New Fuel Cell Membranes with Improved Durability and Performance

Mike Yandrasits

3M Fuel Cell Components

June 17, 2014

FC109

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

Overview

Timeline

- Start October 1st, 2013
- End September 30th, 2016
- 17% complete

Budget

- Total Project funding $4.2 million
  - $3.1 million - DOE
  - $1.1 million - contractor cost share (26%)
- Funding in FY 2014
  - $321,000 (Through March 2014)

Barriers

Durability

Performance

Cost

Partners

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

General Motors *C. Gittleman*

Vanderbilt University *Professor P. Pintaro*

Project Objectives

The program objective is to 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.

The overall goal of the project is to develop;

- New proton exchange membranes;
  - based on Multi Acid Side Chain (MASC) ionomers
  - reinforced with electrospun nanofiber structures
  - contain additives to enhance chemical stability

- These membranes should have;
  - improved mechanical properties
  - low area specific resistance and
  - excellent chemical stability compared to current state of the art membranes.

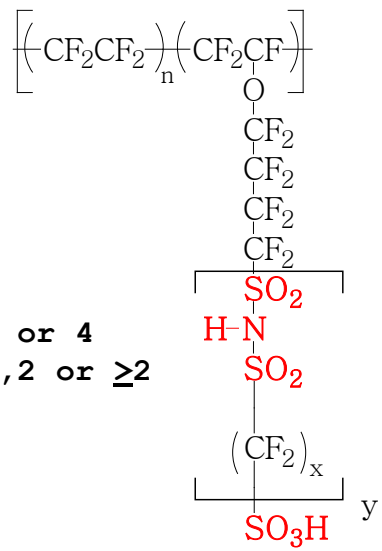
- Evaluation of membrane electrode assemblies (MEAs)
  - Single fuel cells.
  - Fuel cell stacks.

Project Approach

- **Develop Multi Acid Side Chain (MASC) Ionomers**
  - **Further develop PerFluoro Imide Acid (PFIA) chemistry developed under DE-FG36-07GO17006**
  - **New Ionomers with improved performance**
- **Develop mechanical support technology based on electrospun nanofibers**
  - **Study the effect of fiber type and volume fraction on performance and durability**
  - **Compare dual spun (ionomer and support) to traditional ionomer filled fiber membranes**
- **Integrate new ionomers with improved nanofiber supports and stabilizing additives**
- **Ex-Situ membrane testing**
- **Single Cell MEA testing**
- **Stack Testing**
- **Post Mortem Analysis**

Project Approach

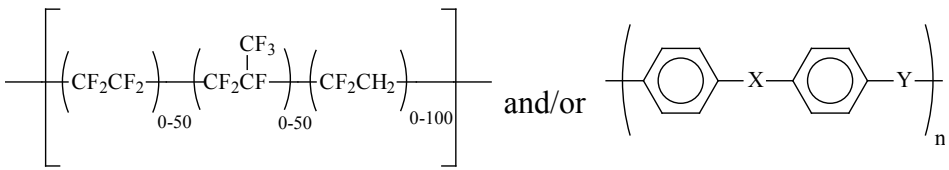
Ionomer Development

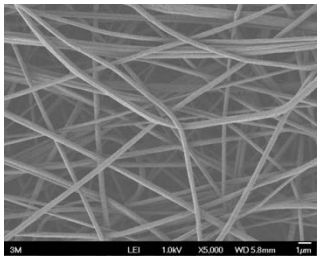


x = 3 or 4
y = 1,2 or ≥2

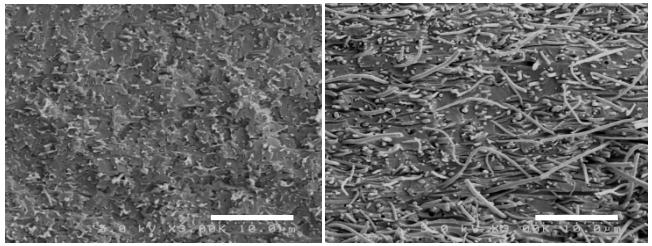
+

Nanofiber Support Development



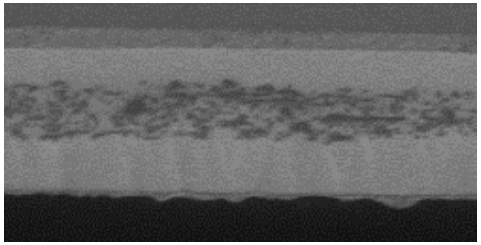


Membrane Development



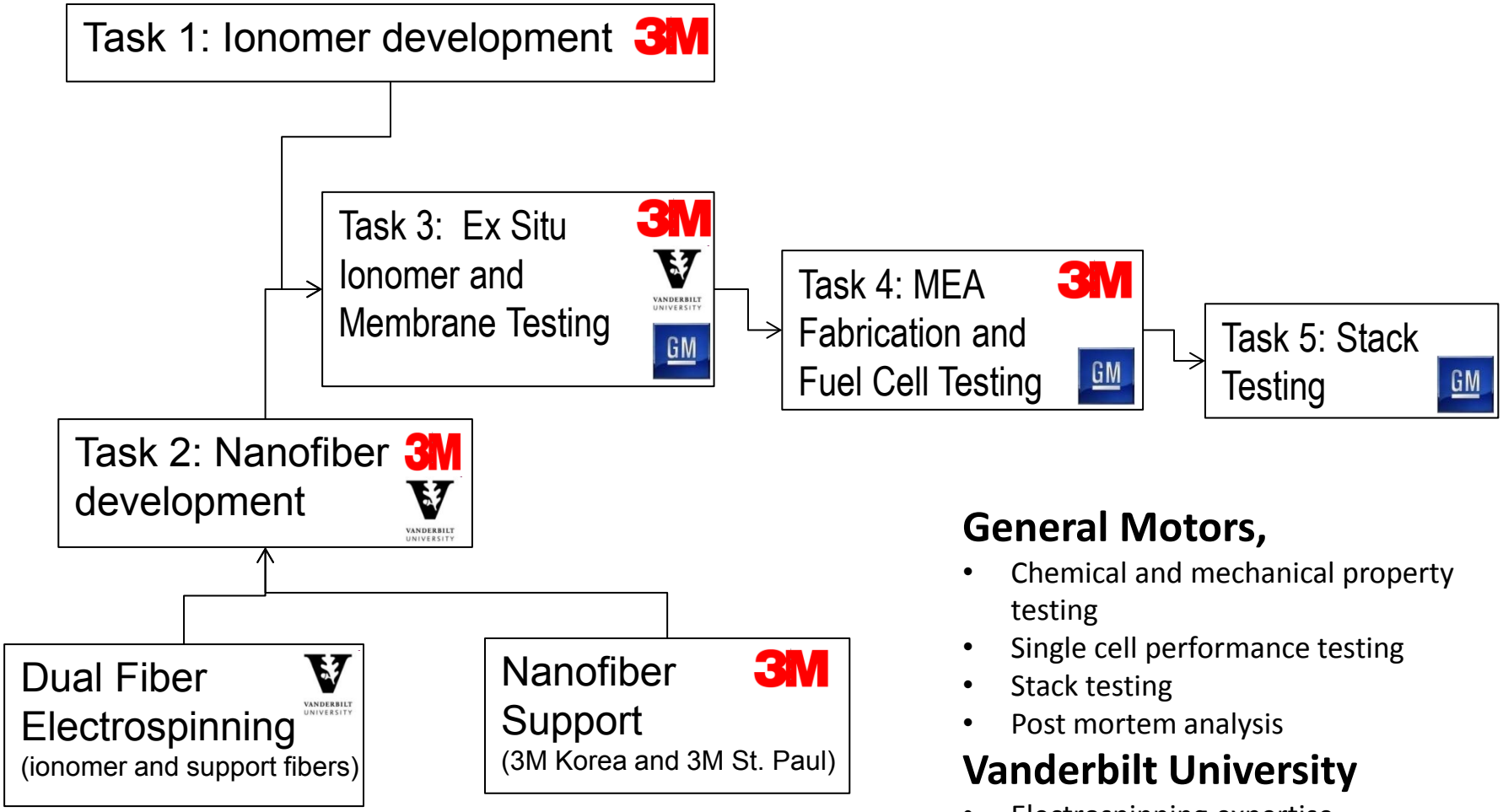
Ionomer fibers in inert matrix

Support fibers in ionomer matrix



Ionomer/Fiber composite center layer with ionomer skin layer

Collaborations:Flow Of Samples & Information



General Motors,

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

Vanderbilt University

- Electrospinning expertise
- Dual fiber electrospinning

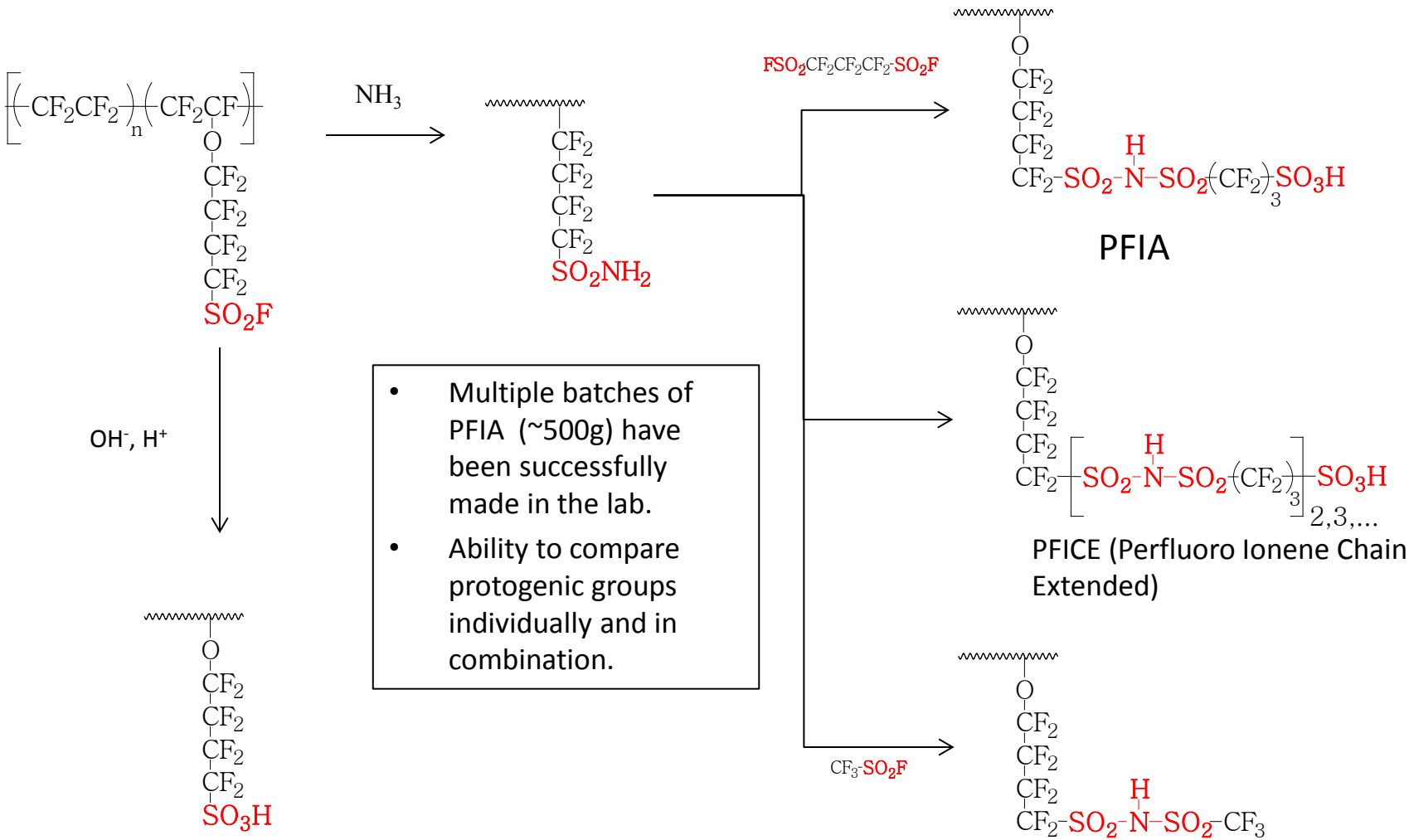
Milestones

Milestone ID	*Full Milestone*	*Brief 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.	Baseline: Conductivity of 2 controls and 1st MASC 0.1 S/cm @80°C, 50% RH (Task 1)	**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.	Identify 1 or more nanofiber polymers (Task 2.1 or 2.2)	**April 8, 2014**
3	Develop electrospinning conditions for one or more 3M ionomers that provides fiber diameter of <1 micron.	Develop spinning conditions for 3M ionomer (Task 2.2)	July 1, 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).	Lab made membrane to pass OCV, RH cycle, and performance >725 supported	October 1, 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.	At least one MASC with 0.1 S/cm @80°C, 40%RH	January 1, 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.	Nanofiber surface treatment selection	April 1, 2015
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.	MASC ionomer with additives. OCV >500hr, ASR < Q4 membrane. Ionomer for Q8.	July 1, 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.	Final membrane construction to meet DOE 2020 targets	October 1, 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)	Fabrication process for Q10 membrane	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.	30 MEAs for stack testing	April 1, 2016
11	Begin post mortem analysis of MEAs to determine failure mode.	Postmortem analysis	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.	MEAs for DOE testing. Complete 2,000hs on stack	October 1, 2016

completed

New Ionomers – Task 1

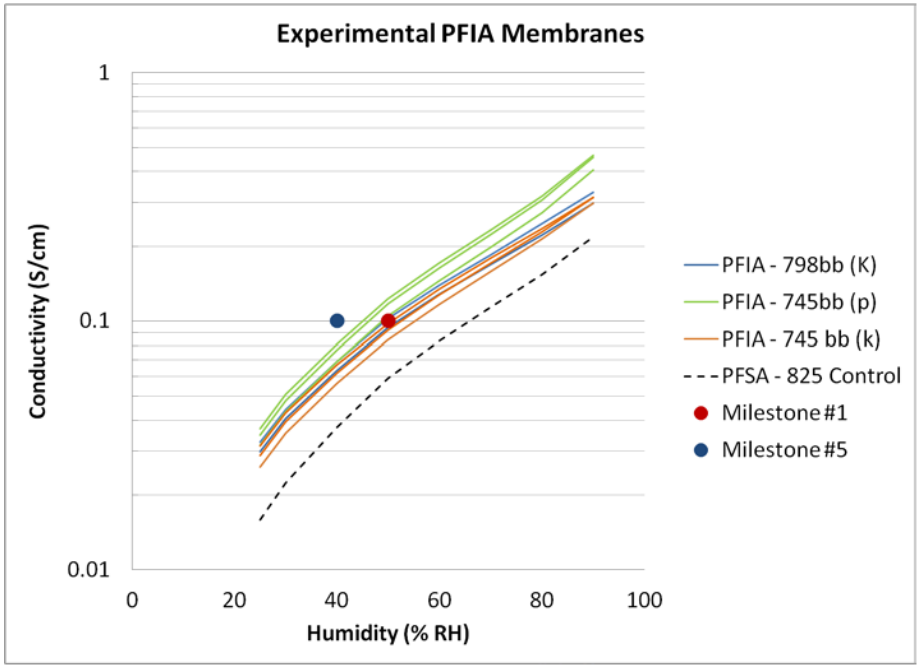
Synthetic Options

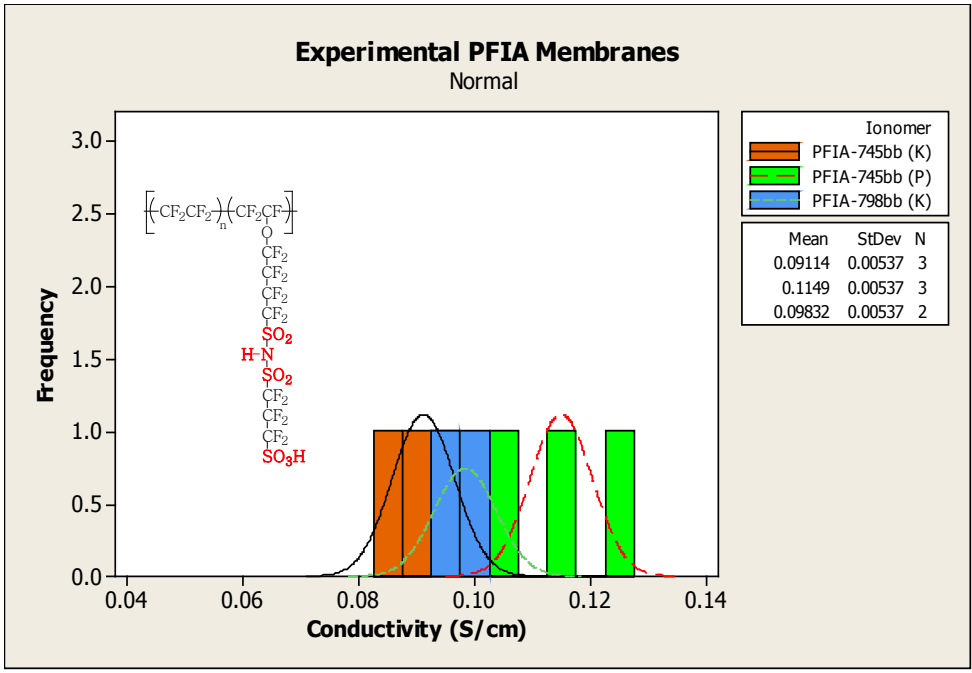


- Multiple batches of PFIA (~500g) have been successfully made in the lab.
- Ability to compare protogenic groups individually and in combination.

Milestone #1

Demonstrate MASC ionomer with conductivity of 0.1 S/cm or higher at 80°C and <50% RH.

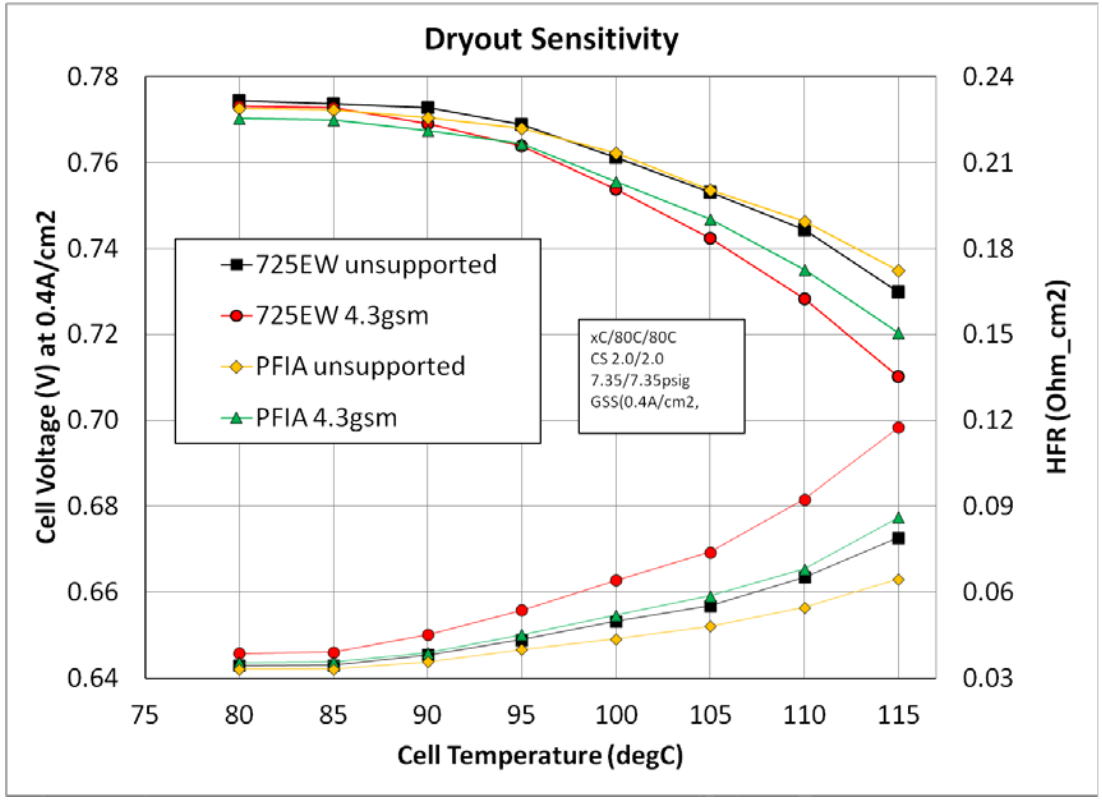




798bb or 745bb denotes a starting ionomer backbone EW
K and p denote liner used to cast ionomer

Accomplishment: Several Lots of PFIA polymer have demonstrated conductivity of 0.1 S/cm within experimental error

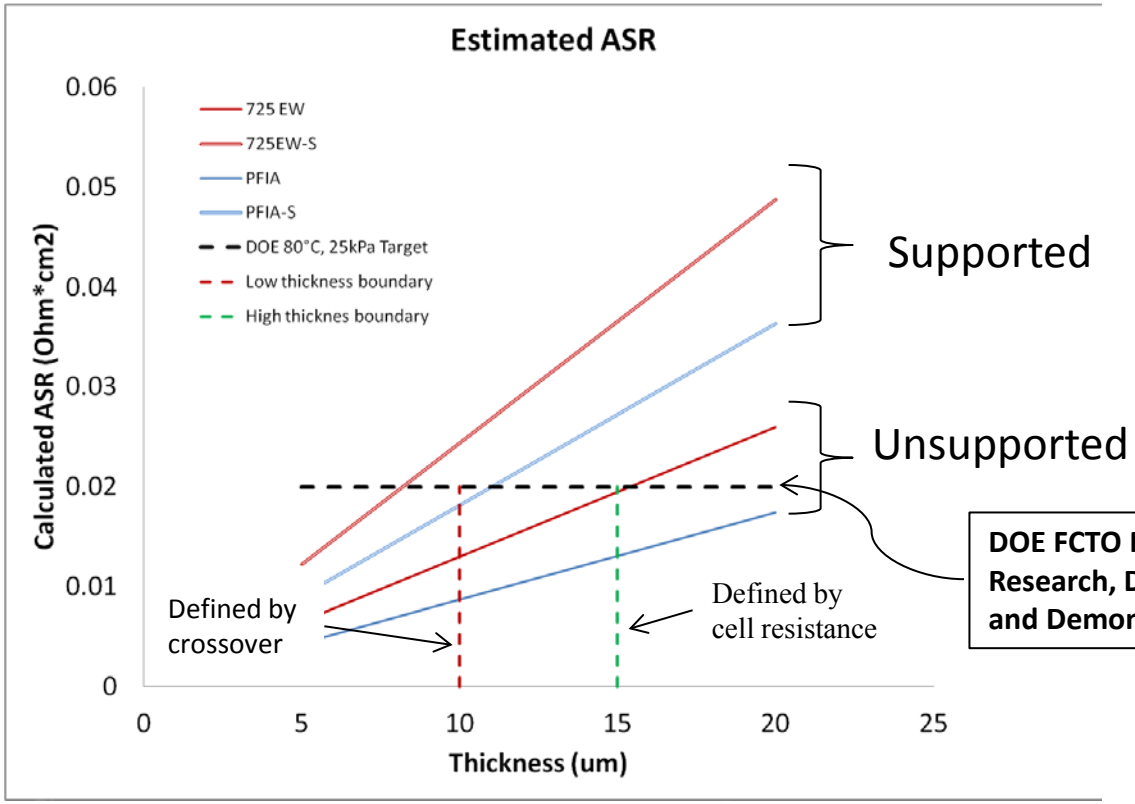
Hot/Dry Performance



- PFIA (620EW) shows lower resistance and improved performance at hot/dry conditions
- Nanofiber supported membranes have increased resistance compared to unsupported

Performance Gaps

Membrane Benchmarks						
Membrane			725EW	725-S	PFIA	PFIA-S
Test	Condition	Units				
In Plane Conductivity	80°C, 50% RH	mS/cm	77 ±8	41 ± 7	115 ± 8	55 ± 7
Est thickness @ ARS Target	80°C, 50% RH	µm	15.4	8.2	23.0	11.0



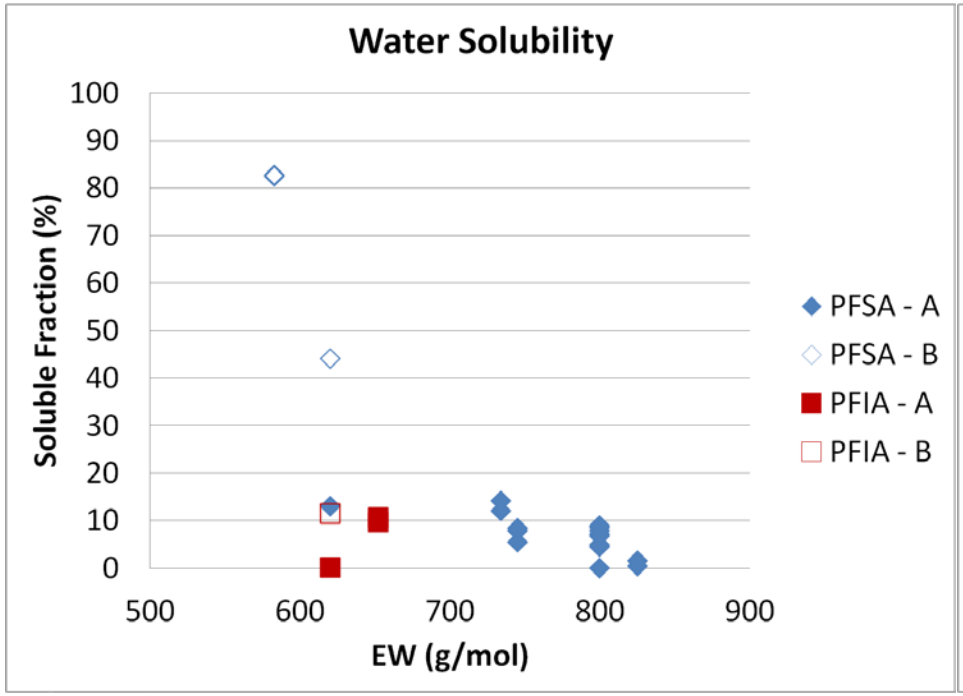
- Unsupported membranes easily meet ASR target at 80 C, 25 kPa H_20 partial pressure
- Supported 725EW PFSA does not meet target
- Supported PFIA marginally meets target

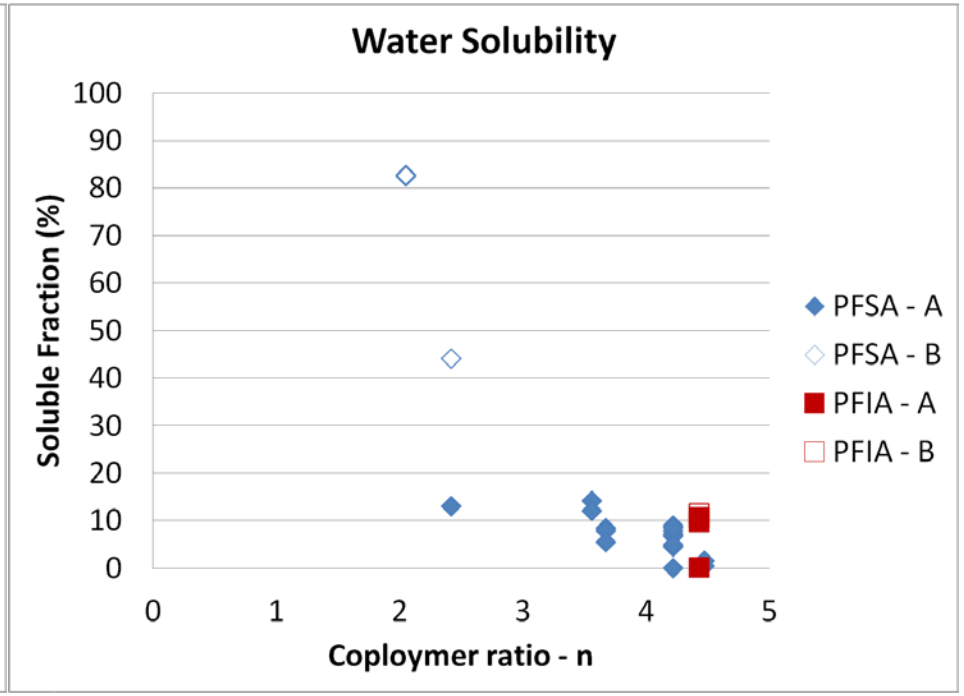
DOE FCTO Multi-Year Research, Development and Demonstration Plan

Thickness boundaries estimated from : C. Gittleman *"Engineering a Proton Exchange Membrane for Automotive Fuel Cell Applications"* Fuel Cell Seminar,Columbus, Ohio,October 24, 2013

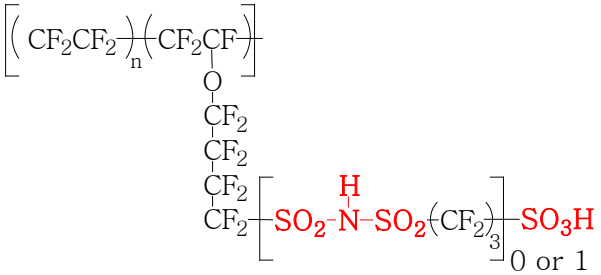
Water Solubility Test

Samples refluxed in Soxhlet extractor for 4 hrs
A and B designate process differences





- Water solubility is a key limiting factor in very low EW PFSAs
- PFIA solubility defined by copolymer ratio not EW



Nanofiber Fabrication Task 2.1

Nanofiber Samples Fabricated in Q1 and Q2					
Coded Sample	Form	Coded polymer	Coded Source	Basis weight (g/m2)	Objective
S1	roll	B1	P1	4.3	Control
S2	roll	B2	P1	3.2	Improved tear strength
S3	roll	B2	P1	4.3	Improved tear strength
S4	test patch	FC3	L2	n/a	Electrospining feasibility
S5	test patch	FC4	L2	n/a	Electrospining feasibility
S6	test patch	FC5	L2	n/a	Electrospining feasibility
S7	test patch	FC6	L2	n/a	Electrospining feasibility
S8	roll	HC3	P1	4.3	Modulus study
S9	roll	FC1	P1	4.3	Modulus study
S10	roll	FC1	P1	4.3	Modulus study
S11	sheet	FC3	L1	5	Improved tear strength
S12	sheet	FC3	L1	5	Improved tear strength
S13	sheet	HC2	V	5.7	Modulus study
S14	sheet	HC2	V	14.2	Modulus study

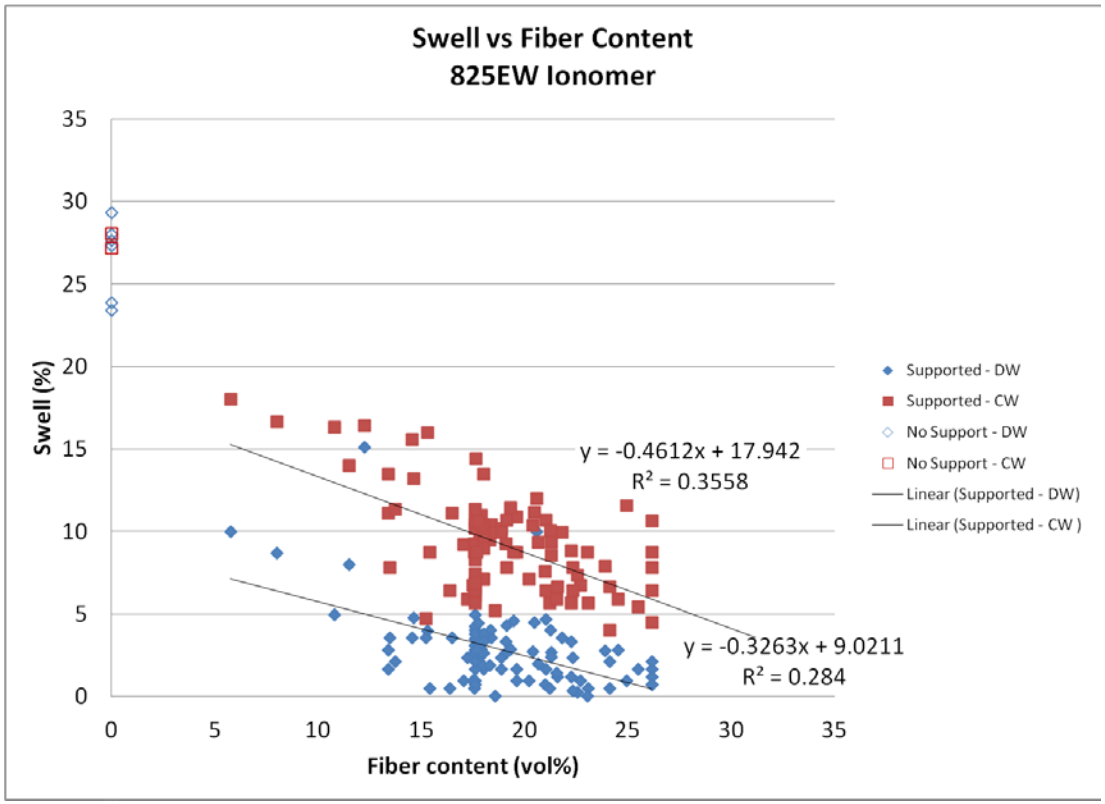
Polymer Codes	
	HC = Hydrocarbon
	FC = Fluorocarbon
	B = Blend

Source Codes	
	L = Lab
	P = Pilot or production line
	V = Vanderbilit

Milestone #2

Identify a support that provides a membrane with x-y swelling of < 5% after boiling in water.

Historical data based on a aromatic polymer/fluoropolymer blend (B1)
Down web and cross web differences need to be addressed

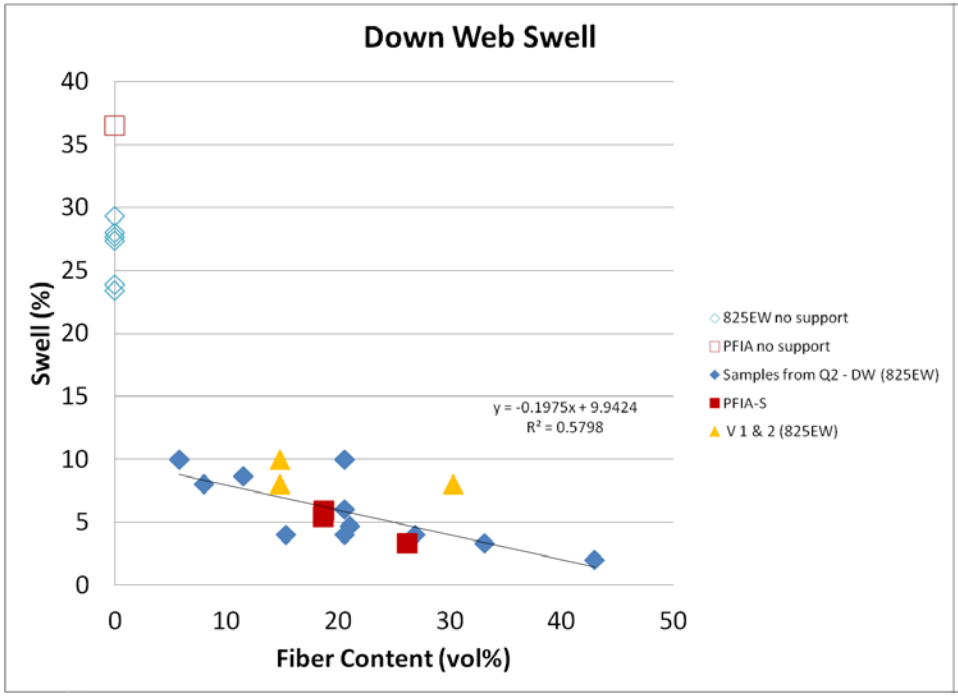


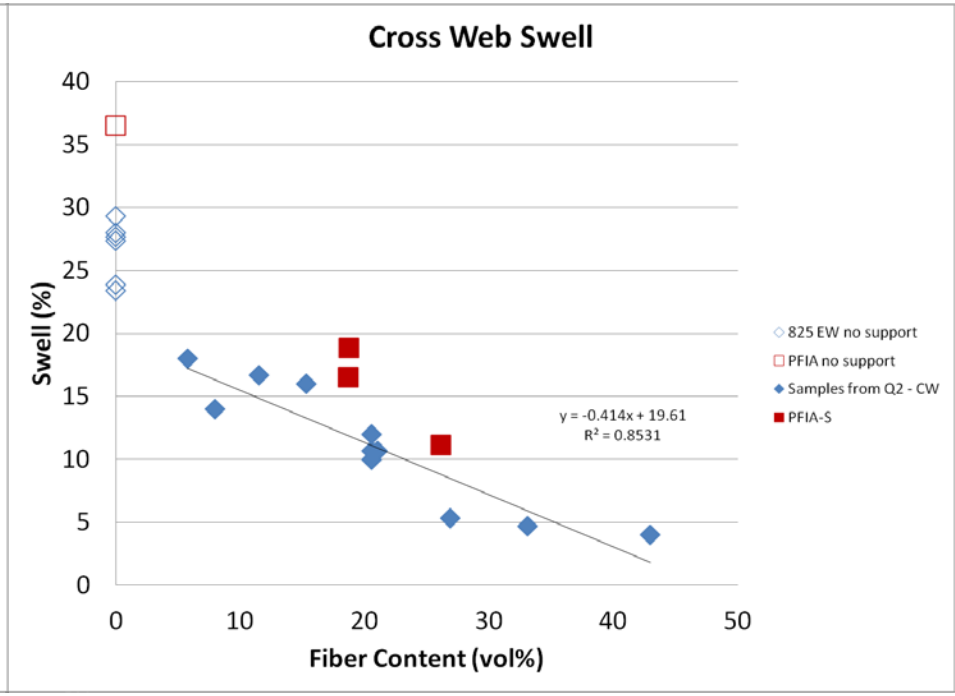
- Down web and cross web swell differences observed
- Less than 5% swell when fiber content is;
  - >12% in the DW direction
  - > 30% in the CW direction

Milestone #2

Identify a support that provides a membrane with x-y swelling of < 5% after boiling in water.

New data based on a aromatic polymer/fluoropolymer blends (B1 & B2) and HC2 from Vanderbilt

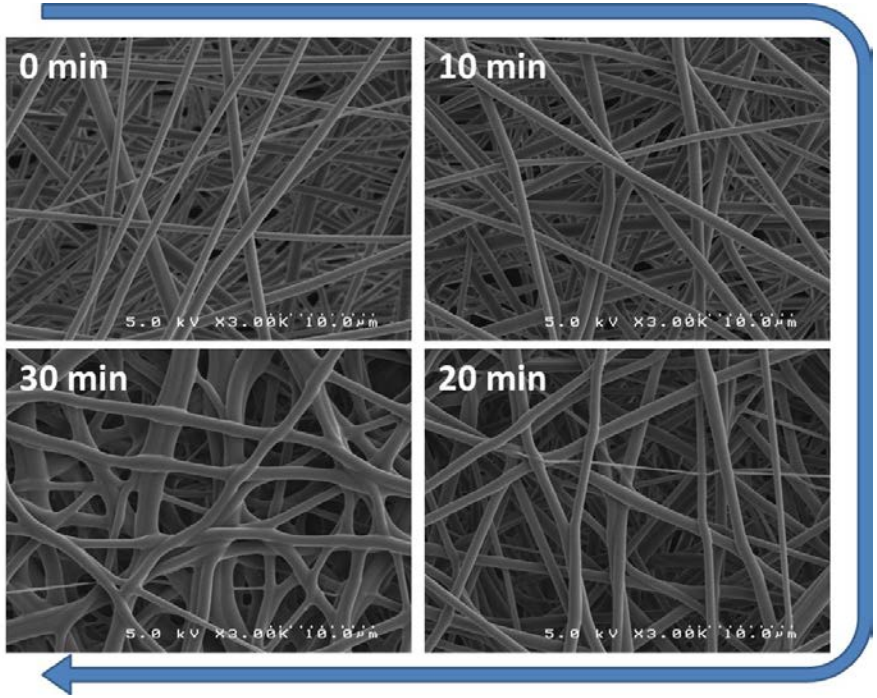




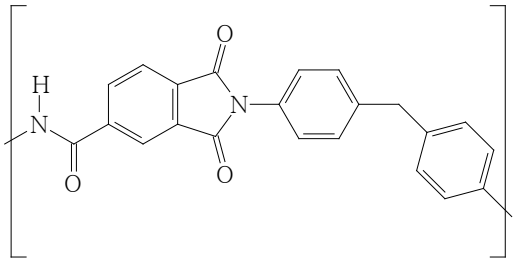
Accomplishments:

- Less than 5% swell in the:
  - down web direction when fiber content is above 12%
  - cross web direction when the fiber content is above 30%
- High swell (low EW) membranes may need higher fiber content (or stiffer supports)

Electrospinning and Welding of Torlon™ – Task 2.1



Interfiber welds start to form between 20-30 minutes of room temperature exposure of the mats to DMAc vapors.



Torlon™ Polyamide imide (PAI)

1) Nanofiber PAI mats were electrospun from DMAc solution
2) Selected mats were exposed to DMAc vapors for 10-60 minutes at RT to weld the fibers at the intersections

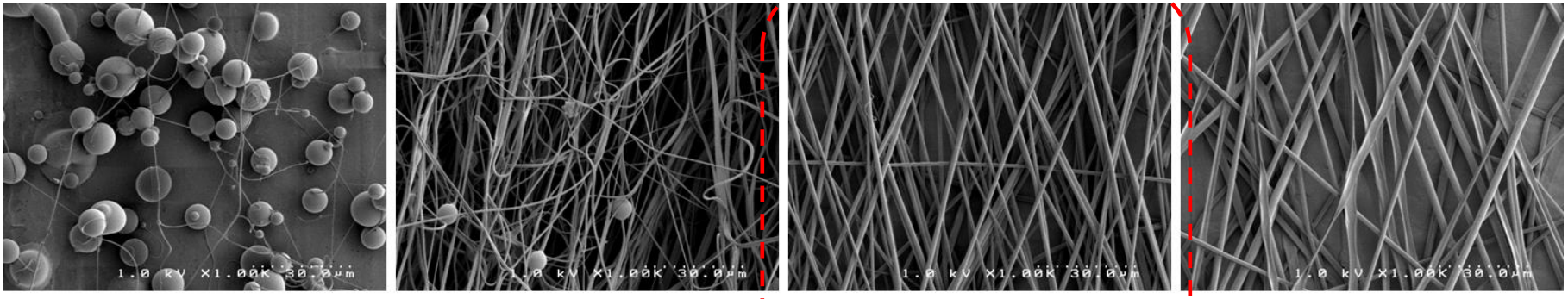
Two Torlon sample mats shipped to 3M for testing:

Mat #1 - 10 cm x 10 cm in area and 25 microns in thickness. Not welded, fiber diameter ~800 nm, pore volume ~80%

Mat #2 - 7 cm x 7 cm in area and 25 microns thick. Welded, fiber diameter~800nm, pore volume ~50%

PFIA Electrospinning – Task 2.2

Great Mat! Fiber diameter 750 nm



0.25wt% PEO | 0.50wt% PEO | 1.00wt% PEO | 4.00wt% PEO

Conclusions:

(1) No fiber formation is possible without the added PEO carrier

(2) The best fiber quality (no beads and uniform fiber diameter) is obtained with 1wt.% PEO (M=400,000). (Milestone #3)

(3) Increasing the accelerating voltage beyond 0.6kV/cm leads to increased fiber orientation and increased bundling.

(4) No significant effect of humidity (25-45%RH) and PEO molecular weight (400,000-600,000) was observed.

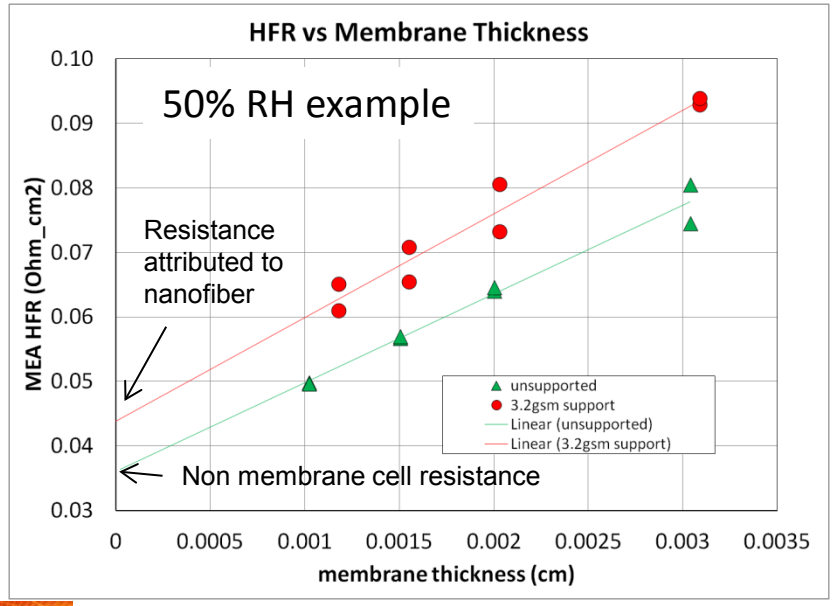
	Electrospun	Solution cast
Proton Conductivity (S/cm)	0.135	0.138

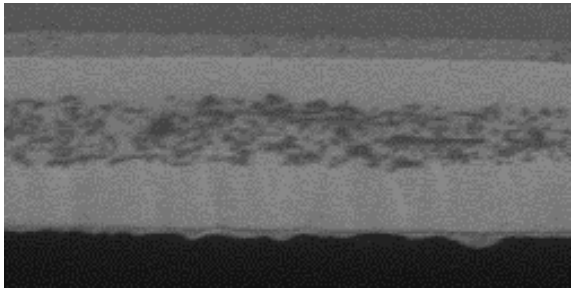
Membrane Characterization Task 3.1

Goal: Decouple ionomer conductivity from composite conductivity

Two Methods:

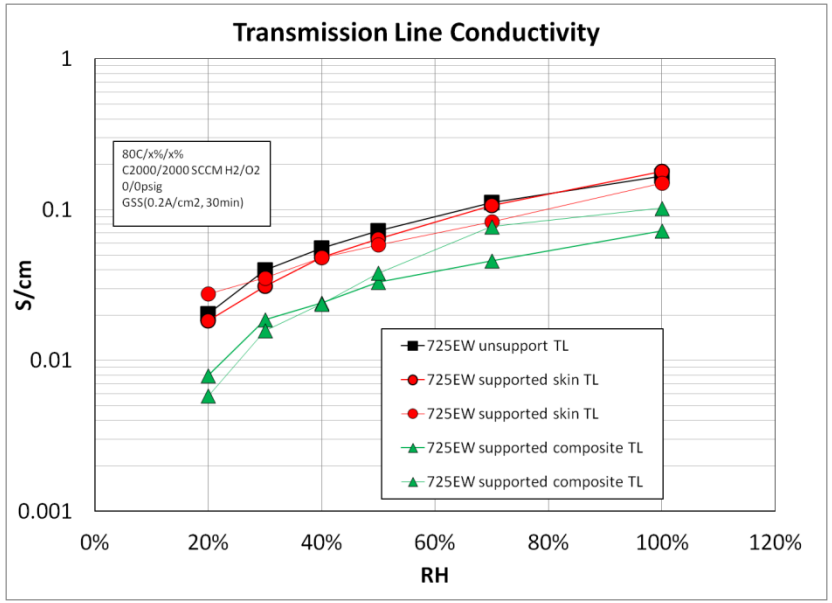
- Transmission line (multiple thicknesses)
  - Ionomer skin resistance derived from slope
  - Composite layer resistance derived from intercept
- Calculation based on SEM thickness measurements
  - Ionomer skin resistance derived from measured thickness and known conductivity
  - Composite layer resistance derived from total resistance minus skin resistance

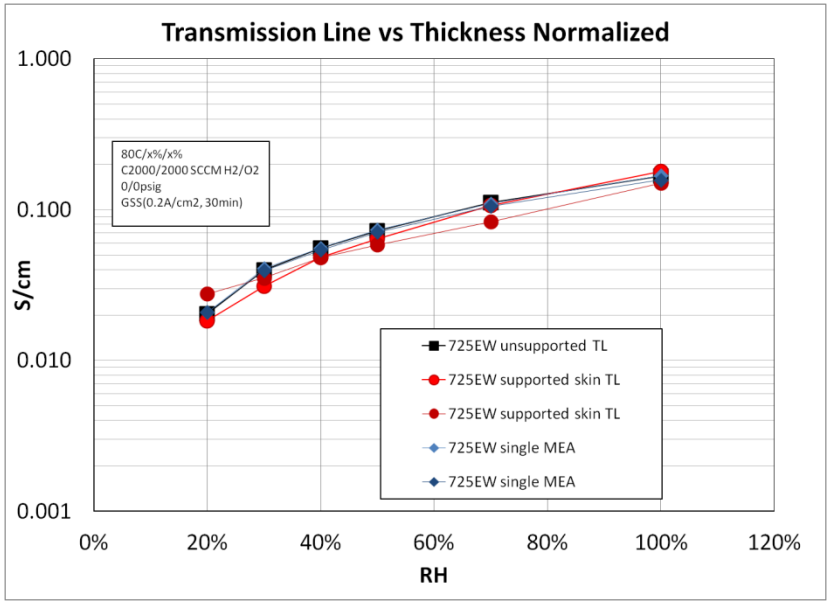




Typical SEM cross section

Membrane Characterization Task 3.1





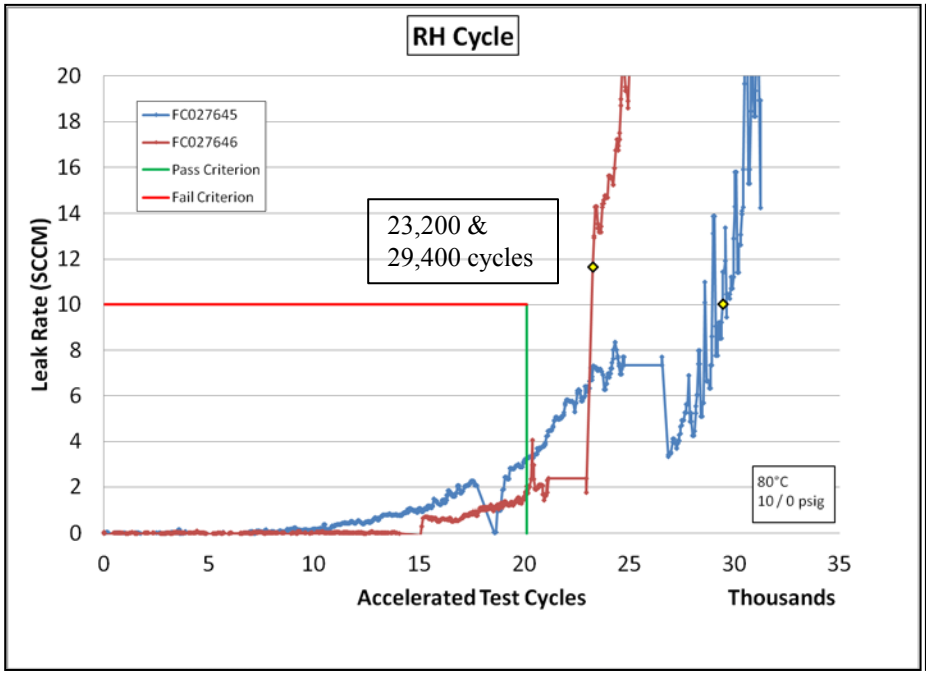
Membrane Conductivity from HFR data (Z-Axis)

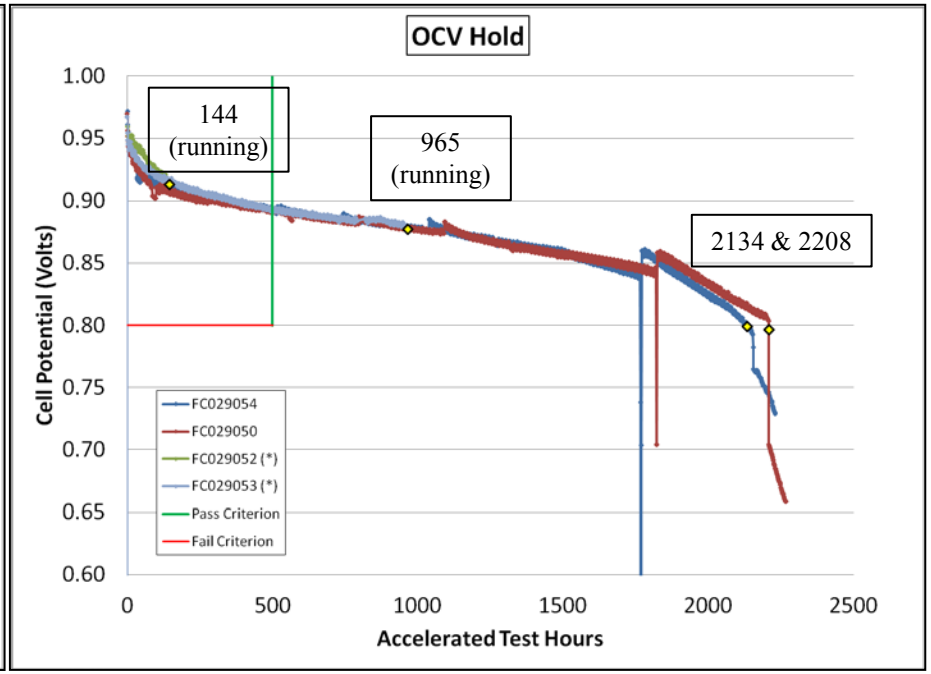
- Values for skin layer and composite layer can be calculated
- Single membrane data agree with transmission line method
- Method established to evaluate conductivity of center composite layer
- Similar analysis underway for hydrogen crossover

Accelerated Durability Test Task 4.3

Milestone # 4 includes passing RH cycle and OCV test

80/20 blend of PFIA and 825EW PFSA supported with nanofiber B1 (4.3gsm)





Test D4 – RH Cycle

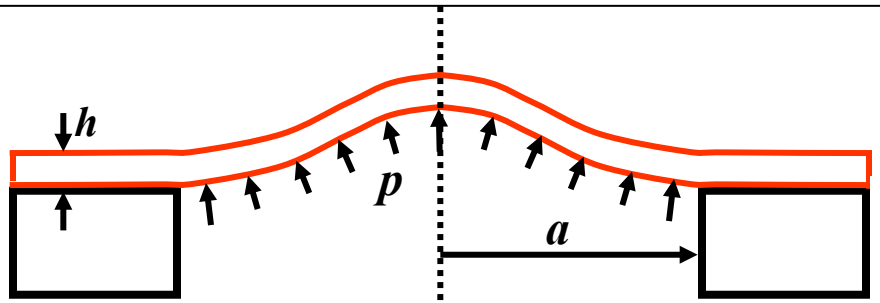
Membrane oriented down web parallel to flow channels (worst case)

Test D3 – OCV

MEA contains stabilizing additives

- Durability targets achieved with supported PFIA membranes

Blister Test – Task 3.2



Schematic of blister testing.

$$\sigma = \frac{1.724}{4}\left(\frac{E(t,T,RH)p^2a^2}{h^2}\right)^{1/3}$$

where

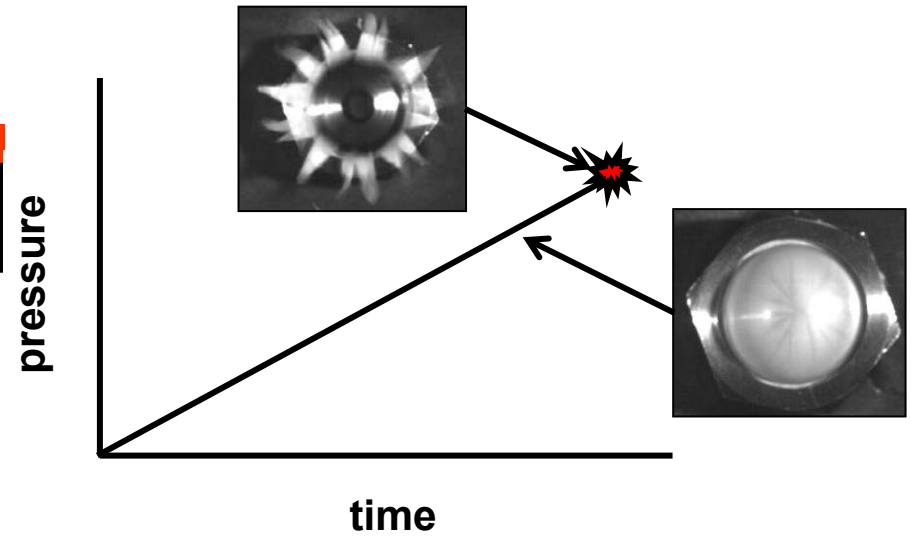
σ is the stress at the center of blister;

E is the relaxation modulus;

p is the applied pressure;

a is the radius; and

h is the thickness of blister.



Burst mode.

- **16 blister samples per test**
- **6 Pressure ramp rates: 1, 0.2, 0.1, 0.05, 0.02, and 0.01 kPa/sec.**
- **Test condition: 90 C, 10%RH**

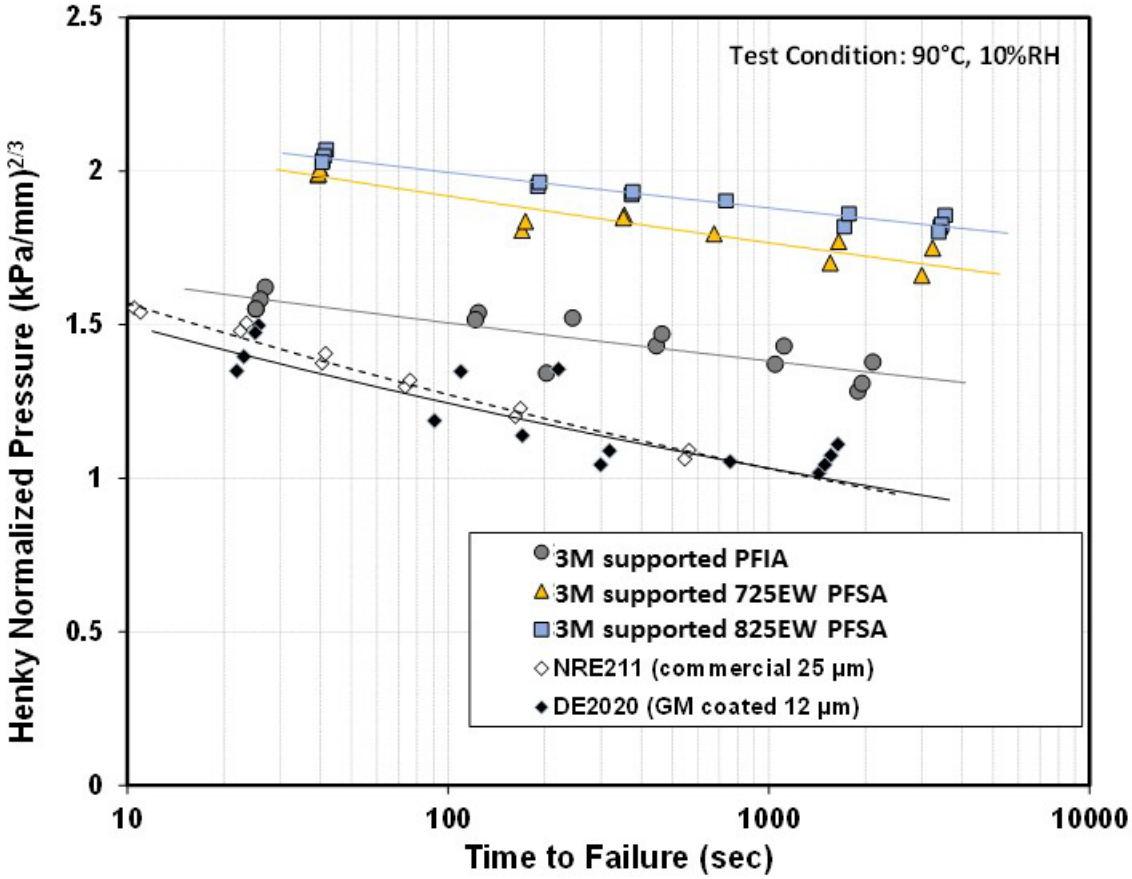
Blister strength

∝ Hencky normalized pressure $(p/h)^{2/3}$

References:

- Li, Y., Grohs, J., Pestrak, M. T., Dillard, D. A., Case, S. W., Ellis, M. W., Lai, Y. H., Gittleman, C. S., and Miller, D. P., "Fatigue and Creep to Leaking Tests of Proton Exchange Membrane Using Pressure-Loaded Blisters", *J. Power Sources,* Vol 194, pp. 873–879, 2009.
- Dillard, D. A., Li, Y., Grohs, J., Case, S. W., Ellis, M. W., Lai, Y. H., Budinski, M. K., and Gittleman, C. S., "On the Use of Pressure-Loaded Blister Tests to Characterize the Strength and Durability of Proton Exchange Membranes". Journal of Fuel Cell Science and Technology, Vol 6 (3), pp. 031014-1 – 031014-8, 2009.

Blister Strength – Task 3.2



- 3M PFSA membranes with reinforcement have higher strength than PFIA membrane.
- 3M 825EW membrane (051223A) is slightly stronger than 725EW membrane (0513277A).
- Unreinforced Nafion® membranes (commercial and GM coated from dispersion) are lower than 3M reinforced PFSA and PFIA membranes.

Summary

Goal: Meet all targets with a single membrane
- Multiacid side chain ionomers (improved performance)
- Nanofiber supported (improved durability)

Characteristic	Units	2017 & 2020 Targets	725 EW (20um)	725EW-S (14um)	PFIA (20um)	PFIA-S (14 um)
Maximum oxygen cross-over[b]	mA / cm²	2				
Maximum hydrogen cross-over[b]	mA / cm²	2	<2		<2	
Area specific proton resistance at:						
120°C and water partial pressures from 40-80 kPa	Ohm cm²	0.02			0.023	
80°C and water partial pressures from 25-45 kPa	Ohm cm²	0.02	0.026	0.034	0.017	0.025
30°C and water partial pressures up to 4 kPa	Ohm cm²	0.03			0.02	
-20°C	Ohm cm²	0.2			0.1	
Minimum electrical resistance	Ohm cm²	1,000				
Cost[c]	$ / m²	20	n/a	n/a	n/a	n/a
Durability[d]						
Mechanical	Cycles with <10 sccm crossover hours	20,000	8,300	>20,000	12,000	26,300
Chemical	hrs	>500				2,170

Future Work

- **Ionomer**
  - **First pilot scale (>5 kg) run of PFIA scheduled for August of 2014.**
  - **PFICE ionomer to be made in small lab batches (2014/2015).**
  - **Additional pilot scale batch planned for 2015.**
- **Nanofiber**
  - **Aromatic and fluorinated polymers to be evaluated for electrospinning feasibility (2014).**
  - **Nanofiber surface treatment evaluations (2014 /2015).**
  - **Dual-fiber electrospinning of PFIA with inert polymer (2014/2015).**
- **Membrane**
  - **Combine new ionomers and nanofiber supports to make improved membrane (mid 2015).**
  - **Compare dual fiber to ionomer filled fabrication methods (2014/2015).**
  - **Chemical and mechanical characterization (2014/2015).**
- **Single Cell Testing**
  - **Performance (2014/2015).**
  - **Accelerated durability (2014/2015/2016).**
- **Stack testing**
  - **Fabrication of final membrane and MEAs (end of 2015).**
  - **Stack testing to start early 2016.**

Technical Back-up Slides

Project Objectives

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).

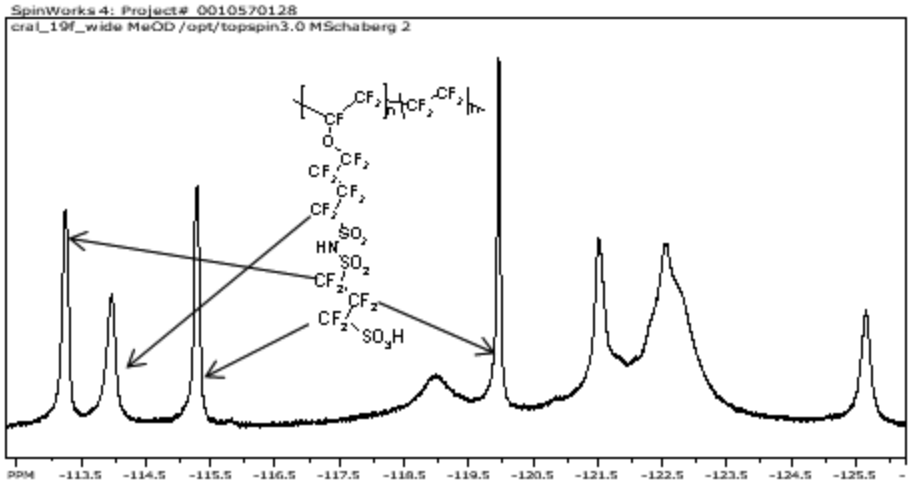
d: http://www.uscar.org/commands/files_download.php?files_id=267Protocol for mechanical stability is to cycle a 25-50 cm^2 MEA at 80°C and ambient pressure between 0% RH (2 min) and 90°C dew point (2 min) with air flow of 2 SLPM on both sides. Protocol for chemical stability test is to hold a 25-50 cm^2 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

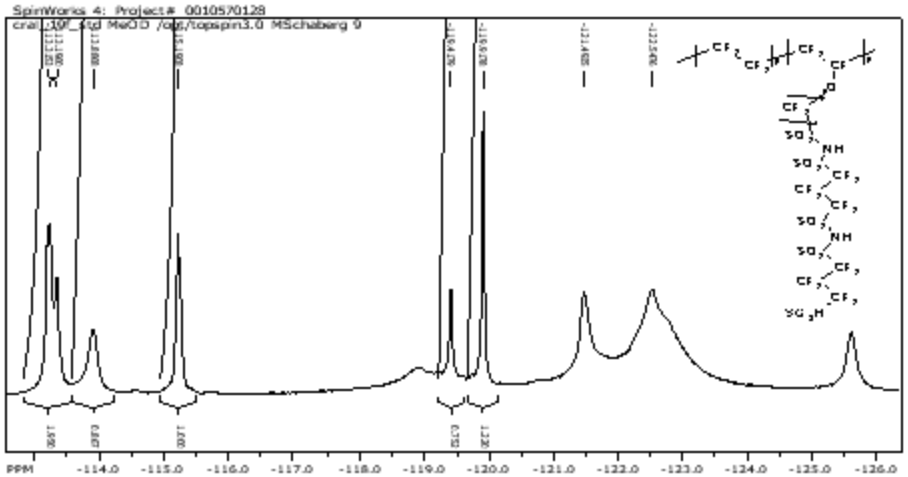
Table 1. Project Milestones and Timing	
Milestone ID	**Milestone**
1	Measure conductivity and fuel cell performance on at least two different control PFSA membranes and initial samples of MASC ionomer membranes. Demonstrate MASC ionomer with conductivity of 0.1 S/cm or higher at 80°C and <50% RH.
2	Identify 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.
3	Develop electrospinning conditions for one or more 3M ionomers that provides fiber diameter of <1 micron.
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).
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.
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.
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.
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.
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)
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.
11	Begin post mortem analysis of MEAs to determine failure mode.
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.

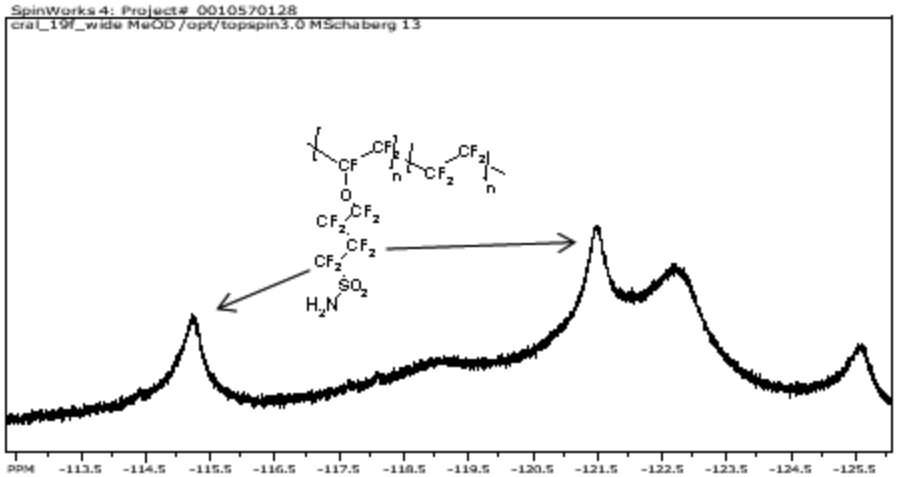
Ionomer Development Task 1

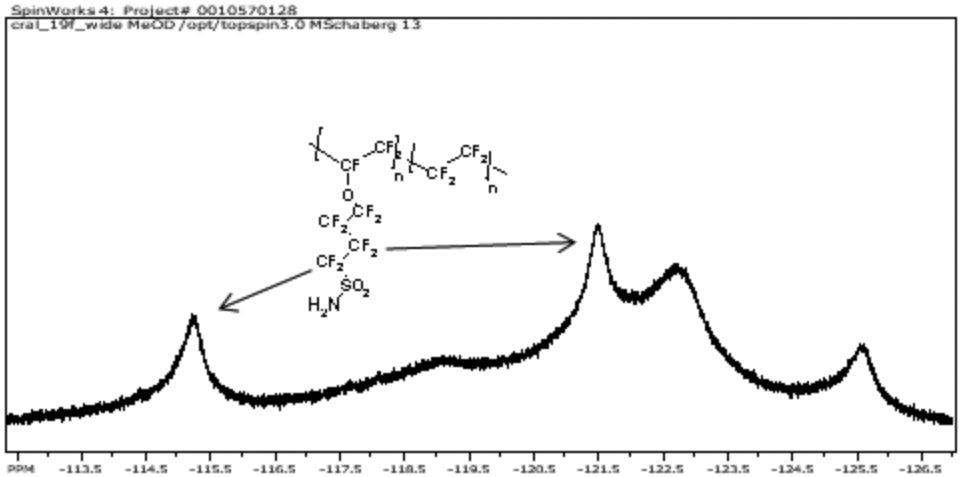
PFIA



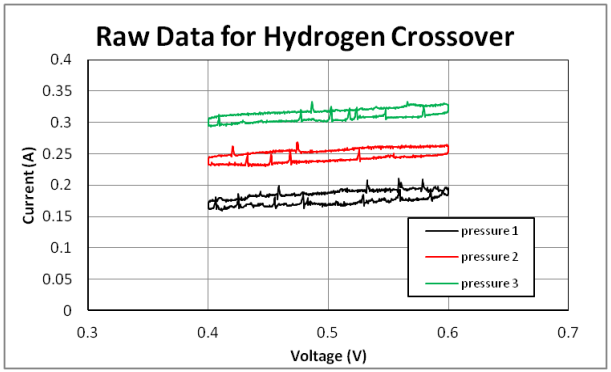
PFICE

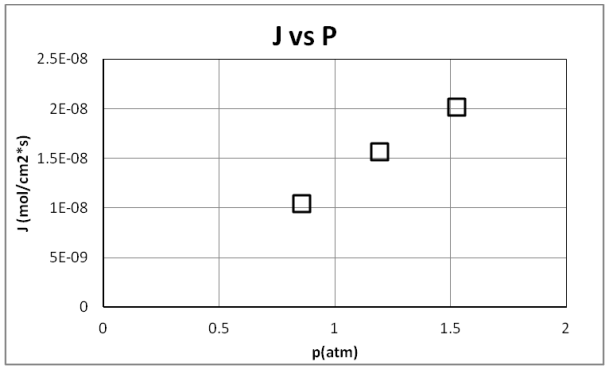


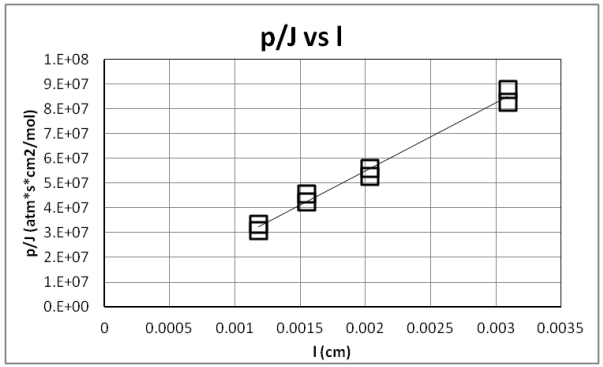




Diffusive Hydrogen Crossover Analysis



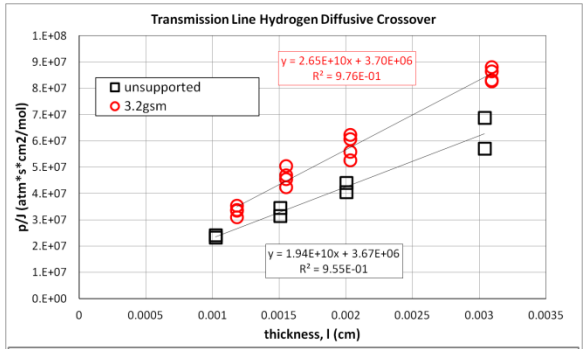


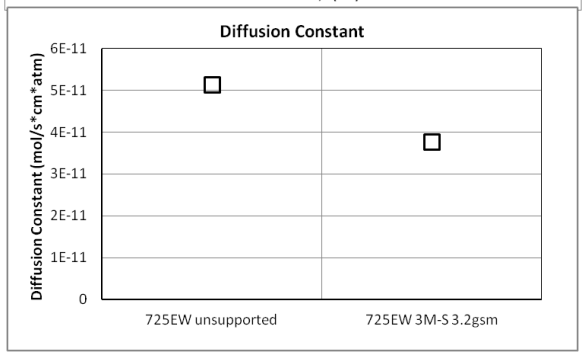


Measure crossover current density as a function of anode hydrogen partial pressure

Plot flux versus hydrogen partial pressure. The inverse of the slope of this linear relationship (p/J) has the units **atm*s*cm²/ moles**,

Plot p/J versus membrane thickness. The inverse of the slope of this linear relationship is the diffusion constant (**moles/ atm*cm*s)**

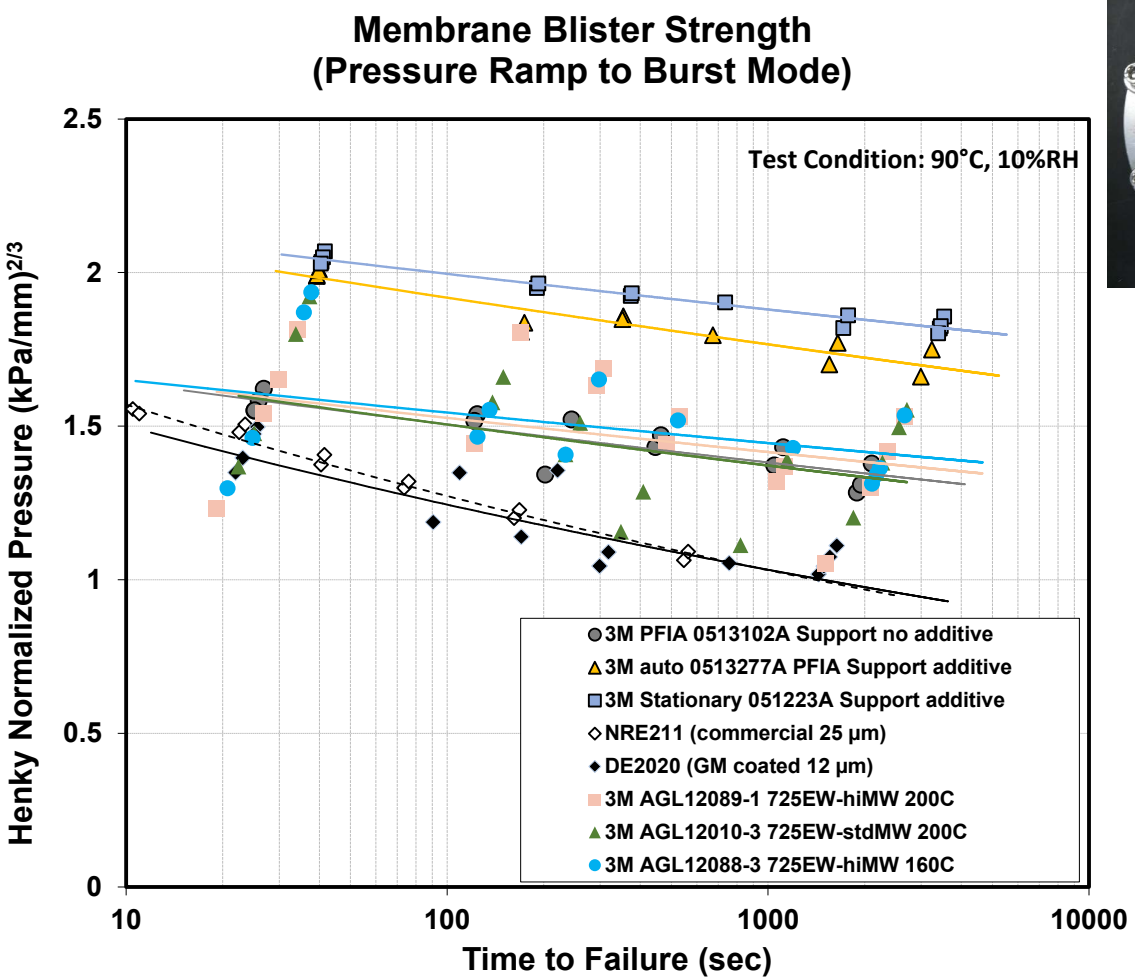




- The plot of p/J versus thickness for 725EW PFSA with and without support show differing slopes. This is an unexpected observation since the it is the same material responsible for the increasing thickness in both construction, namely additional 725EW PFSA ionomer.

- From Fick's Law:
  - J = D * (p/l)
    - J is flux (mol/s*cm2) = i / n*F
  - i = crossover current density (A/cm2)
  - n =2 electrons per molecule H_2
  - F is Faraday's constant
    - p is the anode H2 partial pressure over pressure (atm)
    - l is the membrane thickness (cm)
    - D is the "Diffusion Constant" (mol/s*cm*atm) <- value of interest

Blister Strength



- 3M PFSA membranes with reinforcement have higher strength than PFIA membrane.
- 3M 825EW membrane (051223A) is slightly stronger than 725EW membrane (0513277A).
- 3M un-supported membranes have similar strength as the supported PFIA membrane.
- 3M support significantly increases the membrane strength.
- Nafion® membranes (commercial and GM coated from dispersion) have lower strength than 3M un-supported 725EW membranes.