

V.D.1 New Polyelectrolyte Materials for High Temperature Fuel Cells

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Objectives

- Develop durable water-free membrane materials with properties that meet the 2015 DOE targets as set out in the Multi-Year Research and Development Plan:
 - Conductivity: 0.1S/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 $\leq 2\text{mA}/\text{cm}^2$.
 - Durable membrane electrode assemblies (MEAs) with rated power at $1,000\text{ mW}/\text{cm}^2$ 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

Fuel Cell Technologies Program Multi-Year Research, Development and Demonstration Plan:

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

Technical Targets

- Development of membranes that contain tethered heterocyclic bases (imidazole, triazole), which do not require added water to achieve adequate conductivity and can achieve performance with only the presence of the water produced by the fuel cell reaction: 0.1 S/cm (120°C), 0.07 S/cm (20°C) and 0.01 S/cm (-20°C) at relative humidity (RH) values between 25 and 50%.
- Achieved 0.005 S/cm at 120°C under bone dry conditions and 0.01 S/cm at 25% RH.
- Conductivities at ambient temperatures (10^{-3} S/cm $> 80^\circ\text{C}$) are too low to be practical without a high degree of morphological control to provide connectivity through the membrane.
- Demonstrated that morphological control to achieve high connectivity through the membrane is possible through use of phase separating polymers (block and random copolymers) but is hard to maintain.
- Plasticization of the polymers by water can lead to significantly improved conductivities but at a potential cost of loss of connectivity.
- The presence of imidazole and other heterocyclic bases in the polymers leads to increased conductivity at low water content (RH 25-50%) and to significantly lower water uptake in some cases.
- Three-dimensional (3-D) modeling shows that loss of connectivity can be compensated for by multiple pathways through the membrane.

The provision of membranes and MEAs that need no humidification provides significant system simplifications and large cost advantages over conventional materials

Accomplishments

- It has been determined that solid state membranes with imidazole as proton solvating solvent cannot achieve 0.1 S/cm without added mobile solvents such as water unless a high degree of connectivity through the membrane can be achieved.

- It has been shown that the presence of imidazoles tethered to the polymer backbones improved the conductivities of sulfonated polyetherpolysulfones and poly fluoro sulfonic acid (PFSA) polymers at low water content (25% RH). It has been further shown that presence of bases affects the water uptake and can be used to control swelling as well as to improve conductivity.
- Synthesis of polymers with tethered imidazoles has been achieved with several different polymer backbones – polystyrene, polyether polysulfone, and polyfluorinated ethylene with different side chain lengths.
- Studies of proton conducting ionic liquids in polymer matrices show that they support Grotthuss transport and morphological control in block copolymers can maintain high conductivities at lower temperatures.
- Composite electrode and MEA fabrication methods have been developed for hydrocarbon polyelectrolytes in anticipation of the availability of imidazole-containing material for testing.



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 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 (FY) 2008-2009 annual reports, 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 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(a) shows a schematic of the type of polymer structure that appears to be desirable to achieve fast proton transport through the membrane. Results obtained in FY 2009 on ionic liquid models and on synthesized polymers with tethered imidazoles indicate that the nanoscale 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. Figure 1(b) shows how the pore structure could be arranged on the microscopic scale in order to provide connectivity across the membrane. The molecular-level mechanism of

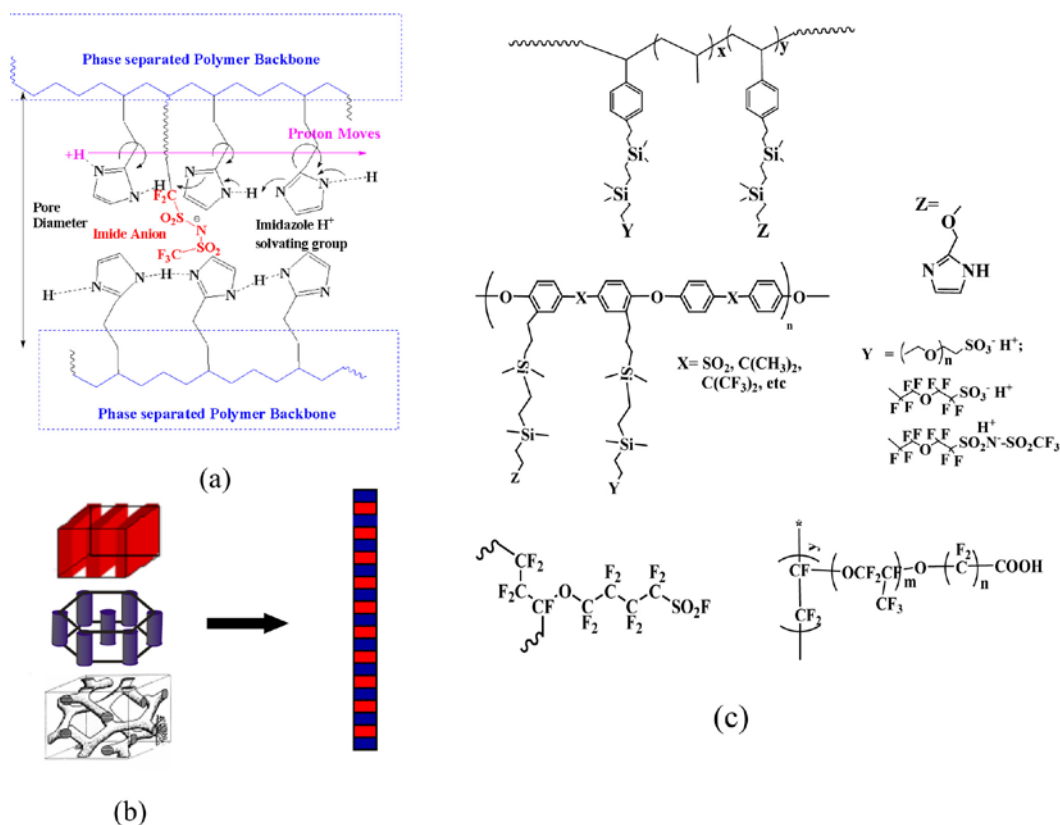


FIGURE 1. (a) Schematic representation of desired polymer morphology to promote high conductivity based on results obtained in FY 2009. (b) Schematic of different morphologies that could contain the proton-conducting pores to achieve connectivity through the membrane. (c) Examples of polymer structures prepared and under study in FY 2010.

proton transport 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. In previous years of this project the low activation energy for proton transport associated with the Grotthuss mechanism has been inferred from the temperature dependence of the conductivity. Pulsed field gradient spin-echo nuclear magnetic resonance measurements on ionic liquid samples prepared from imidazole and bis(trifluoromethylsulfonyl)imide have indicated faster diffusion of the positively charged protons in the liquid than diffusion of the other solvent molecules. These results confirm the reports of Watanabe et al. [6] and support the proton hopping mechanism of proton transport. Experiments are now underway to examine the effect of a block co-polymer matrix on the mechanism to observe whether ordering may result in more efficient operation of the proton hopping mechanism.

The phase separation is best promoted by use of block copolymers with appropriate backbones. Figure 1(c) shows two examples of the polymer structures

that have been prepared for this purpose (polystyrene and polyether polysulfone) and which are under continuing study. Also shown are two fluorinated polymers which can be used to immobilize heterocyclic bases. The imidazole group (e.g. Z in Figure 1(c)) 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 attachment of the imidazole through positions other than the nitrogen is not trivial and generally requires the use of protecting groups on the nitrogen which can be cleanly removed once the polymer is prepared. However, some success has been obtained with syntheses that avoid the use of protecting groups. The use of triazoles has also been explored to avoid some of the synthetic difficulties involved with the imidazoles although in general triazoles have shown slightly lower conductivity than imidazole.

Figure 2(a) shows the results of conductivity measurements made on polymers that contain the imidazole tethered in the 2-position as shown by the structure of the polymer denoted IMVBCI. The polymers are blended with Nafion[®] where the

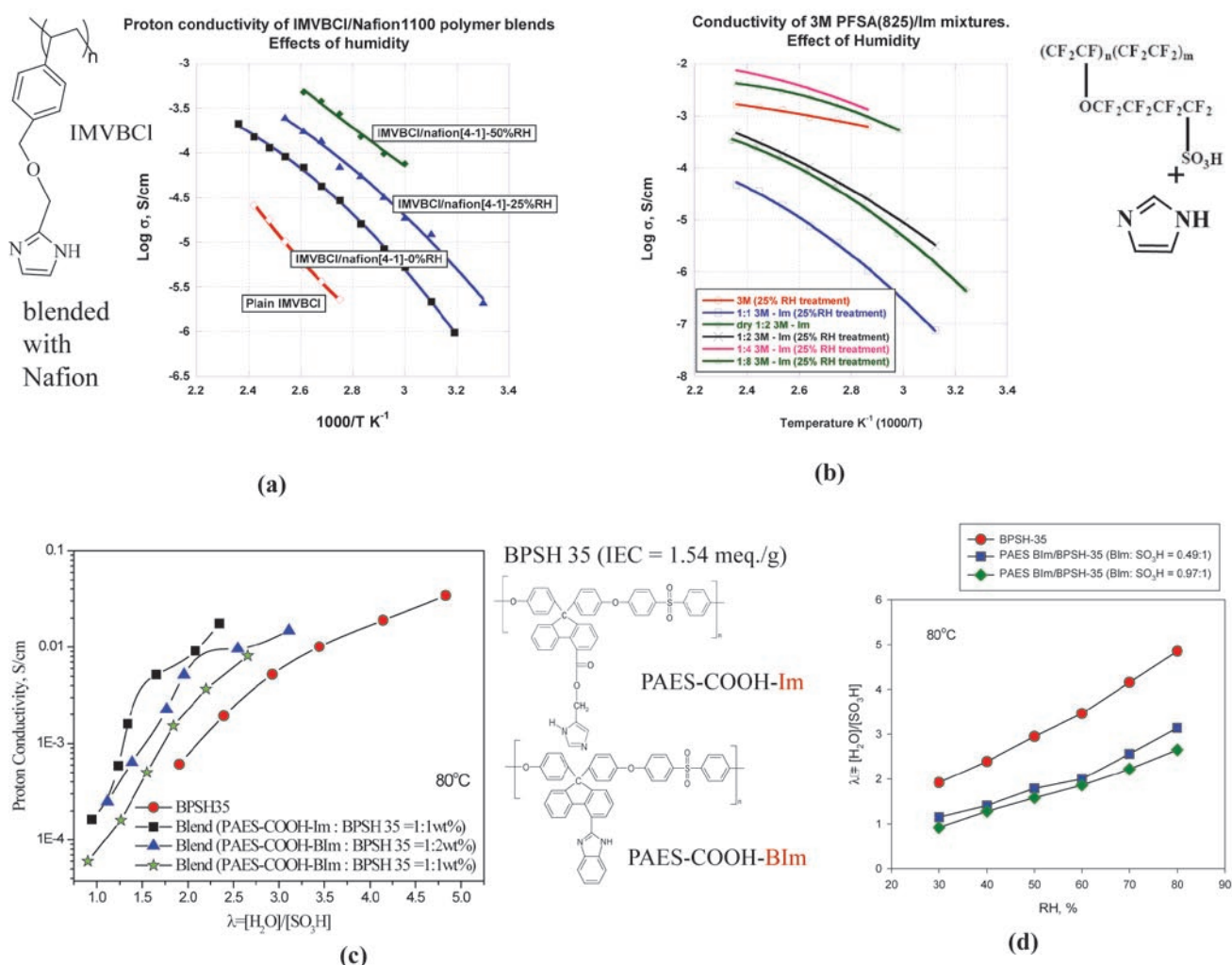


FIGURE 2. Conductivity measurements as a function of temperature and humidity of imidazole containing polymers blended with acid containing polymers. (a) Polystyrene backbone with short chain imidazole blended with Nafion® 1100; (b) 3M PFSA material blended with imidazole; (c) polyether polysulfones blended with BPSH-35; (d) water uptake of polyether polysulfones blended with BPSH-35. Structures shown.

numbers 4-1 represent the ratio of the imidazole molecules to the acid groups in the blend. The unblended, neat polymer exhibits very low conductivity as expected since the self-dissociation of the imidazole does not provide a sufficient concentration of charge carriers. Provision of acid groups from the Nafion® results in higher conductivity under dry conditions. Measurements performed under 25% and 50% RH show increasing conductivity as the water content is increased although they are still too low to be practical. The shape of the conductivity curve as a function of temperature is very characteristic of ion transport control by segmental motion of the polymer indicating that no proton hopping occurs in this case. Dynamic mechanical analysis (DMA) of the polymer blends indicate that considerable plasticization of the polymers occurs which results in inefficient phase separation. This hypothesis remains to be confirmed with small angle X-ray scattering measurements.

Figure 2(b) shows the effect of humidity on the through-plane conductivity of 3M PFSA doped with imidazole. The undoped material measured at 25% RH shows a low dependence upon temperature that is characteristic of proton hopping. While the low ratio of imidazole to acid (1:1) blend has a poor conductivity even in the presence of water, the more highly doped blends (1:4 and 1:8) show better conductivity at these low RH values indicating that combinations of water with imidazole may well lead to higher conductivities. Interestingly, the bend in the curves at low temperatures for the doped polymers indicates that phase separation is not as complete with the doped polymers, which is consistent with the previously reported DMA of the doped polymers that shows increased plasticization of the PFSA by the imidazole. Figure 2(c) shows conductivities of polymer blends of imidazole and benzimidazole-containing polymers with sulfonated polyether polysulfone (BPSH-35). Again, the presence of

the heterocyclic bases clearly improves the conductivity at low water content. However, Figure 2(d) shows that the presence of the bases lead to lower uptake of water so that at a given RH value the actual conductivity of the blend is lower than that of the acid polymer alone. These results illustrate that the heterocyclic bases such as imidazole can provide increased conductivity at low water contents and they also potentially can be used to control water uptake and swelling of a polymer material. These results are intriguing and indicate how greater understanding of the action of the bases for both conduction and water uptake could lead to greater control of the behavior of membrane materials that includes more than just conductivity.

The plasticization effects of the solvent molecules such as water and imidazole upon the polymer morphology are of considerable importance. Figure 3 demonstrates the changes that result in morphology

upon uptake of water that can seriously impact the conductivity. A block copolymer consisting of styrene and hydrogenated isoprene blocks was prepared with a variety of block lengths. The styrene units were sulfonated to different degrees. This resulted in various different morphologies which could be altered by variation of the block lengths and sulfonation degree. The morphologies were determined by tunneling electron, scanning electron, and atomic force microscopy and scattering measurements such as small angle X-ray scattering (SAXS) and small angle neutron scattering (SANS) an example of which is shown in Figure 3. During the course of SANS measurements at 90% RH it was noted that the morphology would change from one temperature to another. Conductivity measurements were also affected by the uptake of water and time at elevated temperature. The conductivity plot shown in Figure 3 shows that the initial high conductivity decreases irreversibly with time. These observations

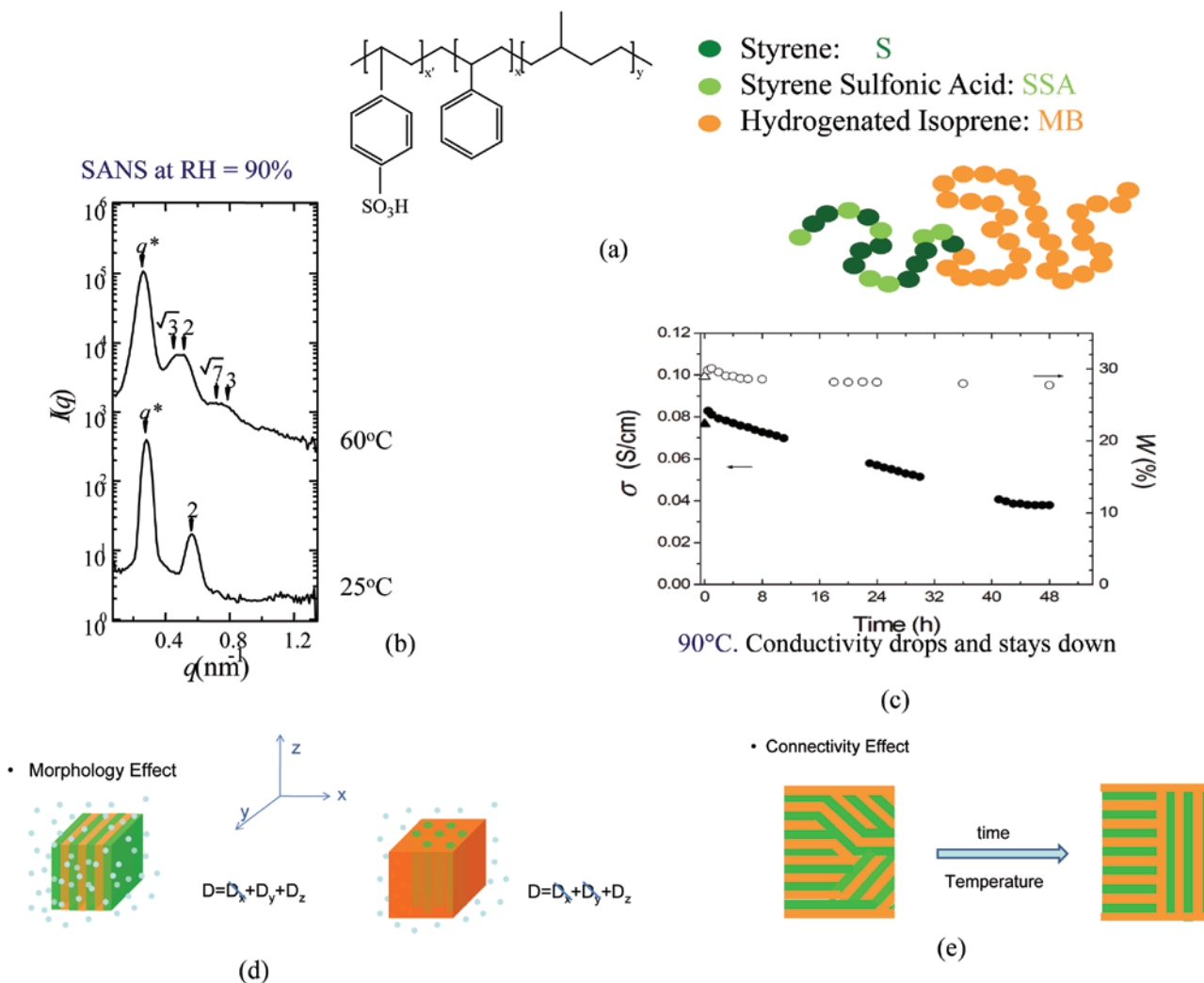


FIGURE 3. Structure of sulfonated polystyrene, hydrogenated polyisoprene block copolymer; Evolution of SANS results at 90% RH as function of temperature; evolution of conductivity and water content at 90% RH and 90°C.

are rationalized by the schemes shown at the bottom of Figure 3. The left hand scheme represents the change in morphology from lamellar to cylindrical upon uptake of water while the right hand scheme represents the loss of connectivity across the membrane that results from the change in morphology and leads to the loss of conductivity. When experiments such as this are carried out with imidazole present in the polymer changes in the morphology were observed in SAXS experiments depending upon the amount of imidazole present. The presence of the imidazole did not suppress the water uptake and the conductivity was lower but stable over time. These results are consistent with plasticization of the polymer by the imidazole which results in lower conductivities but prevents the motion of the polymers that leads to loss of connectivity.

To understand the conductivity results and also the impact of morphology, acid and base site concentrations, etc. on conduction, a network model was developed in FY 2009 to ascertain the importance of bottlenecks on performance and provide guidance to the membrane

synthesis efforts. The concept of the bottlenecks is shown in Figure 4 in the cartoon of the classical Gierke model of Nafion[®] where the fast proton transport pores are interspersed with bottlenecks where transport is controlled by segmental motion of the polymer. In the initial results shown in the top graph of Figure 4, relatively simple calculations in a one-dimensional mode showed that in a membrane with only a few linkages where the vehicle or segmental motion mechanism dominates, the overall conduction suffers greatly due to the much slower diffusion. Extension of the model to two-dimensional and 3-D cases where alternative connection pathways become available, shows that the effects of the segmental motion bottlenecks need not be so severe as can be seen in the lower two plots in Figure 4. Hence there is reason to believe that some degree of plasticization of the polymer morphology can be tolerated without ruining the connectivity through the membrane.

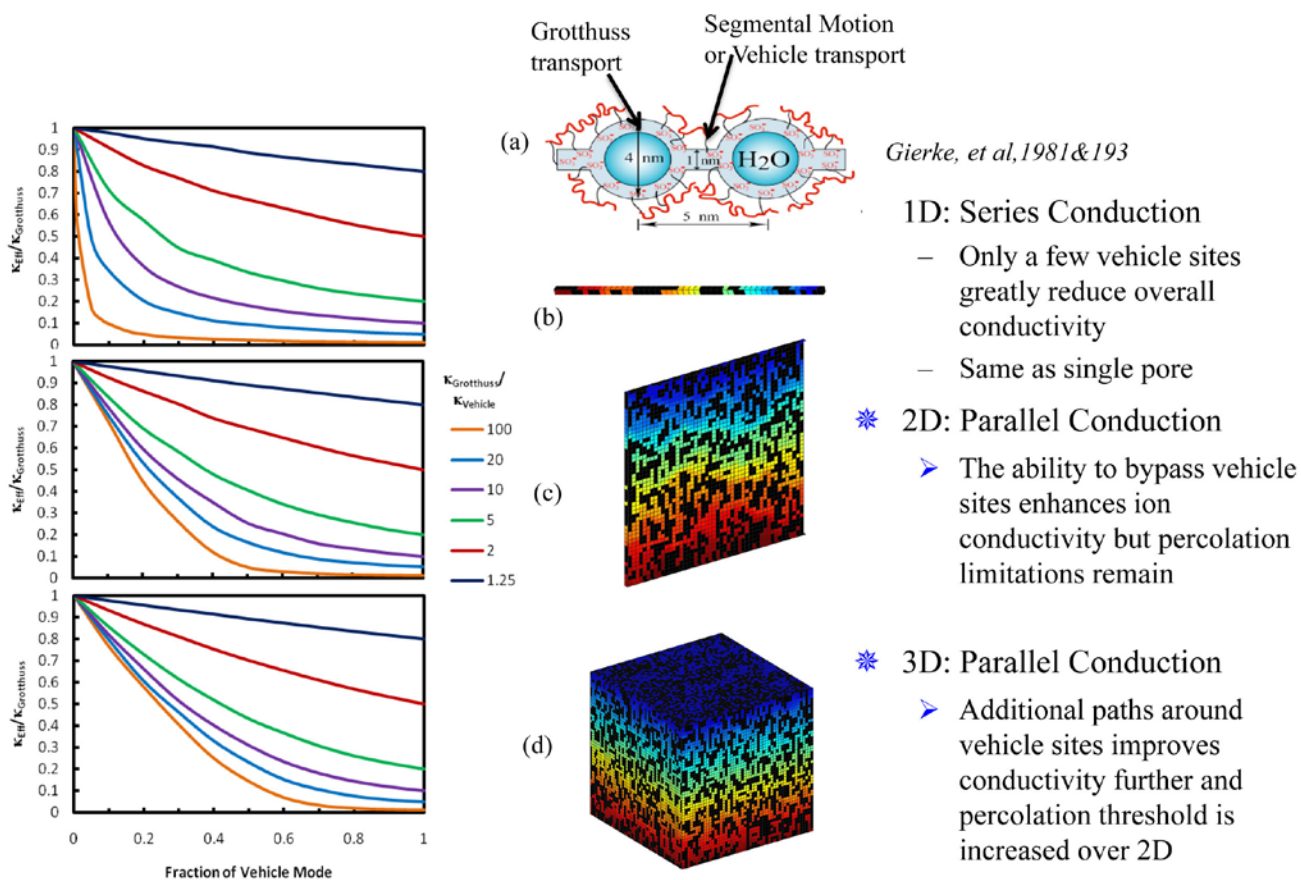


FIGURE 4. Models of the effect of segmental motion bottlenecks on overall conductivity. (a) Gierke model of Nafion[®] showing slow segmental motion segments and fast proton transport segments; (b) effect of bottlenecks on overall conductivity for one, two, and three dimensions.

Conclusions and Future Directions

Conclusions

- Conductivity of polyelectrolyte systems that contain no mobile solvents appears to be too low unless a high degree of connectivity is achieved through the membrane.
- Connectivity through the membrane is very difficult to achieve and to maintain.
- Conductivities of imidazole-containing systems are improved considerably by the presence of some water in the system. However, water uptake by many polymer systems is suppressed by the presence of the imidazole.
- Modeling shows that increasing the segmental motion transport by plasticization of the polymer by water or other solvents increases the overall conductivity but also increases the loss of connectivity. Polymer dynamics are of critical importance.
- 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.
- 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.
- 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.
- Gas permeability and crossover measurements will be initiated.
- Modeling of the system and cell issues (conductivity, low catalyst activity at low RH) will continue to guide experimentation.

FY 2010 Publications/Presentations

1. “New Polyelectrolyte Materials for High Temperature Fuel Cells”, John Kerr, DOE Hydrogen, Fuel Cells, and Infrastructure Technologies Program Review Meeting, June 11, 2010, Washington DC, presentation FC 35.

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6. X Wang, S Yakovlev and N Balsara, Slow Changes in Ionic Conductivity of Model Block Copolymer Electrolyte Membranes, American Physical Society Meeting, Portland, OR, March, 2010.
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