

# 2006 DOE Hydrogen Program Review Presentation

Advanced Materials for Proton Exchange Membranes

**James E. McGrath, Ph.D. NAE**

**University Distinguished Professor of Chemistry  
Macromolecules and Interfaces Institute  
and Department of Chemistry**

**Virginia Tech  
Blacksburg, VA 24061**

**[Jmcgrath@vt.edu](mailto:Jmcgrath@vt.edu)**

# McGrath Group 2006



Front Row (L to R): Dr. W. Harrison (Ph.D. 2004), Prof. Y.J. Kim (Sung KyunKwan Univ, Korea), J.E. McGrath, A. Badami, H. Wang.

Back Rows (L to R): M. Paul, X. Yu, A. Roy, E. Morazzani (undergrad), A. Cleaton (undergrad) N. Arnett, M. Hill, Dr. Z. Zhang, R. Hopp, O. Lane, Y. Chen, H.S. Lee, Y. Li, Dr. G. Fan, Dr. M. Sankir, J. Yang, S. Takamuku (visiting scientist)

# Acknowledgements

- McGrath Research Group: past and present
- May 2006” DOE Contract on “*High Temperature, Low Relative Humidity, Polymer-type Membranes Based on Disulfonated Poly(arylene ether) Block and Random Copolymers Optionally Incorporating Protonic Conducting Layered Water Insoluble Zirconium Fillers*”

# OUTLINE

- **Research Progress Objectives**
  - Approach and Strategy
  - Partially fluorinated systems
  - Multiblocks
  - Crosslinking
  - Blends
  - Film Casting

# Objectives

- Design, identify, and develop the knowledge base to enable proton exchange membrane films and related materials to be utilized in automotive fuel cell applications, particularly for H<sub>2</sub>/Air systems at 120°C/low RH.

# Research Approach/Hypothesis

- Thermally, hydrolytically, and oxidatively stable aromatic ionomers with high  $T_g$ , ductility, and controlled hydrophilicity are required
- Synthesis
  - Linear and crosslinked statistical hydrophobic/hydrophilic copolymers
  - Linear multiblock hydrophobic/hydrophilic copolymers (current & future)

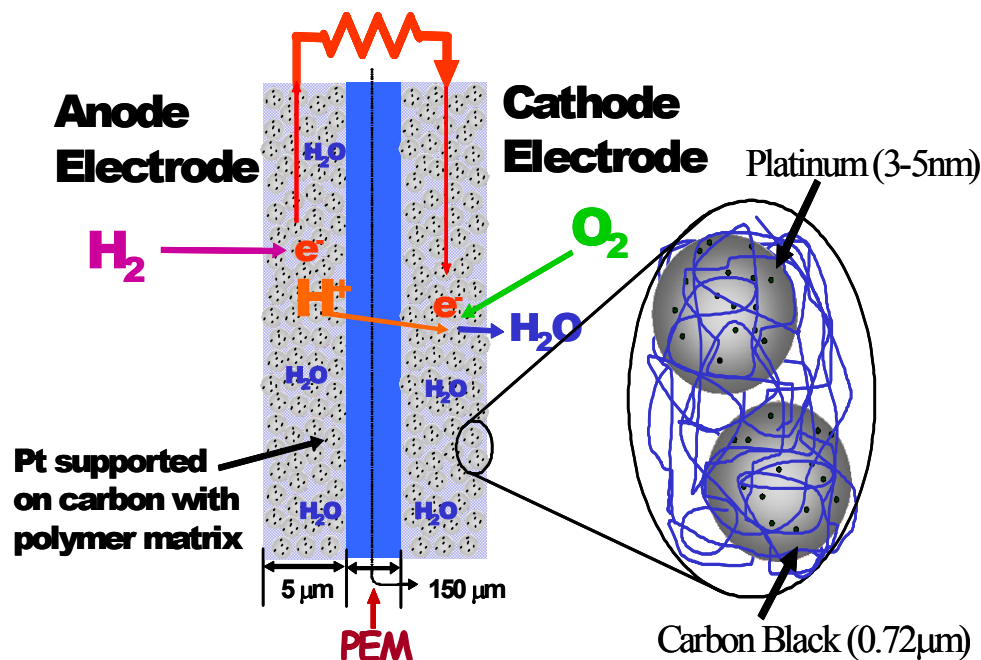


# Proton Exchange Membrane (PEM) Requirements

- **CRITICAL PEM PROPERTIES**

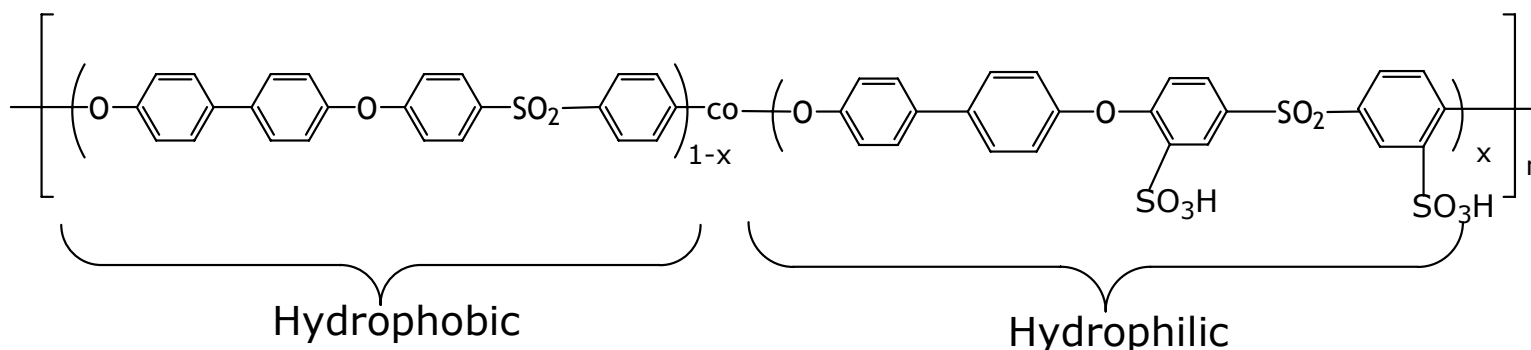
- high protonic conductivity, even at low RH
- low electronic conductivity
- low permeability to fuel and oxidants
- low water transport - diffusion and electro-osmotic drag
- oxidative and hydrolytic stability under acidic conditions, for thousands of hours!
- Good dry and wet mechanical properties at ambient and higher temperatures
- Cost effective and able to be fabricated into robust membrane electrode assemblies (MEAs)

## Membrane Electrode Assembly (MEA)



The benchmark is Nafion™  
for the membrane and electrodes

# Sulfonated Poly(arylene ether sulfone)s (BPSH)



## ❖ Acronym: BPSH-xx-Mx

Bi Phenyl Sulfone: H Form (BPSH)

xx= molar fraction of disulfonic acid unit, e.g., 30, 40, etc.

Mx: Acidification method, e.g., M1, etc.

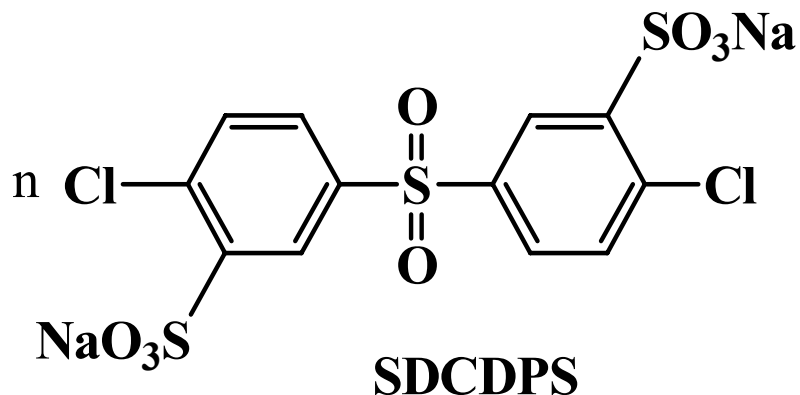
## ❖ Acidification Treatment

**Method 1:** 1.5M  $\text{H}_2\text{SO}_4$ , 30°C, 24hrs, then deionized  $\text{H}_2\text{O}$ , 30°C, 24hrs.

**Method 2:** 0.5M  $\text{H}_2\text{SO}_4$ , boil, 2hrs, then boiled deionized  $\text{H}_2\text{O}$ , 2hrs.

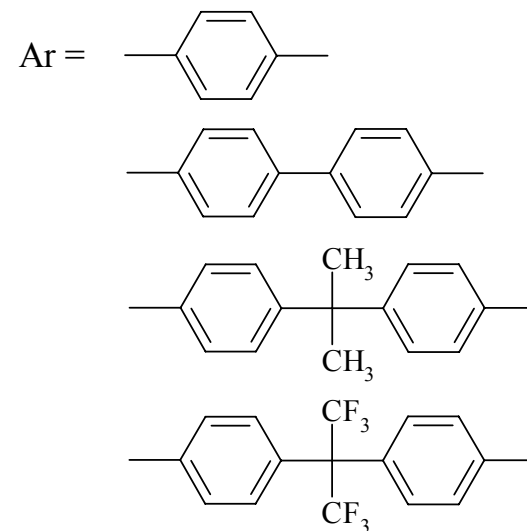
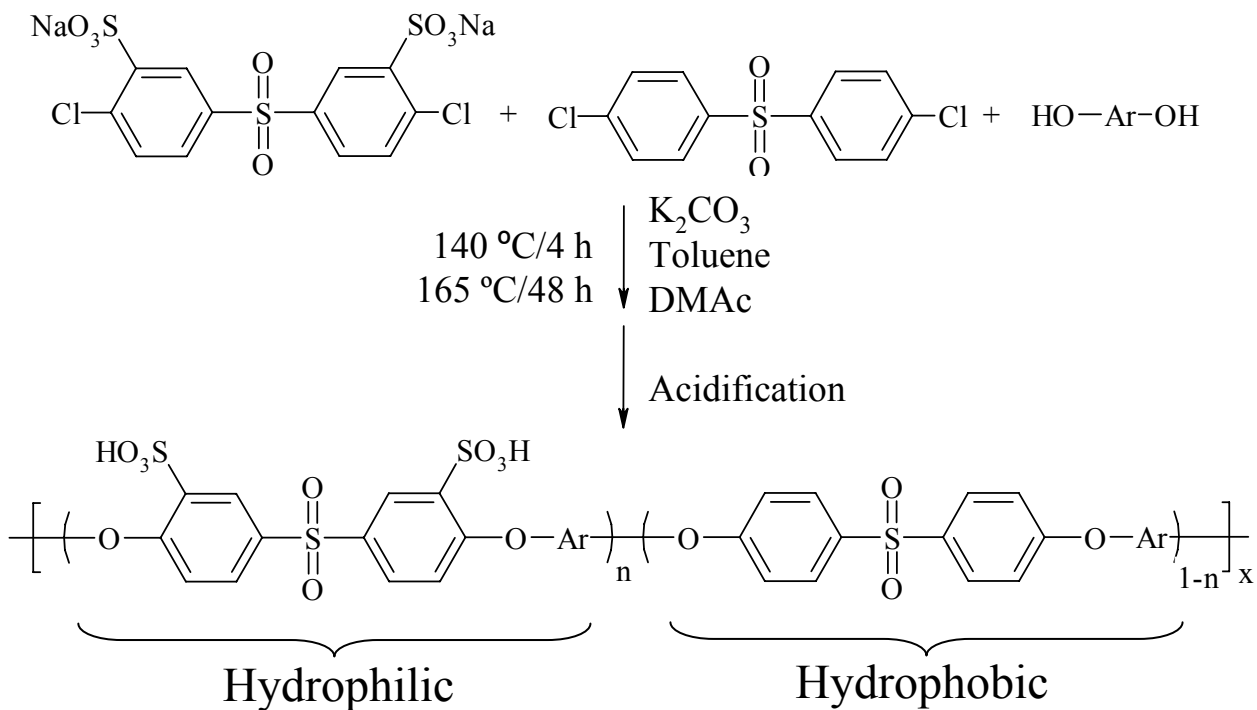


# Advantages of Direct Polymerization



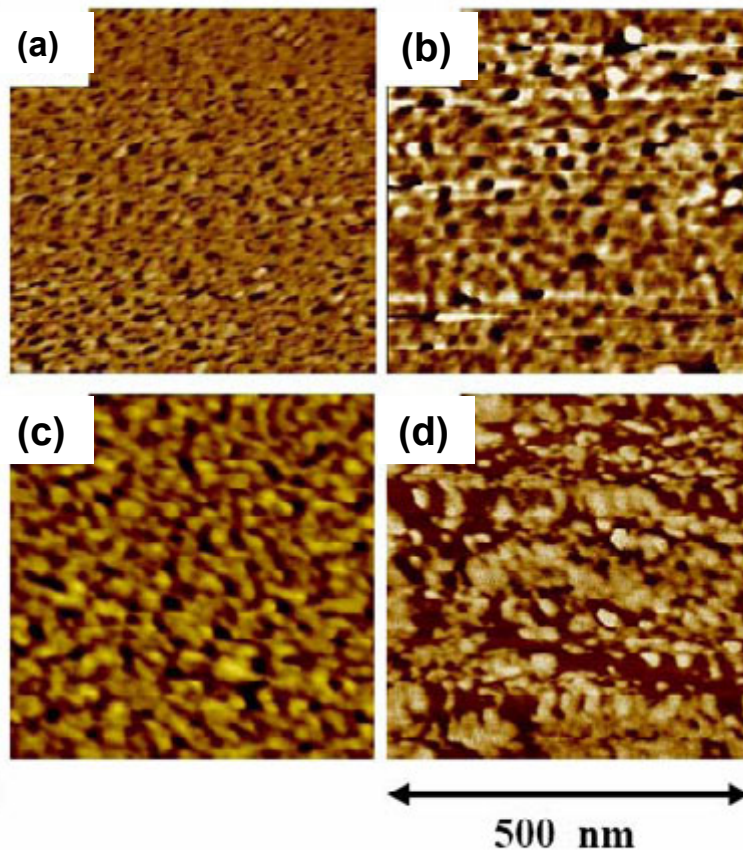
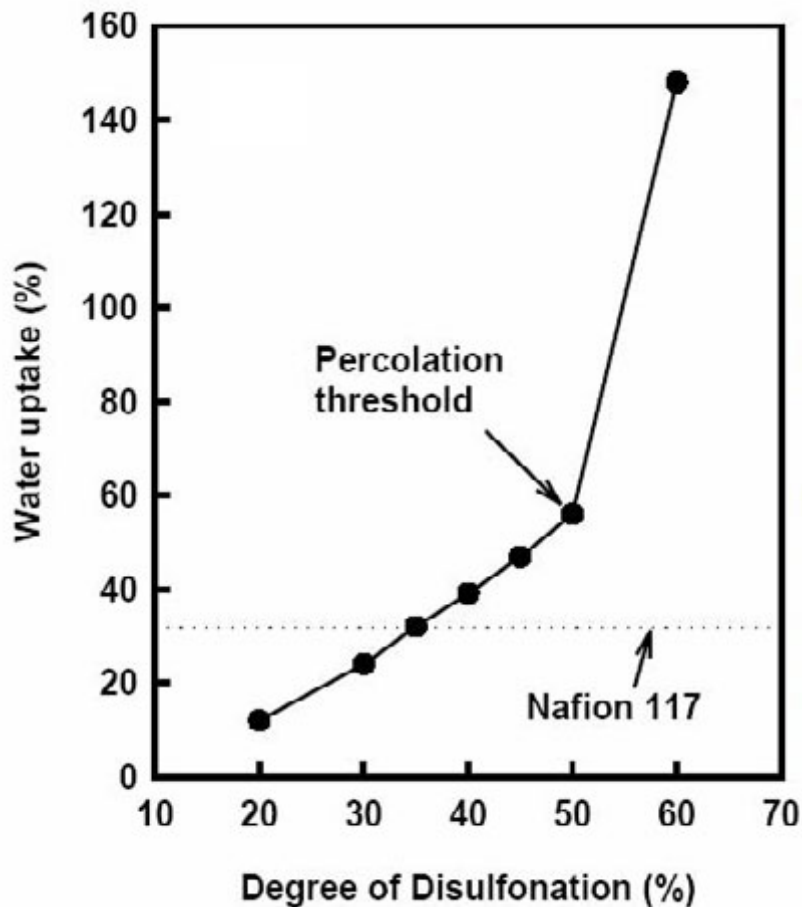
- ✓ High yields from 40MM lb/year precursors
- ✓ Precise control of ionic concentration during synthesis
- ✓ Well-defined ion conductor location; morphology control
- ✓ High H<sup>+</sup> conductivity
- ✓ Enhanced stability due to deactivated position of -SO<sub>3</sub>H
- ✓ Compatible with additives for >100°C studies
- ✓ Very high molecular weight copolymers possible

# Copolymer Synthesis by Nucleophilic Aromatic Substitution



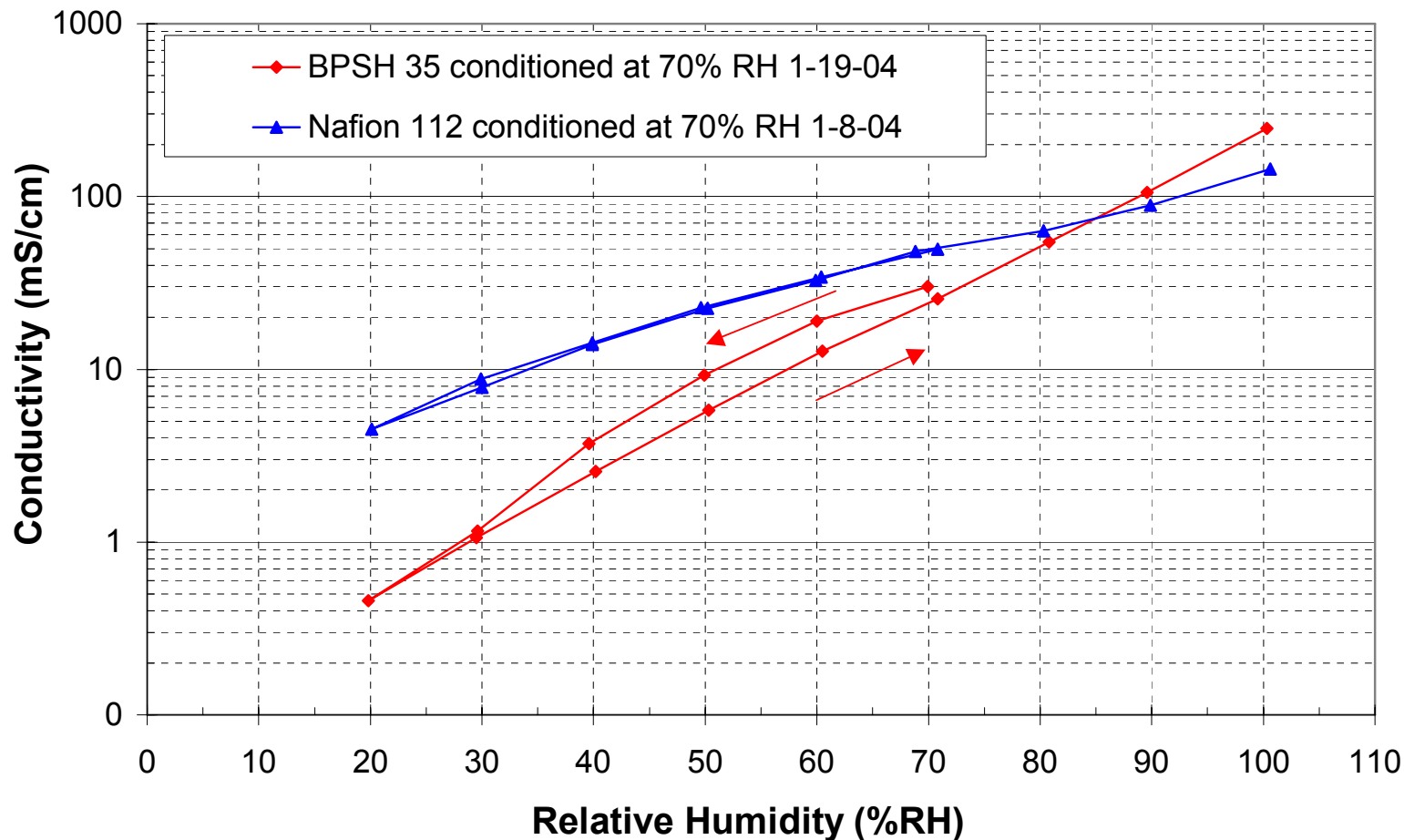
- Monomer and copolymers are scaleable to multi-kilogram quantities

# Water Uptake of BPSH Random Copolymers is Dependent on Morphology

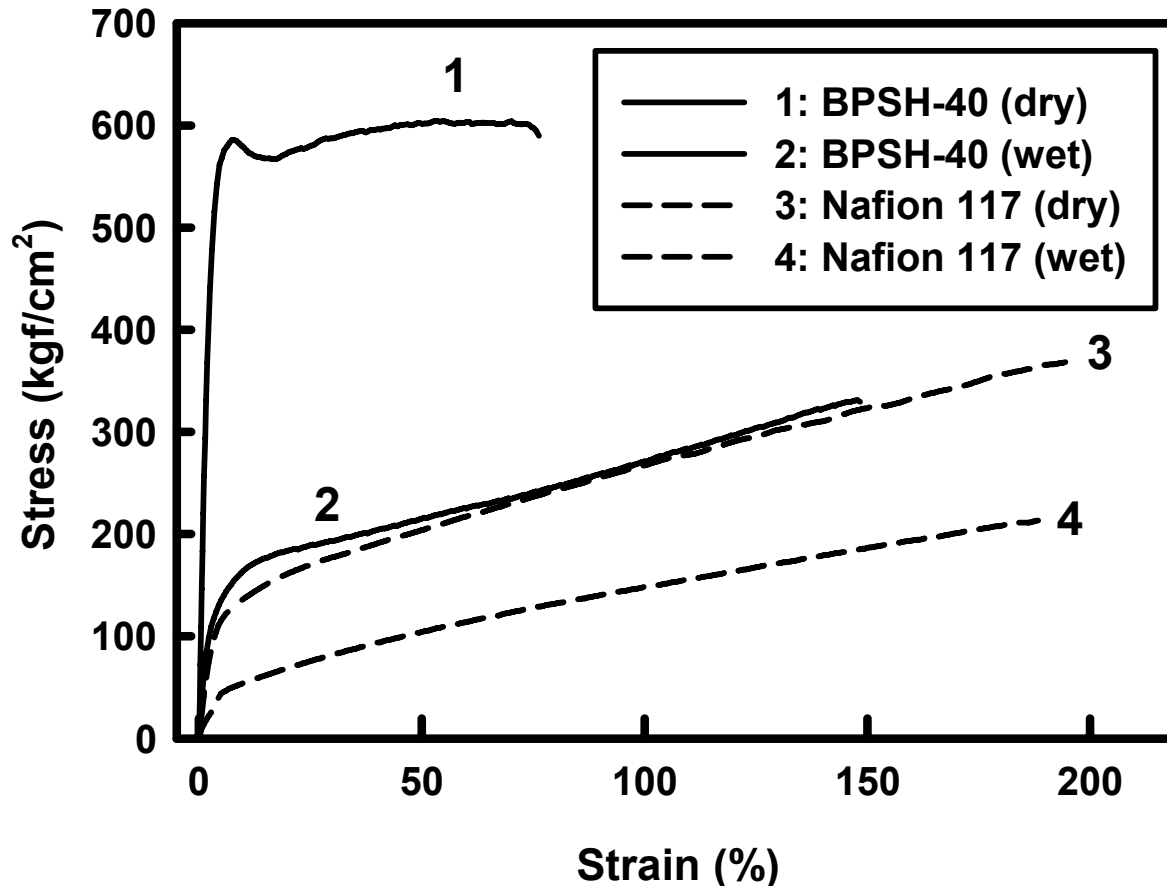


(a) Control; (b) 40% ionic content; (c) 50% ionic content; (d) 60% ionic content

# Comparing Four Electrode Conductivity of BPSH 35 120°C, 500 sccm H<sub>2</sub>, 230 kPa



# Comparison of Stress-Strain Behavior of BPSH-40 and Nafion 117\*

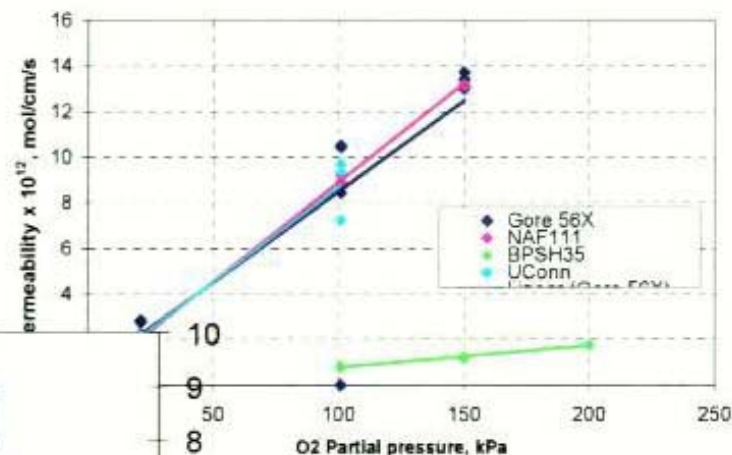


The wet state of BPSH-40 and Nafion 117 had 22% and 16%, total water, respectively.

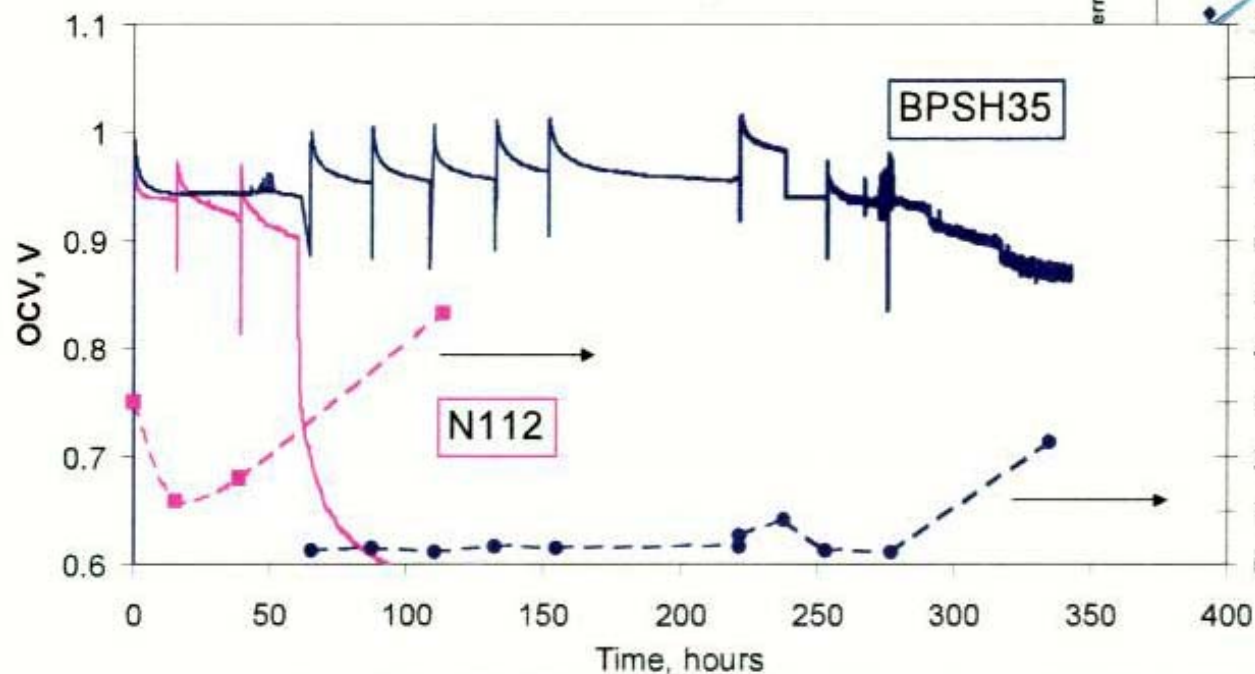
# Colleagues at UTC (Dr. Protsailo/Dr. Haug) have shown BPSH outperforms the benchmark membrane as judged by open circuit voltage (OCV) in H<sub>2</sub>/O<sub>2</sub> accelerated tests

- BPSH O<sub>2</sub> permeability is 10x lower than that of PSFA-like membrane - significantly increases durability

Oxygen Permeability Measurements



Accelerated Membrane Degradation Test

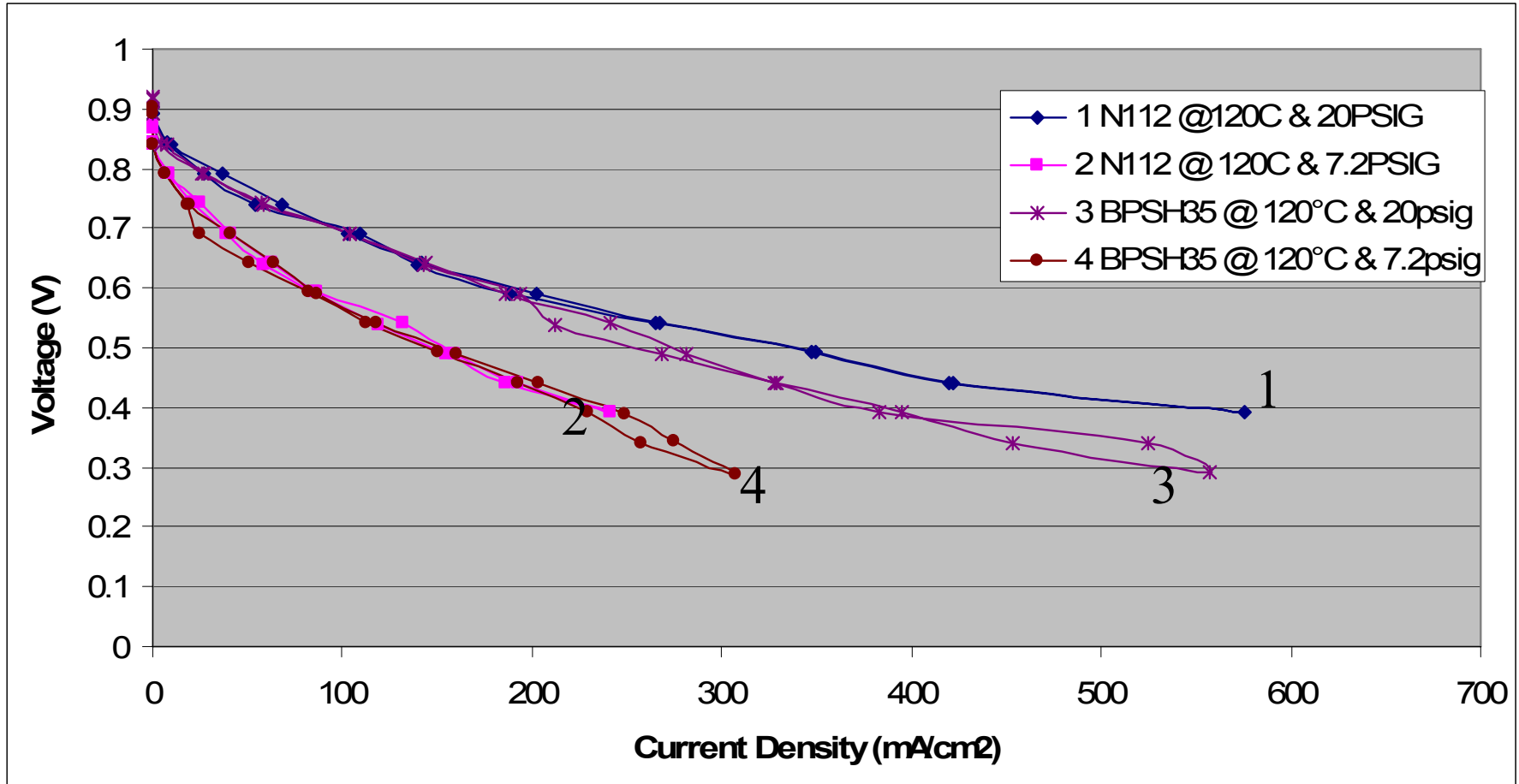


**Accelerated  
Membrane  
Degradation Test  
Conditions:**

100°C, 25%RH,  
1.5atm  
H<sub>2</sub>/O<sub>2</sub>



# N112 and BPSH35-1mil at 120°C and 50%RH



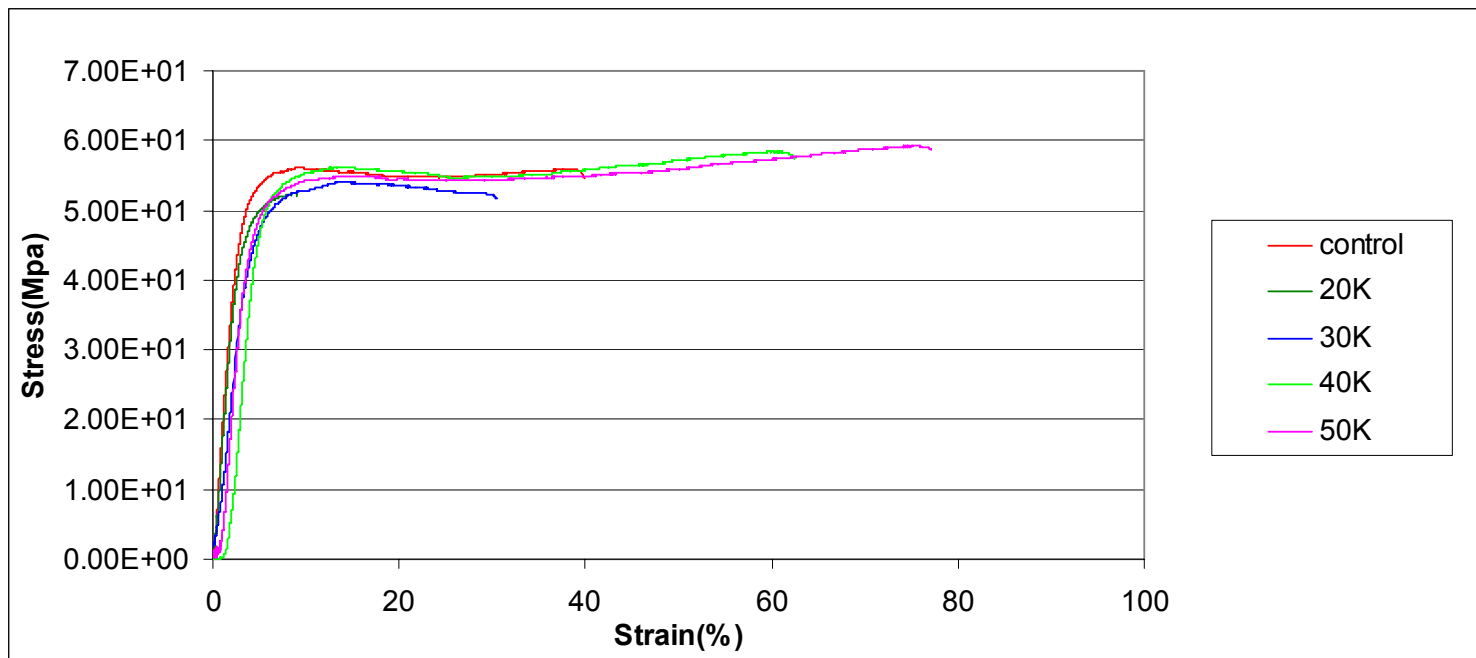
At cell temperature of 80°C: Anode bottle=105°C  
Cathode bottle=90°C

At cell temperatures of 100°C and 120°C: Anode bottle=100°  
Cathode bottle=100°C

# AGING STUDIES (no failures)

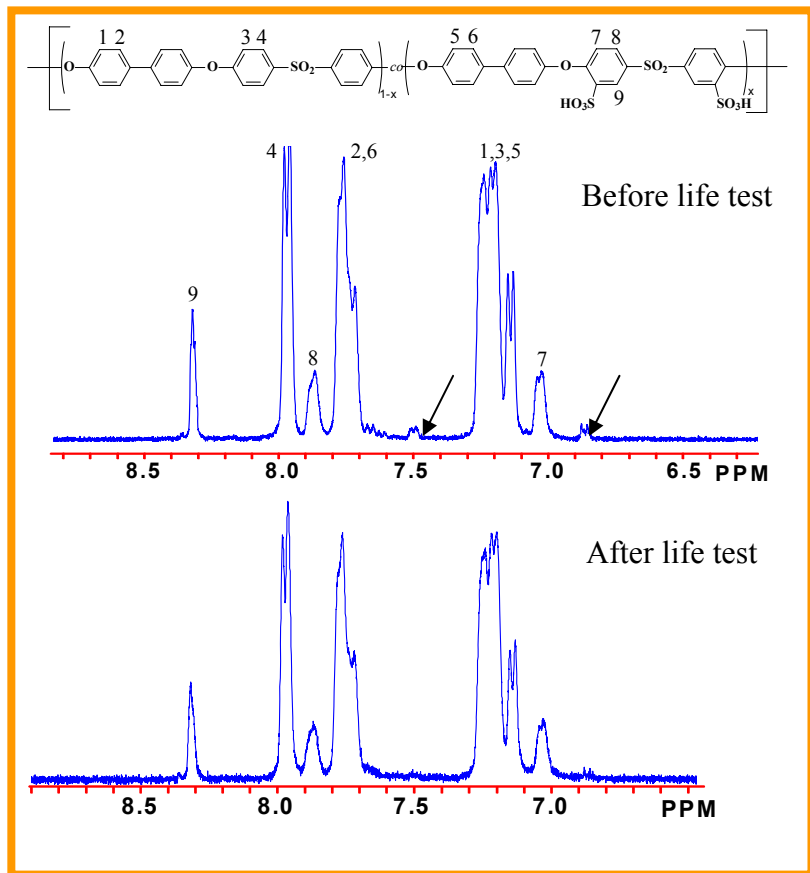
- Boiling water for 10,000 hours
- High pressure (2 atm) steam at 120°C for 1000 hours
- MEA H<sub>2</sub>/air fuel cell, 80°C, 1500 hours
- MEA, DMFC, 80°C, 3000 hours

# Comparisons of Stress-Strain Curves of BPSH35 Samples with Different Molecular Weights



The tensile testing was performed using a universal Instron machine at room temperature (23°C) and 40% R.H, with a crosshead displacement speed of 5mm/min.

# Chemical Composition, IEC, Molecular Weight, and Water Uptake are Not Changed After a 700 hr Fuel Cell Test at 80°C



Life test	Disulfonation by $^1\text{H}$ NMR (%)	IEC (meq/g)		IV (dL/g)	Water uptake (wt.%)
		Calc.	Experimental		
Before	36	1.5	1.4	0.7	34
after	34		1.4	0.8	37 (33) <sup>a</sup>

<sup>a</sup> after life test and recast

**No major chemical degradation of BPSH membrane was found**

**$^1\text{H}$  NMR spectroscopy of BPSH-35 before and after life test**

In cooperation with Dr. Y.S. Kim from LANL

# States of Absorbed Water in a Hydrophilic Polymer

At Least Three States of Water

1. **Non-freezable, tightly-bound water**

plasticises polymer – lowers  $T_g$

water that is strongly bound to sulfonic acid groups

2. **Freezable, loosely-bound water**

broad melting behavior from -20 to 20°C

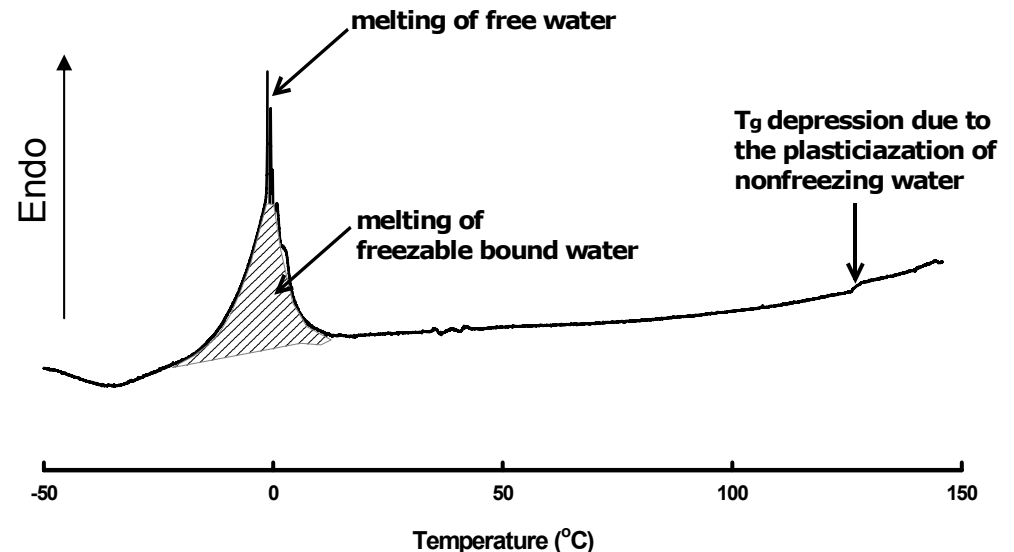
water that weakly bound to the polymer chain

3. **Free water**

sharp melting point at 0°C

water that has the same phase transitions as bulk water

DSC Thermogram



Nakamura, K.; Hatakeyama, T.; Hatakeyama, H. *Polymer* **1983**, 24, 871.

Kim, Y. S.; Dong, L.; Hickner, M. A.; Glass, T. E.; Webb, V.; McGrath, J. E. *Macromolecules* **2003**, 36(17), 6281<sup>19</sup>

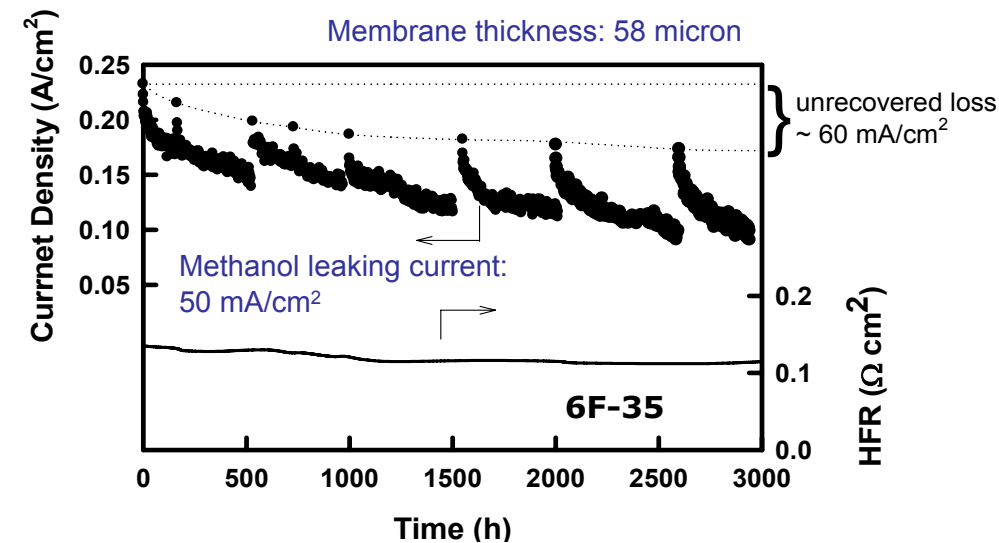
# Why We Are Interested in States of Water in PEM?

Previous studies and current research show

- Only the bound non freezing water causes the depression in glass transition temperature .
- Presence of free water facilitates the transport process .
- Methanol permeability and conductivity tends to depend on free water and loosely bound water.
- Electro-osmotic drag increases with increase in free water.
- Activation energy for proton transport and methanol transport decreases with increasing amounts of free water.
- Operation of fuel cells under freezing conditions is likely a function of the states of water in the membrane

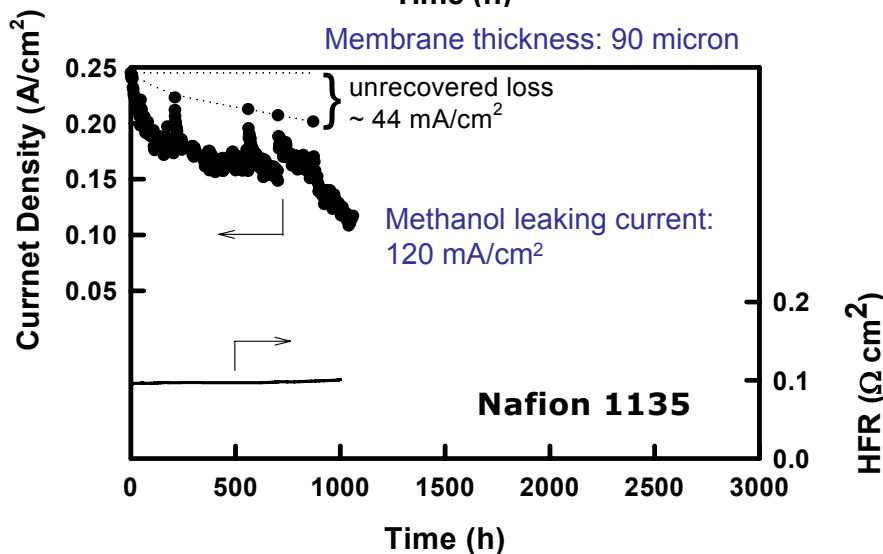


# Long-Term DMFC Performance Studies at LANL (Y.S. Kim) on Partially Fluorinated BPSH(6FSH-35) showed Excellent Stability for 3000 Hours @ 80°C for Portable Power

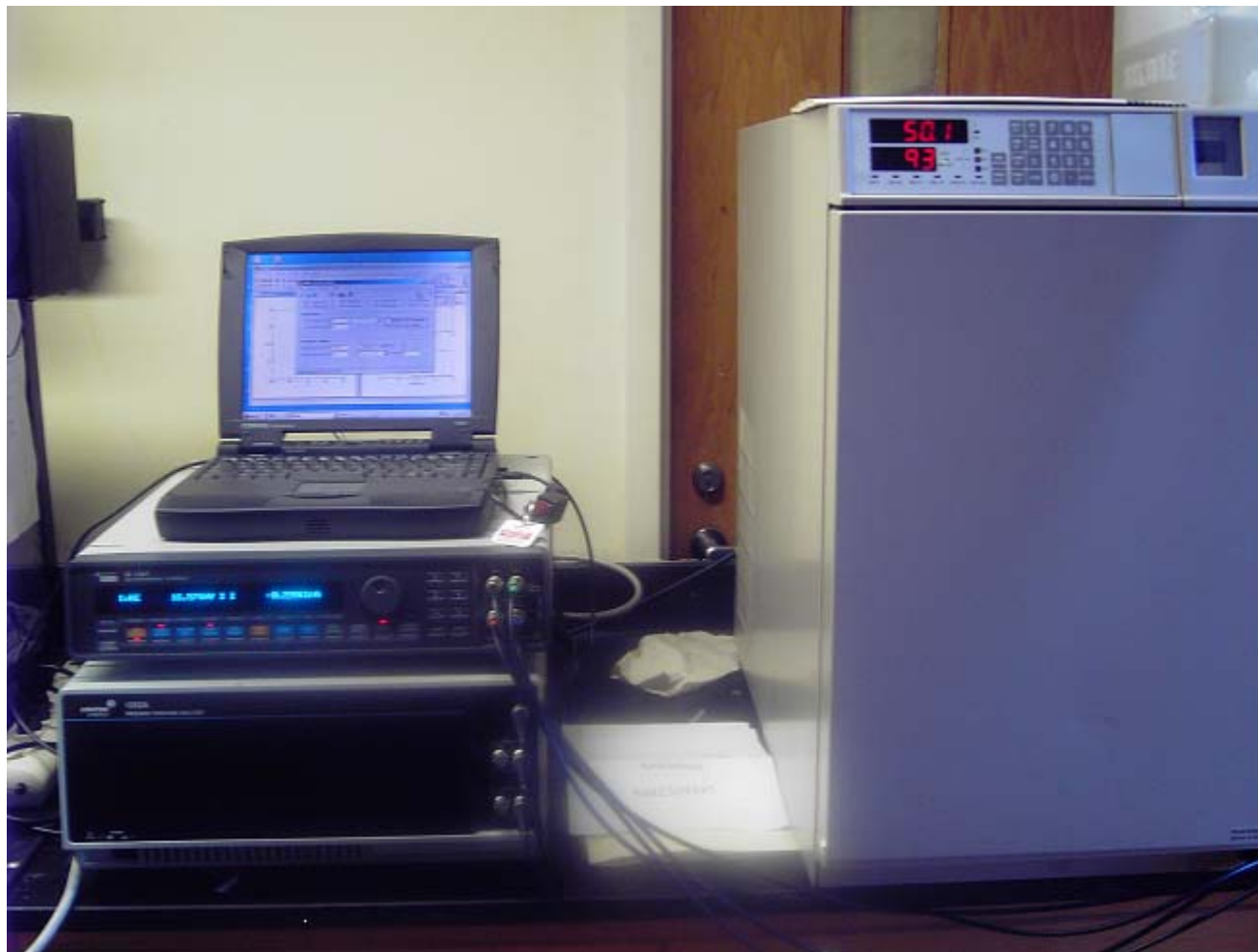


**Optimization of the membrane-electrode interface utilizing a partially fluorinated poly (arylene ether) membrane (6F-35) afforded stable long-term performance (3000 hours) with cell resistance that actually decreased under DMFC conditions.**

**Performance loss after 3000 h of the life test for 6F-35 was only  $60 \text{ mA}/\text{cm}^2$  and the methanol leaking current was reduced more than 50%.**



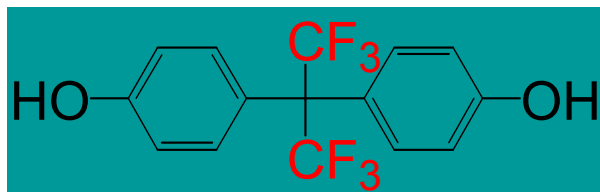
# In situ Determination of Proton conductivity as a Function of RH and Temperature Using ESPEC Humidity Oven and Solartron Impedance Analyzer



Membrane  
conditioning

80°C, 20%RH  
for 16 hr

# Strategy to Achieve the Goal



## Synthesized Copolymers

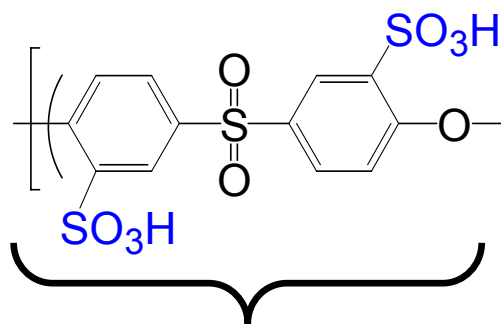
PAEB35 : 35 mol % disulfonation

6F25CN35 : 25 mol % 6F+ 75 mol % BP

6F50CN35 : 50 mol % 6F+ 50 mol % BP

6F75CN35 : 75 mol % 6F+ 25 mol % BP

6F100CN35 : 100 mol % 6F



Controlled  
Amount of  
Fluorinated and  
Non-Fluorinated  
Monomer

Controlled  
Amount of  
Fluorinated and  
Non-Fluorinated  
Monomer

Fixed at 35 or 45 mol  
percent



Copolymer PAEB-XX*	IV** (dL/g)
PAEB35	1.2
6F25CN35	1.1
6F50CN35	1.2
6F75CN35	1.5
6F100CN35	1.4

\*XX: Target Degree of Disulfonation

\*\*IV measurements were done using  
0.05 M LiBr

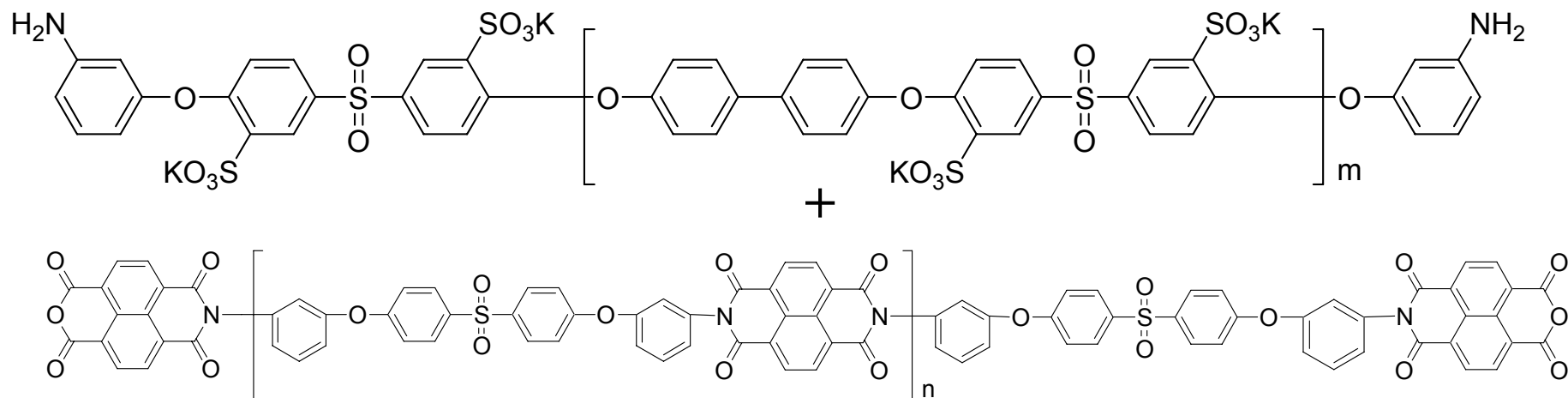
# Multiblock Copolymers with Hydrophilic-Hydrophobic Blocks



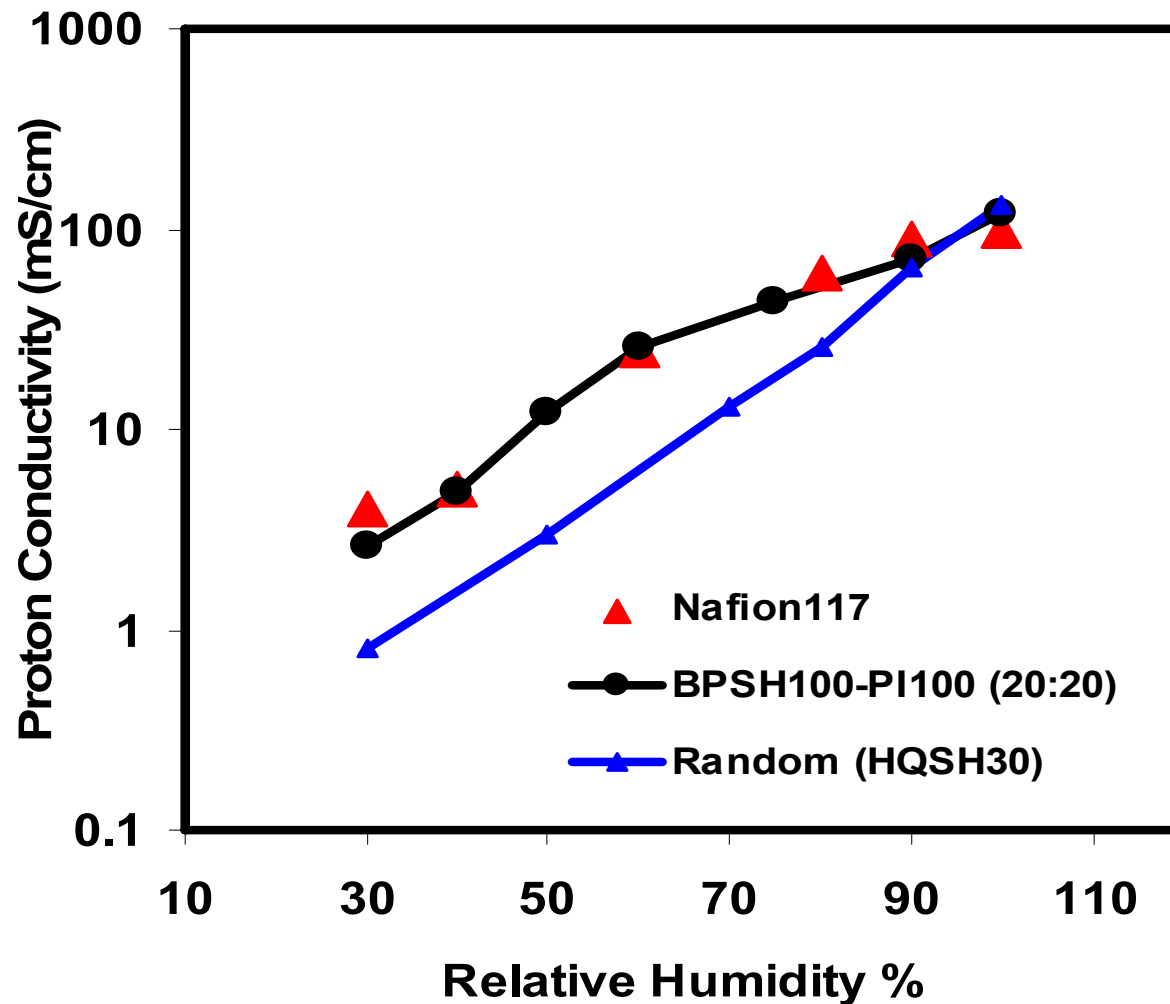
- Micro phase-separated morphology can be precisely controlled by synthesis
- Enhanced mechanical strength, water uptake, and proton conductivity are expected

An Example of an Ideal Cocontinuous Film Morphology in Block Copolymers

# Synthesis of High MW Multiblock Copolymers Employing Mixed Solvent Systems



# Why We Are Interested in Block Copolymers as PEMs?

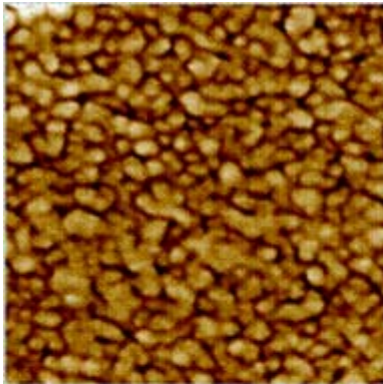


Measured at 80°C



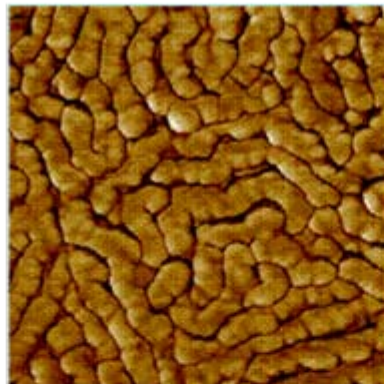
# AFM Images of Multiblock Copolymers

100 nm



BPSH 5 – PI 5

100 nm



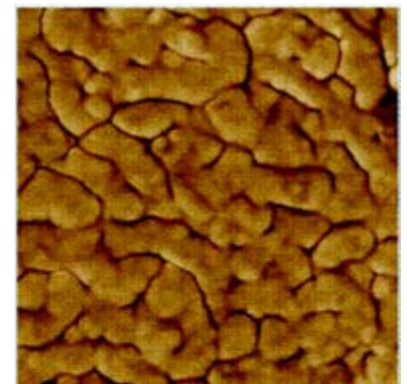
BPSH 10 – PI 10

100 nm



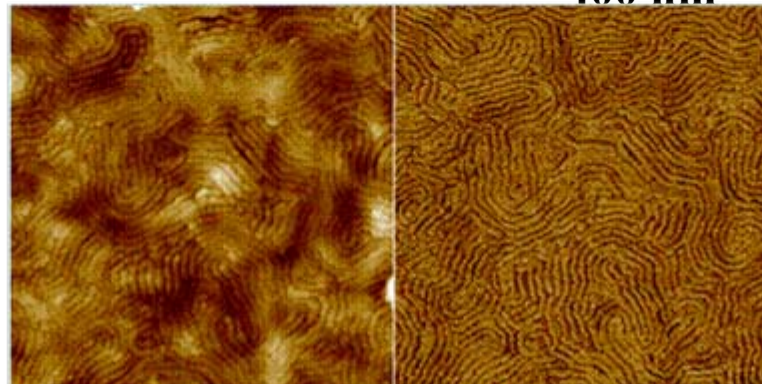
BPSH 15 – PI 15

100 nm



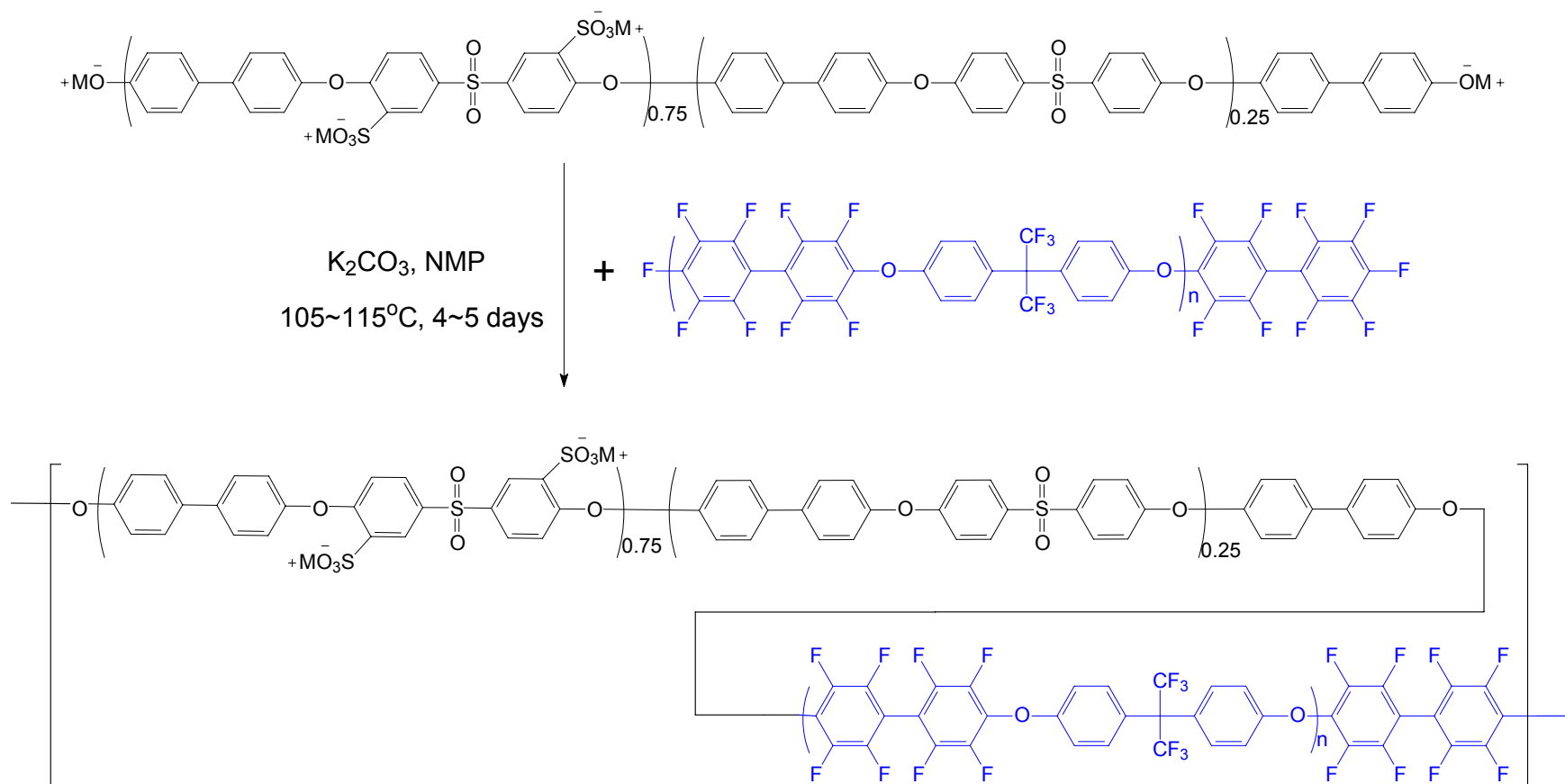
BPSH 20 – PI 20

400 nm

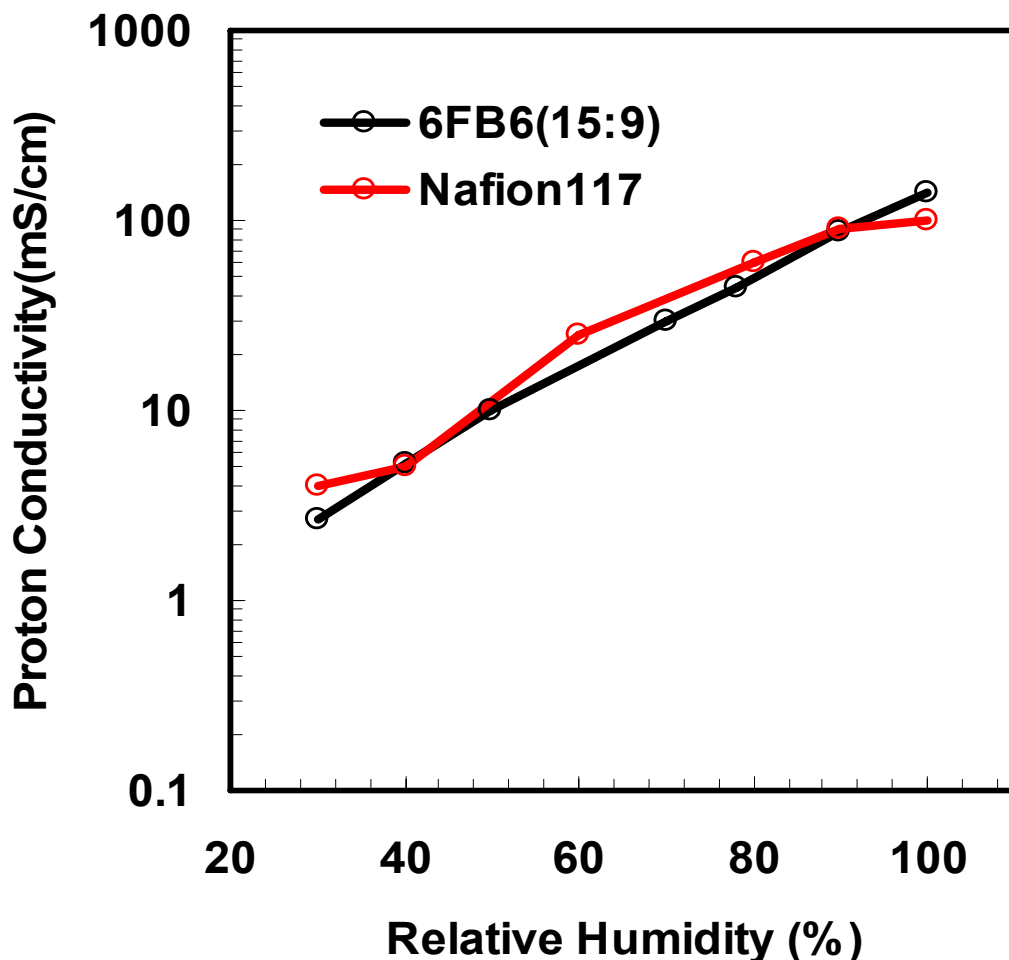


BPSH 15 – PI 15

# Multiblock Perfluorinated Hydrophobic-Hydrophilic Copolymer Synthesis



# Proton Conductivity vs. RH for 6FB6, a 15,000-9,000 gm/mole Multiblock Copolymer

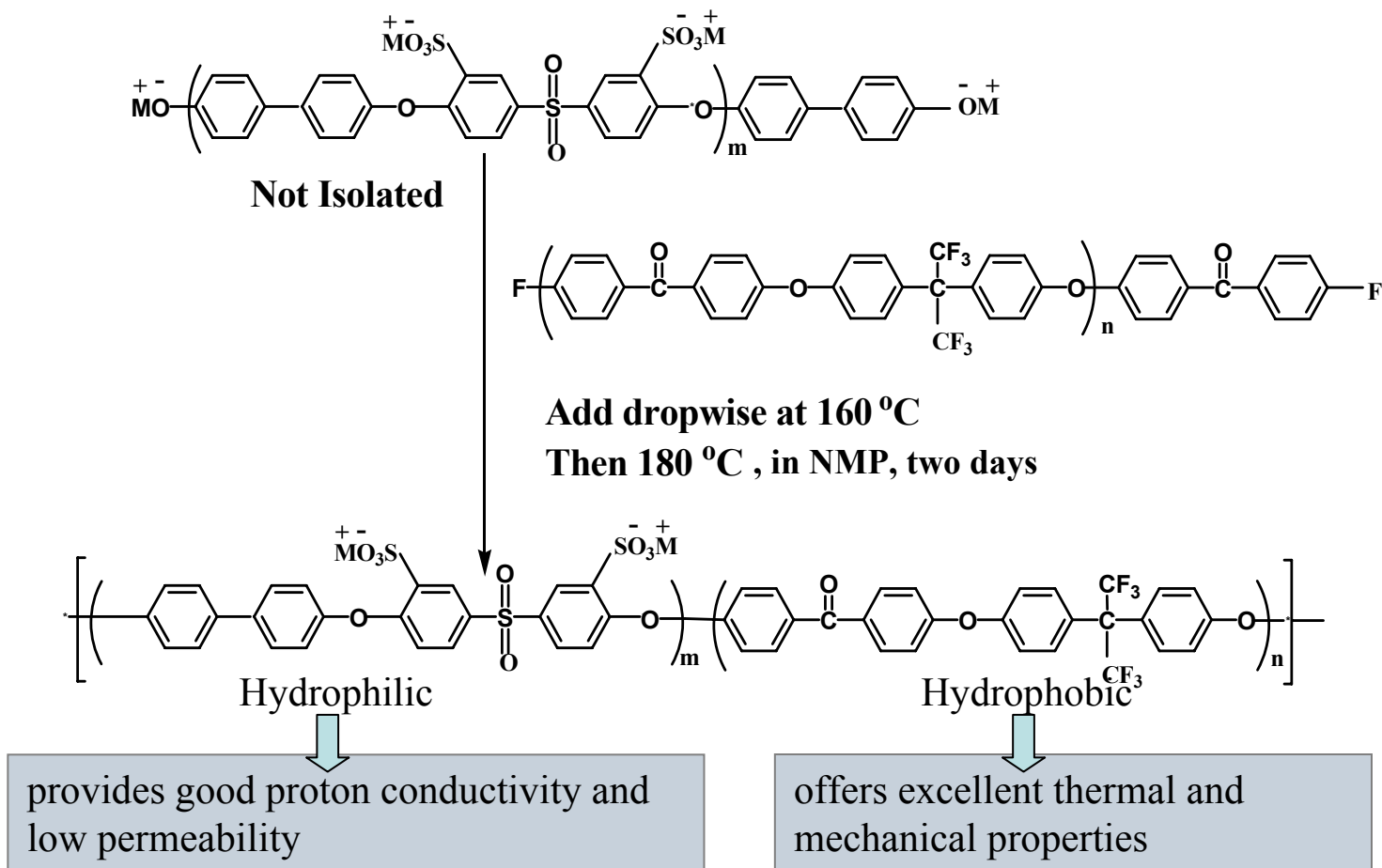


Target IEC: 1.25

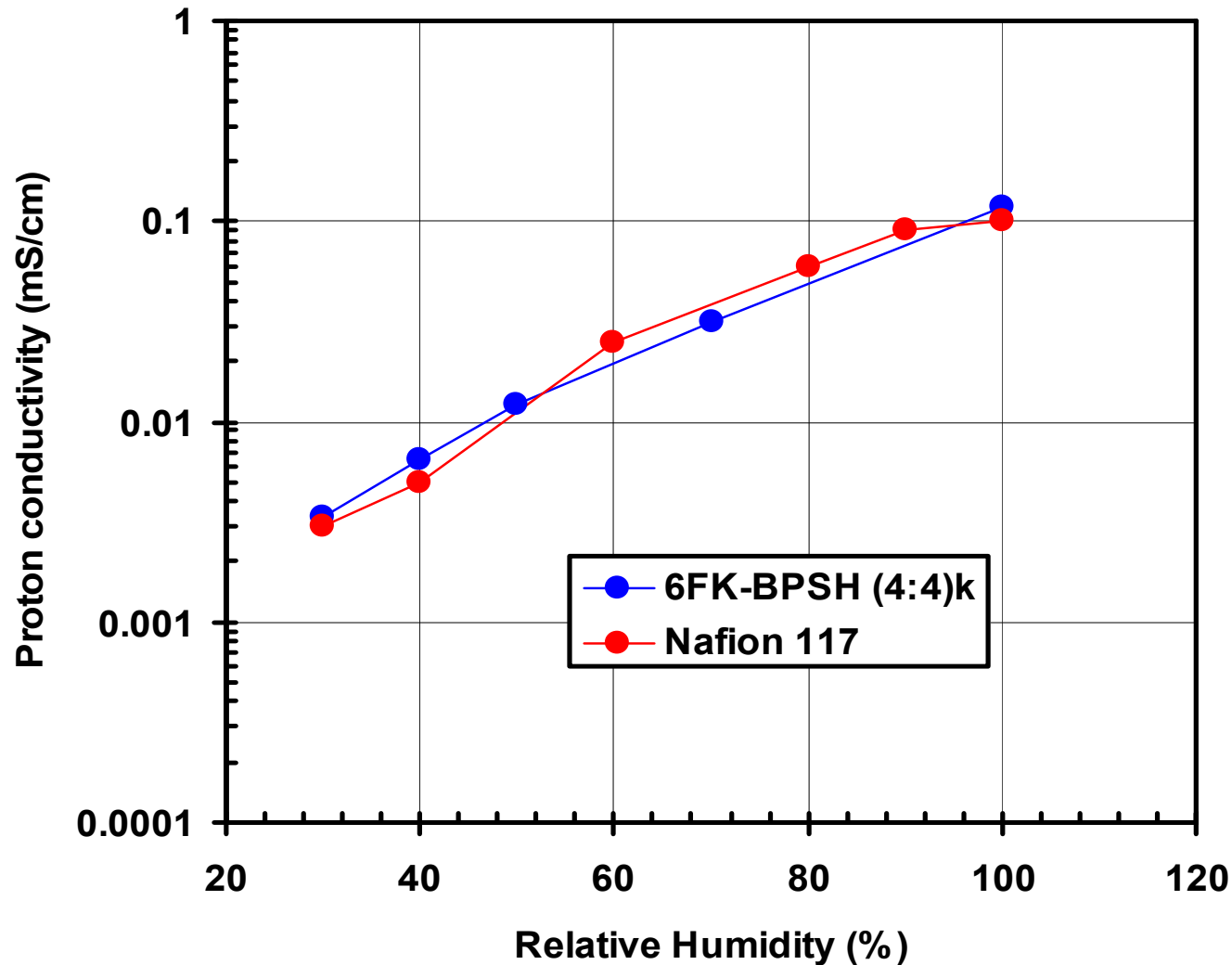
Water uptake: 42%

Proton conductivity in liquid water: 0.09 S/cm

# Synthesis of 6FK-BPSH Multiblock Copolymers

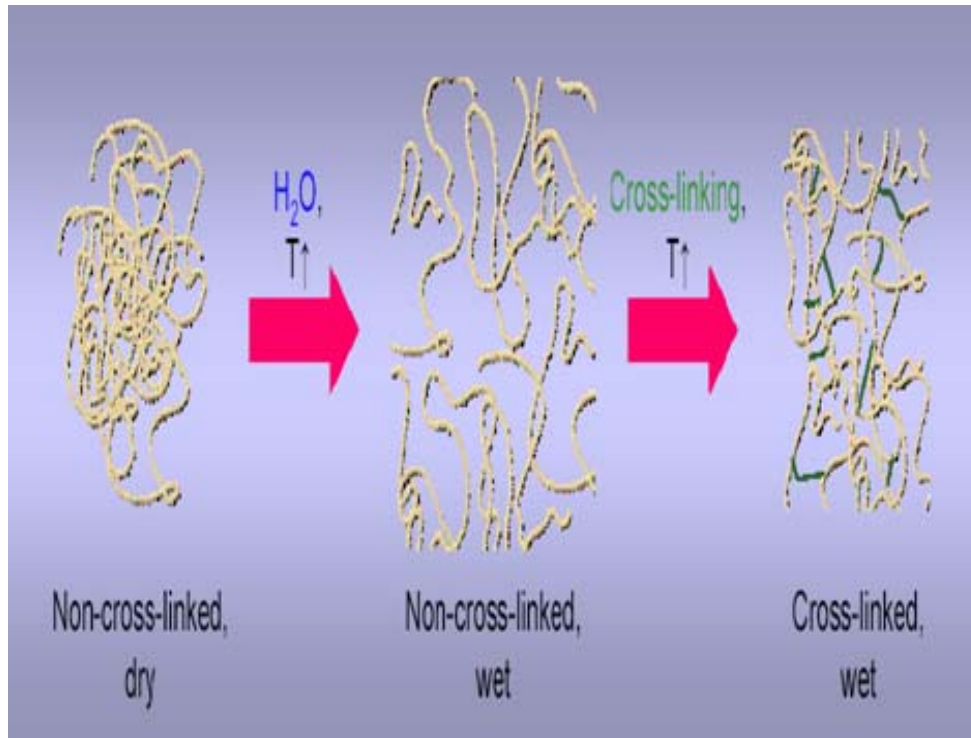


# Comparison of Conductivity vs. RH for 6FK-BPSH Multiblock(4:4)K and Nafion 117



80 °C

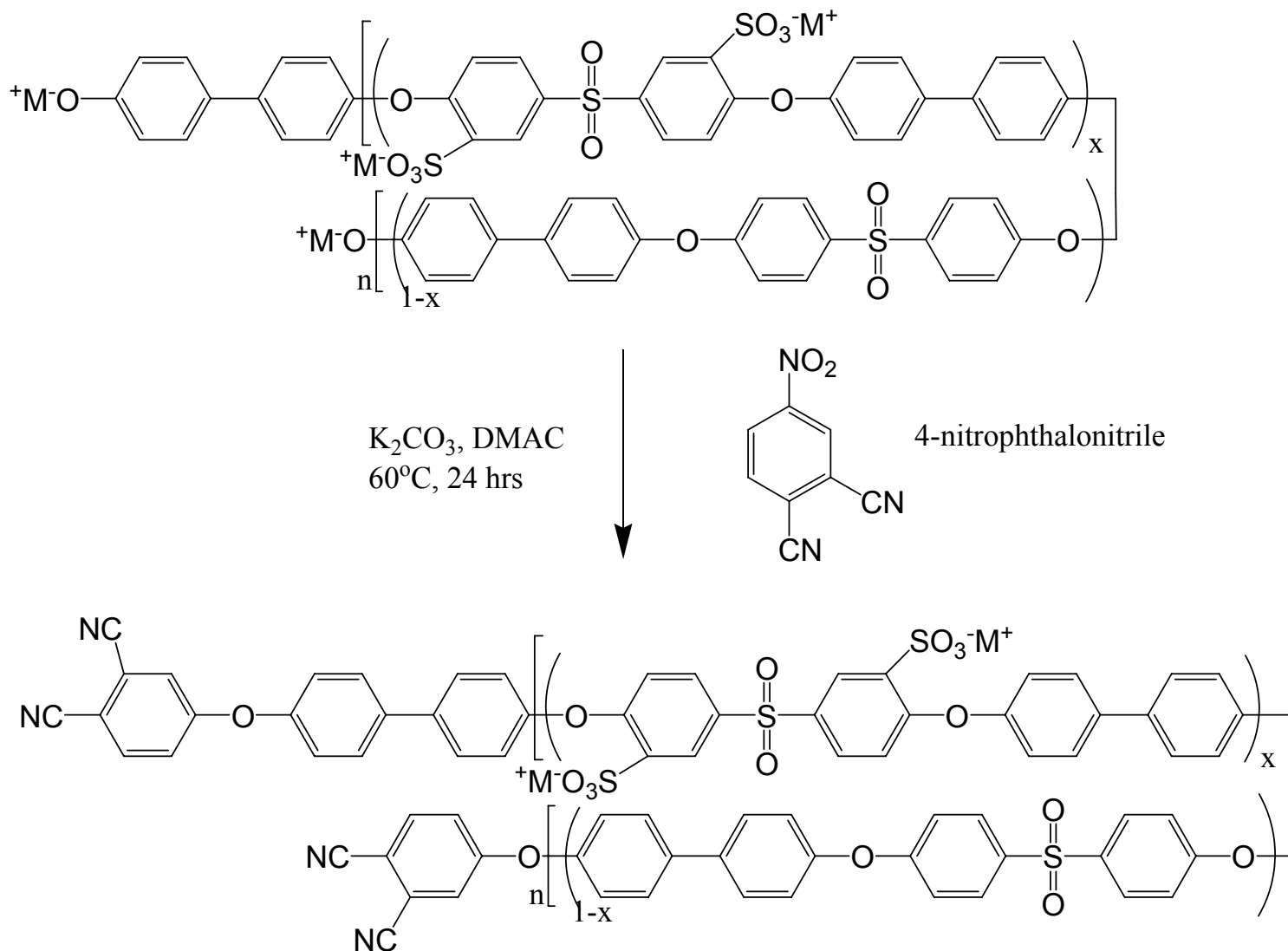
# Why We Are Interested in Crosslinked PEMs ?



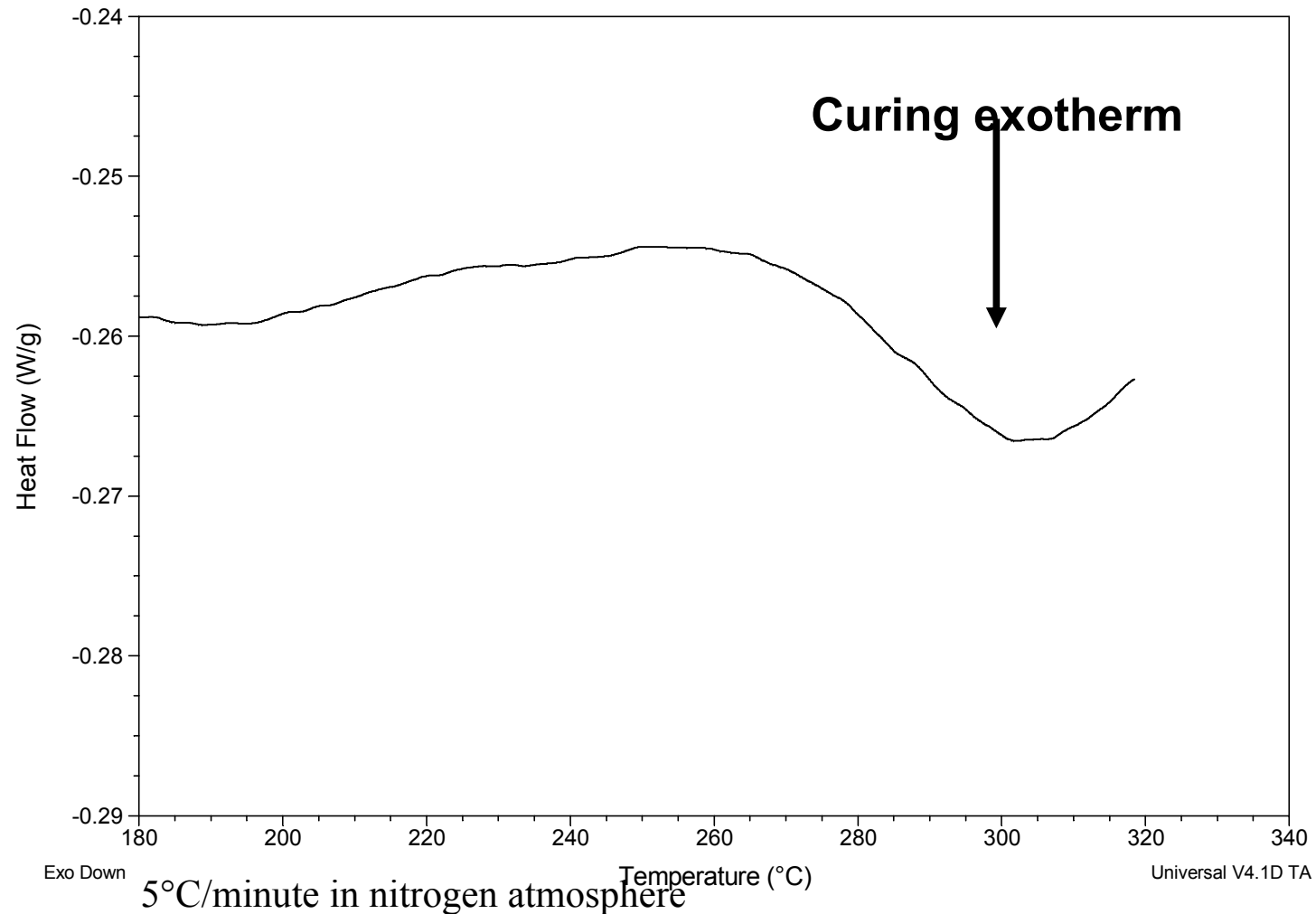
- Proton conductivity increases with increase in IEC or degree of disulfonation .
- But water uptake also increases at the same time causing the membrane to lose its dimensional stability .
- Introduction of crosslink within the membrane may reduce water uptake without losing conductivity . <sup>32</sup>



# Synthesis Route of 4-Phthalonitrile Containing BPS60-15k Copolymer



# DSC Thermogram of a Phth-BPS-60 Film Shows Curing Exotherm Starting from 300°C



# Film Casting of BPSH Polymers



*BPSH-35 Films*

# CONCLUSIONS

- Hydrogen/air PEMFC's based on alternative membranes have good mechanical properties and the potential to provide satisfactory fuel cell performance below 100°C.
  - Conductivity at 120°C and low RH is challenging and may require long sequenced block copolymers to generate co-continuous hydrophilic-hydrophobic morphologies and/or organic-inorganic composite systems.
  - Membrane MW is a critical parameter defining PEM durability.
- Tailored membrane/electrode interfaces are important with Nafion electrodes.