Polymer Blend Proton Exchange Membranes

R. A. Weiss and M. T. Shaw
University of Connecticut

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Objective

Develop new membranes based on polymer blends for operation at temperatures of 120°C or higher

Budget

DOE Funding FY04 = $ 95,000

Technical Barriers and Targets

DOE Technical Barriers For Fuel Cell Components

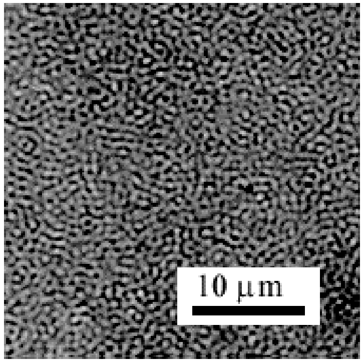
- O. Stack Material and Manufacturing Costs
- P. Durability
- R. Thermal and Water

DOE TechnicalTargets for Membranes (Automotive) for 2005

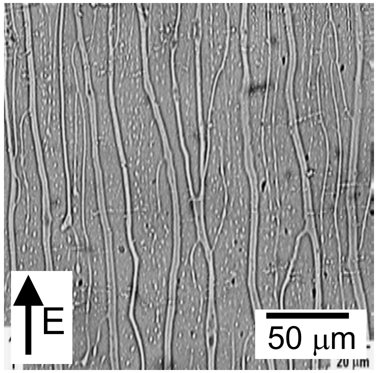
- Membrane conductivity (operating temperature) ~ 0.1 S/cm
- Operating temperature $\geq$ 120°C
- Membrane cost ~ $50/kW
- Membrane durability > 4000 h
- Hydrogen/oxygen cross-over (MEA) ~ 5 mA/cm^2
- Survivability ~ -20 °C

Approach

Develop high temperature PEMs with controlled morphology using acid-base polymer blends



1. Thermodynamics: develop a percolated ionic pathway at the interface of a spinodal morphology of a polymer blend comprising a sulfonated polyketone and a polyimide or similar second component



2. Electro-dynamics: Orient a dispersed phase of the conductive sulfo-polyketone in a polyimide matrix by applying an electric field during membrane casting

Project Safety

- Handling and disposing of SO_3: normal handling procedures for strong acids; disposal by neutralization
- Handling of hydrogen: normal handling procedures of high-pressure gas; high-flow-rate ventilation
- Handling and disposing of solvents: normal OSHA/EPA procedures used

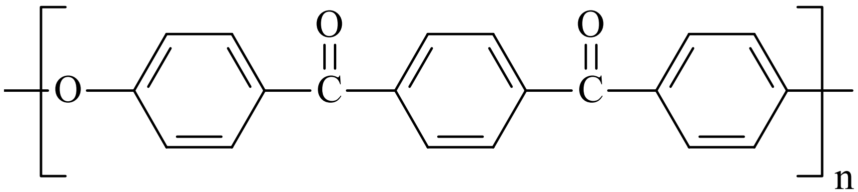
Project Timeline

10/02 – 10/03	10/03 – 10/04	10/04 – 12/06
Phase I	Phase II	Phase III
1 2	3 4 5	6 7

- Phase I: Feasibility
  1 Optimize preparation of sulfonated PEKK (SPEKK) ionomers
  2 Prepare/Evaluate SPEKK/polyether imide (PEI) blend membranes
- Phase II: Morphology Development
  3 Develop spinodal structure for SPEKK/PEI membranes and characterize membrane performance
  4 Develop procedure for orienting SPEKK/PEI membranes and characterize membrane performance
  5 MEA production and testing
- Phase III: System Optimization
  6 Optimize membrane composition and morphology for high temperature SPEKK/PEI PEM
  7 Design and evaluate other blend PEMs

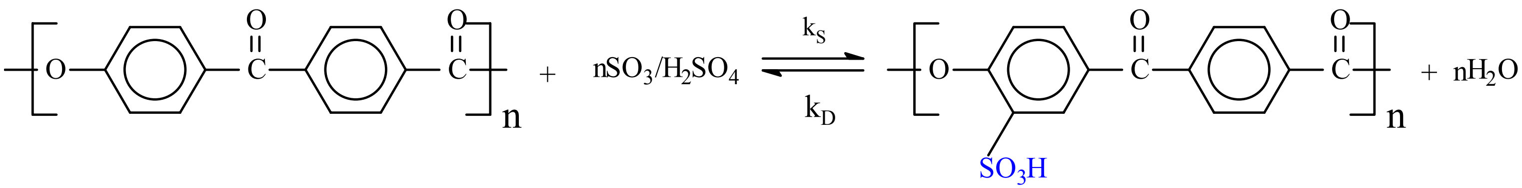
Technical Accomplishments/Progress

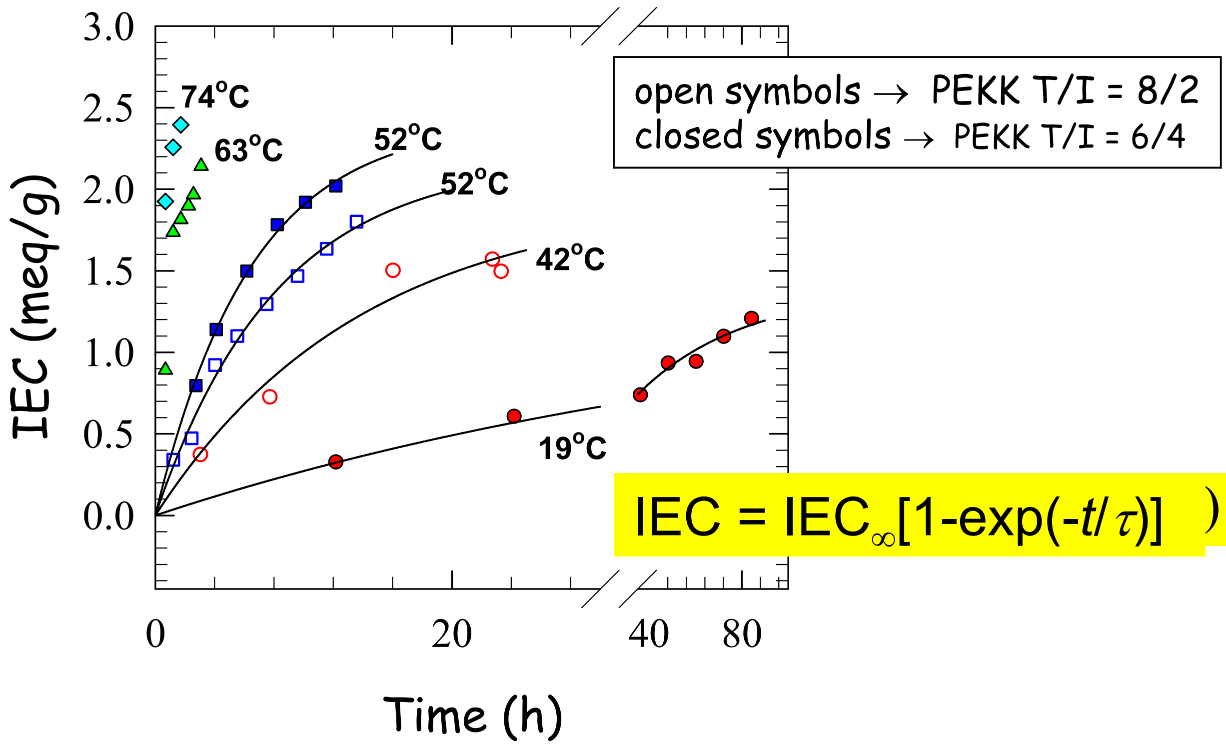
Developed Membranes Based on Poly(ether ketone ketone)



- High temperature stability (T_g ~ 155°C; T_m ~ 360°C)
- Excellent mechanical properties (engineering thermoplastic)
- Excellent chemical and solvent resistance
- Excellent oxidative stability
- Adequate resistance to desulfonation

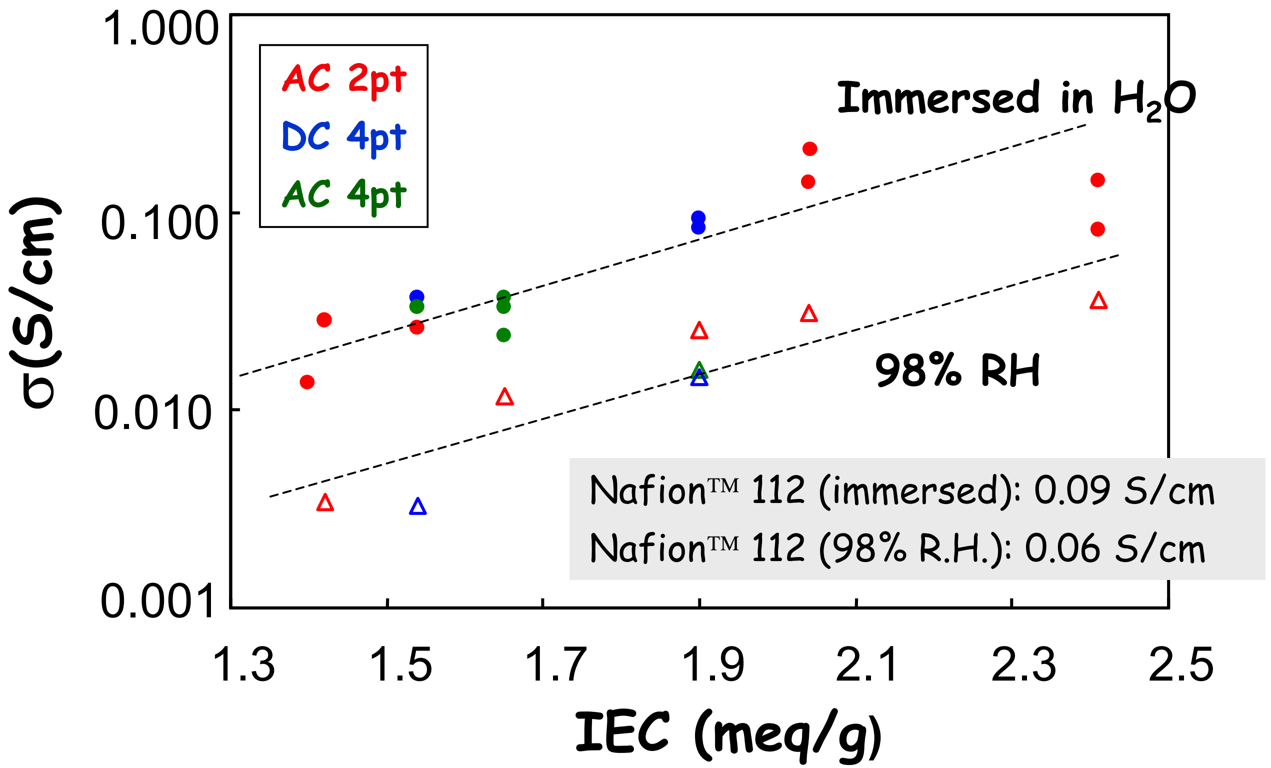
Optimized procedure for preparing sulfonated PEKK (SPEKK)





$$IEC = IEC_{\infty}[1-\exp(-t/\tau)]$$

Proton Conductivity of SPEKK



SPEKKs:

- **For IEC ~ 1.8 – 2.1 meq/g, conductivity ~ 10^{-1} S/cm**
- **Water insoluble when IEC < 2.3 meq/g**
- **20-150 μm membranes can be cast from NMP or DMAc**

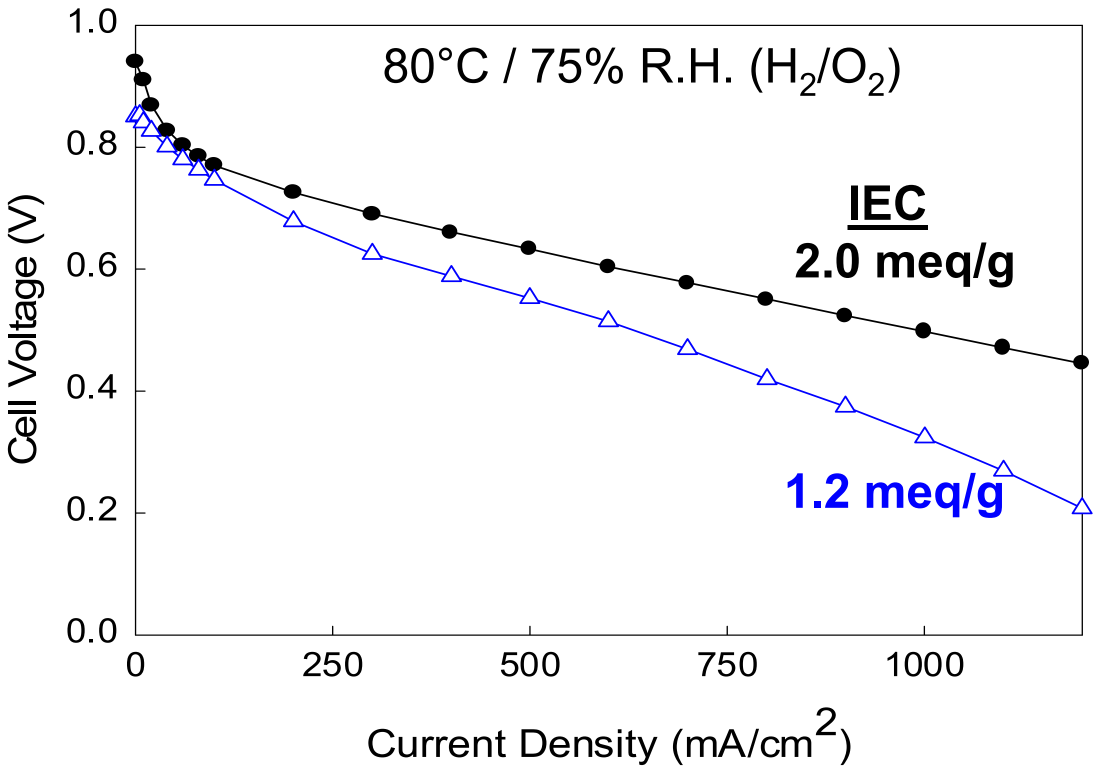
Methanol Crossover for SPEKK in MEA

	Resistance (ohm cm^2) (H_2/O_2, 80 °C)	Methanol Crossover (A/cm^2) (1M MeOH, 80 °C)
SPEKK (1.8 meq/g)	0.07	0.22
Nafion™	0.05	0.40

SPEKK membranes:

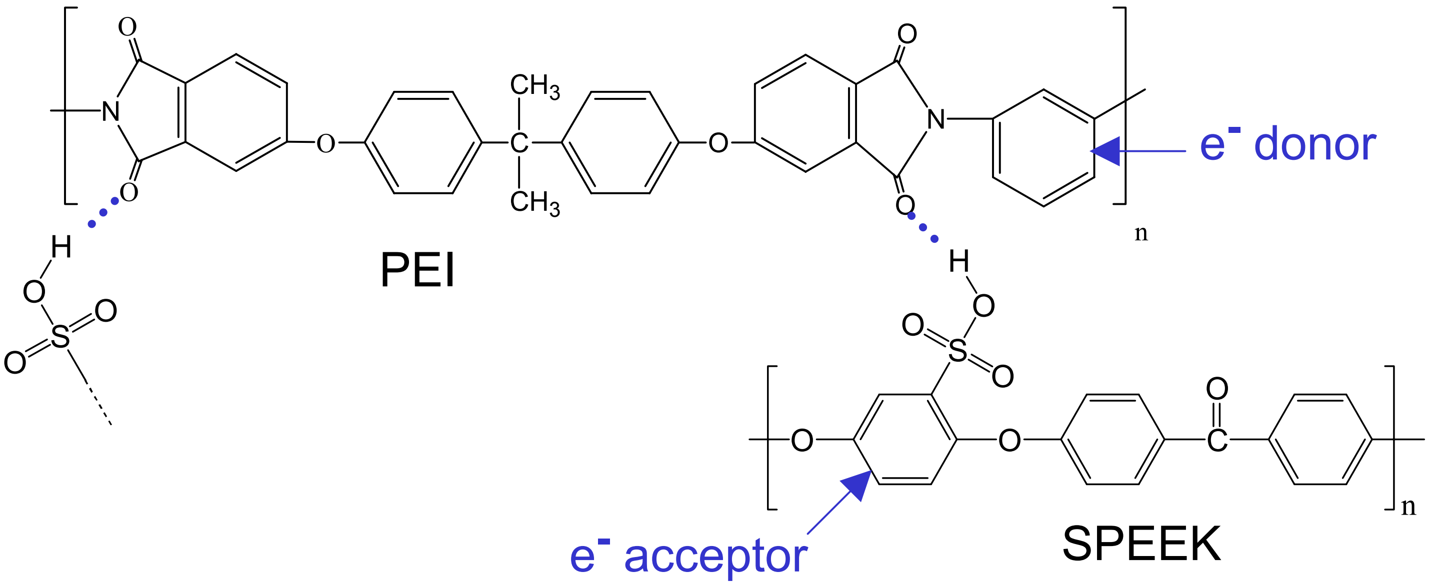
- Good proton conductivity (~ 0.1 S/cm)
- Improved methanol permeability resistance vs. Nafion™

MEA Performance of SPEKK PEMs



Reasonably good MEA performance

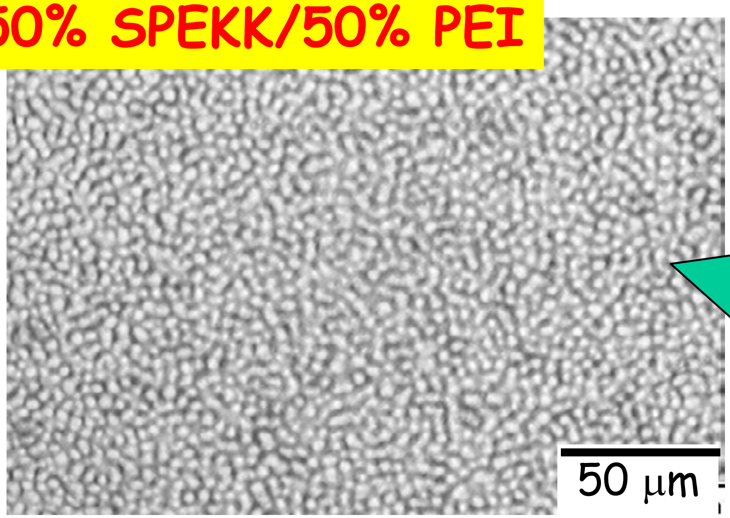
Blends of SPEKK with Poly(ether imide) (PEI)

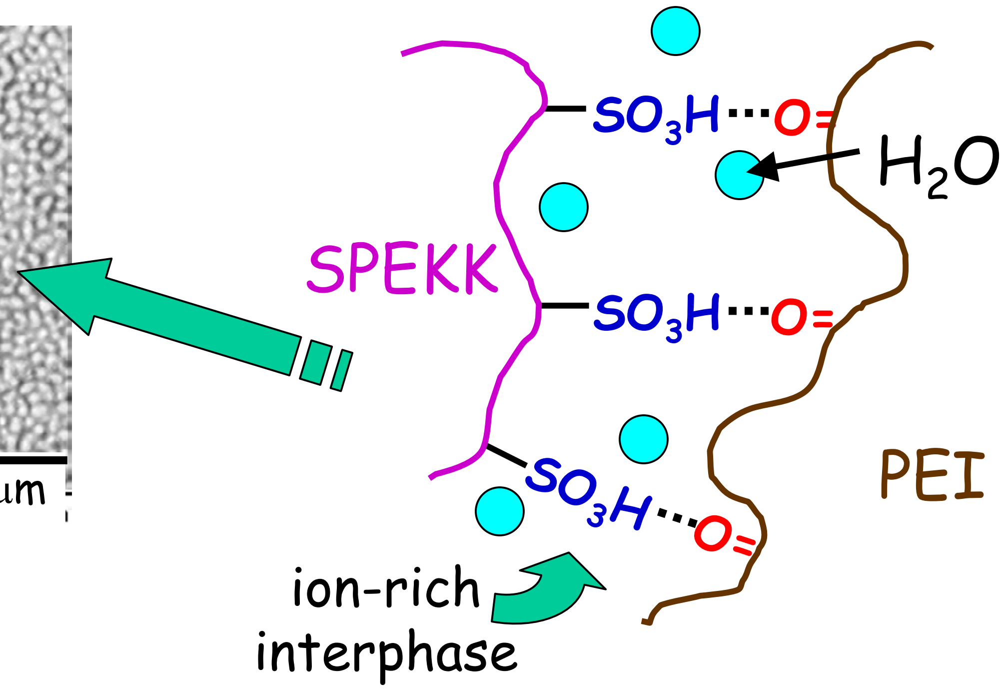


- Strong H-bonding interactions are expected
- Ionomer provides acid groups for proton conductivity
- Relatively hydrophobic PEI provides mechanical integrity

SPEKK/PEI Blend PEMs

50% SPEKK/50% PEI

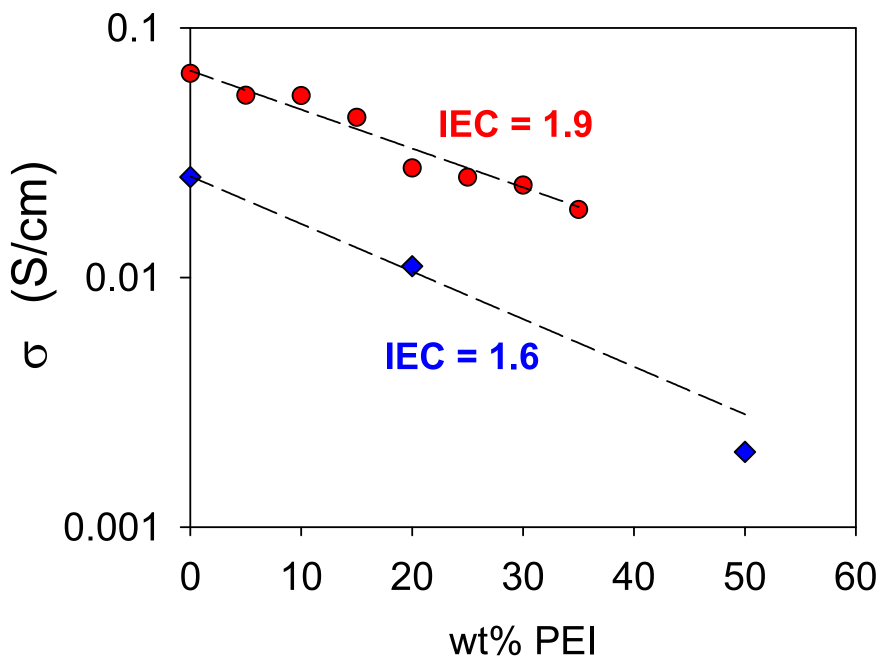




Hypotheses:

- Ion-rich interphase provides pathway for proton conductivity
- Percolated conductive path present before water is added
- Amount of water required for conductivity will be less than for conventional ionomer membrane

Effect of PEI content on conductivity (RT)

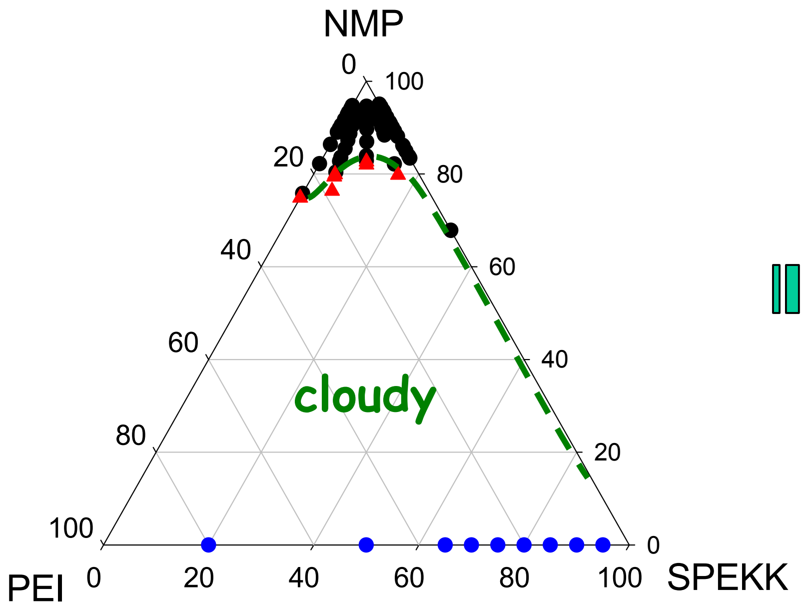


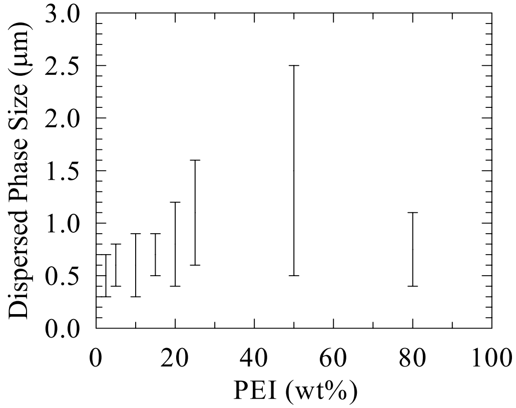
Increasing PEI concentration:

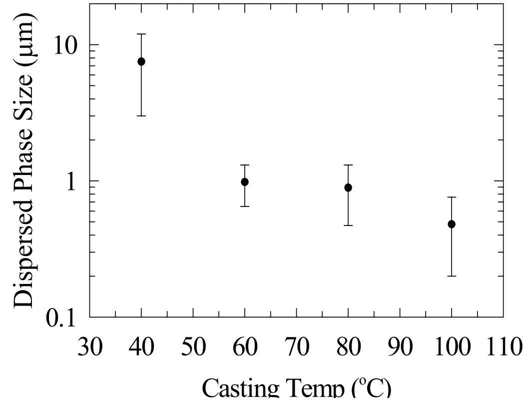
- Lowers conductivity (but still > 0.01 S/cm for c_{PEI} < 30%
- Reduces water concentration
- Improves mechanical properties of wet membrane

Controlling the Blend Morphology: Film Casting T

Ternary Phase Diagram

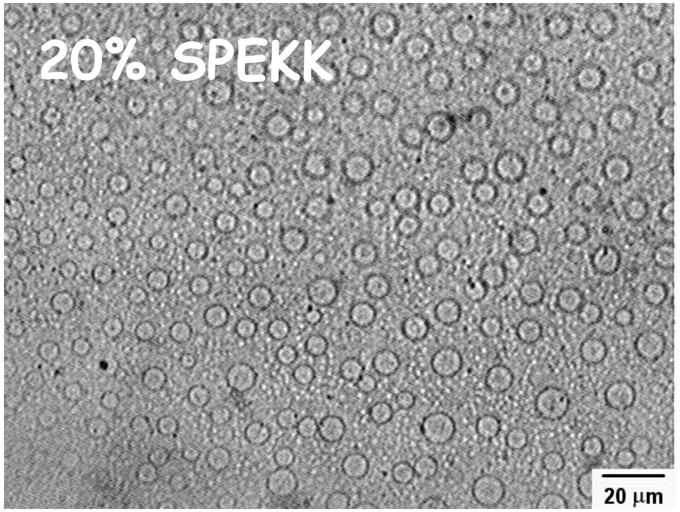




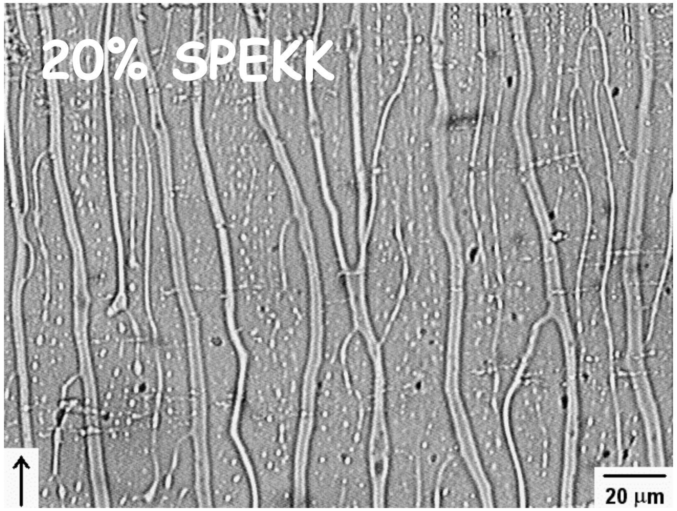


- Dispersed phase size decreases with casting temperature
- Dispersed phase size increases with increasing PEI

Controlling the Blend Morphology: Electric Field Alignment



Cast without Electric Field

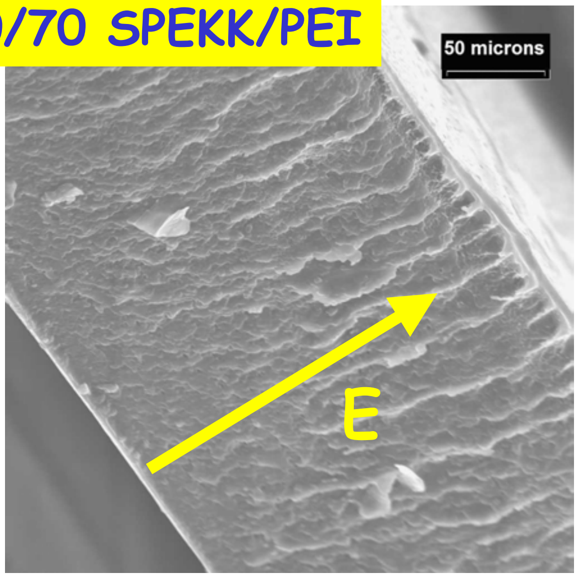


Cast with Electric Field
E = 0.5 kV/cm; f = 20 Hz

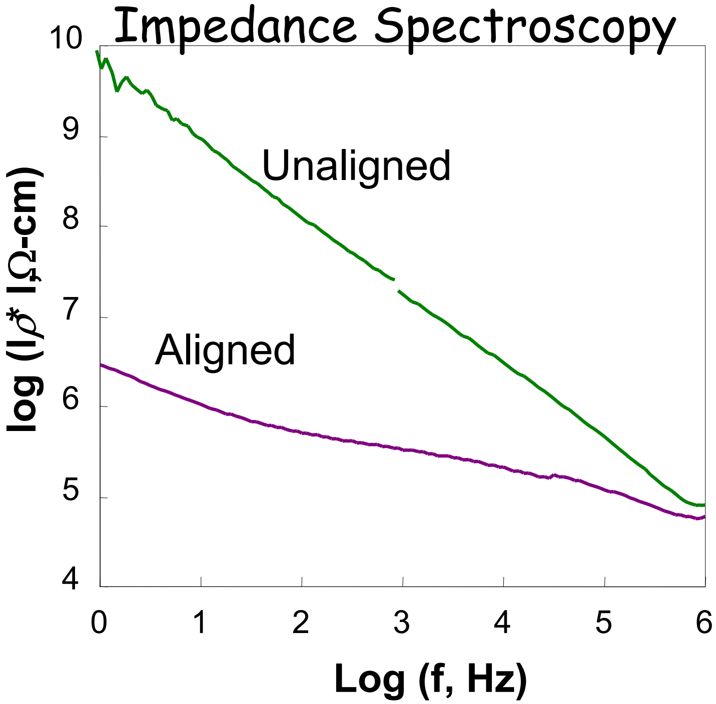
SPEKK dispersed phase can be oriented by applying an AC electric field across the membrane during processing (solution or melt)

Controlling the Blend Morphology: Electric Field Alignment

30/70 SPEKK/PEI



Oriented at 200°C;
E = 10 kV/cm; f = 20 Hz



Electric field alignment of SPEKK phase significantly increases the membrane conductivty

Interactions and Collaborations

Oxford Performance Materials (OPM): SPEKK development and blend membrane development; MEA fabrication and testing

Leveraging Resources:

Agency	Dates	Award	Outputs/Objectives
Connecticut Innovations, Inc. (UConn and OPM)	1999-01	$375K	Development of sulfonated PEKK. Initial evaluation of sulfonated PEKK for PEM fuel cell applications.
Connecticut Innovations, Inc. (UConn and OPM)	2001-03	$375K	Development of reproducible process for sulfonation of PEKK. Demonstrated feasibility of SPEKK PEMs for direct methanol fuel cells.
DOE Inventions & Innovations (OPM)	2003-05	$250K	Ongoing: sPEKK and sPEKK blend based MEAs. (subcontract to UConn)
DOE (UConn)	2003-05	$191K	Ongoing: Development of methods for controlling domain structure of polymer blends for PEM applications using thermodynamics and electric fields
Connecticut Global Fuel Cell Center (UConn)	2003-04	$75K	Development of equipment for electric field orientation of polymer films during film preparation
NSF (UConn)	1994-02	$1.1M	Fundamental studies of the thermodynamics of ionomer blends

Future Plans

Remainder of FY 2004:

- Develop ternary phase diagrams for SPEKK/PEI/solvent, using different solvents
- Produce membranes with spinodal structure
- Optimize equipment and procedures for electric field orientation of membranes
- Fabricate MEAs with controlled morphology blend membranes