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

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

- 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

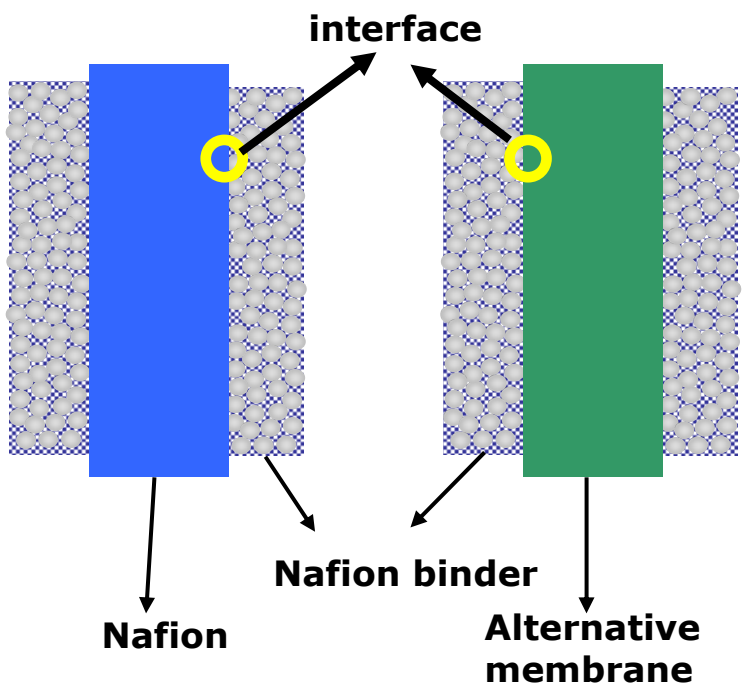
Alternative Polymer Electrolyte Membranes

- 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



Membrane

Nafion

Or

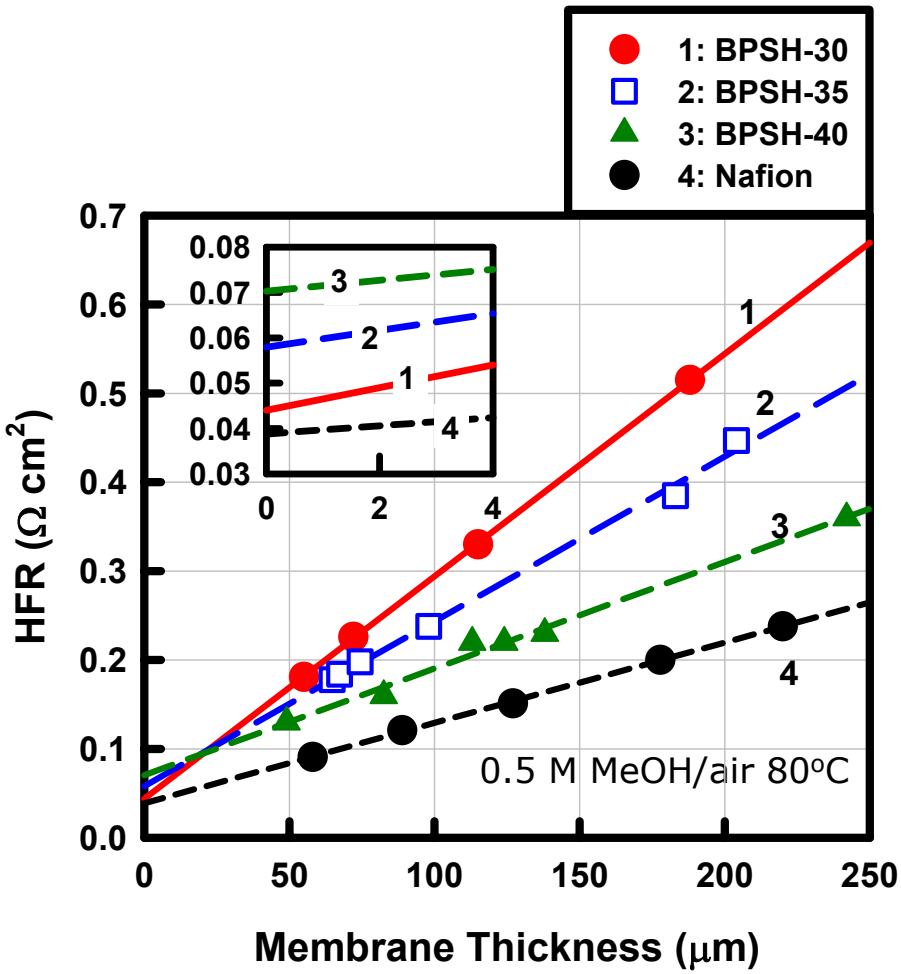
Alternative membrane

Catalyst layers

- **Nafion binder**
  - High reactant permeability (H_2, MeOH, O_2)
  - High proton conductivity
  - Chemically inert
  - Created porous structure
  - Optimized performance (only binder 15+ yrs)

Membrane-Electrode Interface

Effect of Degree of Sulfonation of BPSH* on Interfacial Resistance



Conductivity[a], σ, Interfacial Resistance, $R_{interface}$

Membrane	σ *(mS/cm)*	$R_{interface}$ *(mΩ·cm²)*
BPSH-30	39	16
BPSH-35	54	30
BPSH-40	78	42
Nafion	111	7

[a] *2005 technical target: 70 mS/cm*

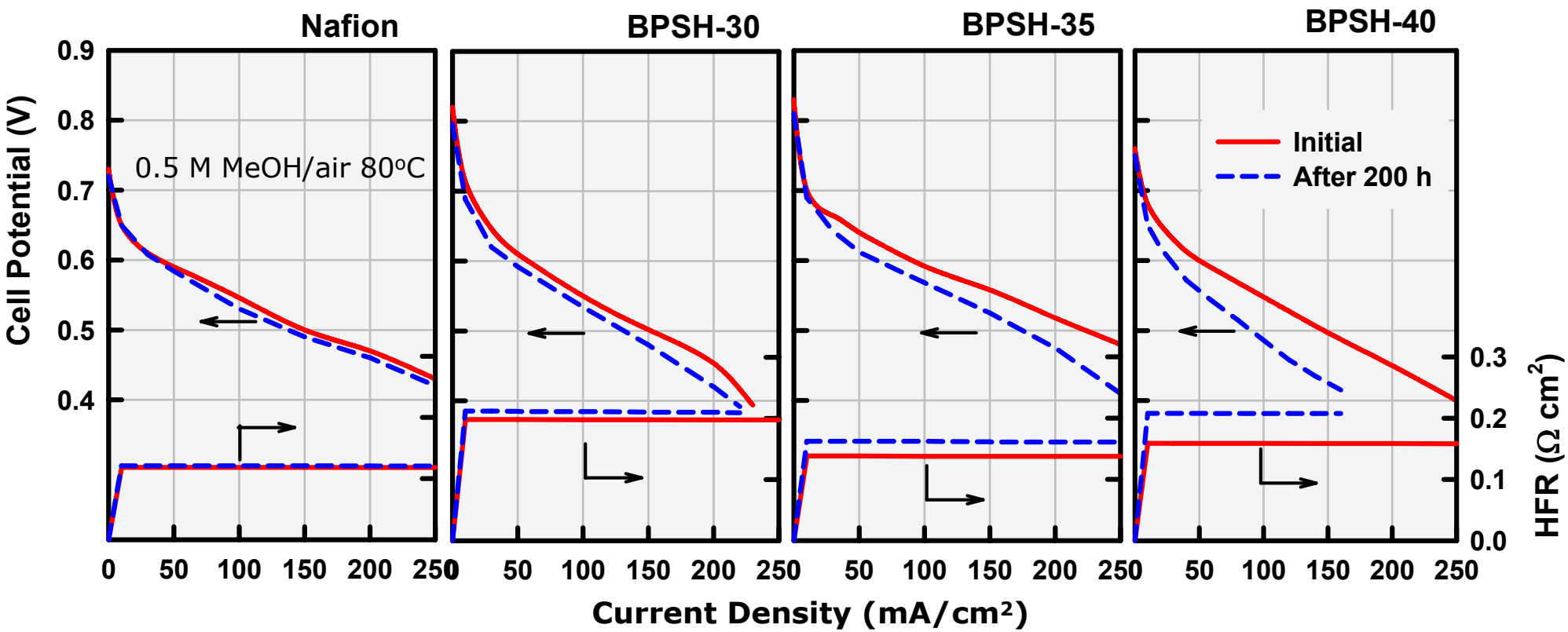
$$HFR = R_{non\text{-}mem} + R_{mem}(x)$$

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

Non-Nafion membranes showed relatively greater interfacial resistance than Nafion

* BPSH: sulfonated polysulfone membrane prepared from Dr. McGrath at Virginia Tech.

Influence of Interfacial Compatibility on Long-Term Performance

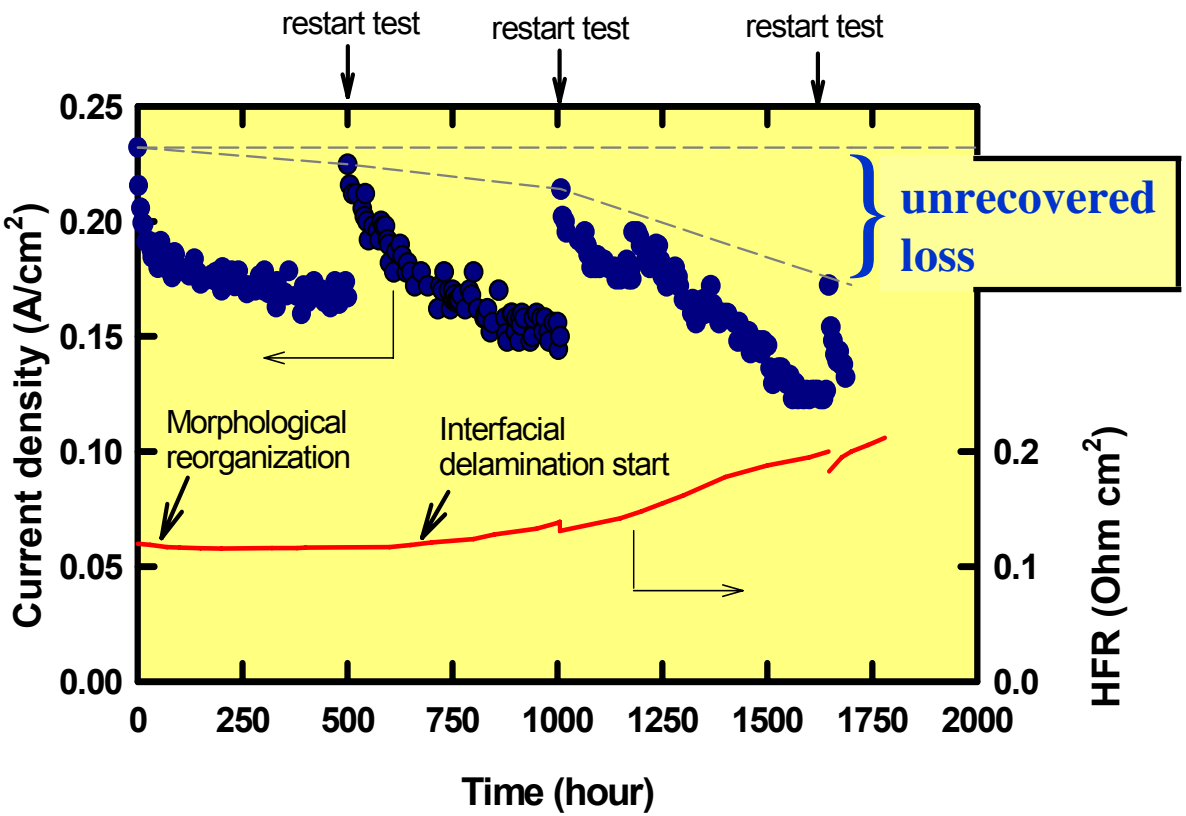


7 16 30 42

Initial Interfacial resistances (mΩ cm²)

Performance degradation increases with increasing initial interfacial resistances.

Importance of Interfacial Compatibility on Long-Term Performance



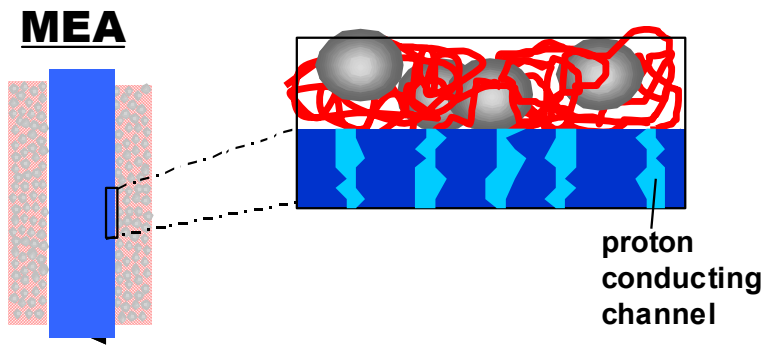
Life test of an alternative MEA at 0.5 V

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

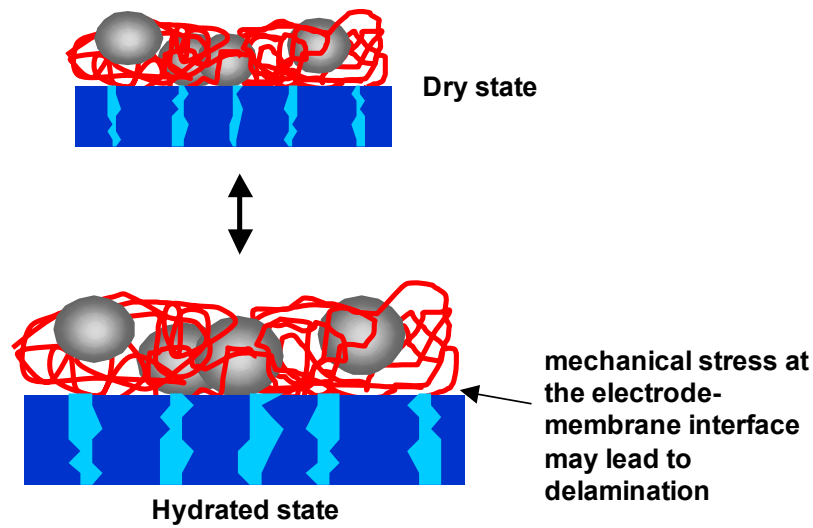
Interfacial delamination is reflected by the HFR increase.

* test was performed under DMFC conditions

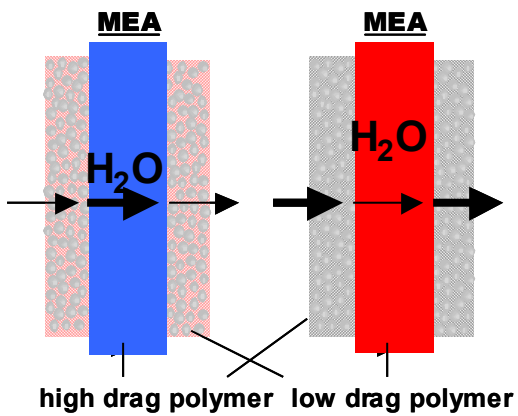
Possible Interfacial Failure Mechanisms



Wetting – Adhesion and conductivity
Adhesion – Performance and lifetime



Swelling – stresses affects performance and lifetime

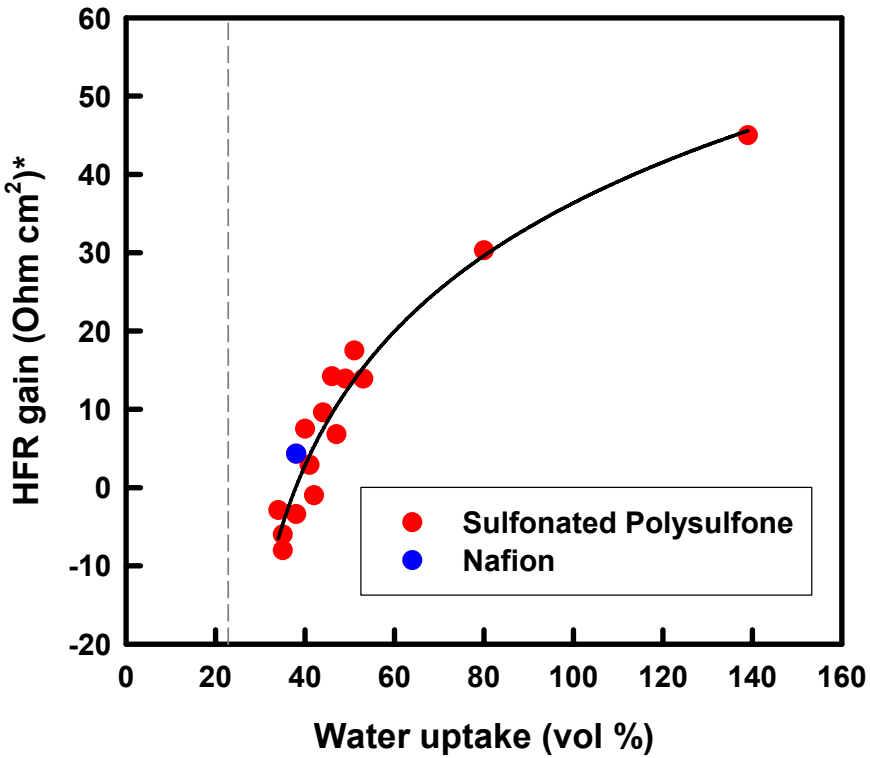


Electro-osmotic drag – stresses affects performance and lifetime

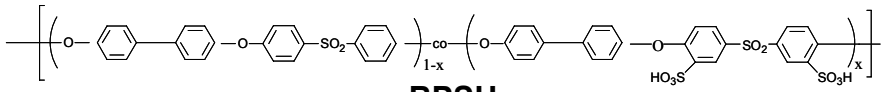
Wetting and adhesion, swelling, and electro-osmotic drag can all contribute to interfacial resistances.

Major Attribute for Interfacial Delamination –Membrane Swelling

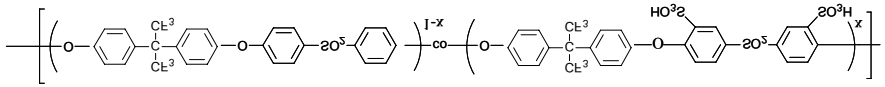
Correlation between membrane water uptake and HFR gain after 100 h life test



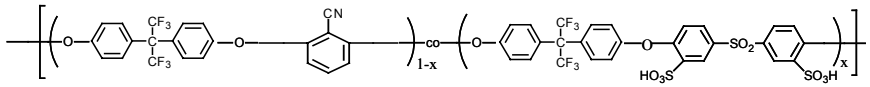
Chemical structural modifications



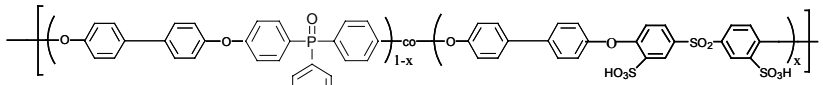
BPSH-x



6F-x



6FCN-x



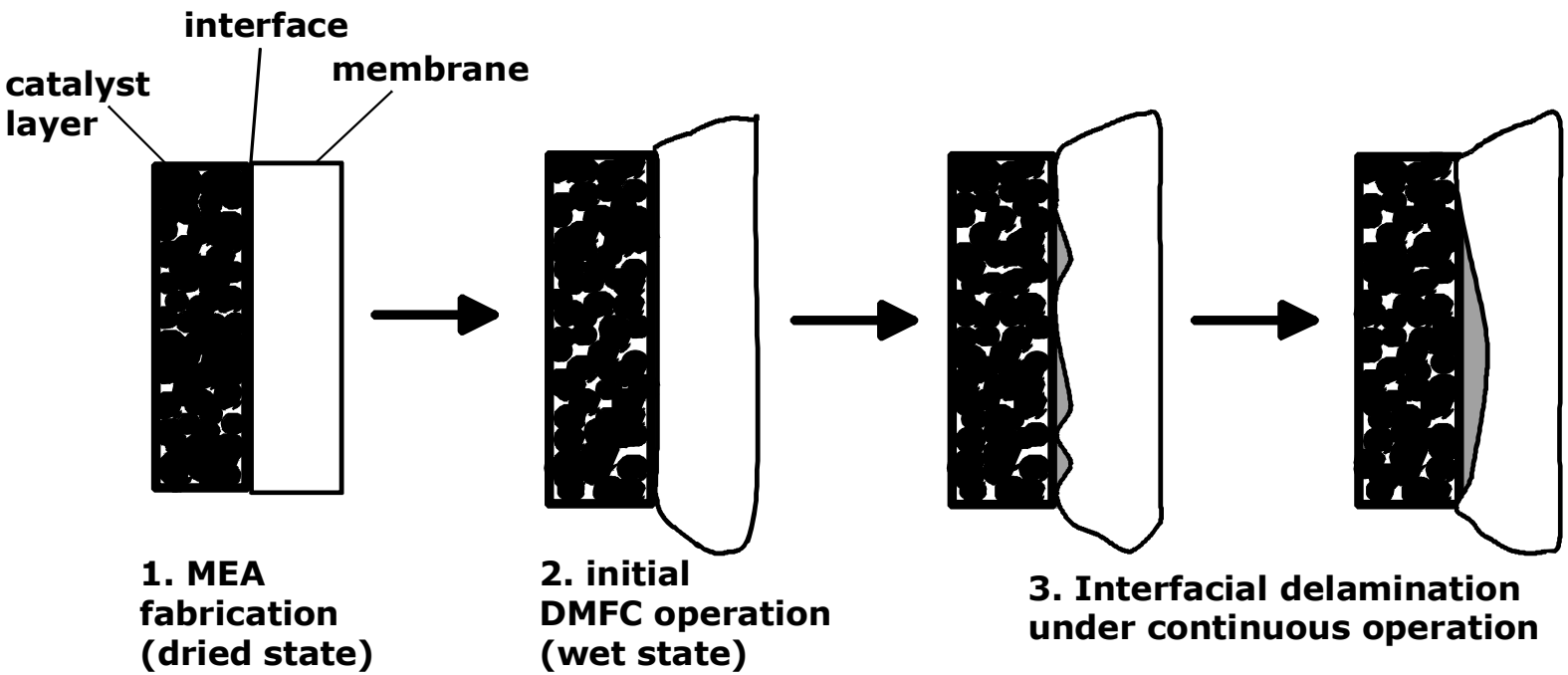
BPPPO-x

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!!

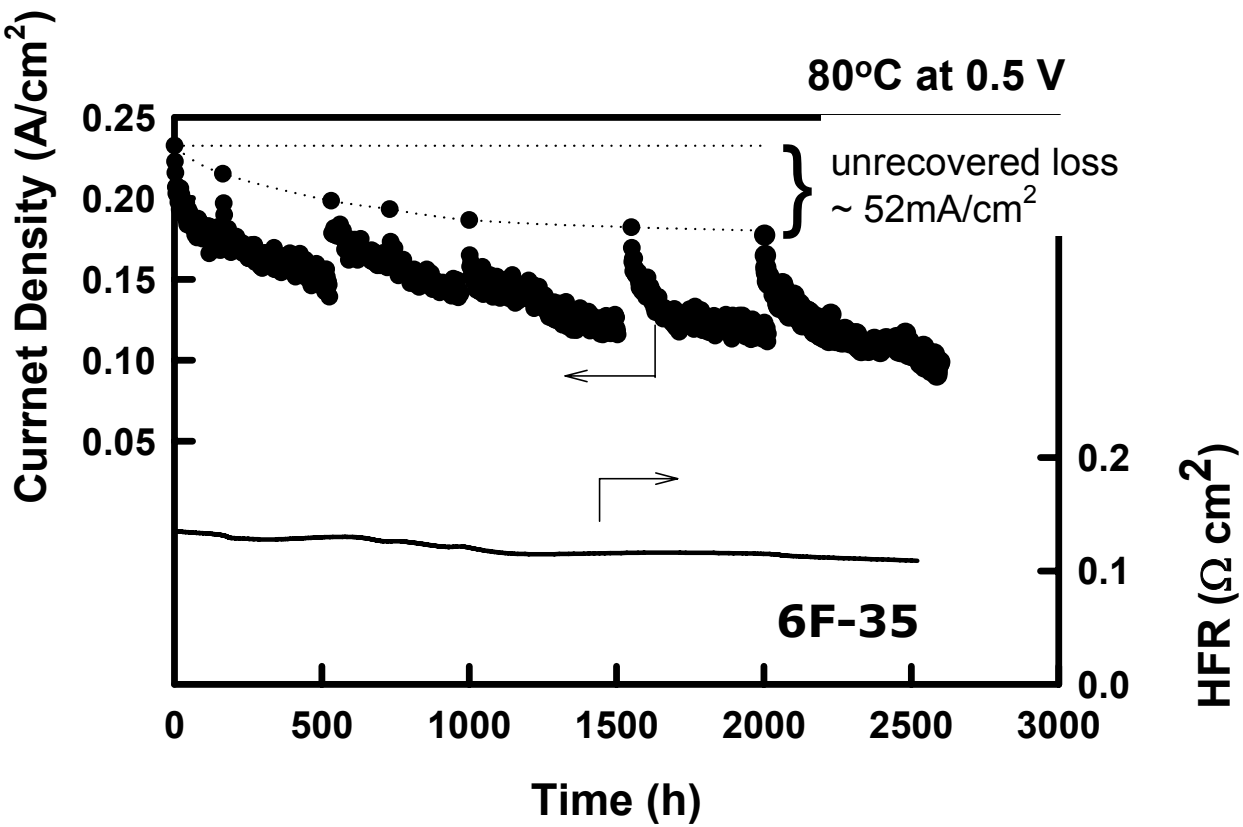
Proposed interfacial delamination during life test



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

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

Long-Term Performance of Interface Optimized Alternative Membrane



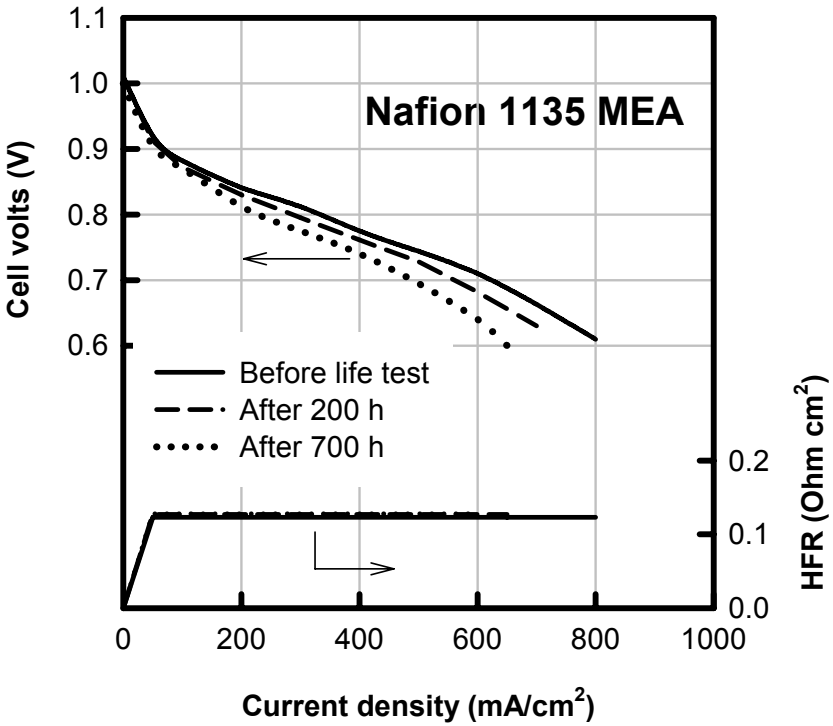
Interface optimized non-Nafion membrane (6F-35) exhibited stable long-term performance* with decreasing cell resistance under DMFC conditions

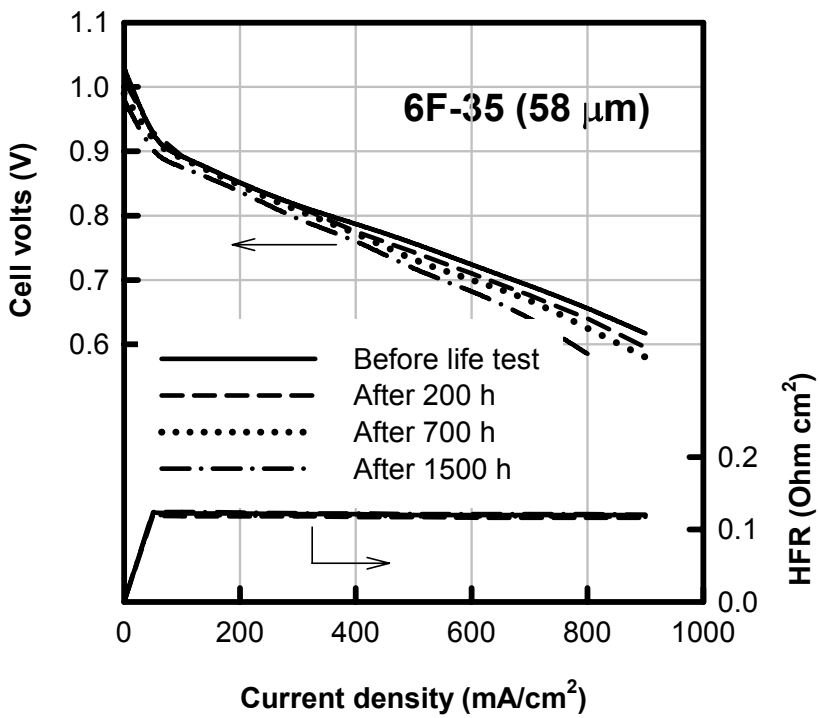
Performance loss after 2000 h life test for 6F-35 was 52 mA/cm^2 (22.4% loss), which was comparable to that of state of the art Nafion MEA.

**2005 technical target for MEA durability 10% loss after 2000 h at < 80°C under H_2/air conditions*

Life test under H_2/air conditions is on going!

H_2/Air Performance Comparison after DMFC Life Test

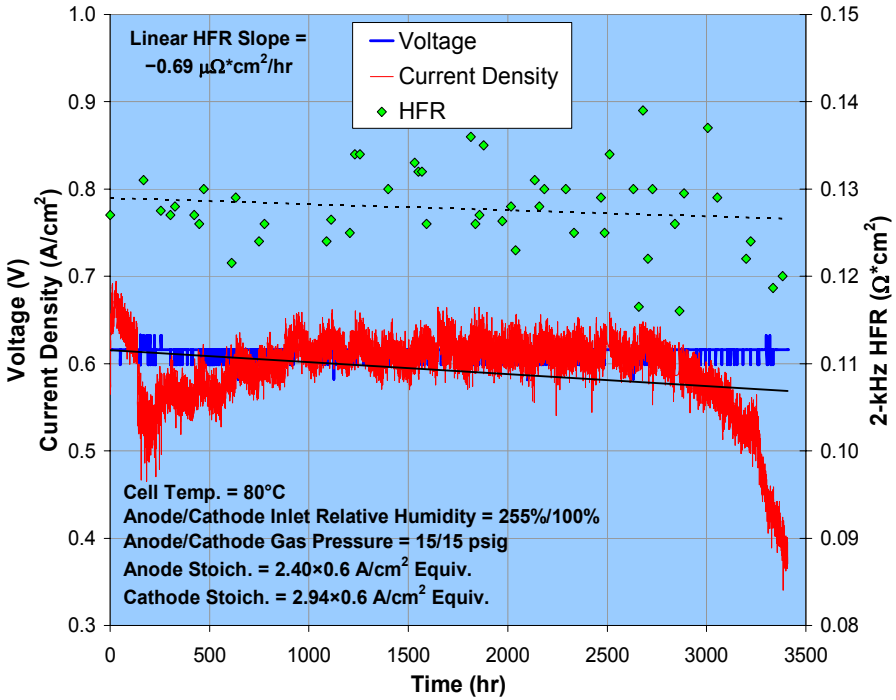


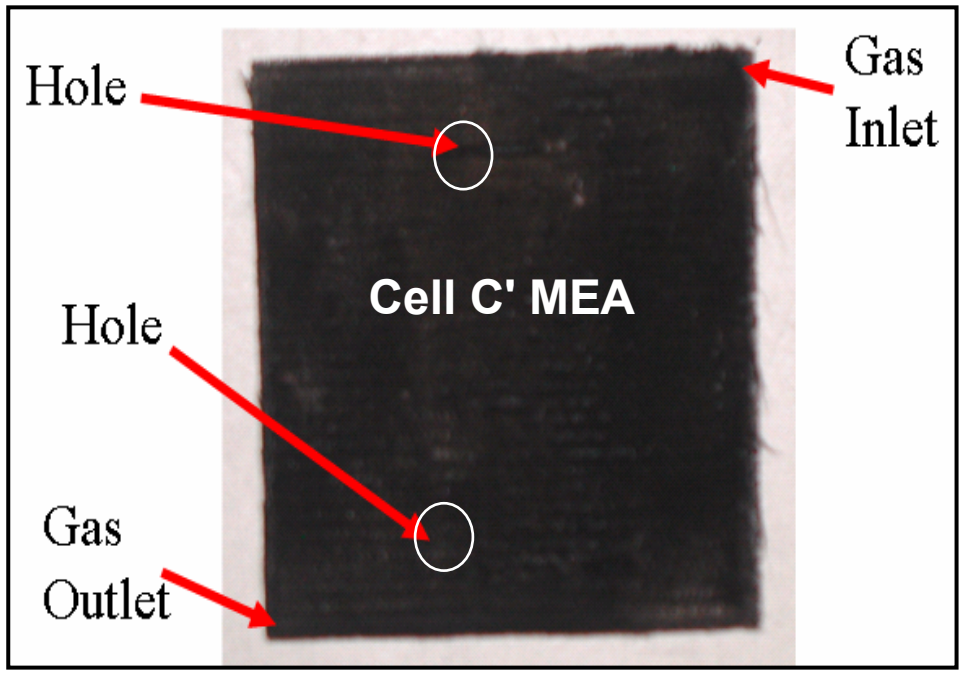


H_2/air, high stoic.
Pt-Ru 8 mg/cm^2 anode
Pt 6 mg/cm^2 cathode
T= 80°C, P back = 20 psig

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

Catastrophic Failure of Nafion*





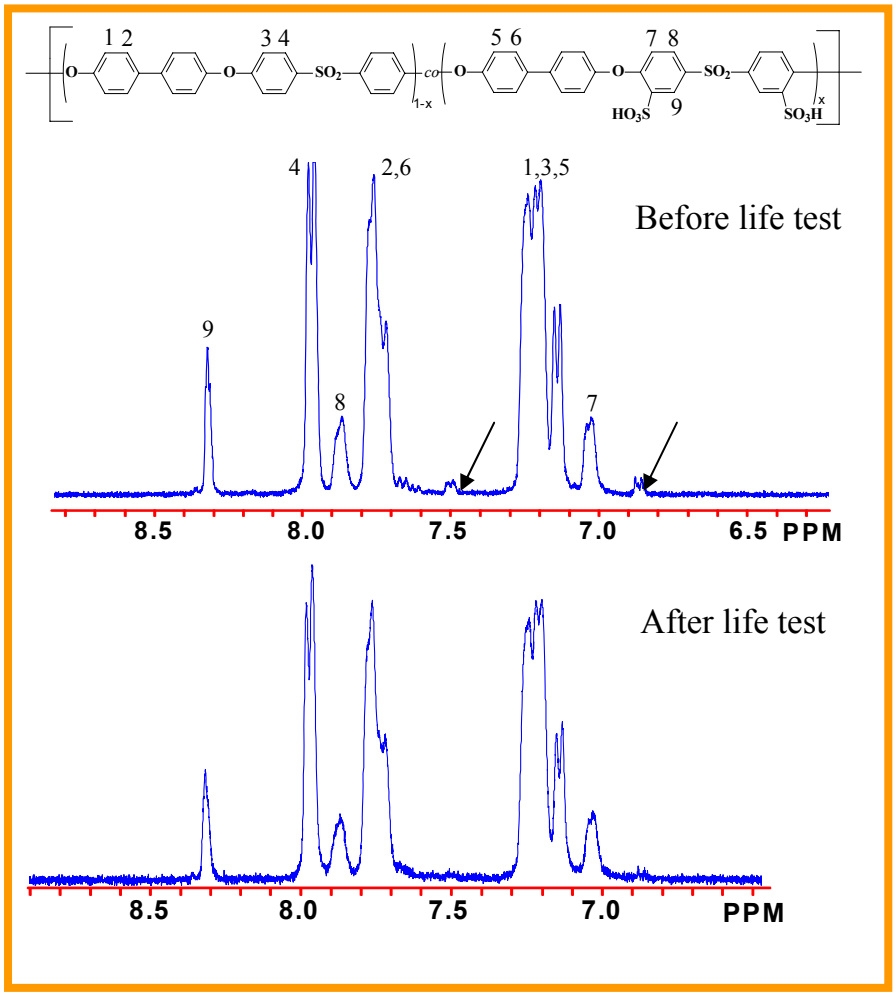
* R. Borup et. al, LANL data presented at 2004 OHFCIT Review

Membrane pinhole formation leads to catastrophic failure and may be due to polymer creep.
Alternative membranes have higher Tg and may resist pinhole formation (catastrophic failure testing using alternative membranes is under way).

copolymer	$T_{g\ dry}$ (°C)	$T_{g\ hydrated}$ (°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?



^{1}H NMR spectroscopy of BPSH-35 before and after 700 h life test

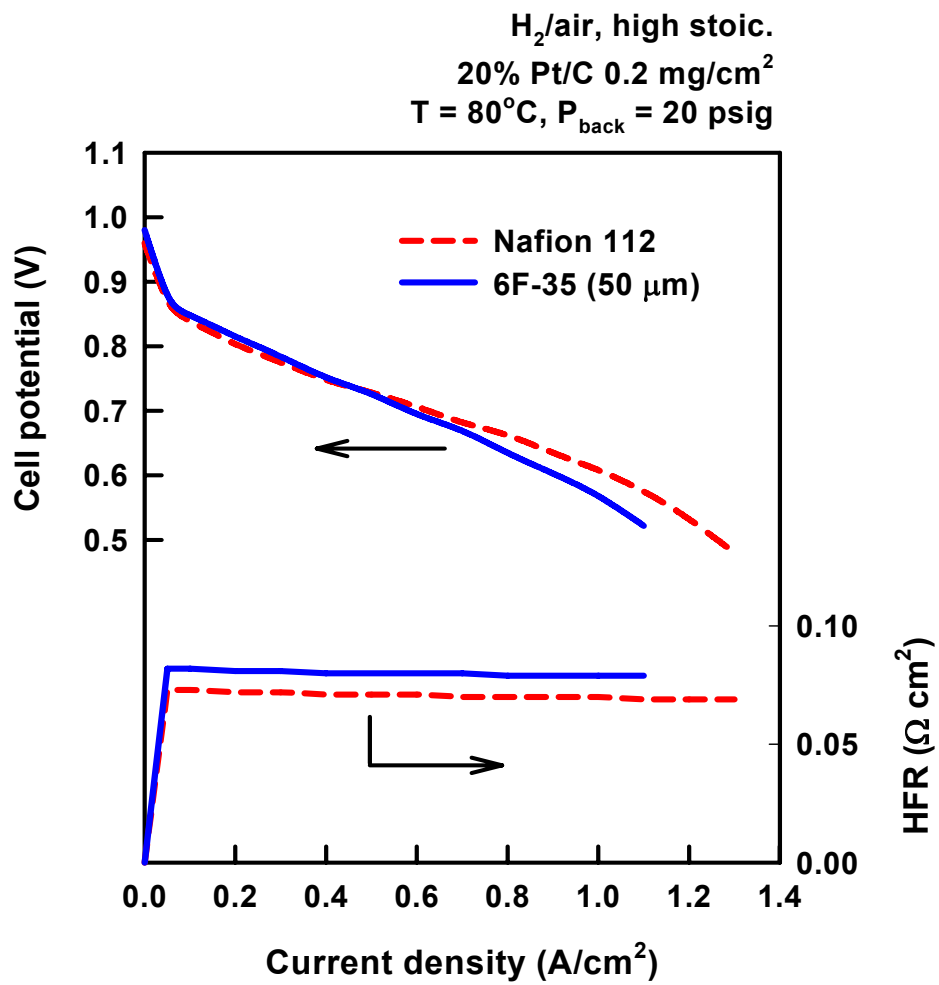
Life test[a]	Disulfonation by ^{1}H NMR (%)	IEC (meq/g)		IV (dL/g)	Water uptake (wt.%)
		calculated	Experimental		
Before	36	1.5	1.4	0.7	34
after	34		1.4	0.8	37 (33)[b]

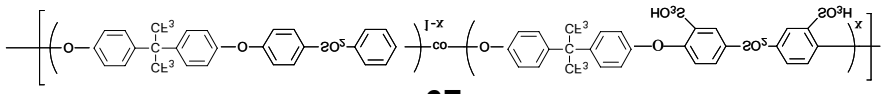
[a] *2005 technical target for membrane durability: 2000 h with cycling*
[b] after life test and recast

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

No significant chemical degradation was found !!

H_2/air Fuel Cell Performance of Alternative Membrane





6F-x

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

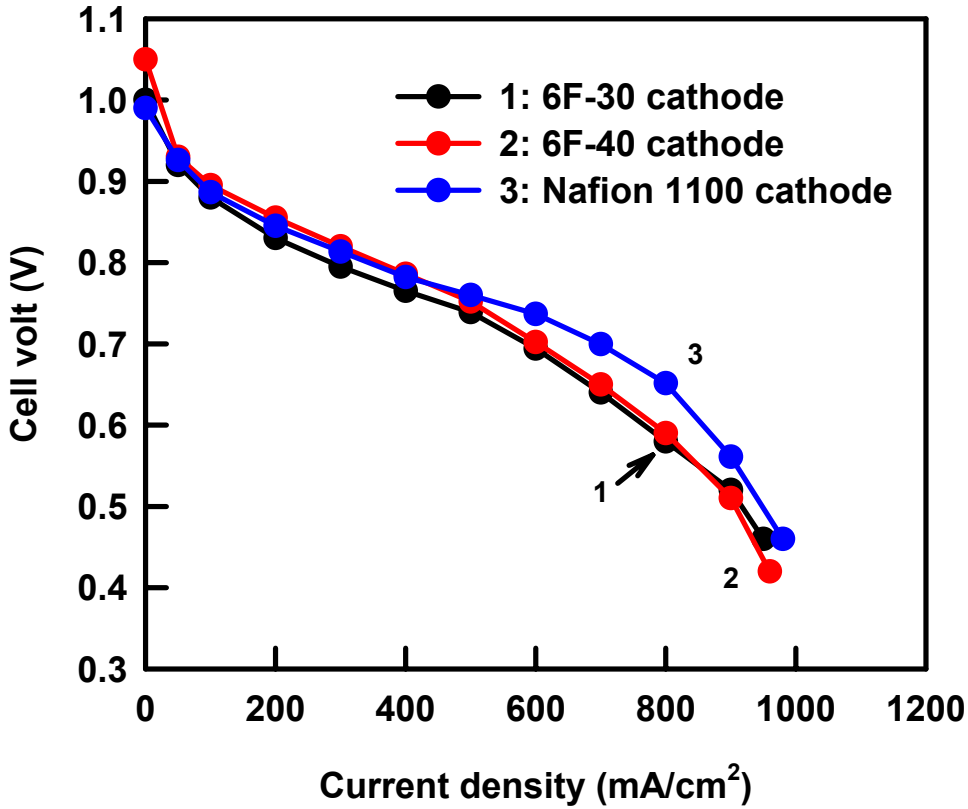
Inferior performance of 6F-35 at higher current density was due to the higher membrane resistance.

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^2) MEAs were prepared

Alternative Polymer Electrodes

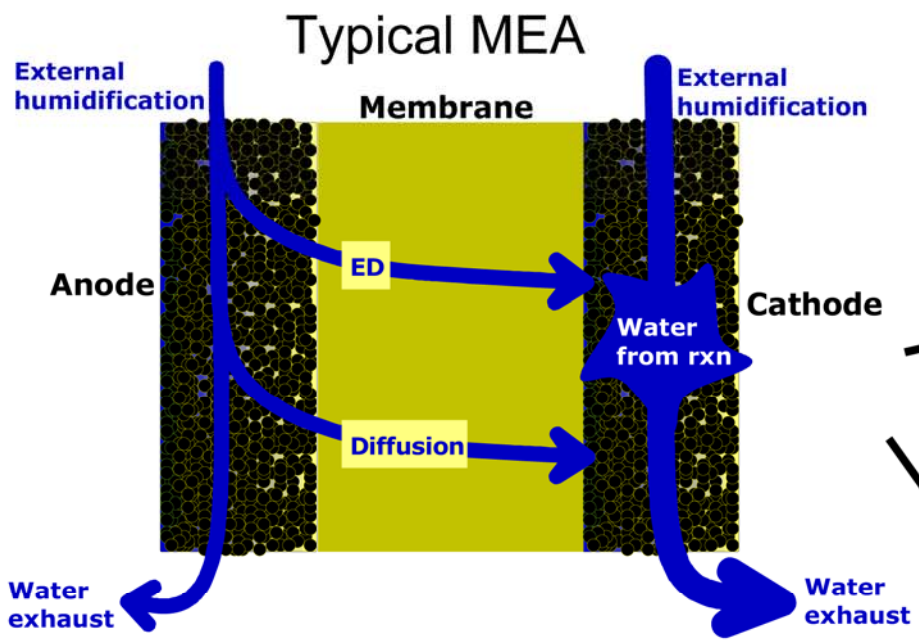


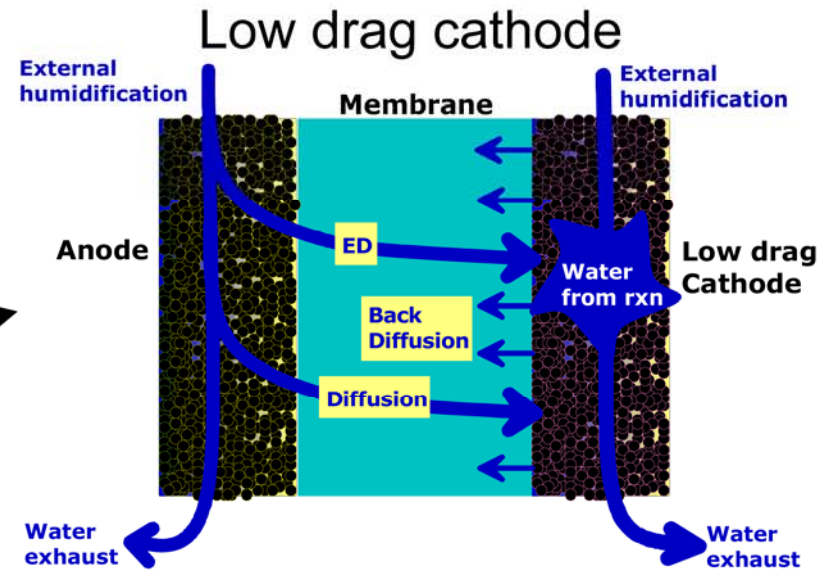
- 6F-30 cathode
  - Ionomer:cat.=1.5:1
- 6F-40 cathode
  - Ionomer:cat.=2:1
- Nafion 1100 cathode
  - Ionomer:cat.=1:1

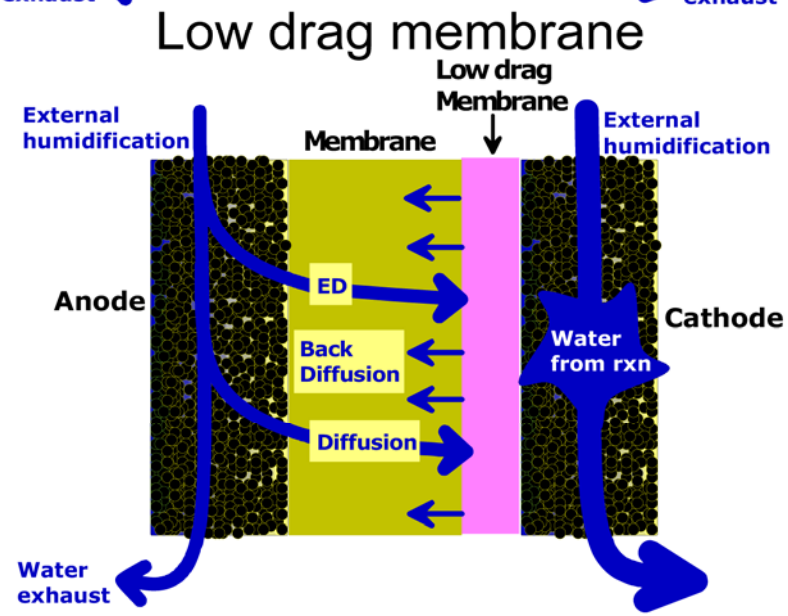
- In common conditions
  - Membrane: Nafion 1135
  - Catalyst loading: 6mg/cm^2
  - Anode Humidity bottle temp.=105°C
  - Cathode Humidity bottle temp.=60°C
  - Cell temp.=80°C
  - 20 psig backpressure on both anode and cathode

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

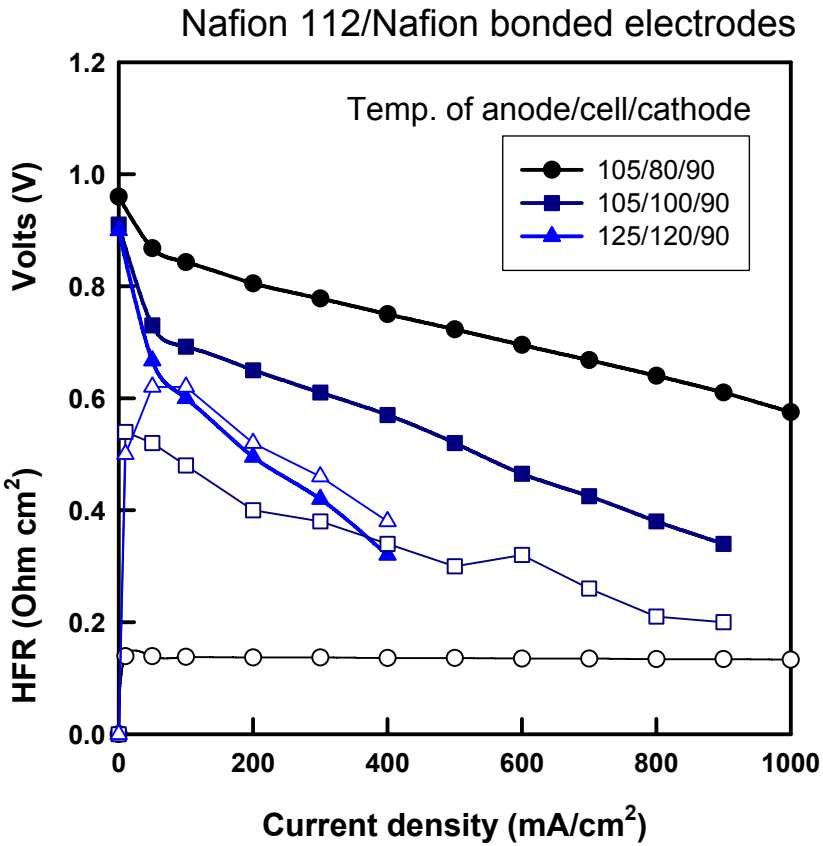


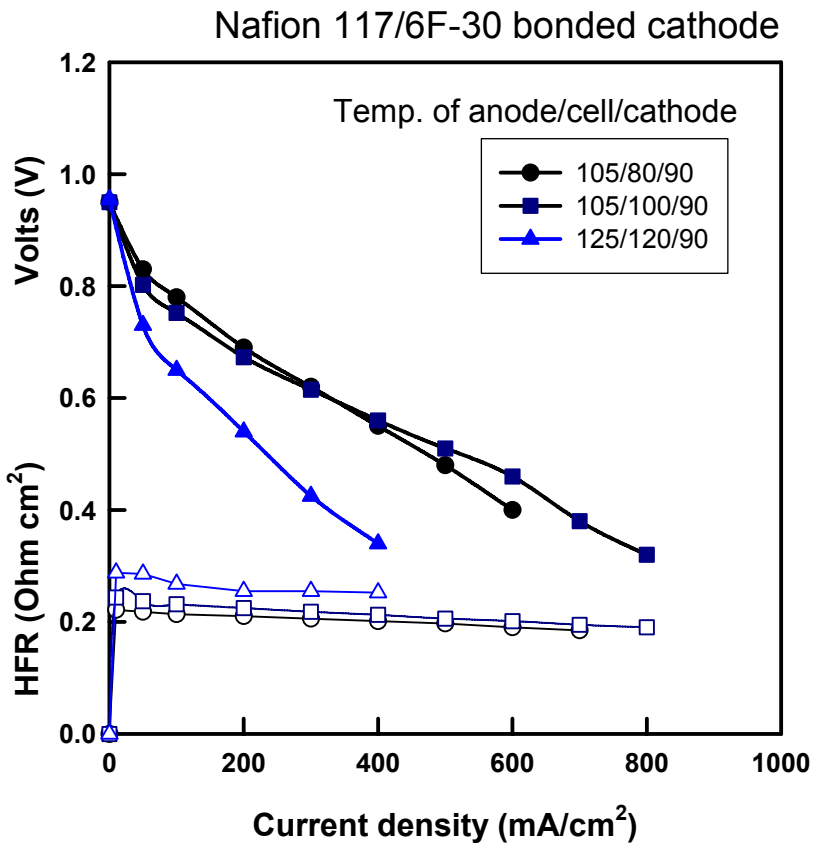




We investigated MEA designs to control water management, by utilizing polymers with different water transport characteristics. (possible advantages in high T, low RH environments).

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^2
Back pressure: 20 psig
High H_2/air stoic.

Future Plans

Remainder of FY 2004:

- **Membrane-electrode interfacial issue**
  - Interfacial resistant measurement of H_2/air fuel cell
  - Complete long-term test under accelerated conditions to > 3000 h
- **Non-Nafion H_2/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_2/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

- ***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, 206th 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, 206th 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, 228th 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.

H2 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)