Improved, Low-Cost, Durable Fuel Cell Membranes

2010 Hydrogen Program Annual Review

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June 8, 2010

Grant ID:
DE-FG36-07GO17008

Project ID # FC059

Overview (DE-FG36-07GO17008)

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

Barriers Addressed
- A) Durability
- B) Cost

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)

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

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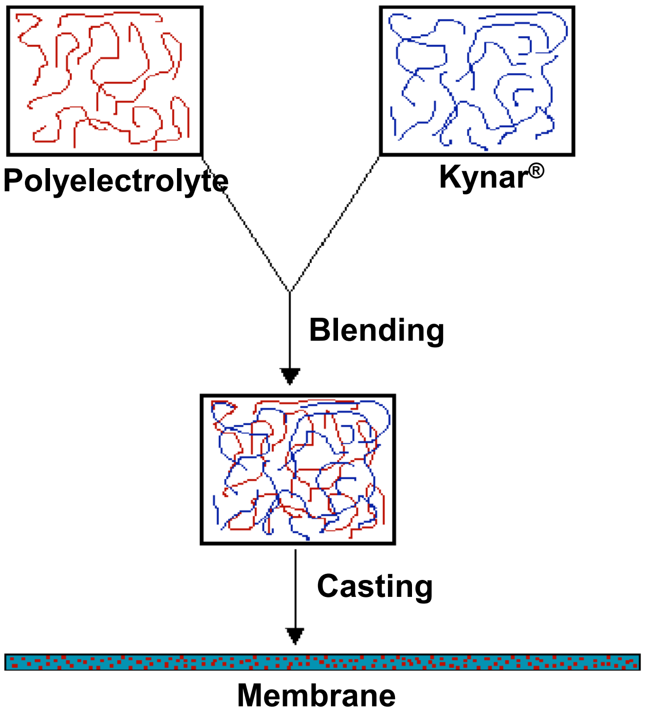
Approach

- 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

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Approach

Milestone	Progress Note	Comments
Improve low RH performance at 80°C	- M70 membranes show improved *ex-* and *in-situ* performance vs. M43	Validated novel disulfonated monomer approach to low RH conductivity improvement
Optimize M70 membrane performance *(ex-situ and in-situ)*	- Ex-situ conductivity vs. RH and in-situ 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

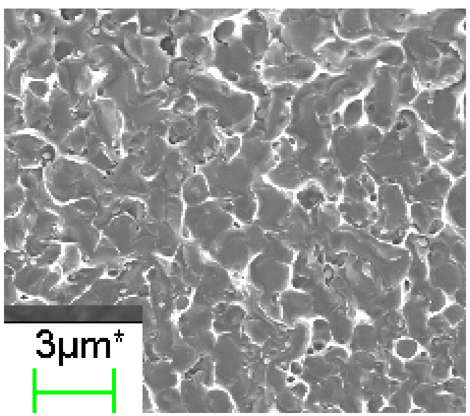
- M70 blending process optimization

Polymer Blend
EW ~ 400 - 600

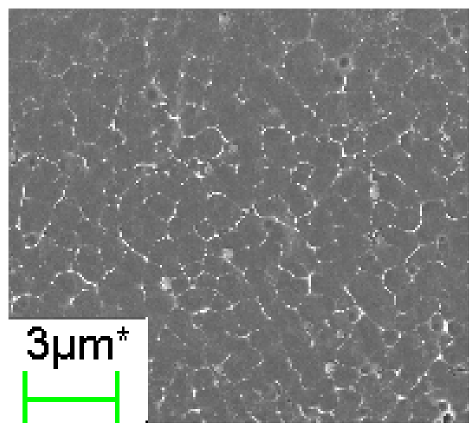
Process 'A'

Process 'B'

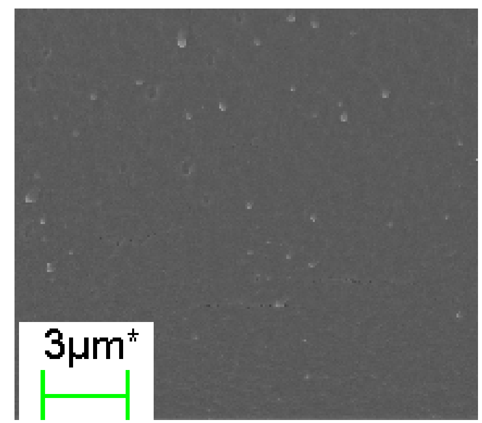
Process 'C'



55±9 mS/cm



63±3 mS/cm



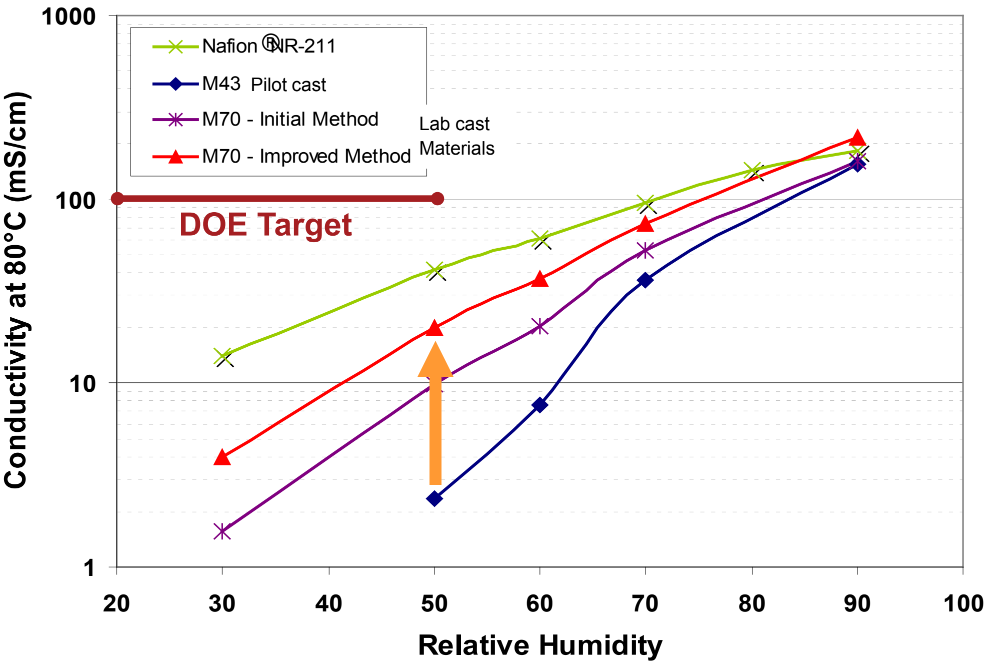
186±17 mS/cm

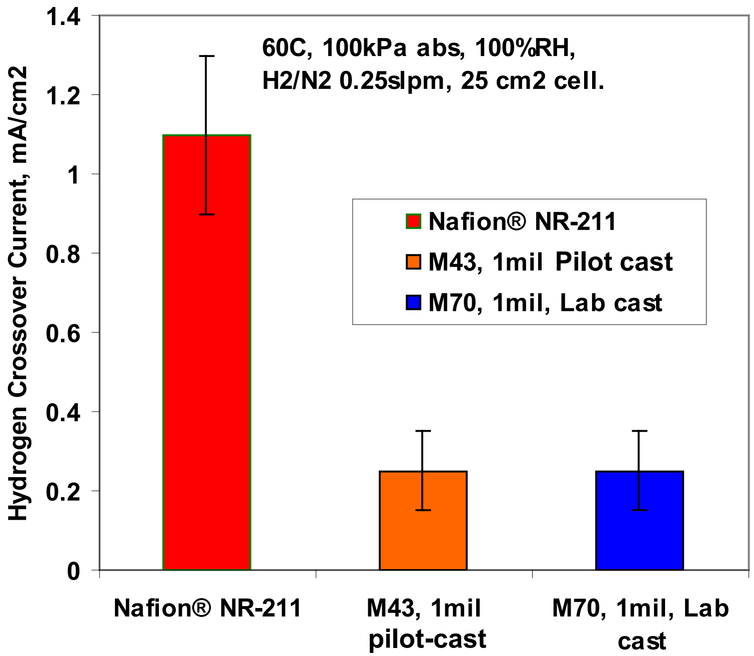
- Membrane transparency → finer morphology → higher conductivity

*Conductivities measured @ 70 ºC, liquid H_2O

Technical Accomplishments and Progress

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



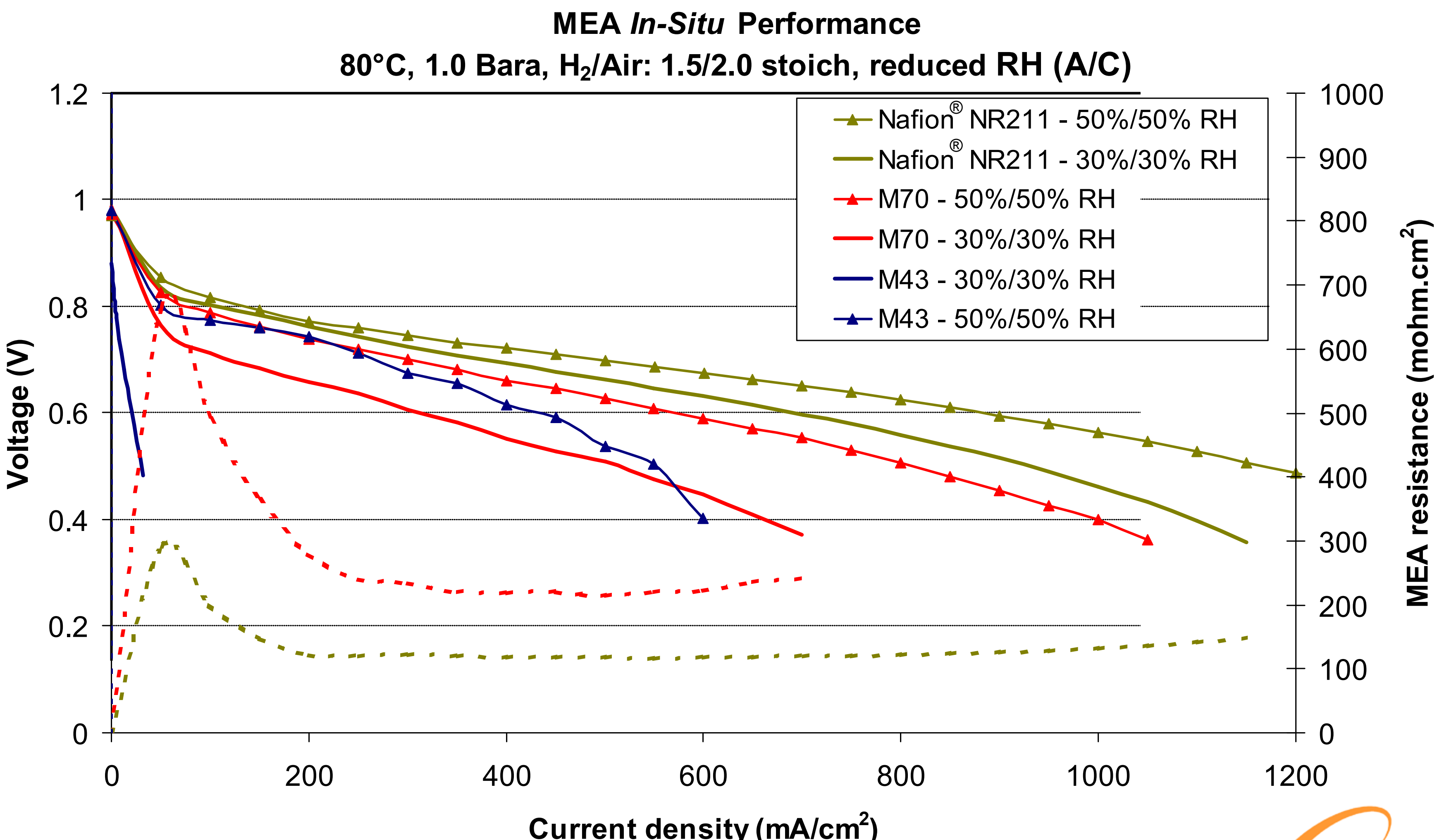


Order-of-magnitude 80°C conductivity improvement vs. previous generation

~75% less H_2 cross-over vs. Nafion® at equivalent thickness

Technical Accomplishments and Progress

- M70 MEA performance – REDUCED HUMIDITY conditions



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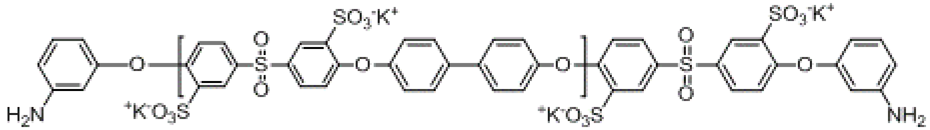
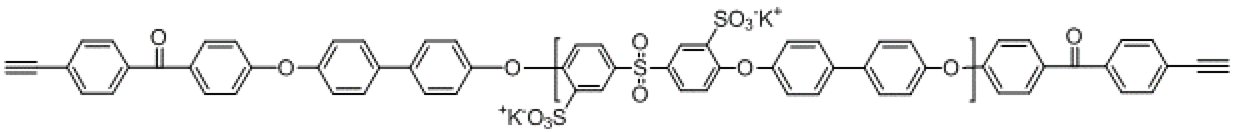
Prof. J.E. McGrath
VirginiaTech
Invent the Future

Collaboration

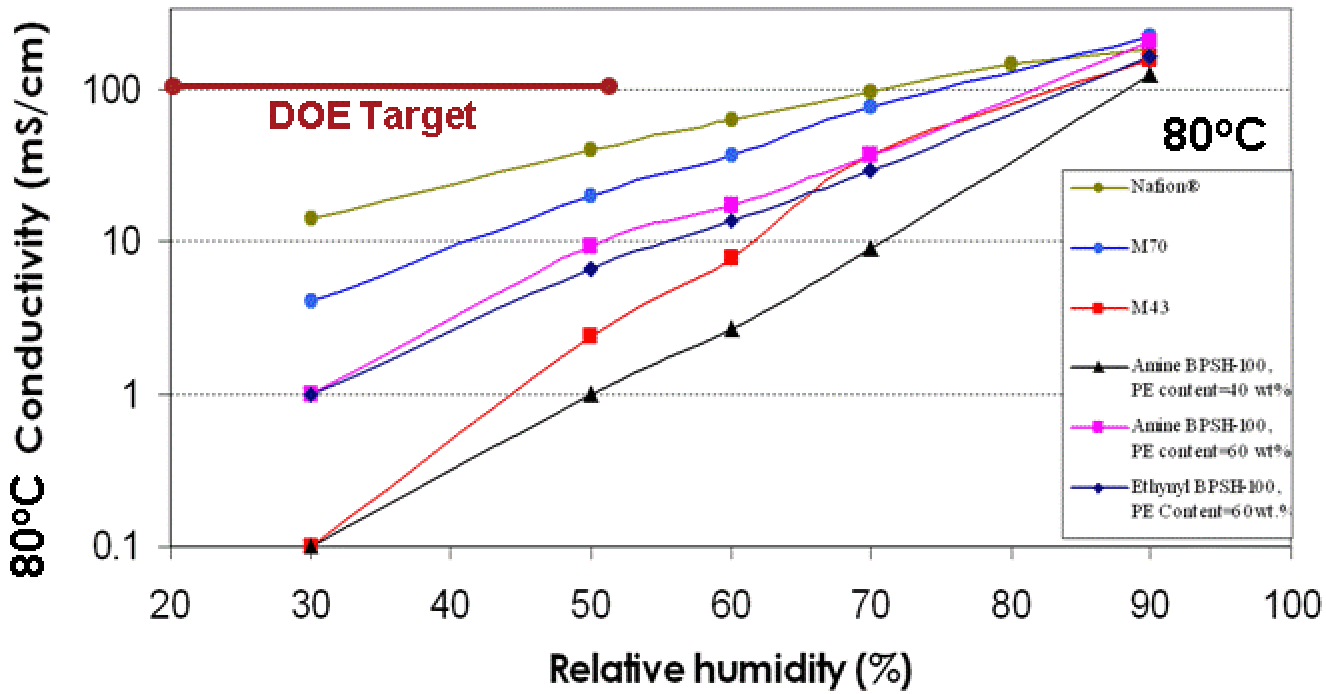
- Increase operating T of PVDF/PE blends – maintain RH conductivity
- Highly sulfonated, cross-linkable BPS-100



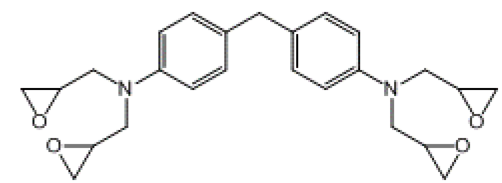
Amine-terminated BPS-100



Ethynyl-terminated BPS-100



Amines reacted with tetraepoxide cross-linking agent



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

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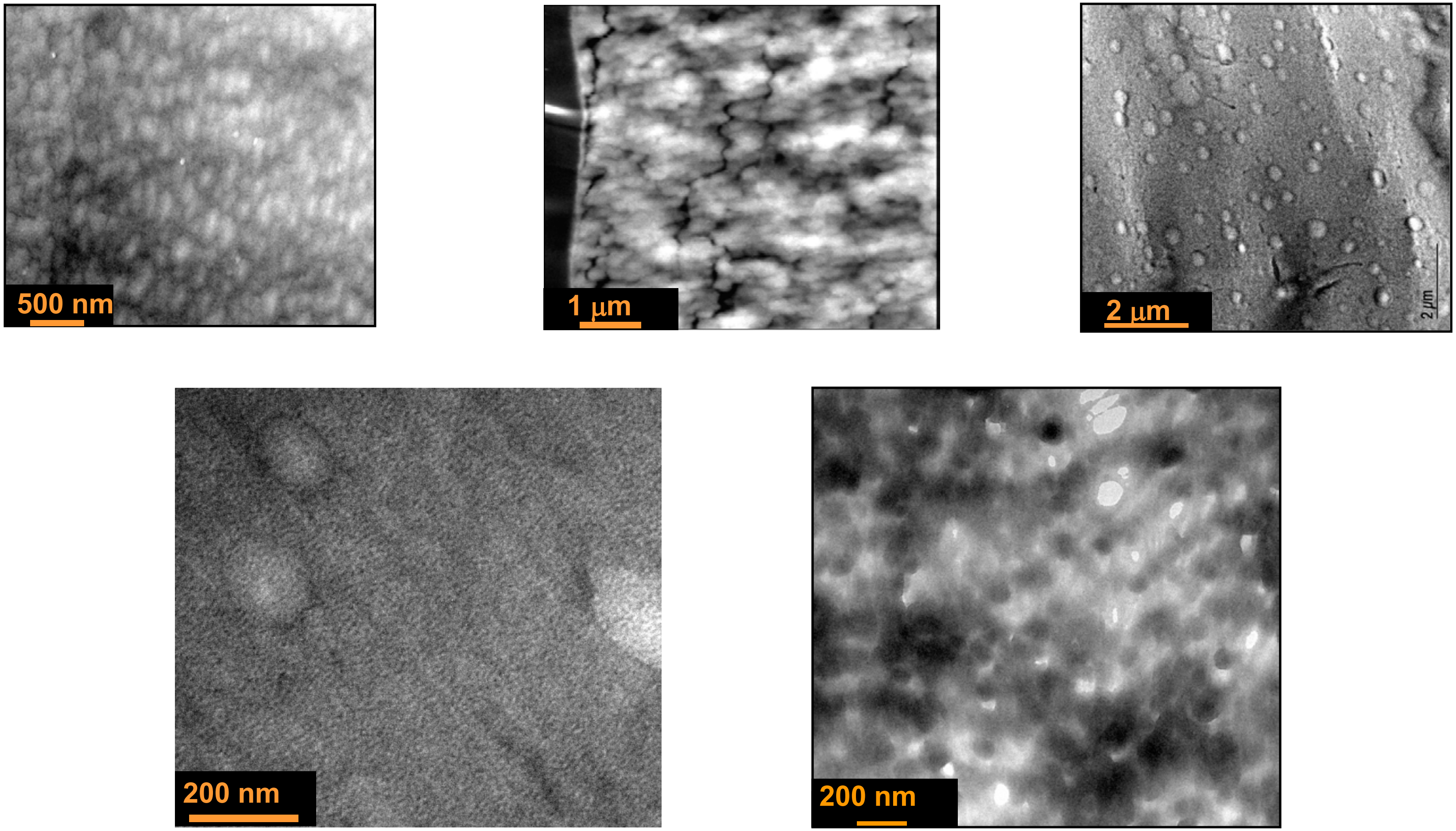
Collaboration



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

*Dr. K. More - ORNL

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

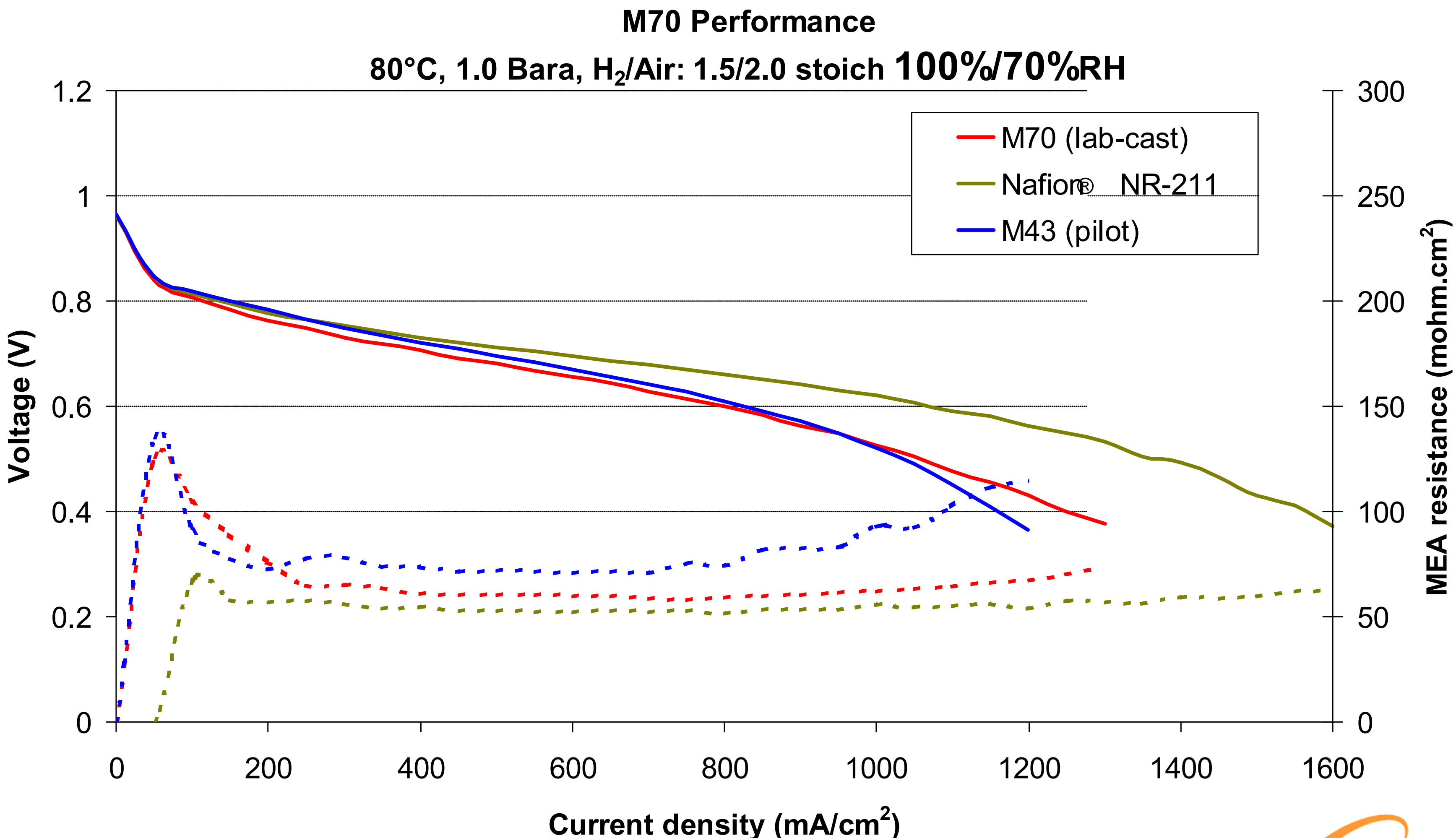
- M70
  - Novel monomer and polyelectrolyte synthesized
  - Multi-kilo scale up achieved; membrane produced on pilot scale
  - PVDF blending and optimization completed
  - Successfully produced blended membranes
  - Encouraging *ex*-situ and *in-situ* low RH performance
  - Validated multi-acid route 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^+

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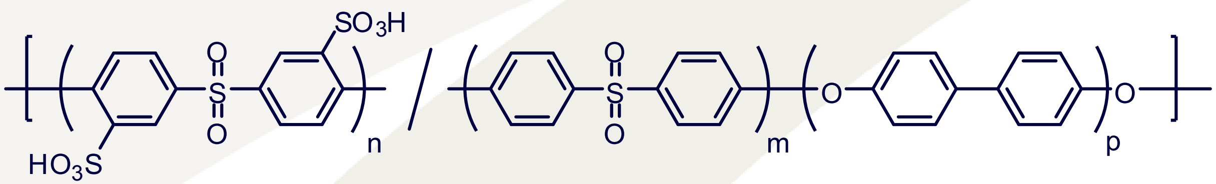
BPSH/Kynar® Blend Membranes

- 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

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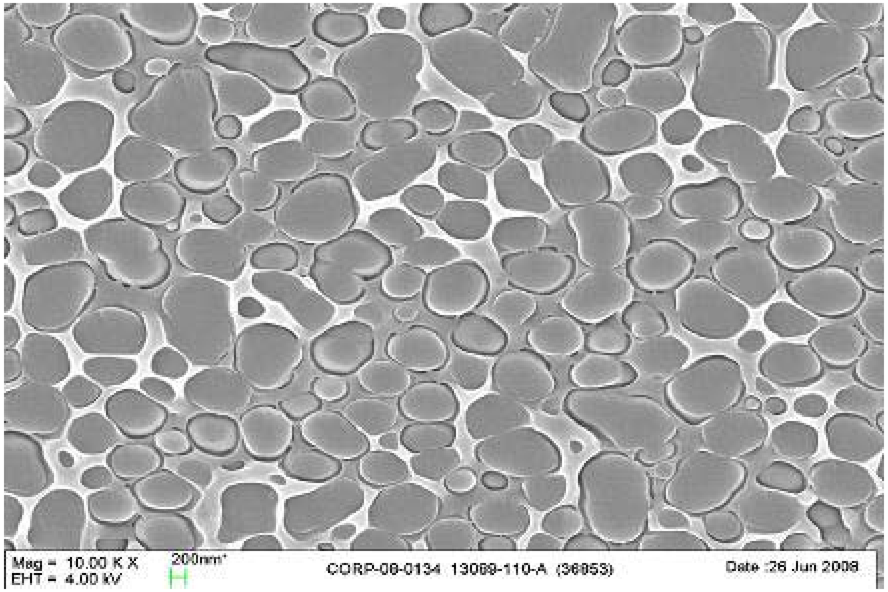
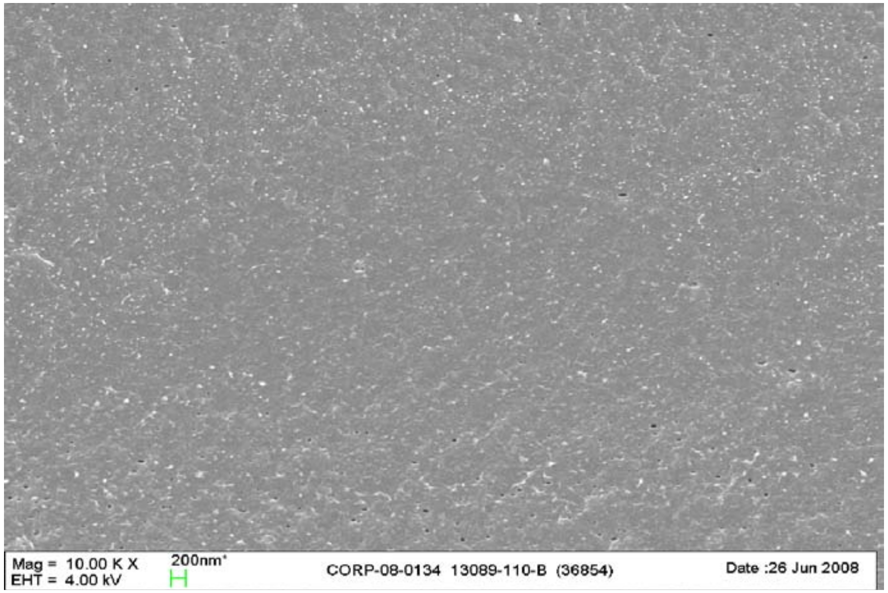
BPSH-60/Kynar® Blend Membranes - SEM



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



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

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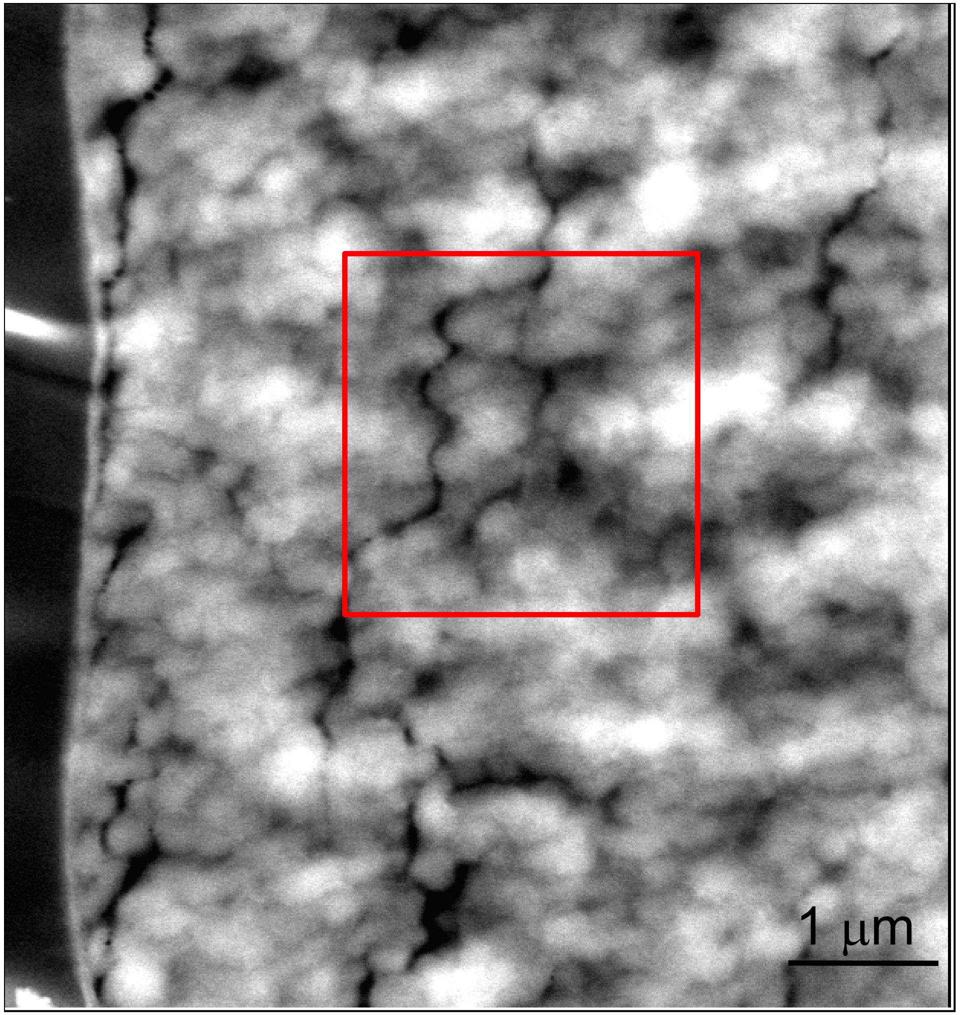
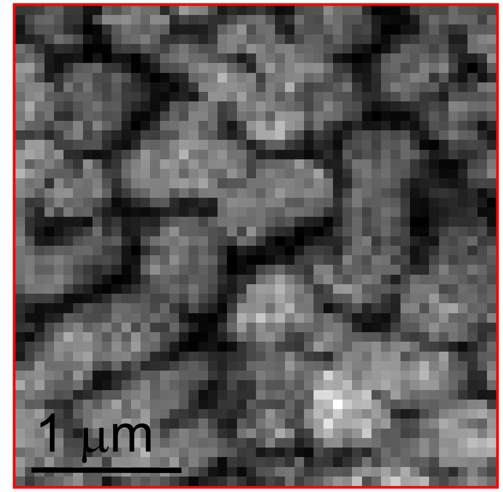
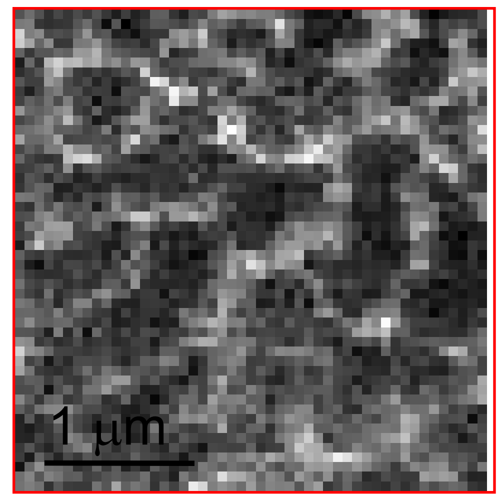
BPSH-60 / Kynar® Blend Membrane TEM





S map



F map

S and F form separate phases F/S=10

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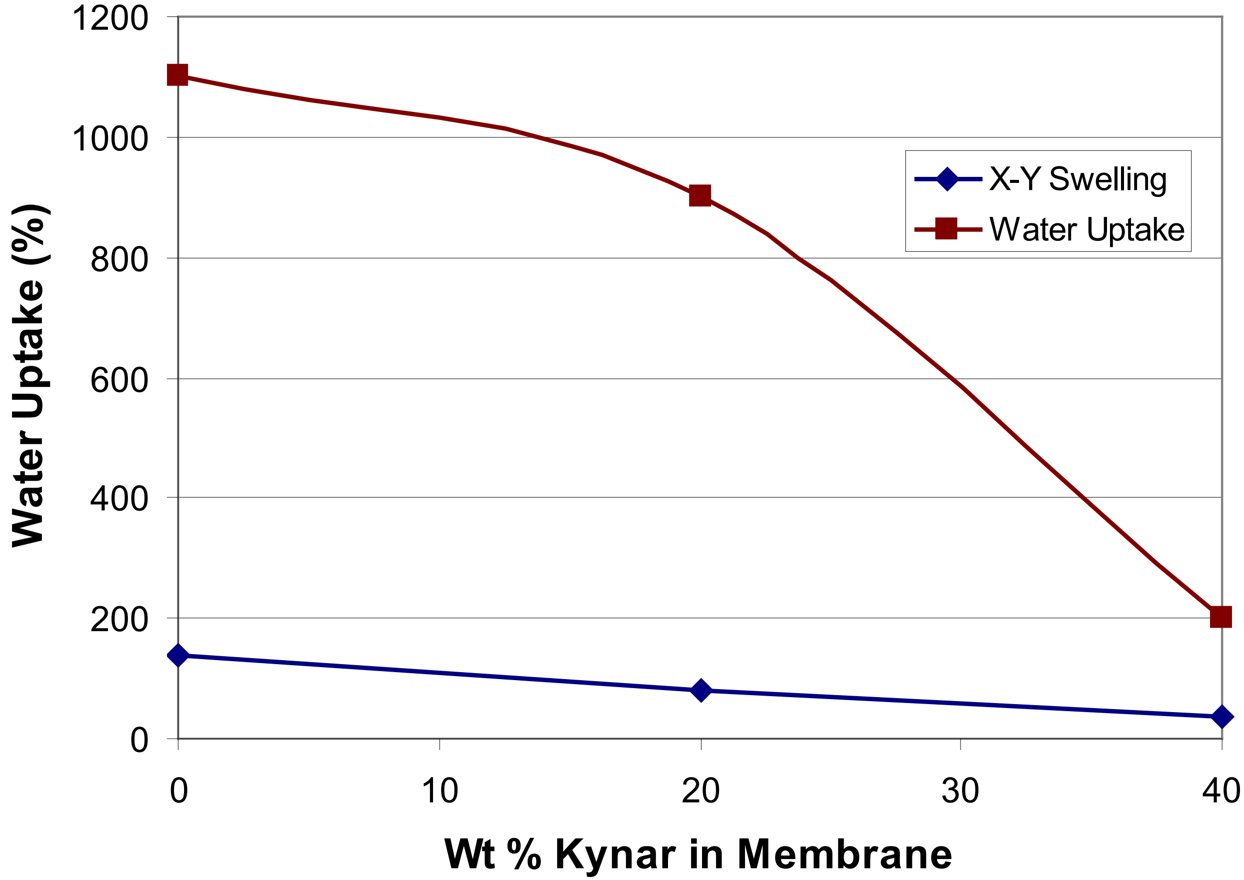
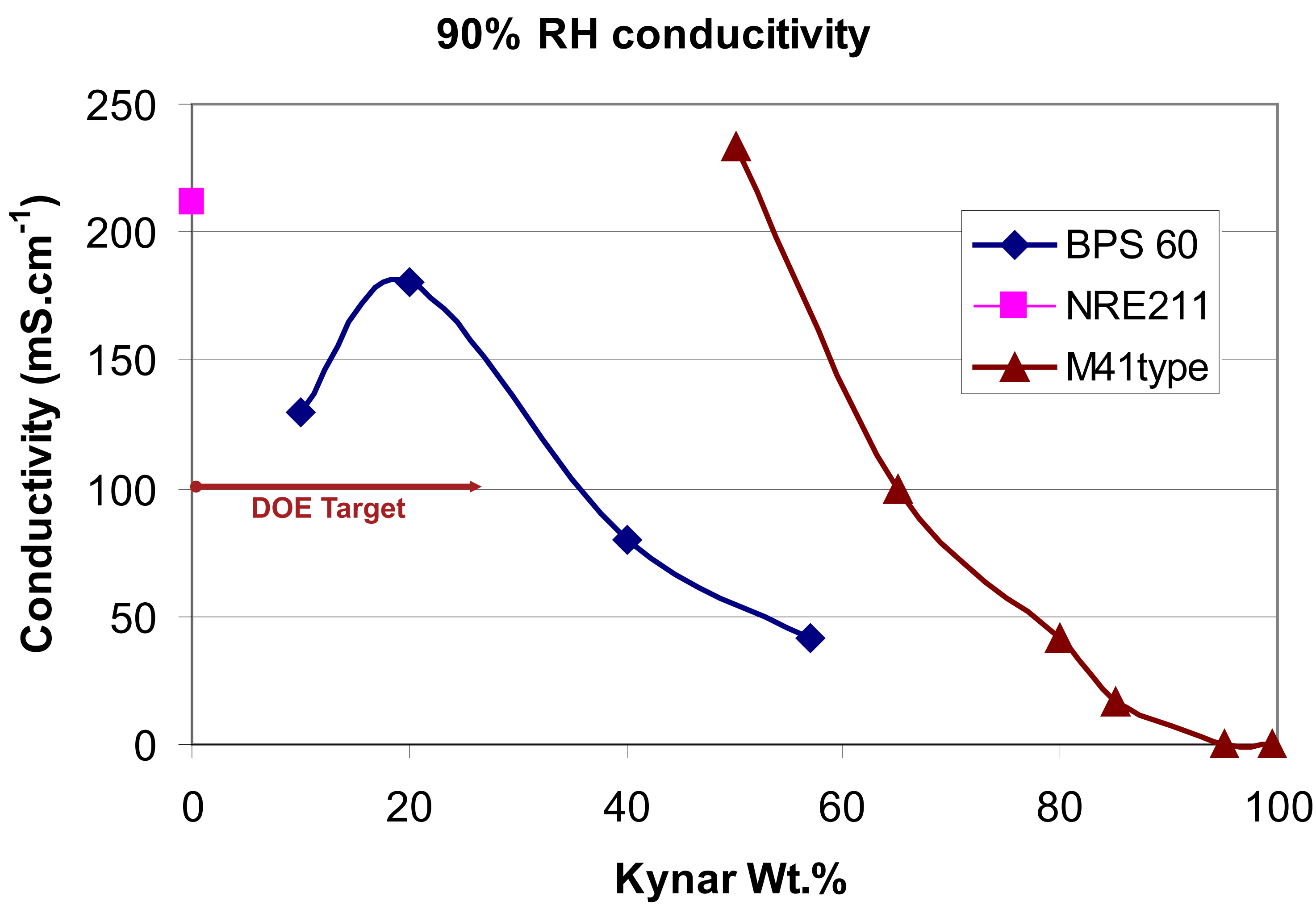
BPSH-60/Kynar® Membranes – Water Uptake



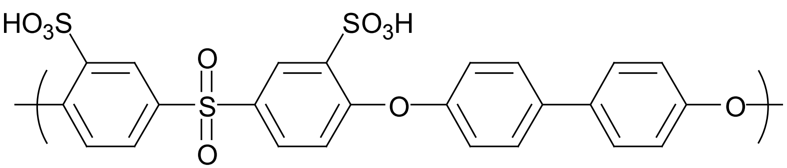
- Water uptake increases substantially with higher loading of BPSH-60
- Swelling greatly reduced with Kynar® blending

BPSH-60/Kynar® Membranes - Conductivity

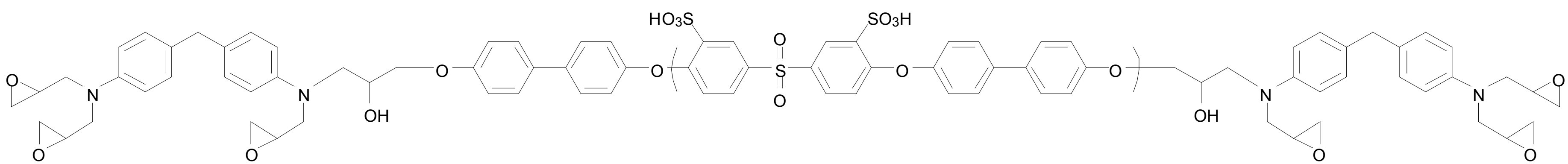


BPSH-100 Copolymer Blends

- 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

VirginiaTech

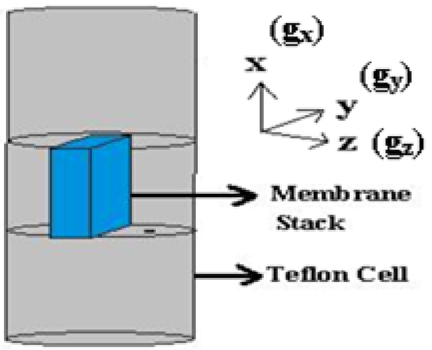
Membrane Preparation

- 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



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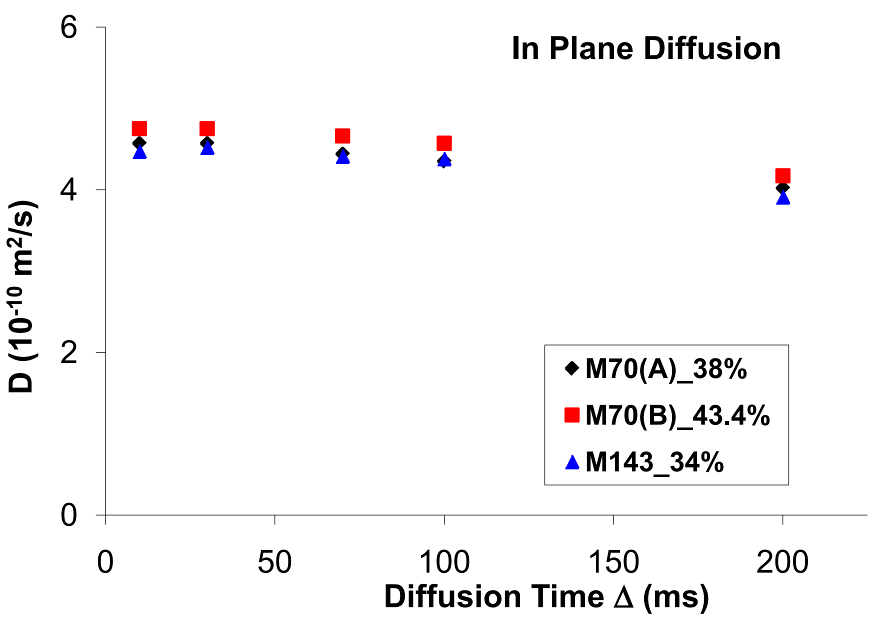
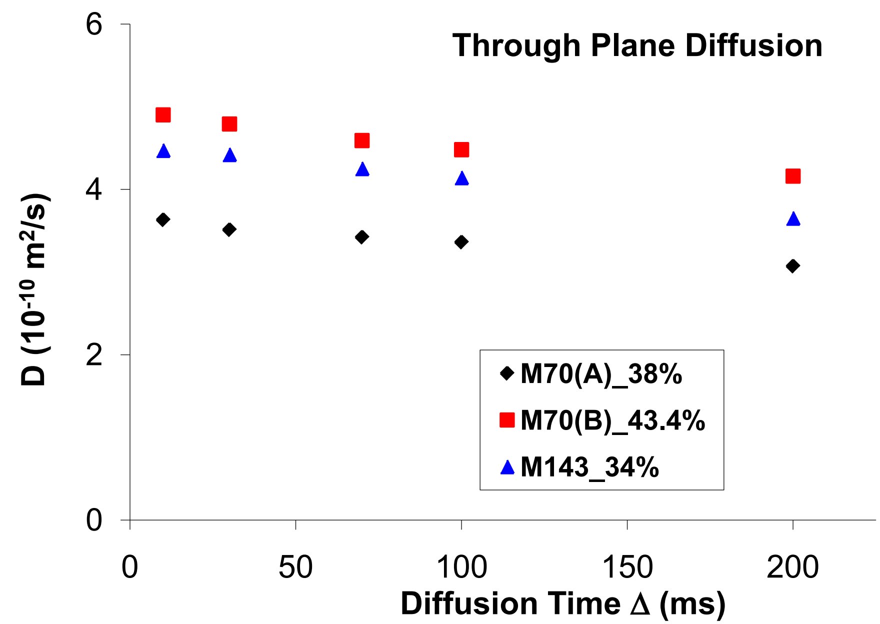
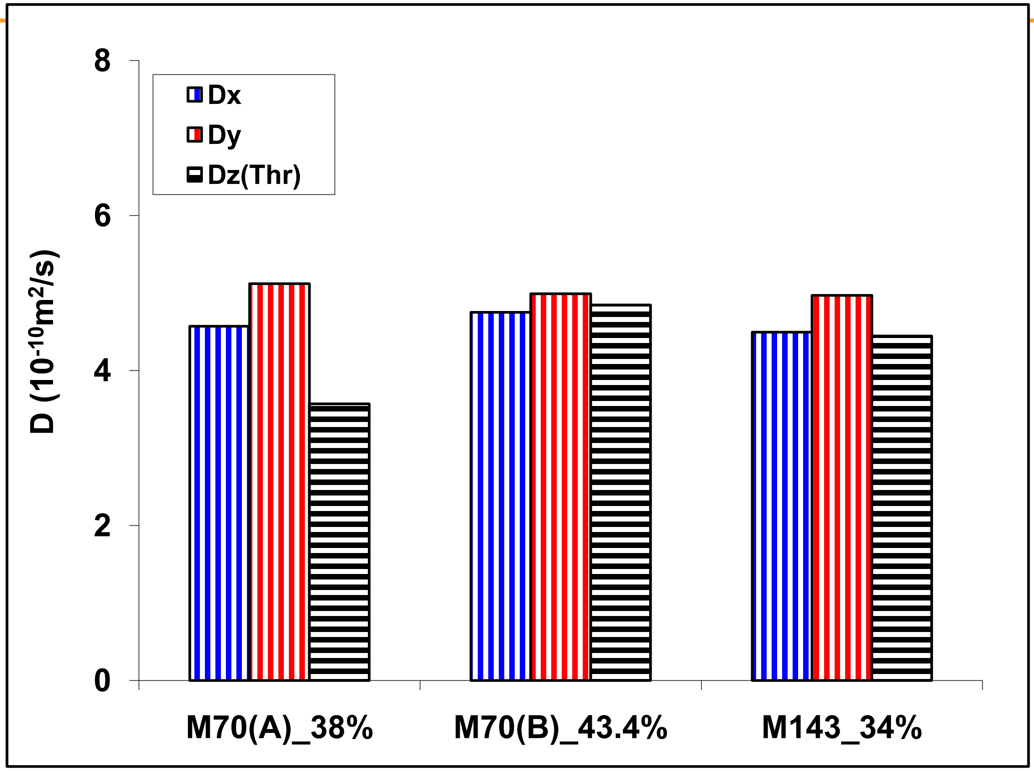
Arkema M70 and M143 Membranes





- 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

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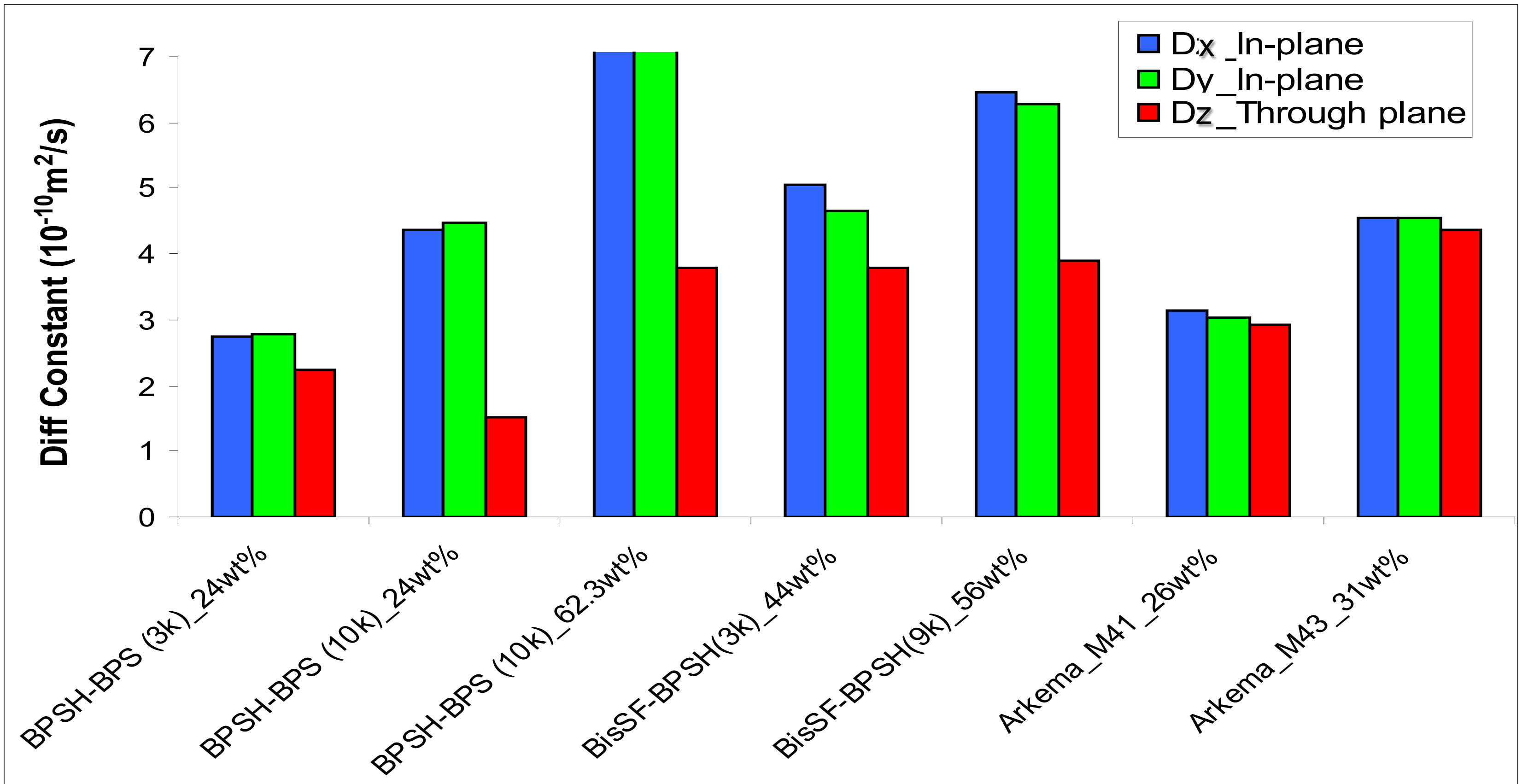
Comparing Diffusion Isotropy and Anisotropy

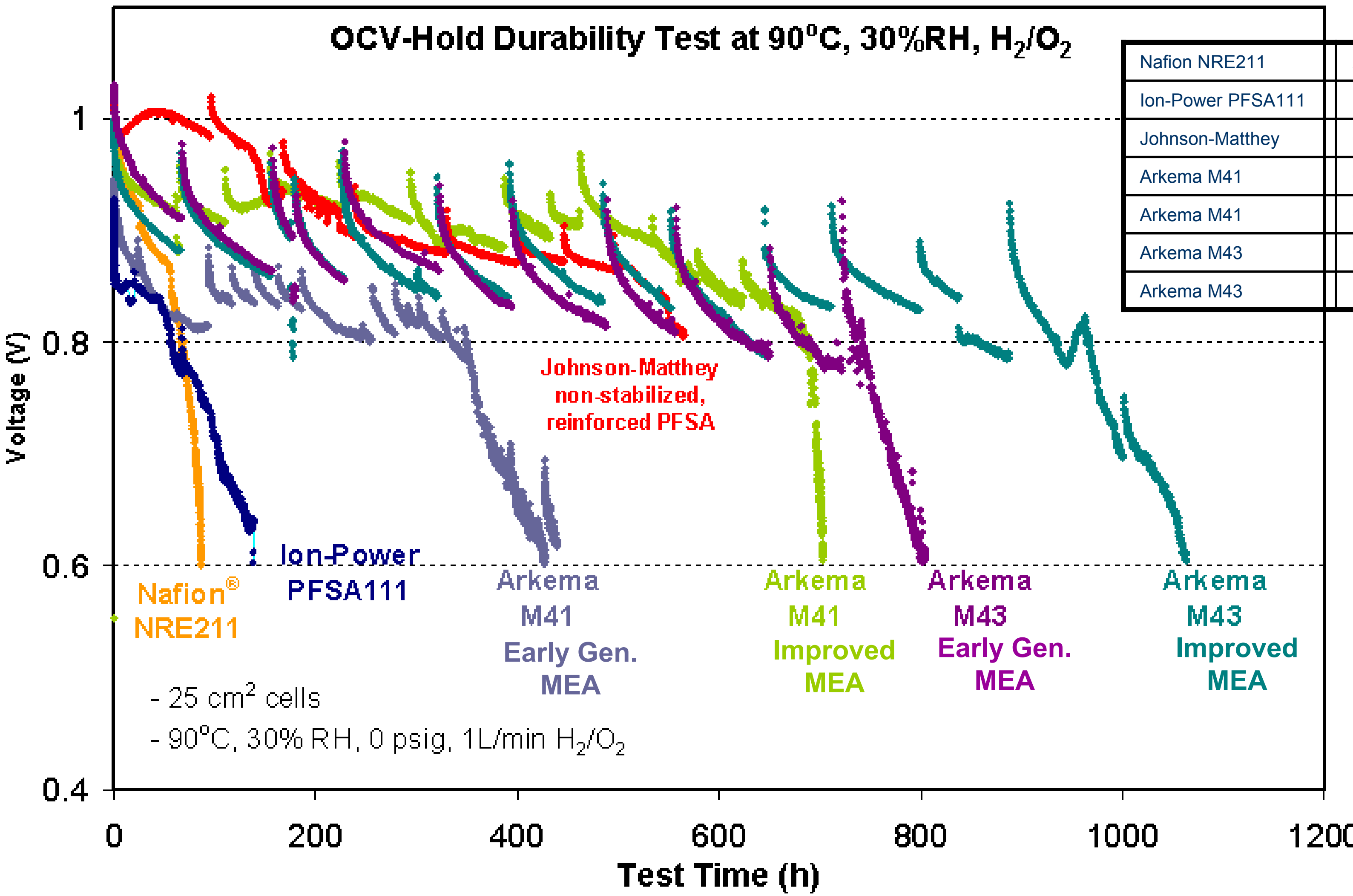
- Diffusion is isotropic in Arkema M41 and M43 membranes
- Anisotropy in diffusion shows up in all block copolymers to different extent



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 ~ 20 %) for all Arkema membranes measured at the same water uptake

M43 OCV Durability



Nafion NRE211	2.3 mV/h
Ion-Power PFSA111	1.7 mV/h
Johnson-Matthey	0.33 mV/h
Arkema M41	0.39 mV/h
Arkema M41	0.26mV/h
Arkema M43	0.32mV/h
Arkema M43	0.20mV/h

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