

# **Non-Nafion Membrane Electrode Assemblies**

**Yu Seung Kim (Point of Contact)  
Ana Siu  
Bryan Pivovar**

Los Alamos National Laboratory  
Institute for Hydrogen and Fuel Cell Research

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This presentation does not contain any proprietary or confidential information

# Overview

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## **FY '05 Milestones (Project ongoing since FY '03)**

- Dec 04: Quantify interfacial impact on fuel cell performance.  
*Status: Complete*
- Mar 05: Examine impact of performance degradation in non-Nafion MEA.  
*Status: Complete*
- Sep 05: Explore MEA operating window dependence on architecture.  
*Status: 30 % complete*

## **Barriers Addressed**

- A. Durability
- B. Cost
- C. Electrode Performance
- D. Thermal, Air, and Water Management
- J. Startup Time/ Transient Operation

## **Total Project Funding**

- Funding in FY04: \$350 K
- Funding for FY05: \$350 K
- Non-cost sharing

## **Collaborators**

- Virginia Polytech and State Univ  
(Prof. James McGrath)
- Simon Fraser Univ.  
(Prof. Steven Holdcroft)

# Objectives

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- **To assist the DOE Hydrogen, Fuel Cells & Infrastructure Technologies (HFCIT) Program by performing the enabling science that will produce high performance membrane-electrode assemblies out of alternative polymeric electrolytes.**
- **To develop a low cost, high performance and durable alternative membrane:**
  - Investigate effect of membrane-electrode interface
  - Design interface optimized non-Nafion MEAs
  - Evaluate fuel cell performance
- **To develop non-Nafion membrane electrode assembly (MEA):**
  - Evaluate non-Nafion electrode performance
  - Optimize MEA structure for high temperature and/or low humidity operations

# Technical Approach

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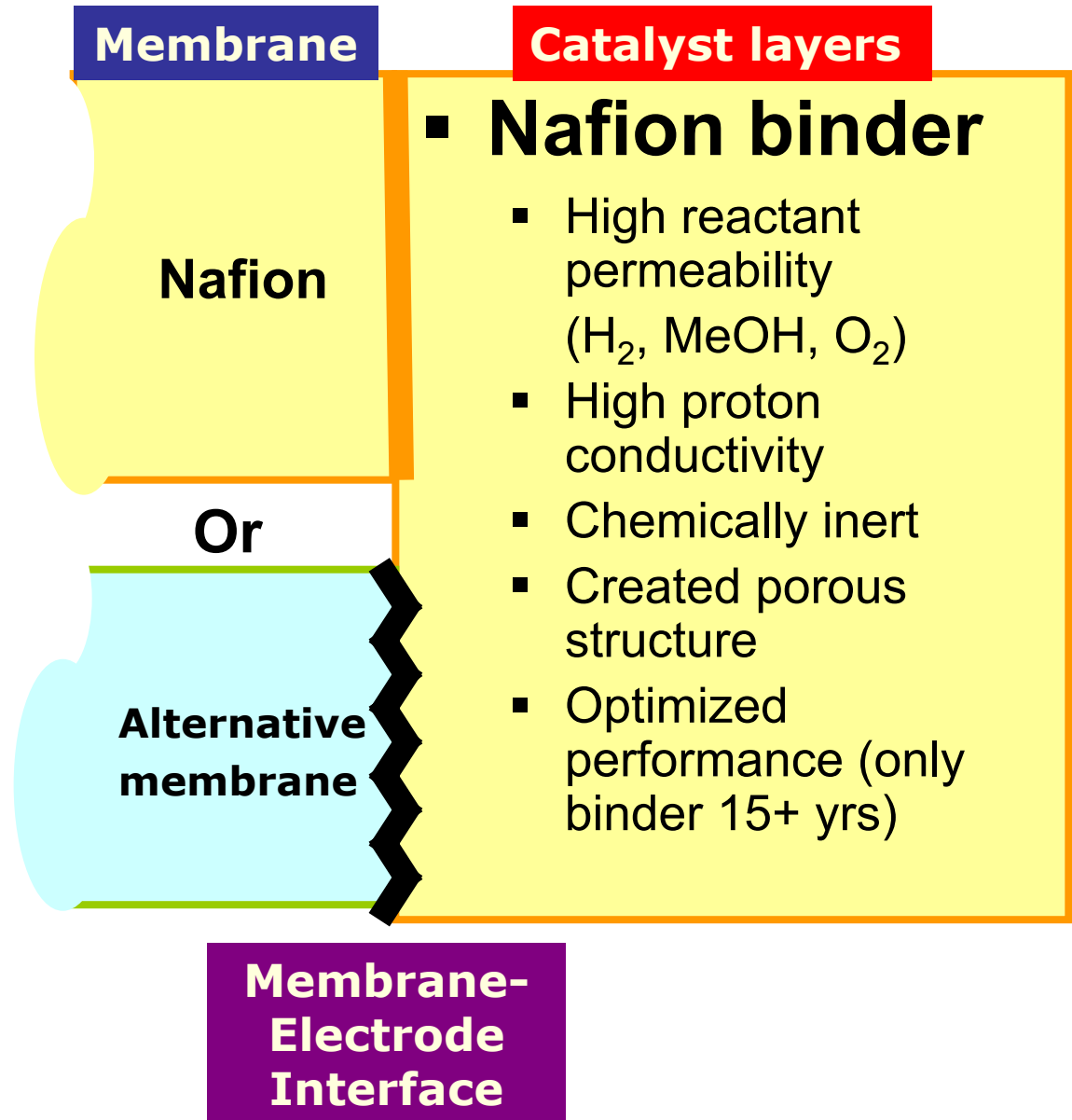
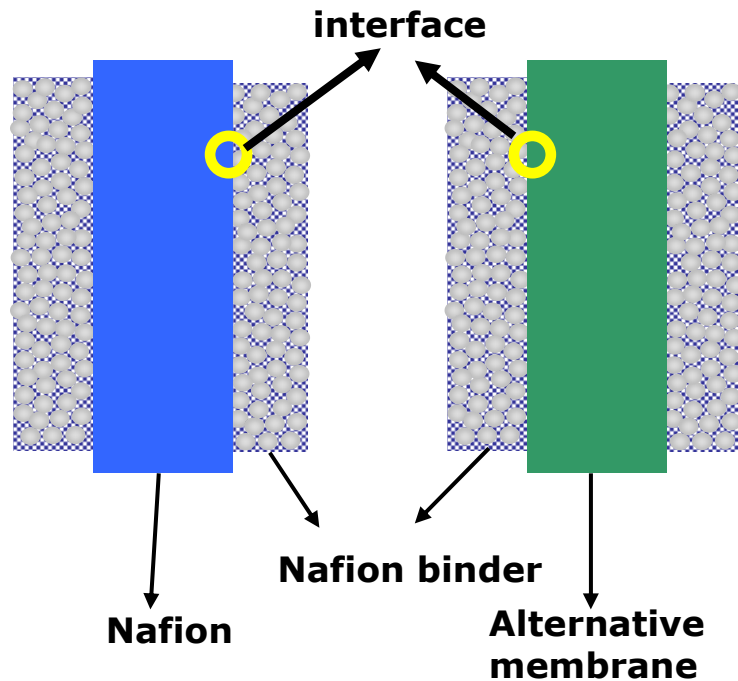
## ***Alternative Polymer Electrolyte Membranes***

- Measure the interfacial resistance between non-Nafion membrane and Nafion-bonded electrodes
- Identify the impact of interfacial incompatibility and origin of interfacial resistance
- Design novel polymer electrolyte having improved interfacial compatibility
- Compare the initial and long-term fuel cell performance of the optimized membrane with Nafion control

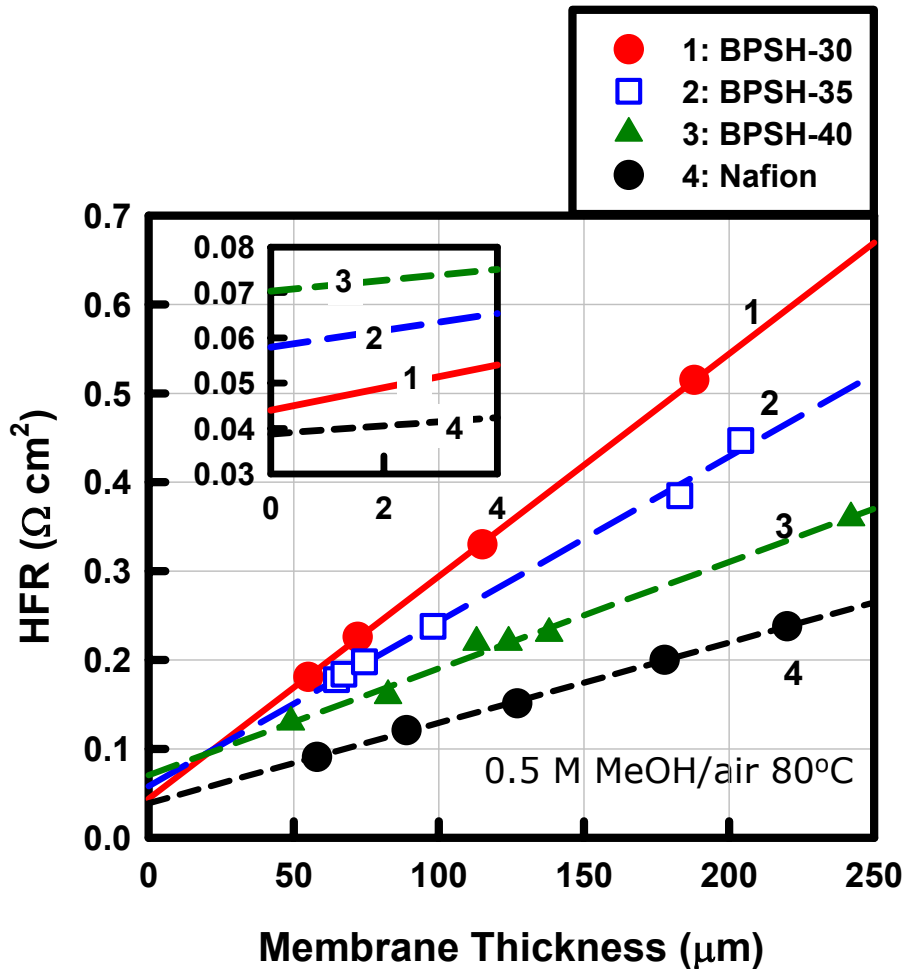
## ***Alternative Polymer Electrodes***

- Optimize catalyst/ionomer composition using alternative polymer binder
- Develop MEAs that tolerate excursions to 120°C and/or operate at RH 25-50%

# Nafion™ Advantages within the Electrodes



# Effect of Degree of Sulfonation of BPSH\* on Interfacial Resistance



Conductivity<sup>a</sup>,  $\sigma$ ,  
Interfacial Resistance,  $R_{interface}$

| Membrane | $\sigma$<br>(mS/cm) | $R_{interface}$<br>(mΩ·cm <sup>2</sup> ) |
|----------|---------------------|--|
| BPSH-30  | 39                  | 16                                       |
| BPSH-35  | 54                  | 30                                       |
| BPSH-40  | 78                  | 42                                       |
| Nafion   | 111                 | 7  |

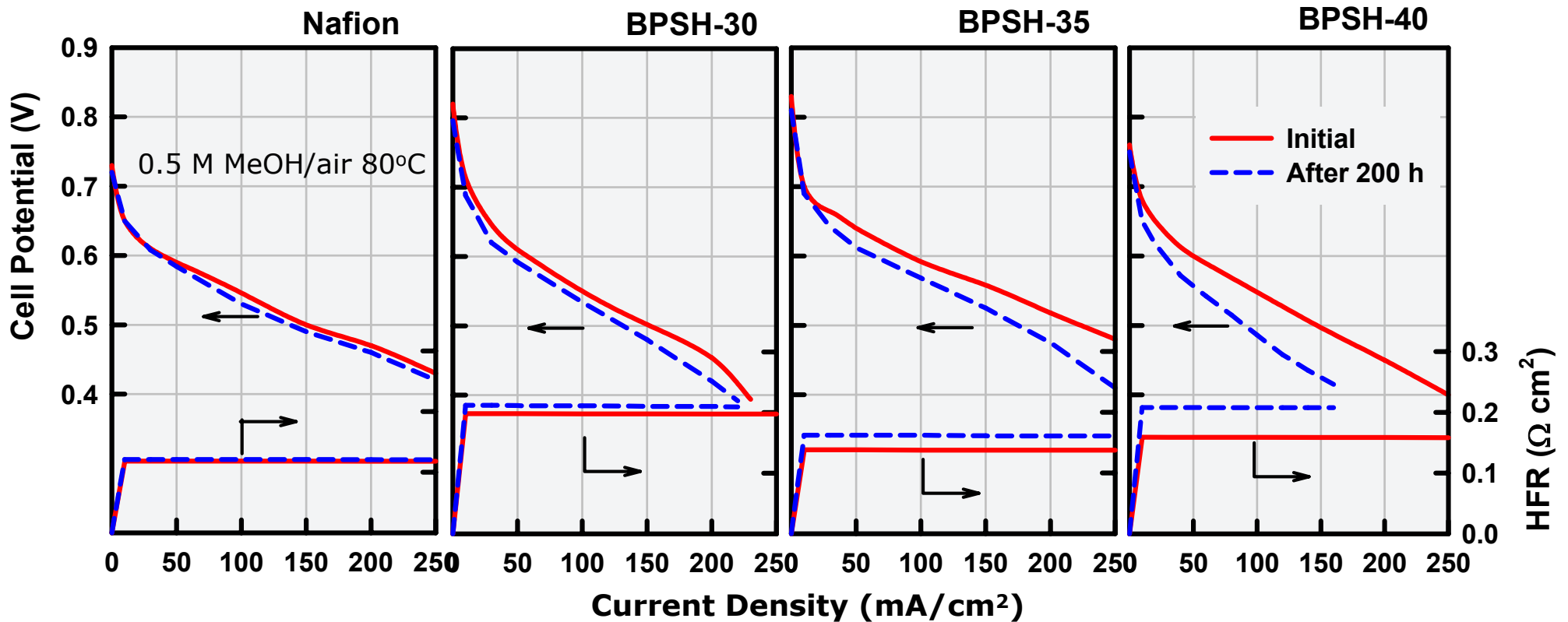
<sup>a</sup> 2005 technical target: 70 mS/cm

$$HFR = R_{non-mem} + R_{mem}(x)$$

$$R_{non-mem} = R_{elec} + R_{int}$$

**Non-Nafion membranes showed relatively greater interfacial resistance than Nafion**

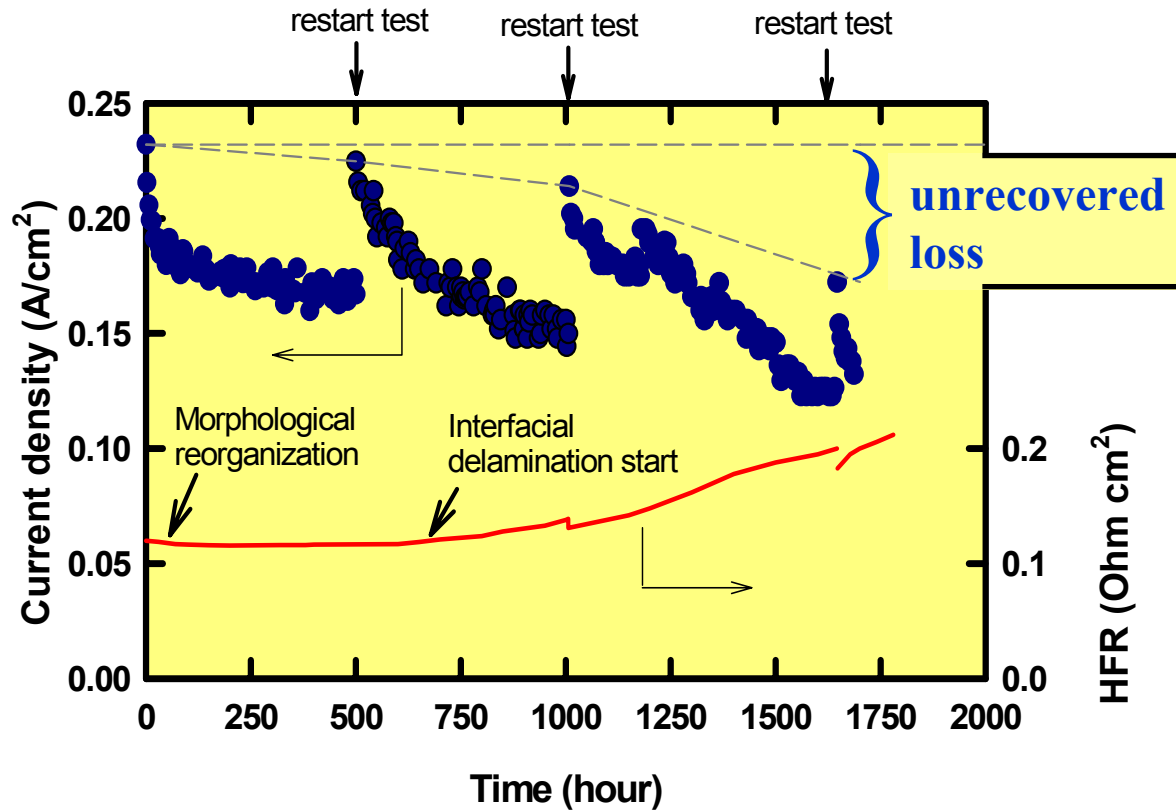
# Influence of Interfacial Compatibility on Long-Term Performance



**7                      16                      30                      42**  
**Initial Interfacial resistances (mΩ cm<sup>2</sup>)**

Performance degradation increases with increasing initial interfacial resistances.

# Importance of Interfacial Compatibility on Long-Term Performance



Non-optimized interface between alternative membrane and electrode (left figure) results in significant unrecovered performance loss during life test.

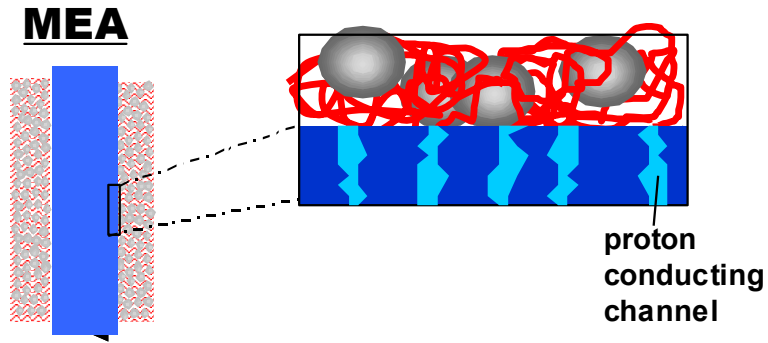
Interfacial delamination is reflected by the HFR increase.

\* test was performed under DMFC conditions

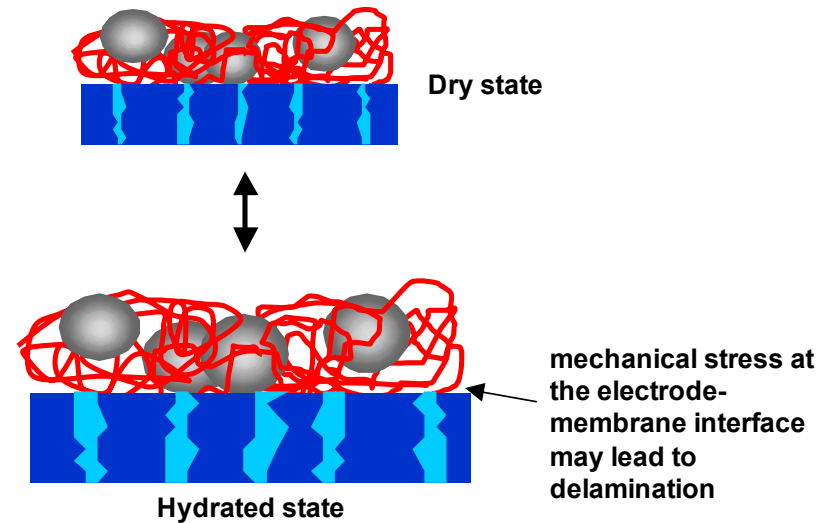
Life test of an alternative MEA at 0.5 V



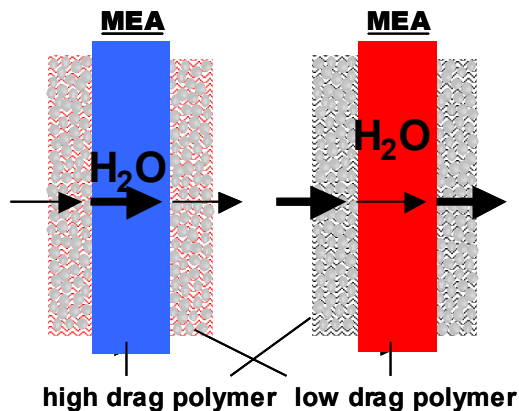
# Possible Interfacial Failure Mechanisms



Wetting – Adhesion and conductivity  
Adhesion – Performance and lifetime



Swelling – stresses affects performance and lifetime

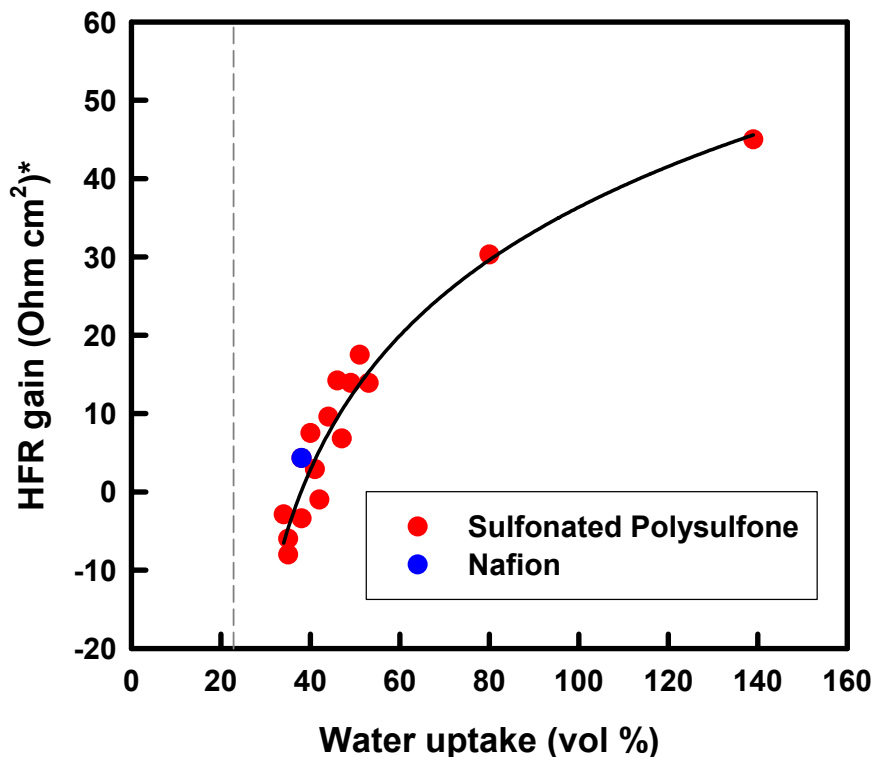


Electro-osmotic drag – stresses affects performance and lifetime

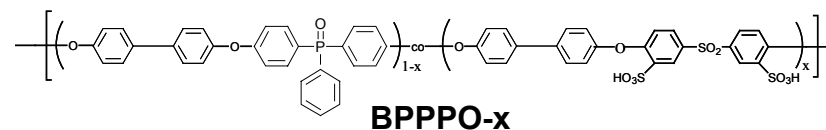
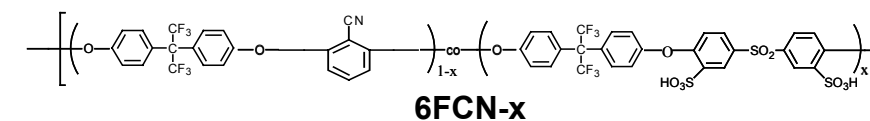
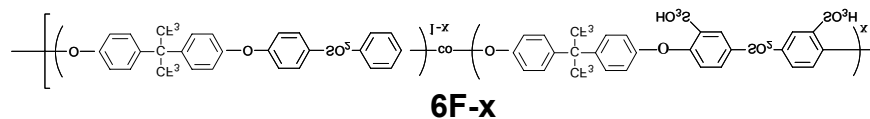
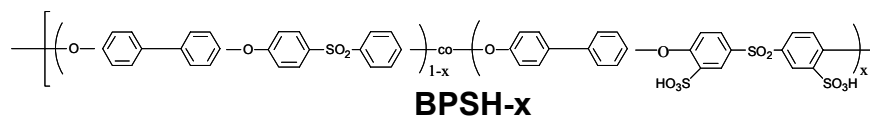
Wetting and adhesion, swelling, and electro-osmotic drag can all contribute to interfacial resistances.

# Major Attribute for Interfacial Delamination – Membrane Swelling

Correlation between membrane water uptake and HFR gain after 100 h life test



## Chemical structural modifications

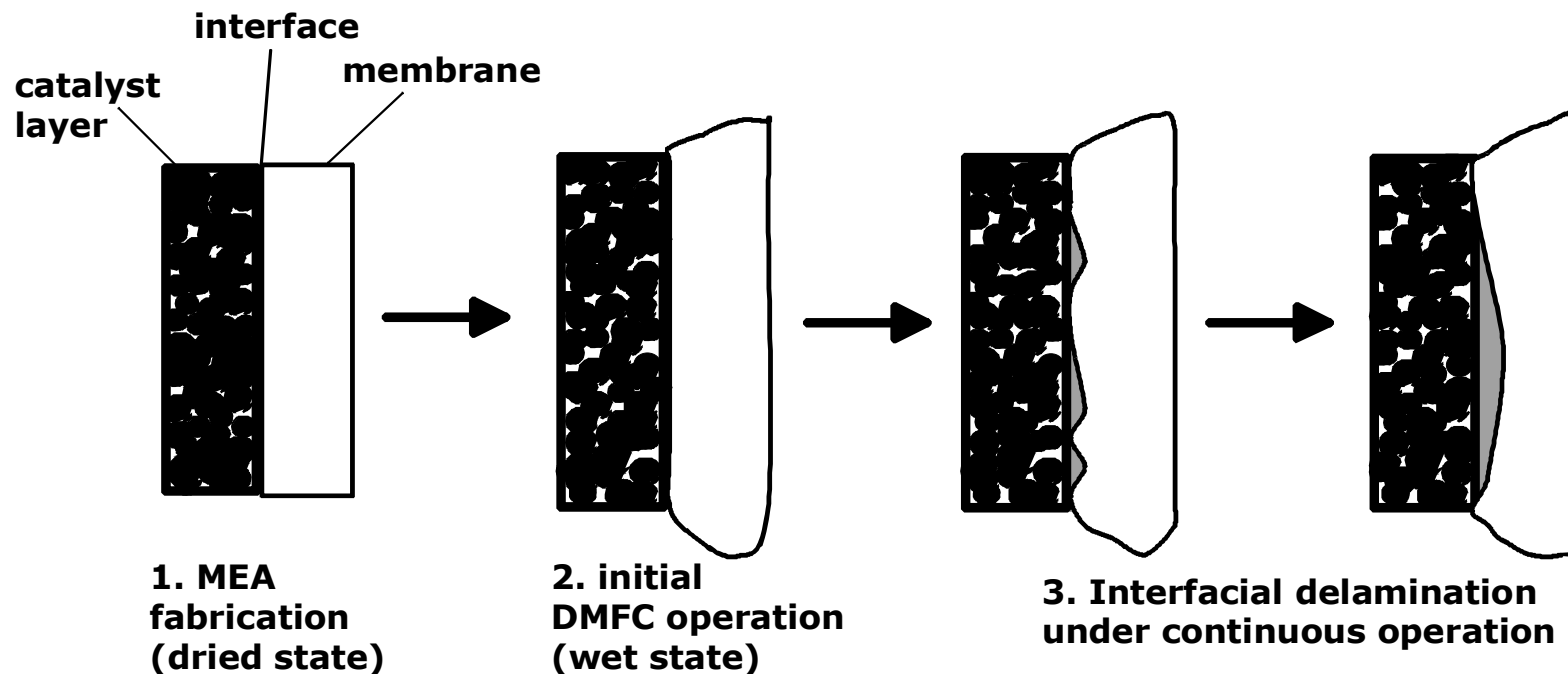


x denotes degree of disulfonation

High frequency resistance (HFR) gain shows a strong correlation with volume change by membrane. By tuning polymer chemistry in terms of sulfonation level and composition, we could reduce membrane water uptake.

**Swelling appears to be key mechanism!!**

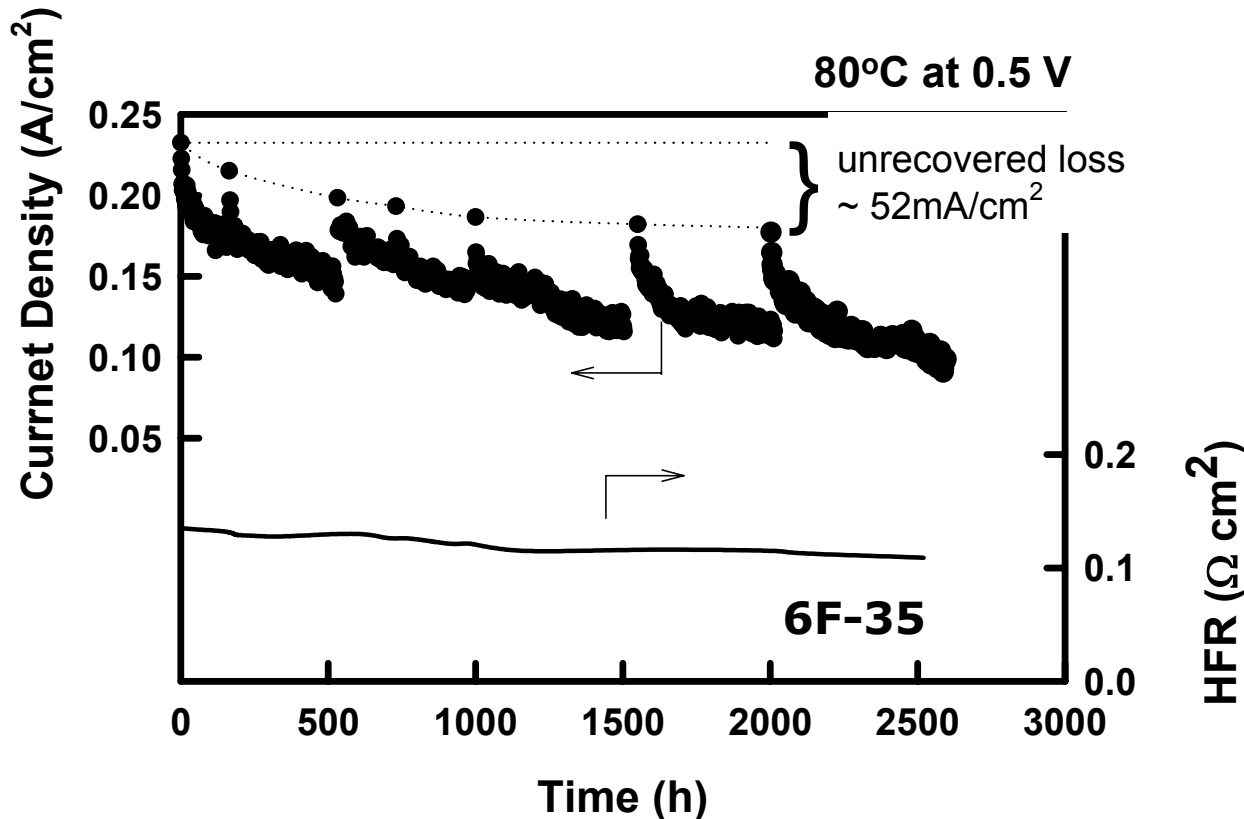
# Proposed interfacial delamination during life test



Interfacial delamination is probably due to the dimensional change from dried condition (state 1) to hydration (state 2).

Interfacial delamination processes seem to proceed under continuous operation of fuel cells (state 3).

# Long-Term Performance of Interface Optimized Alternative Membrane



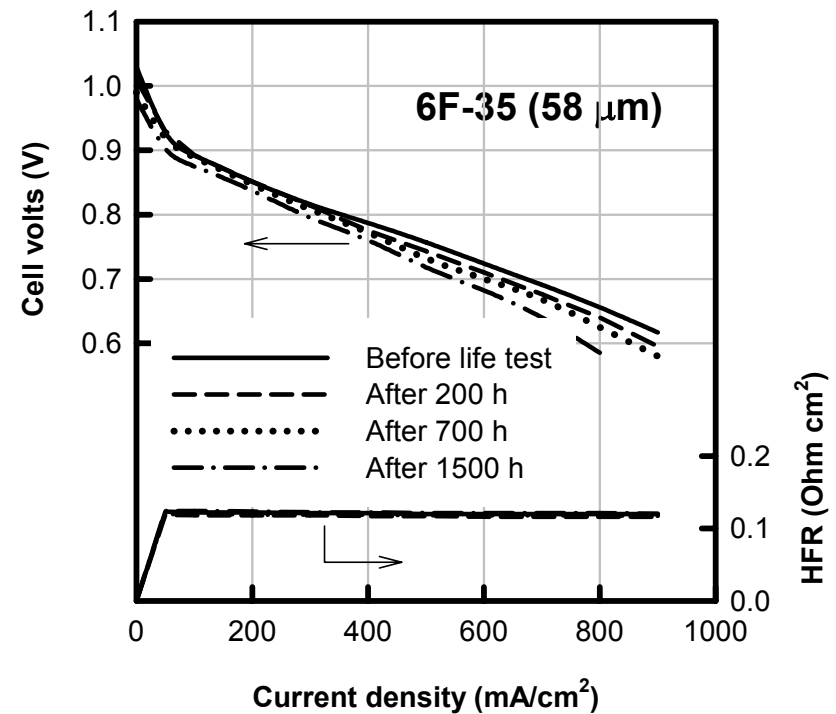
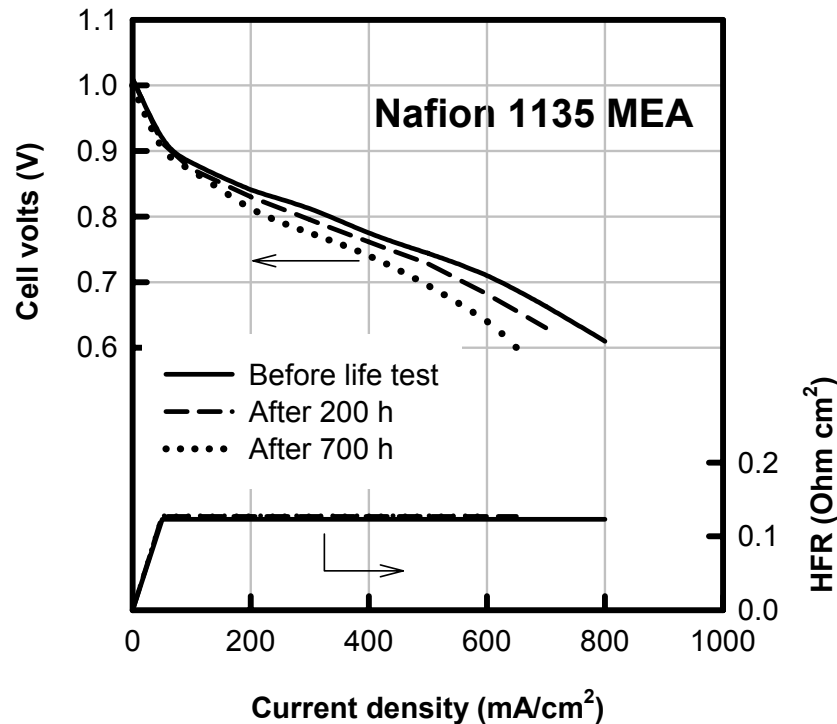
Interface optimized non-Nafion membrane (6F-35) exhibited stable long-term performance\* with decreasing cell resistance under DMFC conditions

Performance loss after 2000 h life test for 6F-35 was 52 mA/cm<sup>2</sup> (22.4% loss), which was comparable to that of state of the art Nafion MEA.

*\*2005 technical target for MEA durability  
10% loss after 2000 h at < 80°C under  
H<sub>2</sub>/air conditions*

**Life test under H<sub>2</sub>/air conditions is on going!**

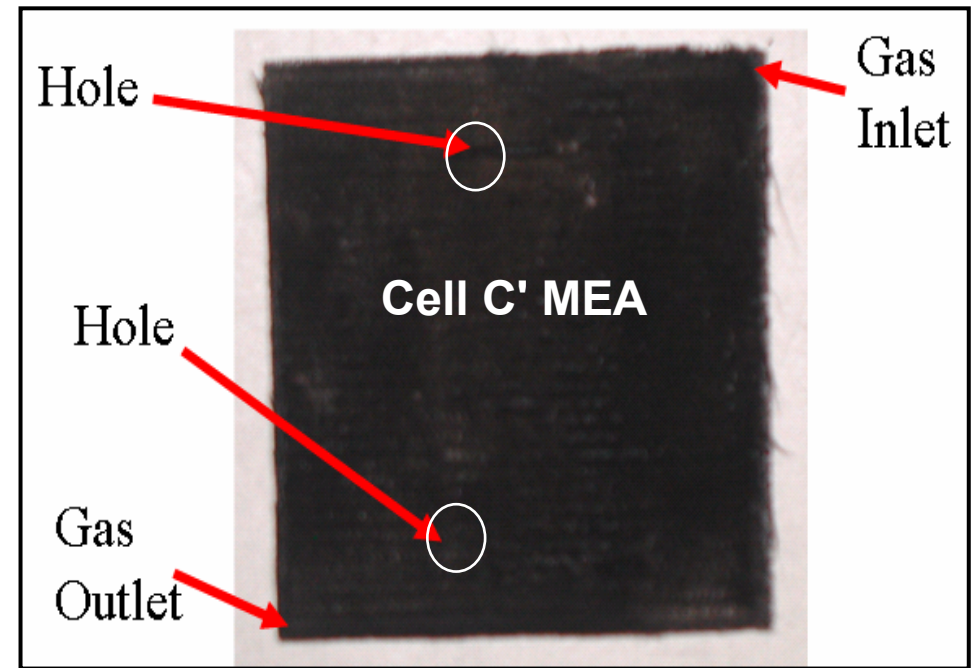
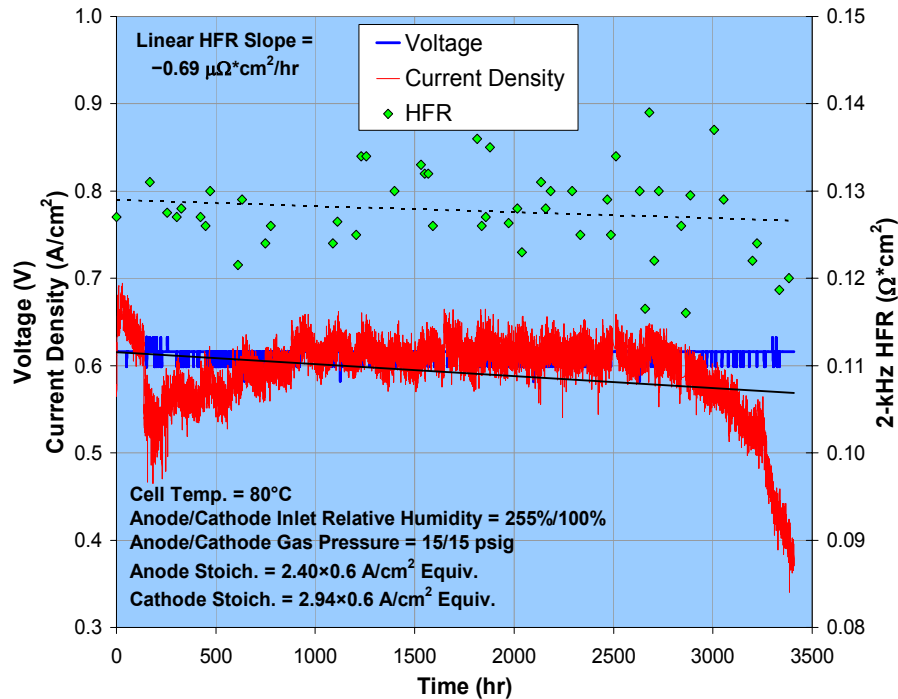
# H<sub>2</sub>/Air Performance Comparison after DMFC Life Test



H<sub>2</sub>/air, high stoic.  
 Pt-Ru 8 mg/cm<sup>2</sup> anode  
 Pt 6 mg/cm<sup>2</sup> cathode  
 T = 80°C, P back = 20 psig

- Performance loss of the 6F-35 membrane after DMFC life test was comparable with Nafion control.

# Catastrophic Failure of Nafion\*



\* R. Borup et. al, LANL data presented at 2004 OHFCIT Review

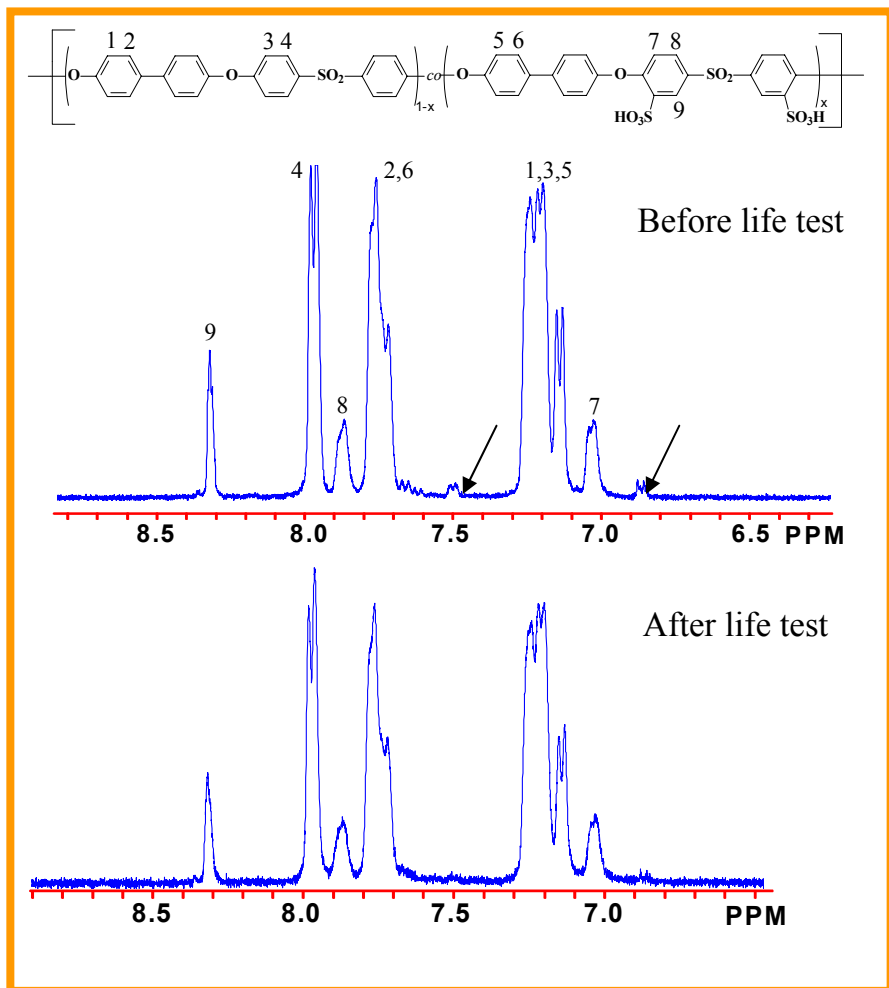
**Membrane pinhole formation leads to catastrophic failure and may be due to polymer creep.**

**Alternative membranes have higher  $T_g$  and may resist pinhole formation (catastrophic failure testing using alternative membranes is under way).**

| <i>copolymer</i> | $T_{g \text{ dry}} (^{\circ}\text{C})$ | $T_{g \text{ hydrated}} (^{\circ}\text{C})$ |
|------------------|--|---|
| BPSH-30          | 257                                    | 136   |
| BPSH-40          | 267                                    | 126   |
| BPSH-50          | 272                                    | 98  |
| Nafion           | 160                                    | 99  |

Tgs were obtained from DSC experiments.

# Is there Chemical Degradation for the Alternative Membranes?



| Life test <sup>a</sup> | Disulfonation by <sup>1</sup> H NMR (%) | IEC (meq/g) |              | IV (dL/g) | Water uptake (wt.%)  |
|------------------------|---|-------------|--------------|-----------|----------------------|
|                        |   | calculated  | Experimental |           |                      |
| Before                 | 36                                      | 1.5         | 1.4          | 0.7       | 34                   |
| after                  | 34                                      |             | 1.4          | 0.8       | 37 (33) <sup>b</sup> |

<sup>a</sup> 2005 technical target for membrane durability: 2000 h with cycling

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

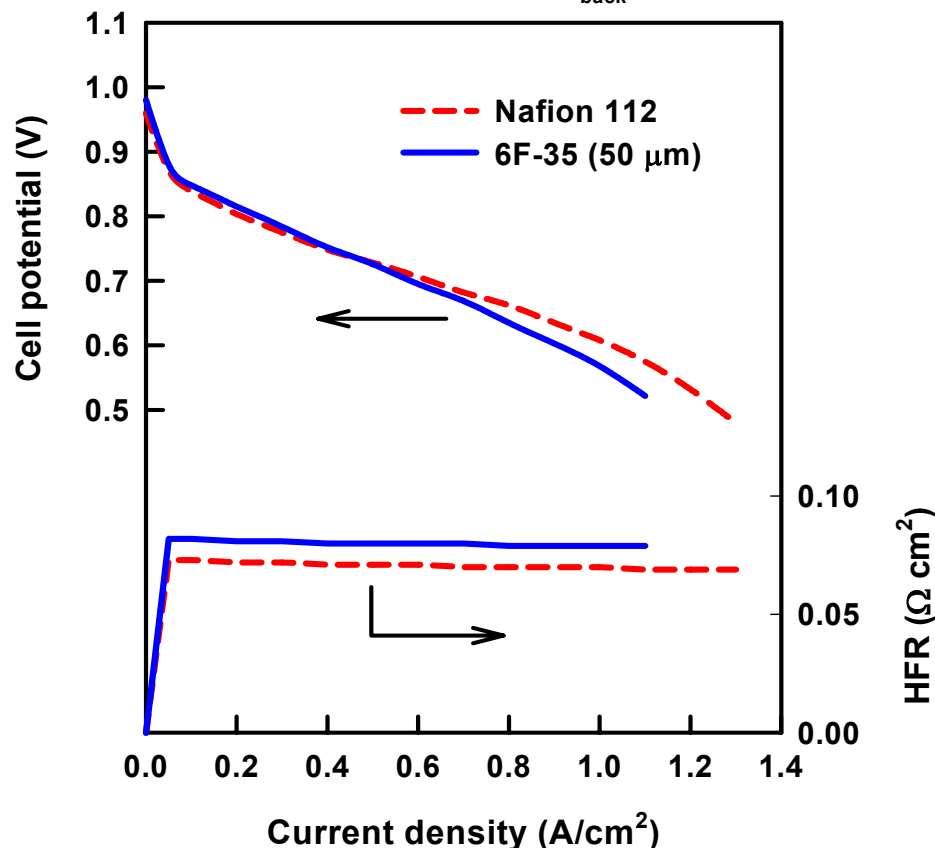
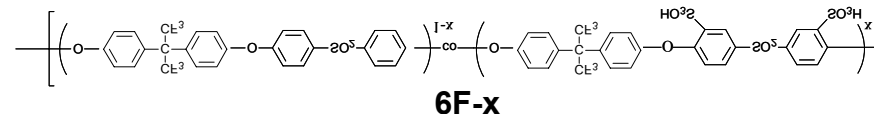
NMR spectrum, IEC, IV and water uptake were stable.

**No significant chemical degradation was found !!**

<sup>1</sup>H NMR spectroscopy of BPSH-35 before and after 700 h life test

# H<sub>2</sub>/air Fuel Cell Performance of Alternative Membrane

H<sub>2</sub>/air, high stoic.  
 20% Pt/C 0.2 mg/cm<sup>2</sup>  
 T = 80°C, P<sub>back</sub> = 20 psig



Fuel cell performance of 6F-35 membrane (50 μm thick) was comparable to Nafion 112 at lower current density (< 0.6 mA/cm<sup>2</sup>)

Inferior performance of 6F-35 at higher current density was due to the higher membrane resistance.

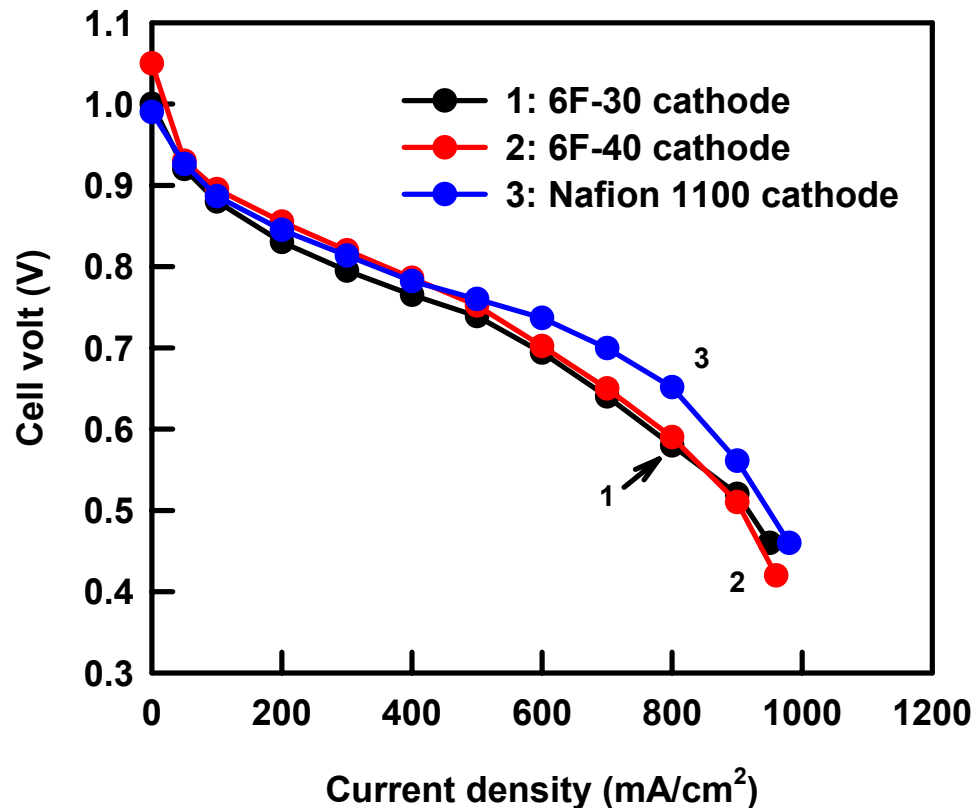
Increasing membrane conductivity while maintaining water uptake is critical for performance improvement.

Performance at > 80°C – under investigation.

Low catalyst loaded (0.2 mg/cm<sup>2</sup>) MEAs were prepared



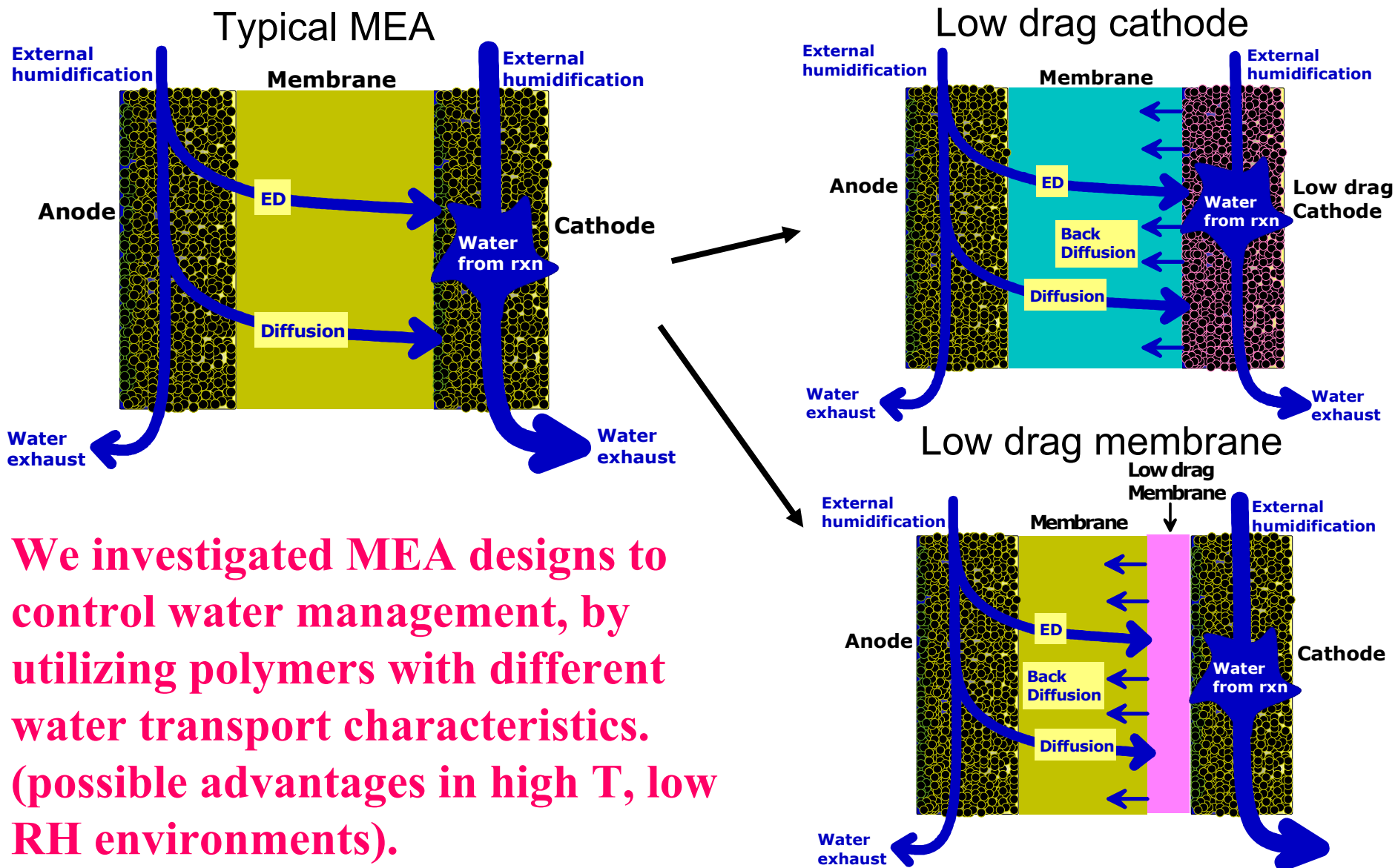
# Alternative Polymer Electrodes



- **6F-30 cathode**
  - Ionomer:cat.=1.5:1
- **6F-40 cathode**
  - Ionomer:cat.=2:1
- **Nafion 1100 cathode**
  - Ionomer:cat.=1:1
  
- **In common conditions**
  - Membrane: Nafion 1135
  - Catalyst loading: 6mg/cm<sup>2</sup>
  - Anode Humidity bottle temp.=105°C
  - Cathode Humidity bottle temp.=60°C
  - Cell temp.=80°C
  - 20 psig backpressure on both anode and cathode

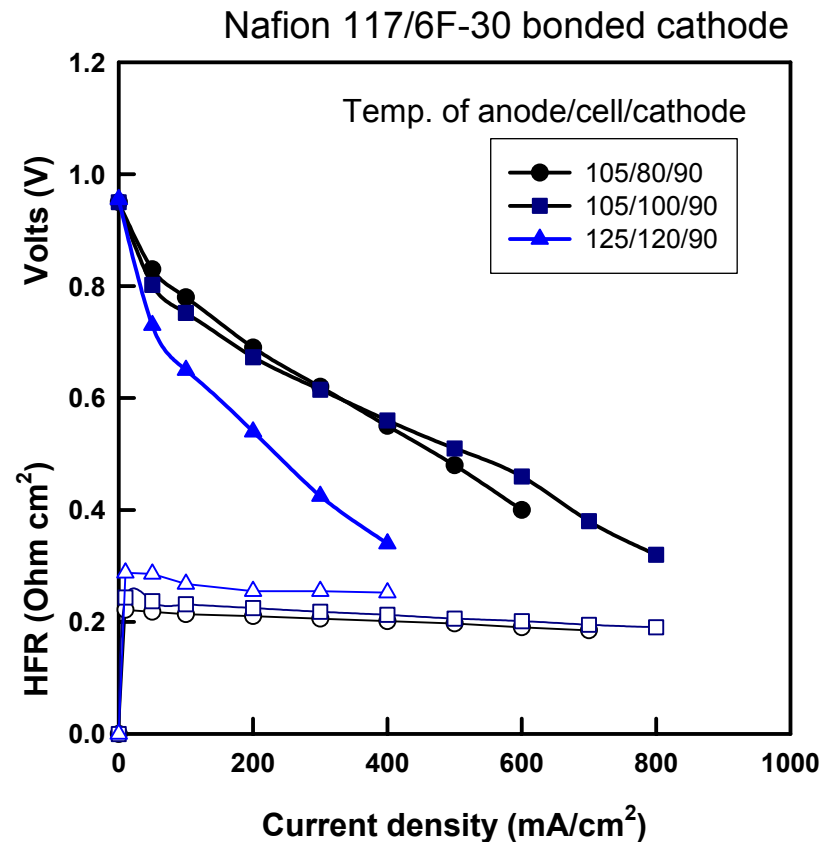
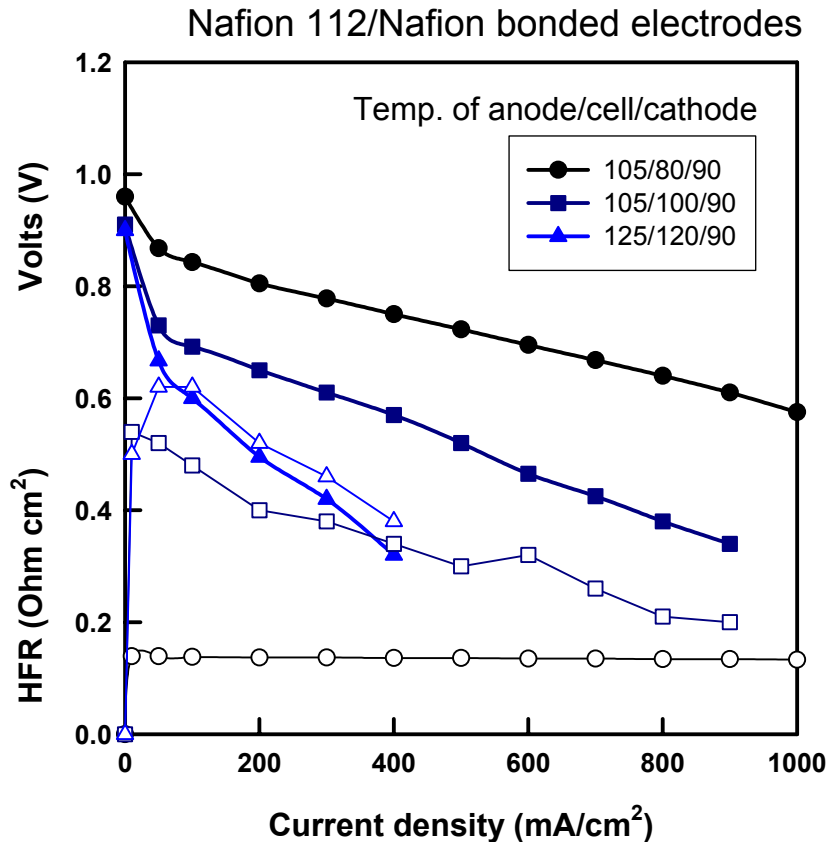
Fuel cell performance using 6F polymers in the cathode layer showed competitive performance with Nafion, representing a significant accomplishment that may lead to better incorporation of alternate, low-cost membranes.

# MEA Designs for Elevated Temperature Operation



We investigated MEA designs to control water management, by utilizing polymers with different water transport characteristics. (possible advantages in high T, low RH environments).

# Preliminary Results on MEA using Low Drag Cathode



**MEA using low drag cathode showed slightly better performance at 120°C (25% RH). Stable HFR (open symbols) shows water is effectively held within the membrane, even though cathode is dry.**

Catalyst: 20 % Pt/C 0.2 mg/cm<sup>2</sup>  
 Back pressure: 20 psig  
 High H<sub>2</sub>/air stoic.

# Future Plans

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## ***Remainder of FY 2004:***

- **Membrane-electrode interfacial issue**
  - Interfacial resistant measurement of H<sub>2</sub>/air fuel cell
  - Complete long-term test under accelerated conditions to > 3000 h
- **Non-Nafion H<sub>2</sub>/air fuel cell membrane**
  - Membrane optimization (conductivity, water uptake and thickness)
  - Effect of operation parameters (temperature, humidity and reactant stoic.) on fuel cell performance

## ***FY 2005***

- **Non-Nafion H<sub>2</sub>/air fuel cell membrane**
  - Durability with cycling at 80°C to 2000 h
  - Long-term test under elevated temperature and either low or high RH
- **Non-Nafion electrode binder**
  - Study long term durability of alternative ionomers in catalyst layers (peroxide effects?)
  - Non-Nafion electrode design for elevated temperature and low relative humidity

# Presentations and Publications

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- **Publications**

1. Direct Methanol Fuel Cell Performance of Disulfonated Poly(Arylene Ether Benzonitrile) Copolymers, Yu Seung Kim, Mike Sumner, William Harrison, James E. McGrath, Bryan Pivovar, *J. Electrochem. Soc.* **151**, 12, A2150 (2004).
2. New Proton Conducting Sulfonated Poly(Arylene ether) Copolymers Containing Aromatic Nitriles, M.J. Sumner, W.L. Harrison, R.M. Weyers, Y.S. Kim, J.E. McGrath, J.S. Riffle, A. Brink, M.H. Brink, *Journal of Membrane Science*, **239**, 2, 199-211 (2004).
3. Alternative Polymer Systems for Proton Exchange Membranes (PEMs), Michael Hickner, Hossein Ghassemi, Yu Seung Kim, Brian Einsla, and James E. McGrath, *Chemical Reviews*, **104**, 4587-4612 (2004).

- **Presentations**

1. The Importance of Membrane-Electrode Interface on Long-Term Fuel Cell Performance, Yu Seung Kim, Bryan S. Pivovar, Advances in Materials for Proton Exchange Membrane Fuel Cell Systems 2005, Asilomar Conference Grounds, Pacific Grove, CA, Feb. 20-23 (2005)
2. Membrane-Electrode Interfacial Degradation in Nafion based PEMFCs and DMFCs, Ana Siu, Yu Seung Kim, Bryan S. Pivovar, 206<sup>th</sup> Meeting of the Electrochemical Society, Oct. 3-8 (2004). (Paper no. 1925)
3. Sulfonated Poly(arylene ether sulfone) as Candidates for Proton Exchange Membranes: Influence of Substitution Position on Membrane Properties, J. E. McGrath, W. L. Harrison, B. Einsla, N. Arnett, Y. S. Kim, B. Pivovar, 206<sup>th</sup> Meeting of the Electrochemical Society, Oct. 3-8 (2004). (Paper no. 1973)
4. Novel sulfonated proton exchange membranes for fuel cell applications: partially fluorinated copolymers, C. N Tchatchoua, W. L. Harrison, B. Einsla, Y. S. Kim, B. S. Pivovar, J. E. McGrath, Division of Fuel Chemistry, 228<sup>th</sup> ACS National Meeting, Philadelphia, PA, August 22-26, (2004).

# Non-Nafion Membrane Electrode Assemblies

2005 DOE Hydrogen Program Review

Yu Seung Kim

Los Alamos National Lab

Tuesday May 24, 2005

Project #:  
**FCP4**

This presentation does not contain any proprietary or confidential information

# Hydrogen Safety

The most significant hydrogen hazard associated with this project is:

*Hydrogen leak in the hydrogen supply leading to accumulation in the room with ignition leading to an explosive event.*

# Hydrogen Safety

Our approach to deal with this hazard is:

*In labs with hydrogen supply from cylinder banks or from a hydrogen generator, hydrogen sensors have been installed and are interlocked with the hydrogen gas supply.*

*Two sensors are installed in every room for redundancy.*

*Sensors installed at ceiling level where accumulation is most severe.*

*H<sub>2</sub> sets off the alarm at 10% of Lower Flammability Limit (LFL).*

*In rooms that use only bottled hydrogen, only a single cylinder is in the room at any given time and bottle sizes are limited to ensure being safely below the LFL of the room even with complete release of a full cylinder.*

*Work has been reviewed and approved through Los Alamos National Lab's safety programs:*

*Hazard Control Plan (HCP) - Hazard based safety review*

*Integrated Work Document (IWD) - Task based safety review*

*Integrated Safety Management (ISM)*