



Improved, Low-Cost, Durable Fuel Cell Membranes

2010 Hydrogen Program Annual Review

James Goldbach, David Mountz, Tao Zhang,
Wensheng He, and Chris Roger

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Project ID # FC059

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Overview (DE-FG36-07GO17008)

Timeline

- Start Date: Sept. 30, 2007
- End Date: Sept. 30, 2010
- % Complete: 90%

Budget

- Total Funding
 - DOE: \$6,278k
 - Partners: \$1,569k
- Funding Received
 - FY2007: \$0
 - FY2008: \$2,369k
 - FY2009: \$1,932k
 - FY2010: \$226k
 - Through (02/28/2010)

Barriers Addressed

- A) Durability
- B) Cost

Partners

- Johnson Matthey Fuel Cells
- Virginia Tech
- Oak Ridge National Lab
- University of Hawai'i
 - Hawai'i Natural Energy Institute(HNEI)

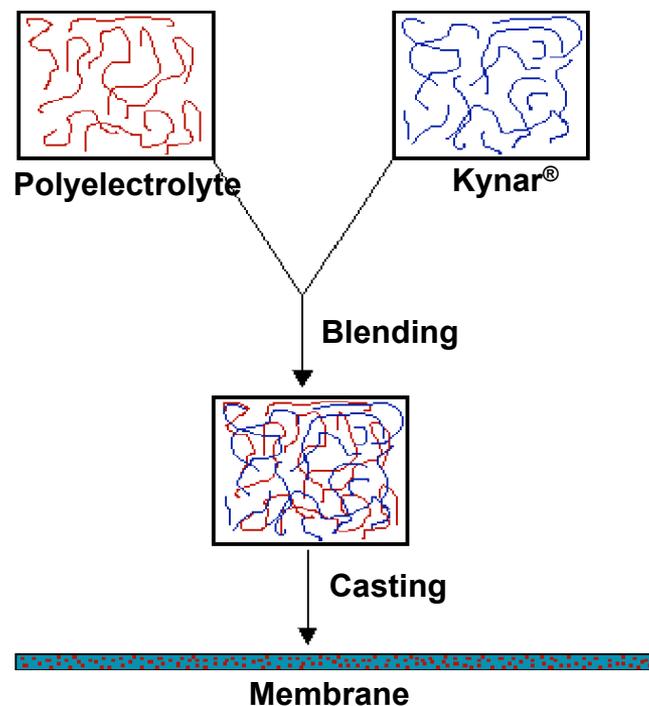
Relevance

● Objectives

- To develop a membrane capable of operating at 80°C at low relative humidity (25-50%).
- To develop a membrane capable of operating at temperatures up to 120°C and ultra-low relative humidity of inlet gases (< 1.5 kPa).
- To elucidate ionomer and membrane failure and degradation mechanisms via ex-situ and in-situ accelerated testing.
 - Develop mitigation strategies for any identified degradation mechanism.
- Use commercially-available matrix materials as low-cost approach

Approach

- **Polymer blend**
 - Decouples conductivity from other requirements
 - Kynar® PVDF
 - Chemical and electrochemical stability
 - Mechanical strength
 - Polyelectrolyte
 - H⁺ conduction and water uptake
- **Robust blending process**
 - Compatible with various polyelectrolytes
 - Morphology and physical property control
- **Lower cost approach compared to PFSA**
 - Kynar® PVDF - commercial product
 - Polyelectrolyte – hydrocarbon based
- **M43 – highly sulfonated polyelectrolyte**
 - Maximize conductivity at high RH



Approach

Milestone	Progress Note	Comments
Improve low RH performance at 80°C	- M70 membranes show improved ex- and <i>in-situ</i> performance vs. M43	Validated novel disulfonated monomer approach to low RH conductivity improvement
Optimize M70 membrane performance (<i>ex-situ</i> and <i>in-situ</i>)	- Ex-situ conductivity vs. RH and <i>in-situ</i> MEA performance remain slightly lower than Nafion®	Much improved vs. M43 generation
Produce pilot quantities of M70	- Synthesis scale-up completed - Pilot membrane trial conducted	Produced >500ft ² of high-quality membrane
Improve thermal stability to 120°C	- Validated BPSH blending with PVDF - Validated cross-linking strategy for BPSH materials in PVDF blends	Using arylene polyelectrolytes for improved temp. stability
Improve low RH performance at 120°C	- Validate BPSH-100 blending and stability	Using BPSH-100 to improve low RH properties of blends

Technical Accomplishments and Progress

- M70 blending process optimization

Polymer Blend
EW ~ 400 - 600



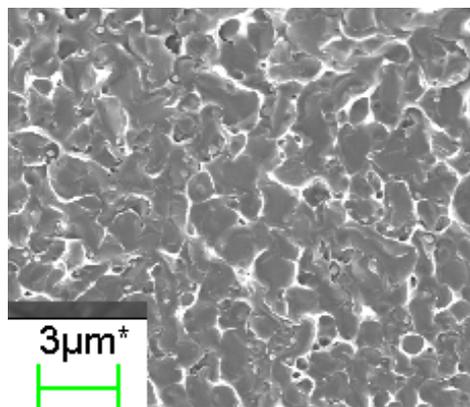
Process 'A'



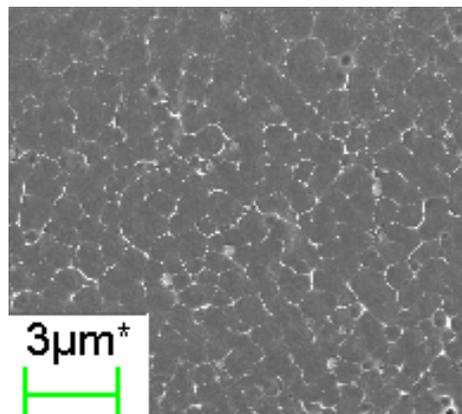
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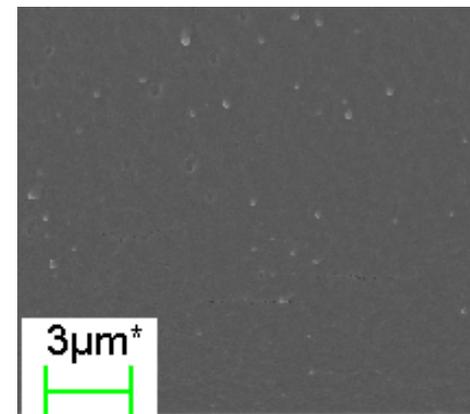
Process 'C'



55±9 mS/cm



63±3 mS/cm



186±17 mS/cm

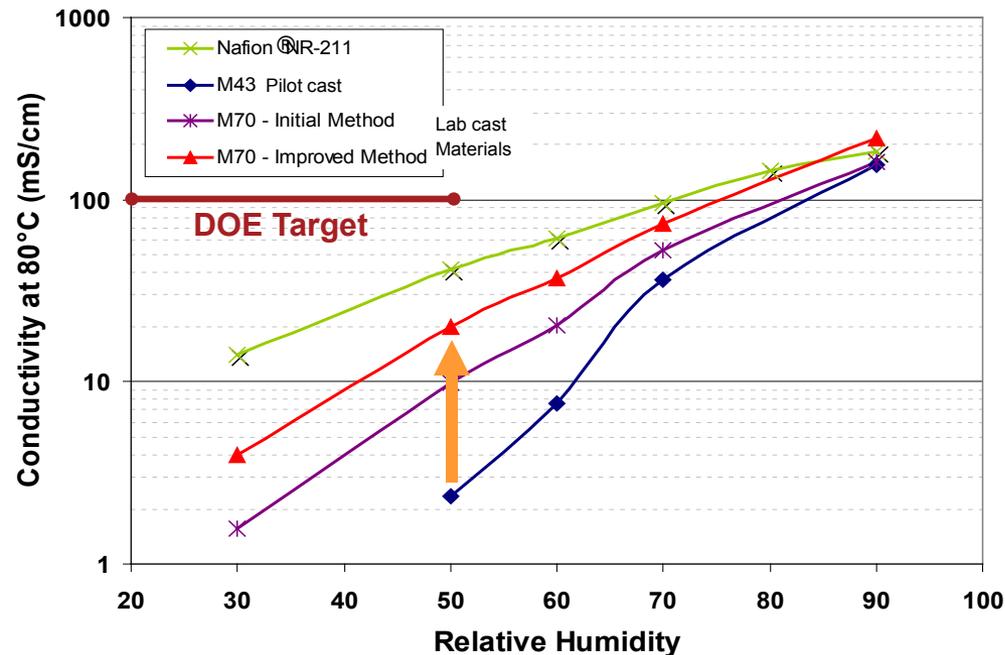
- Membrane transparency → finer morphology → higher conductivity



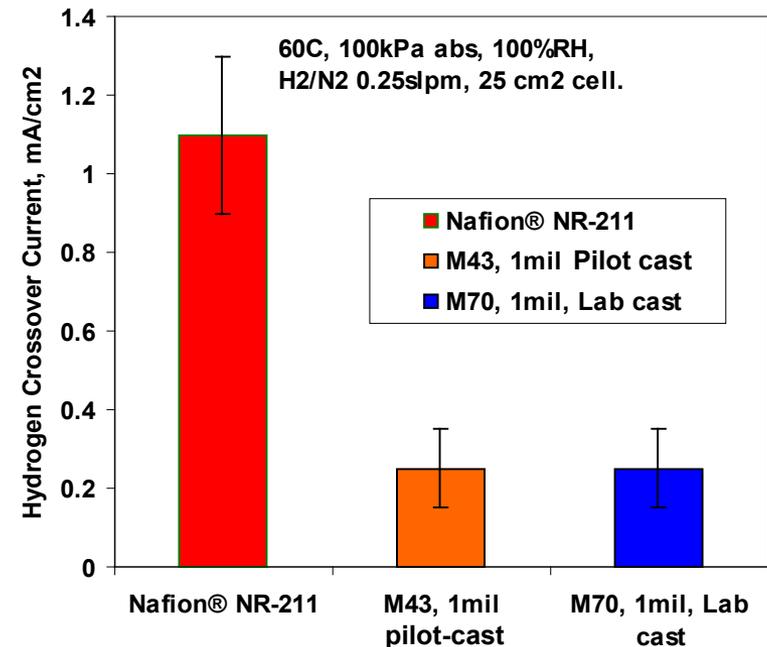
*Conductivities measured @ 70 °C, liquid H₂O

Technical Accomplishments and Progress

- M70 shows a significant increase in conductivity vs. M43
- Maintains excellent resistance to hydrogen cross-over



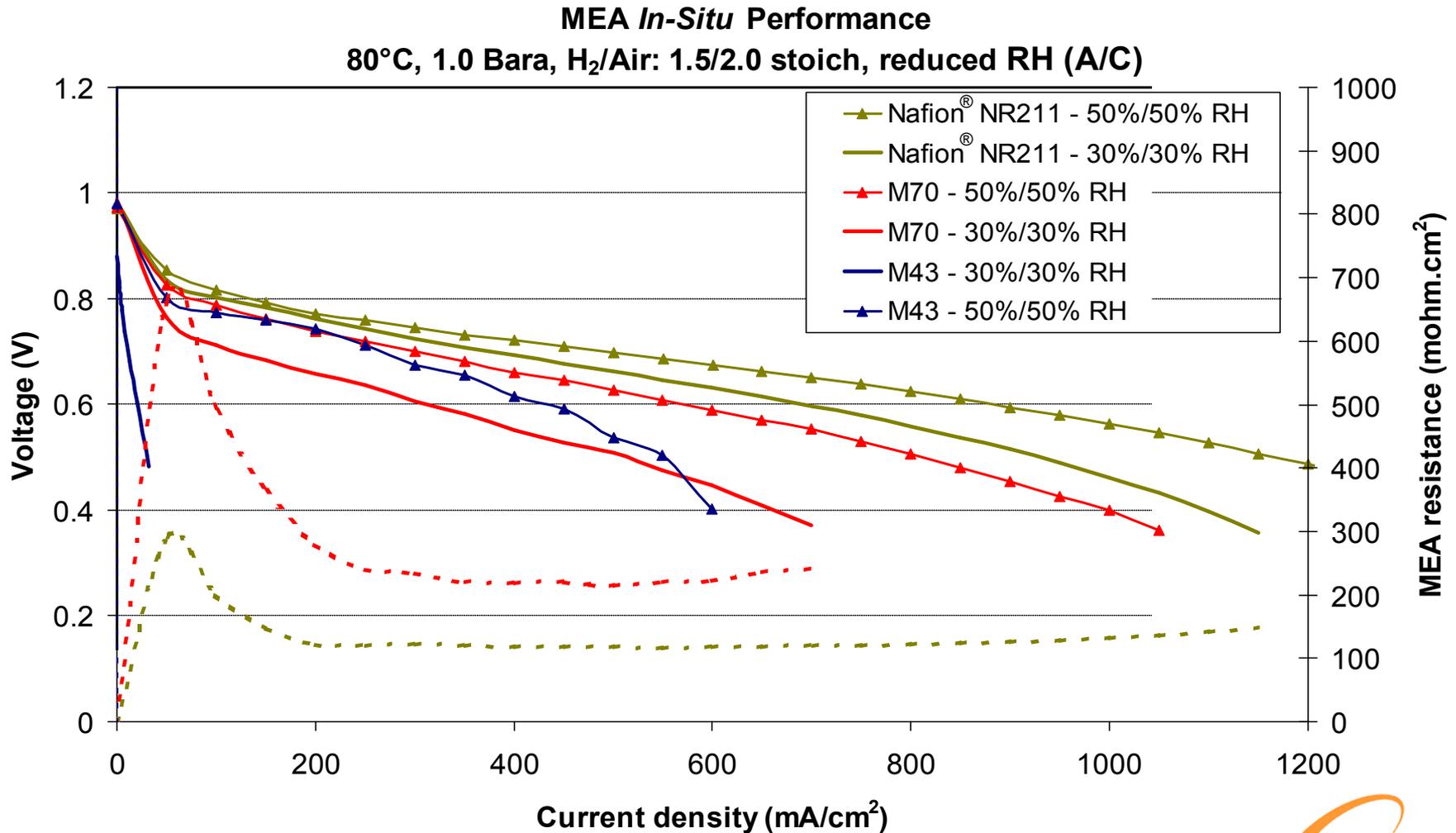
Order-of-magnitude 80°C conductivity improvement vs. previous generation



~75% less H₂ cross-over vs. Nafion® at equivalent thickness

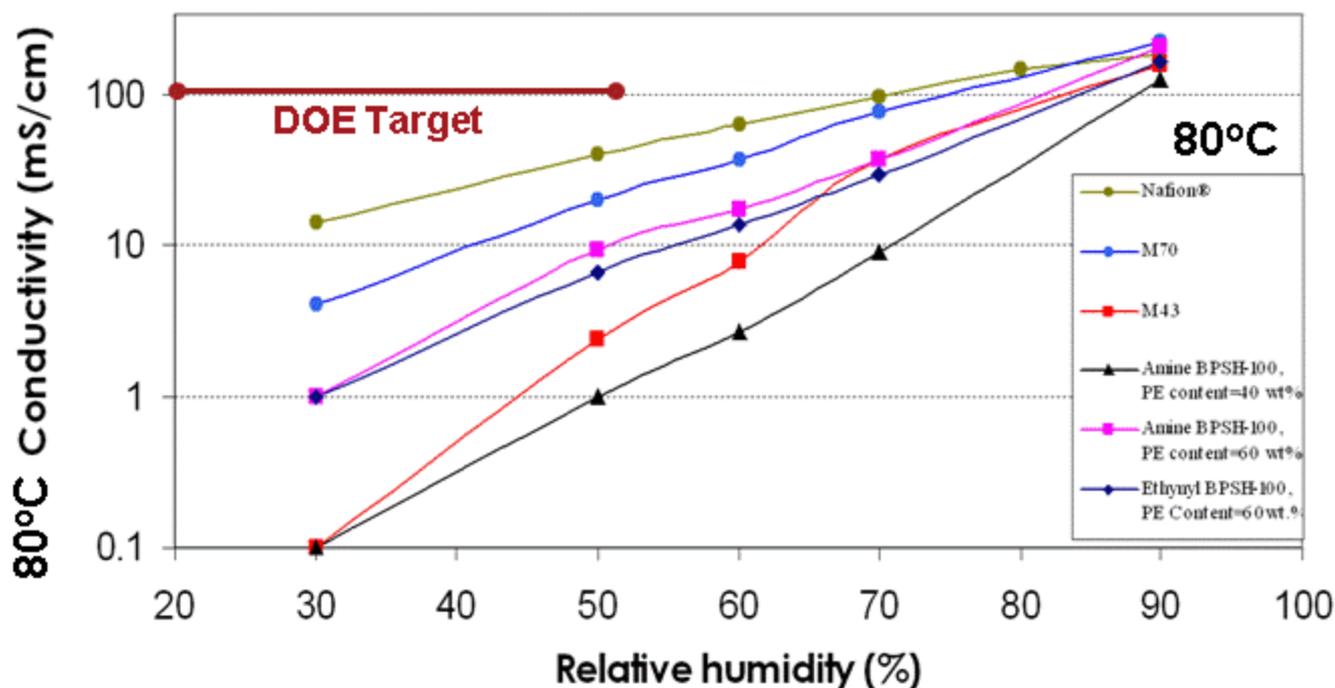
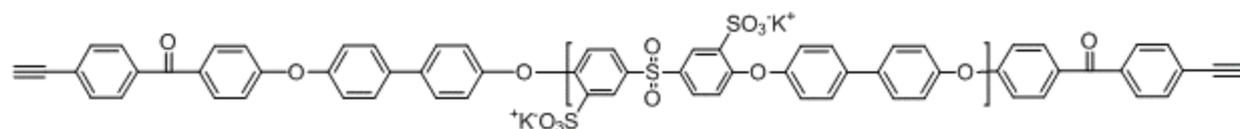
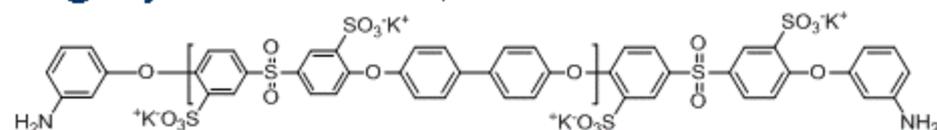
Technical Accomplishments and Progress

- M70 MEA performance – REDUCED HUMIDITY conditions



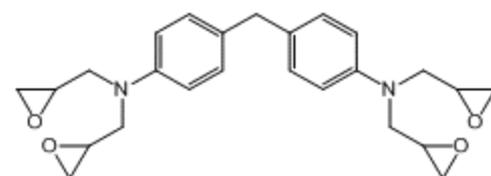
Collaboration

- Increase operating T of PVDF/PE blends – maintain RH conductivity
- Highly sulfonated, cross-linkable BPS-100



Ethynyl-terminated BPS-100

Amines reacted with tetraepoxide cross-linking agent



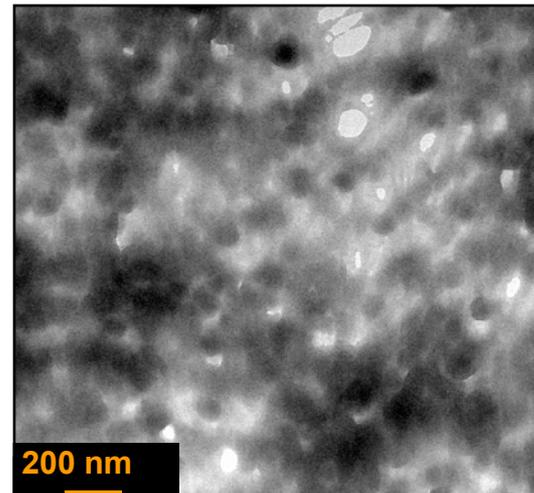
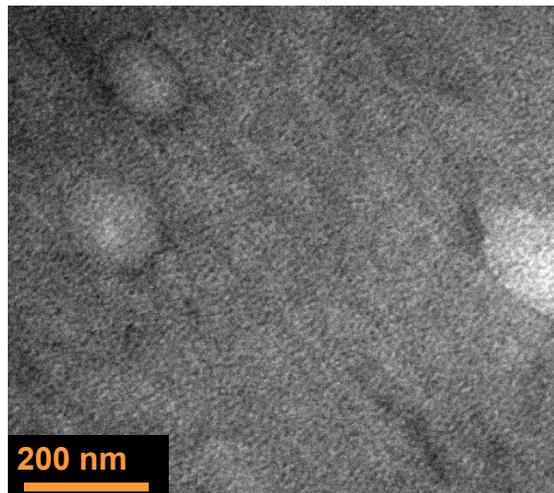
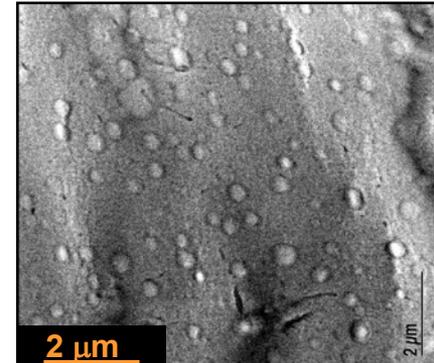
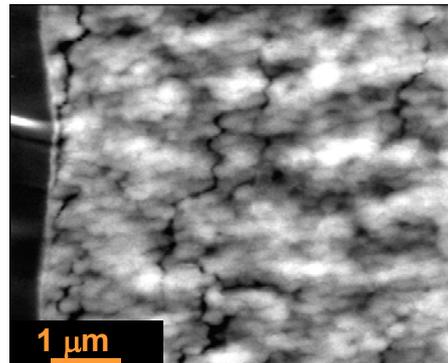
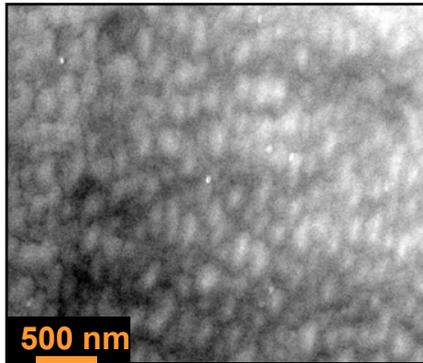
[2+2] cycloaddition / radical intermediate thermal cross-linking end-groups

Collaboration



OAK RIDGE NATIONAL LABORATORY

Managed by UT-Battelle for the Department of Energy



TEM characterization* of varying polyelectrolyte types blended with PVDF
Membranes with conductivities > 100 mS/cm



Proposed Future Work

- M70 membranes

- Continuing membrane optimization
- Characterize pilot-produced membranes for performance vs. RH
- Continuing membrane *ex-* and *in-situ* durability and performance testing
- MEA OCV and RH cycling durability testing

- BPSH/Kynar[®] PVDF blend membranes

- Optimize BPSH-100 (cross-linkable) blending with PVDF
- Validate efficient BPSH-100 cross-linking
- BPSH-100 / Kynar[®] PVDF blend *ex-* and *in-situ* durability and performance testing

- Process development

- Streamline membrane blending process to position for further scale-up
- Correlate process changes to structure properties and performance

Summary

● M70

- Novel monomer and polyelectrolyte synthesized
- Multi-kilo scale up achieved; membrane produced on pilot scale
- PVDF blending and optimization completed
- Successfully produced blended membranes
- Encouraging *ex-situ* and *in-situ* low RH performance
- Validated multi-acid route for low RH performance
- Process development / scale-up continuing

● BPS100

- Relatively low conductivity vs. RH for PVDF blends even at high BPS100 loadings
- Continue testing BPS materials with even higher acid contents

● Acknowledgements

● US DOE

- Nancy Garland
- Kathi Epping
- Reg Tyler
- Tom Benjamin

● Johnson Matthey Fuel Cells

- Rachel O'Malley, Graham Hards, Jonathan Sharman

● Oak Ridge National Laboratory

- Karren More, Harry Meyer, Shawn Reeves

● Virginia Tech: Profs. Jim McGrath, Lou Madsen

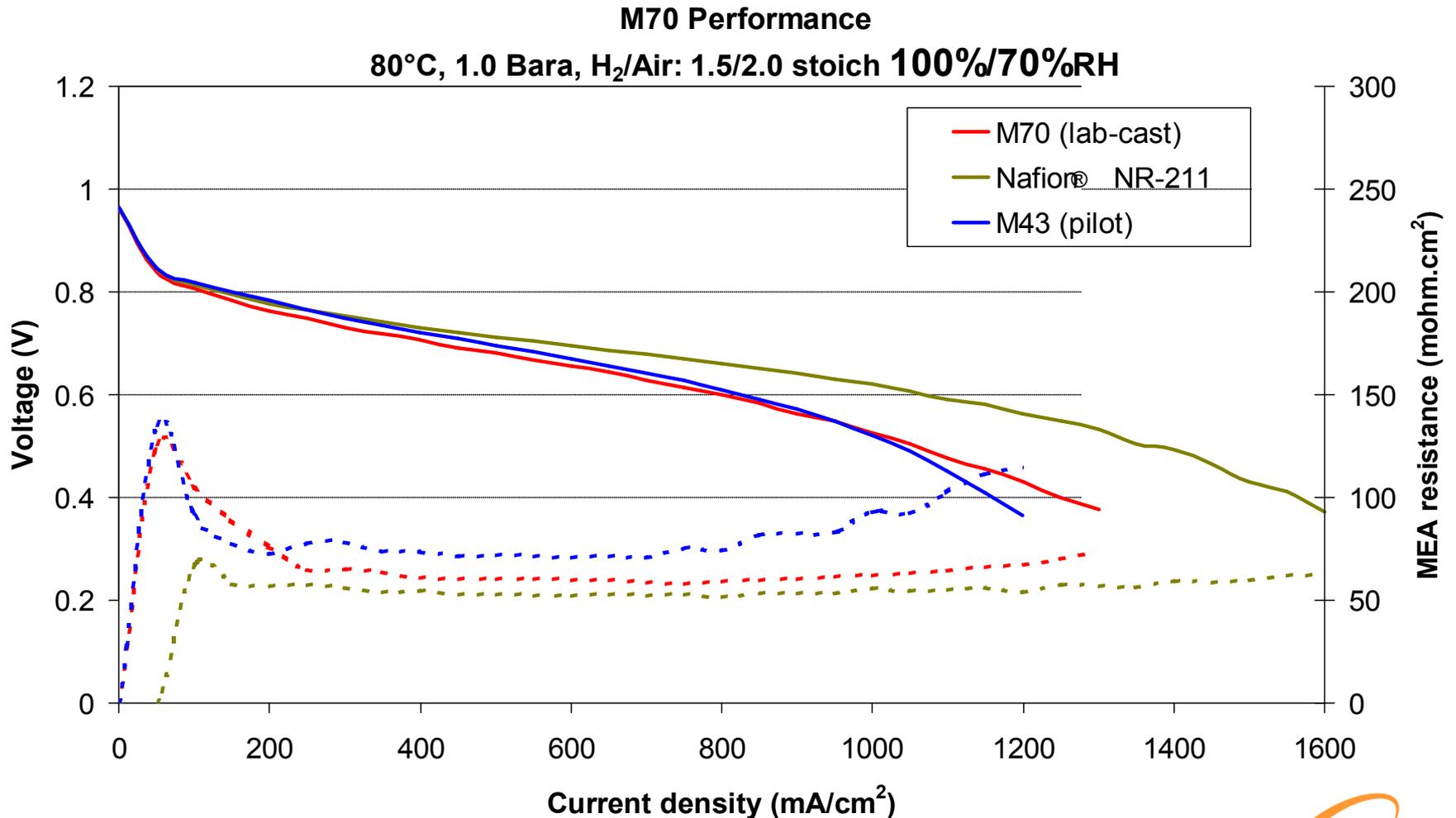




Supplemental Slides

Technical Accomplishments and Progress

- M70 MEA performance – HIGH HUMIDITY condition

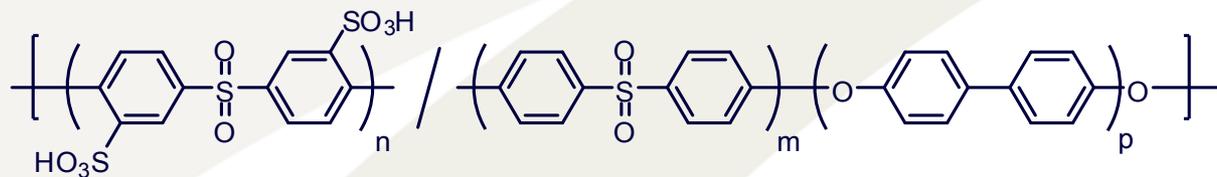


Membrane Chemistry: M70

- EW of M43 is ~800, this is too high.
 - Membrane densities: 2.0 for Nafion[®] and 1.4 for M43
 - Sulfonic acid molality is 2.2 mol/l for Nafion[®] vs. 1.75 mol/l for M43.
 - The distance between two sulfonic acid groups is larger for M43.
 - (0.8nm has been estimated for Nafion[®])
- Solution: use of multi-sulfonated monomers for the polyelectrolyte to drive the EW down.
 - Concurrently increasing the local concentration of acid groups
- M43 EW ~ 800 g/mol H⁺
- M70 membrane EW 400-600 g/mol H⁺

BPSH/Kynar[®] Blend Membranes

- Collaborative effort – J. McGrath (VT)



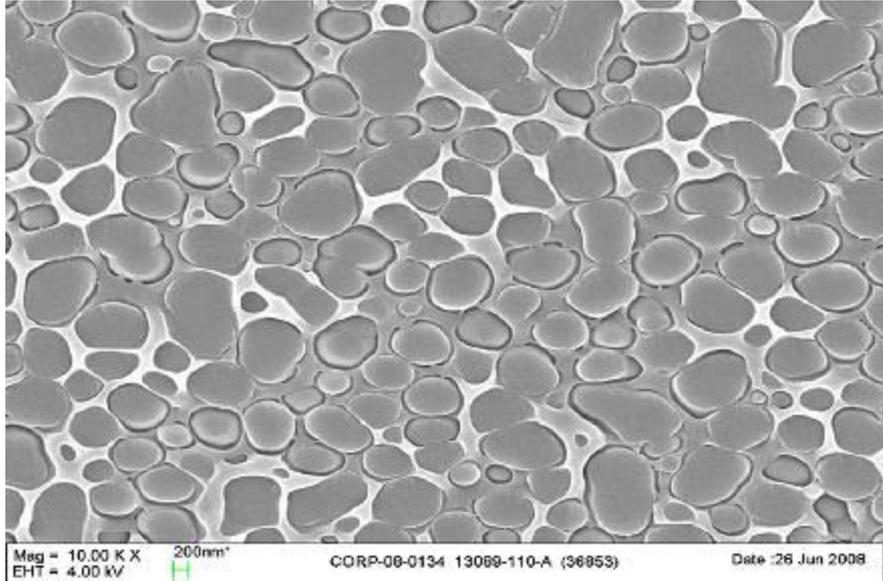
+ Kynar[®] PVDF

Blending BPSH-60 with Kynar®

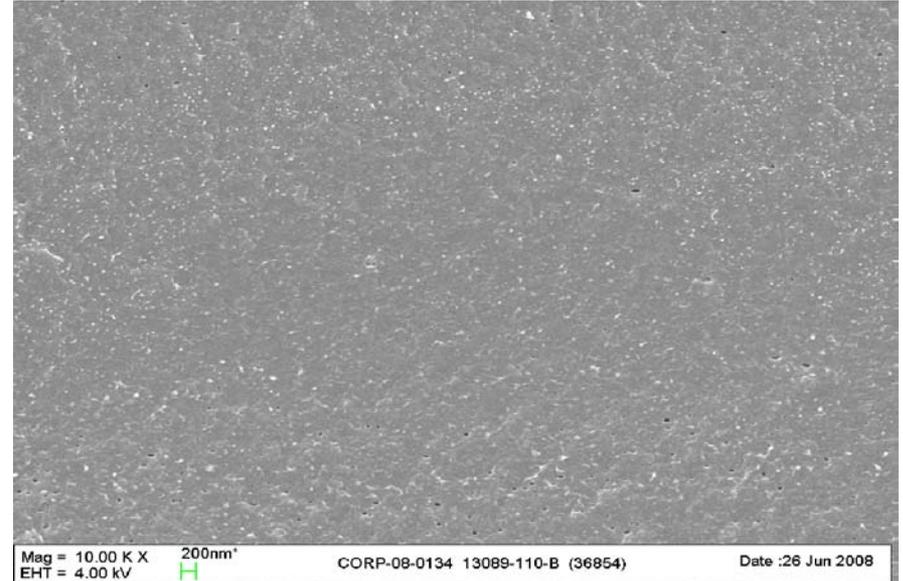
- Membrane solution gelling required process optimization
 - Moisture level in BPSH polyelectrolytes caused some uncertainty
 - Problem addressed by rigorously drying the BPSH before use.
- Narrow window for processing to generate well-blended membranes without gellation of the formulations.

Kynar®/BPSH-60 wt ratio	Process	Membrane Description
40/60	A	Opaque
40/60	B	Transparent
40/60	C	Formulation gelled

BPSH-60/Kynar[®] Blend Membranes - SEM

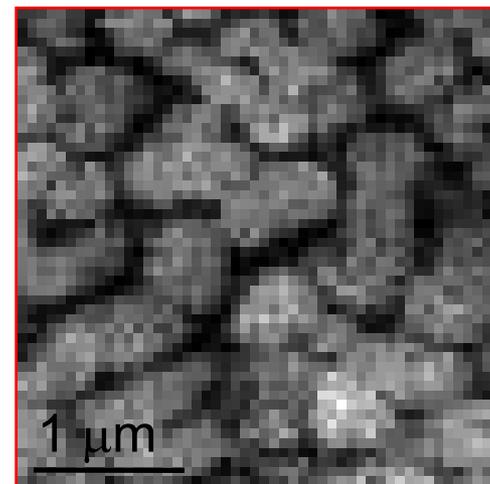
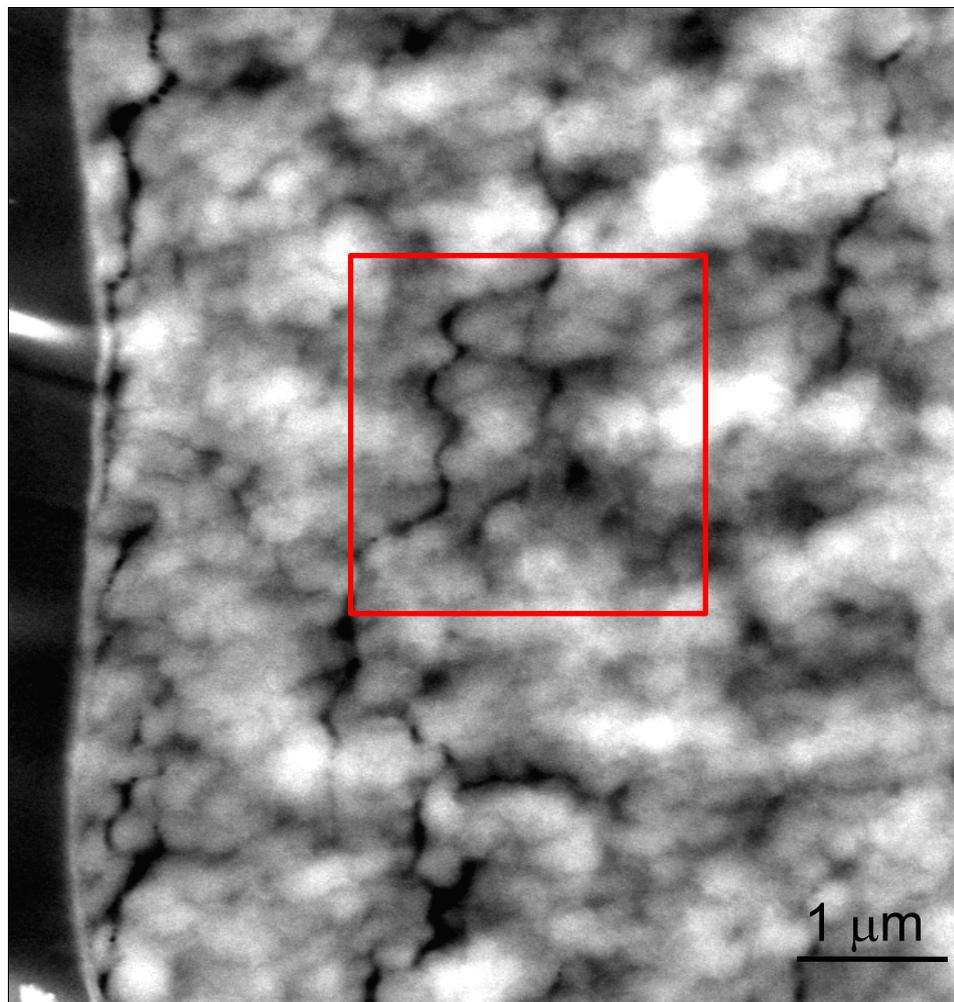


Kynar[®]/BPSH-60 wt ratio
60/40 Process A

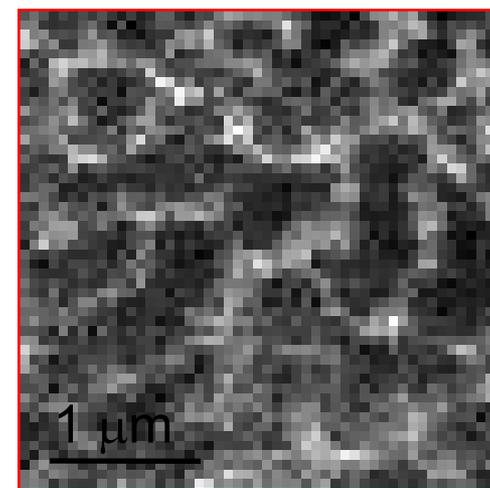


Kynar[®]/BPSH-60 wt ratio
60/40 Process B

BPSH-60 / Kynar[®] Blend Membrane TEM



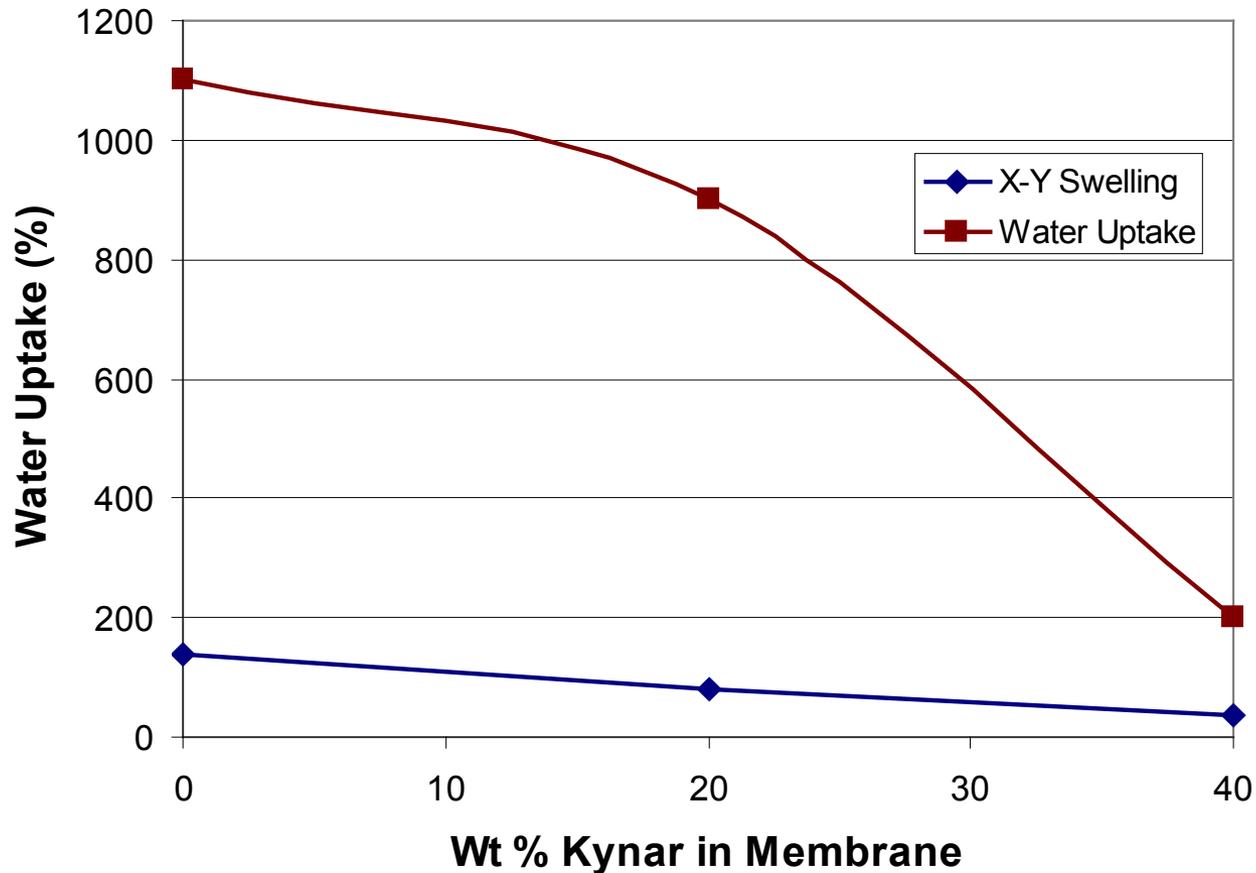
S map



F map

S and F form separate
phases F/S=10

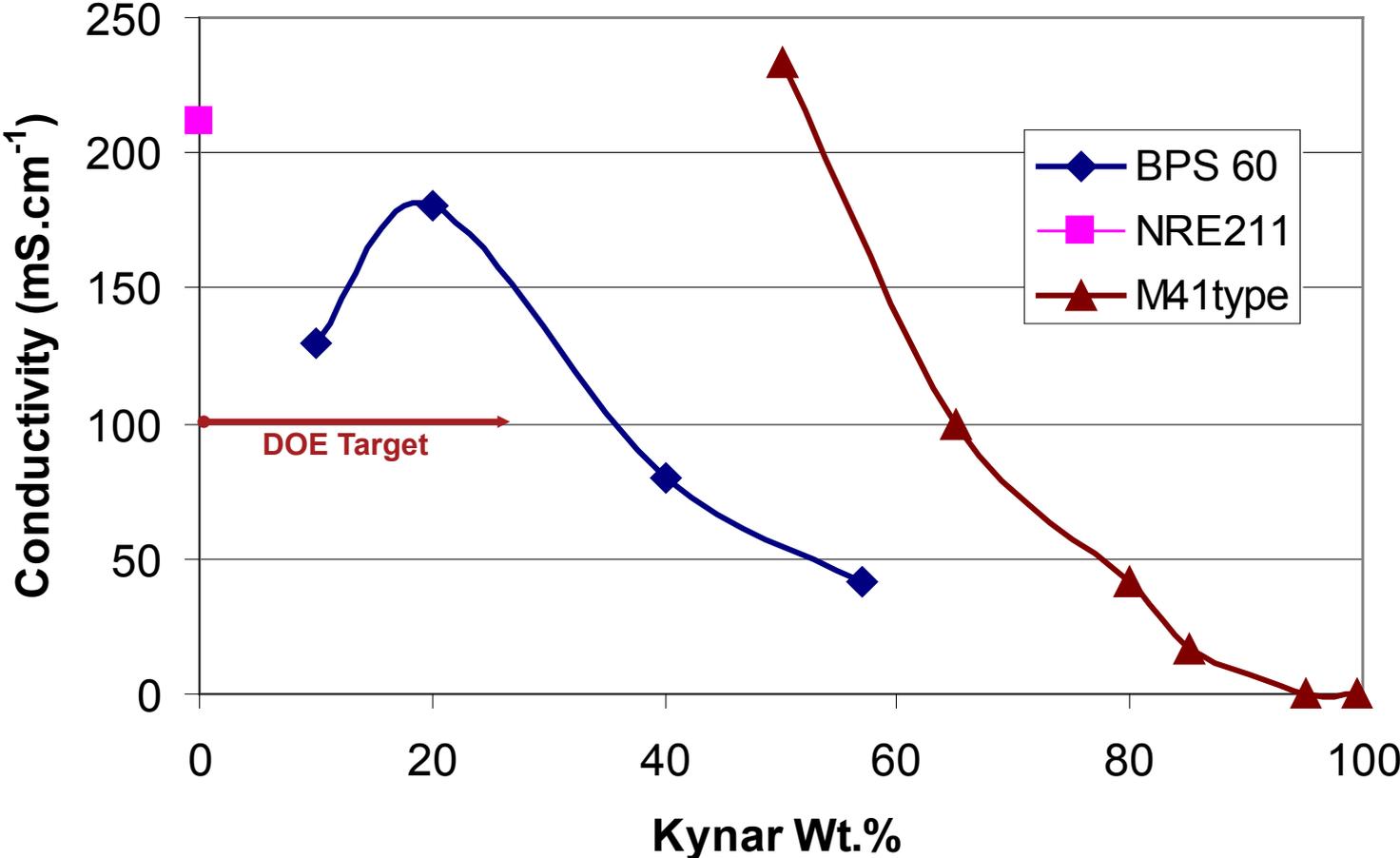
BPSH-60/Kynar[®] Membranes – Water Uptake



- Water uptake increases substantially with higher loading of BPSH-60
- Swelling greatly reduced with Kynar[®] blending

BPSH-60/Kynar[®] Membranes - Conductivity

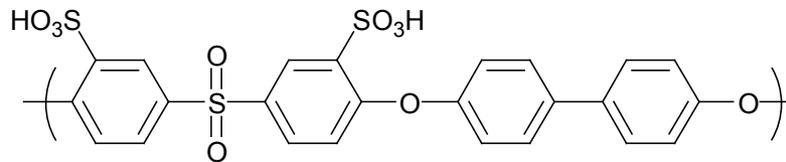
90% RH conductivity



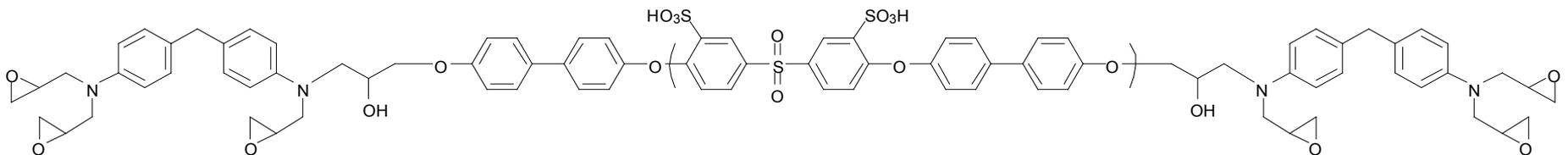
BPSH-100 Copolymer Blends

- **Kynar® / BPSH-100 Blends**

- Rationale: Increase sulfonate content to increase low RH conductivity
- Main issue: BPSH-100 is water-soluble and must be immobilized
- BPSH-100
 - 100% of possible disulfonated monomer
 - 50 mol.-% of overall monomer units



- **BPSH-100 Cross-linkable**



Paul, M., McGrath, J.E., et.al.; Polymer, 49, 2008, 2243-2252.

BPSH Blending Conclusions / Ongoing Work

- BPS-60/Kynar[®] narrow processing window
 - Moderate proton conductivity
 - Interesting swelling / mechanical characteristics
 - Observed hole formation upon boiling water treatment
 - Likely due to BPS-60 leaching
- Transition to a cross-linkable, higher conductivity system
 - BPSH-100 cross-linkable
 - Improve processing window
 - Reduce hole formation from leaching

NMR Diffusion Studies of M70(A/B) and M143 Membranes

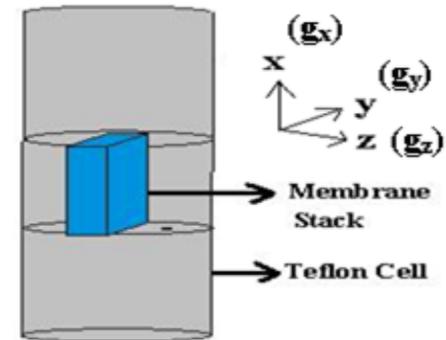
Prof. Lou Madsen & Jianbo Hou

6/10/09

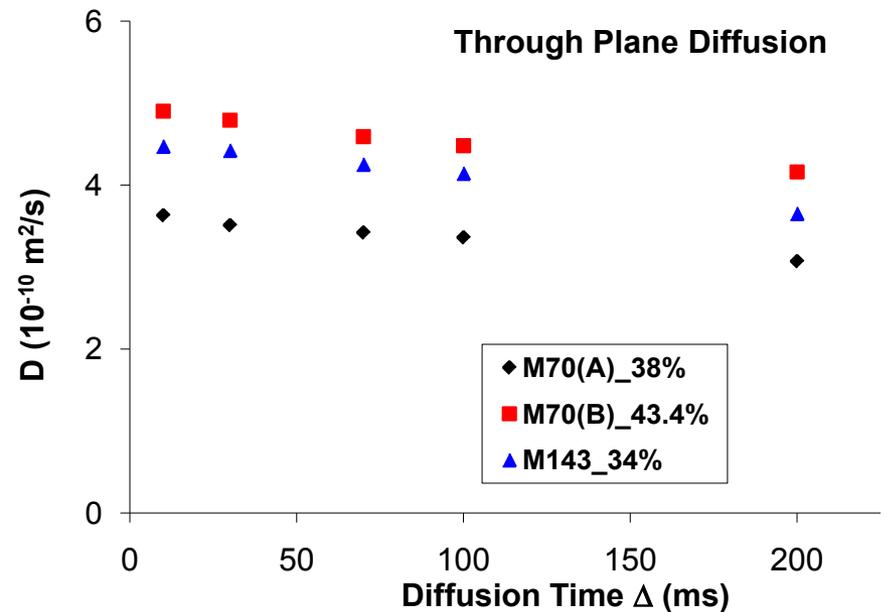
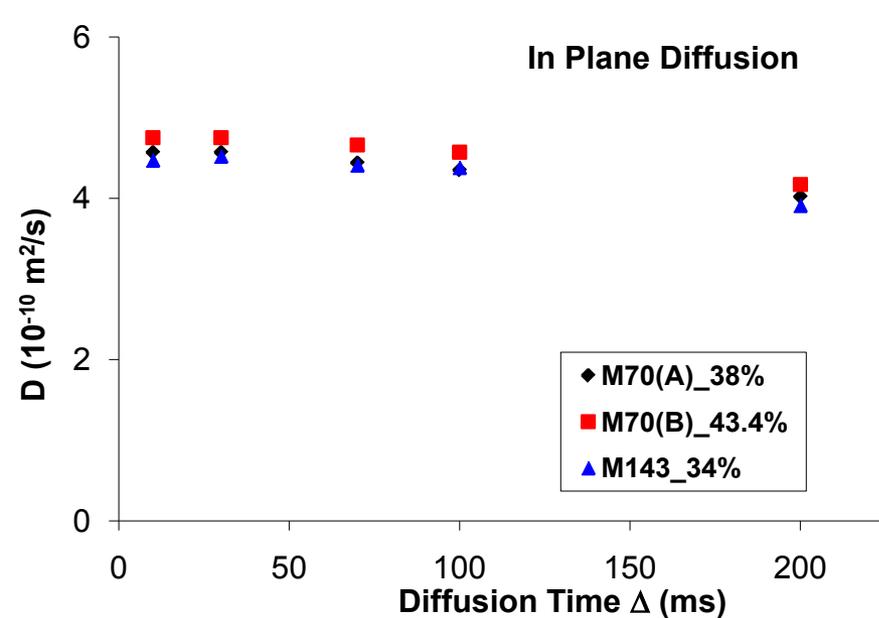


Membrane Preparation

- All membrane samples are cut into pieces of 5 x 5 mm
- Samples are stacked closely and wrapped together by Teflon[®] tape
- Samples are dried with desiccant over night under room temp
- Samples are soaked in DI water for more than 24 hr
- Free water is blotted from sample by clean soft paper
- The blotted sample is equilibrated in a Teflon[®] cell in stack over night before NMR expt. (> 12 hr)
- Sample is equilibrated under 25°C for 2 hr in the NMR tube
- Diffusion coefficient of water is measured in 3 directions:
 - Z: Through-Plane
 - Y: In-Plane
 - X: In-Plane

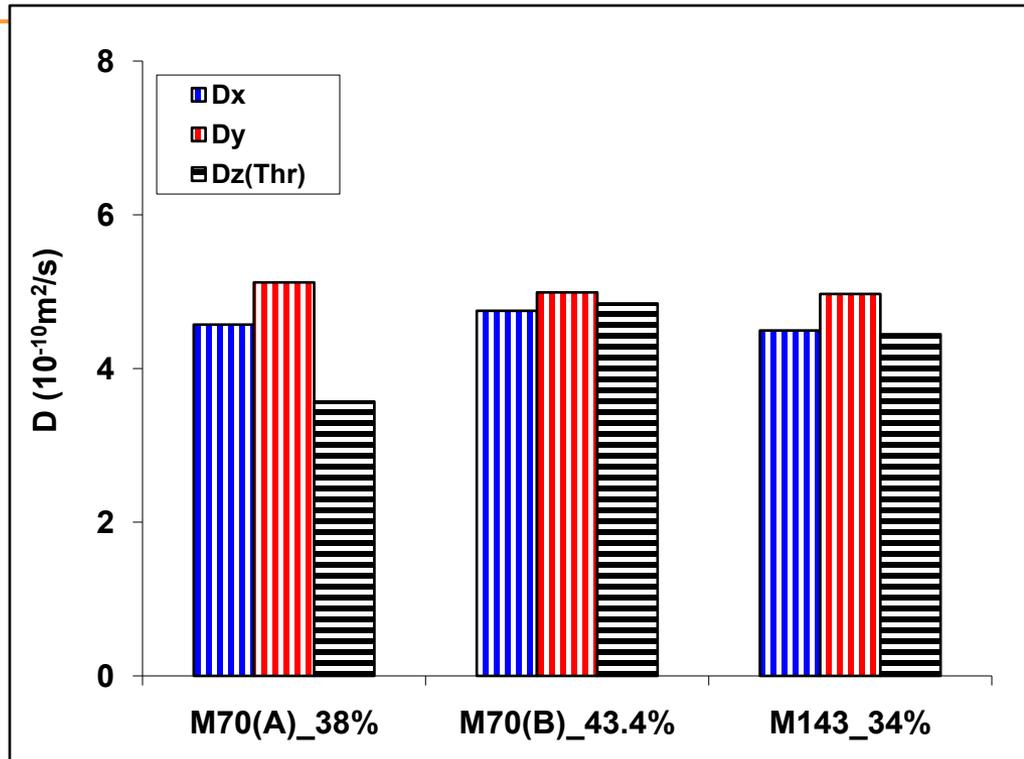


Arkema M70 and M143 Membranes



- Diffusion constant measured along x, y, and z directions (**in plane and through plane**)
- Drop off in D's value versus diffusion time Δ indicates morphological restrictions on 5-10 μm length scale
- T_1 shows single component for M70(A/B) and M143 membranes (~ 400 ms)
- Diffusion constants are roughly similar to M41 and M43 membranes and similar water uptake

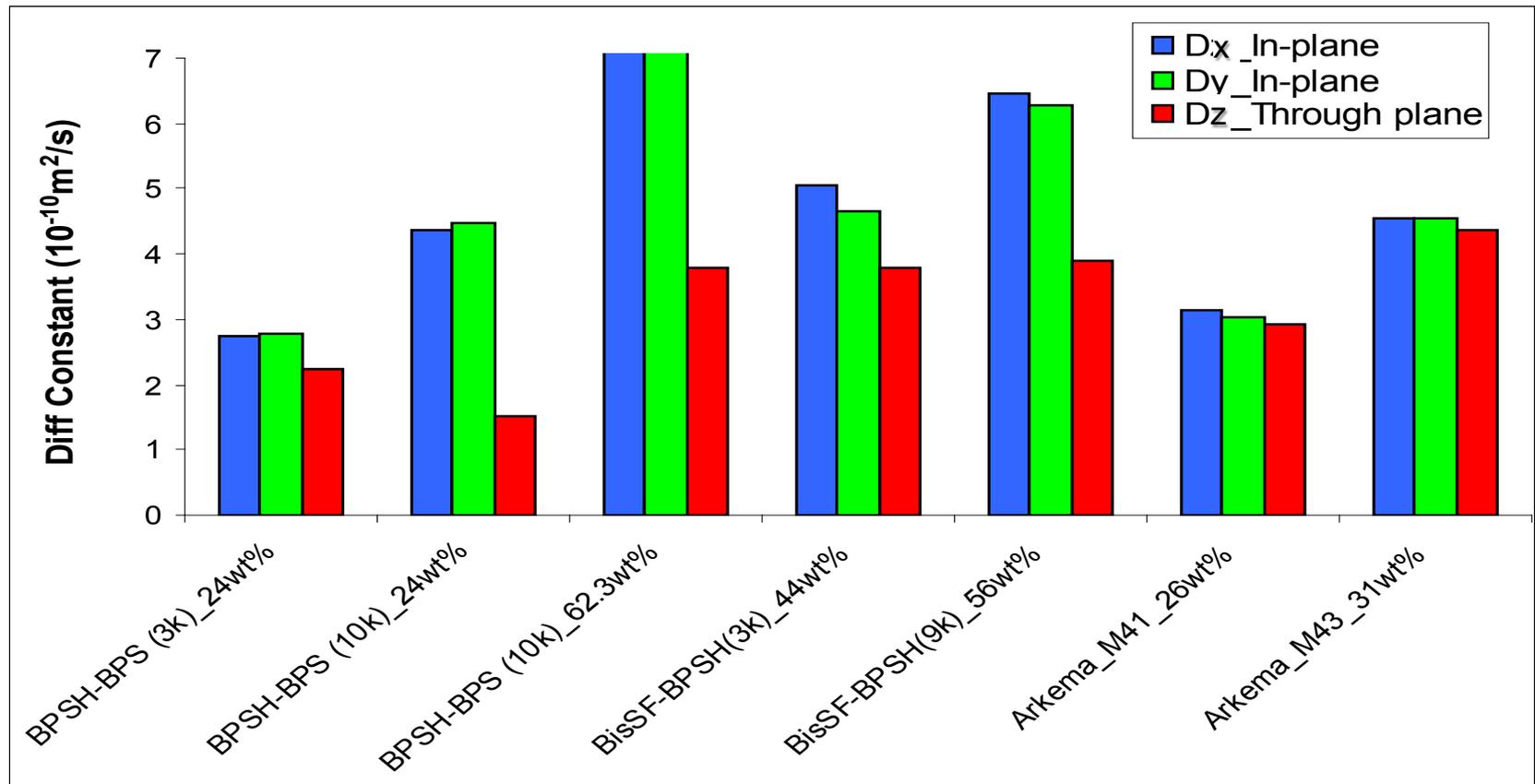
Diffusion Anisotropy and Isotropy



- Only one peak (^1H) appears in each NMR spectrum
- Diffusion anisotropy exhibited (through-plane vs in plane) by M70(A), and also some apparent (not strong) anisotropy in the two in plane directions for M70(A) and M143
- M70(B) is isotropic, similar to the M41 and M43 materials
- Diffusion studied only at one hydration level per membrane

Comparing Diffusion Isotropy and Anisotropy

- Diffusion is isotropic in Arkema M41 and M43 membranes
- Anisotropy in diffusion shows up in all block copolymers to different extent



Conclusions

- For M70 and M143 membranes, only one peak (^1H) shows up in the NMR spectra, and only one T_1 time is present
- Water molecules diffuse more quickly in plane than through plane for M70(A)
- Decrease in D with diffusion time Δ indicates some restrictions on the 5-10 μm length scale
- Arkema M70 and M143 membranes both show only one distinct T_1 time, indicating more uniform morphology on small length scales (10s of nm) than M41 and M43
- Diffusion constants are similar (within $\sim 20\%$) for all Arkema membranes measured at the same water uptake

M43 OCV Durability

