Improved, Low-Cost, Durable Fuel Cell Membranes

2009 Hydrogen Program Annual Review

James Goldbach, David Mountz, Tao Zhang, Wensheng He, and Michel Fouré

May 19, 2009

Grant ID:
DE-FG36-07GO17008

Project ID # FC_12_Goldbach

This presentation does not contain any proprietary, confidential, or otherwise restricted information

Overview (DE-FG36-07GO17008)

Timeline

- Start Date: Sept. 30, 2007
- End Date: Sept. 30, 2010
- % Complete: 53%

Barriers Addressed

- A) Durability
- B) Cost

Budget

- Total Funding
  - DOE: $6,278k
  - Partners: $1,569k
- Funding Received
  - FY2007: $0
  - FY2008: $2,369k
  - FY2009: $360k
    - (as of 2/28/09)

Partners

- Project Lead
  - Arkema Inc.
- 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%).

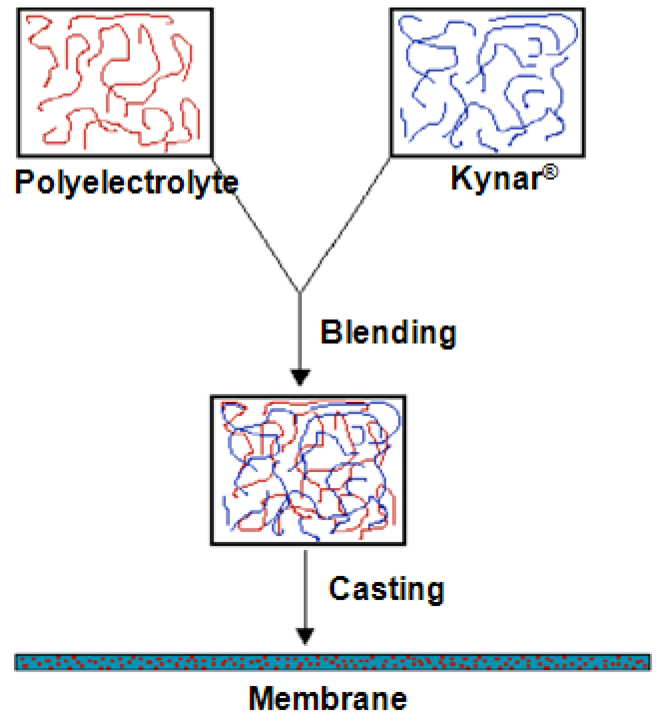
- To develop a membrane capable of operating at temperatures up to 120°C and ultra-low relative humidity of inlet gases (< 1.5 kPa).

- 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

Overall 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

ARKEMA

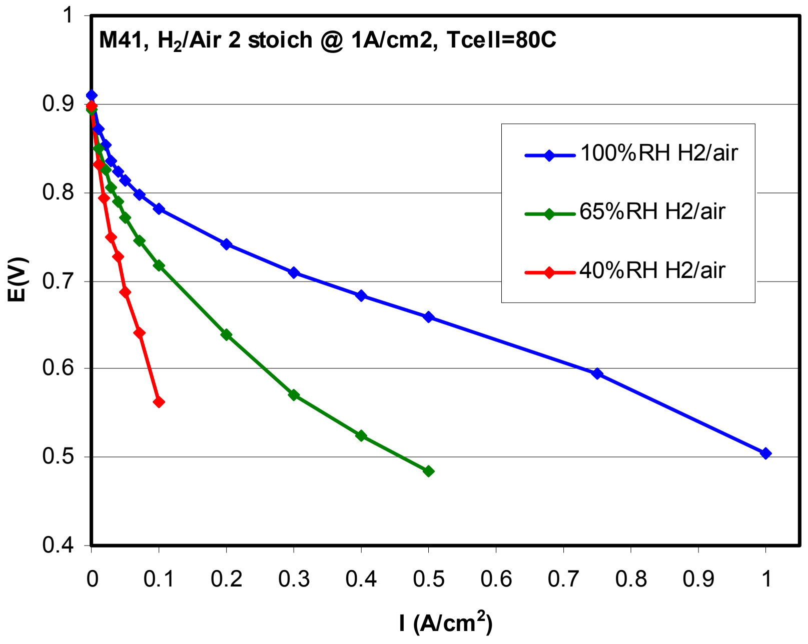
Milestones – Low RH Membranes

Milestone	Progress Note	Comments
Improve low RH performance at 80°C	M70 membranes show improved *ex-* and *in-situ* performance	Validated disulfonated monomer approach
Produce pilot quantities of M70	Scale-up in progress	Pilot production planned for 3Q09
Improve thermal stability to 120°C	Validated BPSH blending with PVDF	Narrow processing window with BPSH-60; Move to BPSH-100
Improve low RH performance at 120°C	Validate BPSH-100 blending and stability	TBD

ARKEMA

Background – Arkema Membranes

- M4x Series –polyelectrolyte /w monosulfonated monomer
  - Proton conductivity ~ 130 mS/cm
  - Mechanical properties > PFSA
  - <10% creep @ 120 ^oC, 40% RH
  - OCV-Hold testing > 1000h (90^{o}C, 30%RH, O_2, no backpressure)
  - RH cycling > 50,000 cycles (DOE protocol)



- Insufficient low RH performance

  <2mS/cm *ex-situ* conductivity @ 50% RH

  MEA operation to ~65% RH

Low RH Membranes: Approach

1) New polyelectrolyte blend membranes

- Alternate sulfonated monomer (drop-in replacement): **M60/61** membranes
- Multiacid-functional polyelectrolytes (novel syntheses): **M70** membrane
- Highly sulfonated BPSH polyelectrolytes (J. McGrath)

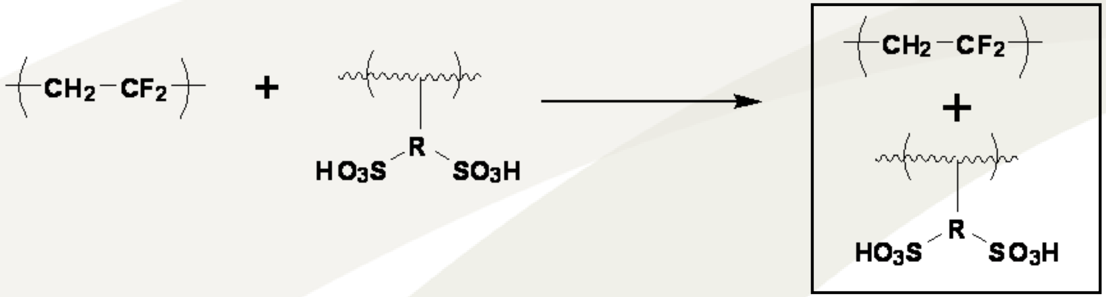
2) Control morphology of Kynar® blends

- Understand/baseline blend morphology
- Understand/control morphology←→bulk property relationship
  - Extremely complex nano-morphology – under investigation

ARKEMA

M7x – Series Membranes

- Disulfonated monomer-containing polyelectrolyte
- Membrane EW ~ 400 g/mol H^+



Polymer Blend
EW ~ 400 - 600

Novel Polyelectrolyte Synthesis

- Novel disulfonated monomer
- Optimized polymerization

(readily scalable syntheses)

- Optimizing blending parameters
- Optimizing membrane production process

M70 Polyelectrolyte Hydrolytic Stability

- Polyelectrolyte only hydrolysis test
  - Initial screening test for all new polyelectrolytes
  - 5.0 wt.-% polyelectrolyte solution in acidic H_2O, 80 ^oC, sealed tube
  - Periodically remove samples for ion chromatography analysis

- M70 polyelectrolyte
  - Nearly unmeasurable levels of hydrolysis
  - 0.036 wt.-% S loss as SO_4^{2-} over 500h
  - Would take ~14,000h to lose just 1.0% of sulfonate groups

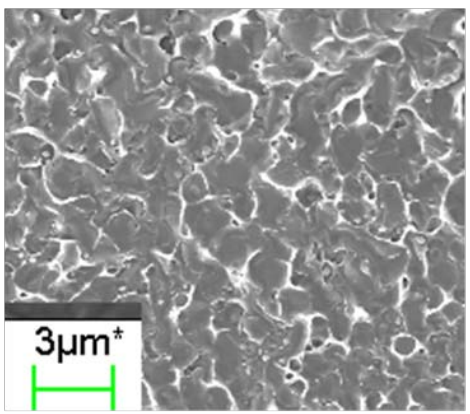
ARKEMA

M70 Blending Optimization

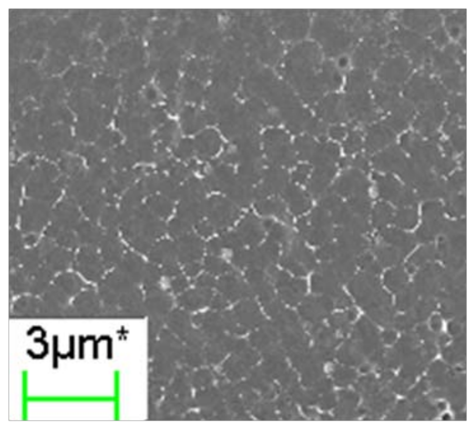
Process ‘A’

Process ‘B’

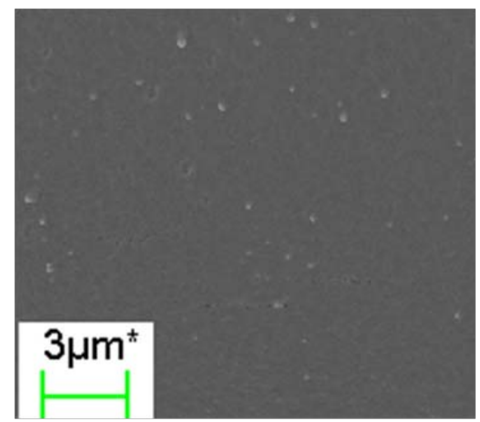
Process ‘C’



55±9 mS/cm



63±3 mS/cm

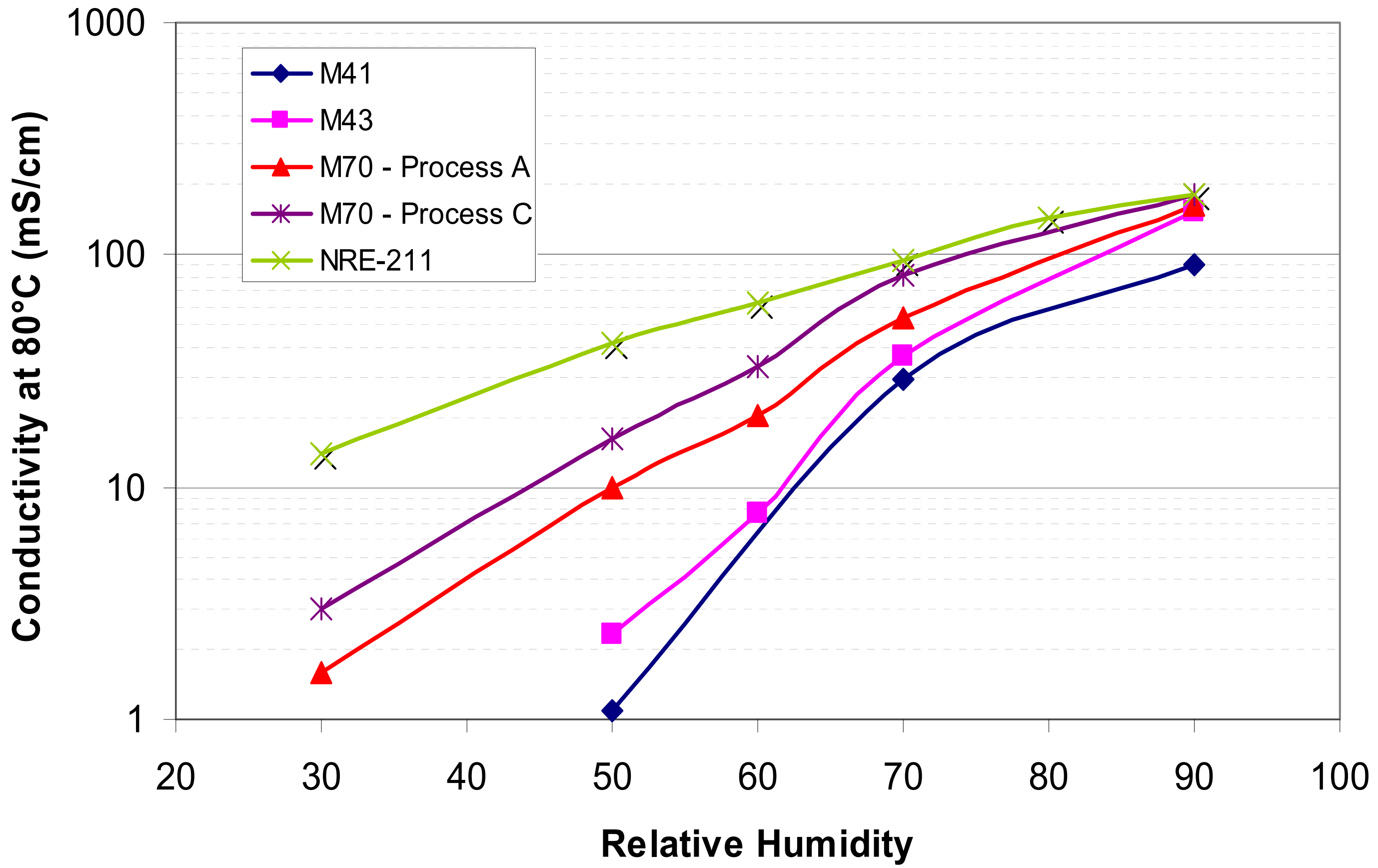


186±17 mS/cm

- Membrane transparency → finer morphology → higher conductivity

*Conductivities measured @ 70 ºC, liquid H_2O

M70 Conductivity vs. RH – Initial Membranes



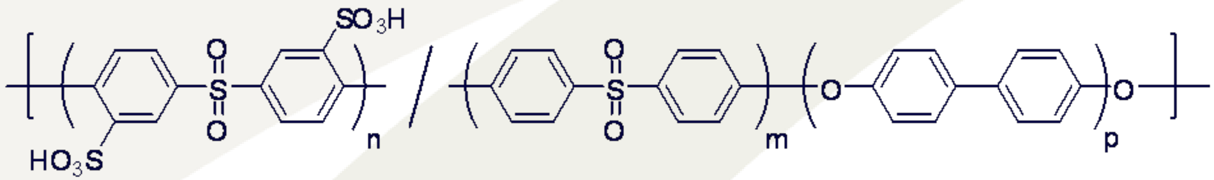
- *Unoptimized membranes*: Order-of-magnitude increase vs. M41
  - Continued optimization underway

M70 Summary To Date

- Novel monomer and polyelectrolyte synthesized
  - Initial scale up achieved - >500g scale
- Initial blending investigation completed
  - Successfully produced blended membranes
  - Encouraging *ex*-situ low RH improvement
- Validates multi-acid approach for low RH performance
- Process optimization underway
  - Potential for further improvement
- Synthesis and process readily scalable to pilot
- Begin *in-situ* performance and durability testing

BPSH/Kynar® Blend Membranes

- Collaborative effort – J. McGrath (VT)



+ Kynar® PVDF

BPSH Copolymer Blends

- Rationale
  - >80°C-stable aromatic-type polyelectrolytes
  - Use highly-sulfonated BPSH polyelectrolytes
    - Potential to improve low RH conductivity
  - Improve mechanical properties / swelling of BPSH materials
    - Important for BPSH-60 and higher sulfonate content

- Challenges
  - PE leaching vs. SO_3H content
  - BPS / Kynar® compatibility vs. SO_3H content
  - BPS vs. Kynar® ratio
    - Effect on proton conductivity
    - Effect on mechanical properties

BPSH / Kynar® Blends

- Project Plan

	Completed?
Test blending of BPS-60 with Kynar®	☑
▪ Random copolymer (BPS) synthesis (VT)	☑
▪ Vary blending process parameters	☑
▫ Maximize compatibility (small domain sizes)	☑
▫ Test proton conductivity and mechanical properties	☑
Test blending of BPS-100 with Kynar®	
▪ Random copolymer (BPS) synthesis (VT)	☑
▪ Vary blending process parameters	in progress ↓
▫ Maximize compatibility (small domain sizes)	
▫ Test proton conductivity and mechanical properties	
Test blending of BPS-100 (cross-linkable) with Kynar®	
▪ Random copolymer (BPS) synthesis (VT)	☑
▪ Use blending parameters from previous investigation	in progress ↓
▪ Investigate cross-linking reaction effect on leaching	
▫ Test proton conductivity and mechanical properties	

ARKEMA

Kynar®/BPSH-60 Conversion Table

Kynar®/BPSH60 wt ratio	Theoretical EW (mg.meq-1)
0/100	469
10/90	521
20/80	587
40/60	782
57/43	1091

M41 Membrane

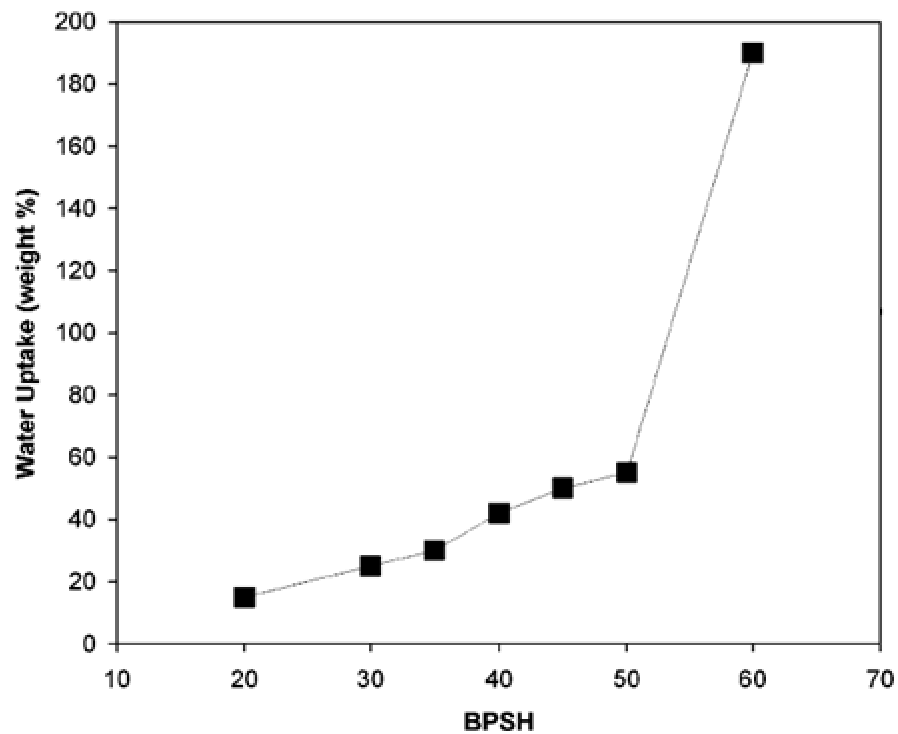
EW~ 800 $mg.meq^{-1}$

M41 polyelectrolyte

EW ~ 250 $mg.meq^{-1}$

BPSH Copolymer Swelling

- Solubility vs. swelling
- Mitigate high swelling using Kynar® matrix
- Control SO_3H content to avoid leaching
- Blend with PVDF for added mechanical properties



30°C liquid water

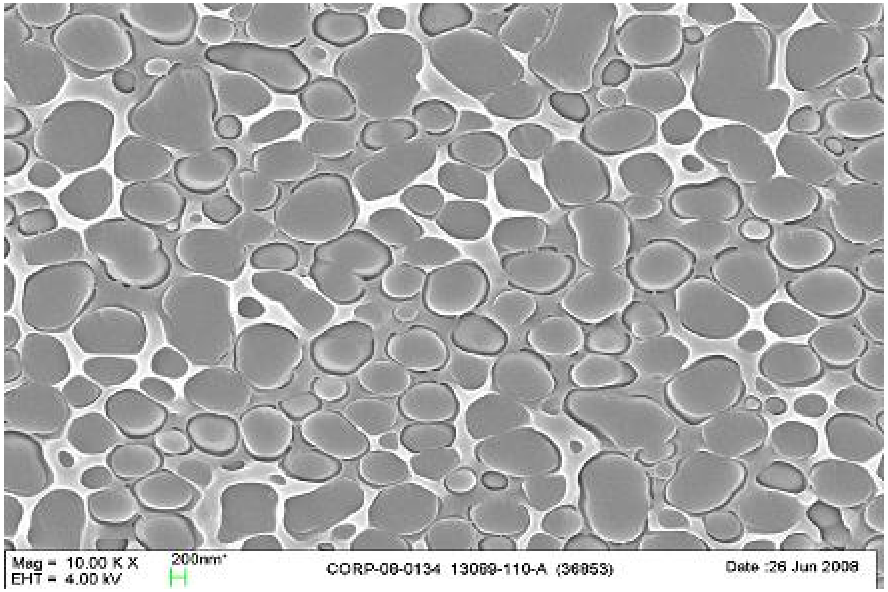
McGrath, J.E., et.al.; *Chem. Rev.*, **2004**, *104*, 4587-4612.

Blending BPSH-60 with Kynar®

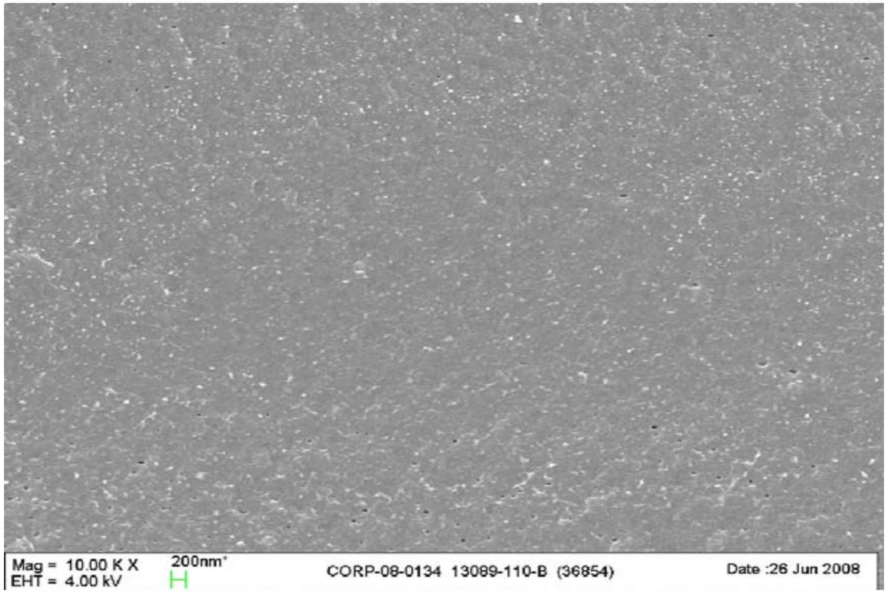
- Membrane solution gelling required process optimization
  - Moisture level in BPSH polyelectrolytes caused some uncertainty
  - Problem addressed by rigorously drying the BPSH before use.
- Narrow window for processing to generate well-blended membranes without gellation of the formulations.

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

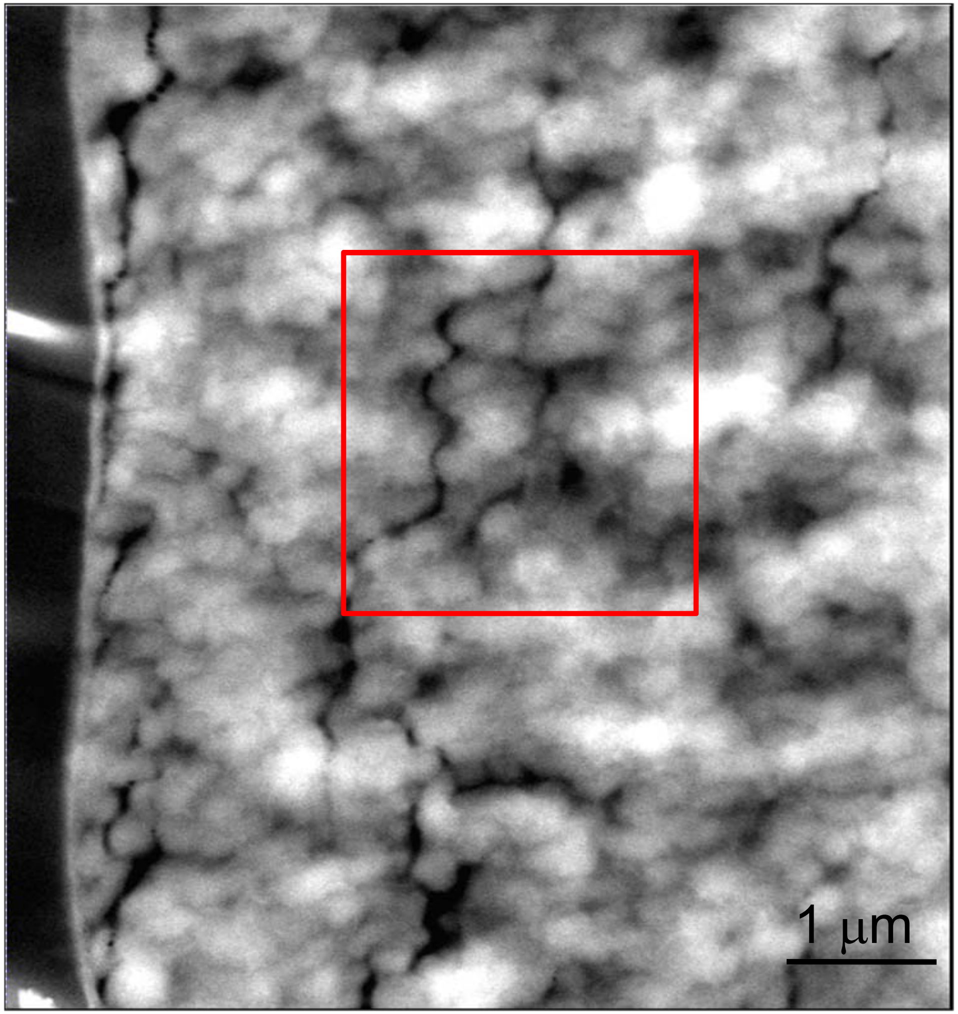


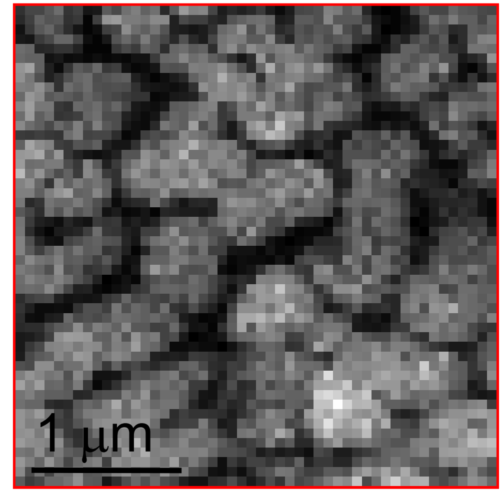
Kynar®/BPSH-60 wt ratio 60/40 Process A



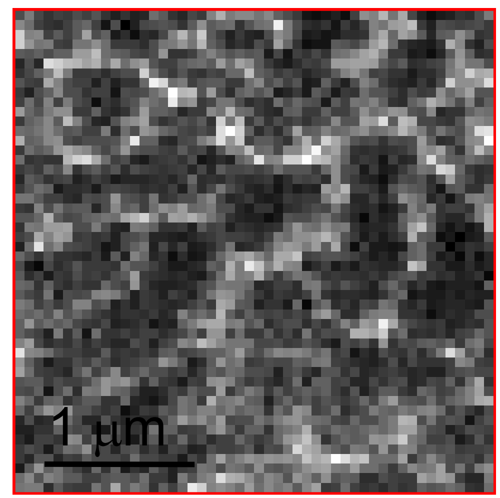
Kynar®/BPSH-60 wt ratio 60/40 Process B

BPSH-60 / Kynar® Blend Membrane TEM





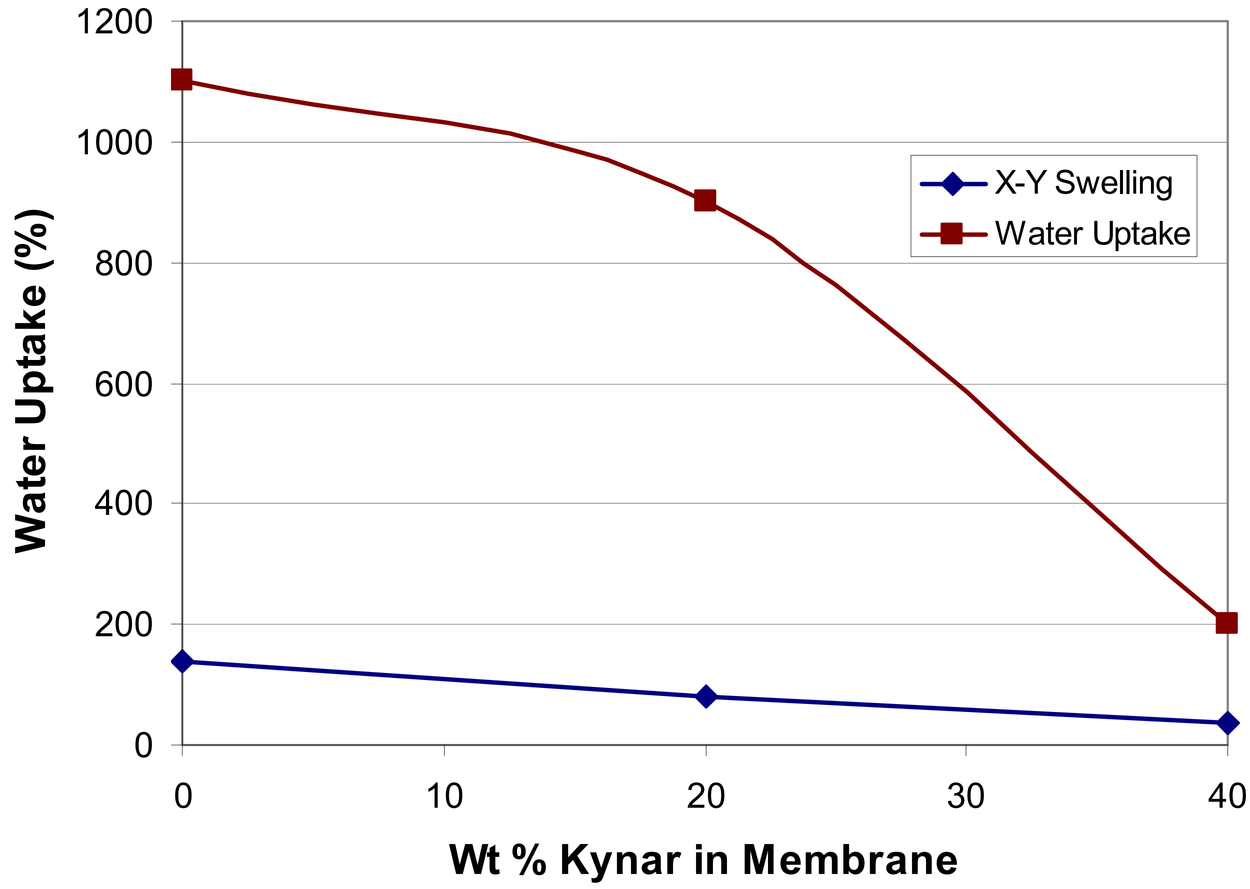
S map



F map

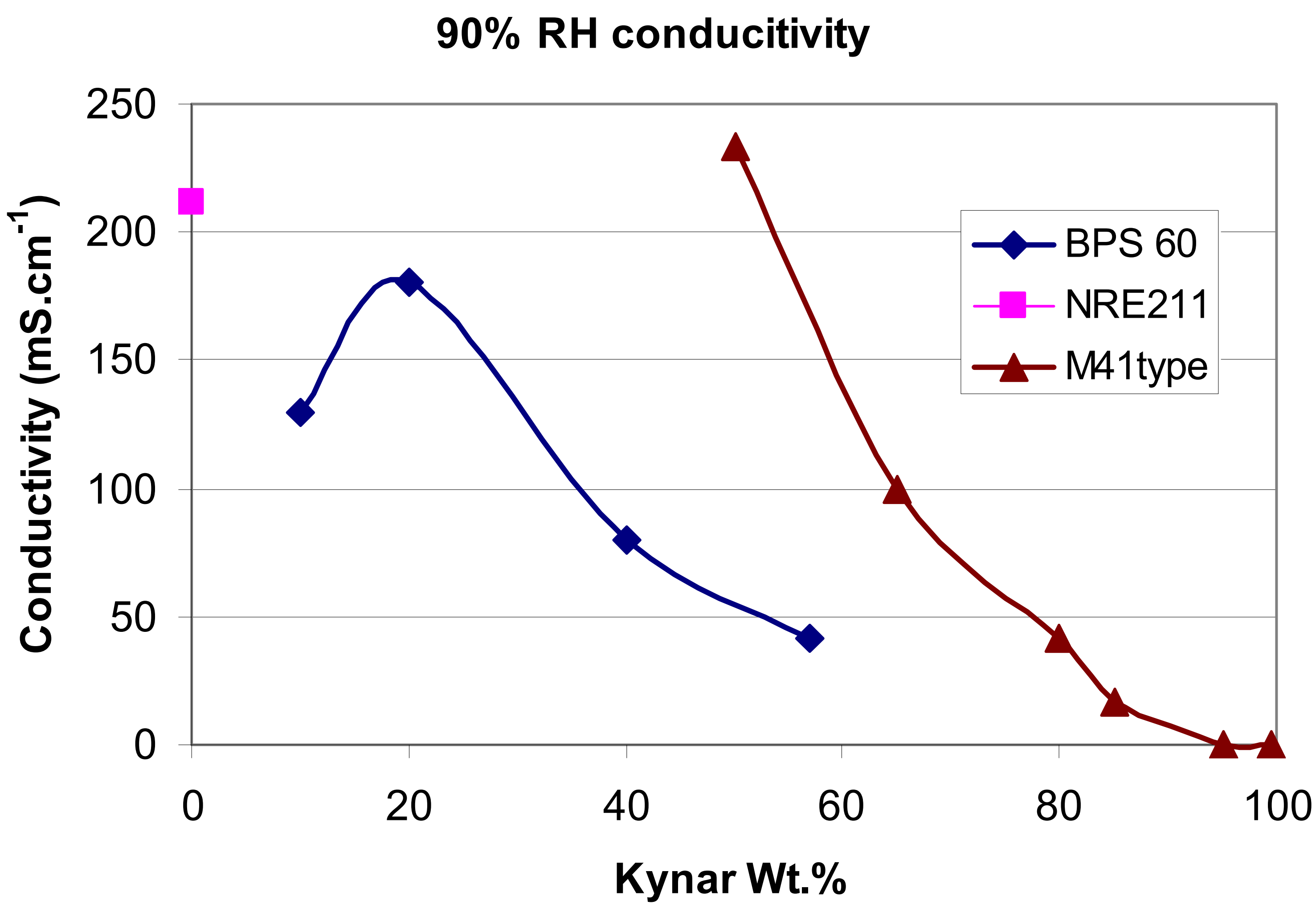
S and F form separate phases F/S=10

BPSH-60/Kynar® Membranes – Water Uptake



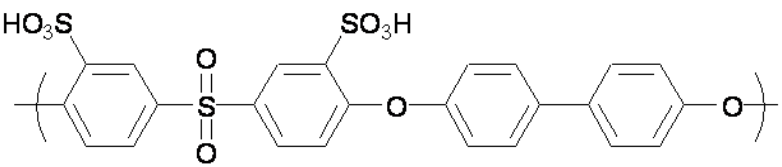
- Water uptake increases substantially with higher loading of BPSH-60
- Swelling greatly reduced with Kynar® blending

BPSH-60/Kynar® Membranes - Conductivity

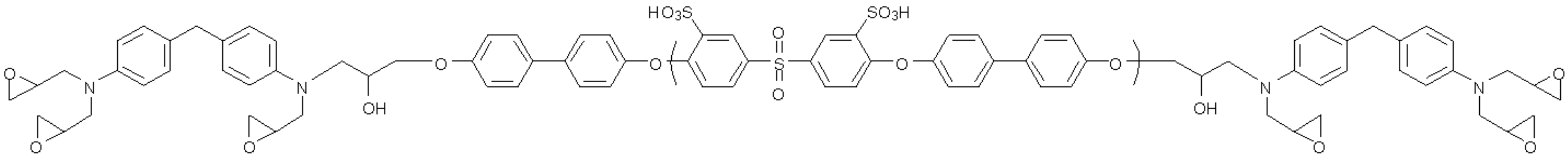


BPSH-100 Copolymer Blends

- 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

Overall Summary

- M41 shows superior durability in accelerated *in-situ* testing
- M41 MEAs shown to operate down to 65% RH (inlet)
- Disulfonated monomer approach validated
- Initial M70 membranes
  - Order-of-magnitude increase in conductivity vs. M43
  - Continuing membrane optimization
  - Continuing membrane *ex-situ* performance testing
  - Starting MEA *in-situ* performance and durability testing

- BPSH-60 polyelectrolytes shown to blend with Kynar®
- BPSH/PVDF blends show marked reduction in swelling
- Transitioning to BPSH-100 to improve low RH conductivity

Future Work

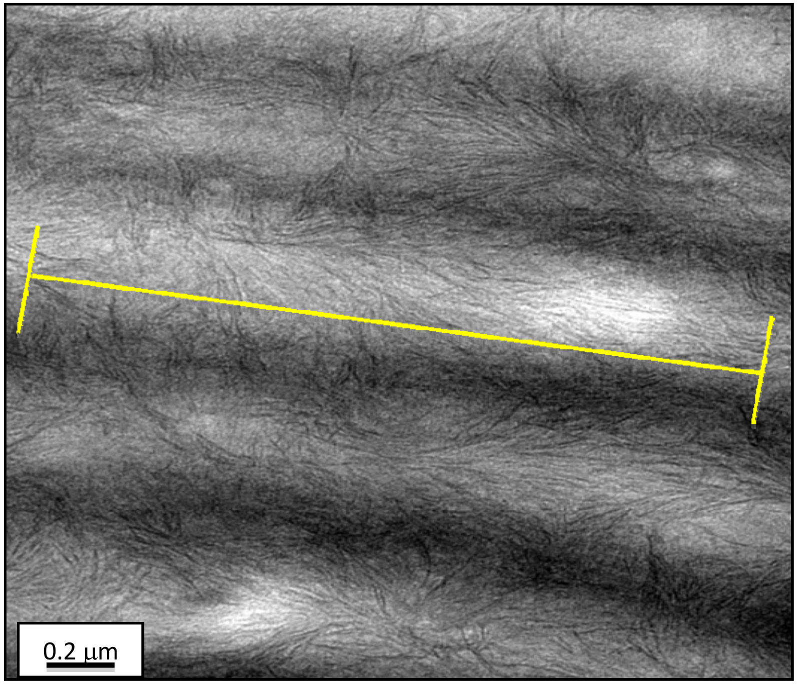
- M70 Membranes
  - Continuing membrane optimization
  - Continuing membrane *ex*- and *in-situ* durability and performance testing
  - Planned pilot production run
  - MEA cycling durability testing
- BPSH/Kynar® Blend membranes
  - Optimize BPSH-100 (cross-linkable) blending with PVDF
  - Validate efficient BPSH-100 cross-linking
  - BPSH-100 / Kynar® blend ex- and in-situ durability and performance testing
- Develop novel monomers/polyelectrolytes with even lower EW
- Polyelectrolyte / PVDF Blend Morphology
  - Continue investigation of complex blend morphology (M43)
  - Correlate morphology changes to performance

Acknowledgements

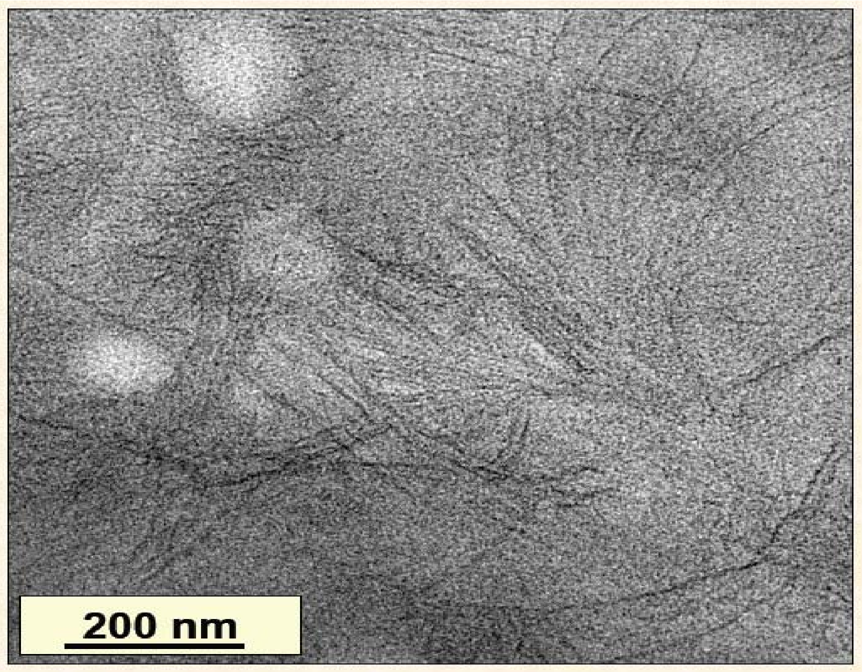
- US Department of Energy
  - Nancy Garland
  - Kathi Epping
  - Reg Tyler
  - Tom Benjamin
- Johnson Matthey Fuel Cells
  - Rachel O'Malley, Graham Hards, Jonathan Sharman
- Oak Ridge National Laboratory
  - Karren More, Harry Meyer, Shawn Reeves
- University of Hawai'i – Hawai'i Natural Energy Institute
  - Rick Rocheleau, Keith Bethune
- Virginia Tech
  - Prof. Jim McGrath
- Arkema Fuel Cells Team

Supplemental Slides

TEM – M43 Membranes



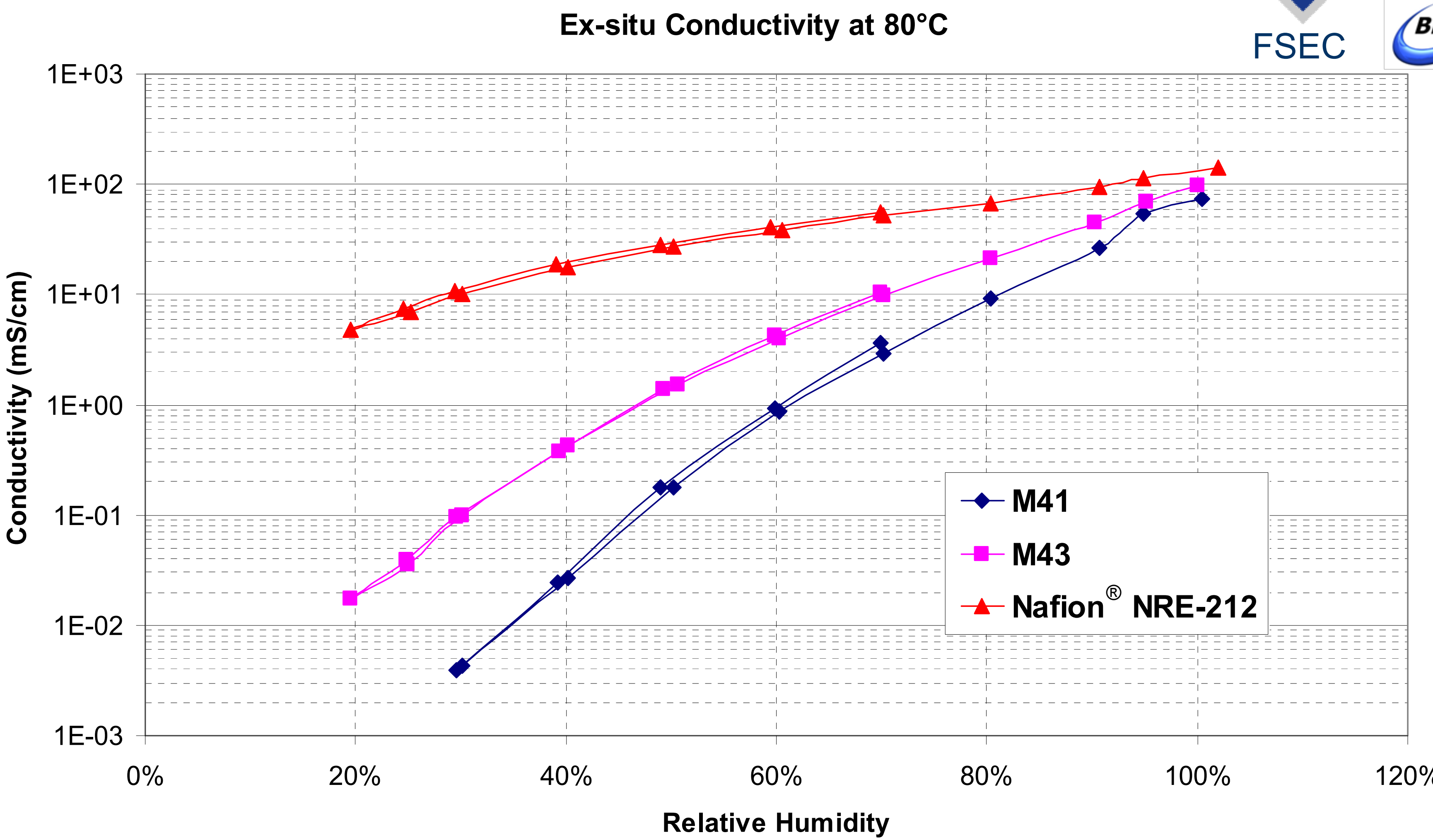
15% Polyelectrolyte



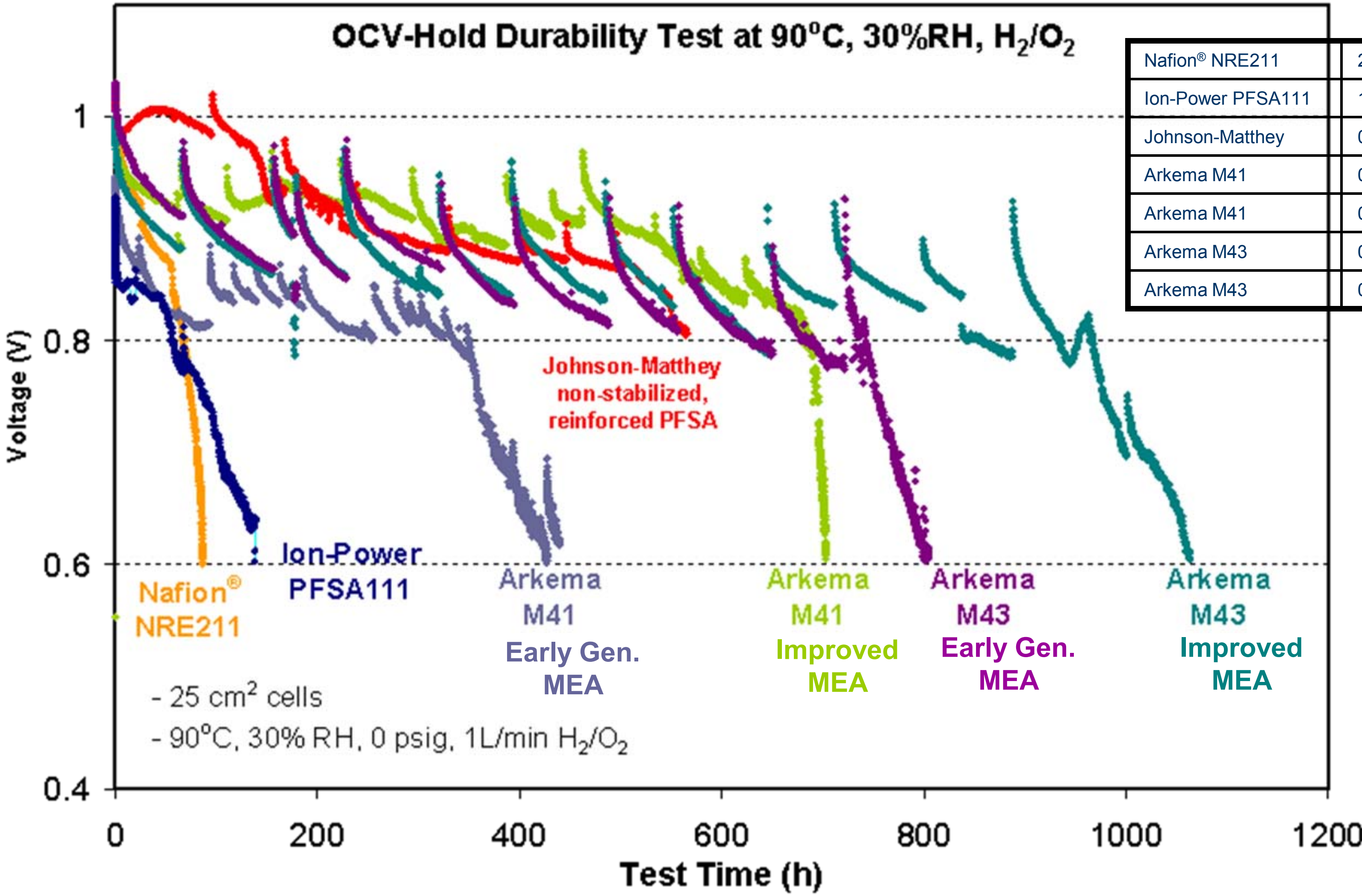
35% Polyelectrolyte

- Very complex morphology in blend membranes
  - Kynar® crystallites, polyelectrolyte domains, very tiny structures
  - Ongoing work using SEM, TEM, STEM, AFM and X-Ray Scattering
  - Determining baseline structure in M43, then adjust process variables
    - Relate process changes to morphology changes to membrane performance

M43 Initial Results

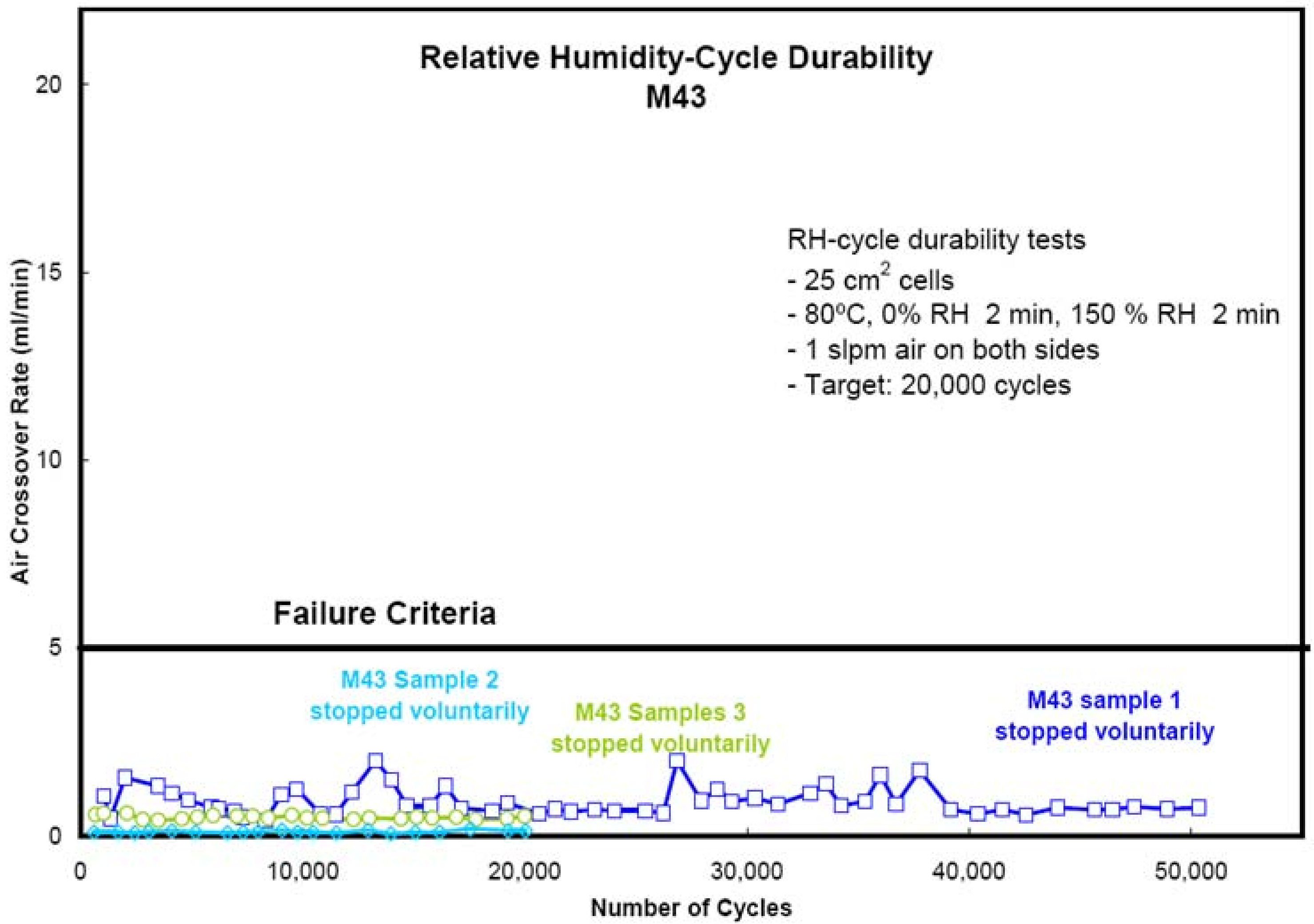


M43 OCV Durability



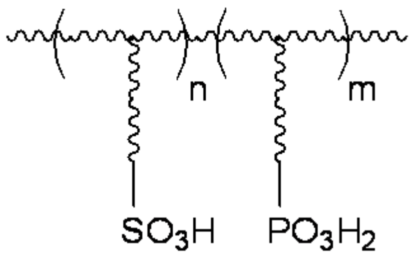
Nafion® NRE211	2.3 mV/h
Ion-Power PFSA111	1.7 mV/h
Johnson-Matthey	0.33 mV/h
Arkema M41	0.39 mV/h
Arkema M41	0.26mV/h
Arkema M43	0.32mV/h
Arkema M43	0.20mV/h

M43 RH Cycling Durability



M5x Membrane Generation

- Polyelectrolyte with phosphonic acid groups
  - M41: Highly sulfonated polyelectrolyte
- M51
  - ¼ of sulfonates replaced with phosphonate
- M52
  - ½ of sulfonates replaced with phosphonate
- M53
  - ¾ of sulfonates replaced with phosphonate



n:m = 3:1, 1:1, or 1:3

- Reoptimized PVDF blending parameters
- Produced new membranes (lab-scale)
- Conductivity and MEA performance poor
  - Approach abandoned in lieu of M70 and BPSH work

ARKEMA