FY 2009. (b) Examples of polymer structures prepared and under studying FY 2009.

some of the polymer structures that have been prepared for this purpose and which are under continuing study.

Particularly noteworthy is the imidazole group (e.g. Z in Figure 1) which is shown as tethered to the polymer through the 2-position. The tether can also be through the 4- or 5-positions. However, the tether cannot be through the 1-position, which is the nitrogen as this would block the operation of the Grotthuss mechanism of proton transport. The mechanism is shown schematically in Figure 1(a) where the arrows represent electronic rearrangements within the imidazole molecules and rotation around the tether bonds. The end result is that the proton is able to hop from one side to another without the need for the solvent molecules to move with it. The attachment of the imidazole through positions other than the nitrogen is not trivial and requires the use of protecting groups on the nitrogen which can be cleanly removed once the polymer is prepared. Considerable effort has been expended upon this problem during FY 2008 and FY 2009 and a completely satisfactory solution is still not in hand. In this, the project contains much in common with peptide chemistry and we are drawing heavily on knowledge from that field to assist in the problem.

Figure 2 shows the results of conductivity measurements made on polymers that contain the imidazole tethered in the 2-position. These measurements are made under completely dry conditions. The polymers are blended either with trifluoromethylsulfonic acid (TFA) or Nafion® where the numbers 1:1, 4:1 or 10:1 represent the ratio of the imidazole molecules to the acid groups. The blends with Nafion® ionomer represent fully immobilized materials where only the proton moves through the membrane. The figure shows results for a polymer backbone which can phase separate (polystyrene) (a) and one which does not (polyether) (b) and each graph shows comparisons of conductivities for short side chains versus long side chains. It can be seen that the short side chain with the polystyrene backbone provides the highest conductivity at 120°C (nearly 10^{-2} S/cm) but with a strong temperature dependence. A similar temperature dependence is observed with the non-phase-separating polymer (imiepi:Nafion®-4:1) but at a lower absolute value of conductivity. This may indicate that the bottleneck for proton transport lies in transport through portions of the polymer which is controlled by segmental motion and that the phase separation may concentrate the ionic conduction medium to achieve a higher local

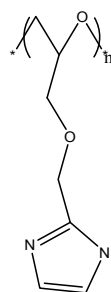
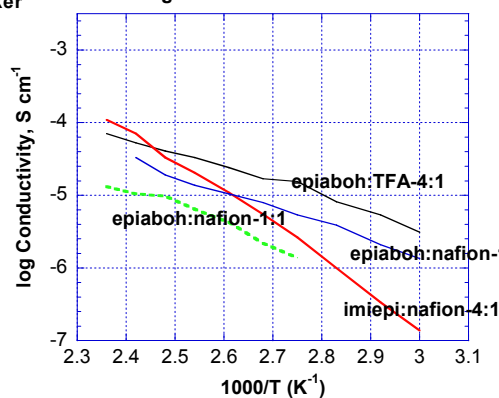
VBCI-ABOH



ImiVBCI

(a)

Proton conductivities of polymers with long versus short side chains



imiepi

(b)

epiaboh

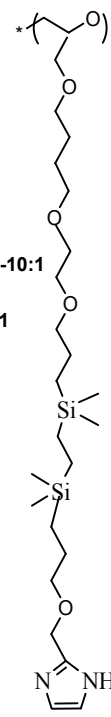


FIGURE 2. Conductivity measurements as a function of temperature of tethered imidazole polymers blended with TFA and Nafion®. (a) Polystyrene backbones thought to promote phase separation; (b) polyether backbones thought not to phase separate. Polymer structures shown.

concentration of charge carriers which can support higher conductivities. The hypotheses concerning the effect of phase separation and side chain length are under continuing study but it appears reasonable that conductivity's in the range of 0.01-0.1 S/cm at 120°C are attainable by appropriately altering the polymer structures.

The temperature dependences of the conductivities shown in Figure 2 are clearly unacceptable for use at lower temperatures. Figure 3(a) shows much more desirable conductivity behavior for imidazolium TFSI ionic liquids (b) both as neat liquids and dispersed in a block copolymer matrix. Small angle X-ray scattering (SAXS) and small angle neutron scattering measurements carried out at LBNL and Oak Ridge National Laboratory respectively show how the presence of the ionic liquid alters the morphology of the polymer structure (Figure 3(c)) and these structures appear to correlate with the conductivity behavior in Figure 3(a). The pure ionic liquid (2VP:IL=0) shows a flat conductivity dependence upon temperature indicating a Grotthuss or "hopping" mechanism of proton transport. Addition of 40% block copolymer to the mix does not reduce the conductivity (2VP:IL=0.6) while the effect of 60% by weight of the polymer is relatively small (2VP:IL=1.36) and only when the polymer is present in

large excess (2VP:IL=3.63) does the conductivity drop to levels that are characteristic of control by segmental motion. The behavior of this sample is similar to the samples in Figure 2(b) which are not phase separated and charge transport is controlled by segmental motion.

To understand the conductivity results and also the impact of morphology, acid and base site concentrations, etc. on conduction, a network model has been developed. The network model uses pore-level effects such as changes in dielectric to corroborate the experimental findings and tune the resistances between the network nodes. These values will also be further explored in the future using model copolymer systems and NMR results. When complete, the network model will be able to ascertain the importance of bottlenecks on performance and provide guidance to the membrane synthesis efforts. As a first result, relatively simple calculations have shown that in a membrane with only a few linkages where the vehicle mechanism dominates, the overall conduction suffers greatly due to the much slower diffusion. These results are shown in Figure 3(d) which demonstrates that even a very small amount of vehicle motion (segmental motion in polymers) has a very significant effect upon the overall conductivity and this is magnified by the greater differences between Grotthuss and vehicle conductivities. Thus the presence

Conductivity of Block Copolymer: S-2-PVP (8.7-12.0kg/mol) in 5:5 IL

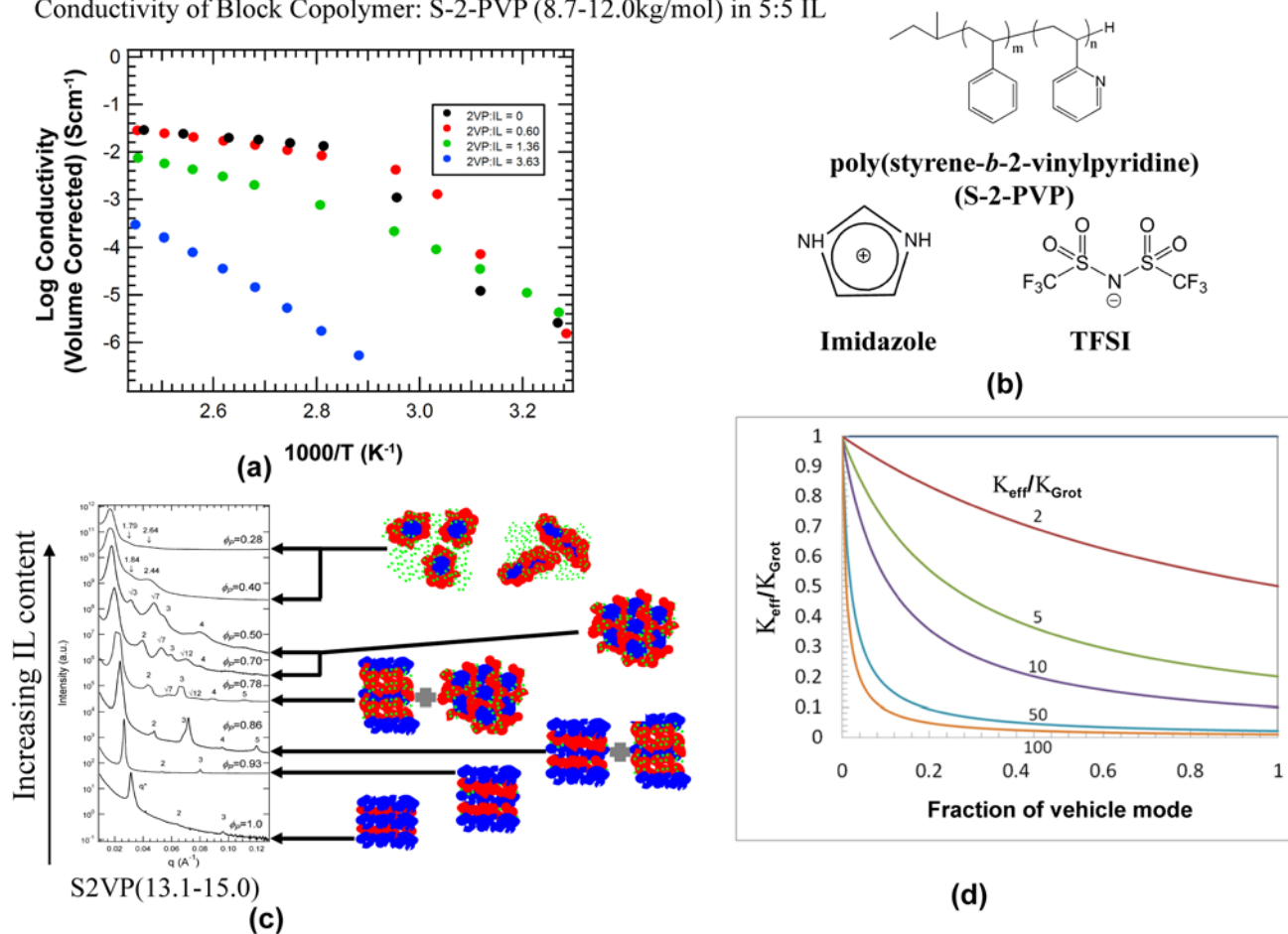


FIGURE 3. (a) Conductivity as a function of temperature of imidazolium TFSI ionic liquids in a poly(styrene-*b*-2-vinylpyridine) matrix for varying compositions; (b) structure of the studies ionic liquids and polymers; (c) SAXS measurements on ionic liquid-polymer mixtures; (d) Model of the effect of non-Grothuss charge transport segments on overall conductivity.

of charge transfer bottlenecks can have severe effects upon the conductivity.

Finally, the polymer materials must eventually be tested in MEAs and to prepare for this, work has been carried out on the preparation of composite electrodes using non-Nafion[®] binders. Figure 4 shows the fuel cell performance of MEAs using ionomers with different levels of fluorination under fully humidified and non humidified conditions. The MEA with a PFSA-bonded cathode performed best, while the MEA using a wholly hydrocarbon binder performed the worst. MEAs using partially fluorinated ionomers gave an intermediate performance, with the performance depending on the degree of fluorination. These observations indicate that fluorination of ionomers improves fuel cell performance probably due to improved gas permeability. This effect is more prominent under non-humidified conditions which may indicate that rejection of water may be occurring allowing easier transport of the gases. In order to accomplish these results considerable experimentation

was required to formulate the electrode inks and patents have been applied for that describe this. These methods will be applied to the imidazole containing polymers as they become available.

Conclusions and Future Directions

Conclusions

- Conductivity measurements indicate that practical conductivities (0.05 S/cm) will be possible only through operation of the proton-hopping (Grothuss) mechanism of charge transfer. This appears to be promoted by phase separation and morphology control. The morphology is best controlled by use of block co-polymers.
- Relatively simple model calculations have shown that in a membrane with only a few linkages where the segmental motion (vehicle) mechanism dominates, the overall conduction suffers greatly

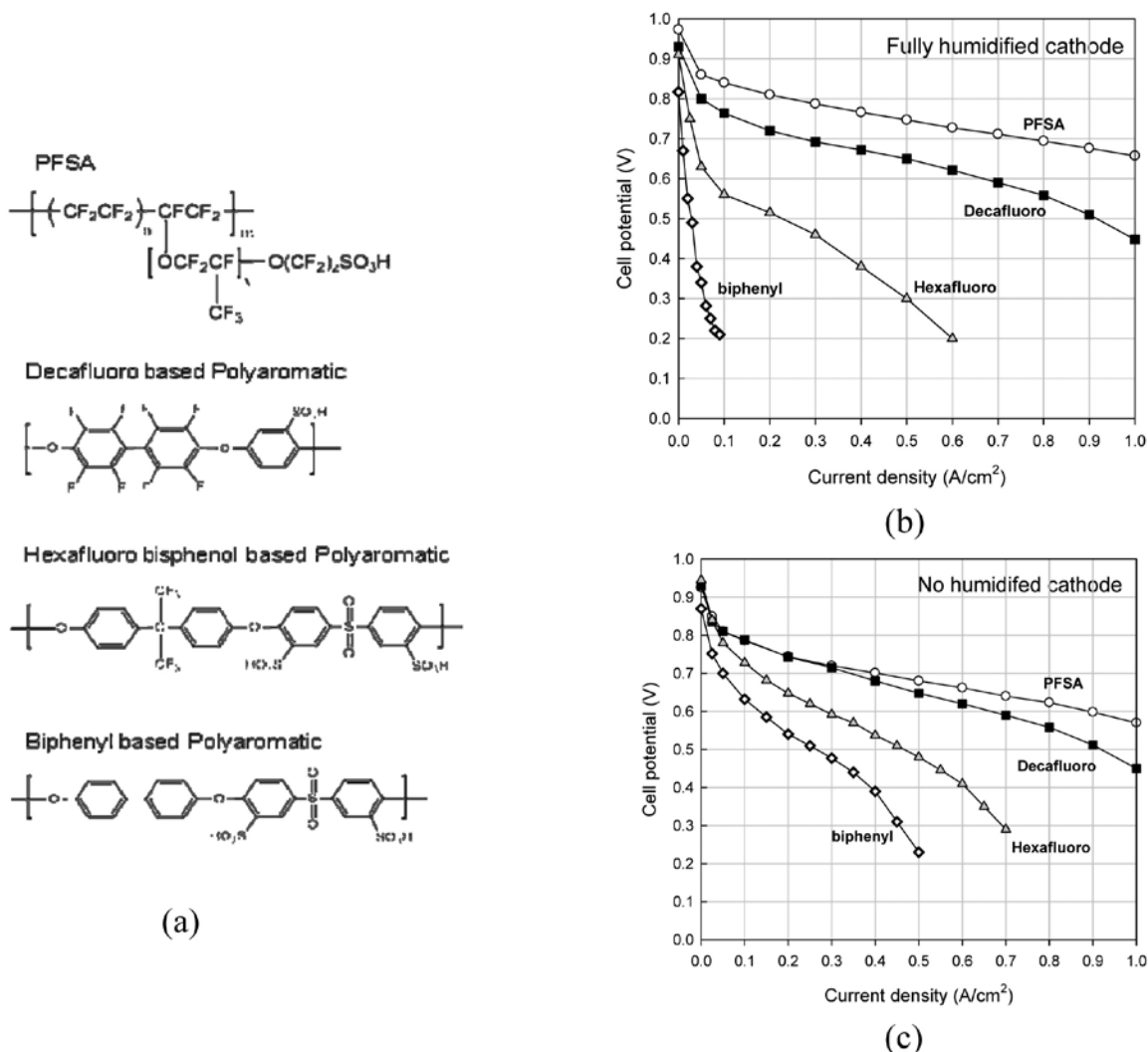


FIGURE 4. Performance of different polymer binders (a) in humidified (b) and non-humidified (c) MEAs.

due to the much slower diffusion. This emphasizes the importance of control of the polymer morphology to avoid such bottlenecks.

- The use of metal-ion initiated Fenton chemistry for degradation studies of imidazole-containing polymers results in much more degradation than in the absence of the imidazoles. This is understandable due to the chelation of the ions by imidazole that results in a more active metal ion initiator. Ultraviolet/visible light or thermal initiation of peroxide decomposition is a more appropriate test but this indicates a vulnerability of imidazole polymers to the presence of metal ion contaminants.
- The preparation of composite electrodes for use in MEAs with non-Nafion[®] polymer binders requires considerable experimentation with ink formulation (concentration, solvent polarity and volatility, particle size, etc.) as well as processing conditions.

The development of the methodology is important for preparing MEAs with the imidazole bases present.

Future Directions

- Synthesis and measurements of polymers as functioning membranes is the highest priority.
- Stability of imidazole, the ionic liquids and the complete polymer architectures under oxidative conditions is a critical issue. Durability and degradation testing of membranes under fuel cell conditions is a priority.
- Preparation of MEAs is a critical issue as conventional electrodes will not allow a proper test to be carried out. Studies on this topic are already under way at LANL.
- Gas permeability and crossover measurements will be initiated.

- Modeling of the system and cell issues (conductivity, low catalyst activity at low relative humidity) will continue to guide experimentation. Molecular dynamics modeling needs to be added.

FY 2009 Publications/Presentations

1. “New Polyelectrolyte Materials for High Temperature Fuel Cells”, John Kerr, DOE Hydrogen, Fuel Cells, and Infrastructure Technologies Program Review Meeting, May 9, 2009, Arlington, VA, presentation FC 14.
2. “Polyelectrolyte Materials for Batteries, Fuel Cells and other Energy Applications”, John Kerr, Pennsylvania State University, Materials Science Distinguished Lecturer, March 26, 2009.
3. “Water-free Proton Conductors”, John Kerr, LANL-NEDO Workshop, San Diego, CA, September 10, 2008.
4. Virgili, J.M.; Hexemer, A., Pople, J.A., Balsara, N. P.; Segalman, R.A., Phase Behavior of Polystyrene-block-Poly(2-vinyl pyridine) Copolymers in Selective Ionic Liquid Solvents. submitted to *Macromolecules*.
5. Virgili, J.M.; Nedoma, A.; Melnichenko, Y.B.; Cheng, G.; Balsara, N.P.; Segalman, R.A.; [Imidazolium][TFSI] Ionic Liquid Distribution in Concentrated Polystyrene-b-Poly(2-vinyl pyridine) Copolymers Solutions. ACS Preprint, 2009.
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11. Y.S. Kim, “PEMs for High Temperature and Low RH Fuel cells” *Advances in Materials for Proton Exchange Membrane Fuel Cell Systems*, Pacific Grove, CA, Feb. 18–21 (2009).
12. Y.S. Kim, “Hydrocarbon Ionomers for PEMFC Electrodes” High Temperature Working Group Meeting, Washington, D.C., May 18, (2009).
13. A.Z. Weber, “Modeling Heat and Mass Transfer in PEFCs,” Fuel Cell Gordon Research Conference, July, 2008.
14. Y. Fu and J.B. Kerr, “New Electrolyte Materials for High Temperature PEMFC”, 214th ECS Meeting on Electrochemical and Solid State Science, Honolulu, Hawaii, October 12–17, 2008.
15. X. Fei and J.B. Kerr, “The Proton Conductivity and Durability of Imidazole / Imidazole Derivatives Containing PFSA Polymer Membranes,” 214th ECS Meeting on Electrochemical and Solid State Science, Honolulu, Hawaii, October 12–17, 2008.
16. X. Fei and J.B. Kerr, “New Functional Polymers for High Temperature Fuel Cell Membranes,” 214th ECS Meeting on Electrochemical and Solid State Science, Honolulu, Hawaii, October 12–17, 2008.

Patents Issued

1. Y.S. Kim, T. Rockward, K.S. Lee, “Methods of Making Membrane Electrode Assemblies” U.S. Patent Application 12/321,466 (2008).
2. Y.S. Kim, T. Rockward, K.S. Lee, “Non-Aqueous Composition Comprising Ion Exchange Polymers” U.S. Patent Application March (2009).

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