FC109

New Fuel Cell Membranes with Improved Durability and Performance

Mike Yandrasits

3M Energy Components Program

June 8th, 2017

Overview

Timeline

- Start October 1st, 2013
- End June 30th, 2017
- 93% complete

Barriers

Durability

Performance

Cost

Budget

- Total Project funding $4.2 million
  - $3.1 million - DOE
  - $1.1 million - contractor cost share (26%)
- DOE Funding to date (through March 2016)
  - $2,725,188 (88%)

Partners

3M Company *M. Yandrasits (Project lead)*

General Motors *C. Gittleman*

Vanderbilt University *Professor P. Pintauro*

Collaborations: Flow Of Samples & Information

Objective: Meet all of the DOE Fuel Cell Technologies Office Multi-year RD&D Plan membrane performance, durability and cost targets *simultaneously* with a single membrane.

Task 1: Ionomer development

Green shading indicates approximate task completion

Task 3: Ionomer and Membrane Testing

Task 4: MEA Fabrication and Fuel Cell Testing

Task 5: Stack Testing

Task 2: Nanofiber development

Dual Fiber Electrospinning
(ionomer and support fibers)

Nanofiber Support
(support fibers only)

Work completed in 2016

General Motors,

- Chemical and mechanical property testing
- Single cell performance testing
- Stack testing
- Post mortem analysis

Vanderbilt University

- Electrospinning expertise
- Dual fiber electrospinning

Milestone Summary

	Milestone	Requirement	Date Completed	Status
Previously Reviewed	1	Ionomer conductivity	Jan, '14	✓
	2	Nanofiber down select	Apr, '14	✓
	3	Electrospin Ionomer	May, '14	✓
	4 Go/No Go	Durability & performance	Oct, 14	✓
	5	Ionomer conductivity	Mar, '15	✓
	6	Fiber surface treatment selection	Apr, '15	✓
	7	Durability & ASR	Jun, '15	✓-✓
	8 Go/No Go	Durability, ASR, short res. H_2&O_2 crossover, & cost	Sep, '15	✓-✓
	9	Produce membrane for stack testing (> 20 meters)	March '16	✓
This Presentation	**10**	**Begin Stack Testing**	**June, '16**	✓
	11	**Post Mortem Analysis, Determine Failure Mode**	**Nov. '16**	✓
	12	**Deliver MEAs to DOE, Complete 2,000hrs stack testing**	**Nov. '16**	X

Full Milestone List in Back-Up Slides

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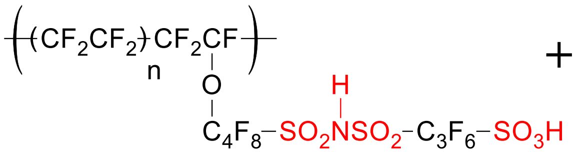
Membrane For Milestones 8 and 10



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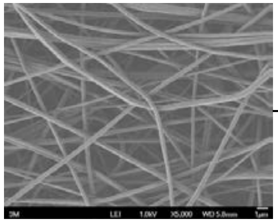

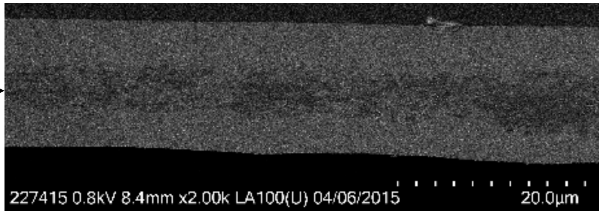

Perfluoro imide acid (PFIA) ionomer

Nanofiber support made using fluoropolymer (FC1)

Electron microscope cross section image of composite membrane

3M ID	Milestone	Ionomer	Fiber type	Additive	Fiber (vol%)	Thickness (um)
0513277A	Control	3M 725EW	B1	Type A	20.6	14
0515079D	#8	PFIA – Lot #1	FC1	Type A	18.0	10
05160081A, B, C,D	#10	PFIA - Lot #2	FC1	Various	18.0	10

Milestone 8: 3M ID 0515079D

Characteristic	Units	2017 & 2020 Targets	MS#8 PFIA-S (10 um)
Maximum oxygen cross-over	mA / cm²	2	0.6[a], 3.5[b]
Maximum hydrogen cross-over	mA / cm²	2	1.9[c]
Area specific proton resistance at:			
120°C, P_{H2O} 40 kPa	Ohm cm²	0.02	0.054
120°C P_{H2O} 80 kPa	Ohm cm²	0.02	0.019
80°C P_{H2O} 25 kPa	Ohm cm²	0.02	0.020
80°C P_{H2O} 45 kPa	Ohm cm²	0.02	0.008
30°C P_{H2O} up to 4 kPa	Ohm cm²	0.03	0.018
-20°C	Ohm cm²	0.2	0.2[d]
Minimum electrical resistance	Ohm cm²	1,000	1,635[e]
Cost	$ / m²	20	Not available
Durability			
Mechanical	Cycles with <10 sccm crossover	20,000	>24,000
Chemical	hrs	>500	614

a. O_2 crossover based on DOE Table 3.4.12 indicating measurement at 0.5V
b. Calculated from GM O_2 permeability data at 80°C, 100% RH, 1 atm air.
c. In cell measurements at 3M 70°C, 100% RH, 1 atm.
d. Calculated from in-plan data
e. Data provided by GM

DOE Table in Back-up Slides

Relevance:

- Lower membrane resistance at low P_{H_2O} and/or high T will allow for fewer cells or simplified balance of plant.
- Membrane cost, especially at low volumes, is an issue for FCEVs.

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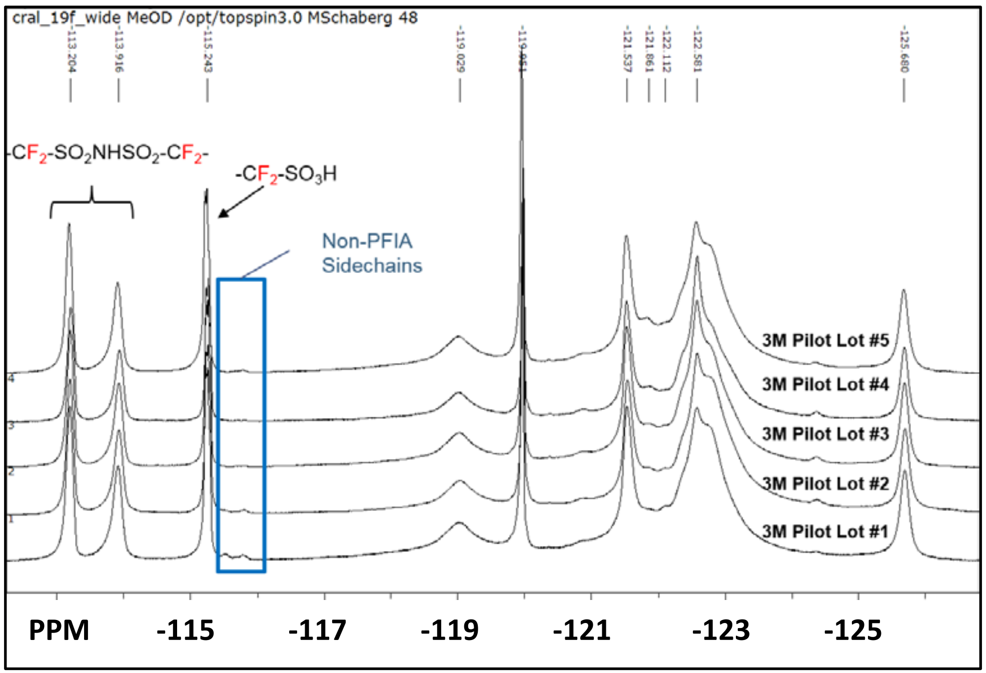
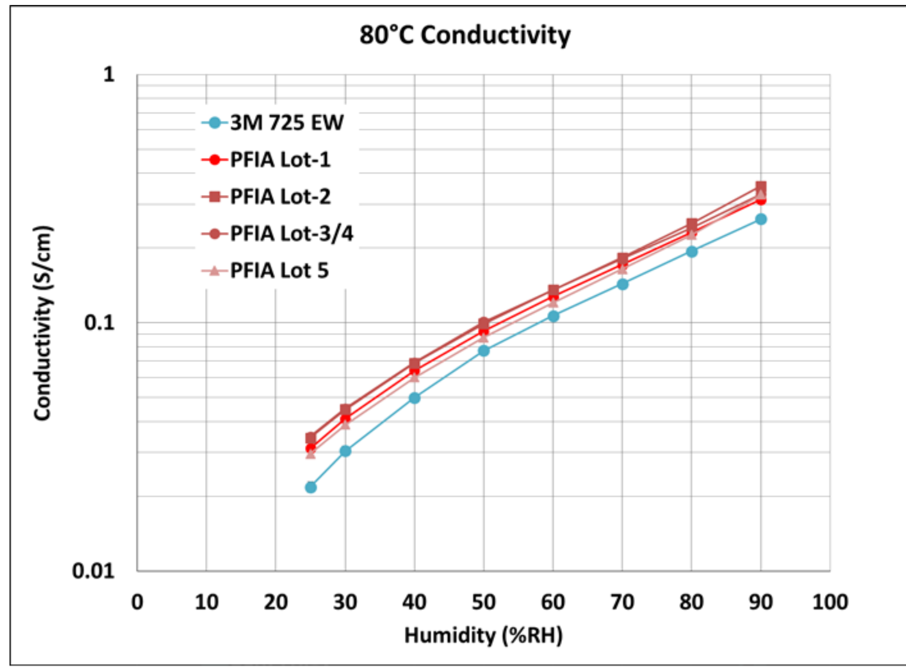
PFIA Pilot Scale

Lot Number	Date	Titrated EW	Program
1	January 2015	660	DOE
2	December 2015	652	3M
3 and 4	March 2016	625	3M
5	Sept 2016	650	3M





- Five pilot scale batches complete
- High degree of conversion in each step

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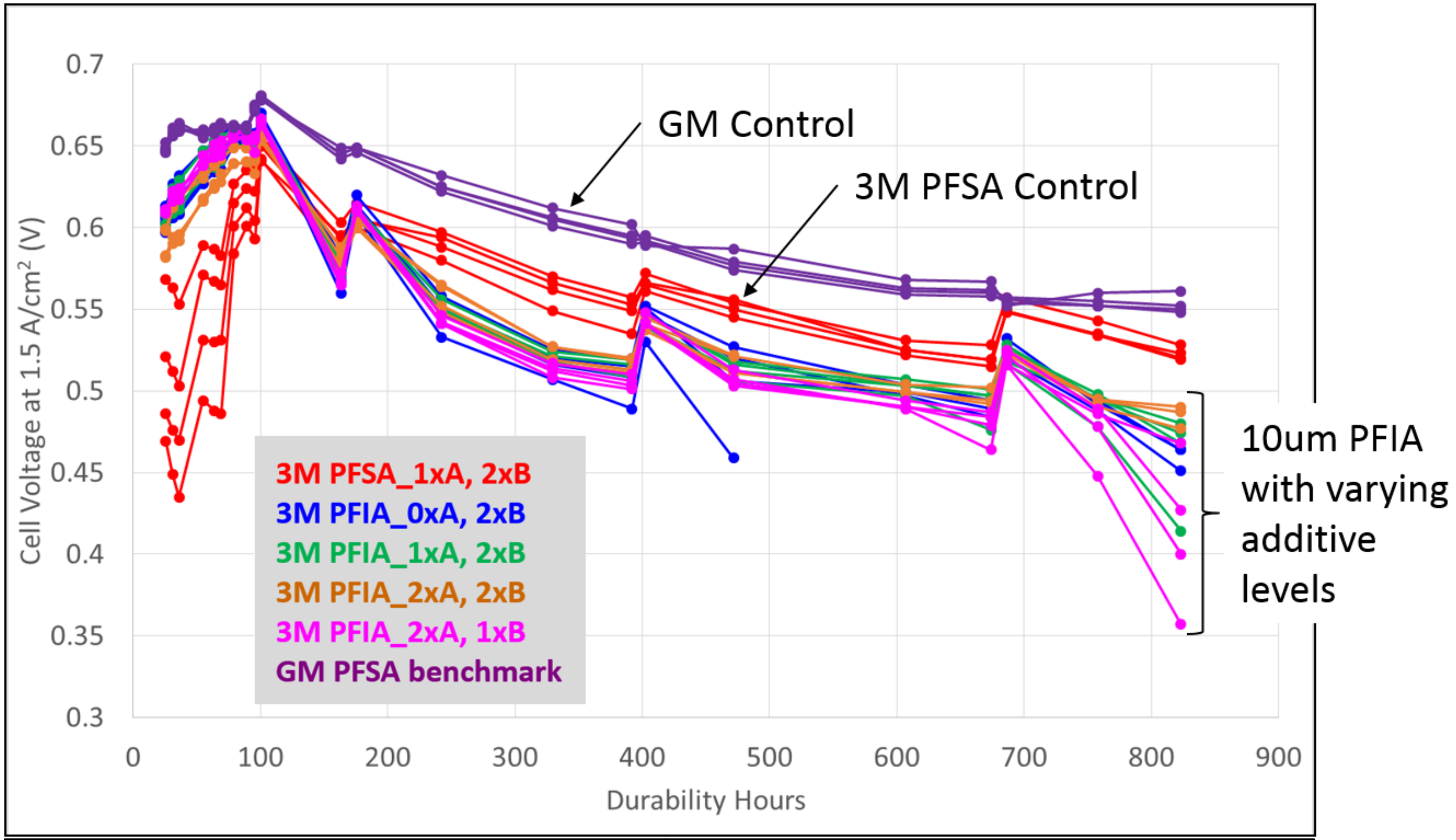
Milestones 10-12: Stack Testing at GM

- Milestone 10: Manufacture for stack testing at least 30 MEAs with a minimum cell area of 250 cm2. Evaluate in fuel cells and ex situ tests. Begin stack testing.
- Milestone 11: Begin post mortem analysis of MEAs to determine failure mode.
- Milestone 12: Prepare the MEAs, the number and size to be determined by 3M and the DOE, and deliver them for testing at a DOE approved facility. Complete stack testing for a minimum of 2,000 hours.

Membrane Types	Ionomer	Ionomer EW (g/mol)	Thickness	Support	3M + GM additive
3M 0513277A	3M PFSA	725	14µm	HC/FC	1X type A, 2XB
3M 05160081A	3M PFIA	650	10µm	FC1	0X type A, 2XB
3M 05160081B	3M PFIA	650	10µm	FC1	1X type A, 2XB
3M 05160081C	3M PFIA	650	10µm	FC1	2X type A, 2XB
3M 05160081D	3M PFIA	650	10µm	FC1	2X type A, 1XB
GM state-of-art PFSA				ePTFE	yes

Controls

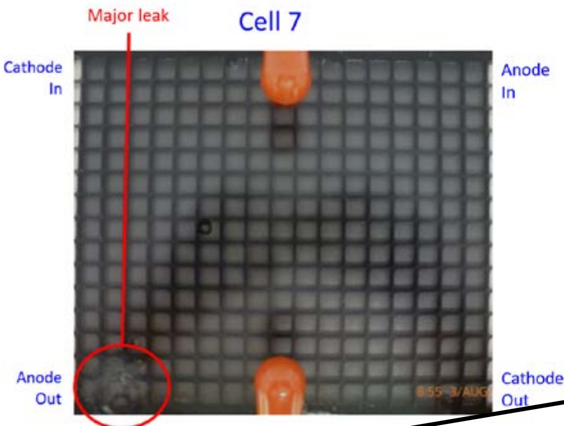
Milestone 12: Stack Test Data from GM



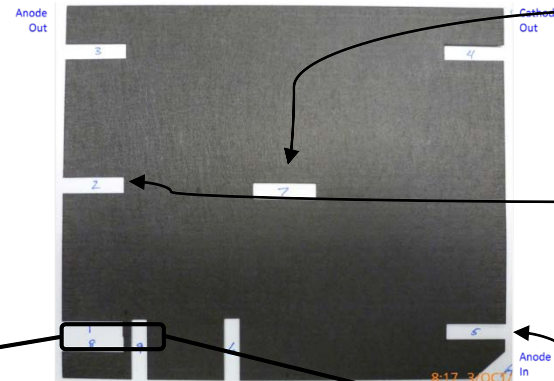
Summary	**Potential reasons for early failure**
• Membranes failed prior to the 2,000 hr target (~830 hrs) • Performance decay was observed for the PFIA that was partially recoverable • No dependence on additive type or level	• Short resistance marginal at BOL (see back-up slides) • 3M determined PFIA lot had high iron content (~50 ppm) • Possible defects in membrane coating • Ionomer stability

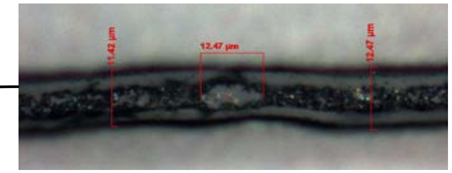
Milestone 11: Post Mortem Analysis

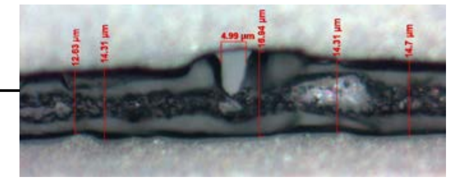
Leaks identified with bubble test

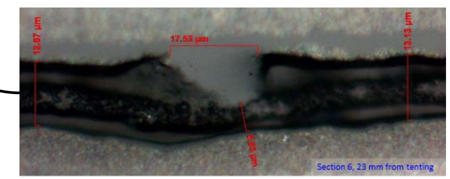


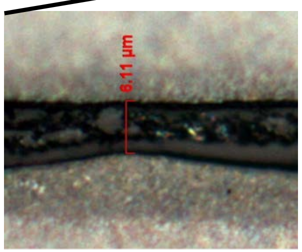
Optical microscope cross sections images

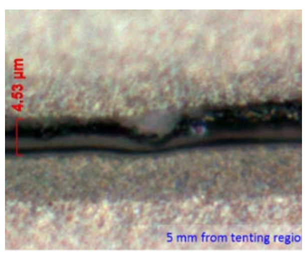


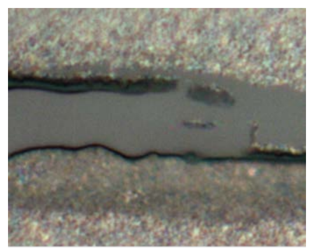


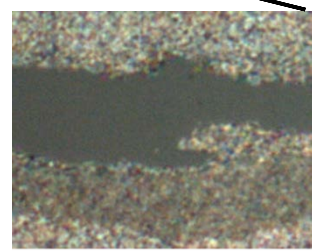












Summary

- Membrane thinning/erosion observed near cathode inlet of cell 7.
- Damaged areas observed in several locations.
- Cracks more severe on anode side.

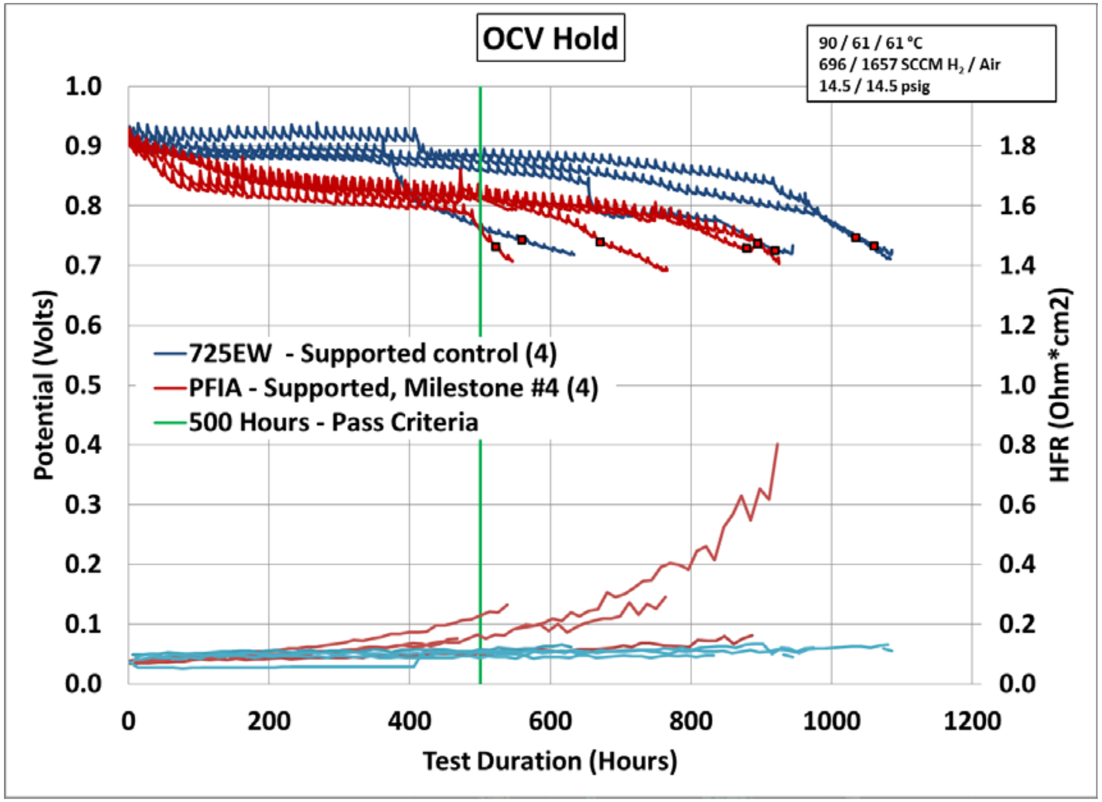
A Closer Look at the OCV Testing

Unexpected OCV decay

- Impurities related to synthesis eliminated as possible cause.
- Cross-over or shorts eliminated (see 2016 AMR)
- Commercial electrodes using alloy catalyst and additional additive appear to delay the effect (see 2016 AMR)
- ~50ppm iron detected in PFIA ionomer lot (2017 AMR)
- Membrane decomposition hypothesis explored (2017 AMR)

Unexpected HFR increase

- Measurement error eliminated (data not shown).
- Formation of resistive layer (i.e. voids in support layer) eliminated (data not shown).
- Commercial electrodes (Alloy and additional additive) appear to delay the effect (see 2016 AMR)
- ~50ppm iron detected in PFIA ionomer lot (2017 AMR)
- Membrane decomposition hypothesis explored (2017 AMR)

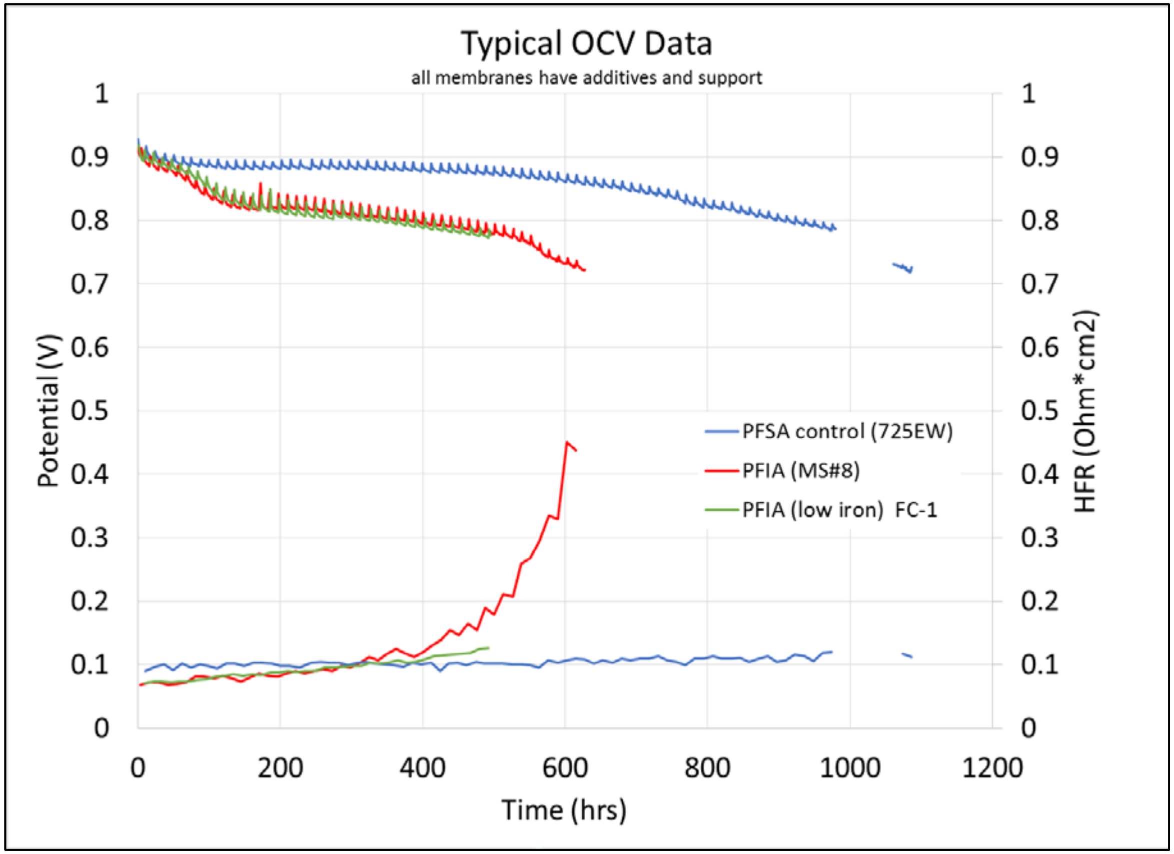


Summary

- Ionomer decomposition hypothesis under evaluation
- OCV decay and resistance increase appear related
- High surface area catalyst with increased additives mitigate effect (See 2016 AMR and back-up slides).

OCV Testing – Low Iron Samples

- Iron Identified in PFIA lot used for MS#8 Membrane (~50ppm)
- Low Iron samples prepared and run in OCV test (~1 ppm)

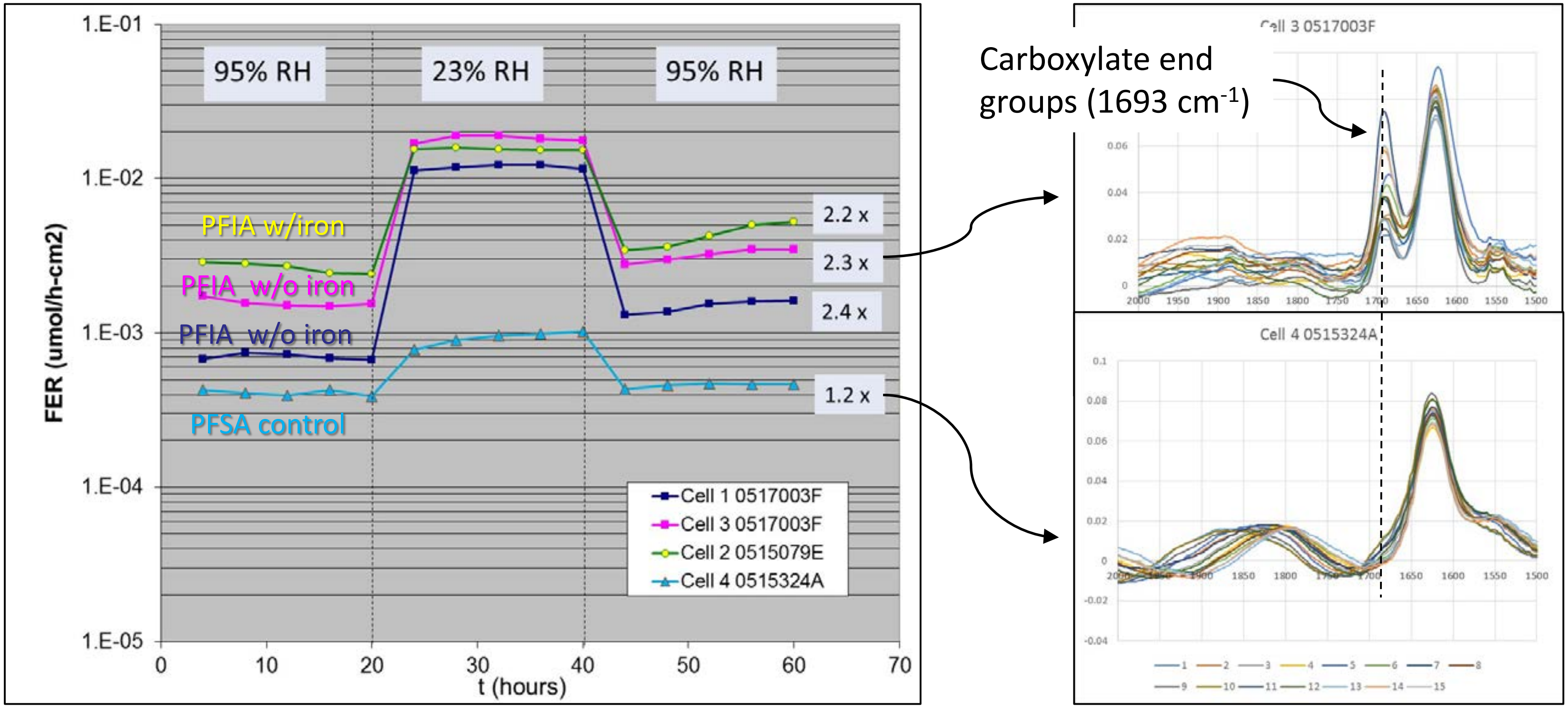


Summary

- Increased degradation due to iron contamination alone is not the likely cause of the observed OCV decay or resistance increase.

Peroxide Vapor Test (30 ppm)

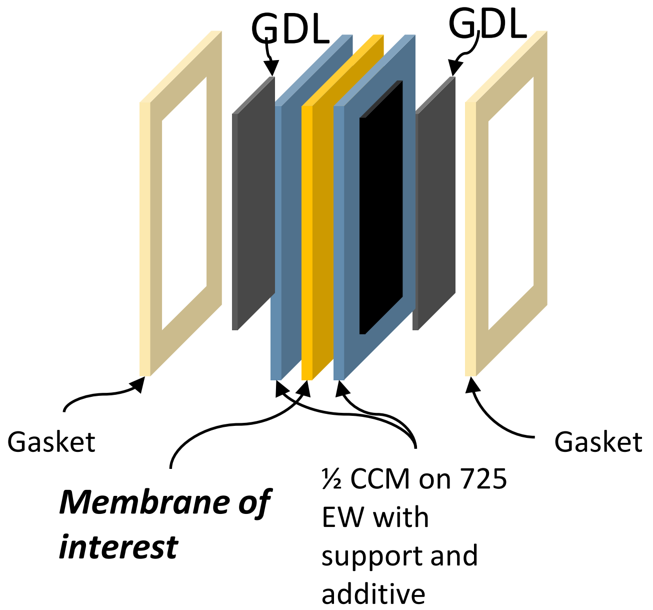
Four, 14 µm thick, ePTFE reinforced membranes with additive were subjected to the standard 60 hour H_2O_2 vapor test



Summary

- 3M PFSA exhibited near zero acceleration at the conclusion of the test (1.2x)
- All PFIA membranes showed about a 2.3x acceleration over the course of the 60 hour test
  - Reason for differences in t=0 degradation rates are unknown
- Membrane damage assessed by FTIR analysis of K^+ salts, increased COO^- observed in PFIA samples

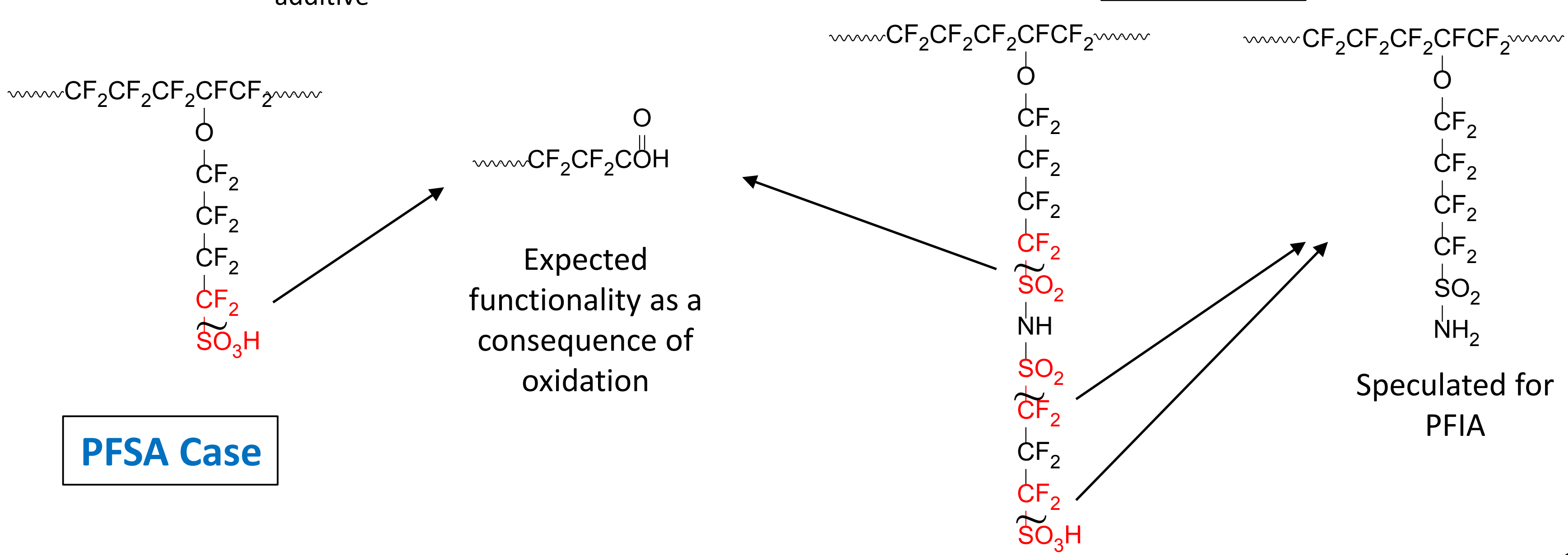
Multilayer Membrane Fuel Cell Testing



Objective:

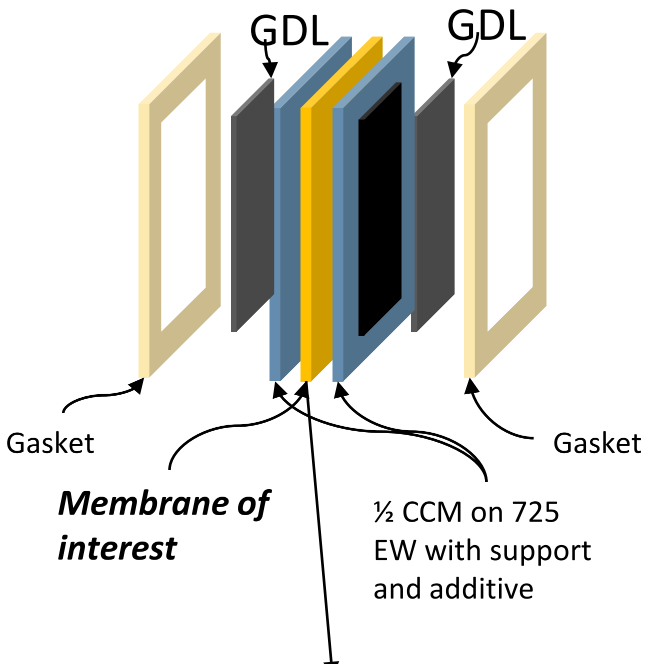
Subject membrane to the same conditions that result in performance decay and analyze separate membrane layers for chemical or physical changes (3-5 layers);

- Conductivity
- ^{19}NMR
- FTIR

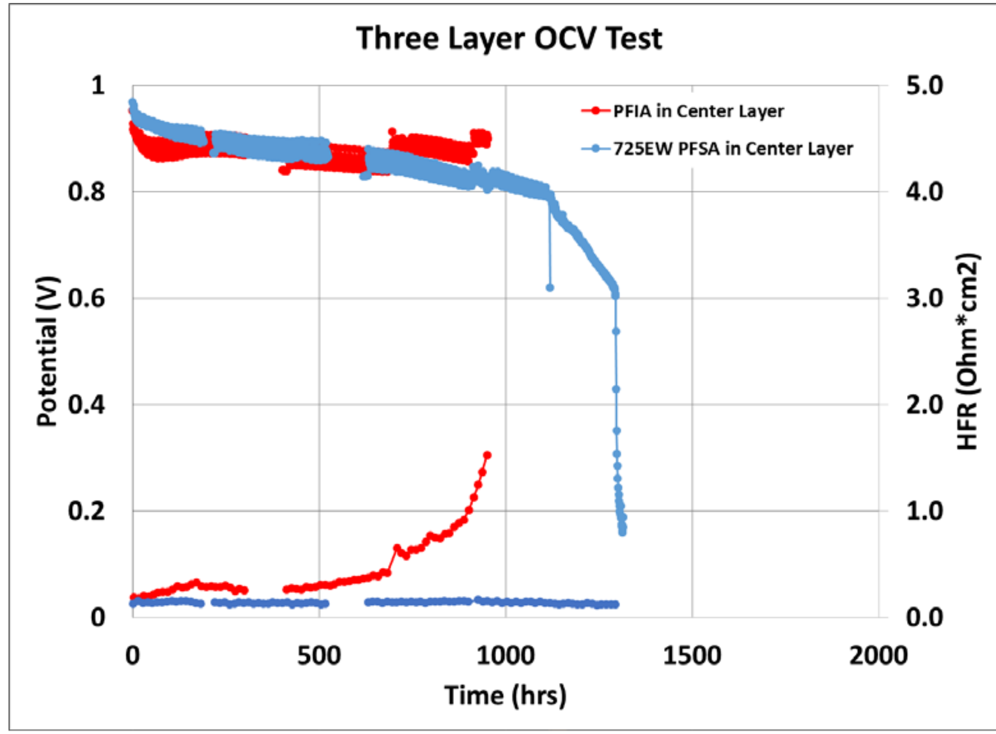


OCV Testing – 3 Layer Samples

Inner layer Membranes:
- 20um 725 EW no add. no support
- 20um* PFIA (CG3/4) no add. no support



Representative Data

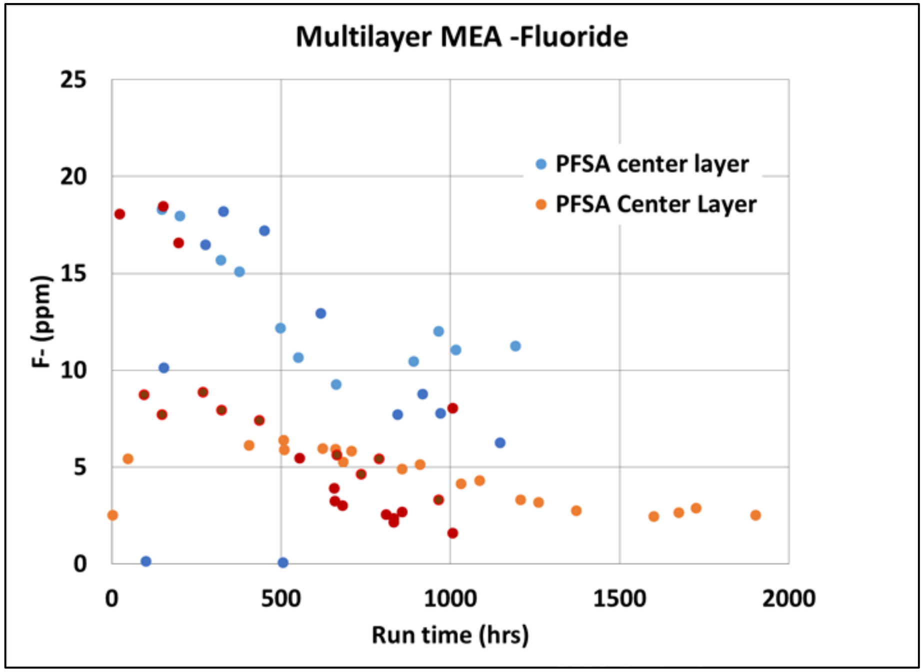


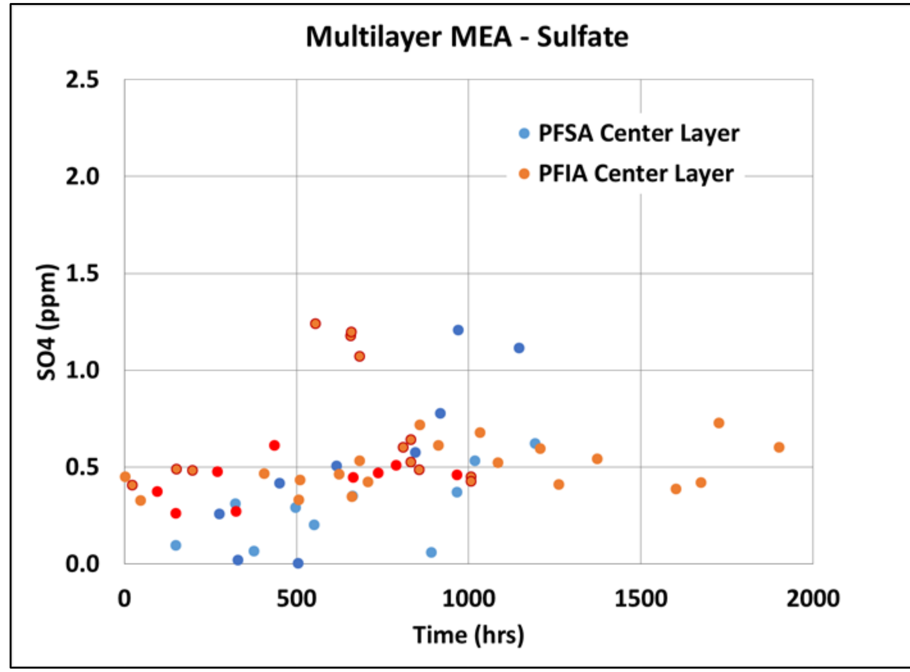
Summary
- PFIA in center layer exhibited OCV decay and resistance increase
- Center membrane isolated for both PFIA and control

Multilayer OCV Test – Effluent Water

Inner layer Membranes:

- 20um 725 EW no add. no support
- 20um* PFIA (CG3/4) no add. no support



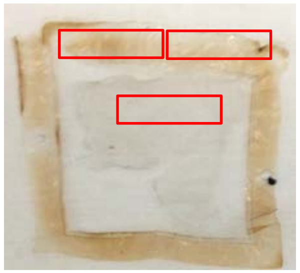


Summary

- Ion chromatography measurements of effluent water (***cathode only***) show fluoride and sulfate levels similar between PFSA and PFIA

Post Mortem Conductivity

In-plane conductivity measured using 4 point probe method

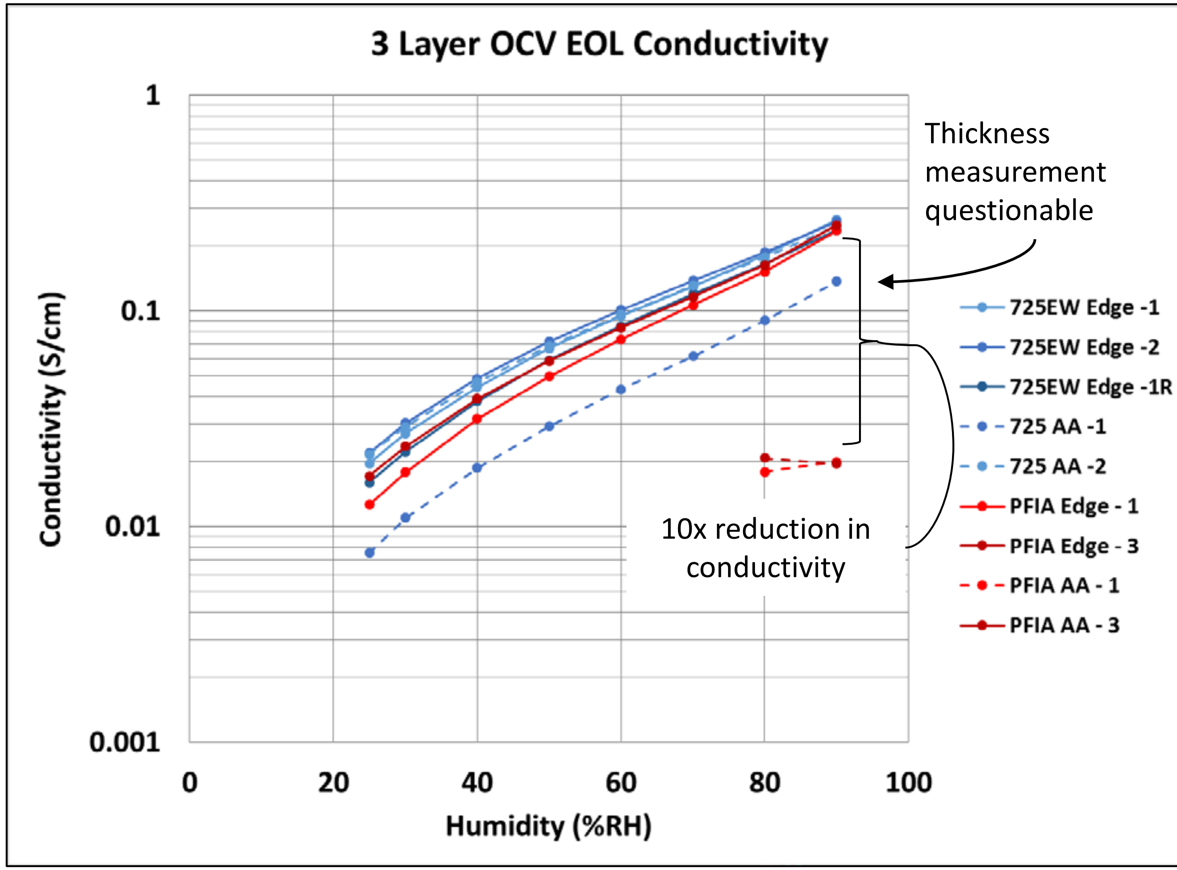


725EW
Sample 1

725EW
Sample 2

PFIA
Sample 1

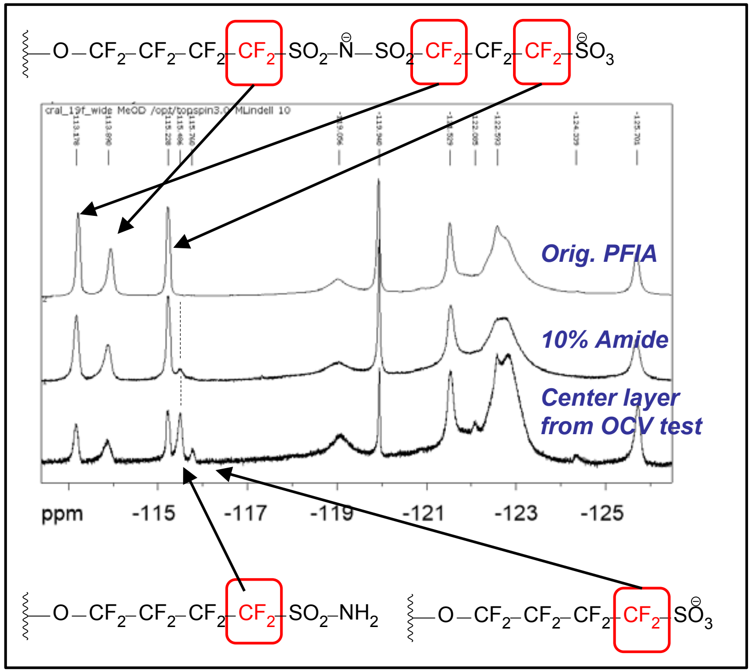
PFIA
Sample 3

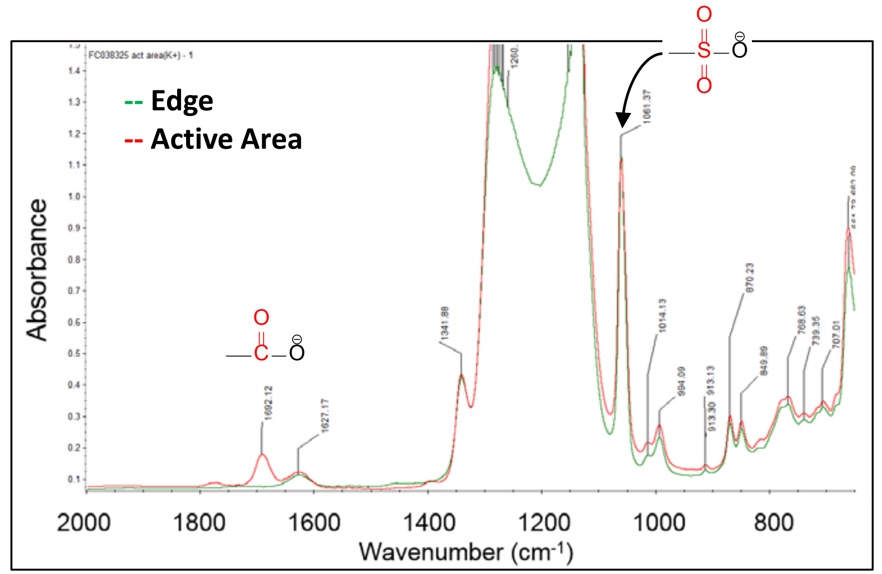


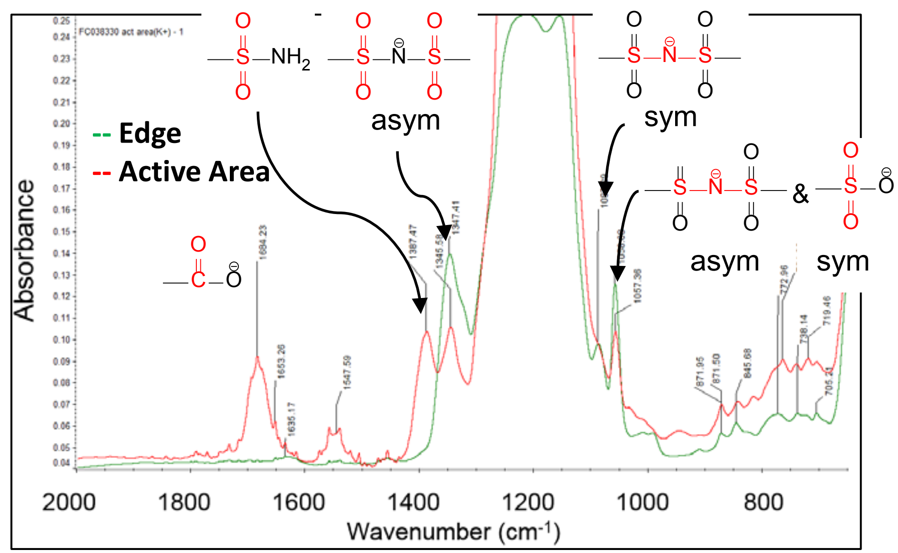
Summary
- All samples showed thinning in active area 20um → 5-15um
- Conductivity for PFSA control membranes are similar between edge and active area
- Conductivity of PFIA active area significantly reduced

Post Mortem ^{19}F NMR and FTIR

Analysis of center layer of 3 layer OCV test (K+ or Li+ form)







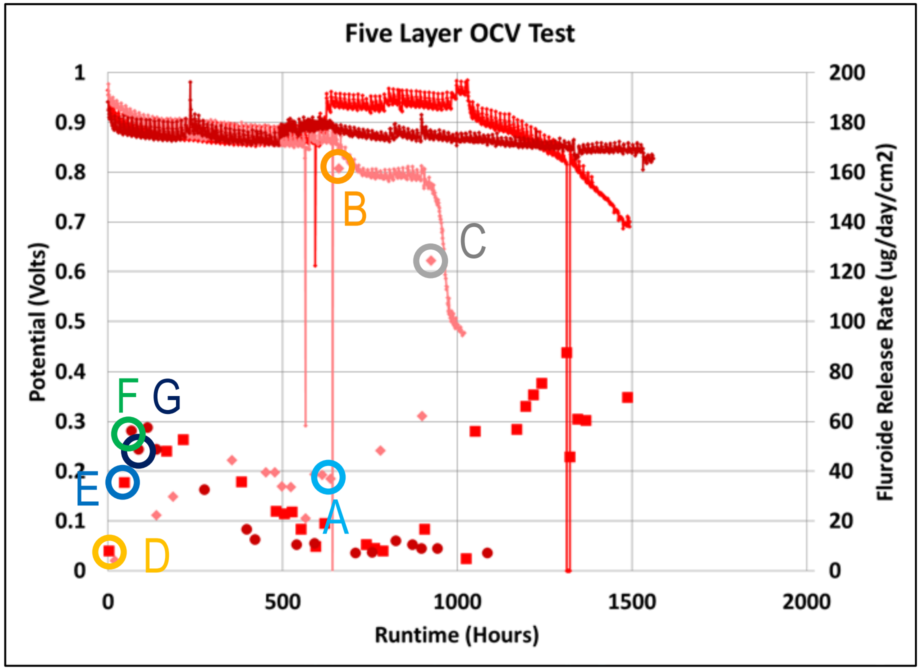
Summary

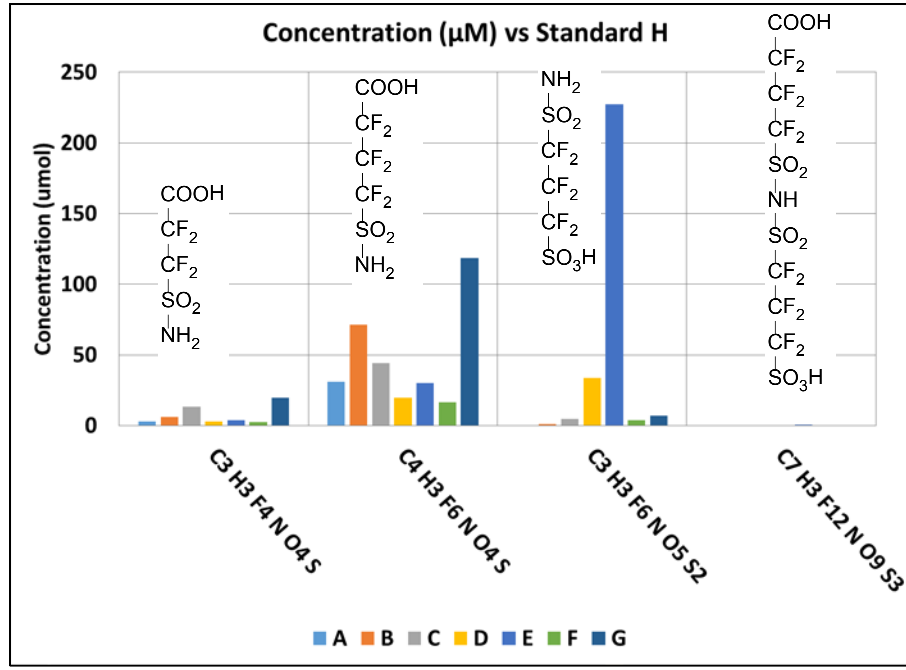
- Carboxylate end groups observed in FTIR for both ionomers as expected.
- FTIR analysis of PFSA shows no meaningful change in side chain functionality
- FTIR and ^{19}F NMR analysis of PFIA layer show loss of the imide functionality and appearance of the amide functionality

OCV Testing – 5 Layer Samples

All membrane layers: **14um PFIA with support and additives**

Water samples retained for fluoride measurements (***cathode only***) were analyzed by liquid chromatography-mass spectroscopy (LC-MS)





Summary

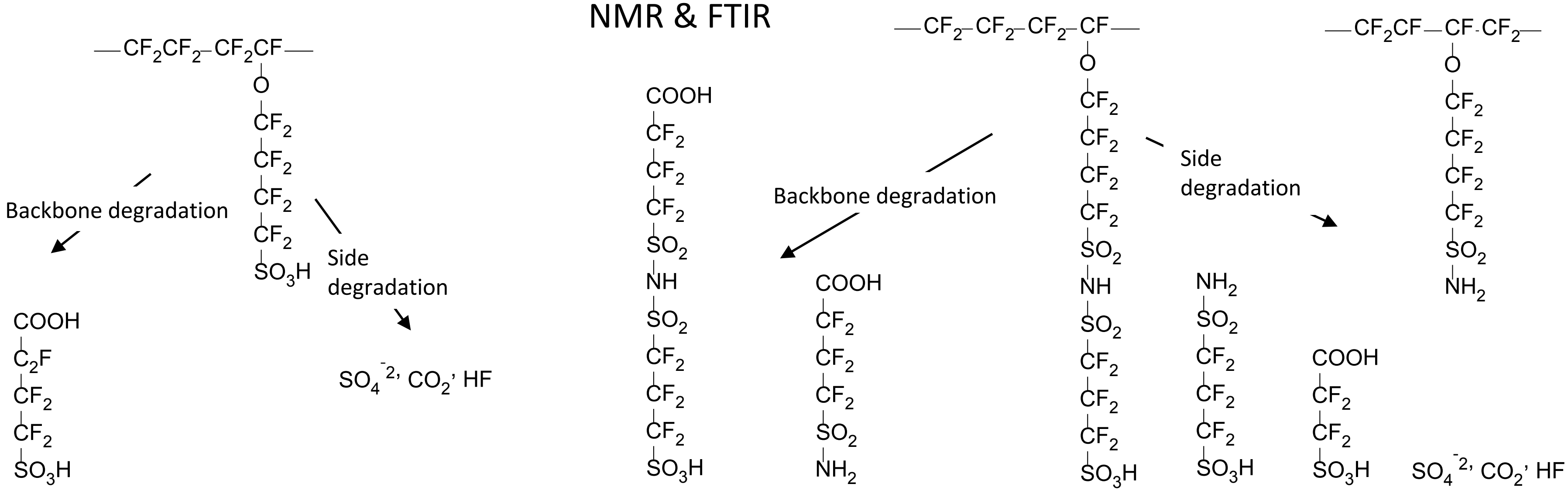
- Layers not able to be effectively separated.
- Water analysis shows low levels of PFIA side chain fragments throughout cell lifetimes.
- Additional fragments detected but not reported here.

Ionomer Stability Summary

PFSA Case

Fragments measure by LC-MS
Amide side chain measured by
NMR & FTIR

PFIA Case



Summary

- Fluoride and sulfate release levels similar between PFSA and PFIA samples.
- Bond strengths and oxidative decomposition likely to be similar between sulfonic acid and imide functionality.
- ***No evidence yet that PFIA is fundamentally less stable than PFSA***
- ***Consequences*** of decomposition are different
  - Potential catalyst poisoning (larger/different fragments)
  - Nonconductive polymer (sulfonamide polymer has very low conductivity)

Summary

- Nearly all milestones met with the exception of final stack test
- Nearly all of the DOE targets for membrane performance, and durability were met simultaneously with a single membrane.
- A new durability concern has emerged;
  - Oxidative decomposition of PFIA has new implications on MEA electrode performance and membrane conductivity.
  - Existing OCV and RH cycle accelerated stress tests did not immediately reveal the problem
  - Mechanism of degradation not fully understood

Future Work

Remainder of project

- Investigate PFIA oxidation mechanism
  - Model compound studies (isolate imide and sulfonic acid functionality)
  - Study imide only ionomers
- Evaluate the effects of peroxide stabilizing additives on PFIA stability
  - Revisit Milestone #7
  - Use mechanism learnings to develop stabilizing strategy
- Study the effects of decomposition products on catalyst activity
  - Rotating disk electrode (RDE) studies at NREL (H., Dinh, G. Bender)
  - Introduce side chain fragments into operating fuel cell
- Assess stabilization strategies by the end of 2017
- Ongoing work in fiber support development

Any proposed future work is subject to change based on funding levels

Technical Back-up Slides

DOE Targets

Table 3.4.12 Technical Targets: Membranes for Transportation Applications				
Characteristic	**Units**	**2011 Status**[a]	**2017 Targets**	**2020 Targets**
Maximum oxygen cross-over[b]	mA / cm^2	<1	2	2
Maximum hydrogen cross-over[b]	mA / cm^2	<1.8	2	2
Area specific proton resistance at:				
Maximum operating temperature and water partial pressures from 40-80 kPa	Ohm cm^2	0.023 (40kPa) 0.012 (80kPa)	0.02	0.02
80°C and water partial pressures from 25-45 kPa	Ohm cm^2	0.017 (25kPa) 0.006 (44kPa)	0.02	0.02
30°C and water partial pressures up to 4 kPa	Ohm cm^2	0.02 (3.8 kPa)	0.03	0.03
-20°C	Ohm cm^2	0.1	0.2	0.2
Operating temperature	°C	<120	≤120	≤120
Minimum electrical resistance	Ohm cm^2	–	1,000	1,000
Cost[c]	$\$ / m^2$	–	20	20
Durability[d]				
Mechanical	Cycles with <10 sccm crossover	>20,000	20,000	20,000
Chemical	hours	>2,300	>500	>500

a: http://www.hydrogen.energy.gov/pdfs/progress11/v_c_1_hamrock_2011.pdf). Status represents 3M PFIA membrane (S. Hamrock, U.S. Department of Energy Hydrogen and Fuel Cells Program 2011 Annual Progress Report, (

b: Tested in MEA at 1 atm O_2 or H_2 at nominal stack operating temperature, humidified gases at 0.5 V DC.

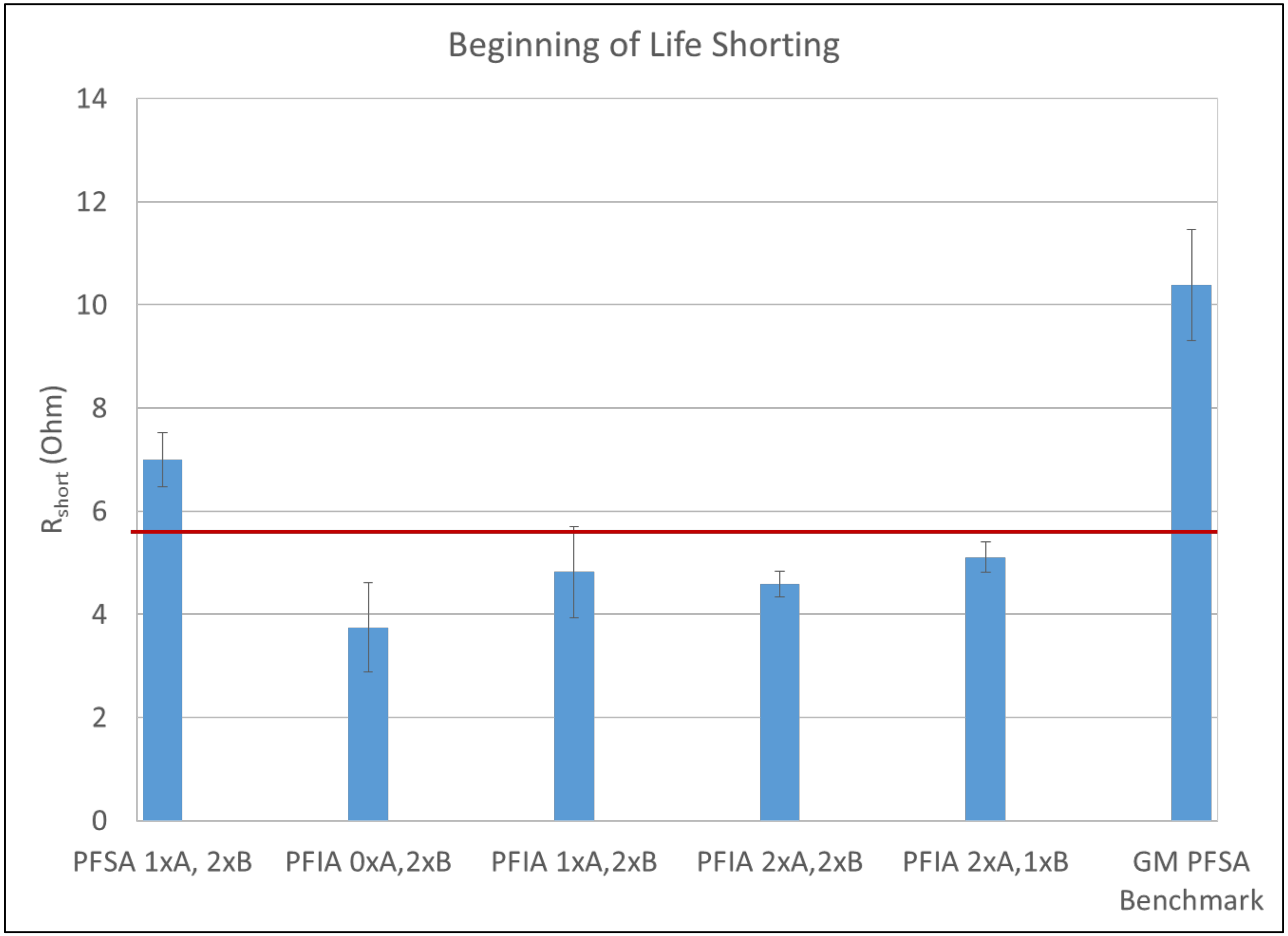
c: Costs projected to high-volume production (500,000 stacks per year).

d: http://www.uscar.org/commands/files_download.php?files_id=267Protocol for mechanical stability is to cycle a 25-50 cm^2 MEA at 80°C and ambient pressure between 0% RH (2 min) and 90°C dew point (2 min) with air flow of 2 SLPM on both sides. Protocol for chemical stability test is to hold a 25-50 cm^2 MEA at OCV, 90°C, with H_2/air stoichs of 10/10 at 0.2 A/cm^2 equivalent flow, inlet pressure 150 kPa, and relative humidity of 30% on both anode and cathode. Based on U.S. DRIVE Fuel Cell Tech Team Cell Component Accelerated Stress Test and Polarization Curve Protocols (), MEA Chemical Stability and Metrics (Table 3) and Membrane Mechanical Cycle and Metrics (Table 4).

Full Milestone Table

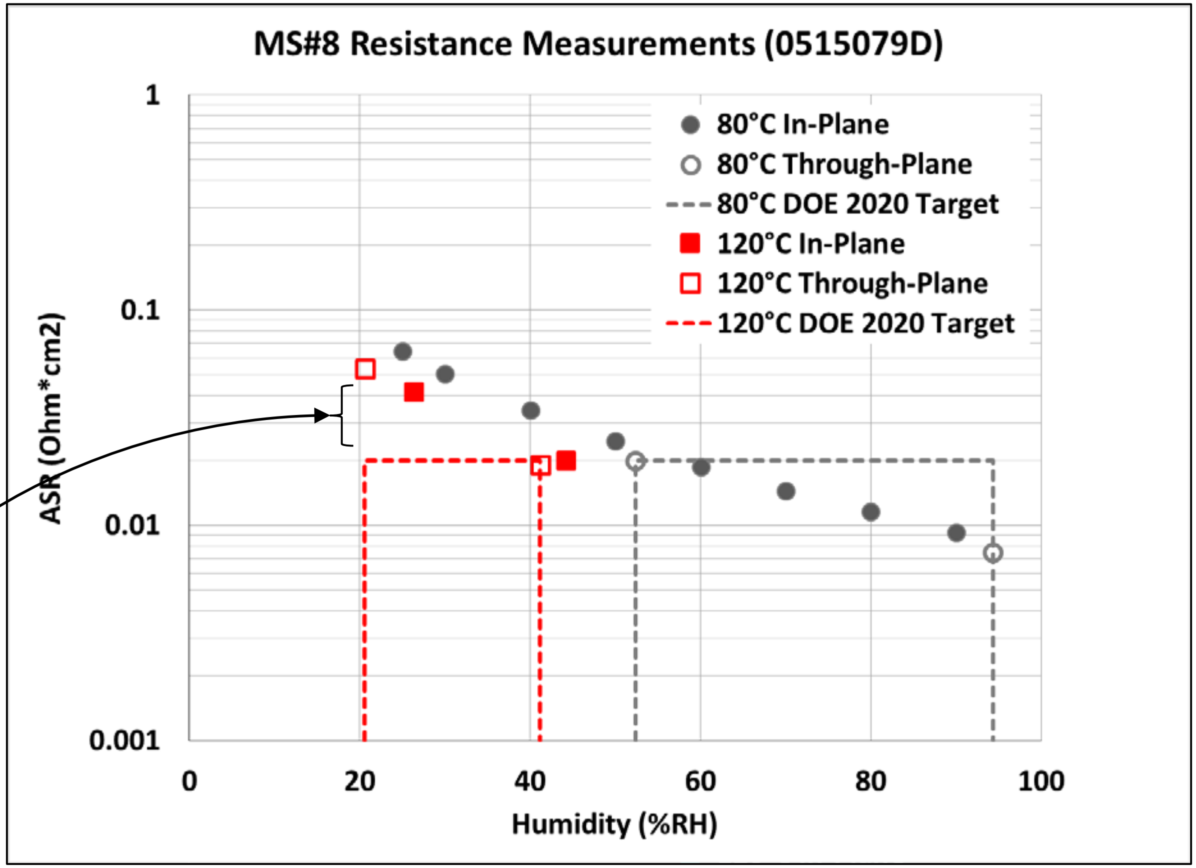
MS ID	Full Milestone	Date
1	Measure conductivity and fuel cell performance on at least two different control PFSA membranes and initial samples of MASC ionomer membranes. Demonstrate MASC ionomer with conductivity of 0.1 S/cm or higher at 80°C and <50% RH.	January 9, 2014
2	Identify one or more polymer systems for further development in a nanofiber support that provides a membrane with x-y swelling of < 5% after boiling in water.	April 8, 2014
3	Develop electrospinning conditions for one or more 3M ionomers that provides fiber diameter of <1 micron.	May 22, 2014
4 - Go/No-Go	Develop a laboratory produced membrane using an optimized ionomer and electrospun nanofiber support that passes all of the tests shown in tables D3 (chemical stability) and D4 (mechanical stability) of the FOA while still showing performance in single cell polarization experiments above state of the art, mass produced membranes (nanofiber supported 725 EW 3M Membranes) tested in the beginning of this program (not to be less than 0.5 V at 1.5 A/cm2 at 95C, 50%RH, 150 kPa inlet pressure, and 0.4 mg/cm2 total pgm catalyst loading).	October 16, 2014
5	Prepare at least one additional MASC polymer. Demonstrate conductivity of 0.1 S/cm or higher at 80°C and <40% RH. Evaluate in a supported membrane in Fuel Cell and ex situ tests.	March 6th, 2015
6	Prepare dense electrospun films with and without surface treatment of the support polymer with a maximum void fraction of <5%. Prepare and characterize the resulting nanofiber composite membranes. Determine if surface treatment impacts swell, tensile or tear properties of the membrane. Select surface treatment, if any.	April 3rd, 2015 - ongoing
7	Prepare an ionomer formulation (ionomer, stabilizing additive) with optimum performance and durability that provides >500 hours in test D3 (chemical stability), and equal or better area specific resistance (ASR) to the membrane described in the Q4 milestone of the same thickness, evaluated in a 50cm2 fuel cell using the same MEA components and same support, to be used for development of the supported membrane described in milestone Q8.	June 30th, 2015
8 - Go/No-Go	Produce membrane comprising a MASC Ionomer, a nanofiber support and a stabilizing additive which meets all of the 2020 membrane milestones in Table 3.4.12 (Technical Targets: Membranes for Transportation Applications) in the DOE Fuel Cell Technologies Office Multi-Year Research, Development and Demonstration Plan, section 3.4, update July 2013.	September 30th, 2015
9	Develop a process for producing the membrane described in Milestone Q8 in quantities large enough to produce membranes for use in Milestone Q10 (at least 20 linear meters)	January 1, 2016
10	Manufacture for stack testing at least 30 MEAs with a minimum cell area of 250 cm2. Evaluate in fuel cells and ex situ tests. Begin stack testing.	April 1, 2016
11	Begin post mortem analysis of MEAs to determine failure mode.	July 1, 2016
12	Prepare the MEAs, the number and size to be determined by 3M and the DOE, and deliver them for testing at a DOE approved facility. Complete stack testing for a minimum of 2,000 hours.	October 1, 2016

Stack Testing at GM



MEA Resistance Quality Check. Red line is GM specification.

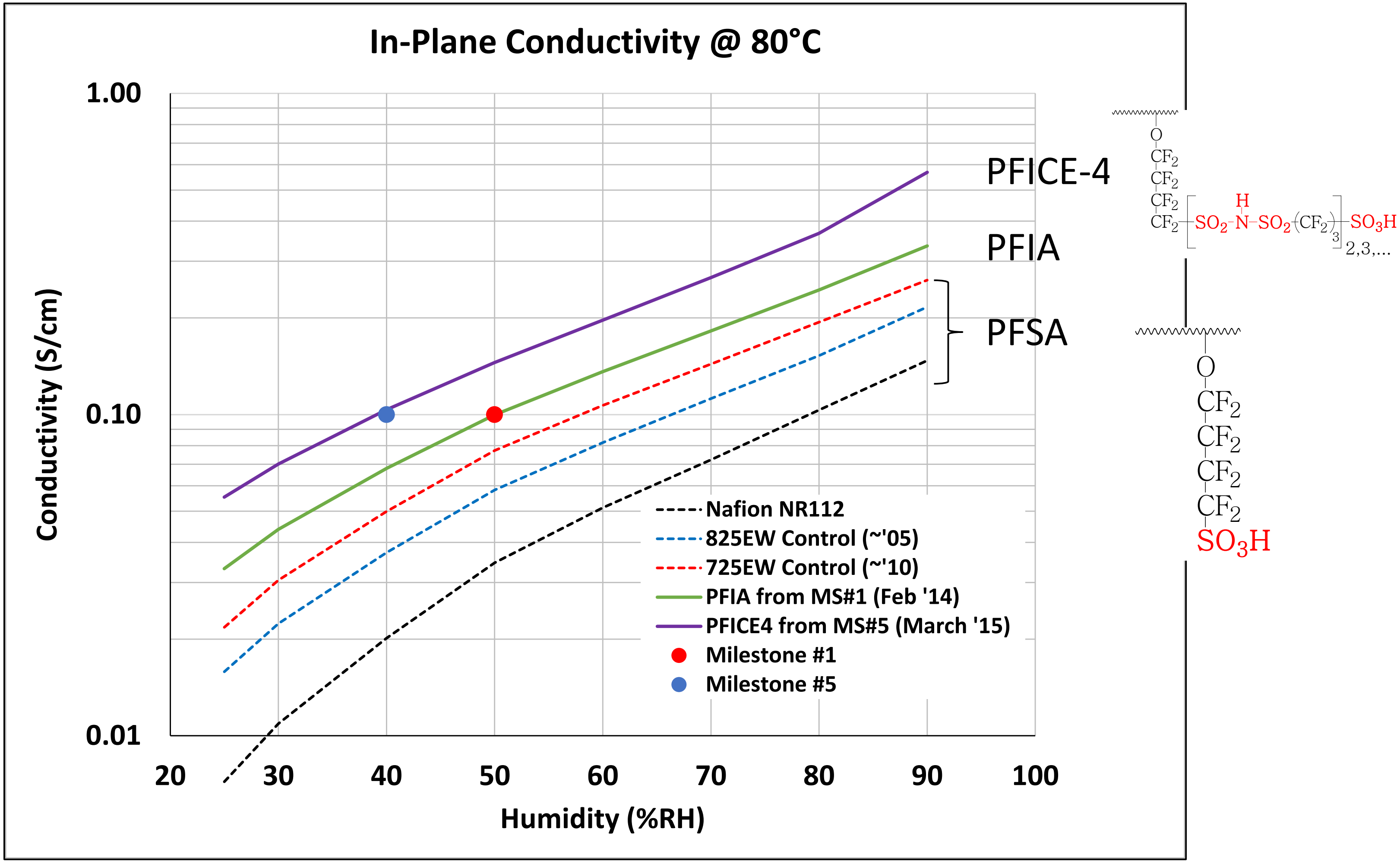
120°C Resistance



Summary

- Ionomer with an Equivalent weight of 450 g/mol is need to meet this target for a 10 um membrane with additive and support (see 2016 AMR).

Milestones #1 & 5

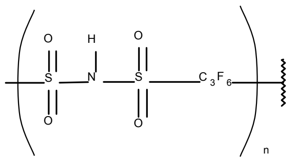


Accomplishments:

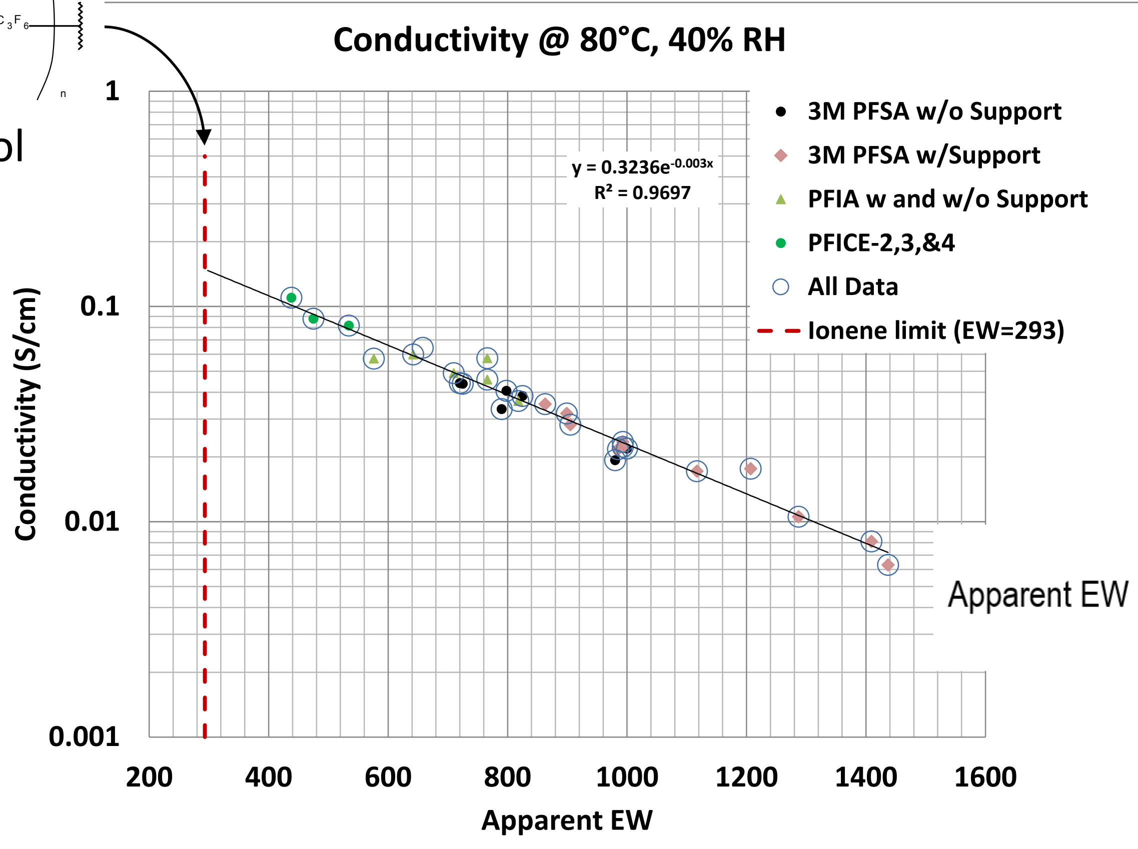
- State of the art conductivity improved by 5x at 80°C and 40% RH.
- 100mS/cm conductivity threshold moved from 80% to 40% RH compared to Nafion™.
- 100mS/cm conductivity threshold moved from 50% to 40% RH since the start of project.

Ionomer Development

In-Plane conductivity (4 point probe)



293 g/mol

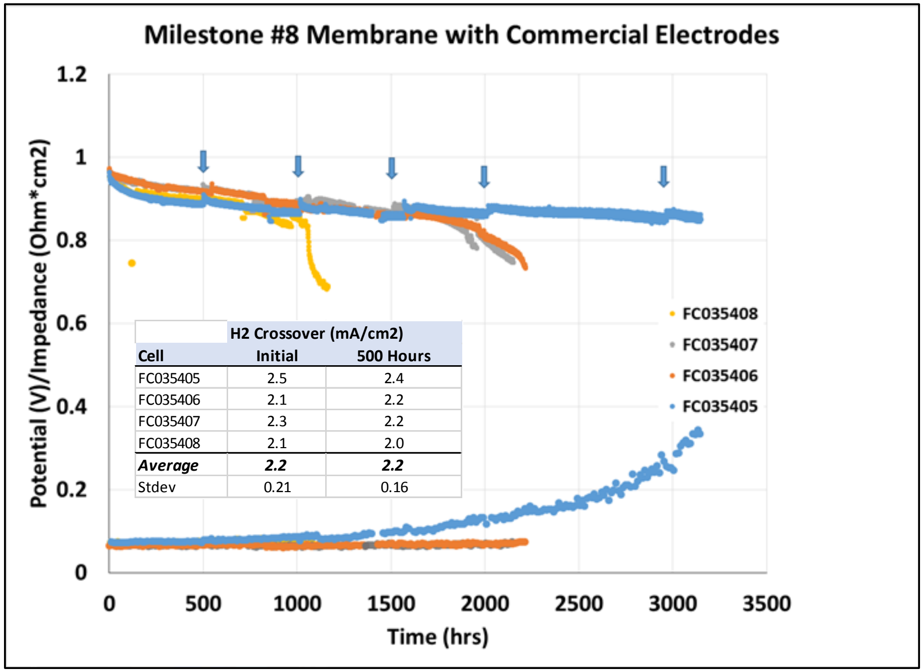


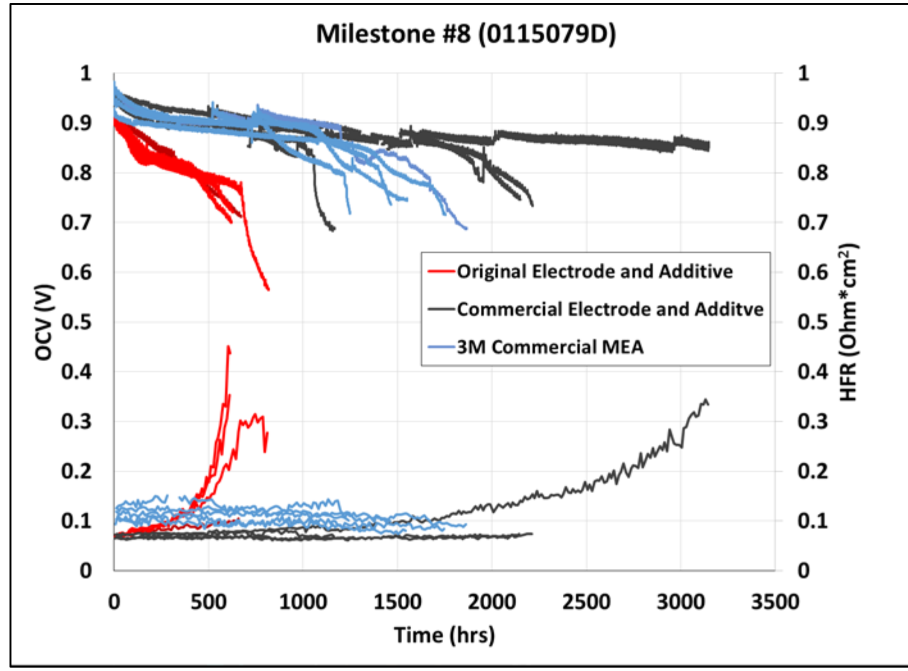
$$\text{Apparent EW} = \frac{1}{\left(\dfrac{1}{EW}\right) * \left(\dfrac{(1\text{-}\%\ \text{fiber})}{100}\right)}$$

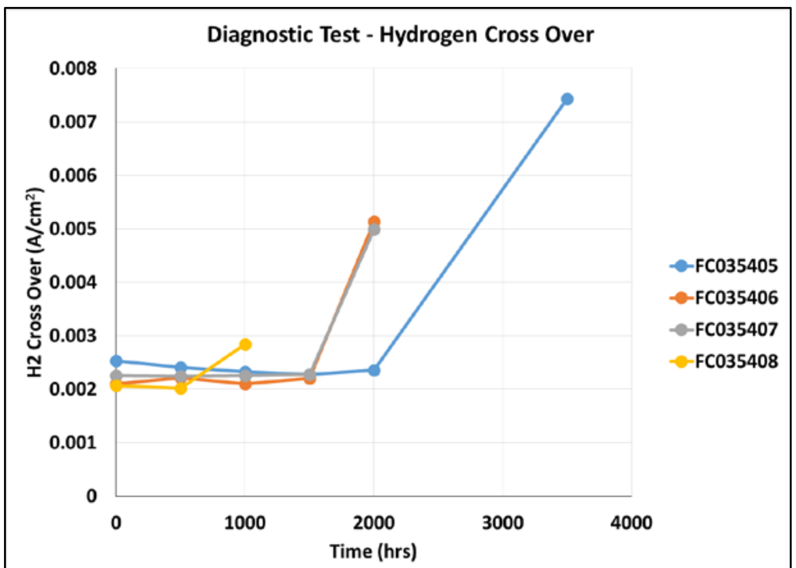
Accomplishments:

- Simple model establishes conductivity as a function of ‘apparent’ equivalent weight
- PFICE-4 conductivity is very close to ‘ionone limit’. – Additional chain extension would provide little addition gains.

OCV Accelerated Durability







Membrane	Electrodes	Lifetime (hrs) 80% OCV
MS#8	Lab control	614 ± 55
MS#8	Commercial	2105 ± 851
3M Commercial	Commercial	1484 ± 209

- MS#8 Membrane passed 500 hrs with lab electrodes.
- OCV decay and HFR increase observed with lab electrodes.
- Commercial electrodes and additive levels appears to have eliminated OCV decay and delayed HFR increase.
- H_2 crossover constant until membrane failure.