New Fuel Cell Membranes with Improved Durability and Performance

> Mike Yandrasits 3M Energy Components Program

June 7th, 2016



FC109

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

Overview

Timeline

- Start October 1st, 2013
- End December 31th, 2016
- 77% complete

Budget

- Total Project funding \$4.2 million
 - \$3.1 million DOE
 - \$1.1 million contractor cost share (26%)
- Funding in FY 2014 FY2015
 - \$1,676,000
- Funding in FY 2016
 - \$450,778 (Through Feb. 2016)

Barriers

Durability

Performance

Cost

Partners

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

General Motors C. Gittleman

Vanderbilt University Professor P. Pintauro



Project Relevance & Project Approach/Collaborations

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 <u>simultaneously</u> with a single membrane.



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Milestone Summary

Milestone	Requirement	Date Completed	Passed
7	Durability & ASR	Jun, '15	\checkmark
8 Go/No Go	Durability, ASR, short res. $H_2 \& O_2$ crossover, & cost	Oct, '15	\checkmark
9	Produce membrane for stack testing (> 20 meters)	March. '16	\checkmark
10	Begin Stack Testing	June, '16	
11	Begin Post Mortem analysis	Sept. '16	
12	Deliver MEAs to DOE, Complete 2,000hrs stack testing	Dec. '16	

Full Milestone List in Technical Back-Up Slides

3M ID	Milestone	lonomer	Fiber type	Additive	Fiber (vol%)	Thickness (um)
0513277A	Control	3M 725EW	B1	Туре А	20.6	14
0514218A	#4	PFIA – Lot#1	FC1	Туре А	17.2	14
0515079D	#8	PFIA – Lot #1	FC1	Туре А	18.0	10



DOE Targets

			Control	MS#4		
		2017 &	(0513277A)	(0514218A)		
		2020	725EW-S	PFIA-S		
Characteristic	Units	Targets	(14um)	(14 um)		
Maximum oxygen cross-over	mA / cm ²	2	<0.5ª	<0.5ª		
Maximum hydrogen cross-over	mA / cm ²	2	1.1 ^b	1.1 ^b		
Area specific proton resistance at:					Statu	us at
120°C, P _{H2O} 40 kPa	Ohm cm ²	0.02	0.147°	0.069°	2015	AMR
120°C P _{H2O} 80 kPa	Ohm cm ²	0.02	0.029	0.027		
80°C P _{H2O} 25 kPa	Ohm cm ²	0.02	0.038	0.028		
80°C P _{н20} 45 kPa	Ohm cm ²	0.02	0.014	0.015		
30°C P _{H2O} up to 4 kPa	Ohm cm ²	0.03	0.027	0.030		
-20°C	Ohm cm ²	0.2				
Minimum electrical resistance	Ohm cm ²	1,000	5,600 ^d	5,700 ^d		
Cost	\$ / m ²	20	n/a	n/a		
Durability						
Mechanical	Cycles with					
	<10 sccm	20,000	>20,000	>23,000		
	crossover					
	hra	. 500	004	740		
Cnemical	nis	>500	094	/42		

Original Table 3.4.12 from the Fuel Cell Technologies Office Multi-Year RD&D Plan is in the Technical Back-Up Slides

- a. In cell measurements at 0.5V.
- b. In cell measurements at 3M 70°C, 100% RH, 1 atm.
- c. Calculated from in-plan data



d. Data provided by GM

Milestone 8: Hydrogen Crossover and Short Resistance

MS#8 0515079D

MS#7 0515079C



- Hydrogen crossover is measured at two different backpressures and extrapolated to 0 psig (101 Kpa) for reporting.
- Values of less than 2 mA/cm² determined for MS#8 membrane.
- Short Resistance is highly dependent on gas diffusion layer (GDL) or catalyst coated backing (CCB).
- Short data shown for MS#7 membrane (14um), full survey of GDLs was not completed for MS#8 membrane but results are expected to be similar.
- Values from GM were used for meeting milestone target of 1,000 Ohm*cm²

Milestone 8: O₂ Crossover



Condition	P ₀₂	mA/cm ²
80°C, 100% RH, 1 atm O ₂ only	1.00	6.50
80°C, 100% RH, 1 atm O_2 and water	0.53	3.45
80°C, 100% RH, 1 atm air and water	0.11	0.72

$$\frac{A}{cm^2} = D(mol * cm * s^{-1} * cm^{-2} * kPa^{-1}) * PO_2(kPa) * F(C * mol^{-1}) * 4e^{-1} * t(cm^{-1})$$

- Original data reported for 3M in-cell measurements at 0.5V (per DOE Table 3.4.12).
- More accurate diffusion measurements at GM and in-cell measurements at 3M show higher crossover at O₂ partial pressure of 1 atm.

Milestone 8: Resistance Data at 80° and 120°C

MS#8 Membrane ID 0515079D



- Both in-plane (x-y) and through-plane (z) measurements are in good agrement.
- The milestone #8 membrane meets the resistance target of 20mOhm*cm²:
 - At 80°C for all humilities.
 - At 120°C only for the highest humidity.

Milestone #8: 120°C, 40KPa

Critical Question: What ionomer EW is needed for a 10 micron or thicker membrane supported with 20 vol% fiber and ~5% iec consumed by additive cation?



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Estimates for ionomer EW based on	
previous data:	

	Membrane Apparent	Estimated
Thickness (um)	EW	Ionomer EW
10	597	454
12	522	397
14	448	340

- Ionomer EWs lower than 450 g/mol are required to meet DOE ASR target at 120°C and 40kPa P_{H2O}
- 3M's PFICE approach might be possible.
- Lowest PFICE EW synthesized is 397 g/mol (PFICE-4)
- Quantities of PFICE-4 lonomer insufficient for fabricating supported membranes.
- Multiple attempts to make PFICE-3
 have fallen short of EW target

PFICE-3	Starting Backbone	Titrated EW
attempt	EW	(g/mol)
1	700	475
2	800	622
3	800	535
4	800	TDB

Milestone #8: RH Cycle

Membrane: 0515079D



- Two cells pass 20,000 mark, one showed leak starting early in life (only when measured in the dry state).
- Cell from original set tested after more than 60,000 cycles with no increase in H₂ crossover.
- Additional beginning of life cells made and tested for H₂ crossover.

OCV Accelerated Durability



- Lifetimes exceed 500hrs and are similar to control when tested at same additive level and same electrodes.
- Membranes made with PFIA show OCV decay within first 200 hrs followed by a plateau.
- Initial decay is reversible when cell is removed from durability station and subjected to start-up protocol.
- C-S bond strength is estimated to be similar for PFSA or PFIA ionomers, however, PFIA has three C-S bonds per side chain which may allow new small molecule fragments to form during oxidative decomposition.





Bond strengths in kcal/mol estimated using DFT calculations with 6-31G* data set.

OCV Accelerated Durability



12

Milestone #8 Performance



- Milestone # 8 membrane (0515079D) performance slightly better than control at humidified condition.
- Milestone #8 membrane has 50 mV higher performance at 1.5 A/cm² compared to 3M725 control when run at 95°C, 50% RH.
- Humidity sensitivity tests show about 100 mV higher performance at 1.5 A/cm² compared to 3M 725EW at the lowest RH (20%).





Milestone 8: 3M ID 0515079D

			MS#8
		2017 & 2020	PFIA-S
Characteristic	Units	Targets	(10 um)
Maximum oxygen cross-over	mA / cm ²	2	0.6 ^a , 6.5 ^b
Maximum hydrogen cross-over	mA / cm ²	2	1.9 ^c
Area specific proton resistance at:			
120°C, P _{H2O} 40 kPa	Ohm cm ²	0.02	0.054
120°C P _{H2O} 80 kPa	Ohm cm ²	0.02	0.019
80°C P _{H2O} 25 kPa	Ohm cm ²	0.02	0.020
80°С Р _{н20} 45 кРа	Ohm cm ²	0.02	0.008
30°C P _{H2O} up to 4 kPa	Ohm cm ²	0.03	0.018
-20°C	Ohm cm ²	0.2	0.2 ^d
Minimum electrical resistance	Ohm cm ²	1,000	1,635 ^e
Cost	\$ / m ²	20	Not available
Durability			
Mechanical	Cycles with <10 sccm		>24.000
	crossover	20,000	>24,000
Chemical	hrs	>500	614

a. O₂ 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 O_2 .
- c. In cell measurements at 3M 70°C, 100% RH, 1 atm.
- d. Calculated from in-plan data



e. Data provided by GM

Technology Transfer

PFIA Pilot Scale

Lot Number	Date	Titrated EW	Program
1	January 2015	660	DOE
2	December 2015	652	3M
3 and 4	March 2016	TDB	3M
5	July 2016		3М
6	December 2016		3M



- Four pilot scale batches complete, two additional runs planned for 2016.
- Equivalent weights are approximately 30 g/mol higher than lab made



Task 4: Membrane Composition Study





3M ionomer filled support

VU 3 layer, dual fiber, electrospun

VU 1 layer, dual fiber, electrospun

- 3M's traditional ionomer filled membrane was compared to VU's dual fiber spinning technique.
- All three membranes used 825EW ionomer and about 20% fiber content by volume.
- For this case, performance appears to be related to total fiber content independent of fiber location.





Task 2: Fiber Diameter Studies



12.5 wt% PVDF, Spin rate 0.15 mL/hr Fiber Dia: 600 +/- 200 nm



17.5 wt% PVDF, Spin rate 0.85 mL/hr Fiber Dia: 2,200 +/- 500 nm

% PFIA	Fiber Diameter [nm]	In-Plane Conductivity [S/cm]	Gravimetric Swell [%]	Lateral Swell [%]	Tensile Strength [MPa]
75	600	0.104	54	14.2	8.6
75	1000	0.101	55	7.9	10.4

PFIA/PVDF composite membranes (75wt% PFIA) were fabricated with greater than usual PVDF fiber diameter (2.2 μ m instead of 0.6 μ m). Minimal drop of conductivity was observed but lateral swelling decreased from 14.2% to 7.9% while tensile strength increased from 8,6 to 10.4 MPa. Very interesting result!

Task 2: Membrane/Fiber Composition



Gravimetric and dimensional (in-plane) swelling of room temperature water-equilibrated membranes was determined for both, the single- and dual-fiber membranes. Below 70 wt% PVDF, conductivity was somewhat lower than predicted based on the mixture law.

Gravimetric swelling of single-fiber membranes was significantly lower than that of dual-fiber membranes (e.g. 40% vs. 60% at 80 wt% PFIA).

On the contrary, dual-fiber membranes had somewhat lower lateral-swelling (below 80 wt% PFIA).

Task 3: Peroxide Vapor Chemical Stability





- Both membrane types show stabilization benefit of additive
- 3M825 PFSA is consistently more robust than analogous PFIA variants
- The FRR profile suggests that the two classes respond somewhat differently
 - Additive apparently suppresses scission in 3M825
 - Some scission does occur in PFIA with and w/o additive
 - Other bonds may be susceptible to peroxide attack
- Membranes to be characterized by FTIR analysis to see which bonds may be breaking





Task 3: Blister Strength vs "Hygral" Stress



- Stress and strength are calculated using quasi-elastic approximation*
 - > Blister strength $\sigma_r(t_f) = \sigma_{\theta}(t_f) = \frac{B_0}{4} \left(\frac{E(t_f)p^2 a^2}{h^2} \right)^{\frac{1}{3}}$

Stress

 $\sigma_{\Delta\lambda}(t_{\Delta\lambda}) = E(t_{\Delta\lambda})\beta\Delta\lambda$

Where β = coefficient of hygral expansion E is the relaxation modulus;

p is the applied pressure;

a is the radius; and

h is the thickness of blister.

RH cycling conditions $\Delta \lambda$ =12 (100% to 0%RH) $t_{\Delta \lambda}$ = 120 sec

*Li, et al., "Fatigue and Creep to Leaking Tests of Proton Exchange Membrane Using Pressure-Loaded Blisters", *J. Power Sources*, Vol 194, pp. 873–879, 2009.

- After adjusting for modulus and swelling, the time to failure for mechanical durability in DOE RH cycling AST ranking is projected to be
 - PFIA/FC1 > PFSA/FC1 > PFIA/ePTFE > PFSA/ePTFE



Task 5: Stack Test Plan

- Rainbow Stack built using GM full active area automotive hardware
- 0.125 total mgPt/cm²
- 4-5 cells of each of the following types



- Beginning of life performance completed in April.
- Stack running GM accelerated durability test projected to be 4X acceleration for membrane life compared to typical automotive drive cycle.
- 2000h planned by Sept 2016.





Future Work

- Remainder of 2016
 - Ionomer development
 - Investigate PFIA oxidative stability both in and out of cell tests (Q2,3, and4)
 - Convert PFIA lots 3 and 4 into membrane for evaluation (Q2)
 - Initiate PFIA lot 5 (Q2)
 - Nanofiber development
 - Study effect of fiber diameter on strength (Q2 and 3)
 - Obtain lower basis weight samples of HC4 fiber for further development (Q3)
 - Stack Testing (Milestone #10)
 - Initiate Stack Testing at GM (Q2)
 - Stack test completed Target run time 2,000 hrs (Q3)
 - Postmortem analysis (Milestone #11)
 - Initiate post mortem analysis on stack cells (Q3)
 - Provide MEAs to DOE test site (Milestone #12)
 - Size and number to be determined (Q4)



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	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 [°]	\$ / m ^²	-	20	20		
Durability [®] 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 or H at nominal stack operating temperature, humidified gases at 0.5 V DC.						
d: <u>http://www.uscar.org/commands/files_download.php?files_id=267</u> Protocol 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 /air stoichs of 10/10 at 0.2 A/cm ² equivalent						
Team Cell Component Accelerated Stress Test and Pola 3) and Membrane Mechanical Cycle and Metrics (Table	rization Curve Protoc (24).	cols (), MEA Chemical	Stability and N	Aetrics (Table		

Blister Test Background





- 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.





- 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



Peroxide Vapor Cell Background:

Chemical Degradation Mechanisms

- Hydroxyl radical (·OH) is the only species capable of abstracting hydrogen atoms at a kinetically significant rate
 F. D. Coms, ECS Transactions, 16
- The unzipping rate is given by:

F. D. Coms, *ECS Transactions*, 16 (2), 235-255 (2008).

f(T, RH)

Unzipping rate = $k_{R_f CO_2 H} [R_f CO_2 H] [\cdot OH]$



Unzipping: [R_fCO₂H] constant Degradation Rate Constant **Dominates at Wet Conditions**



Scission: [R_fCO₂H] increases Degradation rate increases **Plays a Role at Dry Conditions**

- GM developed a Peroxide Vapor flow cell test to probe the degradation mechanism and rate of PFSA membranes
- Temperature, RH and H₂O₂ content of the vapor stream can be readily adjusted to provide a range of reaction conditions



Milestone 8: O₂ Crossover

 $\frac{A}{cm^2} = D(mol * cm * s^{-1} * cm^{-2} * kPa^{-1}) * PO_2(kPa) * F(C * mol^{-1}) * 4e^{-} * t(cm^{-1})$





New Ionomers – Task 1



PFICE (Perfluoro Ionene Chain Extended)

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Approach

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.	July 1, 2015
8 - Go/No- Go	Produce membrane comprising a MASC lonomer, 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.	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)	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

