OPM

OXFORD PERFORMANCE MATERIALS

# Development of Higher Temperature Membrane and Electrode Assembly for Proton Exchange Membrane Fuel Cell Device


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FCP2

# Overview

## TIMELINE

- Start Date: Oct. 1, 2003
- End Date: Oct. 1, 2005
- 65% Complete

## BUDGET

- Total Funding $312K
  - $250K DOE Funded
  - $62K OPM Funded
- Funding for FY04 - $150K
- Funding for FY05 - $162K

## BARRIERS

- Low Proton Conductivity at 25-50% Relative Humidity and 120°C

## TARGETS

- At 120°C, 30% Relative Humidity
  - Membrane Conductance: 0.1 S/cm
  - Membrane Strength: ~ 20kPa
  - MEA Resistance: $0.1\Omega cm^2$

# OBJECTIVES

To develop MEAs based on OPM's novel polymer for operation at 120°C and low RH that approach the performance of Nafion at 80°C and high RH.

- MEA resistance < Nafion
- Demonstrate mechanically stable interfaces after thermal and humidity cycling

# TECHNICAL APPROACH

- **Replace Nafion with Novel Polymer**
  - Sulfonated Polyetherketoneketone (SPEKK)
  - Interconnected interface network – 'Proton Highway’
    - Blend SPEKK with complimentary polymer (polyetherimide (PEI) and polyethersulfone (PES))
- **Engineer Blend Morphology to Improve Properties**
  - Connect isolated ionic domains
  - Improve physical stability
- **Fabricate Prototype Membrane Electrode Assembly (MEA)**
  - Substitute novel polymer for Nafion in membrane and gas diffusion layer
  - Demonstrate MEA feasibility at low relative humidity

# TECHNICAL ACCOMPLISHMENTS

- **Investigated SPEKK, SPEKK/PEI and SPEKK/PES Blends**
  - Conductivity
    - Four point AC method
  - Swelling
- **Application Technique for Gas Diffusion Layer (GDL)**
  - Use MeOH solubility of high IEC SPEKK to advantage
  - Possible enhanced coupling between GDL, electrode and membrane

# TECHNICAL ACCOMPLISHMENTS (Cont'd)

- **Fabricate and Test Membranes to Understand Feasibility**
  - Neat SPEKK
  - SPEKK blends
  - Matrix reinforced high IEC SPEKK
- **Started Up Two Fuel Cell Test Stations**
  - Commercial Nafion MEA proved test station
  - Modifications to prevent accidental introduction of water into test cell
  - Hydrogen safety items

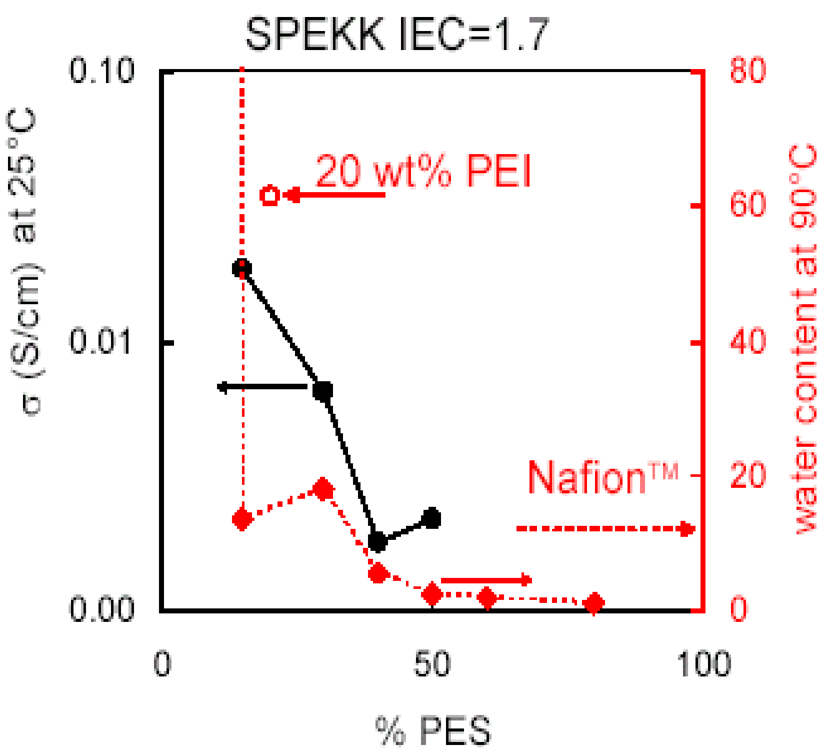
# SPEKK / PEI BLENDS

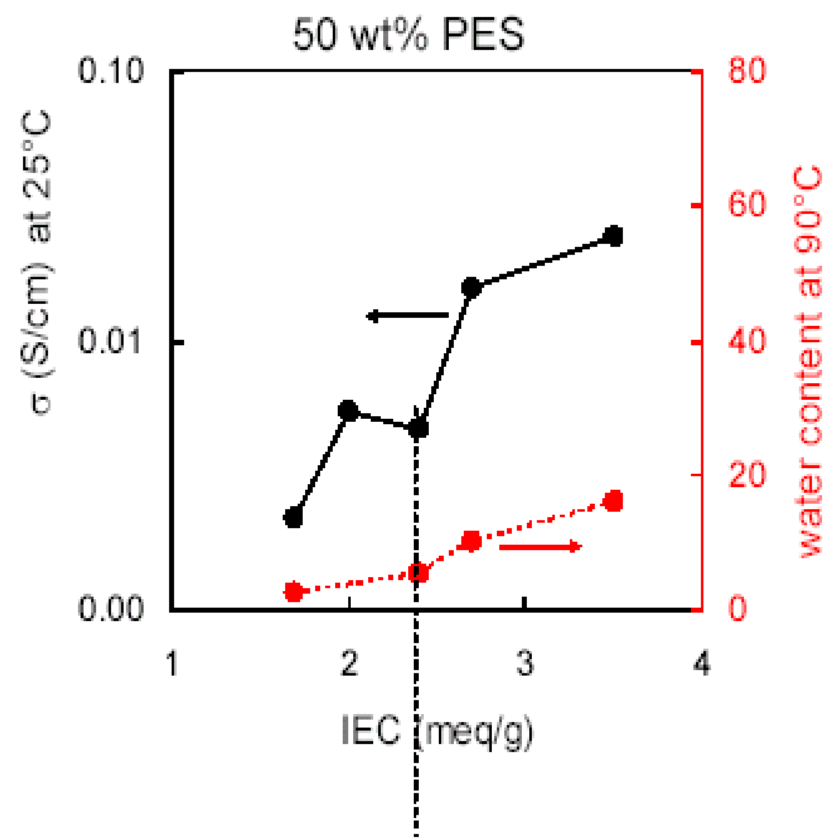
- **Blends of SPEKK and PEI Have a Binary Blend Morphology**
  - Not fully miscible at all proportions
  - Concentration and blend temperature independent
  - Particle morphology spherical due to surface tension
  - Particle size does not significantly affect the conductivity or swelling
  - Conductivity not enhanced due to segregation of conducting domains
  - Good candidate for future EFO process

# SPEKK / PES BLENDS

- **SPEKK & PES Result in Stable Homogeneous Films**
  - Fully miscible in all proportions
  - Minimizes membrane swelling
  - Delays onset of water solubility for high IEC SPEKK
  - Reduces proton conductivity
  - Possible enhancement for DMFC use
  - System warrants further examination

# SPEKK / PES Blends




* Swier, S- 2004

pure SPEKK IEC>2.4 dissolves in water!

# SPEKK / SPEKK BLENDS

- **SPEKK (High IEC) and SPEKK (Low IEC) Result in Continuous 3D Interconnected Homogeneous Films**
  - Miscible if IEC difference is small (<0.5); otherwise not miscible
  - Dominant fraction forms continuous phase
  - Reduces membrane swelling
  - Less reduction of proton conductivity than other blends (**both** phases conduct)
  - System warrants further examination

# MEA FEASIBILITY

- **Neat SPEKK Membranes Not Dimensionally Stable in MEA**
  - Swelling/deswelling in low IEC SPEKK
  - Water solubility in high IEC SPEKK
  - Particulate reinforcement strategy: fumed silica blend with SPEKK
  - Matrix reinforcement strategy: PEEK mesh, woven glass, paper matrix, SPEKK infiltrated
  - Unreinforced membranes of low IEC SPEKK subject to scission in service with RH cycling
  - Reinforced membranes of high IEC SPEKK damaged by back flooding / steaming, even at 120°C
  - Particulate strategy: difficult to implement – fumed silica migration with surface tension
  - Matrix reinforcement strategy: limited success – some data gathered with IEC 2.0 SPEKK indicates matrix approach useful for some applications

# REVIEWER COMMENTS - 2004

- **What Makes PEKK Superior to PEEK and Other Materials Previously Reported in the Literature?**
  - PEKK's chemical structure has more reactive sites for sulfonation and it has a high $T_g$.
- **Gas Transport and Electrode Membrane Interaction**
  - Anode dynamics are **not** limiting fuel cell performance. Current methods will be used until a disruptive technology is discovered.
  - Cathode dynamics **are** limiting fuel cell performance. Gas transport **is** a limiting factor, especially at high current densities. Catalyst inks incorporating pore forming materials to enhance gas transport and other (proprietary) means of forming a more gas permeable electrode layer are under investigation.

# REVIEWER COMMENTS – 2004 (Cont'd)

- Membrane proton conductivity **is** a limiting factor.
- Current focus is to improve proton conductivity and mechanical stability of the membrane material SPEKK for the purpose of incorporating SPEKK into a technically feasible MEA.
- It appears that oxygen is slower to diffuse through SPEKK than Nafion. Given similar configurations, O2 will be less available to a SPEKK cathode than a PFSA cathode. Use of different methods of applying catalysts and GDLs is one method to alleviate this potential performance inhibitor.

# FUTURE WORK – SPEKK MEA

- **Secure Pilot Scale Processor of SPEKK**
- **Improve the Dimension Stability of SPEKK**
  - Crosslinking
  - Matrix reinforcement of low IEC SPEKK (durability)
  - Water replacement (non-volatile swelling agents)
  - Optimize blend /and process (PES, PPEK, Others…)

# FUTURE WORK – SPEKK MEA (Cont'd)

- **Reduce Emphasis on Platinum & Area Loading**
  - Greater need to stabilize membrane
  - Pt loading issues already adequately understood
  - Single anode / cathode system pair is adequate
- **Investigate Cathode Enhancement Strategies**
  - Use of pore forming strategies to facilitate gas transport
  - Investigate feasibility of possible novel structure catalyst material (proprietary)

# SUPPLEMENTAL SLIDES

The following 3 slides are for reviewers only and are not be presented as part of your oral or poster presentation.

# PUBLICATIONS & PRESENTATIONS

Design of Polymer Blends for Proton Exchange Membranes in Fuel Cells, S. Sweir, M. T. Shaw and R. A. Weiss, Am. Chem Soc., Div. Fuel Chem., 2004, 49(2), 532

Influence of Electrolyte Composition on PEFC Performance in Sulfonated PEKK Systems, V. Ramani, S. Sweir, R. A. Weiss, M. T. Shaw, H. R. Kunz, J. M. Fenton, Abstracts of the 206th meeting of the Electrochemical Society, 2005, Abstract 1939

Heteropolyacid/Sulfonated PEKK Composite Membranes for PEFC and DMFC Applications - V. Ramani, S. Swier, R. Weiss, M. Shaw, H. Kunz, and J. Fenton, Abstracts of the 205th meeting of the Electrochemical Society, 2004, Abstract 405

# HYDROGEN SAFETY

The most significant hydrogen hazard associated with this project is entrapment of accidentally vented hydrogen in a closed space (only likely scenario to provide sufficient concentration for detonation). Our approach to deal with this hazard:

- All apparatus allowing a flow of hydrogen are constructed using open mesh or grid wherever function of the device allows.
- Exception: fuel gas humidifier. The function of the device does not allow for free airflow through the hydrogen “wet” areas. Purging of the humidifiers is performed by a single trained operator with the fill cover ajar to avoid any “contained” detonation in favor of an open air “pop”.