

IV.B.11 Polymer Blend Proton Exchange Membranes

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Objectives

- Develop new materials for high-temperature proton exchange membranes (PEMs)
- Demonstrate a PEM based on a polymer blend
- Optimize the morphology of a blend PEM

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:

- O. Stack Material and Manufacturing Cost
- P. Durability
- R. Thermal and Water Management

Approach

- Design polymer blends for PEMs
- Fabricate blend PEMs with controlled morphologies
- Measure conductivity and performance curves
- Optimize blend composition for optimal transport and mechanical properties

Accomplishments

- Optimized preparation of sulfonated poly (ether ketone ketone) {SPEKK} ionomers
- Achieved conductivities of $\sim 10^{-1}$ S/cm for SPEKK membranes
- Prepared and evaluated performance of SPEKK/polyether imide (PEI) blend membranes; conductivities of $\sim 10^{-2} - 10^{-1}$ S/cm were achieved with improvements in mechanical properties of wet membrane by addition of PEI
- Developed procedure for electric field orientation of SPEKK/PEI membranes

Future Directions

- Develop ternary phase diagrams for SPEKK/PEI/solvent and SPEKK/PES/solvent mixtures
- Produce membranes with spinodal-like structure
- Evaluate performance of SPEKK/poly(ether sulfone) (PES) blend PEMs

- Optimize equipment and procedures for electric field orientation of membranes
- Fabricate membrane electrode assemblies (MEAs) with controlled morphology blend membranes

Introduction

The current state-of-the-art fuel cell technology uses perfluorosulfonate ionomer membranes; the most common commercial product is Nafion[®] (Du Pont). Deficiencies with Nafion include high cost, operating temperatures restricted to below 100°C, and poor durability of wet membranes. The majority of contemporary PEM research has considered either modifying the standard perfluorosulfonate ionomer membrane or using lower cost resins to address the problems with the current PEM technology [1]. A variety of materials are being developed for application as high-temperature proton conductors, including polybenzimidazole doped with phosphoric acid, sulfonated polyimides, sulfonated poly(arylene ether sulfones), sulfonated poly(arylene ether phosphine oxides) and sulfonated polyketones, e.g., poly(ether ether ketone), poly(ether ketone) and poly(ether ketone ketone) [1].

Polymer blend technology may represent a more versatile approach for the development of new membrane materials in that the material properties of blends can be varied over a wide range. Relative to a single-component polymeric material, a blend enjoys several degrees of freedom that allow tailoring of the material to meet the membrane requirements. The obvious source of flexibility is the presence of two materials that can have quite different properties, e.g., good mechanical properties and good proton transport. The more subtle differences derive from the fact that there is an interface, and the structure of the interface and the phase structure of the blend can be controlled, e.g., increasing the miscibility of the system can increase the thickness of the interfacial region.

Approach

This project involves the development of polymer blends comprised of one acidic polymer—an ionomer such as SPEKK—and a basic neutral polymer with functional groups complementary to the acid groups, e.g., polyimide or polysulfone. A

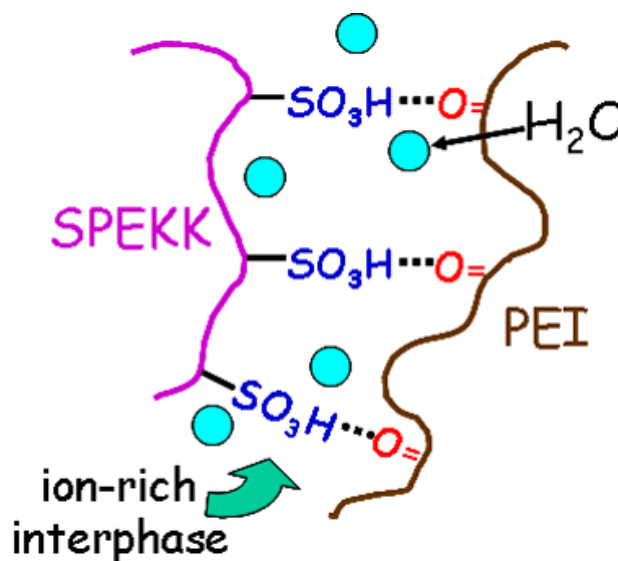


Figure 1. Schematic of Interphase in SPEKK/PEI Blend

key aspect of the work is to develop an understanding of the relationship between blend morphology and PEM performance. That will allow optimization of the morphology for a viable PEM. The working hypothesis is that one can develop an ion-conducting pathway along the interface in a two-phase polymer blend by promoting acid-base interactions. The resulting interfacial region (see Figure 1) is expected to provide an environment conducive to ion-transport, while the components of the blend may be chosen to maintain other needed properties such as thermal stability at elevated temperatures and mechanical strength. By controlling the development of the two-phase structure, it is possible to achieve percolation of the interfacial region through the thickness of the membrane. In that case, the template for the conductive pathway is already in place in the dry membrane, and hydration is needed only to promote ion-mobility and not to create the continuous ion-conducting pathway as is required in conventional ionomer membranes.

Two approaches are being used to develop and control the blend PEM morphology:

- 1) thermodynamics – in which the phase behavior of a ternary mixture (polymer 1 + polymer 2 + solvent) is used to develop a spinodal microstructure, see

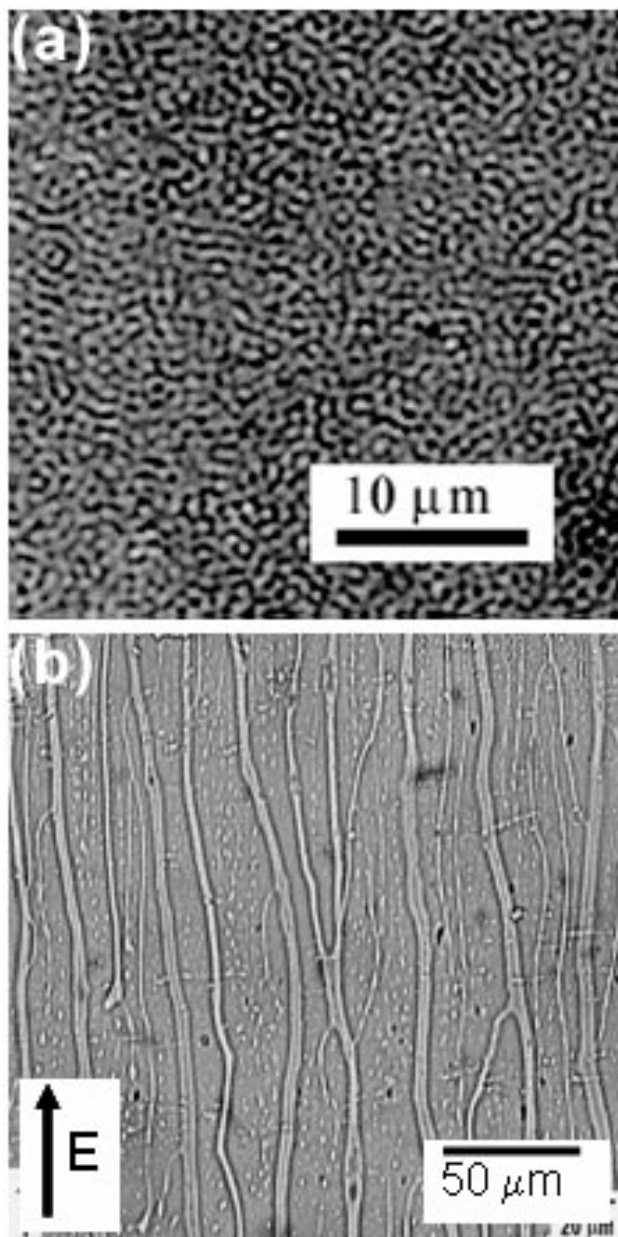


Figure 2. Morphologies of SPEKK/PEI Blends: (a) spinodal structure; (b) dispersed SPEKK domains oriented by an electric field.

Figure 2(a), and 2) electro-dynamics – in which an electric field is employed during film preparation to orient the conductive phase. Figure 2(b) shows electric field orientation of a SPEKK/PEI membrane within the plane of the film, but a technique has also been developed to achieve orientation in the thickness direction.

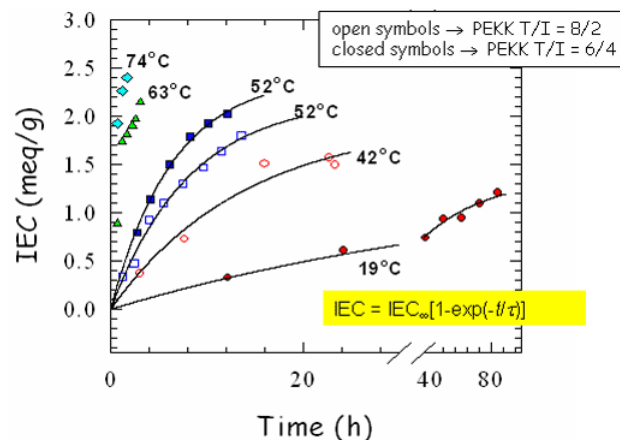


Figure 3. Sulfonation Kinetics of PEKK Using a Mixture of 53/47 (v/v) Concentrated and Fuming Sulfuric Acids

Results

A procedure for reproducibly sulfonating PEKK to an ion-exchange capacity, $IEC = 0.8 - 2.5$ meq/g was developed using mixtures of concentrated and fuming sulfuric acids (see Figure 3). Sulfonation occurs only on the phenyl rings attached to ether and ketone groups. The maximum possible sulfonation level is 4.33 meq/g, but the ionomers become water-soluble for $IEC > 2.4$ meq/g. Typical performance curves in an MEA for the SPEKK membranes are shown in Figure 4. In general, more robust membranes were made when the films were cast from dimethyl acetamide (DMAc) rather than N-methyl-2-pyrrolidone (NMP), primarily because of the higher solubility of PEI in DMAc than in NMP.

The effect of blend composition on the conductivity of SPEKK/PEI blend membranes is shown in Figure 5. The addition of PEI to the SPEKK lowers the swelling of the membrane, improves the mechanical properties of the wet membrane, and for PEI concentrations $< 30\%$, the conductivity of the membrane remained $> 10^{-2}$ S/cm. Similar benefits were achieved for SPEKK/PES blends, which produced homogeneous films and had better durability in an MEA than did the SPEKK/PEI blends.

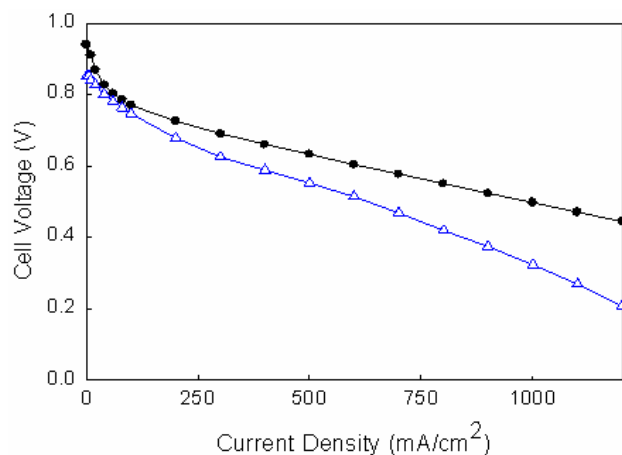


Figure 4. MEA Performance Curves for SPEKK Membranes

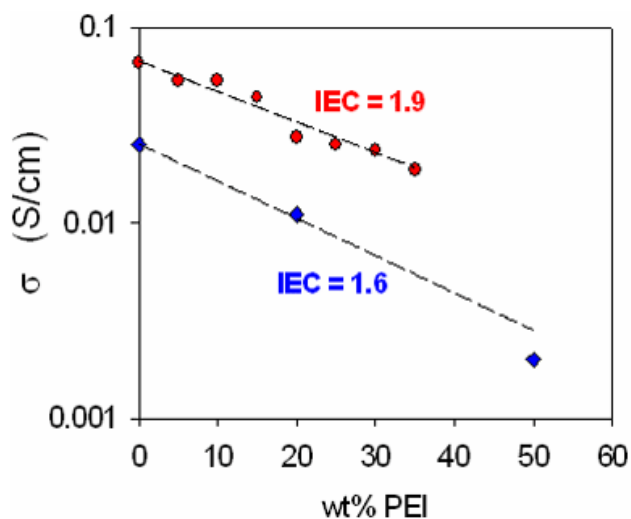


Figure 5. Proton Conductivity of SPEKK/PEI Blend Membranes

A procedure was developed to orient the SPEKK domains in molten blend membranes using an electric field. An example of electric field induced orientation of a 30/70 SPEKK/PEI blend membrane is shown in Figure 6. In that case, the SPEKK domains are oriented in the thickness direction of the film and the conductivity of the membrane increased significantly compared with the unoriented membrane.

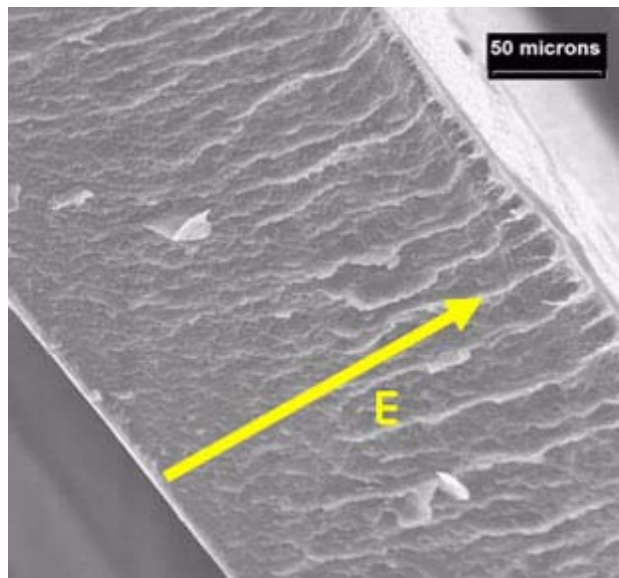


Figure 6. 30/70 SPEKK/PEI Membrane Oriented at 200C with $E=10$ kV/cm and a frequency of 20 Hz

Conclusions

- SPEKK represents a potential material for fuel cell PEMs.
- Polymer blend PEMs, e.g., SPEKK/PEI and SPEKK/PES membranes, provide an improved balance of conductivity and mechanical properties relative to single-component ionomer membranes.
- Electric fields can orient the conductive phase in a blend PEM, providing control of the transport properties.

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