Development of Low-cost, Durable Membrane and MEA for Stationary and Mobile Fuel Cell Applications

2007 Hydrogen Program Annual Review

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Project ID#: FC9

Overview

Timeline

- Start Date: Oct. 2003
- End Date: June 2007
  (with no-cost extension)

Budget

- Total Funding
  - DOE: $5,771K
  - Partners: $2,241K
- FY2006 Funding
  - $2,205K
- FY2007 Funding
  - $2,063K

Barriers

- B: Cost
  - $20/m^2 (Membrane Target)
  - $10/kW (MEA Target)
- A: Durability
  - 5000 hours (Target)

Partners

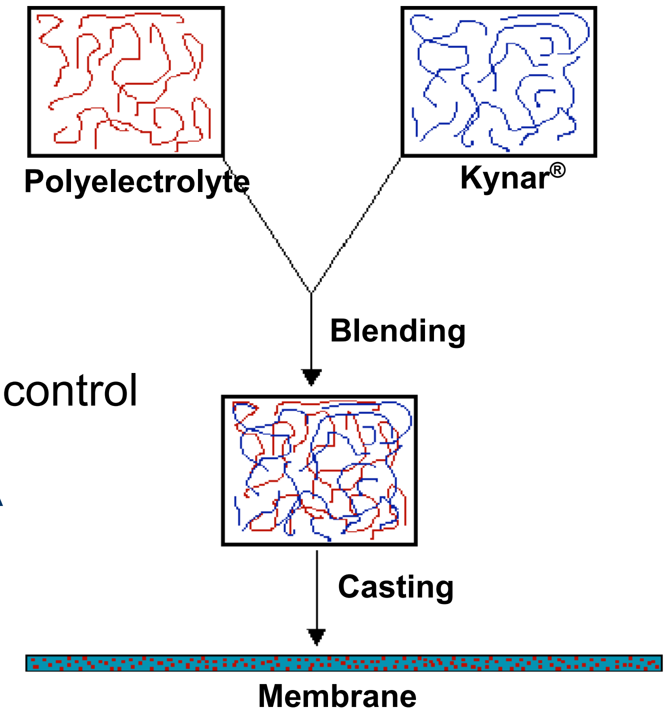
- Arkema:
  - Georgia Tech
- Johnson Matthey Fuel Cells
- UTC Fuel Cells
  - University of Hawaii

Objectives

- Overall
  - Develop low-cost and durable membrane and MEA that can meet DOE targets and help drive the commercial reality of fuel cells
- 2006-2007
  - Development and characterization of new-generation membranes
    - Morphology
    - Transport Properties
    - Mechanical Properties
    - Chemical Stability
  - MEA optimization
  - Durability testing of the membrane in fuel cells

Arkema's Approach

- Polymer blend system to decouple H^+ conductivity from other requirements
  - Kynar® PVDF
    - Engineering thermoplastic
    - High chemical resistance and 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)



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Approach : Project Progress

	Development of Polyelectrolytes	Formulation of Membranes	MEA & Fuel Cell Testing	Large Cell Validation
M31 generation	• Identified the requirements • Down-selected a structure • Synthesized sulfonated copolymer	• Validated blending versatility • Demonstrated comparable properties • Characterized morphology • Developed high throughput methods • Scaled up to pilot	• MEA optimized • Demonstrated comparable FC performance to PFSA • High decay rate observed in long-term testing	• Validation of BOL performance • UEA fabrication • UTC cell testing ($400 cm^2$ active area)
M41 generation	• Elucidated M31 failure mechanisms • Developed *ex-situ* PE screening method • Synthesized new generation chemically stable PE	• Successful membrane formulation • Property & morphology characterization • Scale up to pilot	• MEA fabrication • Electrode optimization • FC performance demonstration • Accelerated durability tests OCV durability RH cycle durability V-cycle durability	• MEA fabrication • UTC cell testing ($400 cm^2$ active area)

Completed **In Progress** (Y06-Y07) **Future Work**

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M41 Physical Properties

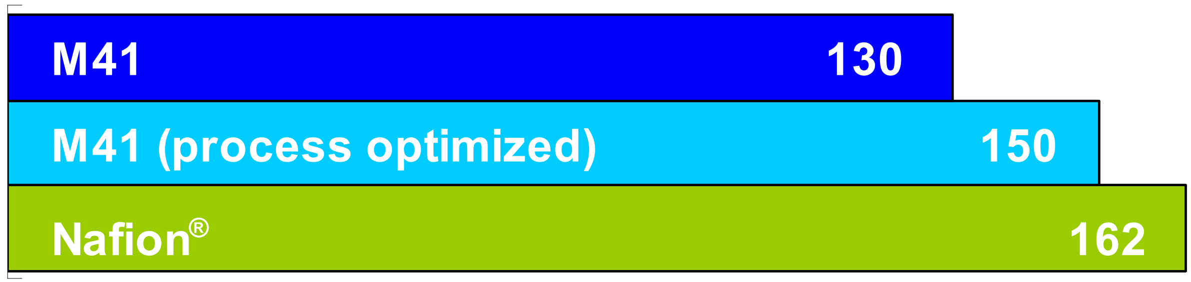
	Nafion®111	M41
Dry Thickness (μm)	25	25
Equivalent Weight	1100	800
Density (g/cm^3)	1.8	1.5
Water Uptake (%)	37	60
X,Y Swell (%)	15	20
Thickness Swell (%)	14	10-15
Tensile Stress Break (MPa)	19	27
Elongation (%)	103	95
Tear Strength(lb_f/in)	404	934
Tear Propagation (lb_f)	0.004	0.018

- 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 property than Nafion membranes

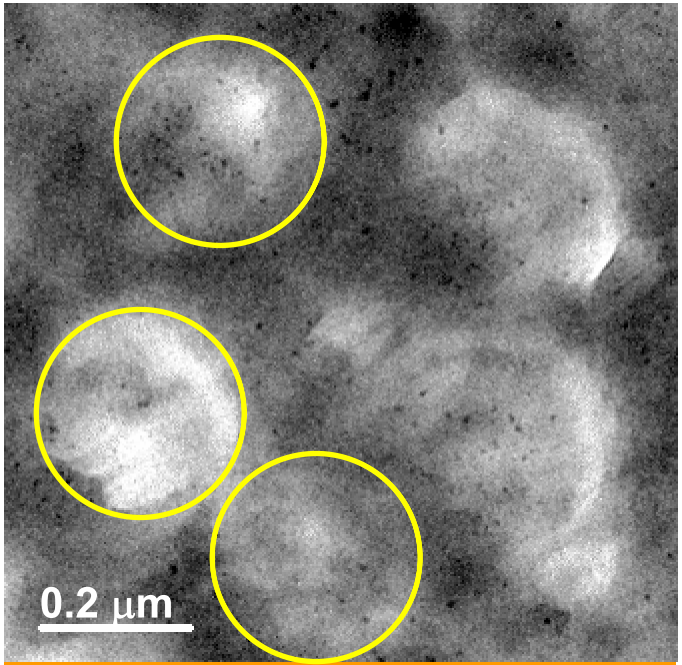
H_2 permeation rate (mA/cm^2)**

* by 4-point in-plane AC measurements in water at 70ºC

** by electrochemical method at 80ºC with 100% RH

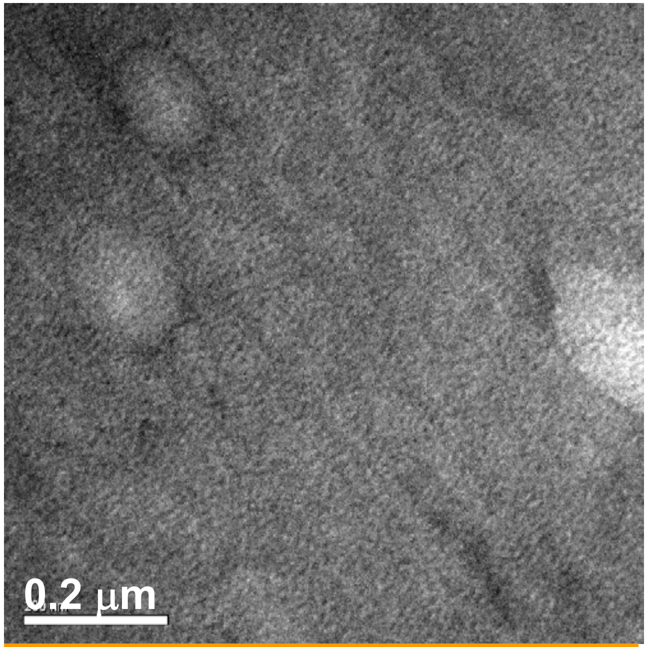
Morphology Characterization and Control

M41 (early development stage)



Conductivity = 100 mS/cm

M41 (Pilot membrane)

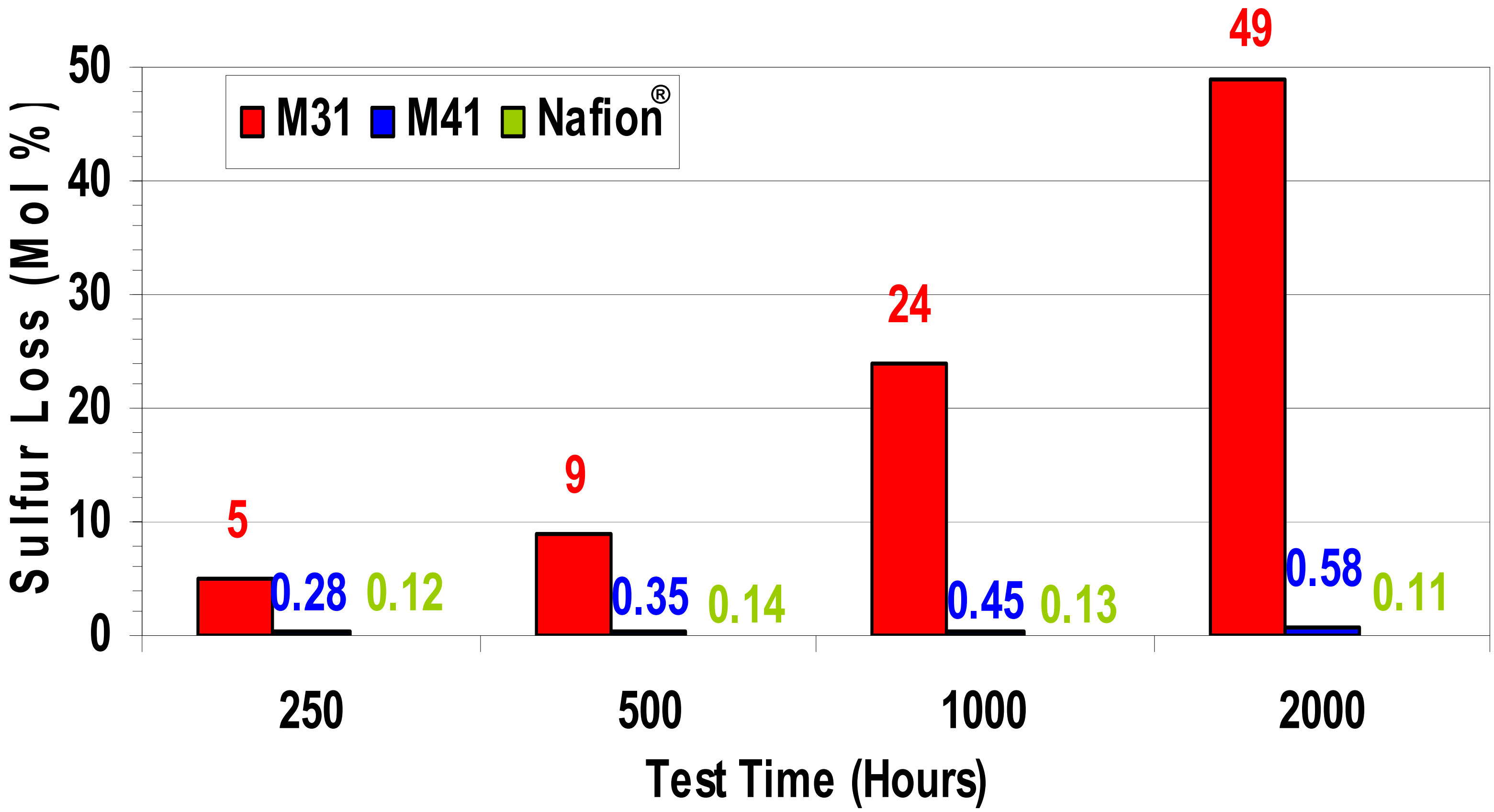


Conductivity = 130 mS/cm

- Range of morphologies possible
- High-resolution TEM characterization (collaboration with ORNL) to gain understanding of structure and property

M41 Chemical Stability

- In-house developed *ex-situ* sulfur loss test



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

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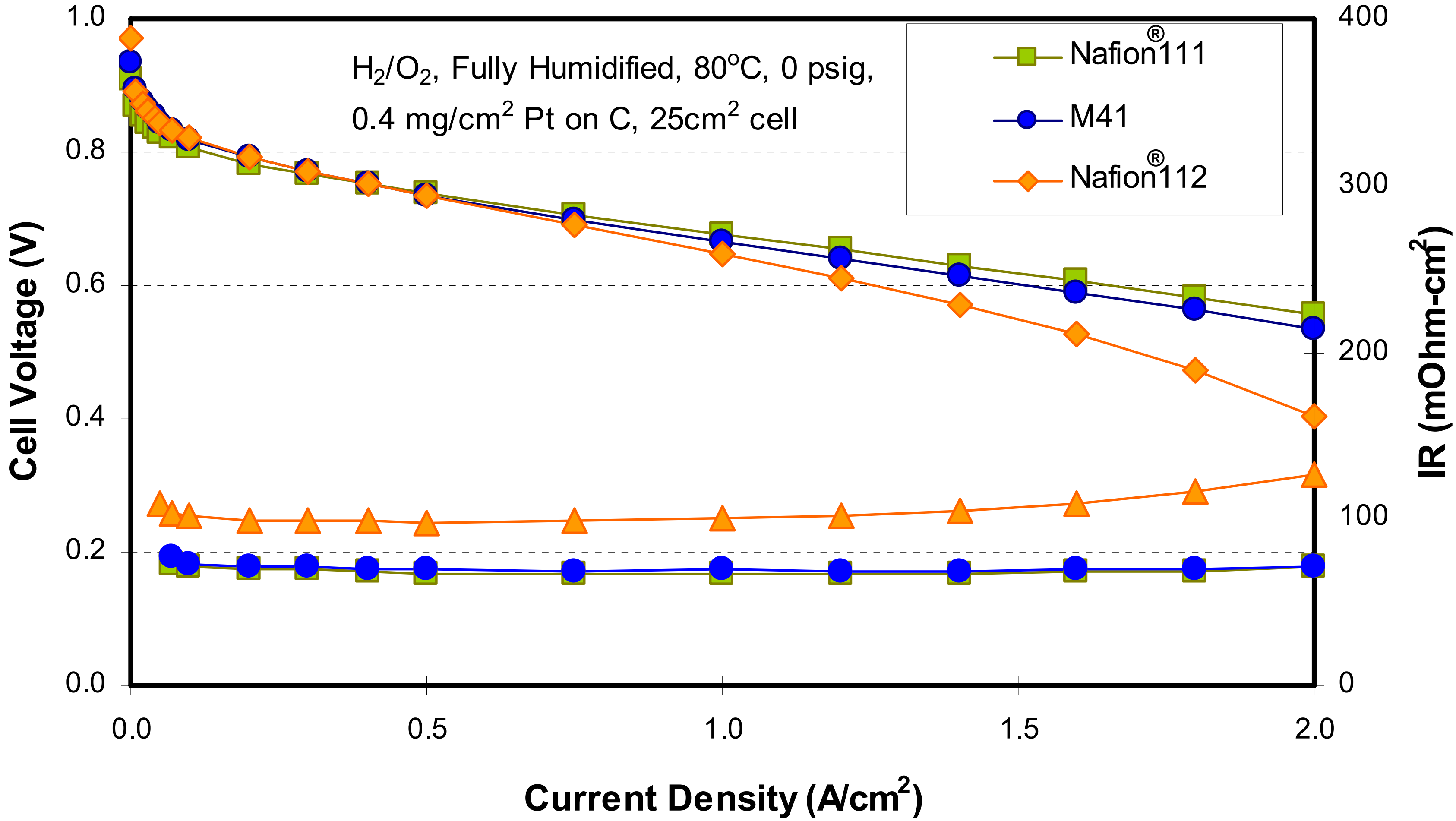
Fuel Cell Testing: BOL Performance



- Comparable in-cell performance to Nafion® 111 demonstrated

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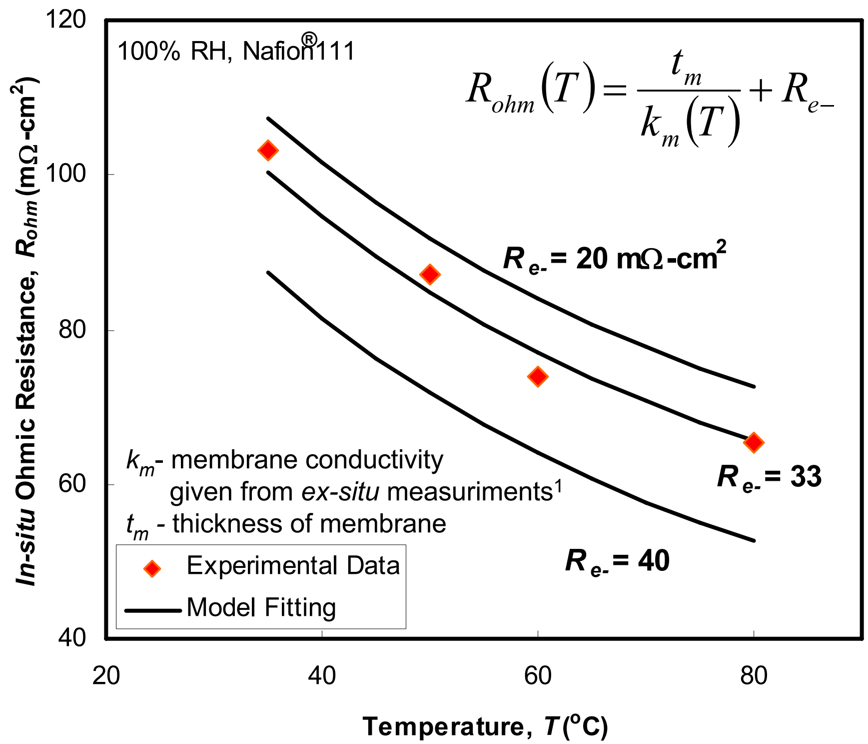
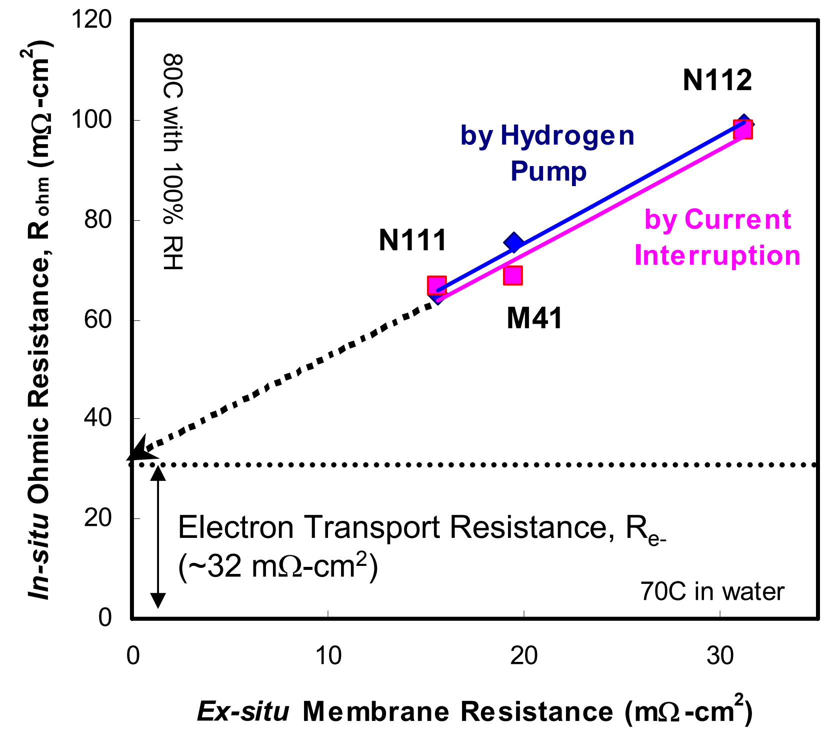
Fuel Cell Performance Diagnostics

- Ohmic resistance (R_{ohm}) by : (1) hydrogen pump and (2) current interruption
- Decouple the proton resistance (R_{H+}) and the electron resistance (R_{e-})by
  - Effect of temperature
  - Effect of membrane resistance





- Good interfacial contact between M41 and electrodes demonstrated

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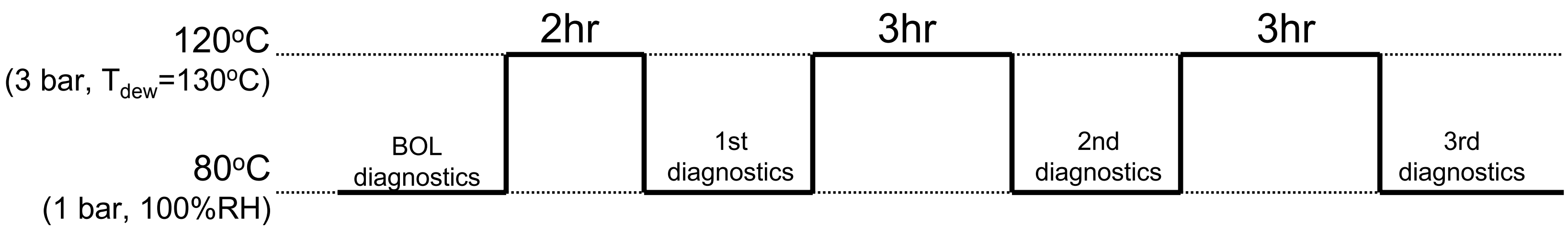
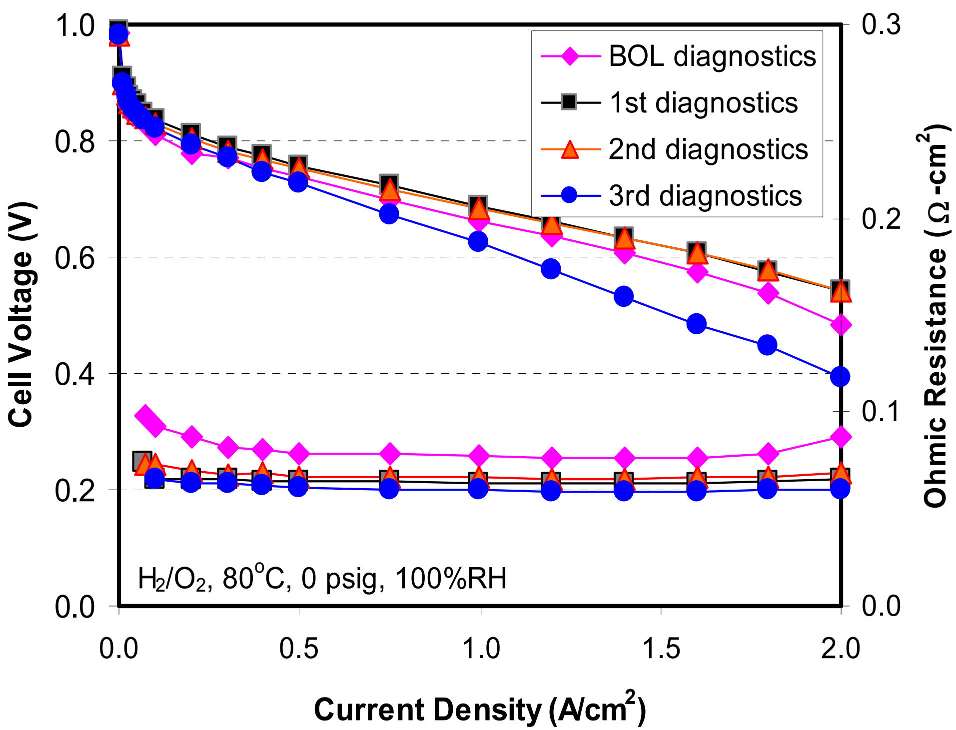
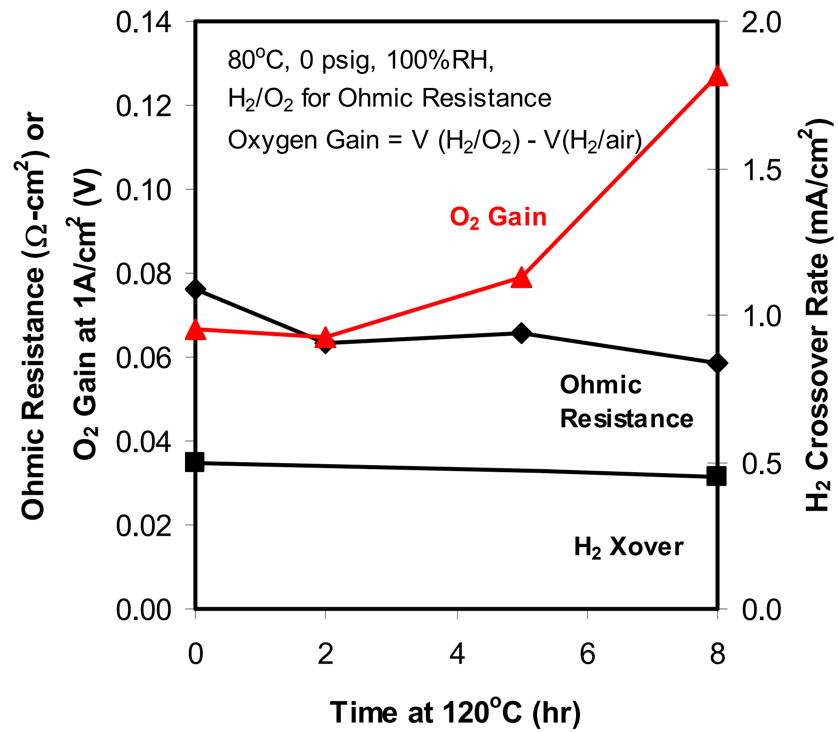
[1] S. Cleghorn, J. Kolde and W. Liu, "Catalyst coated composite membranes," *Handbook of Fuel Cells,* V3, p566, Wiley, 2003

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

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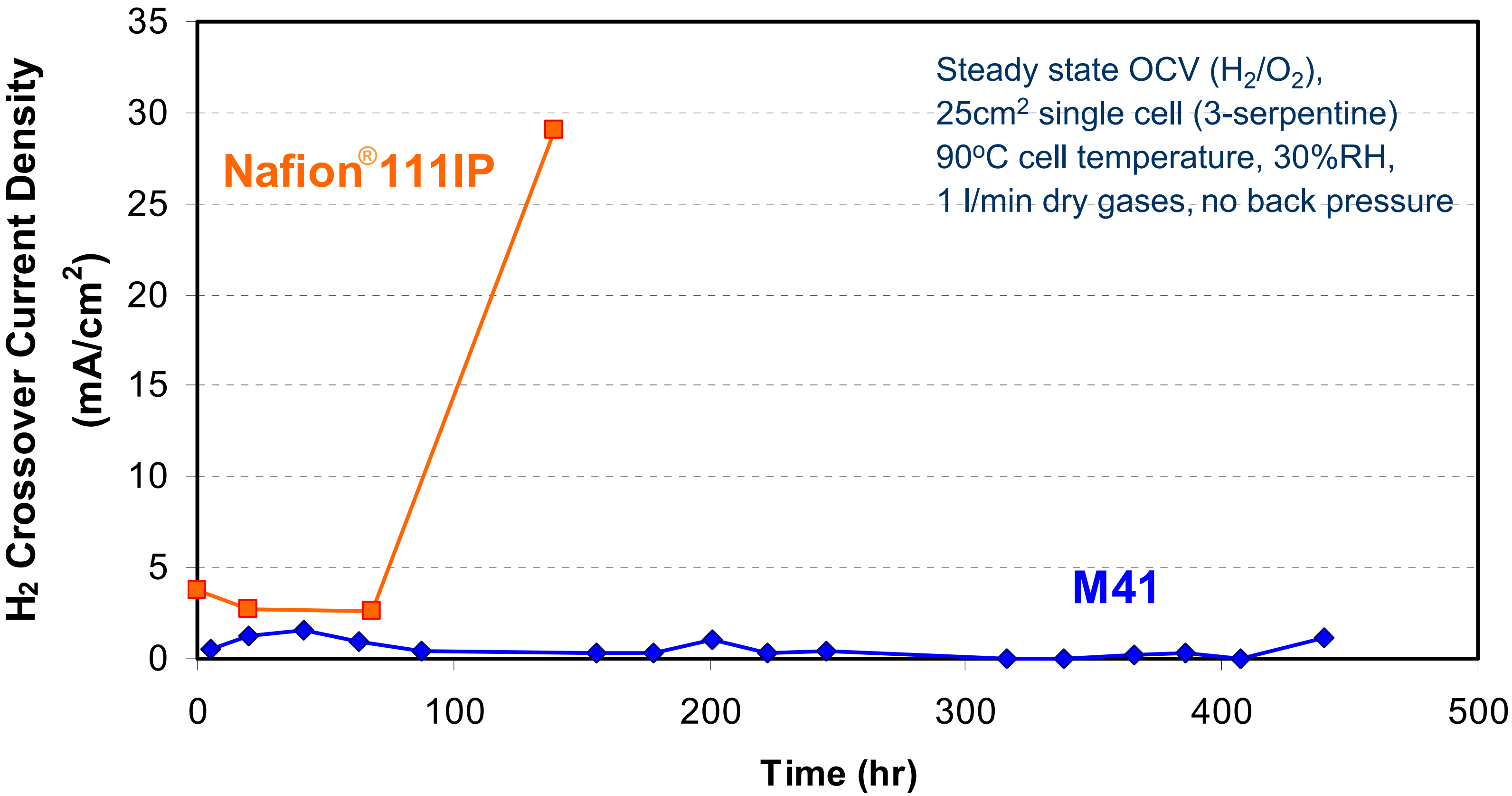
OCV Durability: Hydrogen Crossover



- Nafion® 111IP membrane failed around 100 –150 hrs
- M41 membrane exhibits superior chemical stability in fuel cells

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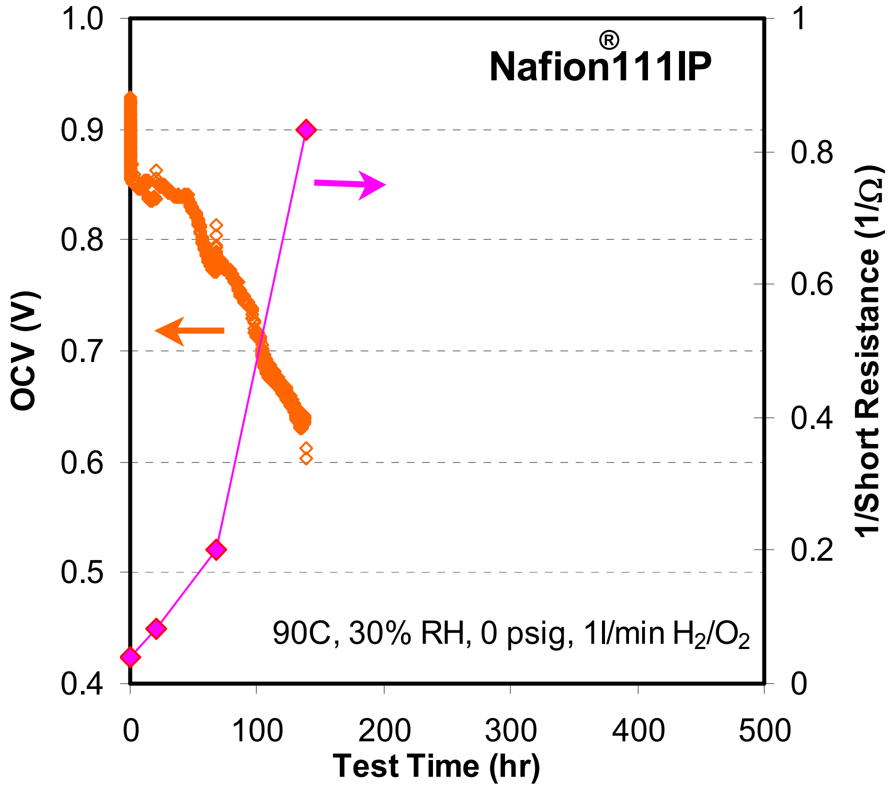
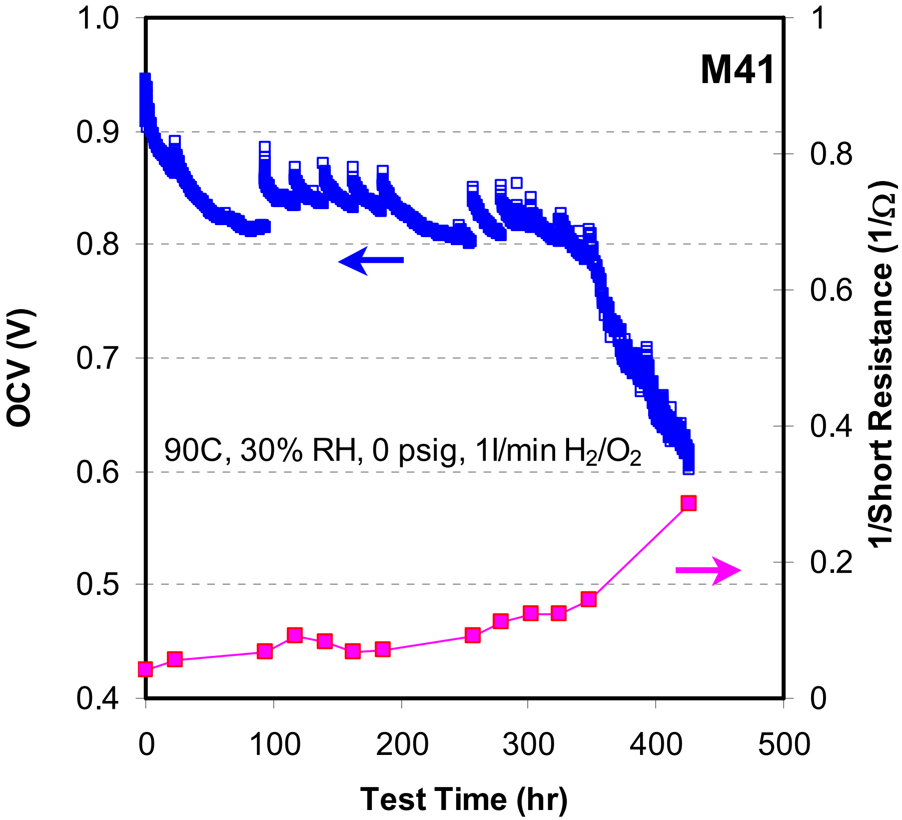
OCV Durability: Effect of Electrical Short





- Electrical short resistance is increased for both Nafion® 111IP and M41
- OCV is dictated by the shorting resistance for both membranes
  - Probably caused by the roughness of gas diffusion electrodes
  - M41 showed no changes in H_2 crossover current density

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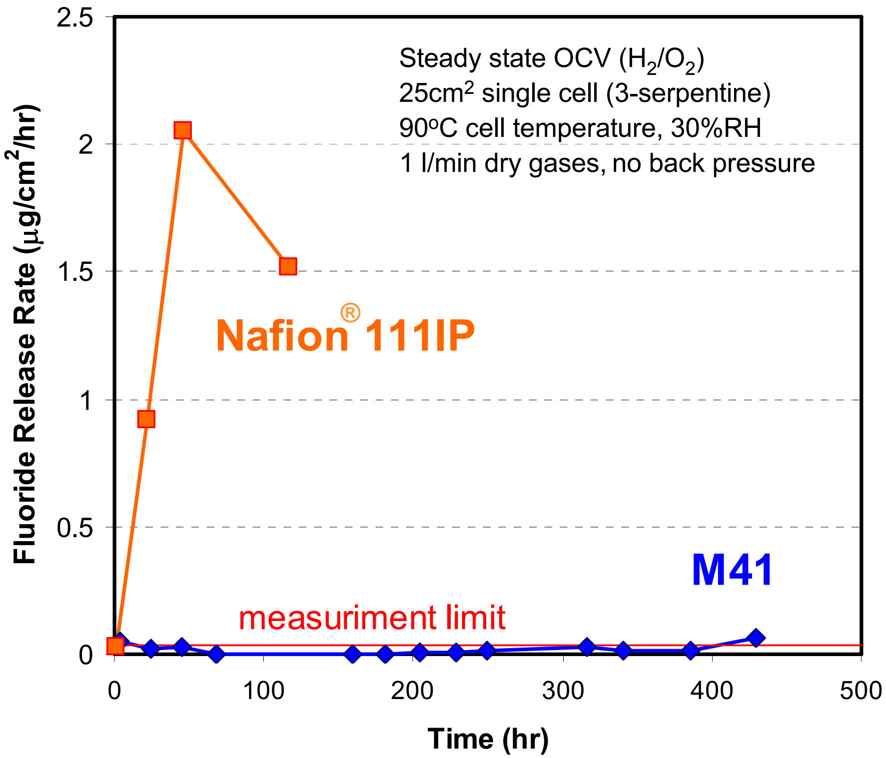
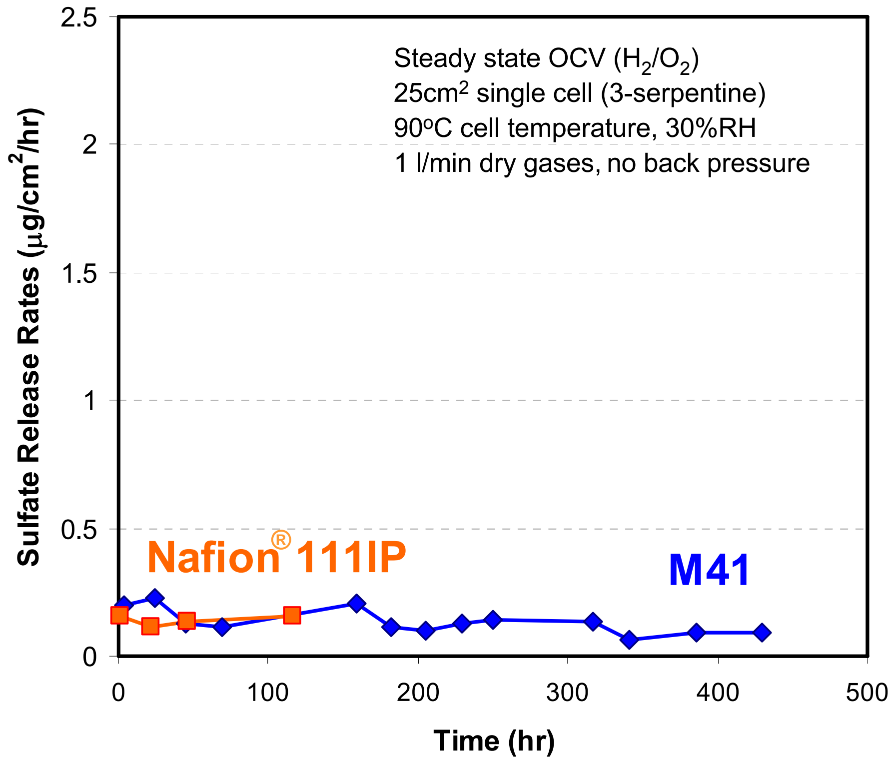
OCV Durability: Effluent Water Analysis

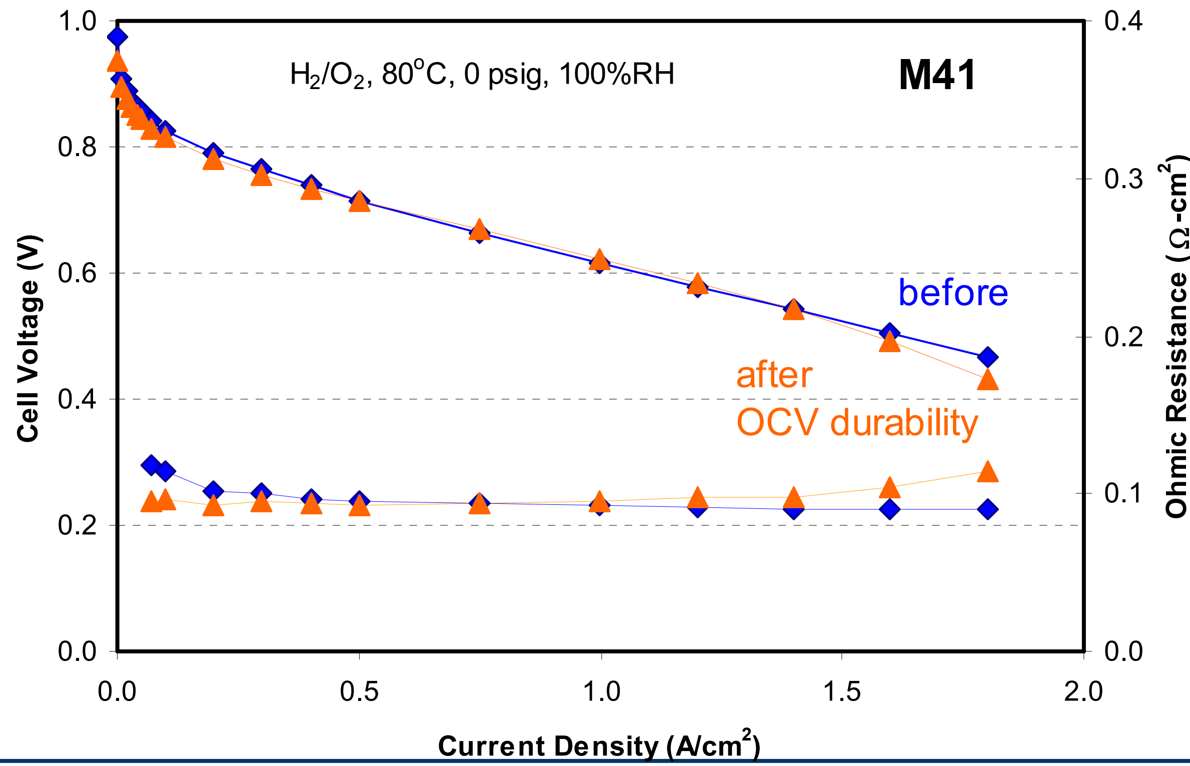




- M41 shows significantly lower F^- release rates
- M41 shows similar sulfate release rates to Nafion® 111IP

OCV Durability: Post-Mortem Analysis

- Nafion® 111IP failed due to chemical degradation leading to local pin-holes (no membrane thinning observed)
- M41 exhibited no sign of membrane failure due to chemical degradation after 400+hr OCV durability test
  - No change in gas crossover rates
  - No change in membrane thickness
  - No change in proton transport resistance
  - Identical performance after OCV test



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Future Work

- Complete accelerated in-cell durability tests (Arkema, JM)
  - Continue OCV durability test
  - RH cycle durability test is in progress
  - Voltage cycle durability test is in progress
- High-resolution morphology characterization for structure-property understanding (ORNL, Arkema)
- Complete large-size fuel cell testing
  - Prepare 400cm^2 MEAs (JM)
  - Testing in UTC Fuel Cell hardware (U of Hawaii and UTC Fuel Cells)
- Develop new-generation polyelectrolytes (new grant award)
  - Optimized for Low RH operation
  - Higher temperature stability (up to120^{o}C)

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Summary

- Arkema developed Kynar®/Polyelectrolyte blending technology and produced membranes suitable for fuel cells (low cost and durability)
  - Equivalent fuel cell performance to Nafion membranes
  - Better mechanical properties
  - Lower gas permeability
  - Pilot scale production
- The new generation membrane (M41) demonstrated superior membrane durability in *in-situ* OCV test
  - At least 4x increase in OCV durability versus Nafion® 111
  - No increase in gas crossover rate after 400+ hrs
  - Significantly lower F^- release rate compared to Nafion® 111
  - Humidity cycle and load cycle tests are underway
- Demonstrated morphology characterization and control capability
  - Further work is in progress to understand structure/property relationships