Improved, Low-Cost, Durable Fuel Cell Membranes

2008 Hydrogen Program Annual Review

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Grant ID:
DE-FG36-07GO17008

Project ID # FC-12

*currently at: Samsung Group, Korea

Overview (DE-FG36-07GO17008)

Timeline

- Start Date: Sept. 30, 2007
- End Date: Sept. 30, 2010
- % Complete: 20%

Budget

- Total Funding
  - DOE: $6,278k
  - Partners: $1,569k
- FY2007 Funding Received
  - $0k
- FY2008 Funding Received
  - $392k

Barriers Addressed

- A) Durability
- B) Cost

Partners

- Project Lead
  - Arkema Inc.
- Partners
  - Virginia Tech
  - Oak Ridge National Lab
  - Johnson Matthey Fuel Cells
  - University of Hawai'i
    - Hawai'i Natural Energy Institute (HNEI)

ARKEMA

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.

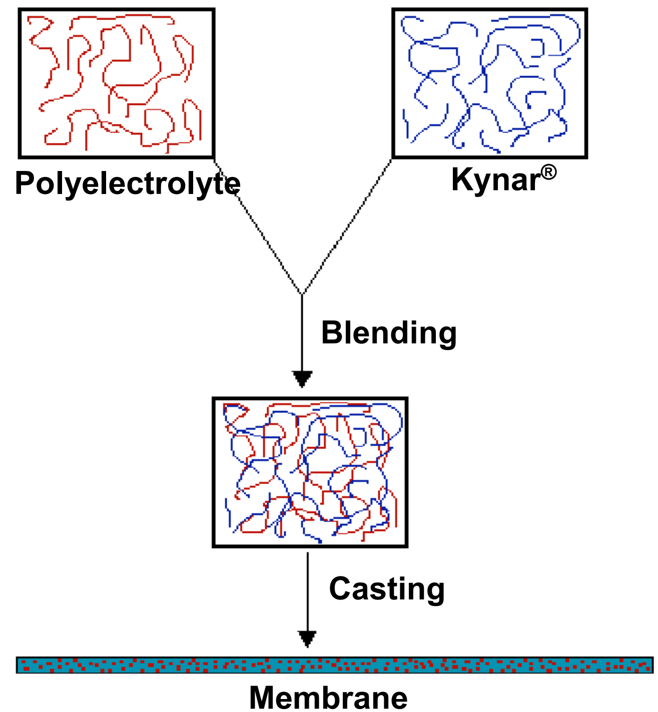
Milestones – Low RH Membranes

Task #	Milestone #	Title	Project Months	Project Deliverable	Go/No-Go Decision
1	1	Membrane meets 80°C requirements	6		X
	2	80°C membrane delivered to JMFC	8	X	
	3	Membrane meets > 100°C requirements	18		X
	4	> 100°C membrane delivered to JMFC	21	X	
	5	Membrane manufacturing plan complete	36	X	
2	6	MEA meets 80°C requirements	15		X
	7	Large MEAs 80°C delivered to HNEI	18	X	
	8	MEA meets > 100°C requirements	27		X
	9	Large MEAs > 100°C delivered to HNEI	30	X	
3	10	80°C MEAs perform per DOE requirements	27		X
	11	> 100°C MEAs perform per DOE requirements	36		X
4	12	Post-mortem analysis of MEAs complete	36	X	
5	N/A	Reporting, Planning, Administration	As Required		

- Task 1 work in progress
  - Develop new membrane candidates

Background

- 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
- M41 – highly sulfonated polyelectrolyte
  - Maximize conductivity at high RH

ARKEMA

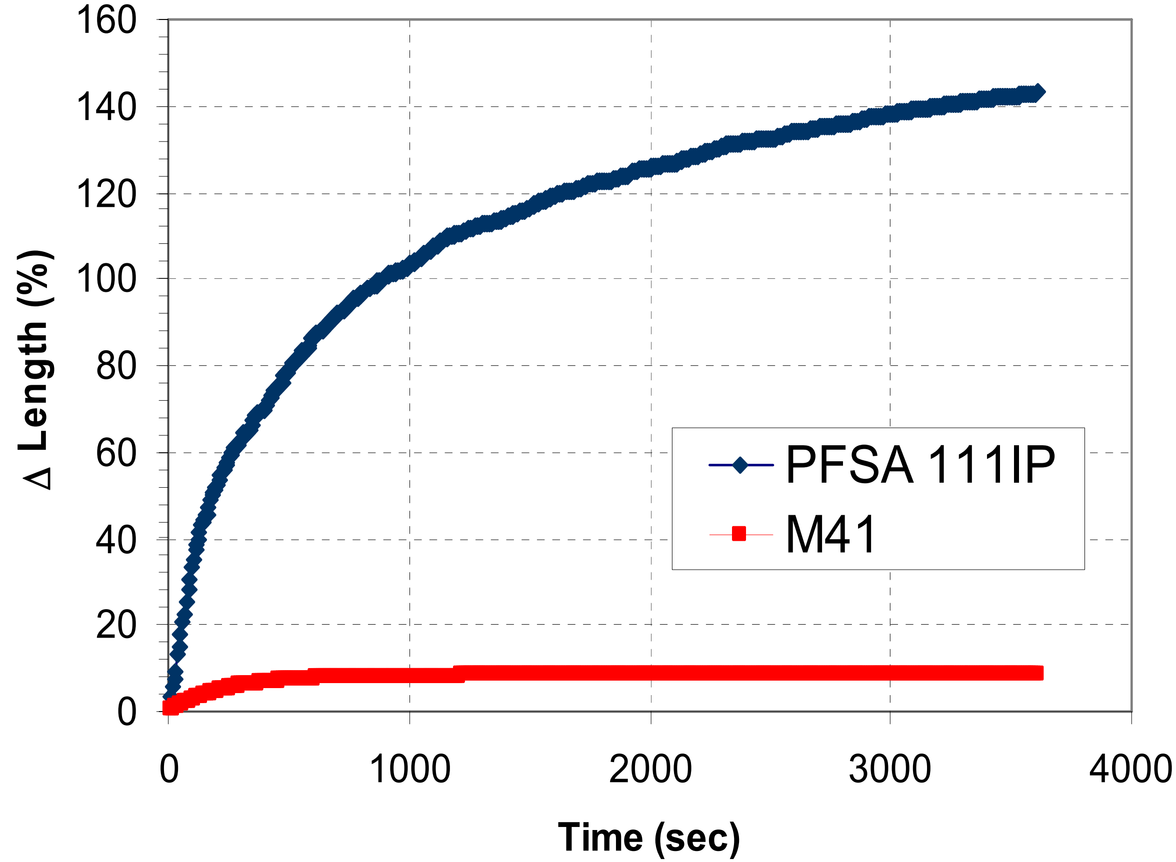
M41 Physical Properties

	PFSA	M41
Dry Thickness (μm)	25	25
Equivalent Weight (g/(mol H^+))	1100	800
Specific gravity (g/cm^3)	1.8	1.5
Water Uptake (%)[a]	37	60
X,Y Swell (%)	15	20
Thickness Swell (%)	14	10-15
Tensile Stress Break (MPa)[b]	19	27
Elongation (%)	103	95
Tear Strength(lb_f/in)[c]	404	934
Tear Propagation (lb_f)[d]	0.004	0.018

[a] gravimetry
[b] ASTM D882
[c] ASTM D1004
[d] ASTM D1938

- M41 shows equal/better mechanical properties than PFSA

Background – M41 Creep Testing



Temp = 120°C
Tension = 5g
Thickness: 25 μm
~40% RH

- M41 shows a significantly larger resistance to flow compared to PFSA (9% vs. 140%)

Background - M41 Transport Properties

- Equivalent proton conductivity compared to Nafion®

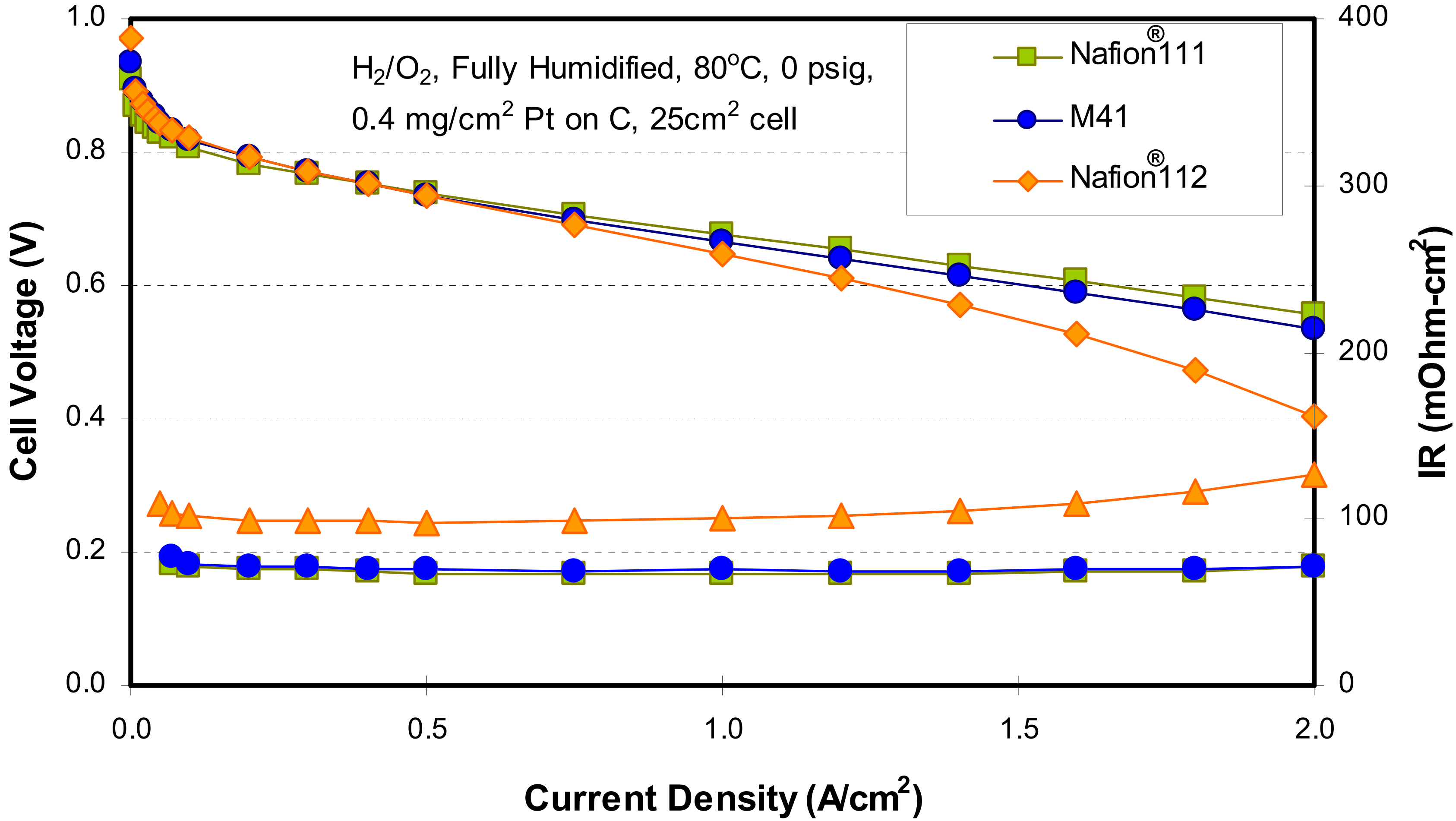
Proton Conductivity (mS/cm)*

- Superior gas barrier property than Nafion® membranes

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

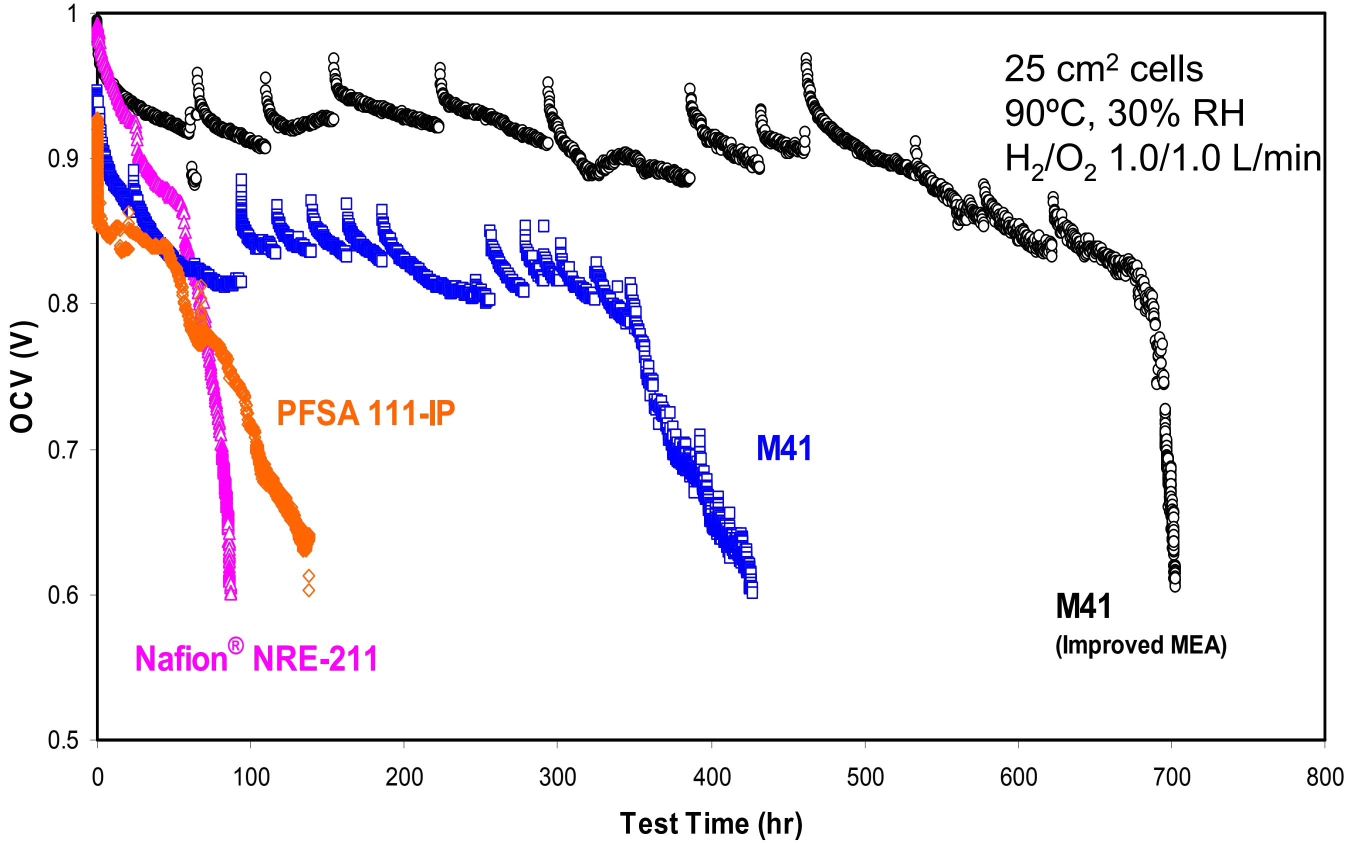
* by 4-point in-plane AC measurements in water at 70°C
** by electrochemical method at 80°C with 100% RH

Fuel Cell Testing: BOL Performance



- Comparable in-cell performance to Nafion® 111 demonstrated

Background – OCV Durability



- Short resistance decreases for PFSA and M41 membranes
- No fluoride and low sulfate emission from M41
- H_2 cross-over remains very low at failure for M41
- Fluoride emission and H_2 cross-over from PFSAs

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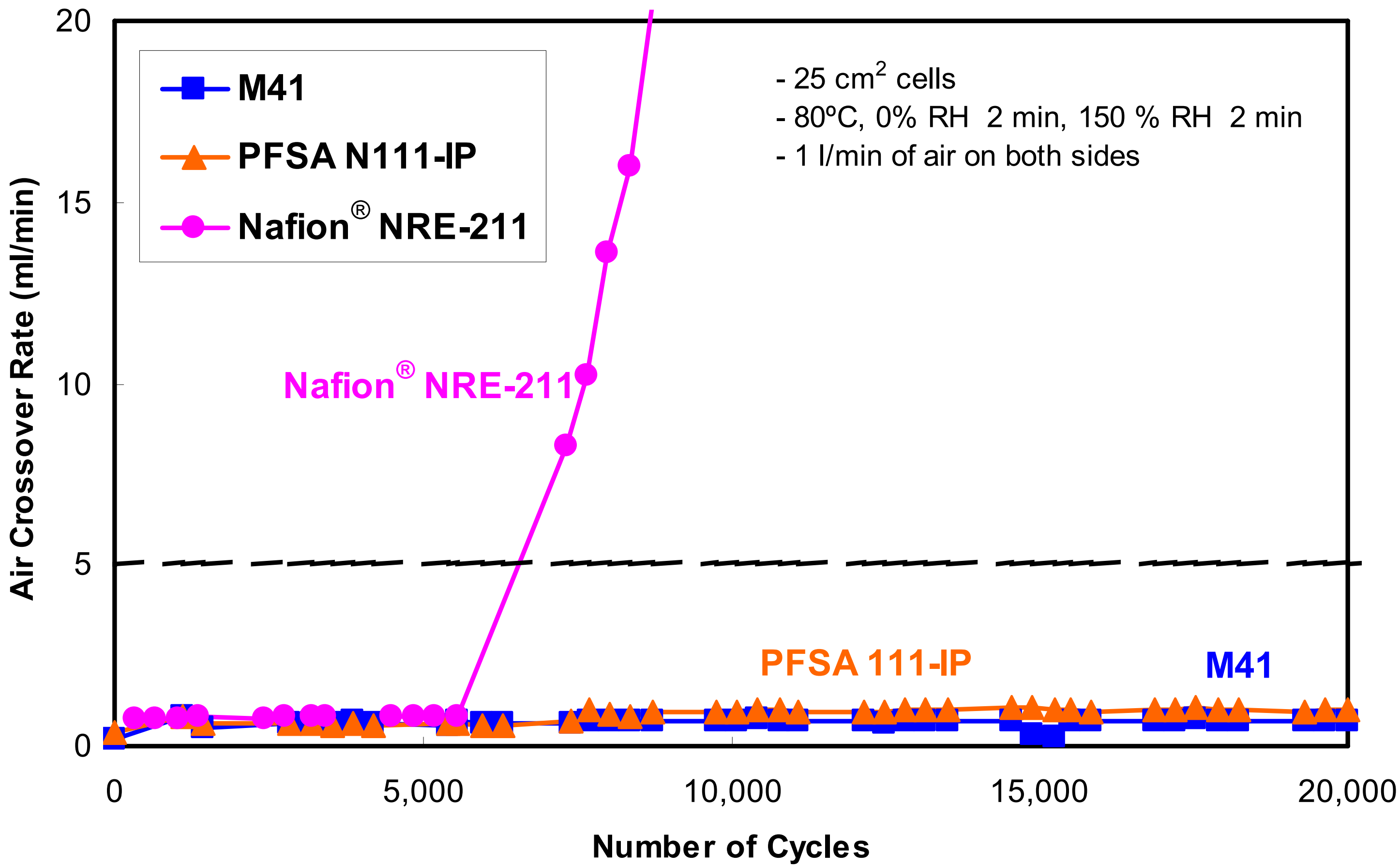
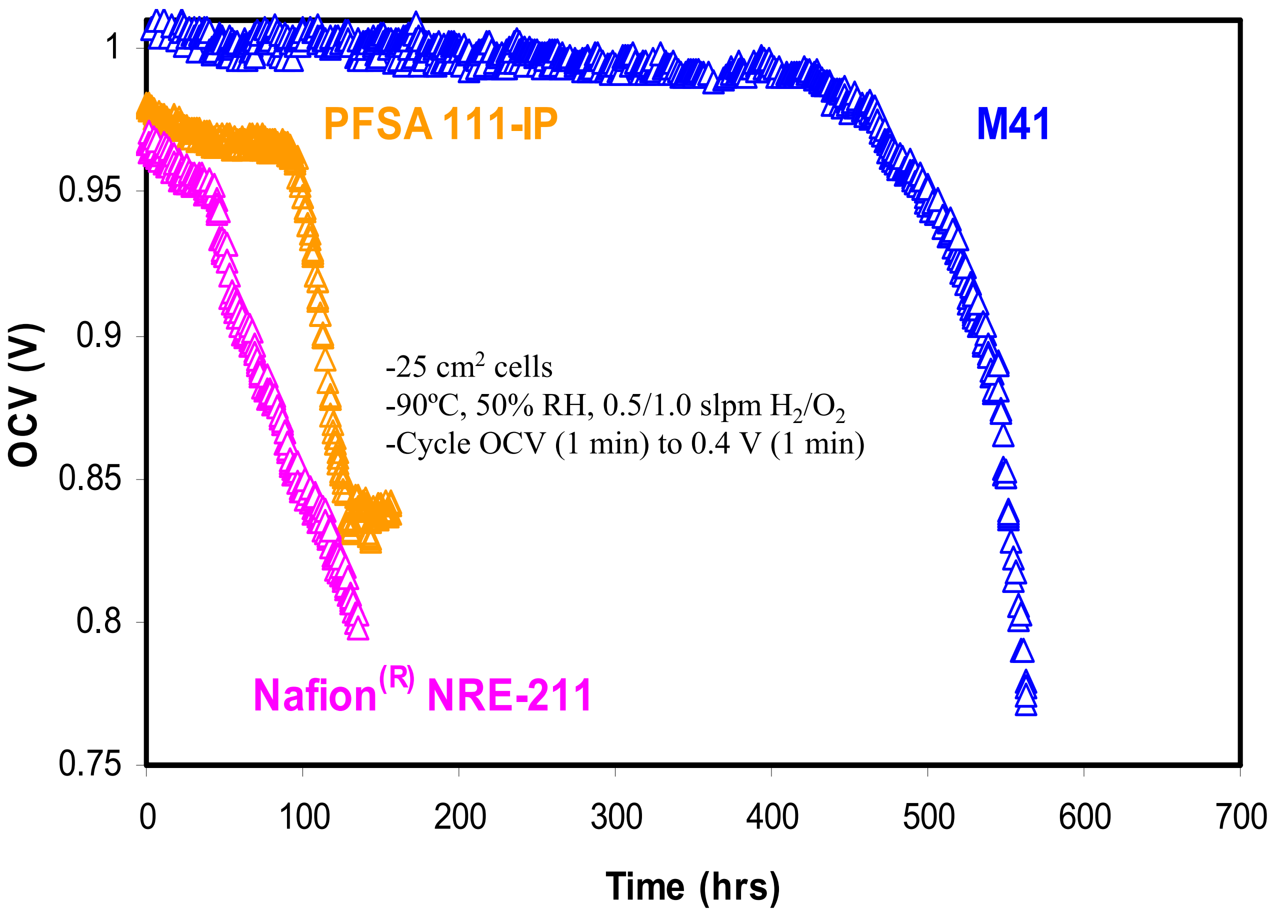
RH Cycling Durability: Gas Crossover



- Nafion® NRE-211 failed at approximately 6,000 cycles
- M41 and PFSA 111-IP MEAs met target of 20,000 cycles

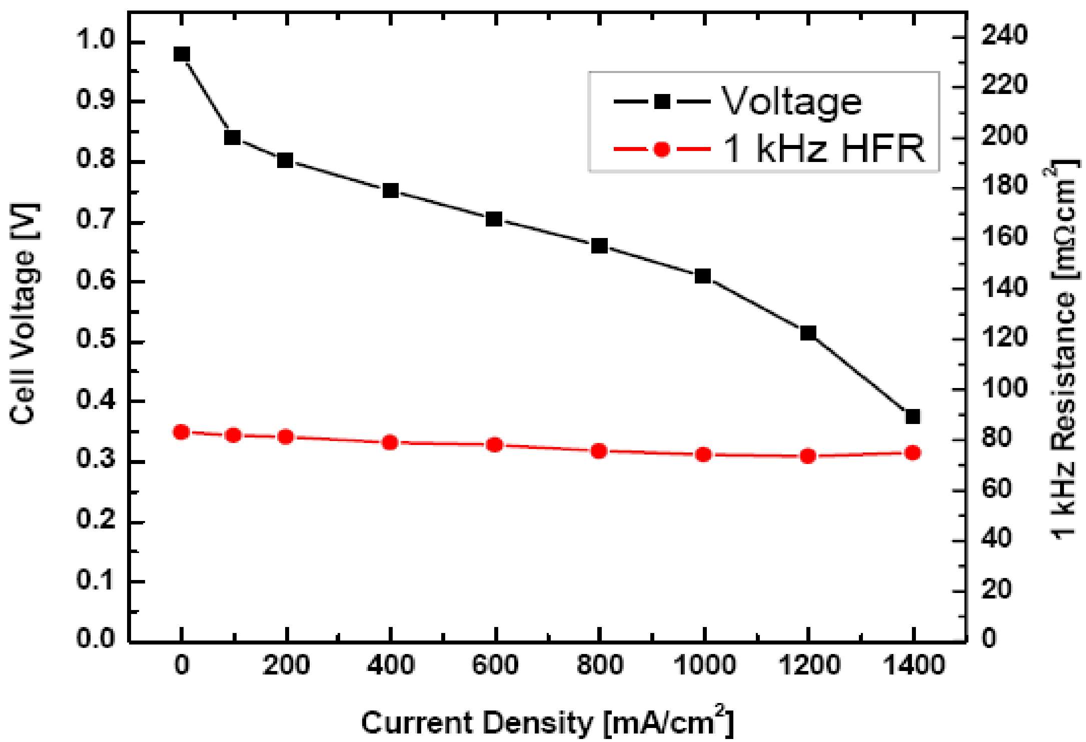
Voltage Cycling Durability: OCV to 0.4 V



- M41 membrane exhibits longer voltage cycling lifetime
- PFSA membranes allow higher current at 0.4V
- H_2 cross-over for PFSA <u>and</u> M41 MEAs at failure

400cm^2 M41 Testing – Preliminary Data

- 400 cm^2 (active area) MEAs fabricated by JMFC
- Preliminary data obtained in UTC Power hardware



Johnson Matthey Fuel Cells
the power within

University of Hawai'i
Mānoa

- M41 MEA H_2/air, 65 ºC, 80/60% utilization, ambient pressure
- Pt loading: Anode: 0.2 mg/cm$^{2;}$ Cathode: 0.4 mg/cm^2

ARKEMA

Development of Low RH Membranes

- Project initiated – Sept 30, 2007
- Objectives
  - To develop a membrane capable of operating at 80°C at low relative humidity (25-50%).
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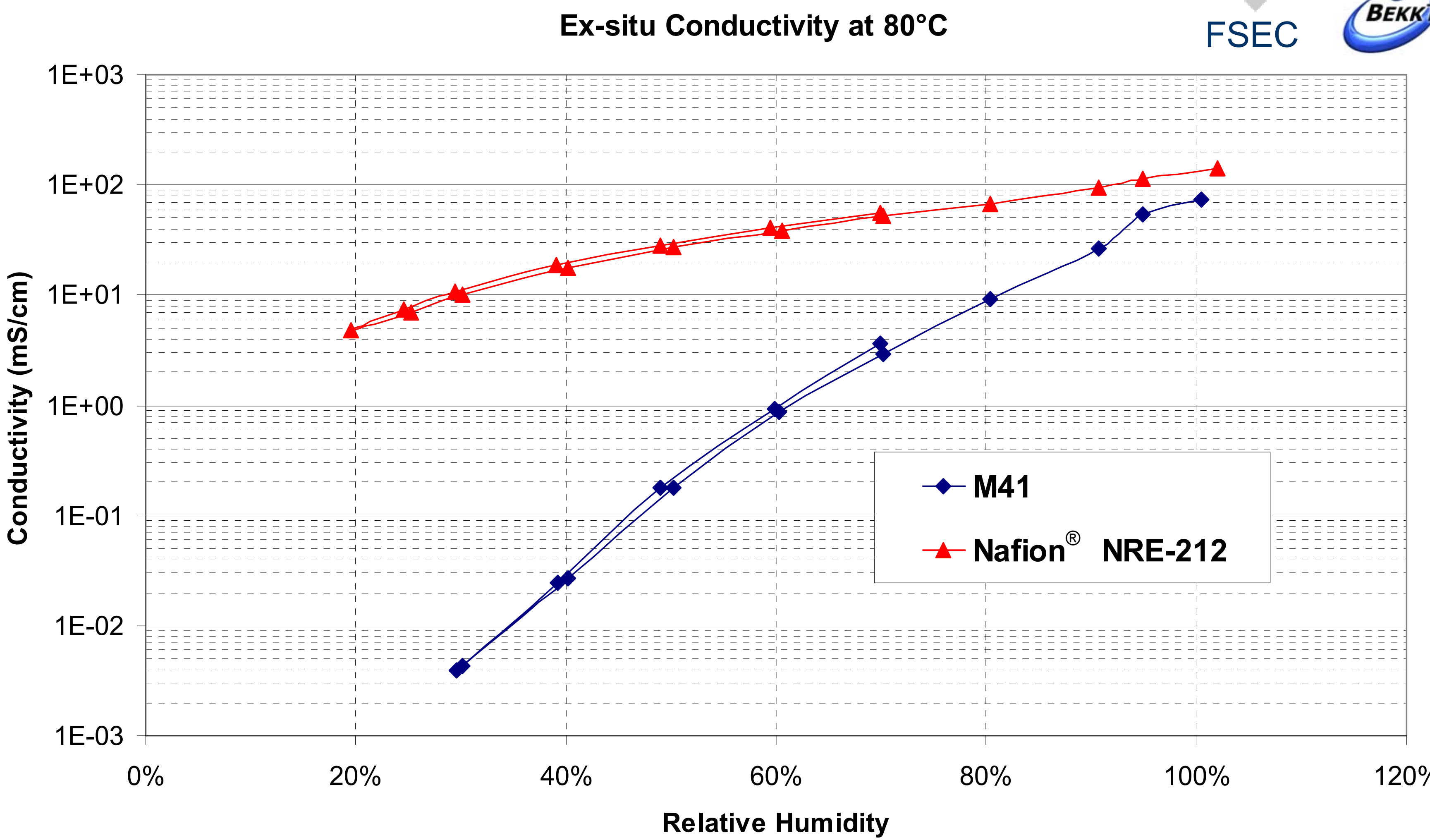
  - To elucidate ionomer and membrane failure and degradation mechanisms via *ex-situ* and *in-situ* accelerated testing.
    - Develop mitigation strategies for any identified degradation mechanism.

M41 Low RH *Ex-situ* Testing

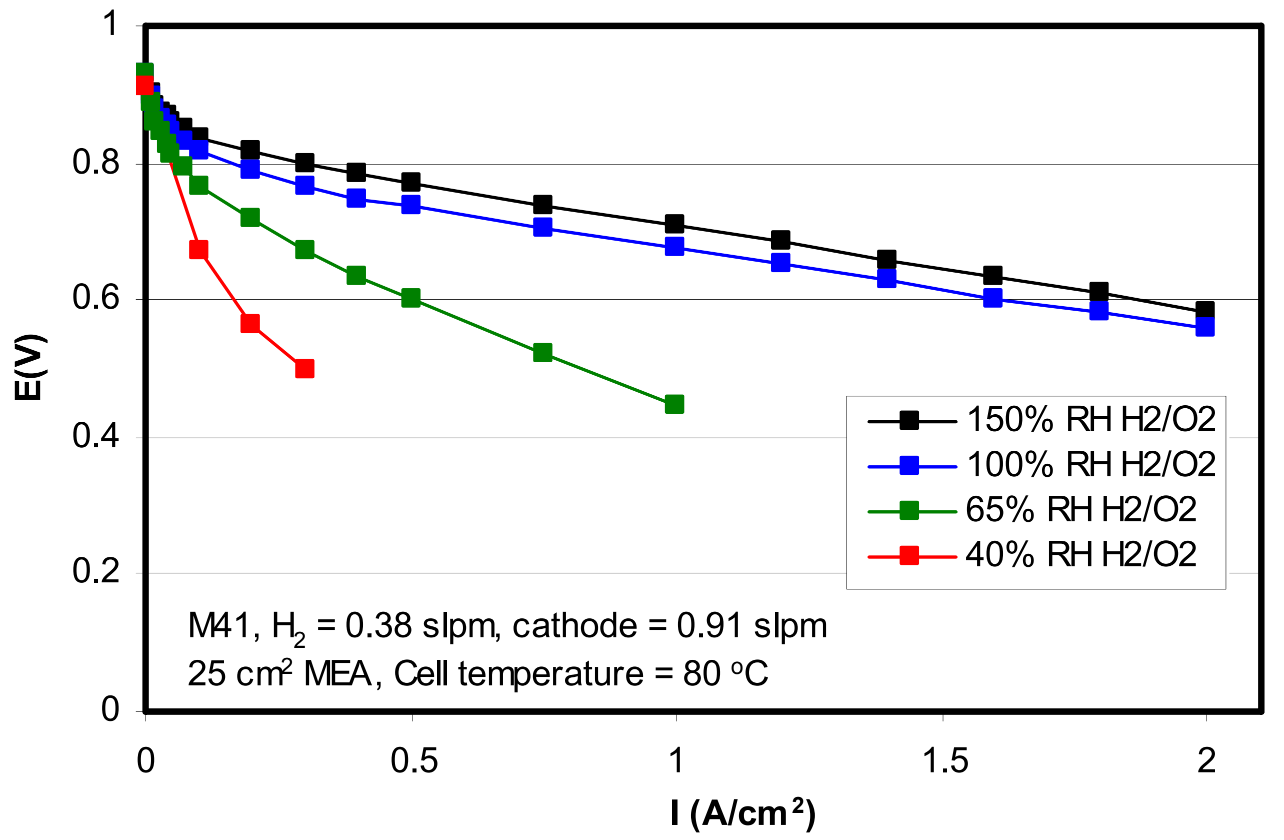
FSEC



- Additional improvement required to meet low RH targets

Low RH Performance of M41-Based MEA

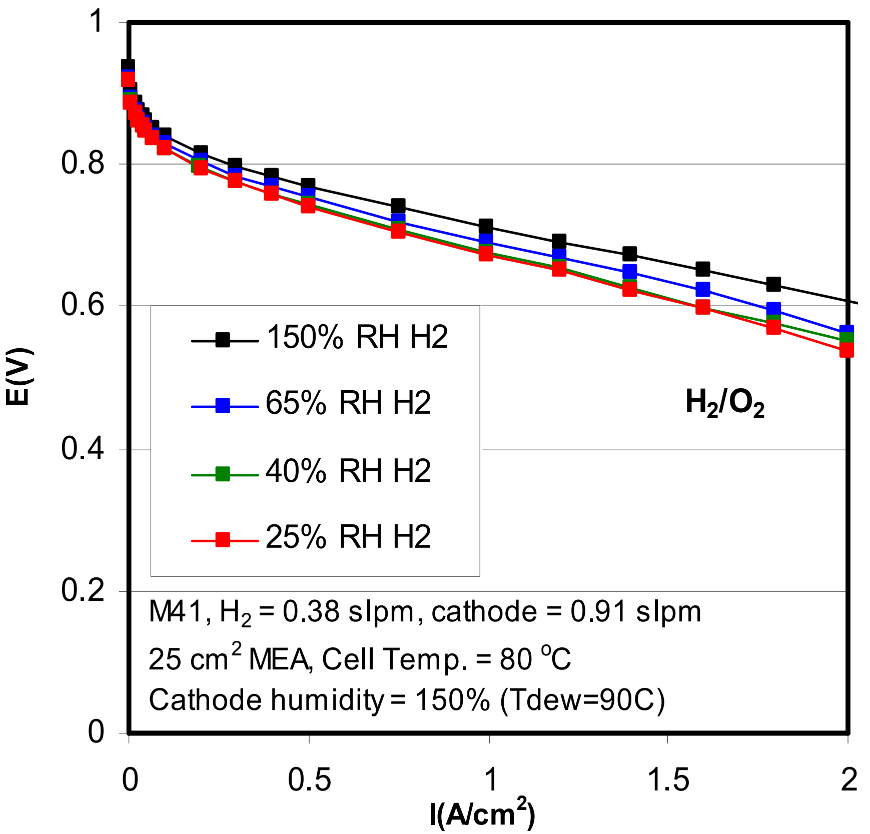
- Inlet RH



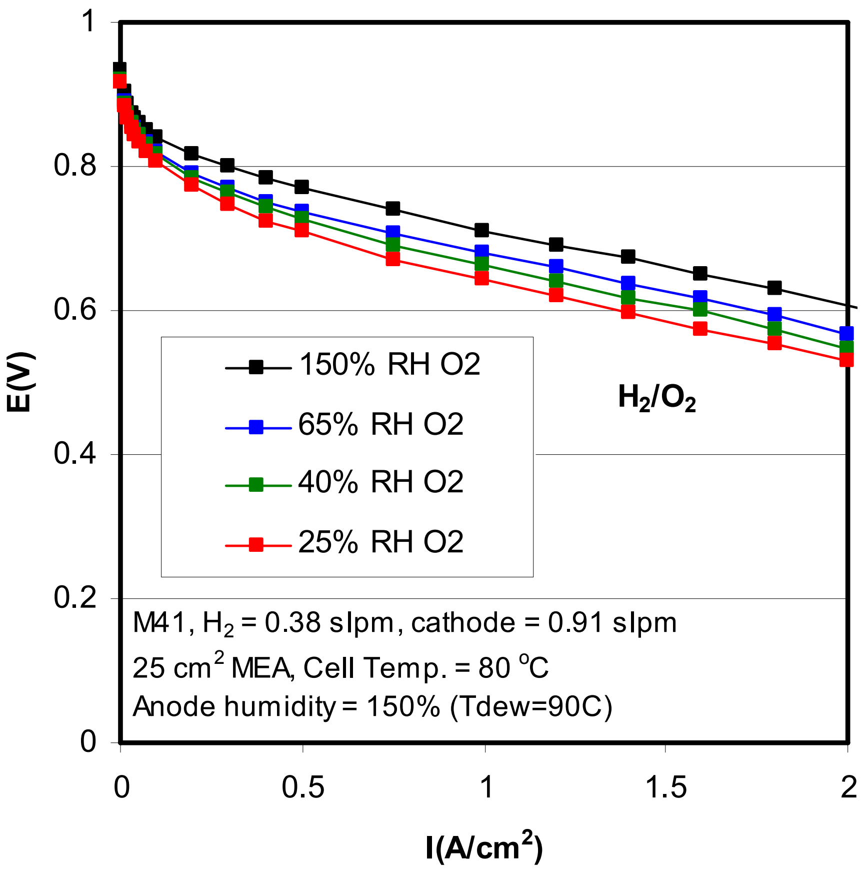
- Significant performance loss at <65% RH on anode and cathode

Low RH Performance of M41-Based MEA

- Effect of Anode Inlet RH



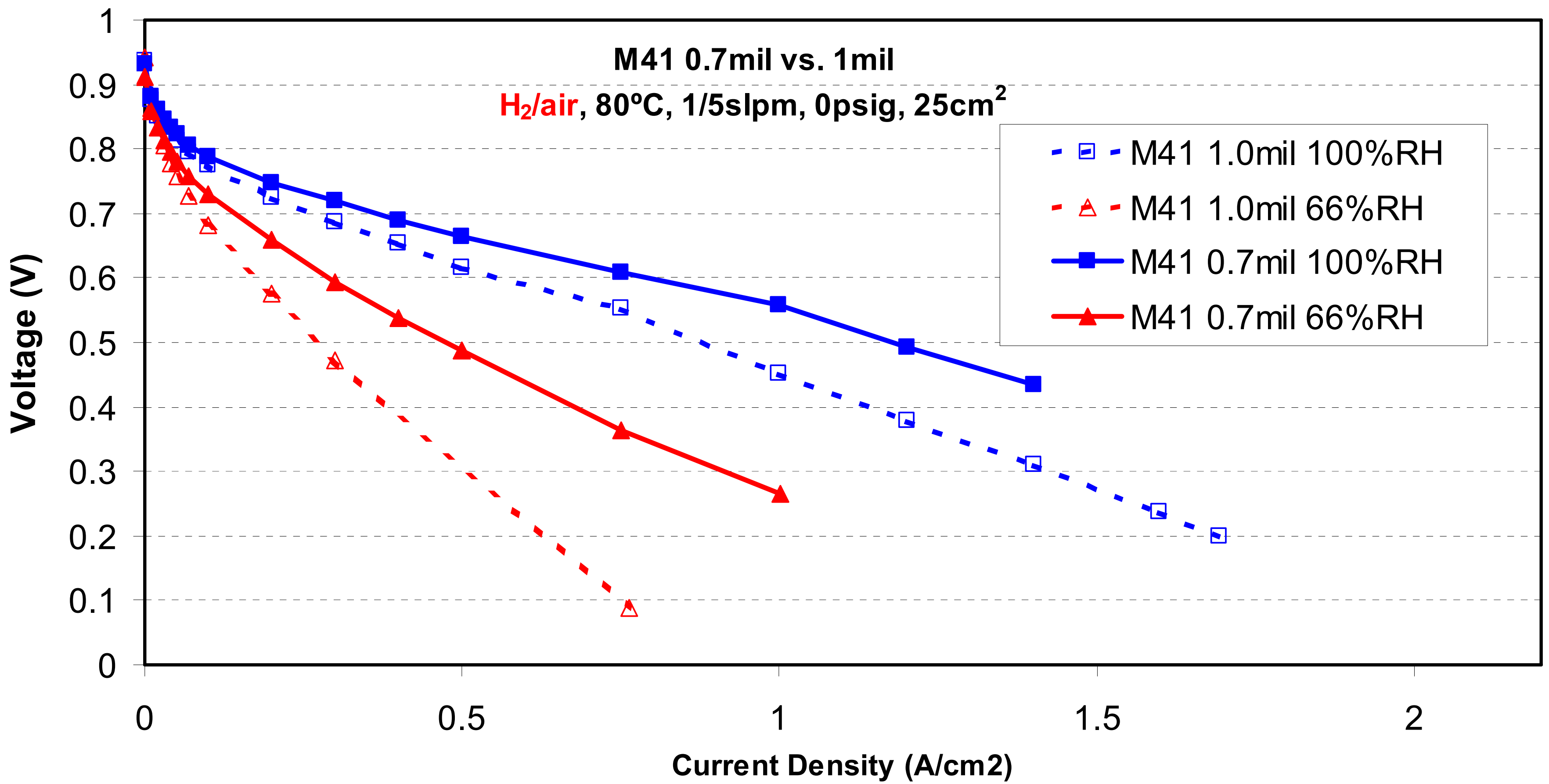
- Effect of Cathode Inlet RH



- With only one-side humidified, reasonable performance is obtained (at ≥25% RH)

Thickness Effect

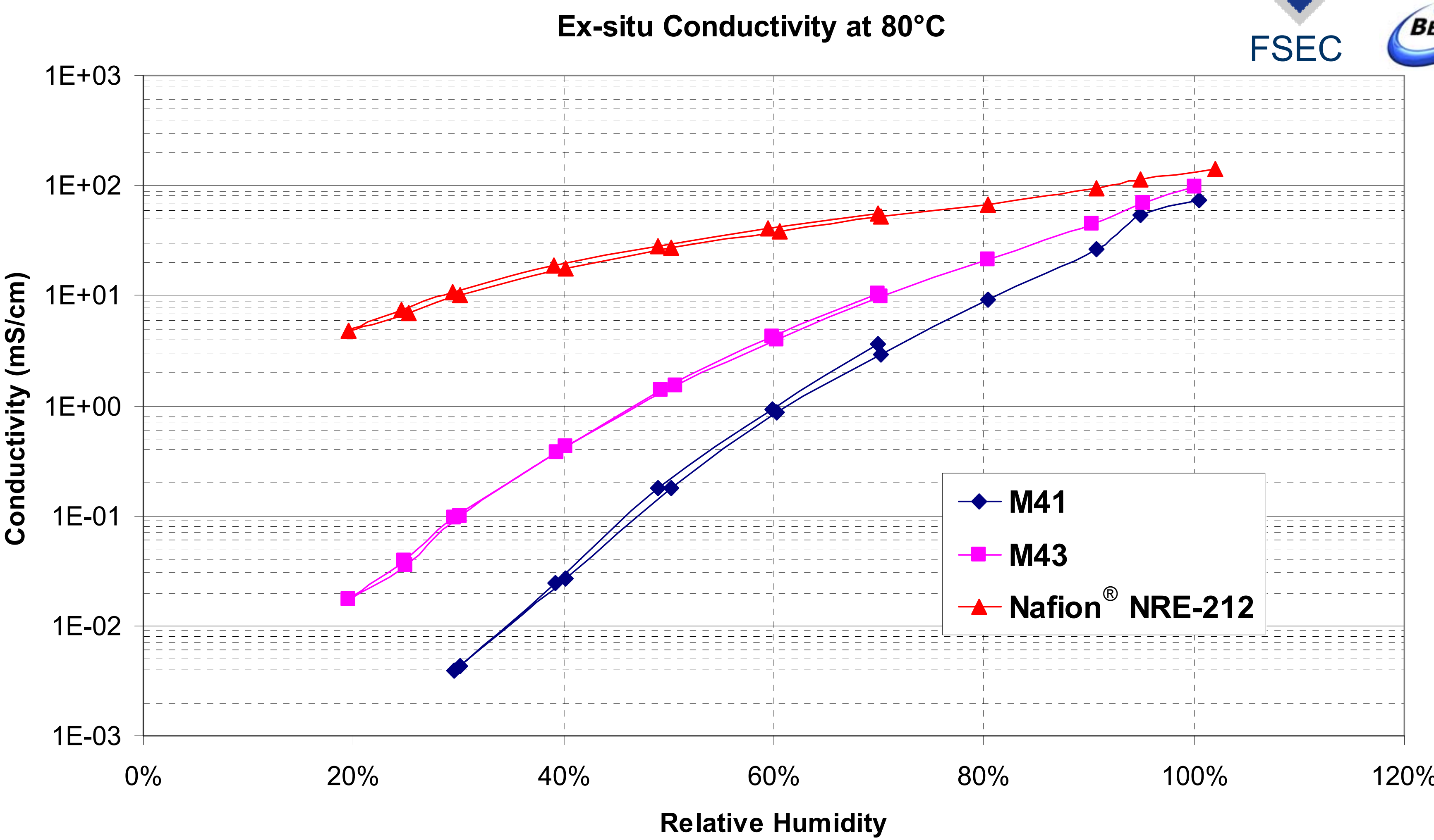
- 0.7 mil M41 – better performance at low RH



Low RH Membranes: Approach

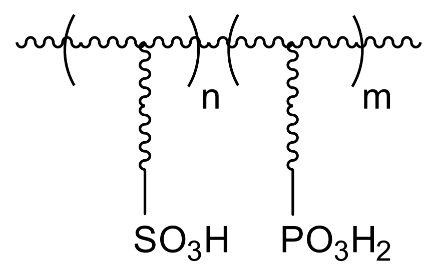
- M41 – good scaffold
  - Good MEA performance at >65% RH
  - 'Bridge the gap' @ lower RH operation
- Blending is transparent to the polyelectrolyte
- 1) Improved M41 production process: M43 membrane
- 2) Analogous approach to phosphoric acid-imbibed membranes
  - Hypothesis: Incorporating bound phosphonic acid groups will increase water retention at low RH
- 3) New polyelectrolytes
- 4) Control morphology of Kynar® blends
  - Vary the hydrophobicity/hydrophilicity of Kynar/polyelectrolyte blends
  - Process control
- 5) Additives

M43 Initial Results



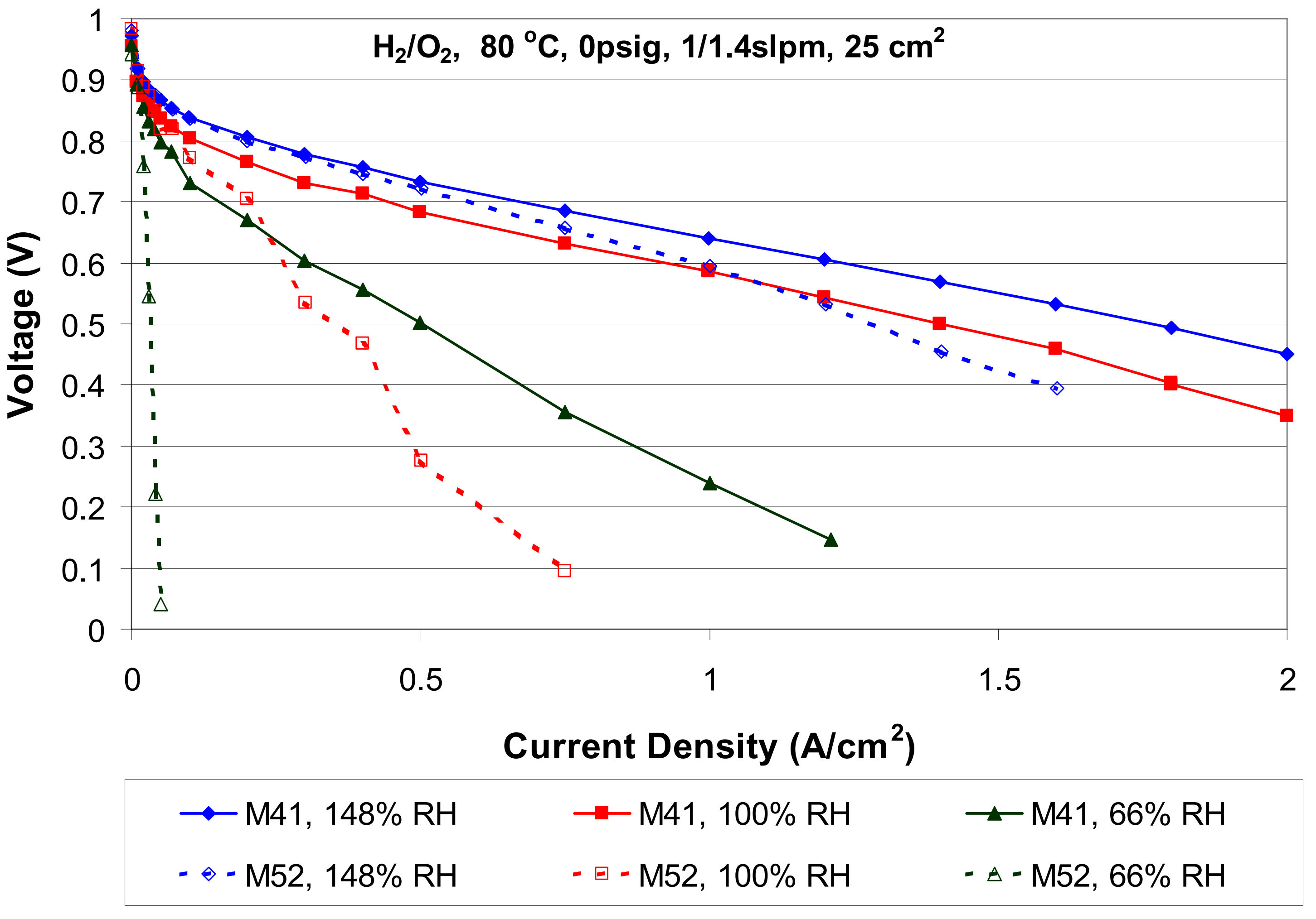
New Membrane Generation

- 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
- Reoptimized PVDF blending parameters
- Produced new membranes (lab-scale)
- Collaboration initiated
  - Prof. V. Ramani (Ilinois Institute of Technology)



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

MEA Testing – Phosphonated Membranes



Representative data:

M52 MEA

Lower performance for phosphonate containing MEAs

Summary

- M41 shows superior durability in accelerated *in-situ* testing
- M41 MEAs shown to operate down to 65% RH (inlet)
- M41 architecture is a good platform for low RH membranes
- New grant targets low RH performance
  - Process improvements show initial gain
  - Phosphonated materials did not show improved performance
- New membrane production, screening, and testing is underway
  - Varying membrane chemistry and/or morphology

Future Work

- Investigation of structure/property/RH relationships
- Approaches
  - Improved blending process
  - Collaboration with Prof. J. McGrath (Virginia Tech)
  - New Arkema polyelectrolyte / Kynar blends
- *Ex-situ* and *in-situ* testing of new membranes
- Validation and optimization of *in-situ*, low RH performance
- Durability testing
- Elucidation of failure mechanisms

Acknowledgements

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- Virginia Tech
  - Prof. Jim McGrath