# VII.B.8 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$^{o}$C

- Prepare membrane and catalytic layers from sulfonated polyether ketone ketone (SPEKK) polymer
- Demonstrate feasibility of membranes
- Optimize performance of membranes operating at 120$^{o}$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:

- A. Durability
- B. Cost
- D. Thermal, Air and Water Management
- I. Hydrogen Purification/Carbon Monoxide Cleanup

## Technical Targets

SPEKK has demonstrated proton conductivity at high temperatures and low humidity. The emphasis of this work has been to develop proton conducting membranes for the targeted operating conditions.

**Table 1.** Technical Targets: SPEKK Membranes for Transportation Applications

| Characteristics | Units | 2005 Target | 2010 Target | 2005 Status |
|---|---|---|---|---|
| Membrane Conductivity at | | | | |
| Operating Temperature | S/cm | 0.1 | 0.1 | 0.1 |
| Room temperature | | 0.07 | 0.07 | 0.08 |
| Durability with Cycling | | | | |
| At operating temperature of ≤ 80°C | hours | 2000 | 5000 | 10 |
| At operating temperature of > 80°C | hours | 2000 | 2000 | <10 |

## Approach

- Design optimized SPEKK polymer
- Engineer membrane using polymer blending, reinforcement, and cross linking
- Test conductivity at target temperatures and RHs
- Fabricate MEAs from SPEKK
- Measure performance in $H_2$/air fuel cell at 120°C and <30% RH
- Measure short term durability

## Accomplishments

- High ion exchange capacity (IEC) SPEKK appears to be self humidifying at 120°C and 30% RH.
- Reinforcements, blends, and cross linking have improved membrane durability.
- Optimized casting solvents have improved membrane properties, improved manufacturing safety, and reduced cost by half compared with previously employed solvents.

## Future Directions

Future directions will focus on additional methods of reinforcing and cross linking SPEKK membranes in anticipation of improving the durability of the MEAs. Additional work will be required beyond the scope of this funding to optimize the durability of SPEKK based-MEAs and should include:

- Synthesis of a new grade of polyether ketone ketone that is optimized for improved membrane durability and maximized conductivity.
- Improve fabrication techniques for polymer blends, reinforced composites, and cross linked structures to further improve durability.

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## 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 (FPS) and hydride-type storage systems. Operating at these low temperatures also renders the cell susceptible to poisoning by carbon monoxide (CO) which is sometimes found in processed fuel and in the air. Recent system studies have identified the potential of higher temperature membranes (>120°C) to simplify PEMFCs, to improve efficiency and to reduce system cost [1-3]. Higher operating temperatures accomplish these benefits by improving CO tolerance in the stack (thereby simplifying the FPS), by providing useful waste heat from the stack to the FPS and hybrid-type storage systems, and by reducing the size of waste heat radiators. The target of this effort is to demonstrate the technical feasibility at higher operating temperatures using MEAs based on novel polymer blends. A MEA is a sandwich-type layer in the fuel cell which contains the required catalysts and a membrane separator and is the part that makes electricity. The critical technical barrier in this work is to maintain sufficient proton conductivity, the specific mechanism the cell uses to make electricity, in the polymer at higher temperatures and lower RH. It should be noted that at the desired operating temperature, which is above the boiling point of water, it is impossible to maintain RH greater than 35% at ambient pressure. Target operating conditions are 120°C and <35% RH. At these conditions, Nafion® conductance drops about an order of magnitude, thereby reducing power and efficiency. The fundamental reasons for this loss are that the proton conductance mechanism depends on a continuous network of "trapped" water inside the polymer membrane, and, Nafion® cannot adequately absorb the available water produced at the cathode as part of the normal operation of the cell.

SPEKK (sulfonated polyether ketone ketone) has the potential to operate as a proton conducting membrane in 120°C operating environments. SPEKK is based on a different chemistry than Nafion® and has a higher affinity for water, as well as good resistance to the environment in an operating fuel cell. These properties make it a prime candidate to replace Nafion® in high temperature fuel cells. We project net system fuel efficiency improvements of 7% when operating at 120°C, and system cost reductions of $375/kW in stationary applications. SPEKK may also provide greater freedom in operating temperature range of the cells as well as extend the operating lifetime.

## Approach

- Design blended and composite SPEKK polymer systems
- Test membranes for durability in a steam environment
- Fabricate MEA and test for conductivity and durability

## Results

A sulfonation process was developed to produce SPEKK with ion exchange capacities of 0.8 to 2.5. As the IEC increases, SPEKK becomes highly proton conductive, but increasingly swells in the presence of steam or water (Figures 1 and 2). SPEKK with IEC 2.0 or greater appears to be self humidifying at 120°C and 30% RH. The largest technical obstacle for the IEC 2.0 SPEKK is its ability to remain intact during start-up and shut-down in a MEA as a result of swelling in excess of 100%. Low IEC SPEKK is more dimensionally stable and has better physical strength in the hydrated state. However, low IEC SPEKK has difficulty meeting the DOE conductivity targets.

Polymer blending and reinforcing strategies have improved the physical strength of the high IEC SPEKK polymers and improve the durability of the MEA. Matrix reinforced membranes show promise as a means to improve durability, though have not yet been well characterized. Blends of SPEKK with poly ether sulfone (PES), poly ether imide and low IEC SPEKK resulted in improved membrane integrity. However the conductivity of the blended membranes was approximately half of the

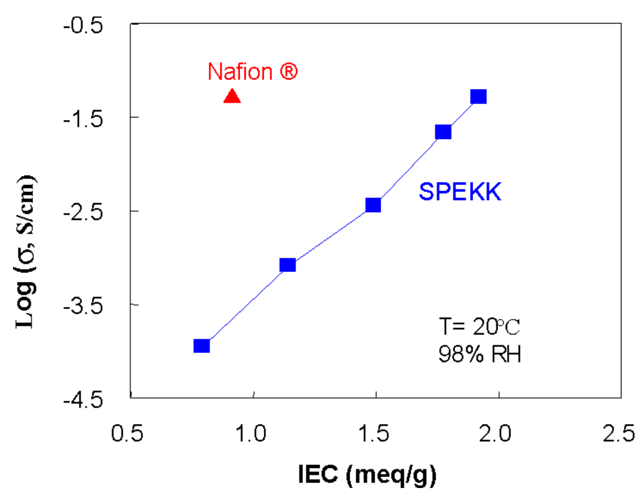


**Figure 1.** SPEKK Proton Conductivity vs. IEC

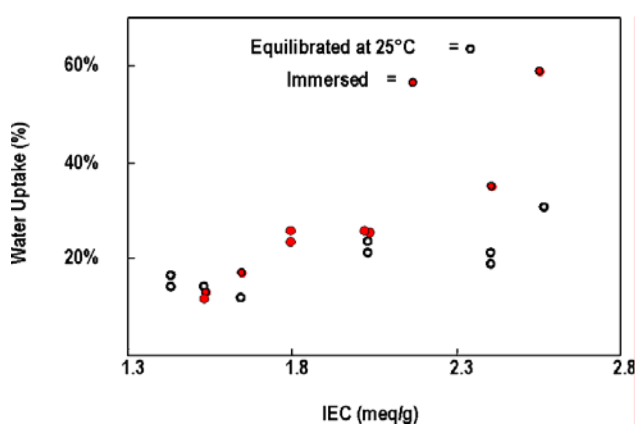


**Figure 2.** SPEKK Water Uptake

conductivity of IEC 2.0 SPEKK. SPEKK blends with PES have shown the most improvement in durability (Figures 3 and 4).

## Conclusions

- SPEKK, by virtue of its hydrophilicity, conductivity, and high temperature stability, is a viable membrane material for high temperature fuel cells.
- Higher IEC SPEKK is capable of meeting the DOE targets for conductivity.
- High IEC SPEKK requires additional engineering to meet the DOE durability targets.
- Mechanical reinforcement, blending, and cross-linking show promise with respect to improving membrane durability.
- A new grade of basis material (polyether ketone ketone) may be required to substantially improve SPEKK membrane durability.

## References


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2. U. S. Dept. of Energy, "Fuel Cell Report to Congress", (ESECS EE-1973) Feb. 28, 2003).
3. T. Zawodzinski, "R&D Plan for High Temperature Membrane Working Group", DOE URL "http://www.eere.energy.gov/hydrogenandfuelcells/tech_teams.html", June 24, 2003 Y. S. Chun and R. A. Weiss, Proc. An. Tech. Conf., Soc. Plast. Eng., 68 (2002).


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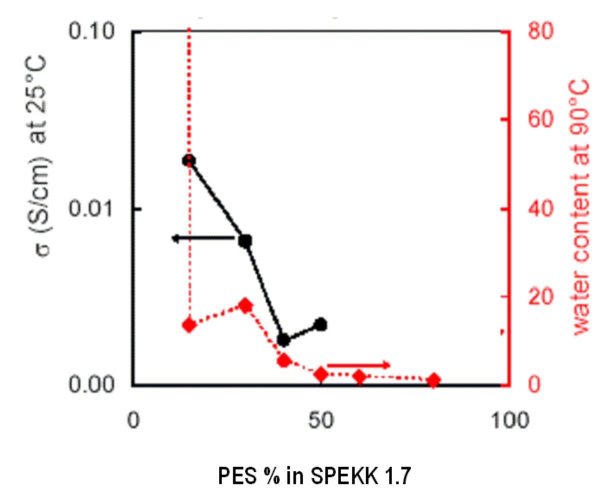


**Figure 3.** Effect of % PES on Conductivity

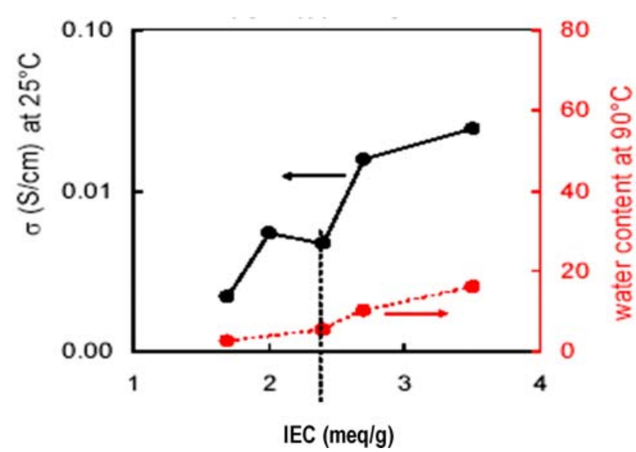


**Figure 4.** Conductivity of PES/SPEKK vs. IEC