Improved, Low-Cost, Durable Fuel Cell Membranes

2007 Hydrogen Program Annual Review

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Arkema, Inc.

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Overview

Proposed Timeline
- Start Date: July 2007
- End Date: July 2010

Budget
- Total Funding
  - DOE: $6,278K
  - Partners: $1,569K

Barriers & 2010 Targets
- Cost
  - $20/m^2$
- Durability
  - 5000 hrs (cycling)

Partners
- Arkema:
  - Virginia Polytechnic Institute
  - Oak Ridge National Laboratory
- Johnson Matthey Fuel Cells
- University of Hawaii

Objectives

- Overall

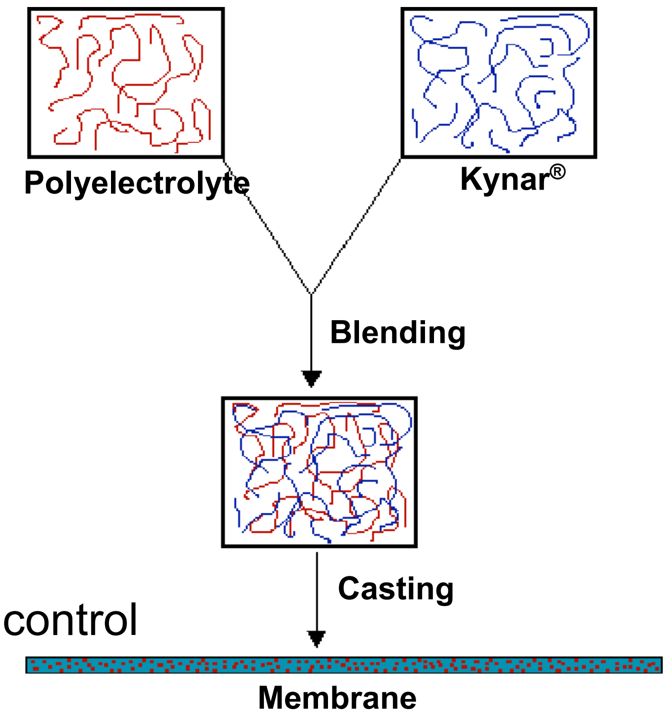
  - Develop a membrane capable of operating at temperatures up to 120°C and ultra-low relative humidity of inlet gases, per DOE targets. A clear road map to attain this goal based on previously developed PVDF/polyelectrolyte blend technology has been devised.

  - Optimize an MEA based on this new membrane that allows full durability characterization under DOE targets conditions.

  - Elucidate ionomer and membrane failure and degradation mechanisms via *ex-situ* and *in-situ* accelerated testing. Develop mitigation strategies for any identified degradation mechanism.

Arkema's Approach

- Polymer blend system to decouple H^+ conductivity from other requirements
  - Kynar® PVDF
    - Engineering thermoplastic
    - High chemical resistance
    - High electrochemical stability
    - Provide mechanical support
  - Polyelectrolyte
    - H^+ conduction
    - Physical properties unimportant
- Robust blending process
  - Applicable for various polyelectrolytes
  - Capable of morphology and physical property control
- Lower cost approach compared to PFSA
  - Kynar® PVDF - commercial product
  - Polyelectrolyte – hydrocarbon based
- Feasibility demonstrated (M31 & M41)

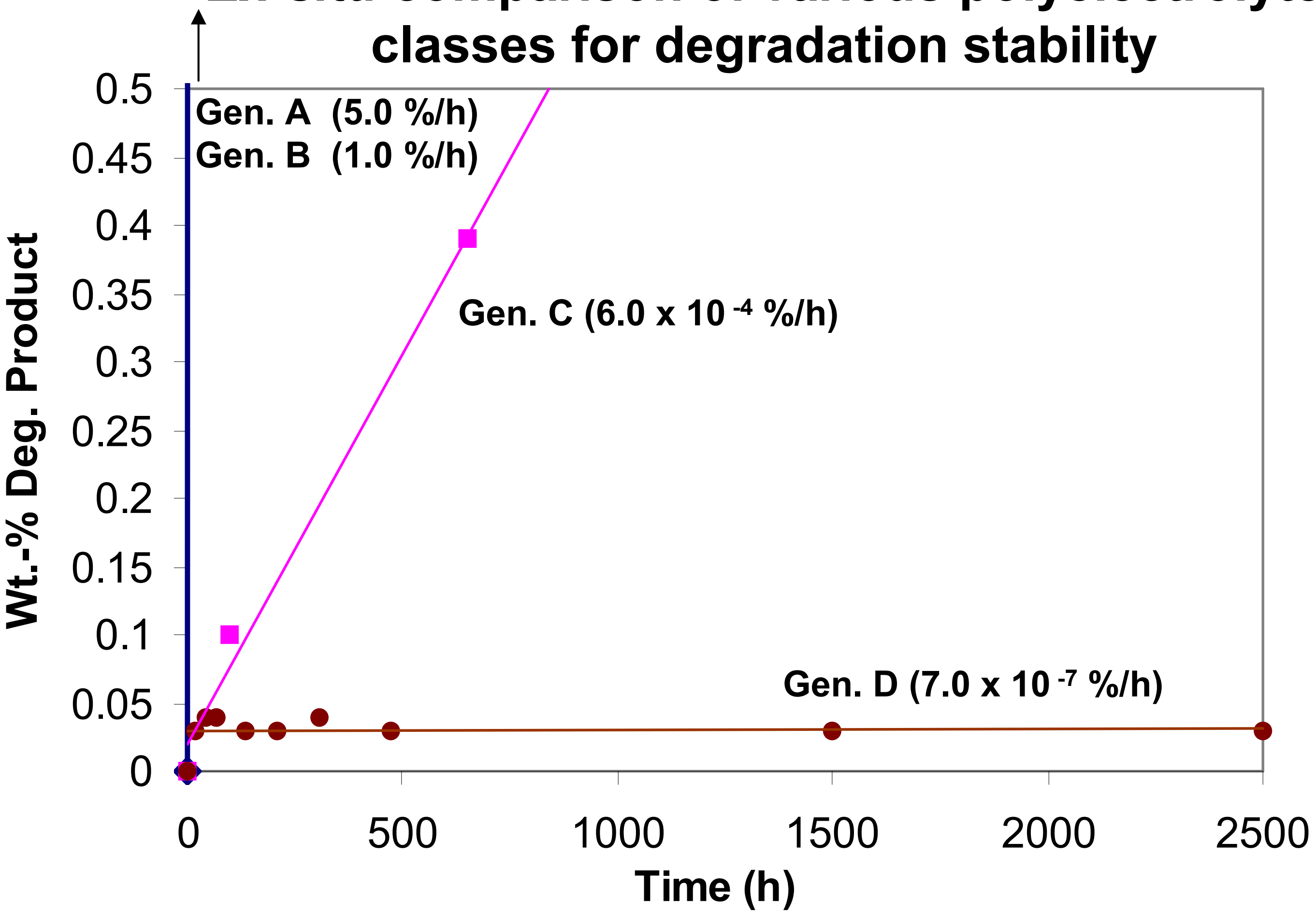


Proposed Project Flow

	I. Polyelectrolyte Development	II. Membrane Development	III. MEA & Fuel Cell Testing	IV. Large Cell Validation
Low RH / High Temp Membrane	• Identify critical go/no go criteria for polyelectrolyte • Prepare and test various polyeletrolyte candidates •Down select polyelectrolyte for membrane evaluations •Arkema & VPI	• Identify critical ex-situ go/no go criteria for membranes • Develop various membrane compositions based on down selected PE and characterize membranes, including morphology • Down select membranes for MEA development • Arkema & ORNL	• Identify critical *in-situ* go/no go criteria, per DOE targets • Develop MEAs optimized for running new membrane under DOE conditions • Conduct EOL testing and accelerated durability • Arkema & Johnson Matthey	• Develop testing protocols • Fabricate large 5 & 7 layer MEAs • Conduct large scale cell testing including BOL & EOL diagnostics • Arkema, Johnson Matthey & U. of HI

I. Polyelectrolyte Development

Ex-situ comparison of various polyelectrolyte classes for degradation stability



- Generation D polyelectrolyte (used in M41) showed no measurable degradation in our *ex-situ* accelerated testing

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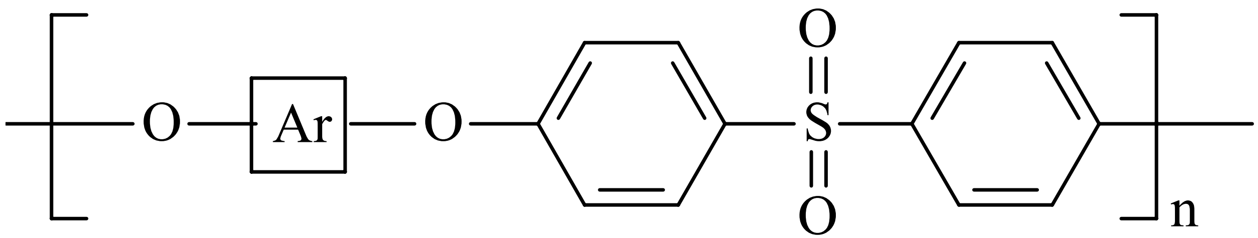
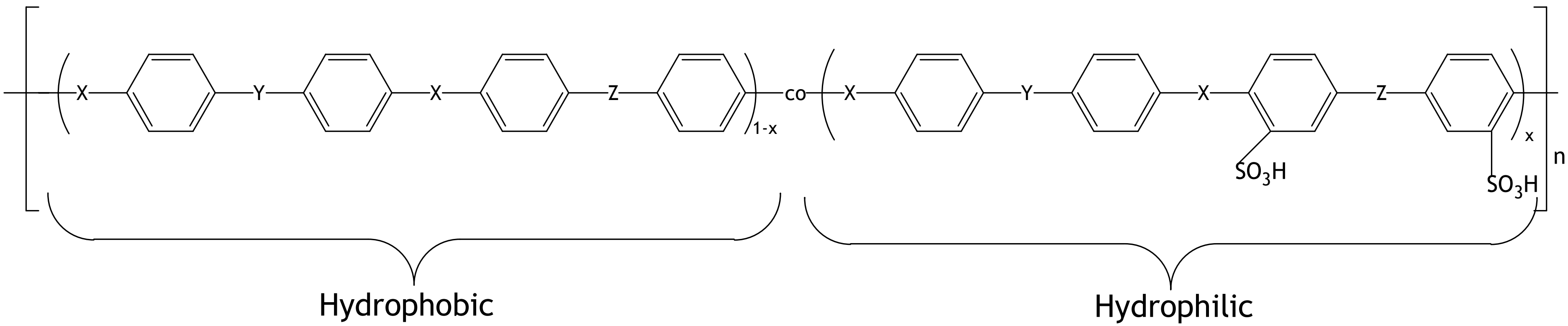
Another possible structure class to be evaluated: Poly(arylene Ether Sulfone)s



- High thermal stability
- Good stability against acid, bases and oxidants
- Good mechanical properties
- Film-forming, high-performance thermoplastics
- Melt processible
- Several monomers are commercially available

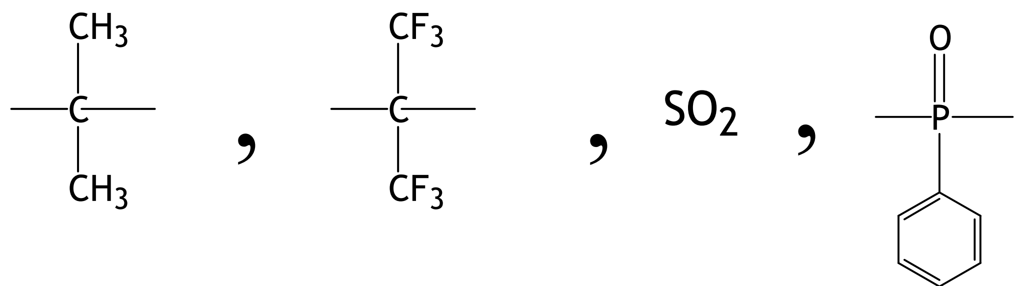
Wang, S. and McGrath, J.E. In: *Polyarylene Ethers*: *A review*, In: *Step Polymerization*, Rogers, M. and Long, T.E., Eds., Wiley, **2003**

Tailoring of Poly(arylene Ether Sulfone)s

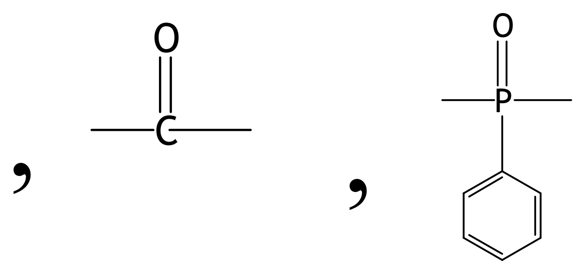


X = O, S

Y = a bond,



Z = SO_2

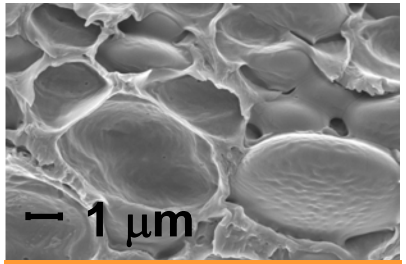


W. Harrison, F. Wang, J. Mecham, V. Bhanu, M. Hill, Y. Kim, and J. E. McGrath, Synthesis of Sulfonated Poly(arylene ether copolymers). J. Poly.Sci. 41, 2264-2276 (2003).

II. Membrane Development

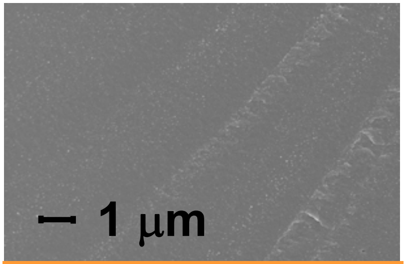
Polyelectrolyte	Conductivity (mS/cm)
• Model materials	
• P(AMPS)	90-120
• Sulfonated Polystyrene	50-90
• Proprietary polyelectrolytes	
• Generation A (M31)	120-150
• Generation B	120-140
• Generation C	60-120
• Generation D (M41)	120 -140

Phase Separated



20 - 40 mS/cm

Compatibilized



>100 mS/cm

Kynar® PVDF blending process is generally applicable for highly protogenic polymers

M41 Physical Properties

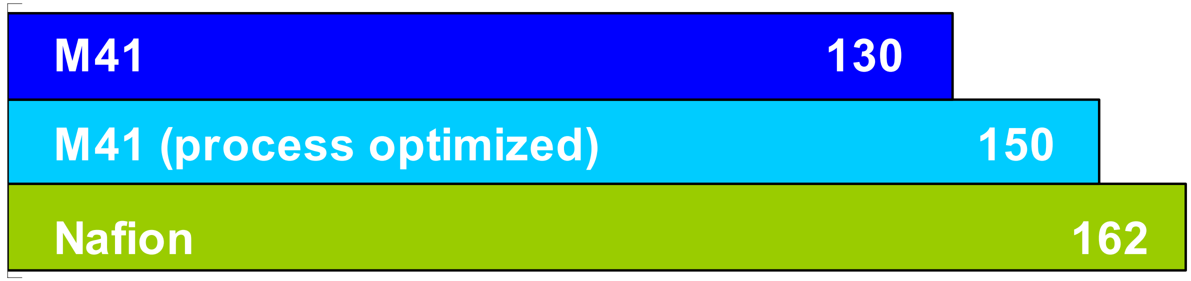
	Nafion® 111	M41
Dry Thickness (μm)	25	25
Equivalent Weight	1100	800
Density (g/cm^3)	1.8	1.5
Water Uptake (%)	37	60
X,Y Swell (%)	15	20
Thickness Swell (%)	14	10-15
Tensile Stress Break (MPa)	19	27
Elongation (%)	103	95
Tear Strength(lb_f/in)	404	934
Tear Propagation (lb_f)	0.004	0.018

- M41 shows equal/better mechanical properties than Nafion® 111

M41 Transport Properties

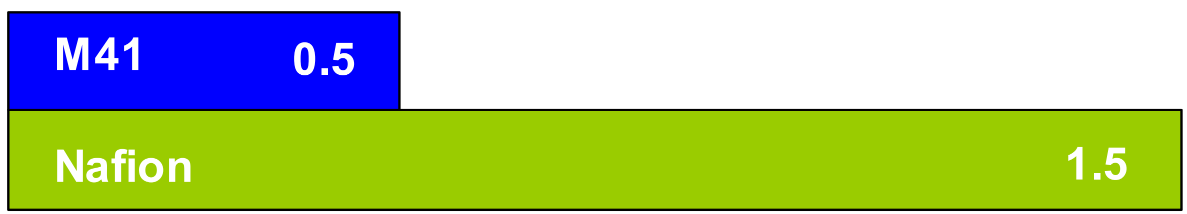
- Equivalent proton Conductivity compared to Nafion®

Proton Conductivity (mS/cm)*



- Superior gas barrier properties than Nafion® membranes

H_2 permeation rate (mA/cm^2)**



* by 4-point in-plane AC measurements in water at 70°C
** by electrochemical method at 80°C with 100% RH

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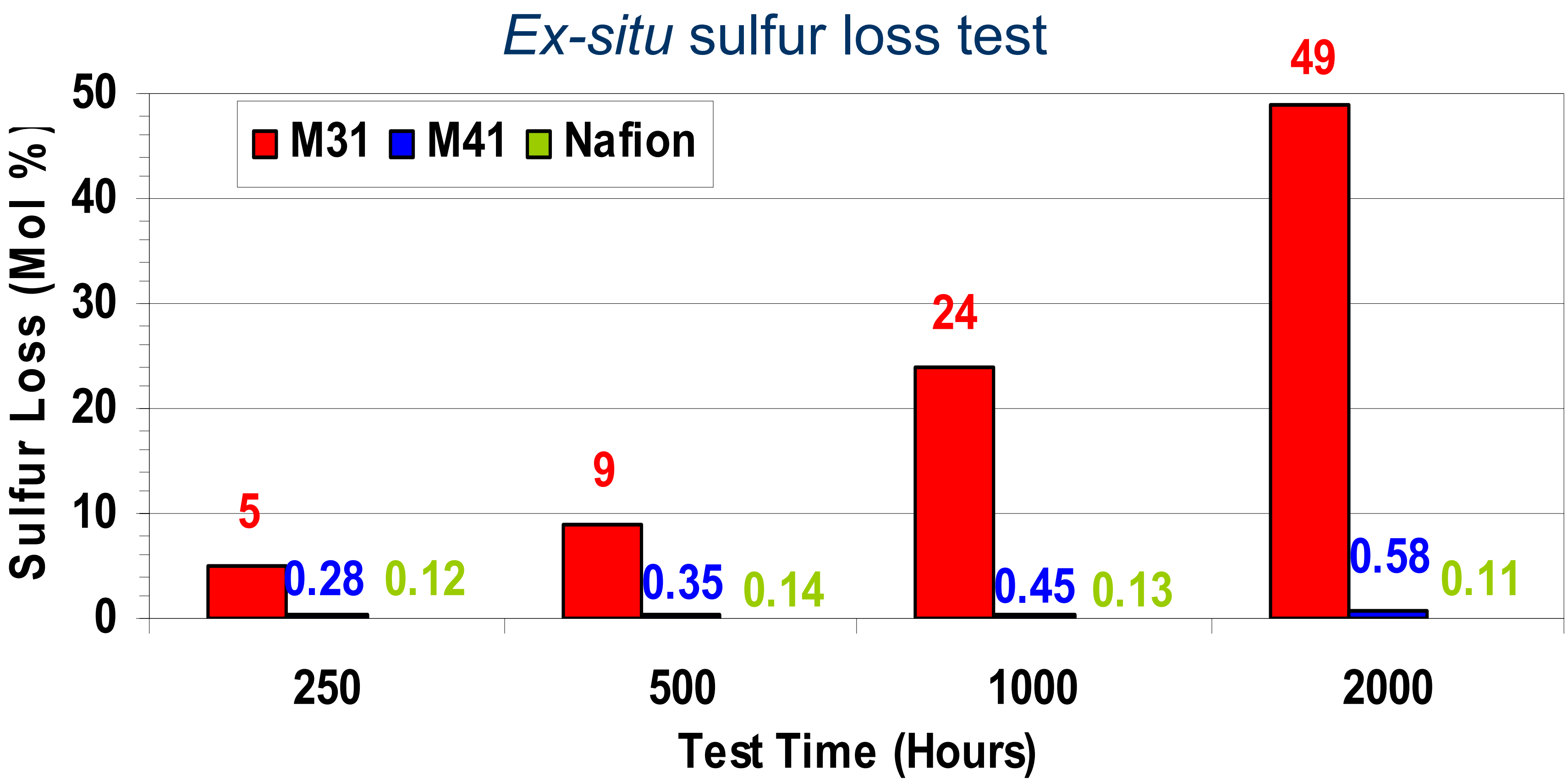
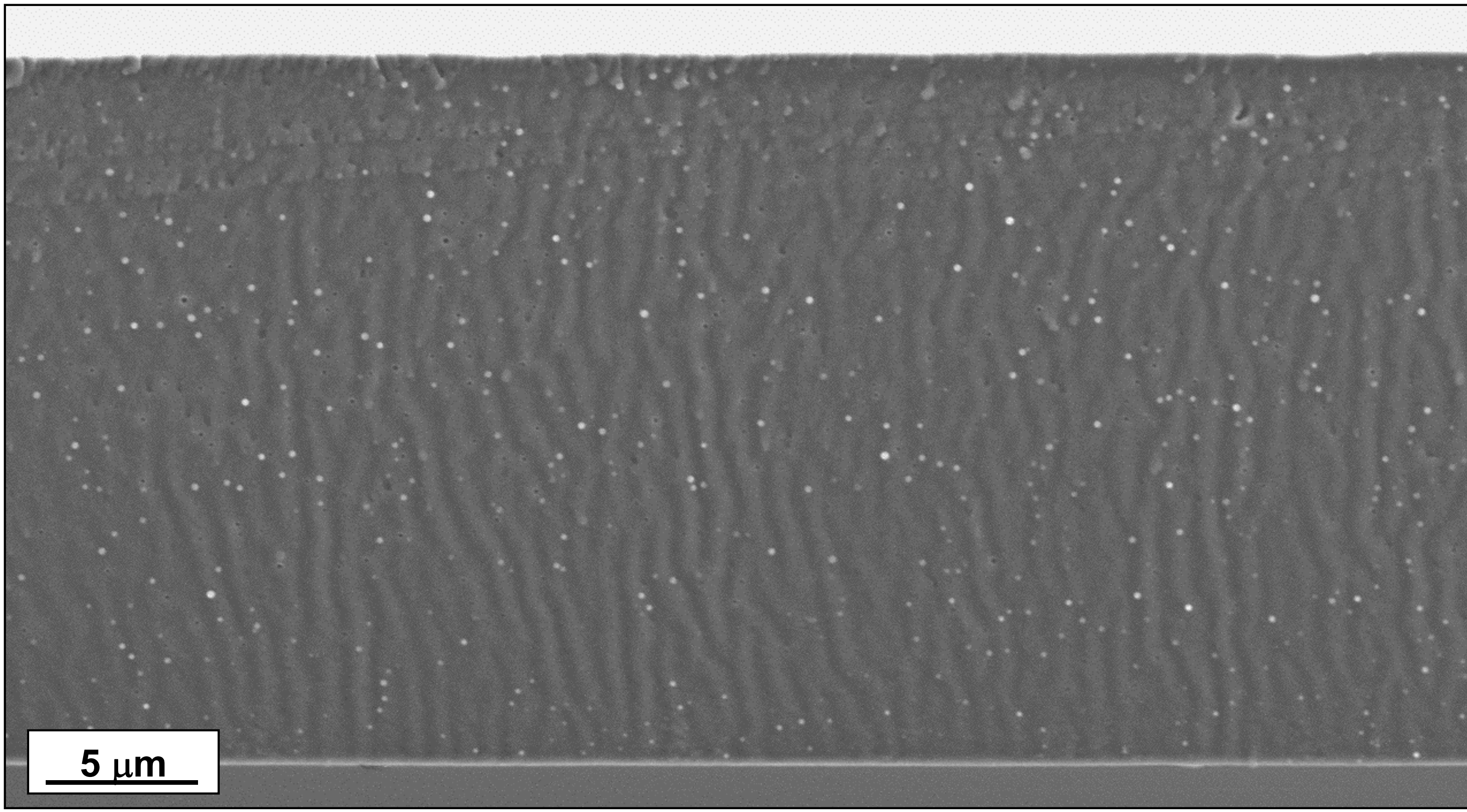
Ex-situ Membrane Chemical Stability



- M41 shows less than 1% sulfur loss over 2000hr

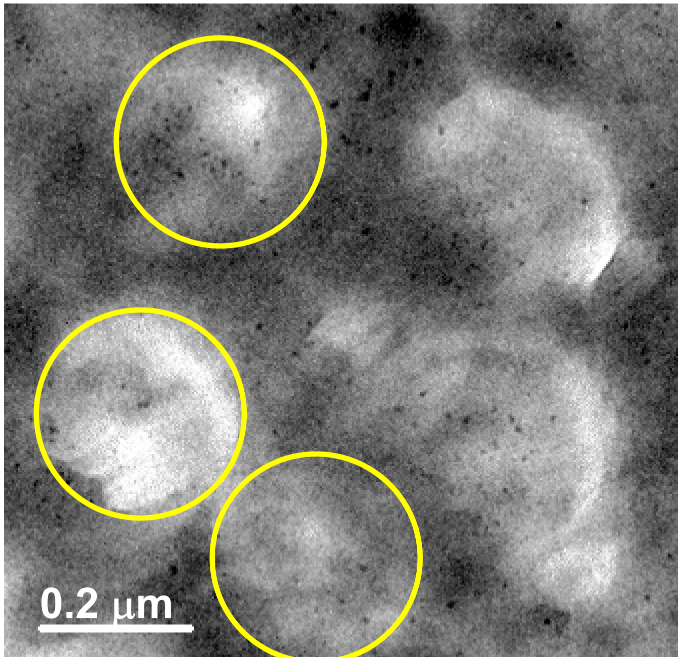
Morphology Characterization: M31 TEM (ORNL)

- ~300 nm-wide striations
  - Possible water diffusion pathways



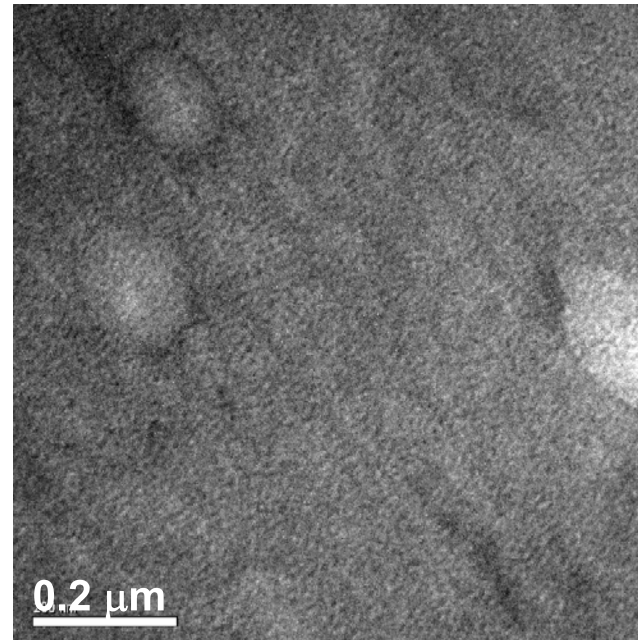
Morphology Characterization: M41 TEM (ORNL)

M41 (early development stage)



Conductivity = 100 mS/cm

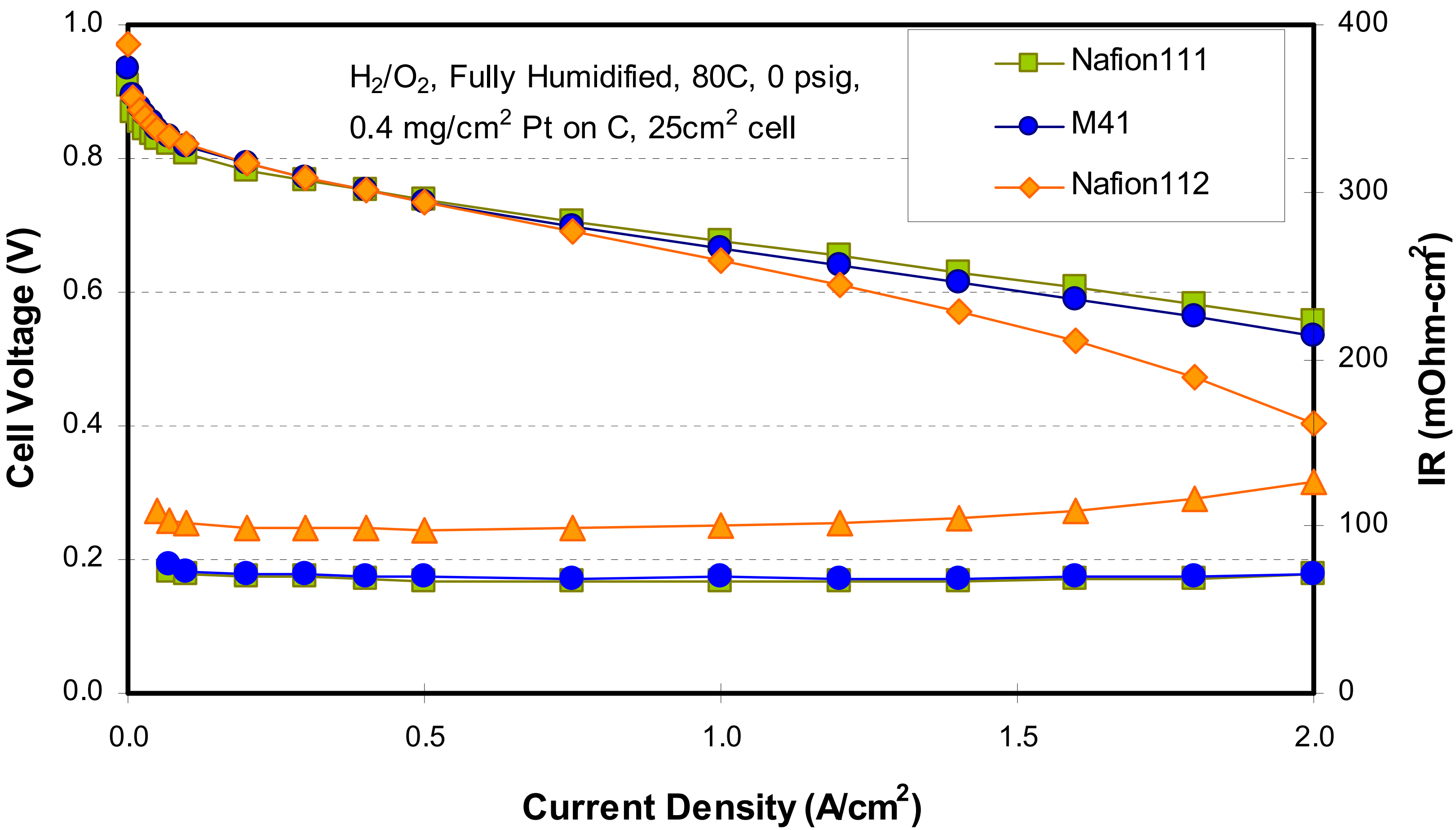
M41 (pilot membrane)



Conductivity = 130 mS/cm

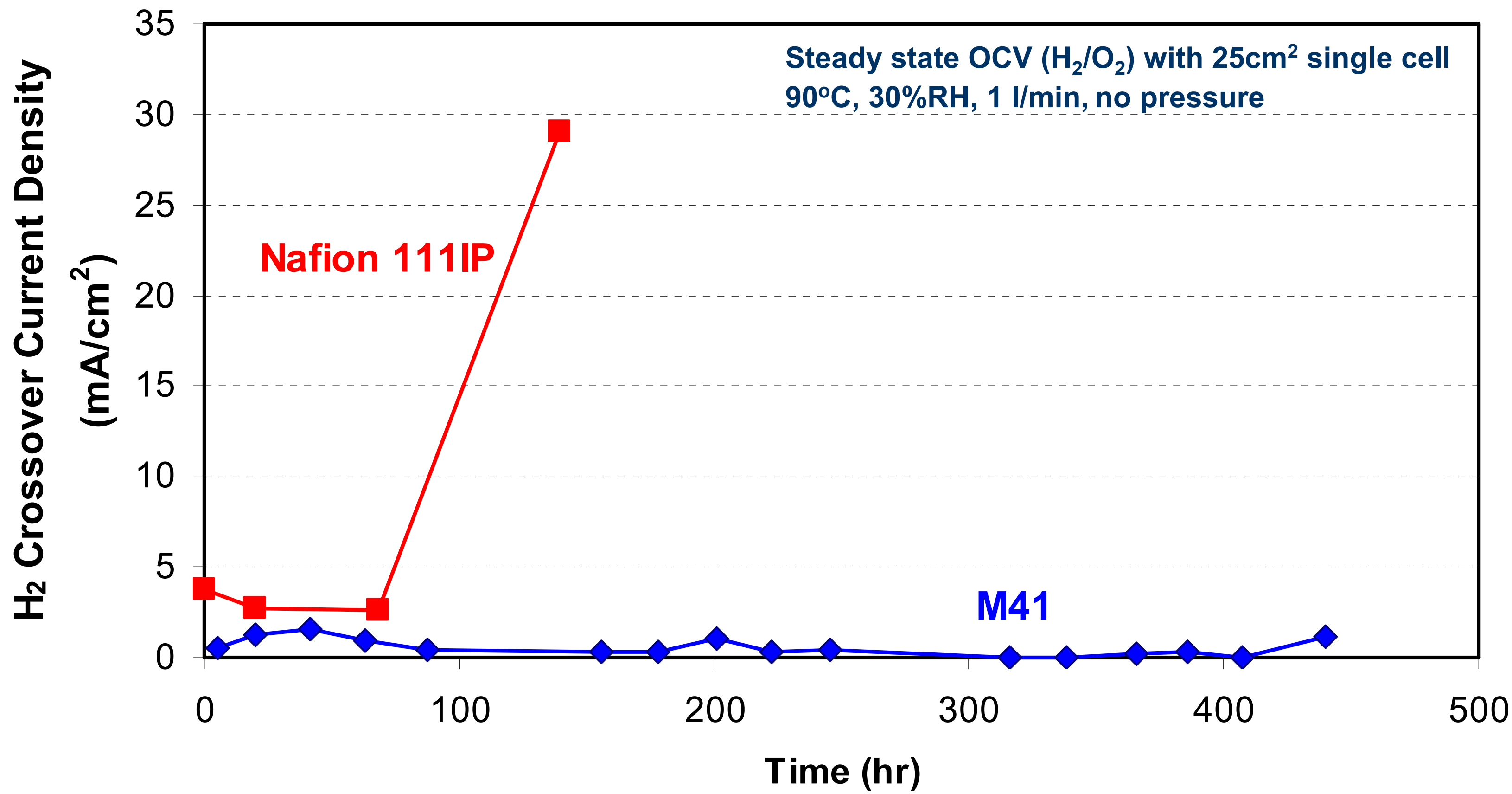
- High-resolution TEM characterization to gain understanding of structure and property

III. MEA & Fuel Cell Testing: M41 Beginning of Life Performance



- Comparable in-cell performance to Nafion® 111 demonstrated

M41 OCV Durability: Hydrogen Crossover



- Nafion® 111IP membranes failed at 100 –150 hrs
- M41 membranes exhibit superior chemical stability in fuel cells

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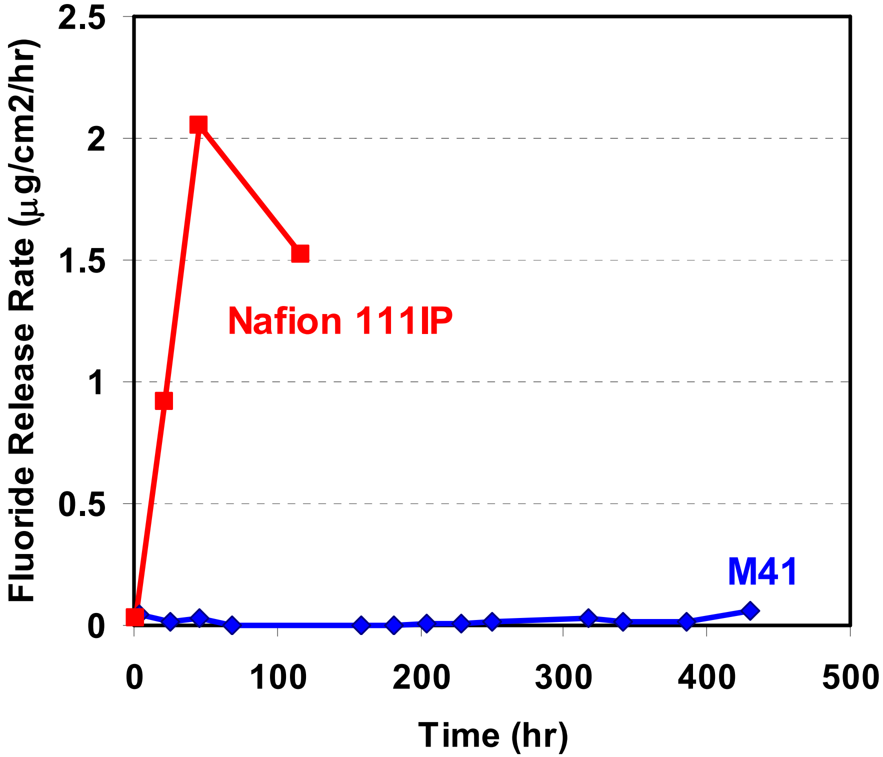
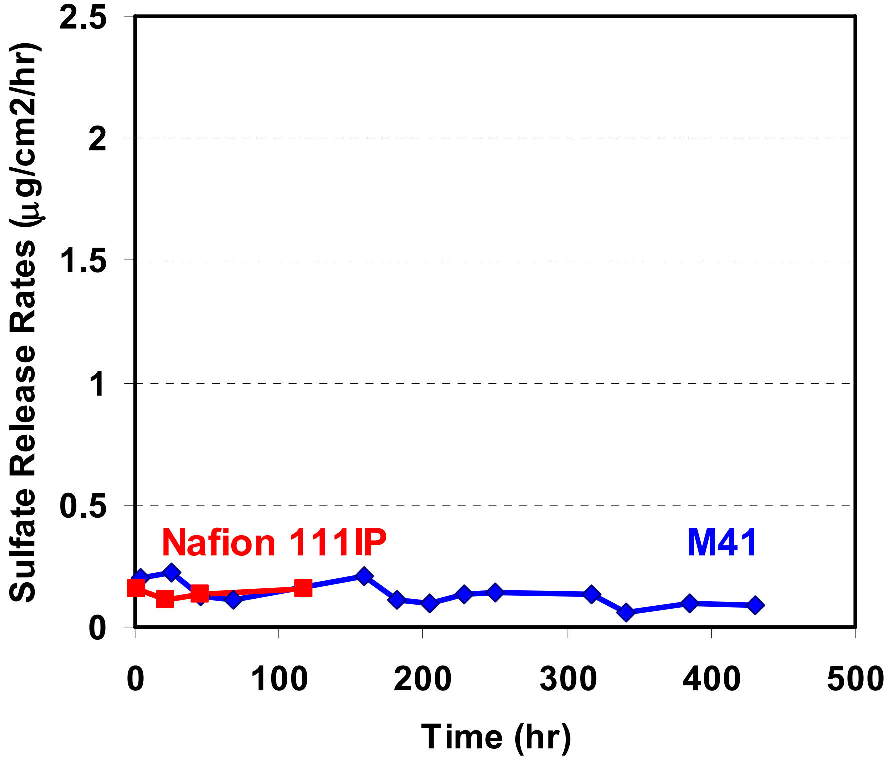
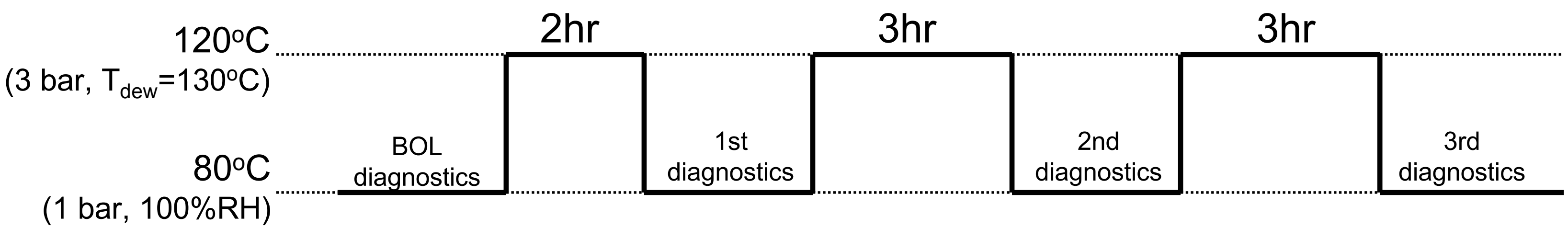
M41 OCV Durability: Effluent Water Analysis

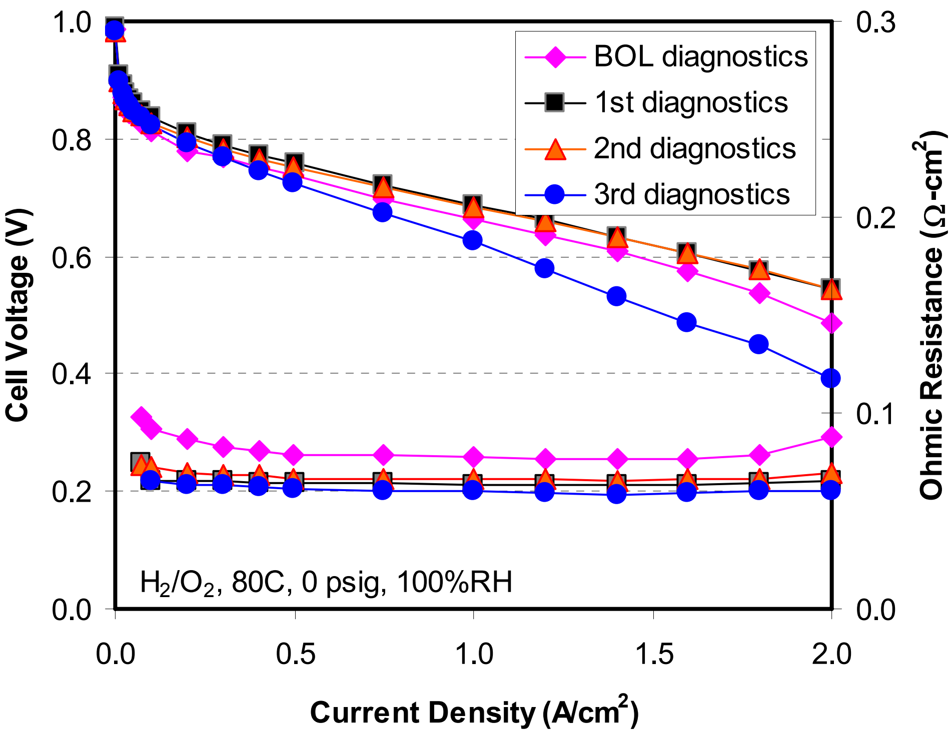


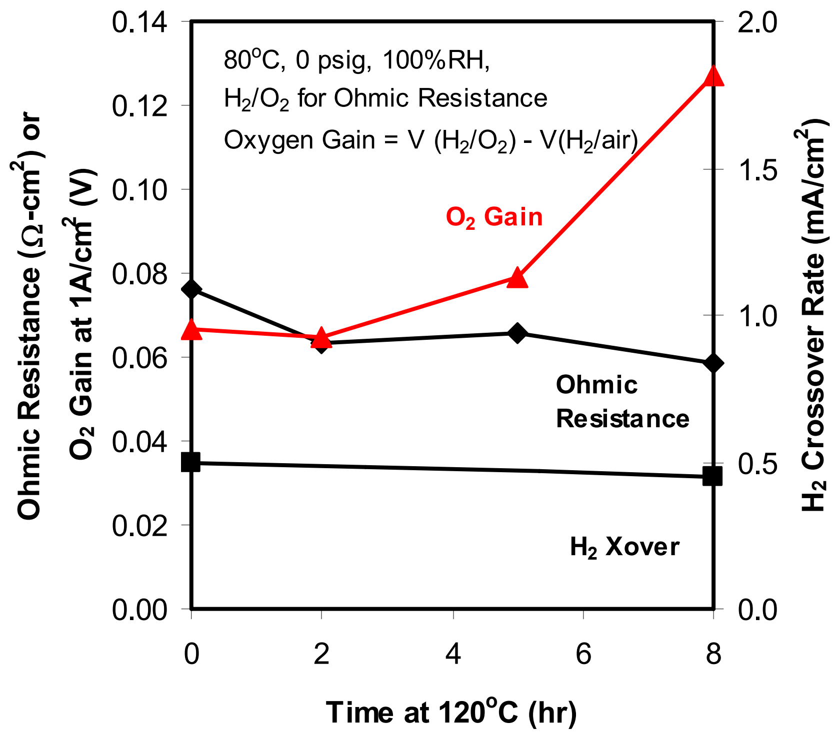


- M41 shows significantly lower fluoride release rates and similar sulfate release rates to Nafion® 111 membranes

M41 High Temperature Excursion Stability







- Stable membrane performance is shown after 8 hrs at 120°C
  - Electrode degradation is shown by higher O_2 gain and 20% loss of ECA

Future Work

- This program is scheduled to begin 2Q2007

- Work for balance of FY07 and FY08
  - Develop new generation polyelectrolytes (Arkema & VPI)
    - Identify key target polyelectrolytes
    - Begin synthesis and *ex-situ* stability of new polyelectrolytes
    - Down select first candidates to carry into membrane development

  - Membrane development (Arkema)
    - Begin blending studies with down selected polyelectrolytes
    - Conduct *ex-situ* membrane testing to DOE targets

  - High-resolution morphology characterization for structure-property understanding (ORNL & Arkema)

Summary

- Arkema has developed a Kynar/polyelectrolyte blending technology capable of incorporating a wide variety of polyelectrolyte chemistries for producing fuel cell membranes

- An iterative process has been developed and used successfully to down select materials at early stages to speed the development cycle

- The latest membrane generation developed (M41) has demonstrated:
  - Equivalent fuel cell performance to Nafion® membranes
  - Better mechanical properties
  - Lower gas permeability
  - At least 4x increase in OCV durability versus Nafion® 111

- The technology and approaches already developed are fully applicable to the development of new membrane families with further improved performance at higher temperatures and lower relative humidities

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