IV.B.10 Development of Higher-Temperature Membrane and Electrode Assembly for Proton Exchange Membrane Fuel Cell Device*

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**Congressionally directed project*

Objectives

Develop membrane electrode assemblies (MEAs) that work at 120°C

- Prepare membrane and catalytic layers (CLs) from sulfonated polyether ether ketone (sPEKK) polymer
- Demonstrate feasibility of MEAs
- Optimize performance of MEAs at 120°C and low relative humidity (RH)

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:

- C. Thermal Management
- F. Heat Utilization
- L. Hydrogen Production/Carbon Monoxide Clean-up
- M. Fuel Processor System Integration and Efficiency
- N. Cost
- O. Stack Material and Manufacturing Cost
- P. Durability
- Q. Electrode Performance
- R. Thermal and Water Transport

Approach

- Prepare membrane films and CLs from blends of sPEKK and other polymers
- Measure conductance at elevated temperatures (120°C) and reduced RH (~30%)
- Prepare MEAs from blends
- Measure performance in H_2/air fuel cell at 120°C and ~30% RH
- Optimize performance
- Measure short-term durability

Accomplishments

- Measured phase diagrams for sPEKK/polyether imide (PEI) blends in N-methyl pyrollidone (NMP) solvent at room temperature
- Cast thin films from sPEKK/PEI blends showing isolated spherical domains with limited conductivity for sPEKK blends at low ratios (~20 wt% sPEKK)
- Demonstrated that casting thin films in high electrical fields orients and connects domains, producing orders of magnitude lower resistance
- Established fuel cell lab capabilities at OPM for conductivity measurements and Instron yield strength measurements, and installed two single-cell fuel cell test stations; presently assembling MEA fabrication equipment
- Demonstrated feasibility of sPEKK-based MEAs at 80°C

Future Directions

- Complete conductivity measurements of improved film blends vs. temperature and RH
- Prepare MEAs from improved blends
- Optimize performance including lower Pt loadings
- Contact fuel cell original equipment manufacturers (OEMs) after this project
- Find optimum polymer blends and use electric field orientation of domains
- Measure CO tolerance at higher temperatures
- Scale up MEAs and build small stacks
- Test for extended durability
- Prepare MEAs for evaluation by OEMs

Introduction

The proton exchange membrane fuel cell (PEMFC) offers many advantages over other types of fuel cells. However, its low operating temperature, ~80°C, creates integration problems with fuel processing systems (FPSs). Recent system studies have identified the potential of higher-temperature membranes (>120°C) to simplify PEMFC power plants, to improve efficiency and to reduce system cost [1-3]. Higher operating temperatures accomplish these benefits by improving CO tolerance in the stack (thereby eliminating 1-3 FPS reactors), by providing useful waste heat from the stack to the FPS and by reducing the size of waste heat radiators. DOE has formed a special Higher Temperature Working Group to support this critical development. We project net system fuel efficiency improvements of 7% and system cost reductions of 375 $/kW in stationary applications by using higher-temperature membranes in PEMFCs.

The target of this effort is to demonstrate technical feasibility at higher operating temperatures using MEAs based on novel polymer blends. The critical technical challenge in this work is to maintain sufficient proton conductivity in the polymer at higher temperatures and lower relative humidity (RH). Target operating conditions are 120°C and 25-50% RH. At these conditions, Nafion conductance drops about an order of magnitude, thereby reducing power and efficiency. The fundamental reason for this loss is that the proton conductance mechanism depends on a continuous network of water between counter-ion sites. Water content in the membrane decreases in higher-temperature operation because of the lower RH.

Approach

Our approach is to develop improved MEAs based on novel polymer blends that maintain their conductivity at higher temperatures and reduced RH.

The critical task is to select an optimum polymer blend and to control its micro-domain structure during MEA fabrication. OPM [4] has developed a novel high-temperature polymer, sulfonated polyether ketone ketone (sPEKK), during previous collaborations with the University of Connecticut. The plan is to blend sPEKK with a complementary high-temperature stable polymer such as polyether imide (PEI) and to fabricate blend-based membranes with a higher level of connectivity between the sPEKK domains to provide better proton conductance at low RH and an interconnected network of PEI to provide superior mechanical properties.

MEAs are multilayered structures incorporating a central membrane and two catalytic layers. Previous efforts at the University of Connecticut have demonstrated MEAs using sPEKK membranes and catalytic layers based on Nafion. This approach was limited at higher temperatures by the reduced conductance of the Nafion. An objective in this project is to demonstrate MEAs containing sPEKK-based blends in both the membrane and the catalytic layer.

Results

Morphology has a dramatic effect on the ionic conductivity of polymer blends. Films were prepared by casting sPEKK/PEI blends from NMP solutions. The phase diagram is shown in Figure 1. Blends near the 50/50 mixture range are normally selected for making spinodal structures (i.e., continuous interconnected domains). At lower ratios (15-30 wt% SPEKK), domains grow into isolated 1-10 μm spheres (Figure 2). In contrast, drying in the presence of an electric field produced an interconnected sPEKK morphology (Figure 3). Both films are compared in Figure 4, showing that resistance is decreased by orders of magnitude. Electric field orientation opens promising new blend ratios for improved conductivity and strength. The plan is to eventually apply this technique to MEA fabrication.

The new laboratory at Oxford is built, and material testing of blends has begun. High-frequency conductivity measurements are taken

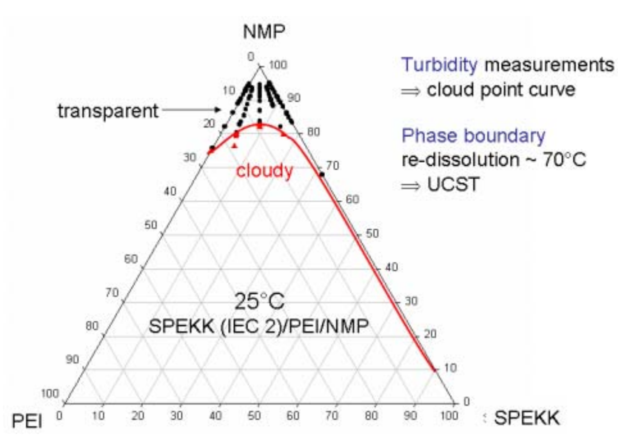

Figure 1. Phase Diagram of sPEKK-PEI Blends in NMP at Room Temperature

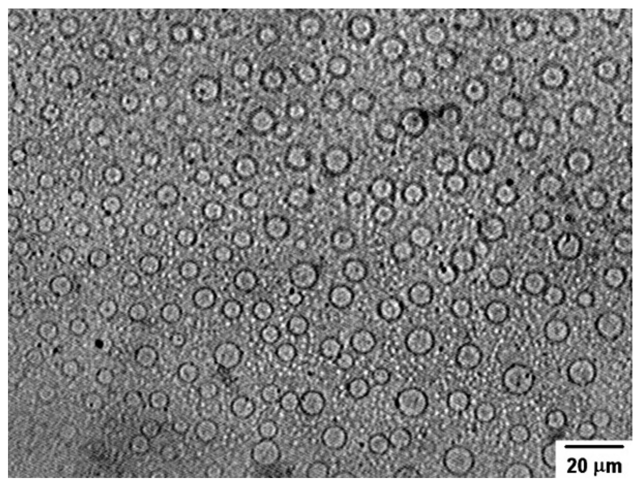

Figure 2. Morphology of 20 wt% sPEKK in PEI Blend Without Electric Field

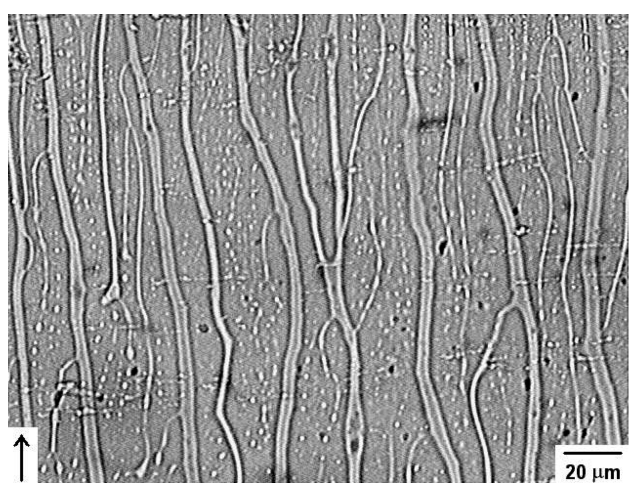

Figure 3. Morphology of 20 wt% sPEKK in PEI Blend Cast in Electric Field

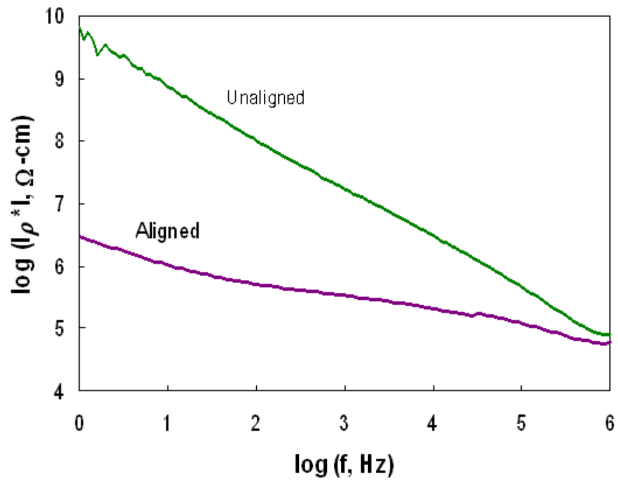

Figure 4. Comparison of Conductivity of 20 wt% sPEKK Cast With and Without Electric Field

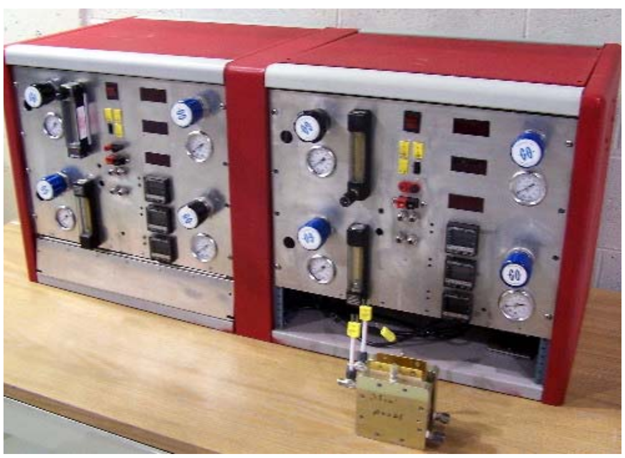

Figure 5. Fuel Cell Test Stands at OPM

using new 4-point probes [5] in a dessicator containing constant-humidity salt solutions [6] within an oven (25-120°C). Film strength is measured using a new Instron with standard ASTM methods. Two new fuel cell test stations are ready for operation (Figure 5). Initial single-cell testing of MEAs using sPEKK in both the membrane and the CLs showed a resistance of 0.35 ohm-cm^2 at 80°C, comparable to Nafion (Figure 6). The operating conditions will next be raised to higher temperatures, followed by the optimization of the blends and then the noble metal content.

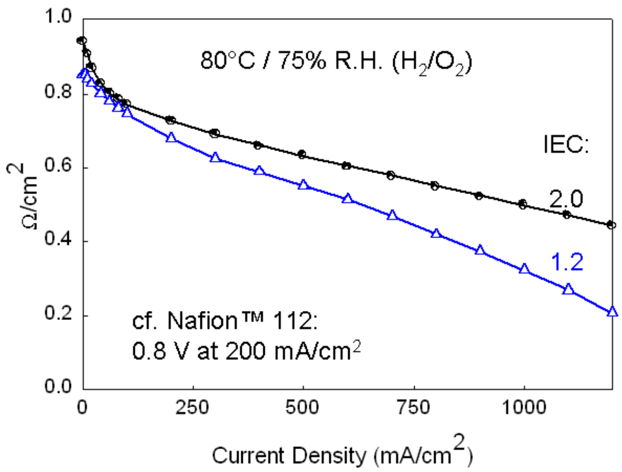

Figure 6. Single-Cell Performance of sPEKK-based MEAs

Conclusions

- Morphology and therefore conductance of sPEKK/PEI blends is a strong function of blend ratios and casting technique, and a weaker function of solvent compositions.
- Casting thin films from blends with low sPEKK loading (~20 wt%) in high electrical fields orients and connects domains, showing orders-of-magnitude higher conductivity.
- The new laboratory is completed, and fabrication of MEAs has begun at OPM.
- MEAs based on all-sPEKK membranes and CLs show performance comparable to Nafion at 80°C.

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2. J. Gaza, R.A. Weiss, M.T. Shaw, Conductivity Enhancement of SPEKK-PEI Blends Using Electric Filed Structuring Techniques, Presentation at American Physical Soc., Montreal, March 23, 2004.

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