Non-Nafion Membrane Electrode Assemblies

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This presentation does not contain any proprietary or confidential information

Overview

Timeline

- Start – Oct. 2003
- Finish – On going

Budget

- Non-cost sharing
- Funding received in FY05: $350K
- Funding for FY06: $350K

Barriers Addressed

- A. Durability
- B. Cost
- C. Electrode Performance

Technical barriers D. Thermal, Air, and Water Management and J. Startup Time/ Transient Operation are also relevant

Collaborators

- Virginia Polytechnic and State Univ. (Membrane supply, prof. James McGrath)
- Simon Fraser Univ. (Membrane supply, prof. Steven Holdcroft)
- Air Force Research Lab. (Membrane supply, Dr. Mitra Yoonessi)
- Hydrosize® Technologies, Inc. (Scale up production)
- Polymer Technology Group, Inc. (Membrane casting)
- Case Western Reserve Univ. (prof. Tom Zawodzinski)
- National Research Council Canada (Ottawa Dr. Michael Guiver)
- International Partnership for Hydrogen Economy (High Temperature Membranes Project Co PI)

Objective and Milestones

- **Develop low-cost, high performance and durable alternative membrane electrode assemblies (MEAs)**

Characteristic	Units	2004 status	2005	2010	2015
Performance @ ¼ power (0.8V)	mA/cm^2 mW/cm^2	200 160	250 200	400 320	400 320
Durability with cycling At operating temp. of ≤80°C At operating temp. of >80°C	 hours hours	 ~ 1000 Not available	 2000	 5000 2000	 5000 5000
Inlet water vapor partial pressure	kPa (abs)	50	25	1.5	1.5

From DOE Hydrogen, Fuel Cells, & Infrastructure Technologies Program, Jan. 2005

FY '06 Milestones

- Mar 06: Explore MEA operating window dependence on architecture.
  Status: Complete

- May 06: Performance evaluation of non-Nafion binder under H_2/air conditions.
  Status: 90 % complete

- Sep 06: Evaluate H_2/air long-term (2000h) performance of non-Nafion membranes under cycling conditions.
  Status: 50 % complete

Technical Approaches

Task 1 Interface

Membrane-Electrode Interface

- Interfacial resistance measurement
- Interfacial failure mechanism
- Membrane property criteria

Task 2 Membrane

Membrane Design

- Effect of hydrophobic fluorine
- Effect of specific interaction
- Electrochemical properties

Task 3 Electrode

Electrode Ionomer Design

- Water/alcohol based catalyst ink
- H_2/air fuel cell performance
- Electrochemical analysis

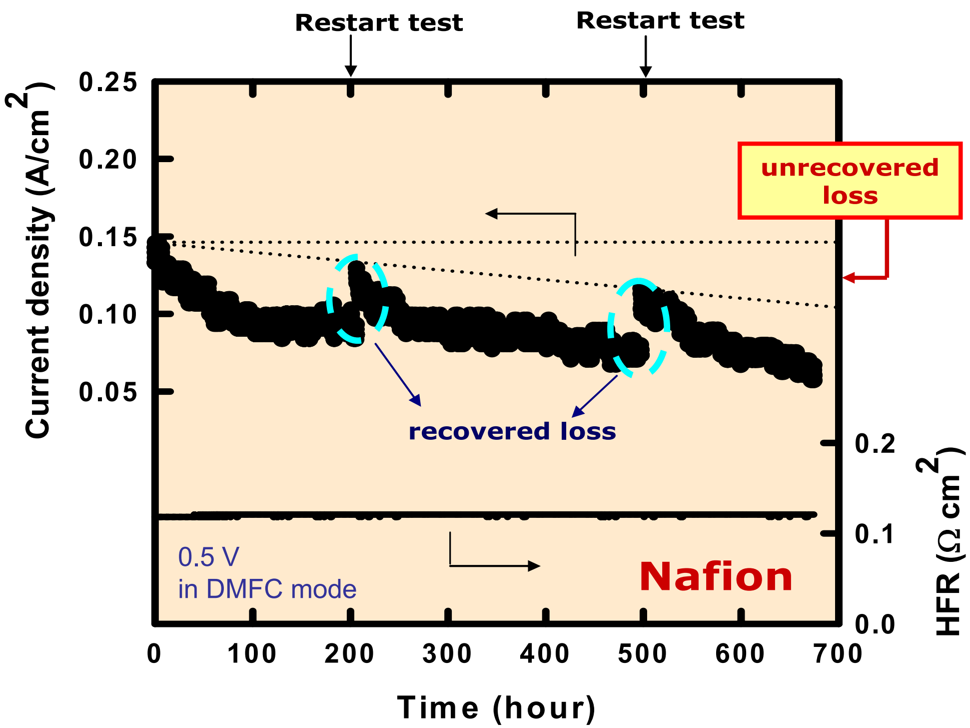
Task 4 Durability

Long-Term Fuel Cell Test

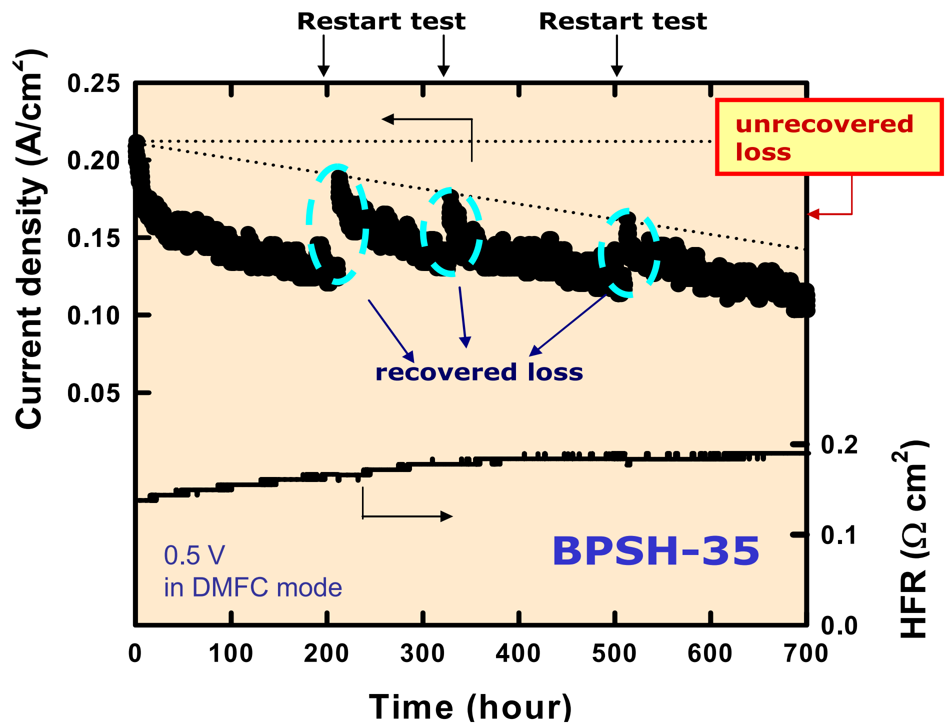
- Fully hydrated conditions
- Start-stop test
- High T, low RH H_2/air conditions

Membrane-Electrode Interfacial Compatibility

Good interface



Bad interface



Poor interfacial compatibility results in greater performance loss with increasing cell resistance over time

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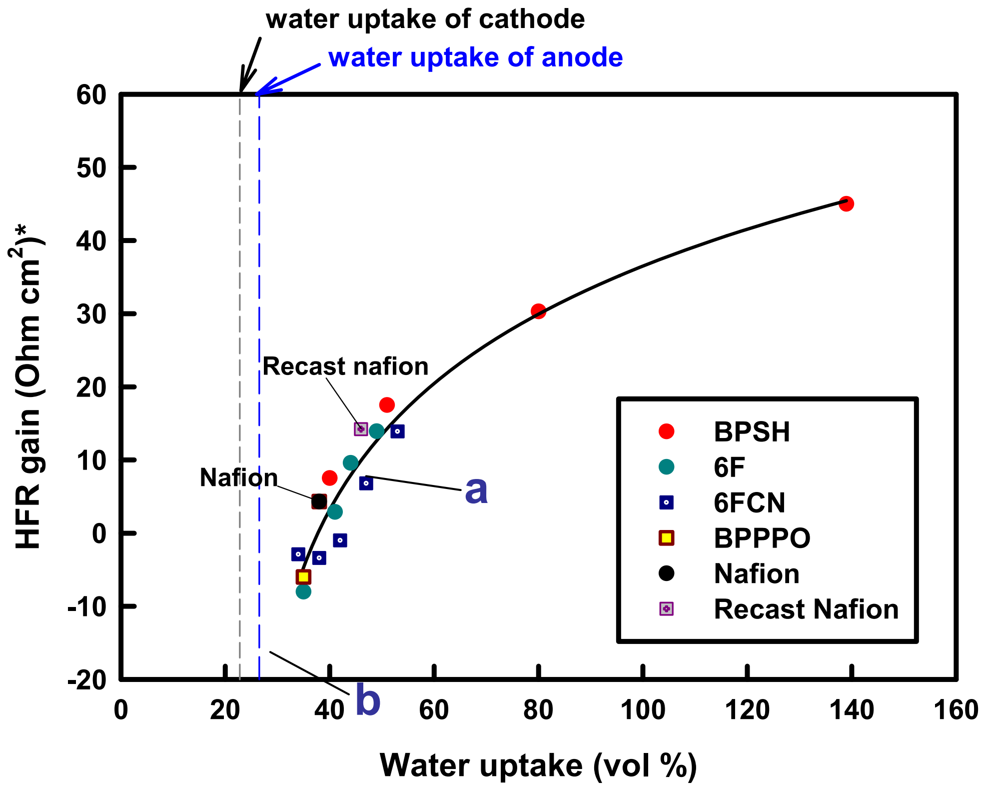
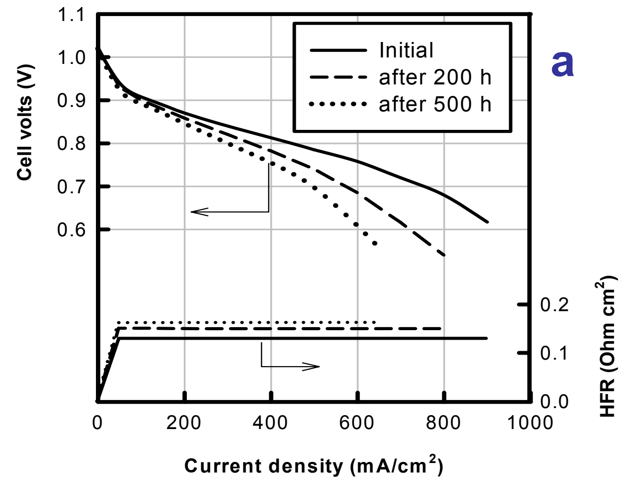
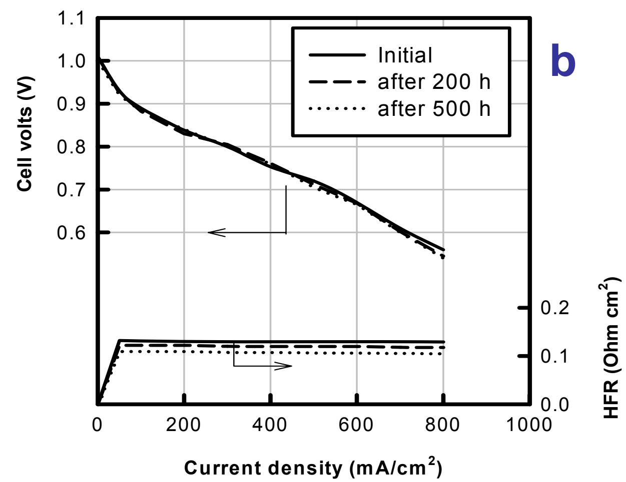
Ref. Y.S. Kim et al. DOE Hydrogen and Fuel Cells Annual Report (2005)

Correlation between HFR Gain and Water Uptake



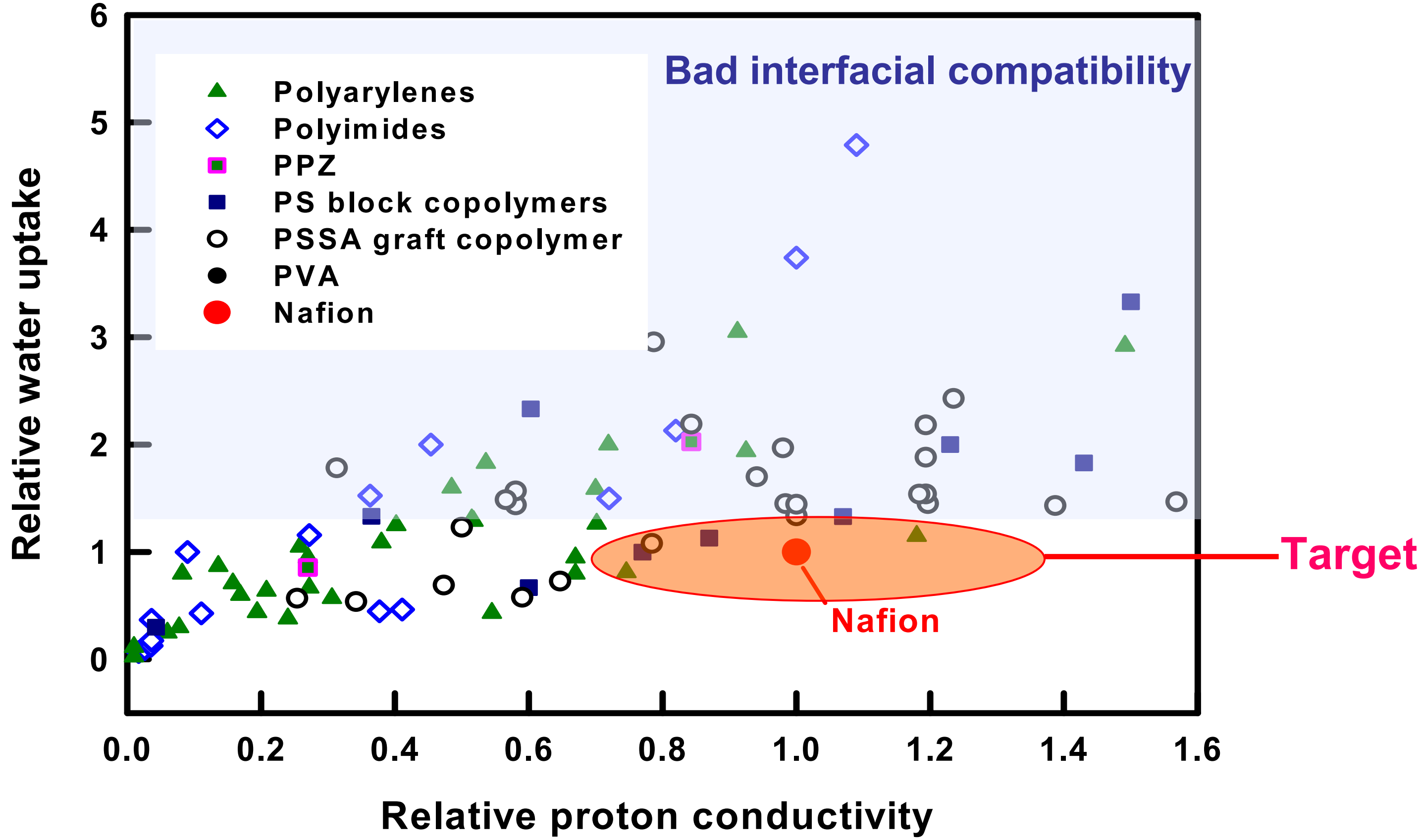




Membrane water uptake is the key durability parameter!!

Ref. Y.S. Kim et al. DOE Hydrogen and Fuel Cells Annual Report (2005)

Membrane Design for Fuel Cells

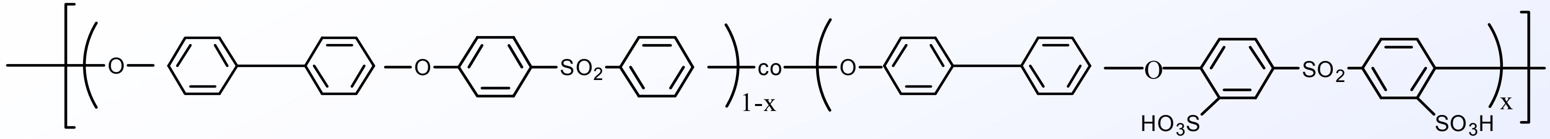


Strategy for Membrane Design:
Reduce water uptake without proton conductivity loss!!!

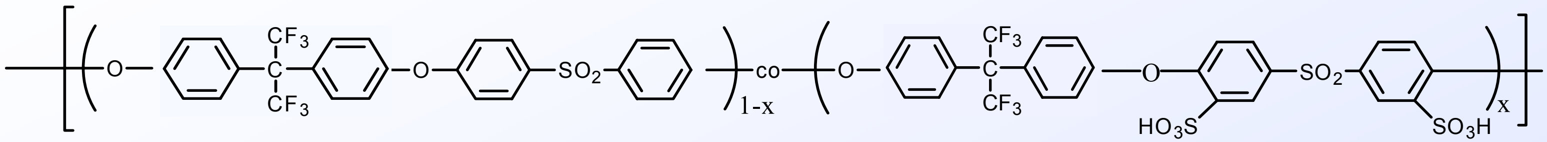
Ref. Y.S. Kim and B.S. Pivovar, Advances in Fuel Cells, Elsevier, to appear (2006)

Chemical Modification of Sulfonated Polysulfone Random Copolymers

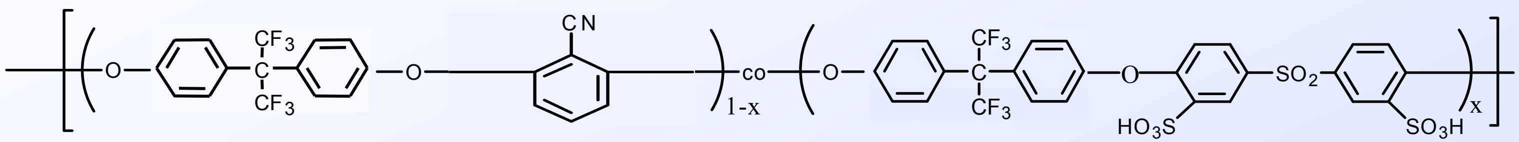
BPSH-*x*



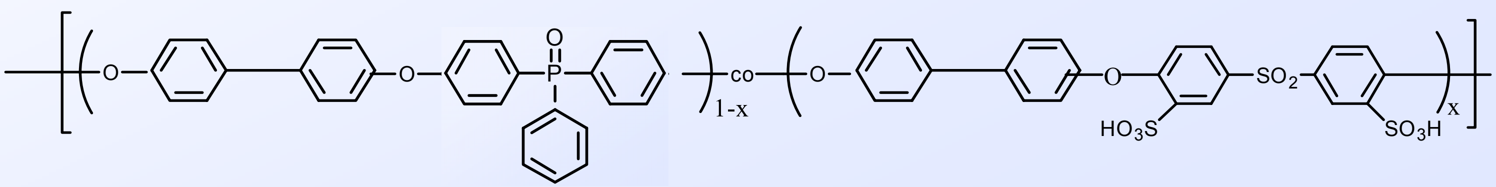
6F-*x*



6FCN-*x*



BPPPO-*x*

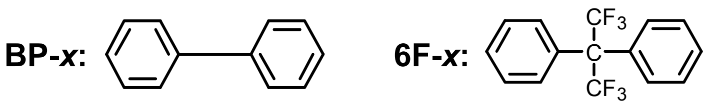


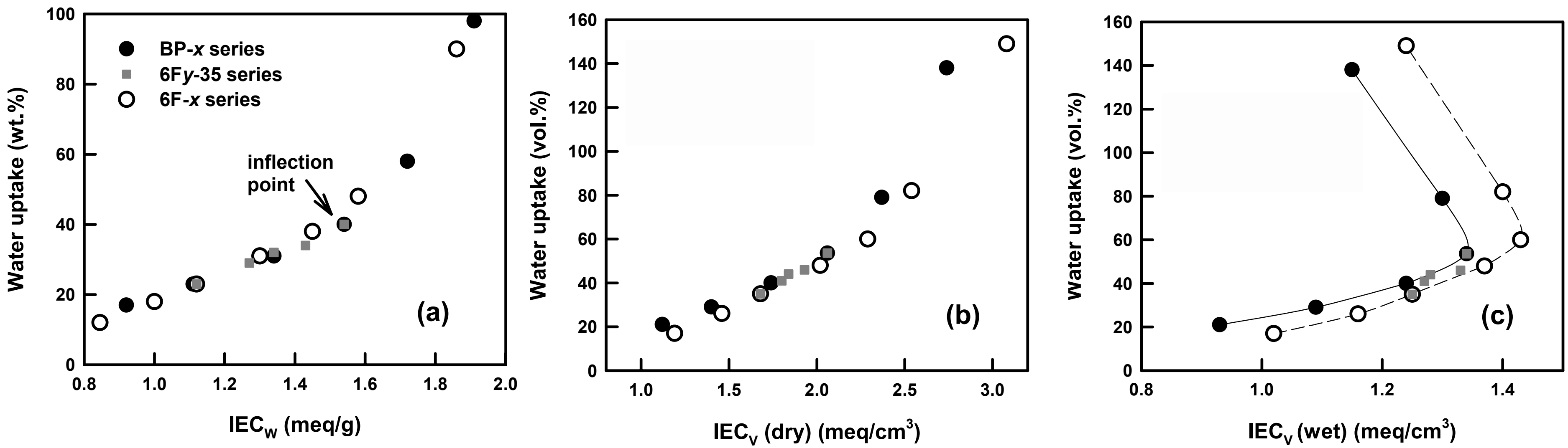
X denotes degree of disulfonation

Membranes were supplied from VT, Hydrosize® INC and Polymer Technology Group, INC

Effect of Fluorine Incorporation on Water Uptake

Bisphenol structure



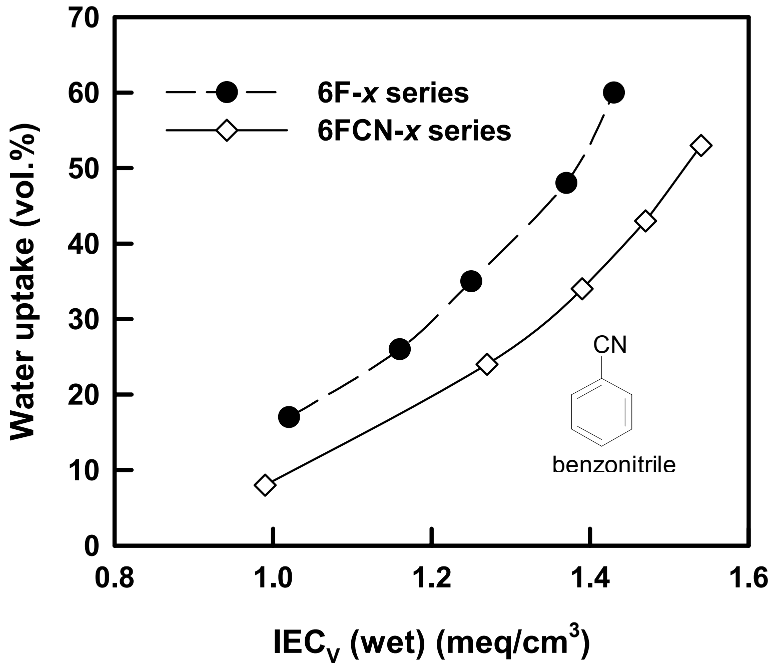


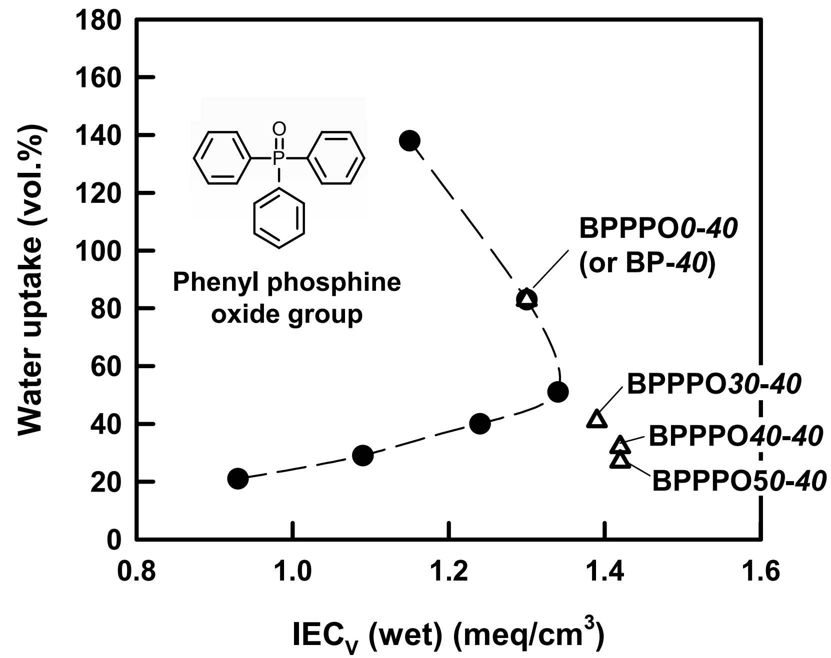
As fluorine content increased, water uptake decreased

Ref. Y.S. Kim and B.S. Pivovar, Polymer, web version available in March 6 (2006)

Effect of Polar Group Incorporation on Water Uptake

Membrane

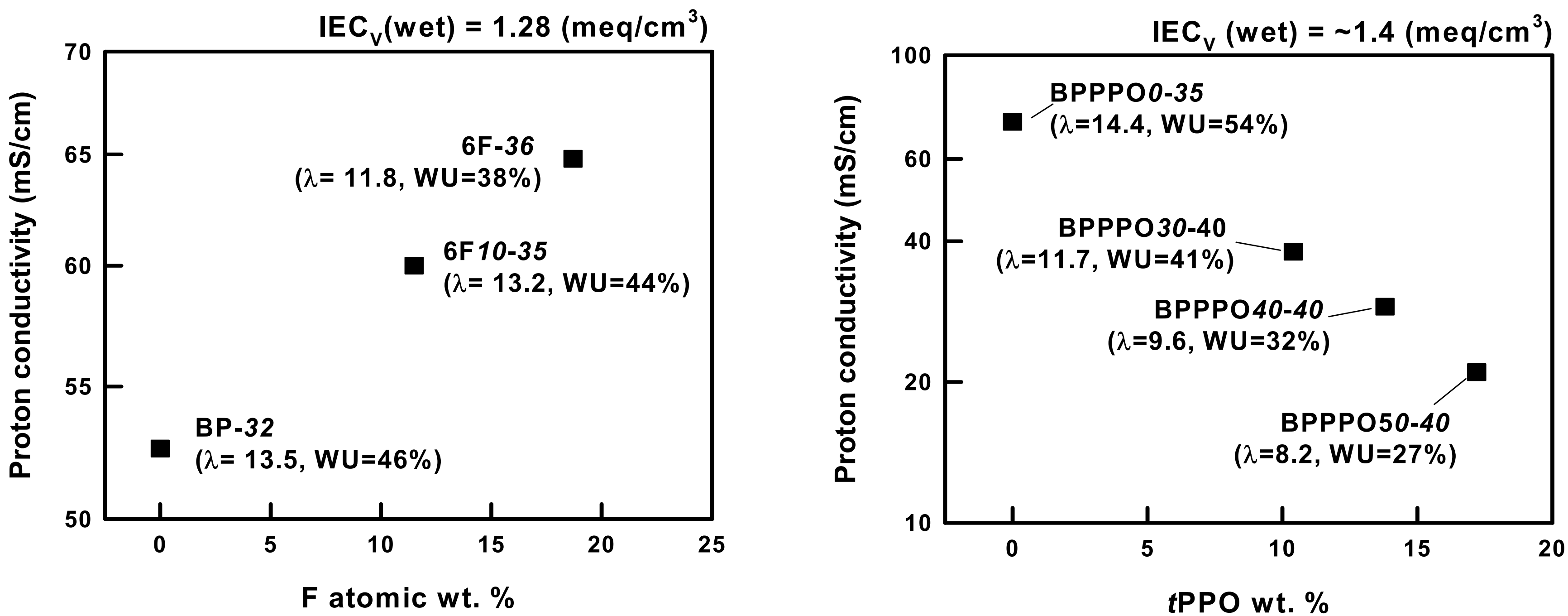




As polar group content increased, water uptake decreased

Ref. Y.S. Kim and B.S. Pivovar, Polymer, web version available in March 6 (2006)

Water Uptake vs. Proton Conductivity



Fluorine incorporation **– increased conductivity and lowered water uptake**
PPO incorporation **– decreased conductivity and water uptake**

Implications to water use in conduction!!!

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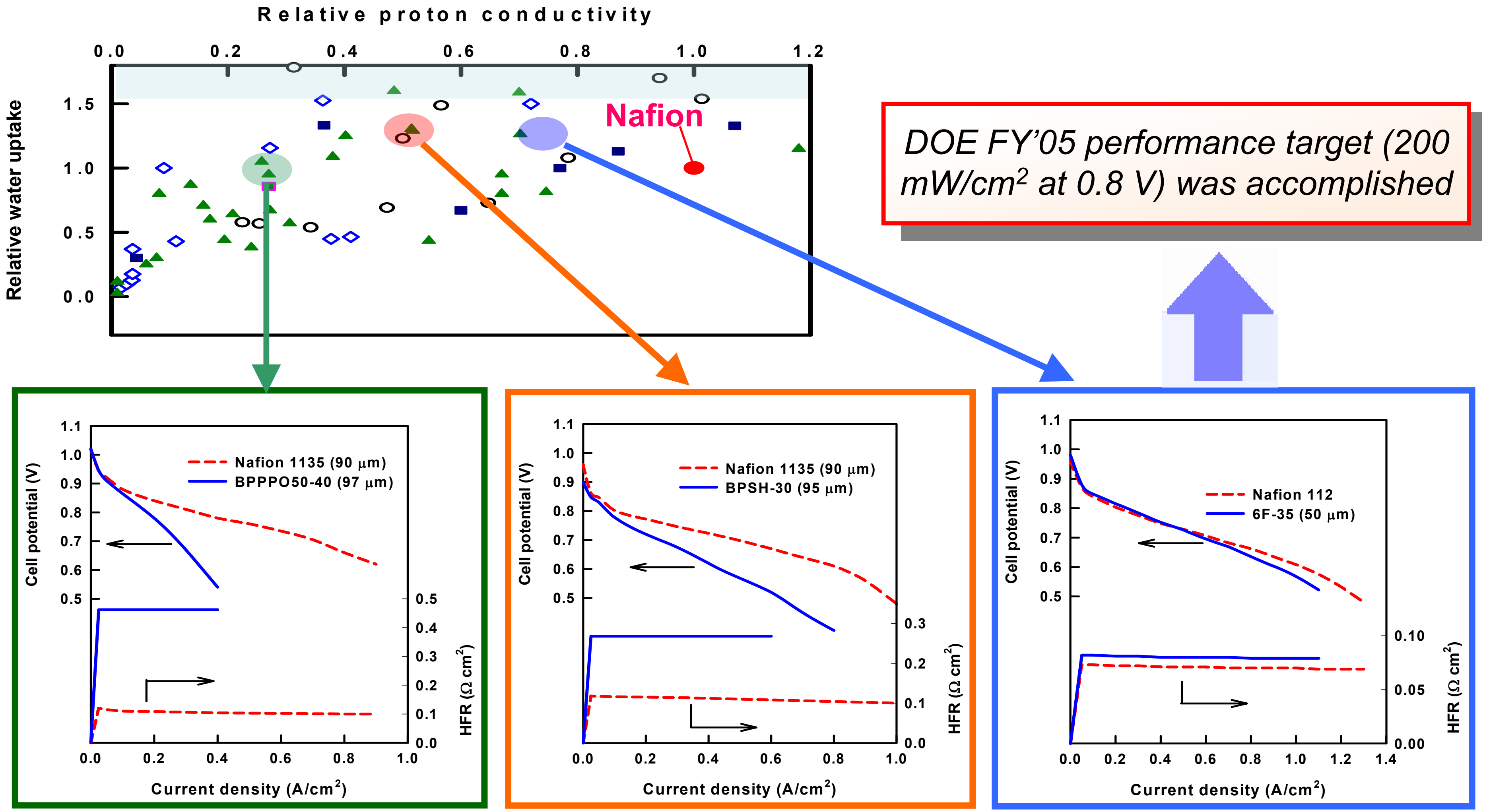
Ref. Y.S. Kim and B.S. Pivovar, Polymer, web version available in March 6 (2006)

Fuel Cell Performance of Non-Nafion Membranes

Membrane

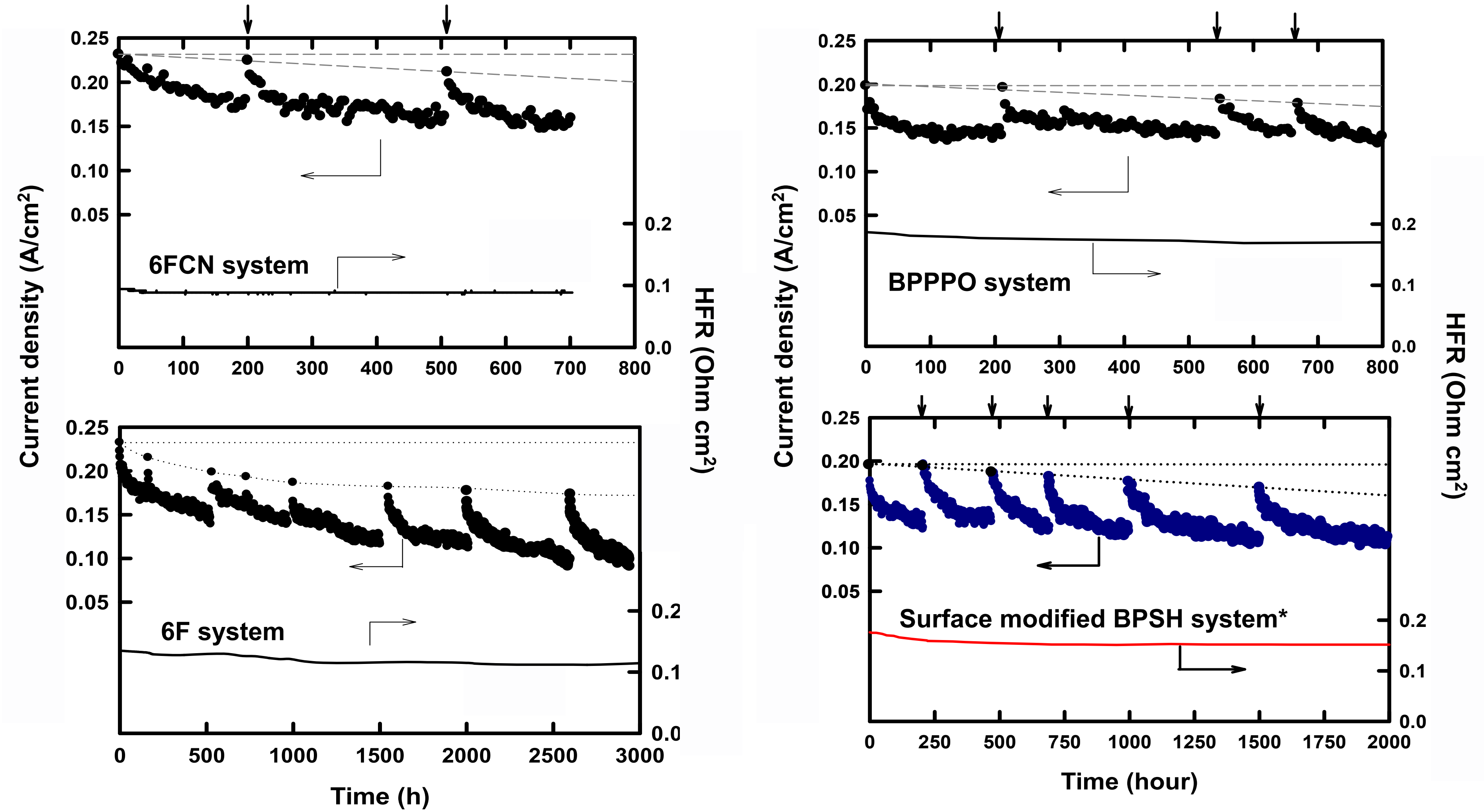


DOE FY'05 performance target (200 mW/cm² at 0.8 V) was accomplished

Catalyst: standard Pt/C (20%), 0.2 mg/cm²

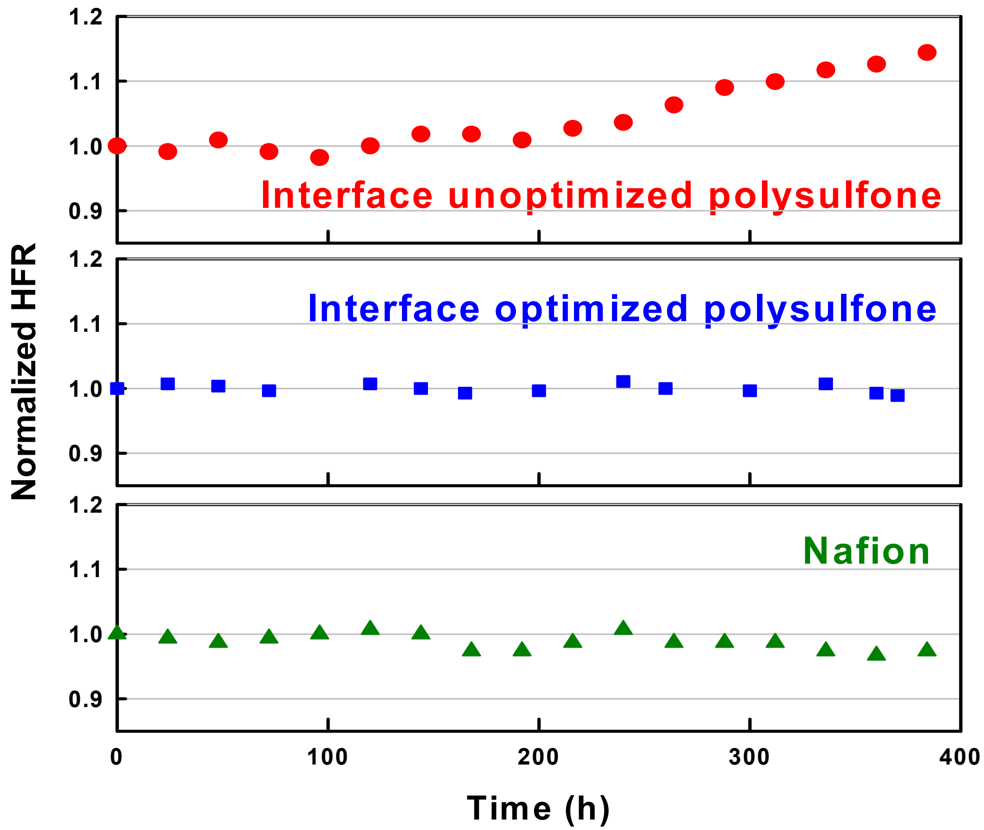
Durability

Long-Term Fuel Cell Performance of Interface Optimized Non-Nafion Membranes



0.5 V in DMFC mode

HFR Change during Start-Stop Testing



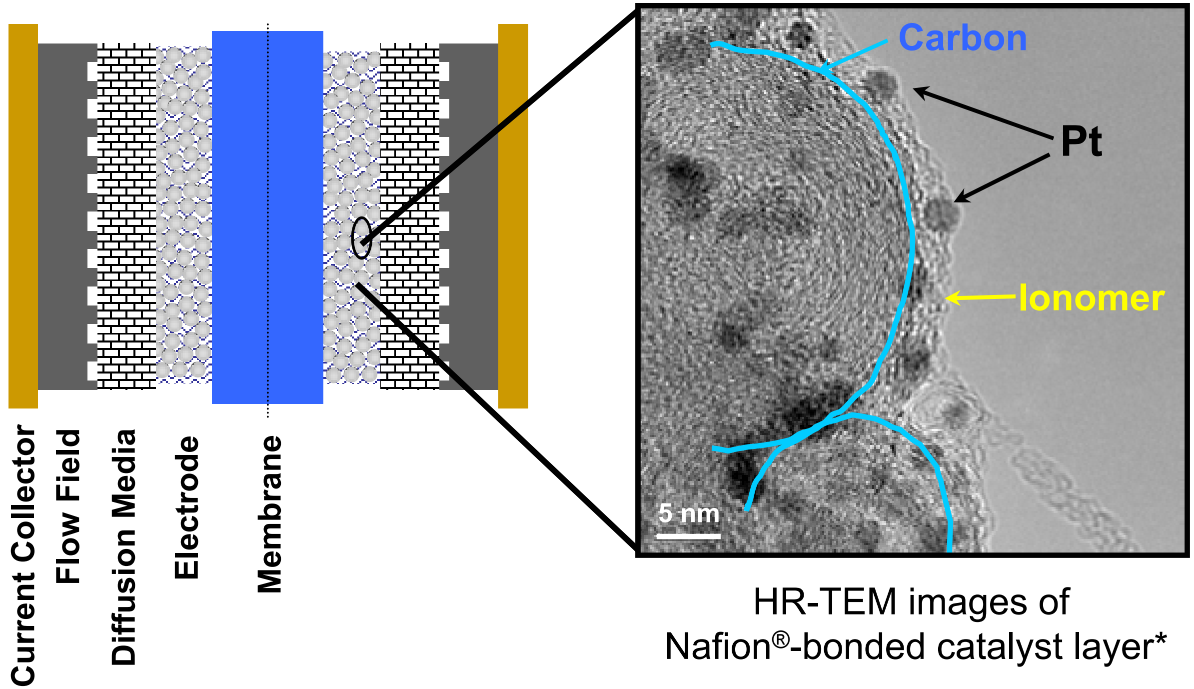
Life test conditions:

- Total duration: 400 h
- *No.* of start-stop cycling: 14~17
- Cell temperature: 80ºC
- Fully humidification
- 20 psig back pressure
- Constant voltage at 0.5 V

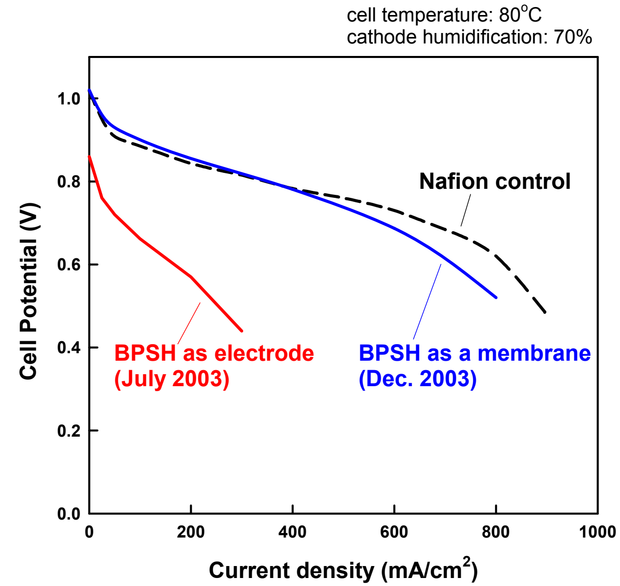
Interface optimized polysulfone membrane showed stable HFR during H_2/air fuel cells (> 400h) with start/stop cycling, while unoptimized polysulfone suffered from increasing HFR after 200 h.

Test for DOE FY '06 long-term performance target (2000h, <5% loss with cycling) will be completed by Sep. '06.

Electrode Ionomer Design



HR-TEM images of
Nafion®-bonded catalyst layer*



Nafion® Ionomer Binder

High reactant permeability (H_2, CH_3OH, O_2)
High proton conductivity
Chemically inert
Created porous structure
Optimized performance (only binder 15+ yrs)

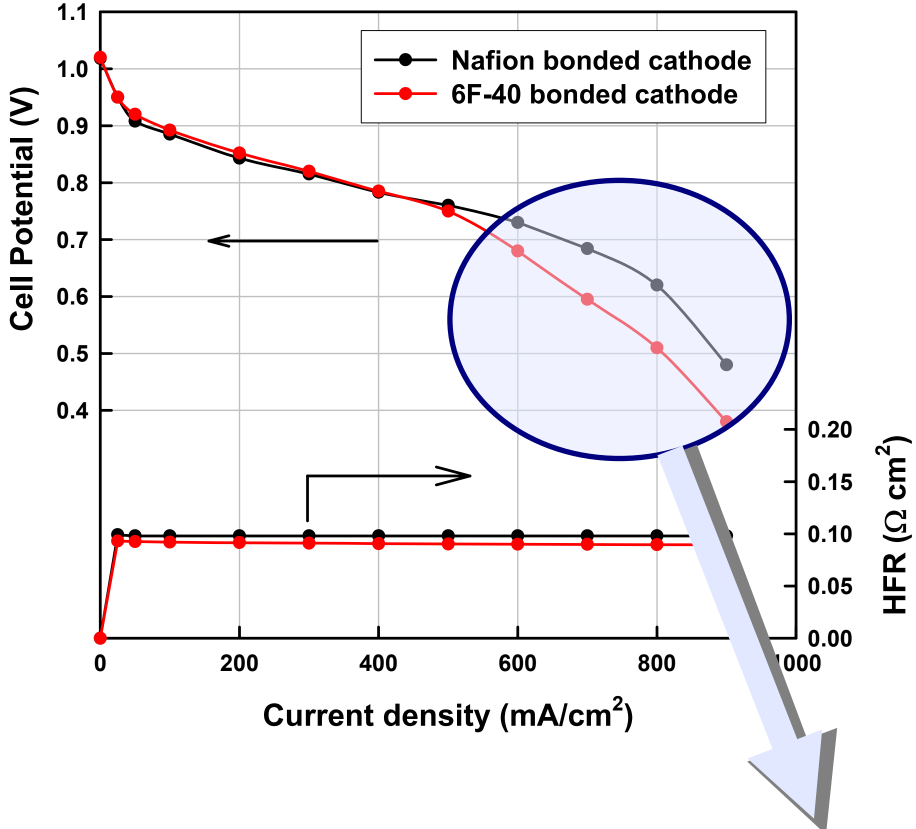
Non-Nafion Ionomer Binder

Good interfacial compatibility with non-Nafion membranes
Good high temperature stability
Tailored chemical structure
LANL started research from 2003

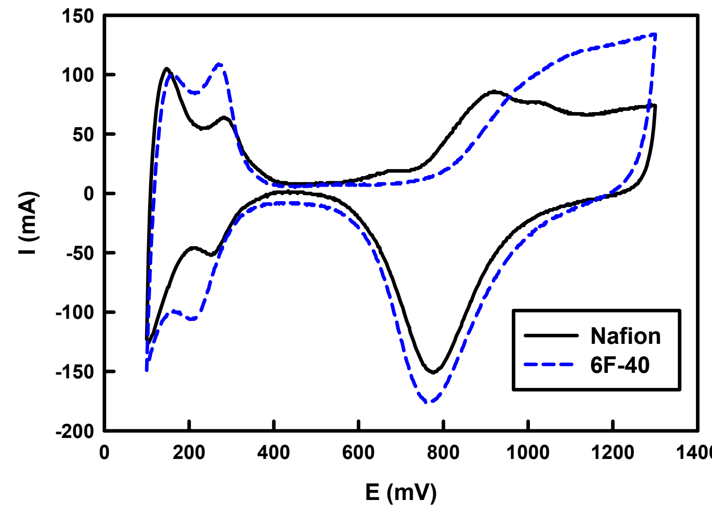
*Ref. Karren More, DOE Hydrogen and Fuel Cells Annual Report (2005)

Fuel Cell Performance of Non-Nafion Bonded Electrode from Alcohol Based Dispersion

cell temperature: 80 °C
cathode humidification: 70%



Catalyst loading: 6 mg/cm^2;
Membrane: Nafion 1135; scan rate 5 mV/sec



- Electrochemical active surface area 6F-40 electrode ≅ Nafion® electrode,
- Hydrogen oxidation and reduction occur at very similar rates with a noticeable difference in the hydrogen desorption and oxidation peak shapes.

Non-Nafion bonded cathode suffered from mass transfer limitation !!!

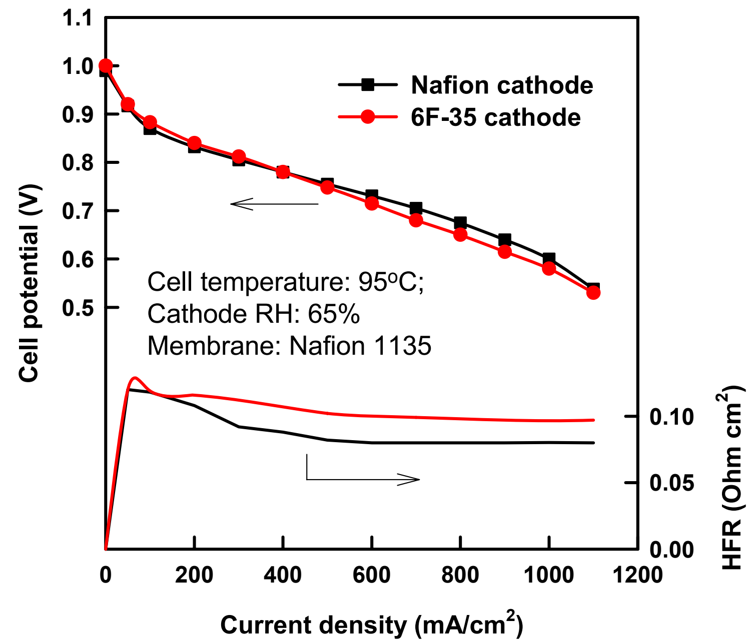
Electrode

Ionomer Optimization of Catalyst Layers

Variables	Fuel Cell Test	Optimum condition
Ionomer:catalyst ratio (vol.)	1:2, 1:1, 1.5:1, and 2:1	1.5:1
Degree of sulfonation (%)	20, 30, 35, 40, and 45	30 to 40
Backbone hydrophobicity	Wholly aromatic (BPSH), and Partially fluorinated (6F)	6F
Catalyst loading* (mg/cm^2)	2, 3, 4, 6, and 8	6

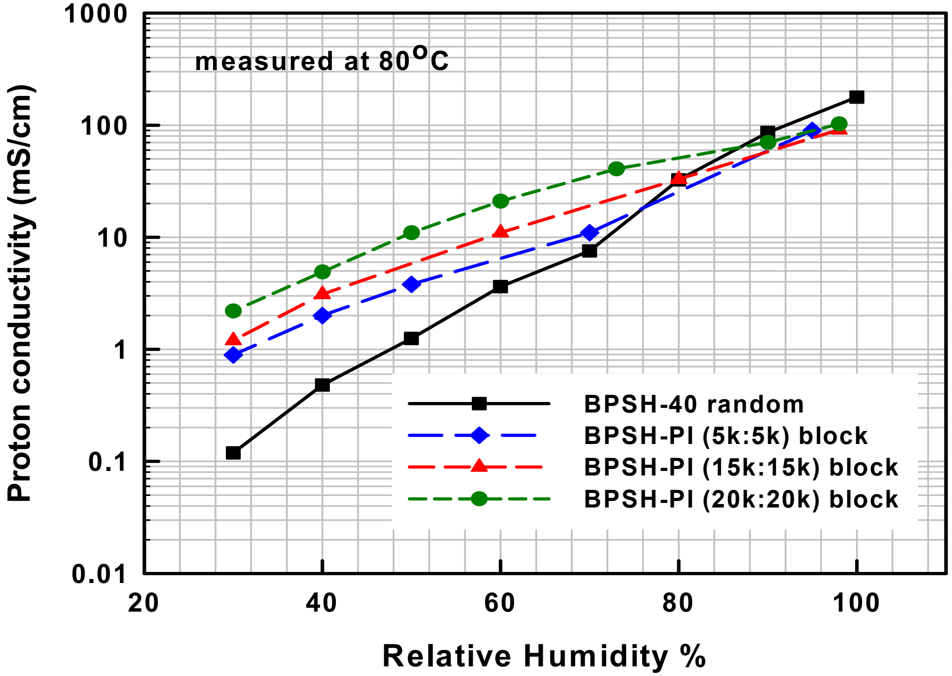
** Carbon supported catalyst may be different optimum loading, since cell performance depends on catalyst thickness.*

H_2/air performance of 6F-35 cathode

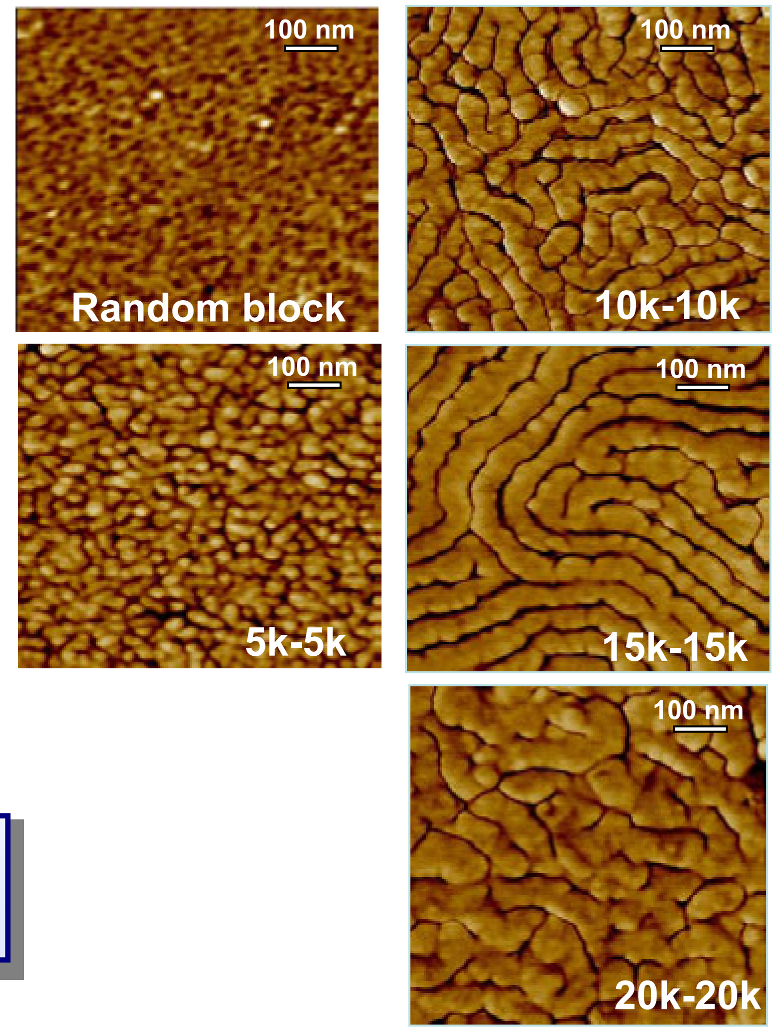


Cathode with optimized non-Nafion ionomer demonstrated 272 mW/cm^2 at 0.8 V which surpassed the DOE FY'05 target (200 mW/cm^2) and approached the FY'15 target (320 mW/cm^2)

Future Work
- Phase Separation



Effect of Block Length of BPSH-*b*-PI Copolymers on Morphology (by TM-AFM)



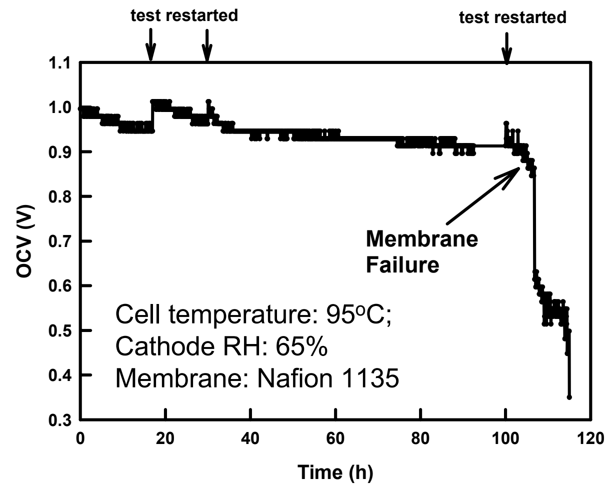
In order to reduce inlet water vapor partial pressure, morphology control is essential !!!

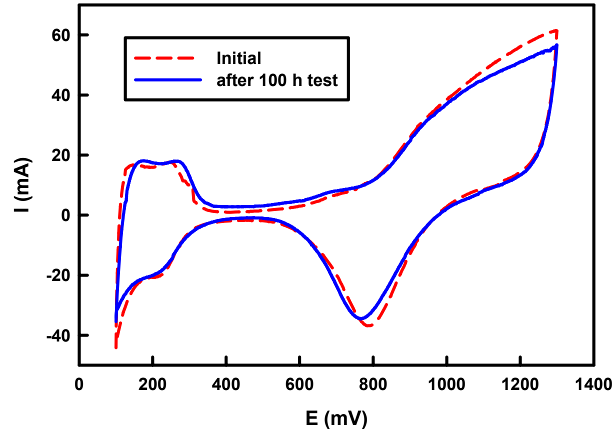
Collaboration with Prof. McGrath (VT)

Future Work
- Non-Nafion Ionomers

Preliminary stability results on 6F-35 bonded electrode

- **Stability test**
  - Long-term life test using non-Nafion membranes
  - Membrane-electrode interfacial study
- **Microelectrode study**
  - Catalyst ionomer interface
  - Transport properties
- **New Ionomer design**
  - Enhance hydrophobicity
  - Effect of specific interaction





6F-35 bonded electrode seems to be stable for at least 100 h under 95°C 65% RH OCV conditions

Project Summary

Relevance:

Develop low-cost, high performance and durable alternative membrane electrode assemblies

Approach:

From the critical membrane-electrode interfacial issue, advanced non-Nafion membranes were prepared and verified their durability under various fuel cell life conditions.

Technical Accomplishments and Progress:

Demonstrated excellent performing and durable Non-Nafion MEAs under standard fuel cell conditions. Demonstrated non-Nafion bonded electrode with promising catalyst activity.

Technology Transfer/Collaborations:

Active collaboration with academia (VT and Simon Fraser), government (AFRL) and industry (Hydrosize® Inc, Polymer Technology Group Inc). Collaborative discussions with CWRU, ORNL and NRC.

Proposed Future Research:

Develop new membranes/ionomers for high temperature, low RH. Continue membrane degradation studies.

Publications and Presentations

1. Yu Seung Kim and Bryan Pivovar, "Polymer Electrolyte Membranes for Direct Methanol Fuel Cells," in Advances in Fuel Cells (Ed. Tim S. Zhao), Elsevier, Oxford, 2006 to appear.
2. Yu Seung Kim, Brian Einsla, Mehmet Sankir, William Harrison, and Bryan S. Pivovar, "Structure-property-performance Relationships of Sulfonated Poly(Arylene Ether Sulfone)s as a Polymer Electrolyte for Fuel Cell Applications," *Polymer*, available March 6 (2006).
3. W.L. Harrison, Y.S. Kim, M. Hickner, and J.E. McGrath, "Poly(Arylene Ether Sulfone) Copolymers from Sulfonated Monomers Building Blocks: Synthesis, Characterization and Performance –A Review," *Fuel Cells*, 5, 2, 201-212 (2005).
4. B.S. Pivovar "An Overview of Electro-osmosis in Fuel Cell Polymer Electrolytes" *Polymer*, available March 22 (2006).
5. B.R. Einsla, Y.S. Kim, M.A. Hickner, Y.T. Hong, M.L. Hill, B.S.Pivovar, J.E. McGrath, "Sulfonated Naphtahlene dianhydride Based Polyimide Copolymers for Proton Exchange Membrane Fuel Cells" *J. Memb. Sci.* 15, 255, 141 (2005).
6. M. Sankir, Y.S. Kim, B.S. Pivovar, J.E. McGrath, "Proton Exchange Membrane for DMFC and H2/air Fuel Cells: Synthesis and Characterization of Partially fluorinated Disulfonated Poly(arylene ether benzonitrile) Copolymers" *J.Electrochem. Soc.* submitted Jan. (2006).
7. B.S. Pivovar, W.H. Smyrl, E.L. Cussler, "Nafion, Polystyrene Sulfonic Acid and Polybenzimidazole as Direct Methanol Fuel Cell Electrolytes" *J. Electrochem. Soc.* 152, A53 (2005)

Publications and Presentations (continue)

8. Utilizing Alternative Polymers in Fuel Cell Applications: Advantages, Difficulties, and Opportunities, Y.S. Kim, B.S. Pivovar, Pacific Polymer Conference IX, Dec. 11-14, Hawaii (2005)
9. Alternative Polymer Performance in Direct Methanol Fuel Cells, Y.S. Kim, B.S. Pivovar, 46th Battery Symposium, Nagoya, Japan, Nov. 16-18 (2005).
10. The Role of the Membrane-Electrode Interface on Fuel Cell Performance, Y.S. Kim, F. Garzon, R. Mukundan, B.S. Pivovar, 2005 Fuel Cell Seminar, Palm Springs, CA, Nov. 14-18 (2005)
11. Durability of Membrane-Electrode Interface under DMFC Operating Conditions, Y. Kim, B. Pivovar, 208th Meeting of the Electrochemical Society, Oct. 16-21 (2005).
12. Proton Exchange Membrane Fuel Cells: II. Synthesis and Characerization of Partially Fluorinated Disulfonated Poly (Arylene Ether Benzonitrile) Copolymers, M. Sankir, Y. S. Kim, W. L. Harrison, A. S. Badami, and J. E. McGrath, Division of Fuel Chemistry, 231th ACS National Meeting, Washington DC, August 22-26 (2005).
13. 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)
14. Disulfonated Poly(Arylene Ether Benzonitrile) Copolymers (PAEB) for Proton Exchange Membrane Fuel Cells (PEMFC), M. Sankir, Y. S. Kim, J. E. McGrath, Advances in Materials for Proton Exchange Membrane Fuel Cell Systems 2005, Asilomar Conference Grounds, Pacific Grove, CA, Feb. 20-23 (2005)

Responses to Previous Year Reviewers' Comments

- **Should not consider the electrode as a fixed entity**
  - We have initiated electrode study for adapting to the Non-Nafion membranes last years
- **Lack of interaction with industrial partners**
  - Pilot plant scale production of membrane synthesis is under way at Hydrosize® Inc and Polymer Technology Group Inc.
- **No clear pathway to meet stabilization requirement and durability targets**
  - We have solved membrane-electrode interfacial degradation issues by reducing membrane water uptake. Other performance degradation issues are under investigation. Transport properties seem to play a critical role in performance stability.
- **Need cost projection**
  - Monomers in sulfonated polysulfones processing cost are generally much cheaper than perfluorinated Nafion® benchmark. Exact cost analysis is out of our research scope.
- **Need publication in order to inform fuel cell community of work**
  - We presented our results in the ECS annual meeting. Articles in peer review journal have been published or will appear in near future.