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Advanced Hybrid Membranes for Next Generation PEMFC Automotive Applications

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FC110

Overview

Timeline

- Project start date: 10/1/13
- Project end date: 9/30/16
- Percent complete: 58%

Budget

- Total Funding Spent as of 3/31/15: $814,366
- Total Project Value: $1,875,300
- Cost Share Percentage: 20%

Barriers

Barrier	2017 Target
A - Durability	Chemical: > 500 hours Mechanical: 20,000 cycles
B - Cost	$\$20/m^2$
C - Performance	ASR ≤ 0.02 Ωcm^2 max operating temp ≤120ºC and 40-80 kPa $P(H_2O)$

Partners

- Colorado School of Mines
- Nissan USA (sub-contractor)
- National Renewable Energy Laboratory
- 3M (in-kind partner)

Relevance

Overall	Demonstrate a low cost hybrid inorganic/polymer from super-acidic inorganic functionalized monomers with: • ASR < 0.02 Ω cm^2 at operating temperature of an automotive fuel cell stack (95-120ºC) at low inlet RH <50% • 50 cm^2 MEA with desired mechanical properties and durability
2014	• Optimize three different candidate hybrid inorganic/polymers in practical systems for low ASR, then eliminate one system • Barrier C
2015	• Optimize two best candidate systems for low ASR, mechanical properties, oxidative stability/durability, and incorporation of electrodes, then eliminate lowest performing system • Barrier A and C
2016	• Incorporate best hybrid polymer system into MEA, deliver 50 cm^2 MEA to DOE with all desired properties for third party testing • Barrier A, B, and C

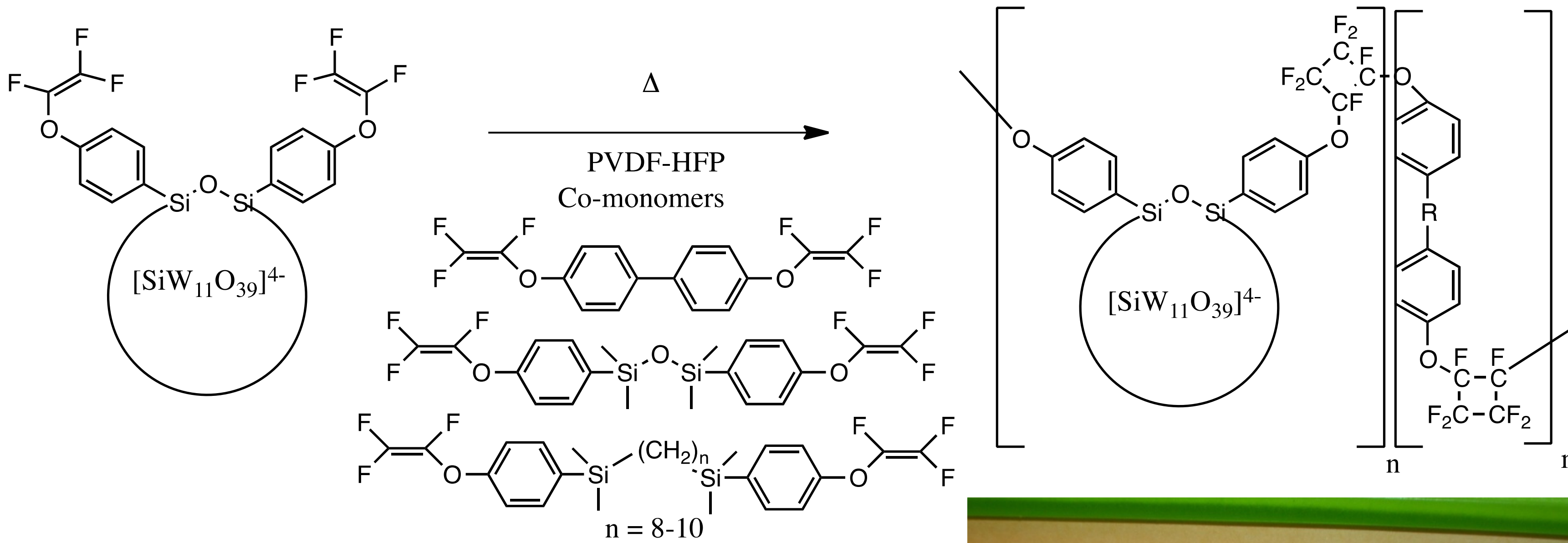
Approach

- Material Synthesis based on functionalized super acidic inorganic moieties, ***Generation II Films (Chemically stable)***
  - Heteropoly acid (HPA) functionalized monomer polymer system
  - FC-2178 functionalized with HPA
  - Zirconyl phosphonate/vinyl phosphonic acid polymers (De-selected, water soluble)
- All systems have tunable properties, either co-monomers for desired mechanical properties, or base polymers with desired mechanical properties.
- Pt/HPA functionalized carbons available for incorporation into electrodes for MEA fabrication
- National lab and Industry partners for scale up and MEA fabrication and testing

FY 2015 Milestones

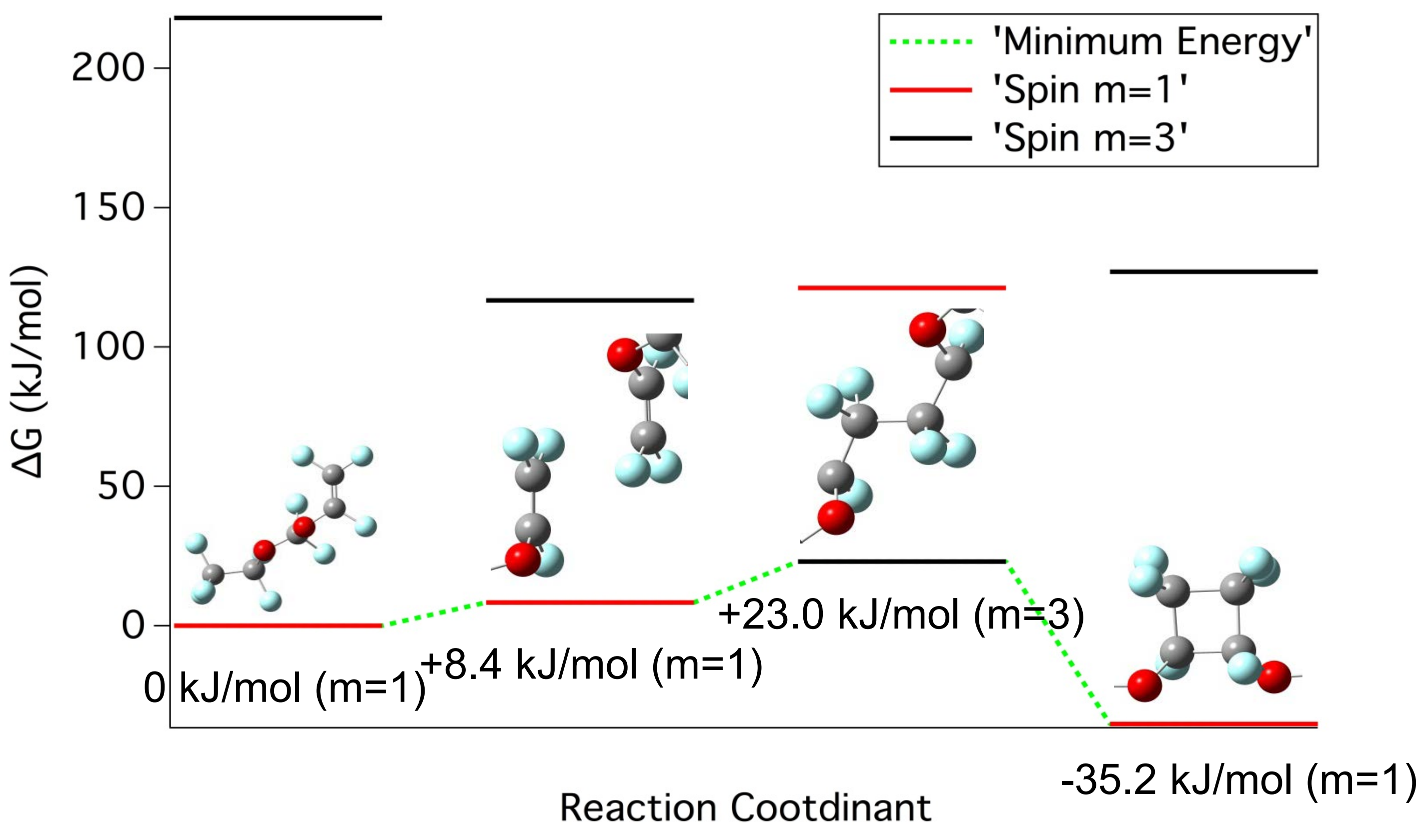
Milestone	Description	% Complete
Year 2 – Q1	Achieve an ASR of ≤0.02 Ω cm2 at 45 kPa and 80° C for the two remaining hybrid systems. This represents a RH of 95% at 80° C.	50
Year 2 – Q2	Demonstrate electrical resistivity of 1000 Ω cm2 for the two remaining hybrid systems.	100
Year 2 – Q3	The electrode system for both hybrid membranes will be optimized. Micro-porous micro-electrode studies will be concluded and the optimized catalyst moved to sub-scale MEAs	50
Year 2 – Q4 Go/No Go	Achieve an ASR of ≤0.02 Ω cm^2 at 80 kPa and 110° C. This is a more aggressive proton conductivity designed as an intermediate step to the project goal. Eliminate one of remaining two polymer systems based on lowest achievable ASR at 80 kPa and 110° C.	10

System I – TFVE - Polymerization



Simply heating this system,
even using defined steps up to high
temperatures led to poor brittle materials

TFVE Reaction Mechanism

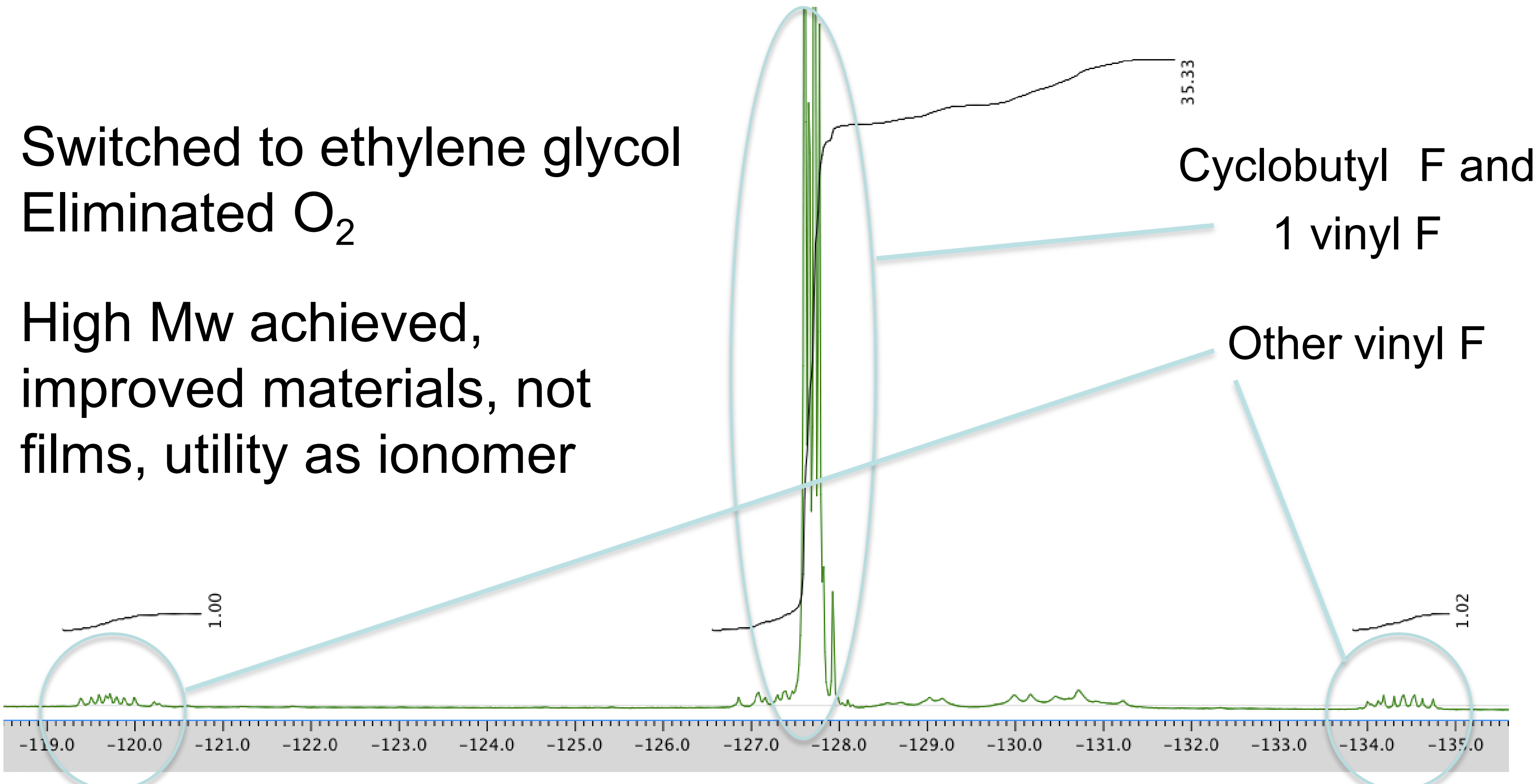


- Computational study shows rotation is likely part of cycloaddition reaction
- Need solvent to minimize viscosity and allow reaction to proceed

TFVE System - ^{19}F NMR

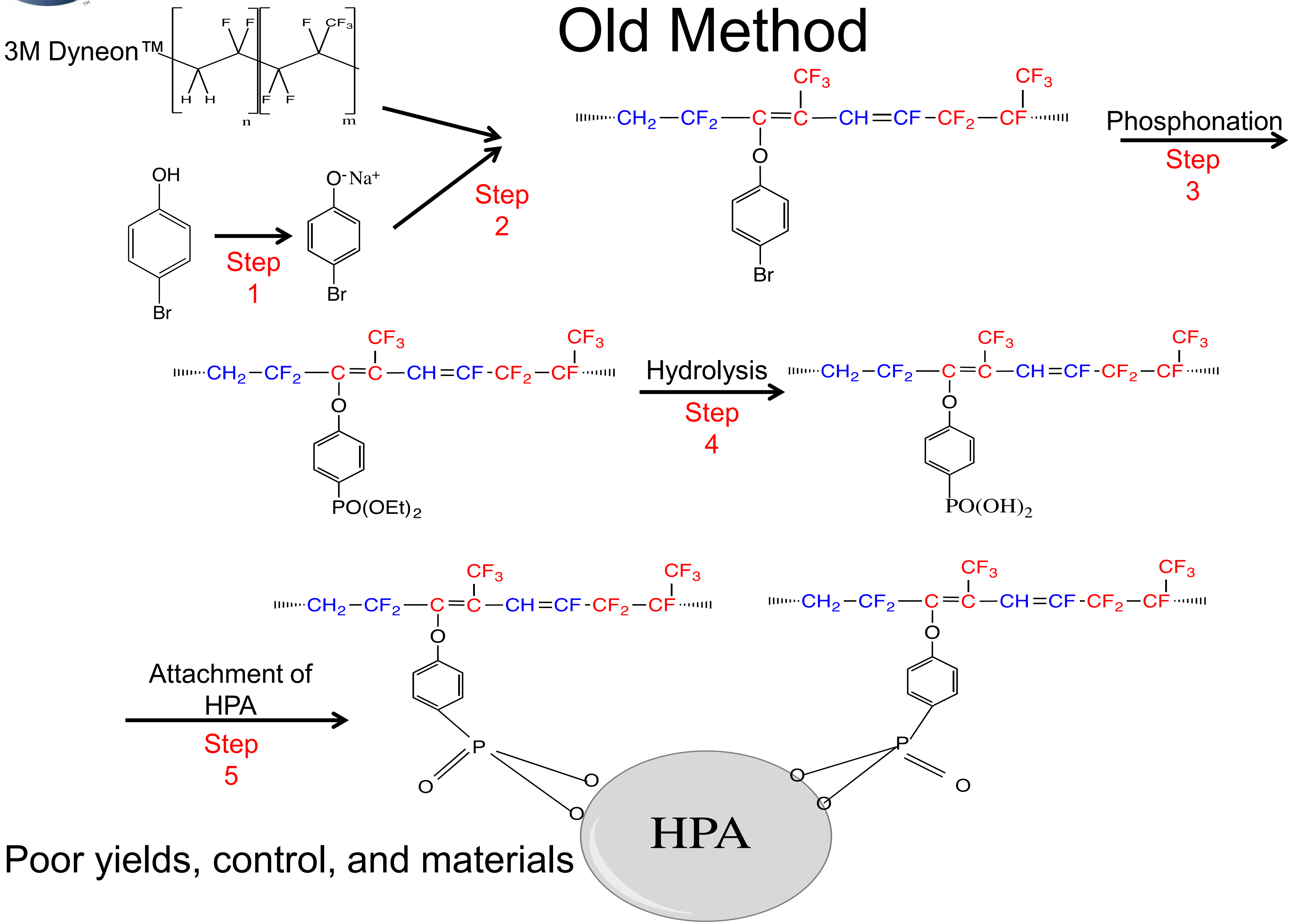
Switched to ethylene glycol
Eliminated O_2

High Mw achieved, improved materials, not films, utility as ionomer



$$Mw = (346 * 0.4 + 2907 * 0.6) * (cyclobutyl / 6) / (vinyl / 2) = 21,500 g / mol$$

System II – Hybrid HPA-3M FC-2178 Old Method



Poor yields, control, and materials

FY14 Go/No-Go at 80^{o}C/95%RH

- Cast on Kapton® Tape from DMAC Solution
- Films had consistent properties
- Stable to water
- Easily meets ASR target <0.02 Ω cm^2
- Large area free standing thin films were not available with this chemistry, due to brittleness

Sample	Trial	Thickness (μm)	ASR (Ohm-cm^2)	Standard Deviation
1	1	12	0.014	1.2e^{-3}
2	1	11	0.021	1.1e^{-3}
3	1	6	0.005	9.4e^{-5}
3	2	6	0.006	6.6e^{-5}
4	1	27	0.016	2.6e^{-4}
4	2	27	0.016	1.0e^{-4}
4	3	27	0.018	5.3e^{-5}
5	1	20	0.019	1.7e^{-3}
6	1	21	0.017	7.4e^{-3}

FC-2178 Functionalization - Improved Process

Step 1, 2, and 4 have standardized procedures, allowing high conversion and purity – previous chemistry left 50% side chains in Br form

Step 3: New Method Developed to Control IEC

Step 5: New in film crosslinking process

Higher yields, good control, much improved materials, over-come solvent, isolation after every step and other criticisms of old method manufacturing assessment, cost should be similar to other fluoroelastomers

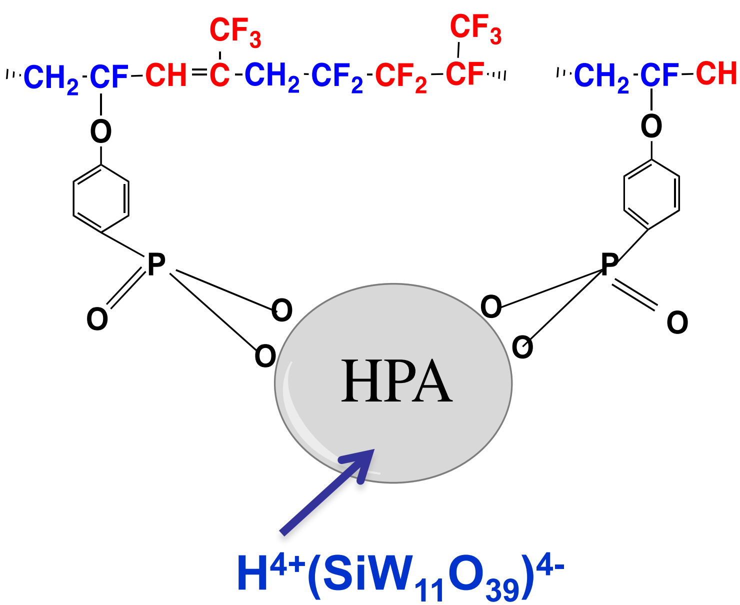
All reactions on large scale >1 Kg of FC-2178 consumed in first 18 months

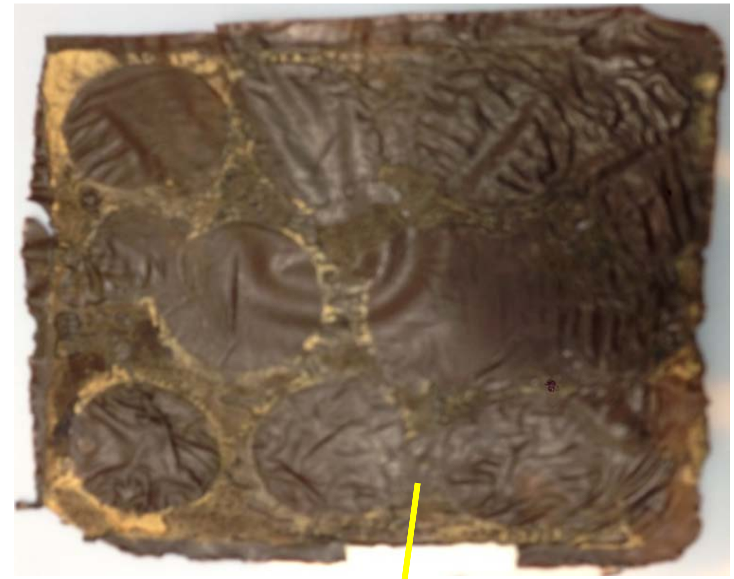
Films of sufficient surface area and uniformity available for partner testing

Full details - proprietary

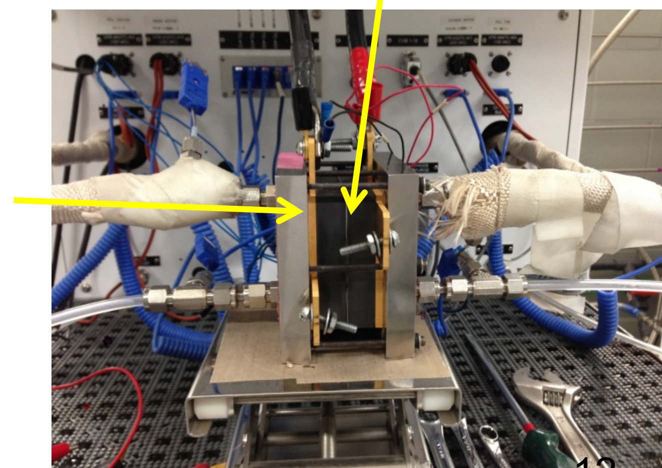
FC-2178 Low HPA Content

This membrane is System II type and is based on dehydrofluorinated 3M FC-2178 polymer and HPA.



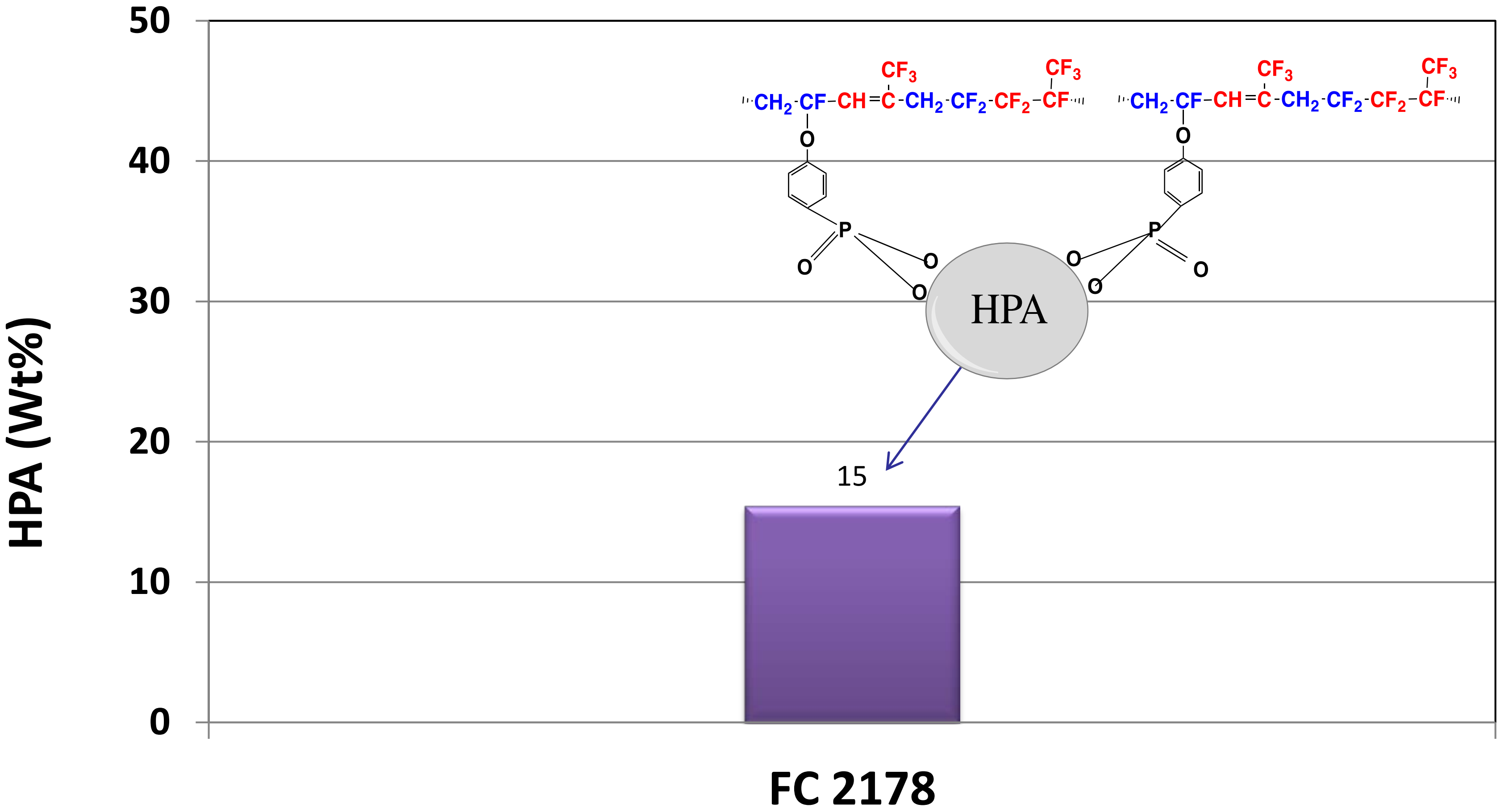


First MEA of 4 cm^2 was fabricated from this sample and assembled in the cell hardware.



HPA Loading

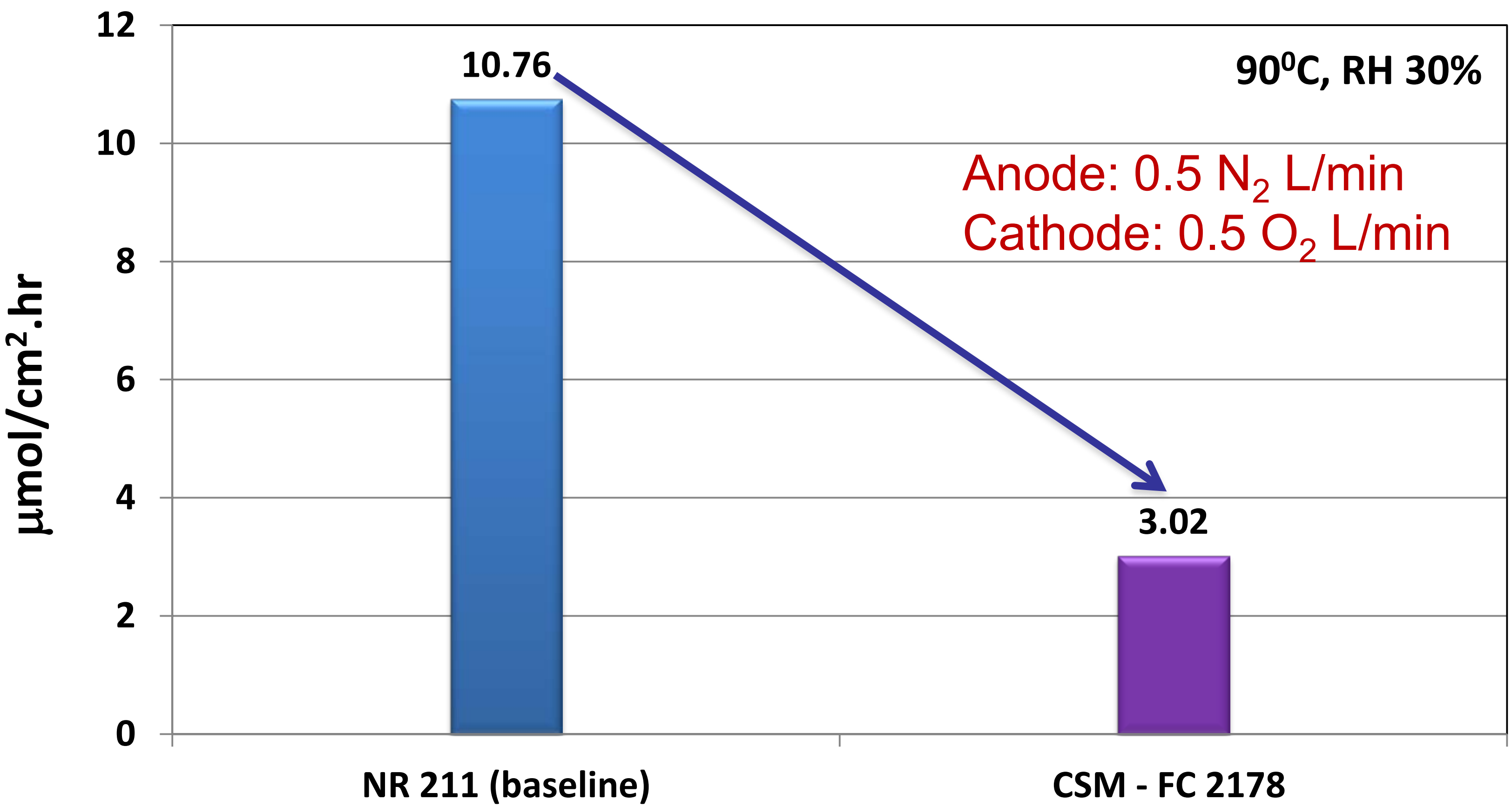
- HPA loading was obtained by PIXE (Proton Induced X-ray Emission) elemental analysis.



- HPA loading was found to be approximately ~15 wt%.

O_2 Crossover

- O_2 crossover was measured to learn about chemical durability behavior of this membrane under OCV hold tests.
- Low O_2 crossover leads to better chemical durability.

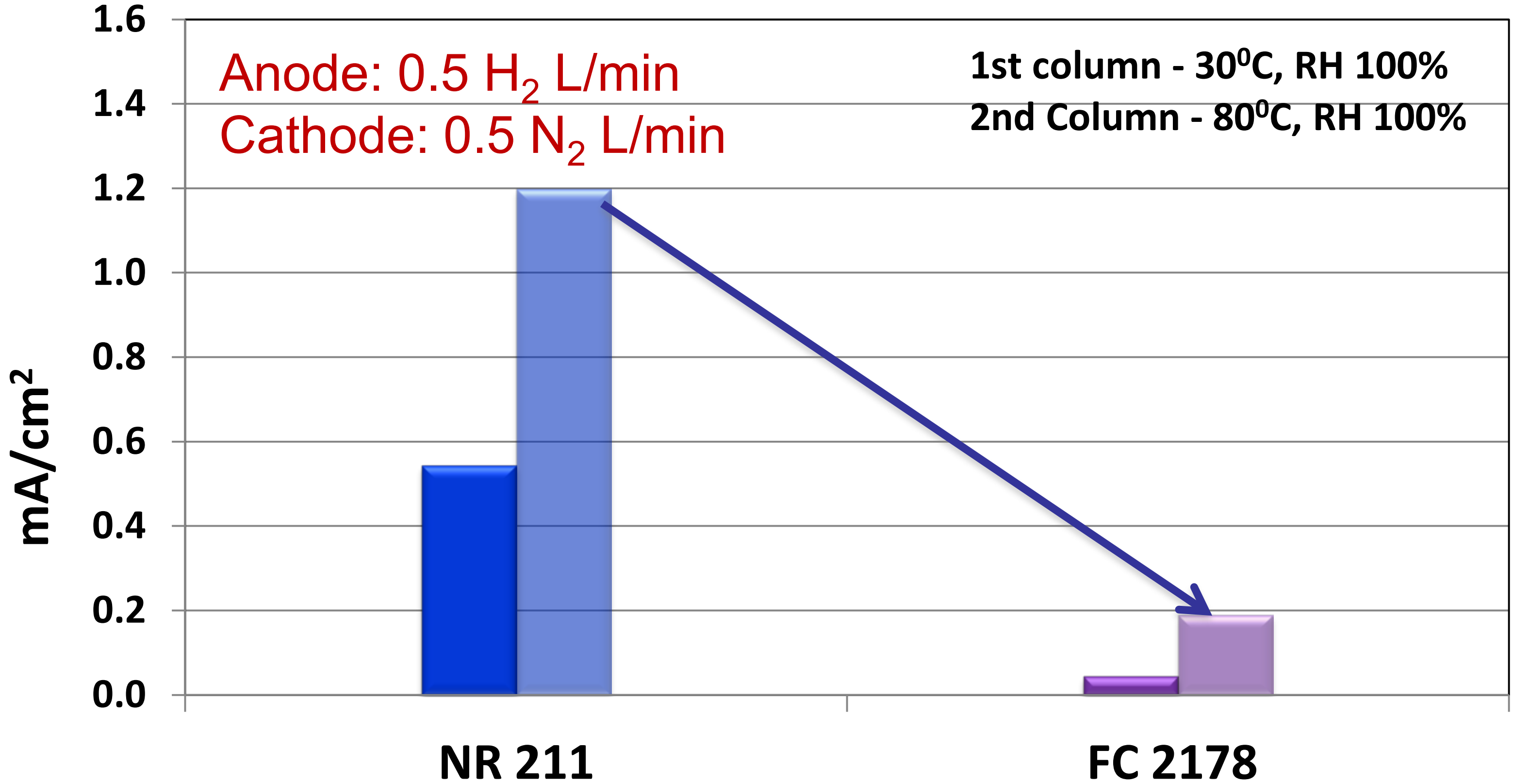


- FC-2178 membrane shows low O_2 crossover probably due to its structure and low HPA loading.
- Low water uptake in FC-2178 in comparison with NR 211 can also lead to low O_2 X-over.

Zero Emission

H_2 Crossover

- This evaluation was done to learn about gas crossover behavior of the membranes.
- Low H_2 crossover allows better IV performance and high chemical durability.



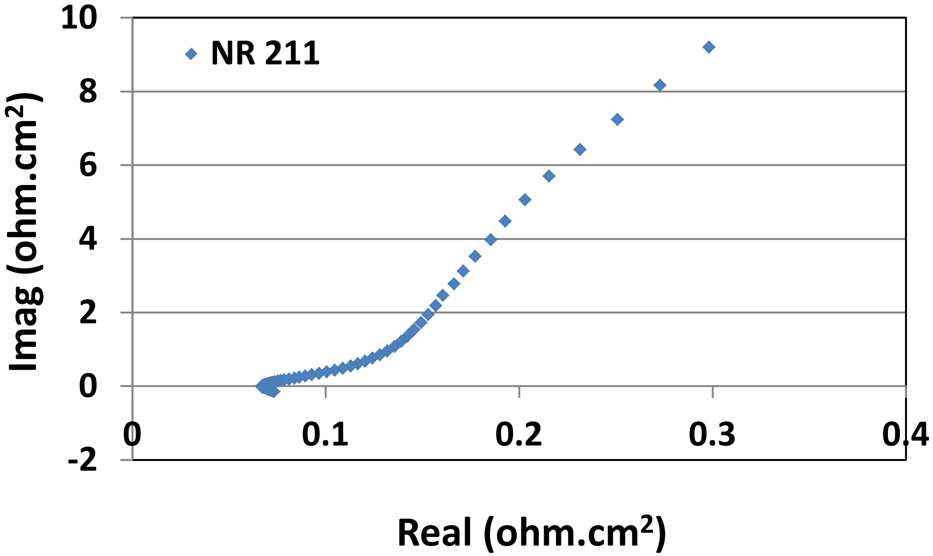
- Very low H_2 crossover in FC-2178 is observed due to low HPA loading or polymer chemistry.
- As expected, both NR 211 and FC-2178 show increase in X-over with increase in temperature from 30 to 80^0C.

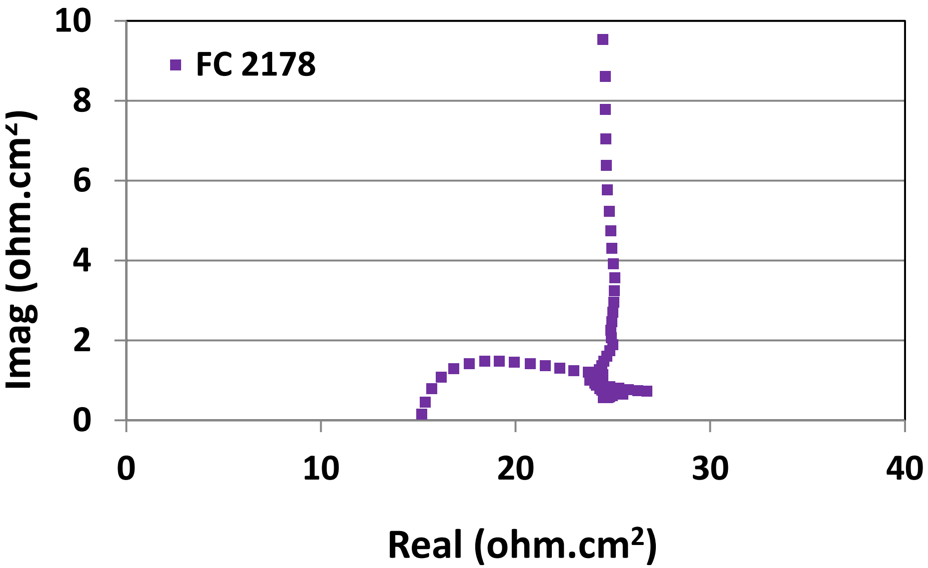
Zero Emission

EIS Analysis of Low Content HPA Film

- EIS was done to learn about ohmic resistance behavior of the membrane
- Low ohmic resistance leads to better IV performance.

80^0C, RH 100%, Anode: 0.5 H_2 L/min, Cathode: 0.5 N_2 L/min





Ohmic Resistance:

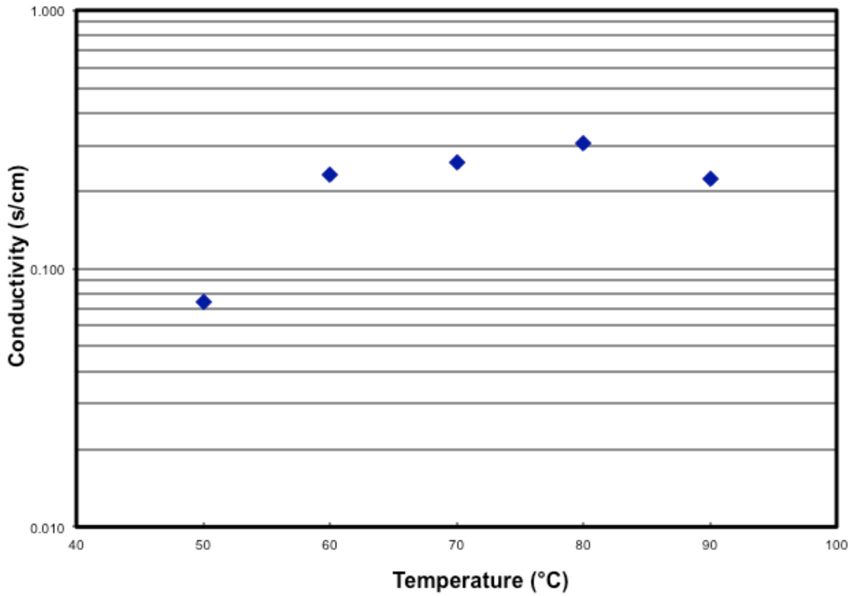
NR 211: 0.073 ohm.cm^2 << FC-2178: 15.20 ohm.cm^2

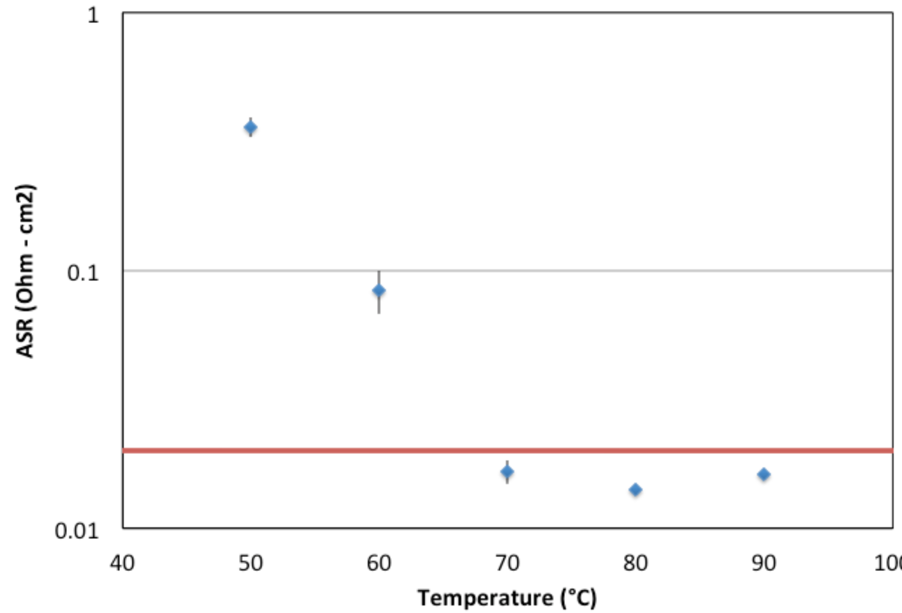
Conductivity: NR 211 >> FC-2178

- This high ohmic resistance could be attributed to low HPA loading and low conductivity in the FC-2178 membrane.

Zero Emission

FC-2178 – Improved HPA Content, Proton Conductivity, 95%RH





σ > 0.2 S/cm, T > 60° C
Free standing, Thick film - 176 μm

(2014 AMR performance was 0.06 S/cm at 80° C)

ASR < 0.02 Ω cm², T > 70° C
Kapton® Supported, Thin film - 12 μm

Collaborations

- Prime: Colorado School of Mines – STEM University
  - Andrew Motz, Tera Dunham, Mei-Chen Kuo, Jim Horan
    Polymer synthesis, membrane fabrication, MEA fabrication
- Sub: Nissan R&D Americas – OEM
  - Nilesh Dale, Rameshwar Yadev
    Membrane testing, MEA fabrication and testing
- National Laboratory: NREL
  - Bryan Pivovar
    Membrane testing, MEA fabrication and testing
- Cost-Share: 3M – Component Supplier
  - Steve Hamrock
    Chemicals, polymer consulting, testing

3M

NREL
NATIONAL RENEWABLE ENERGY LABORATORY

NISSAN
R&D AMERICAS

Zero Emission

Remaining Challenges and Barriers

- Mechanically robust thin films with target ASRs at low RH, synthetic chemistry is now system ready
- Fabrication of MEAs with appropriately integrated electrodes
  - Full Fuel Cell relevant MEA testing protocol to develop membranes with durability, cost, mechanical, and performance metrics

Reviewers Comments

“This project approach is substantially different than other membrane approaches, and the theoretical possibility of successfully producing a high conductive membrane that requires low RH exists. The project is a departure from the approach taken by many of the Office of Energy Efficiency and Renewable Energy (EERE) projects, which show incremental gains; to achieve this gain, the project requires time to make progress, and addressing short-term quarterly milestone could very well take the project in wrong directions.”

- Because the project is now at or above a TRL of 2, BES funding is inappropriate and so we are working with EERE to achieve the desired outcomes in the constraints of the EERE funding model

“The project shows a path to low-cost, low-RH, high-temperature capable membranes. Three paths are included to reduce the risk of failure. There are feasible paths to also meeting durability. Collaborators will provide strong support and ensure the project is commercially relevant.”

- University, industry and national lab partners are becoming fully integrated

“The only recommendation is that if the zirconium phosphonate polymers continue to be water soluble, the work on them should probably be discontinued.”

- This work was discontinued

“Project weaknesses include the team’s inexperience with producing Dyneon and scaling up the batch size, as well as processing quality, reproducible thin films. Hopefully the team will be successful with both during the upcoming year.”

- 3M has had extensive discussions with the project team in regard to the FC-2178 chemistry and many of these issues are now resolved.

TFVE System – Conclusion

- Side reaction was limiting Mw
  - Elimination of O_2 and DMAc fixed the problem
- Reaction in appropriate solvent will better allow twisting part of mechanism
- Needs improved film forming to make stand alone film
  - Blends are currently being investigated
- May work well as ionomer for HT / LH catalyst layers

FC-2178 – Conclusion

- Improved chemistry to avoid excess, un-conducting side chains
  - Previous chemistry left 50% side chains as phenyl-Br
- Developed reliable protocol to make PPA intermediate with controlled IEC and water stable, free standing films
  - These films have not been free standing until now
- Improved mechanics (support) will allow for thinner films
- First films sent to Nissan USA for testing
- There is a trade off between mechanics and IEC
  - Need to find optimum
  - Blends may improve mechanics without significant conductivity loss

Future Work

Remainder of Year 2

- Thin Films, processing, standard ex-situ measurement at CSM
  - Characterization and testing at Nissan, NREL, 3M using DOE, 3M, and Nissan protocols for ASR, cross over, mechanical, and chemical stability
- Scale Up
  - System I, increase MW
  - System II, study IEC property trade offs , optimize HPA loading, supported films as needed (in collaboration with 3M)

Year 3

- Electrode optimization and MEA fabrication, CSM, NREL
- Full membrane protocol testing in MEA, NREL, Nissan, 3M

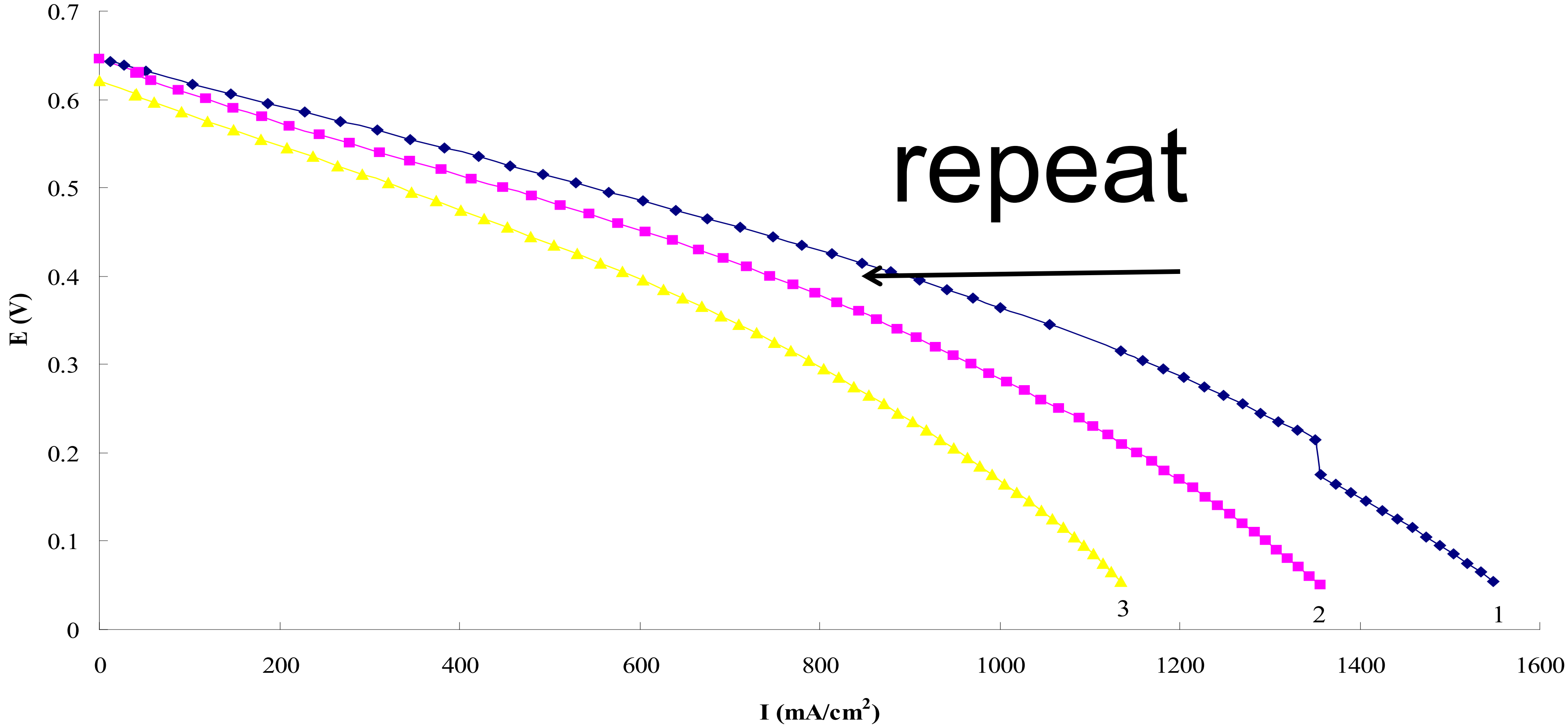
Summary

- Consistently High Proton Conductivity in water stable films
- 2 Film Chemistries under development
- Demonstrated low cross-over with low HPA loaded film

	DOE Target 2017 $\Omega\ cm^2$	**Result** $\Omega\ cm^2$	**Thickness** μm	**Conditions**
System I, TFVE-HPA	0.02	0.3	180	70ºC 95% RH
System II, FC-2178-HPA	0.02	0.01 - 2	10 - 20	> 70ºC 95% RH

Technical Back-Up Slides

12-HPW/PVDF-HFP, 30 μm, No humidity, 0.5 l min^{-1}, H_2/O_2, RT.

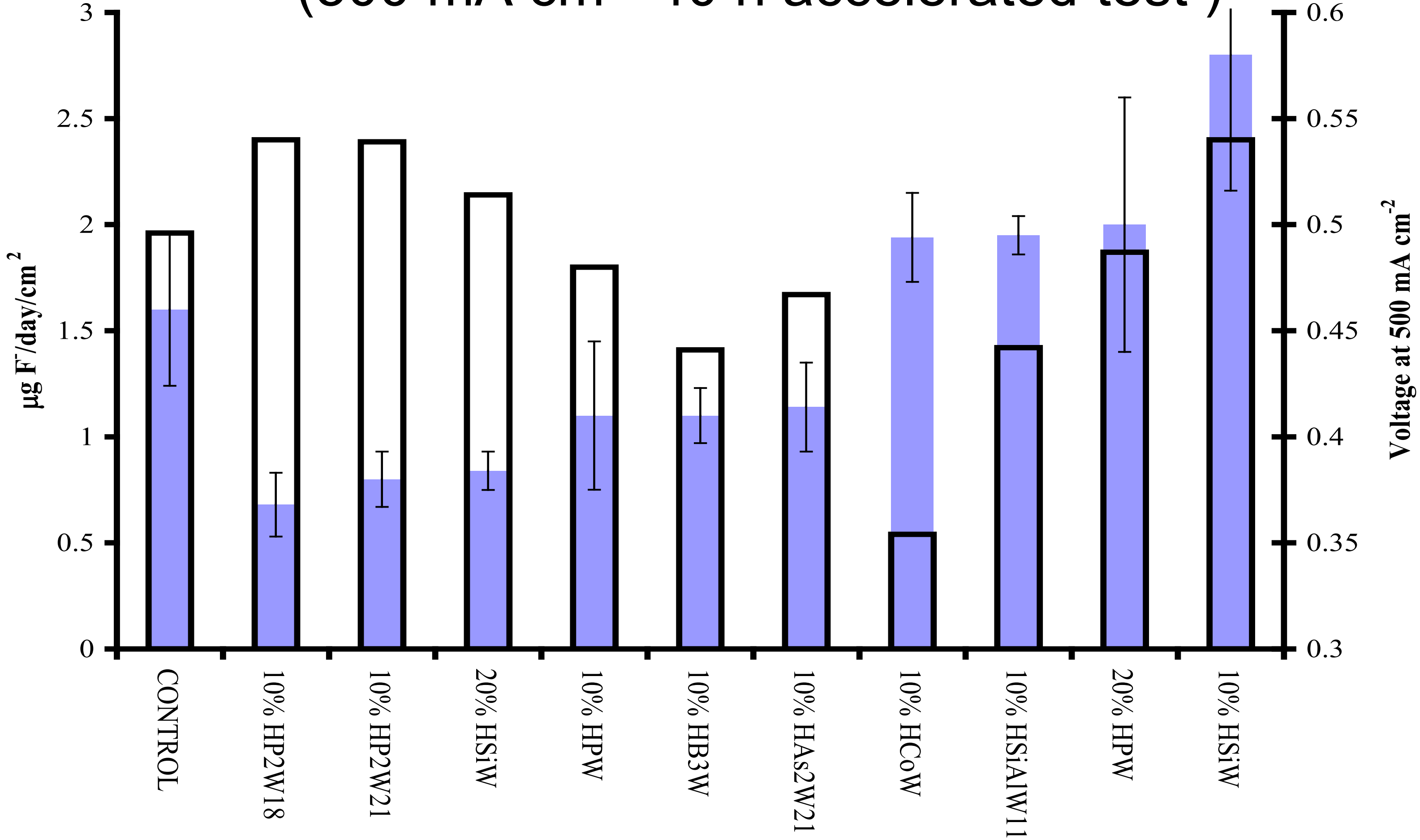


Demonstration that HPA are proton conductors, but water soluble, so need to be immobilized

J.L. Malers, M.-A. Sweikart, J.L. Horan, J.A. Turner, and A.M. Herring,* *J. Power Sources*, **2007**, *172*, 83.

Doping 3M PFSA Membranes

(500 mA cm^{-2} 40 h accelerated test)

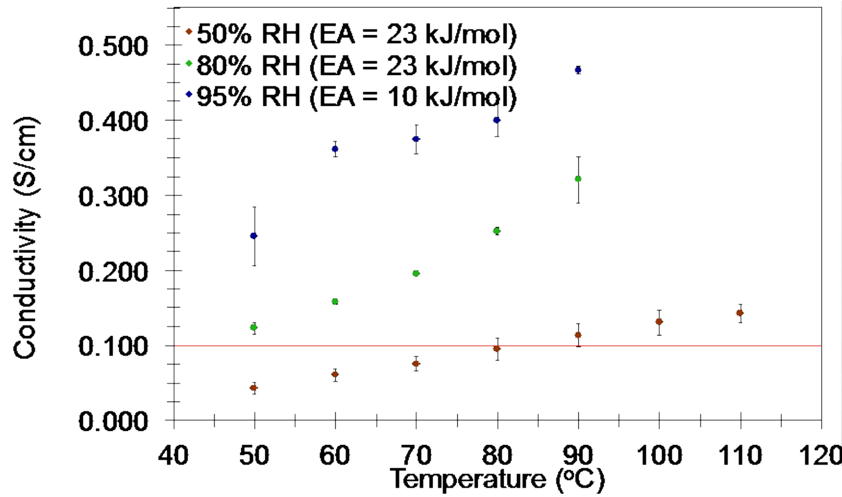


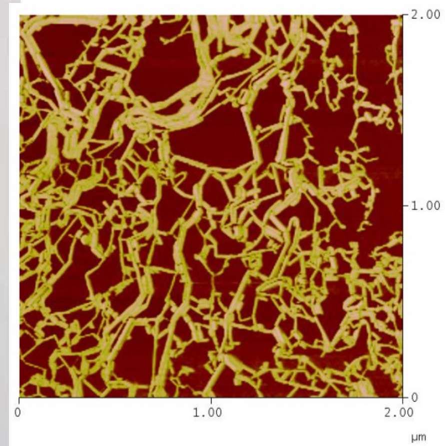
Demonstration that HPA can mitigate oxidative degradation

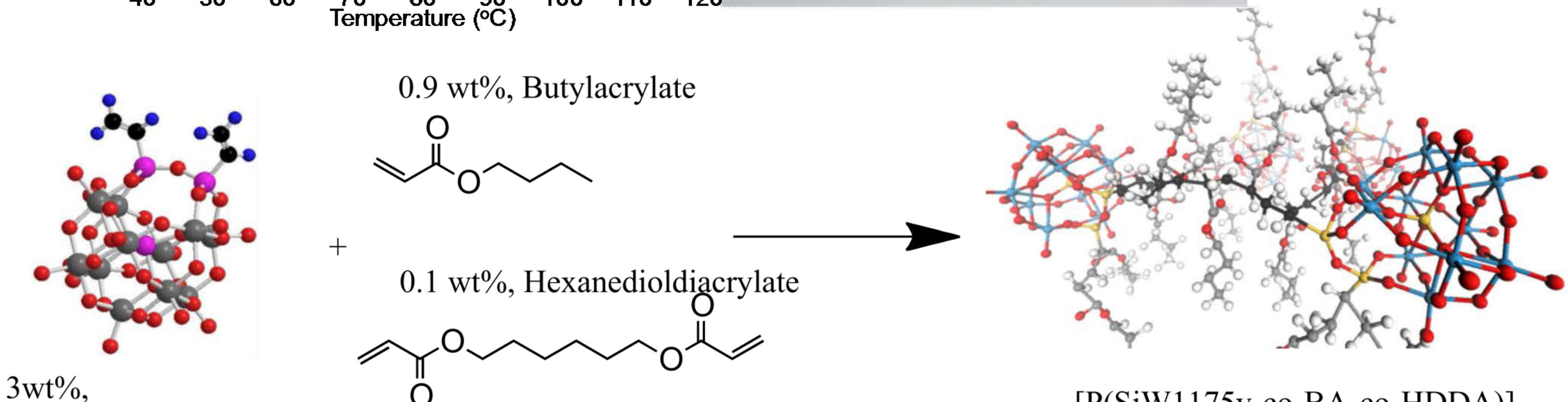
F$^-$ release (solid bars) and average potential at 500 mA cm^{-2}, hours 2 – 7 (Open bars).
G.M. Haugman, F. Meng, M.H. Frey, S.J. Hamrock, N.V. Aieta, J.L. Horan, M.C. Kuo, and A.M. Herring,*
Electrochemical and Solid State Letters, **2007**, *10*, B51.

Generation I Films – PolyPOM85v/BA

High and dry conductivity, but ester linkage susceptible to hydrolysis







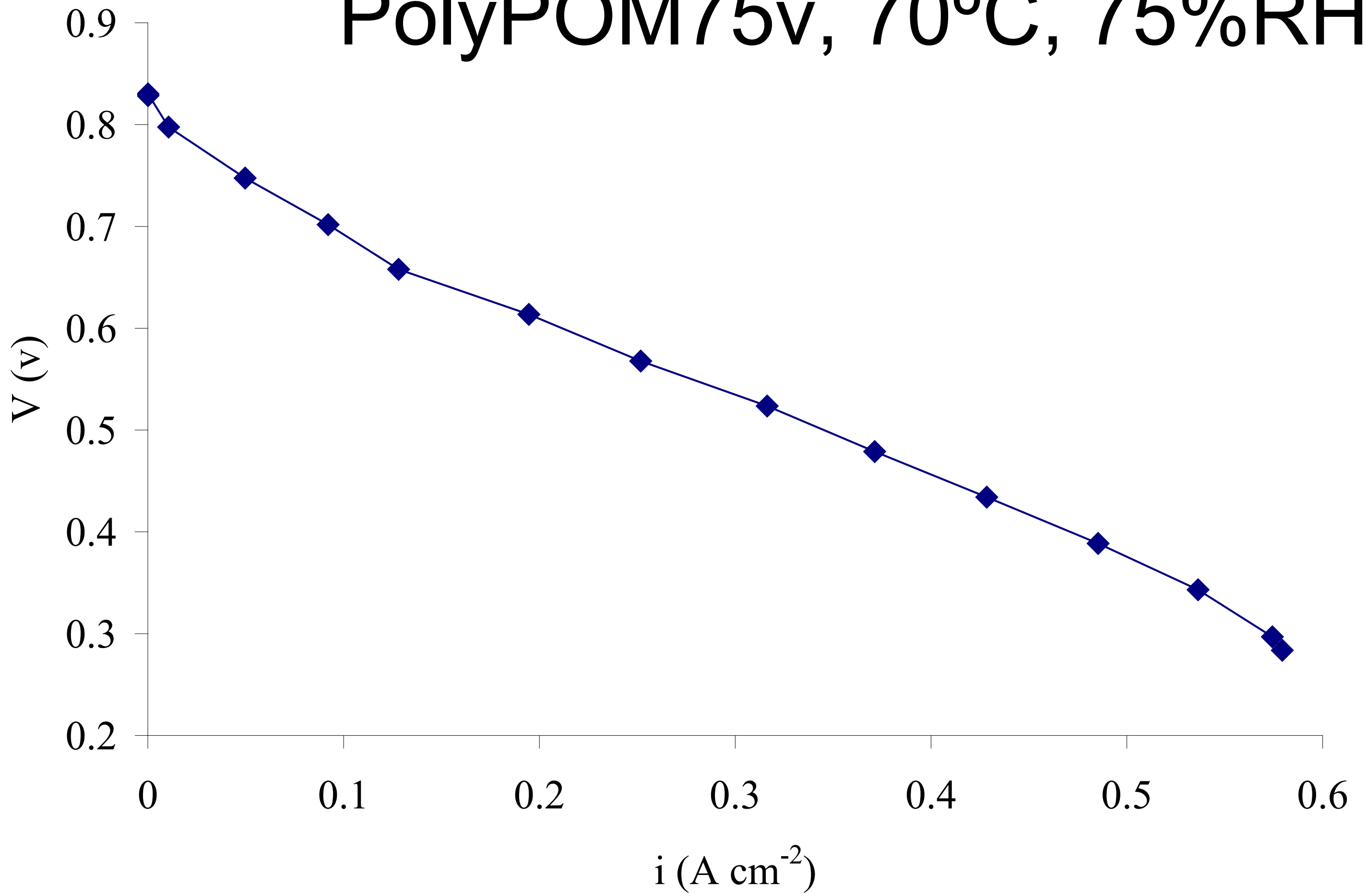
3wt%,
$H_4[SiW_{11}O_{40}(Si(CH{=}CH_2))_2]$

[P(SiW1175v-co-BA-co-HDDA)]
(PolySiW11(75)BA)

Films generally thick but ASR <0.02 Ω cm^2

J.L. Horan, A. Genupur, L. Ren, B.J. Sikora, M.-C. Kuo, F. Meng, S.F. Dec, M.H. Frey, G.M. Haugen, M.A. Yandrasits, S.J. Hamrock, and A.M. Herring,* *Chem. Sus. Chem.*, **2009**, *2*, 226.

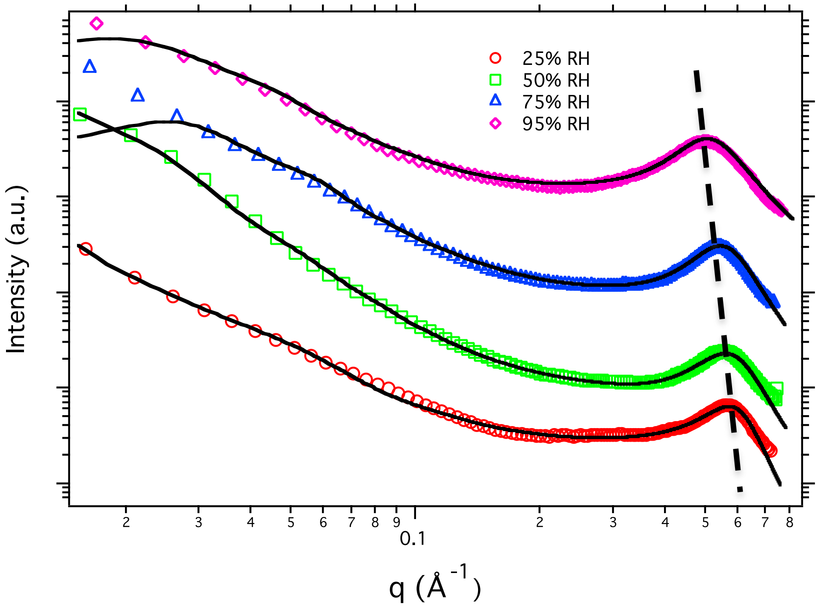
Polarization Curve for PolyPOM75v, 70ºC, 75%RH

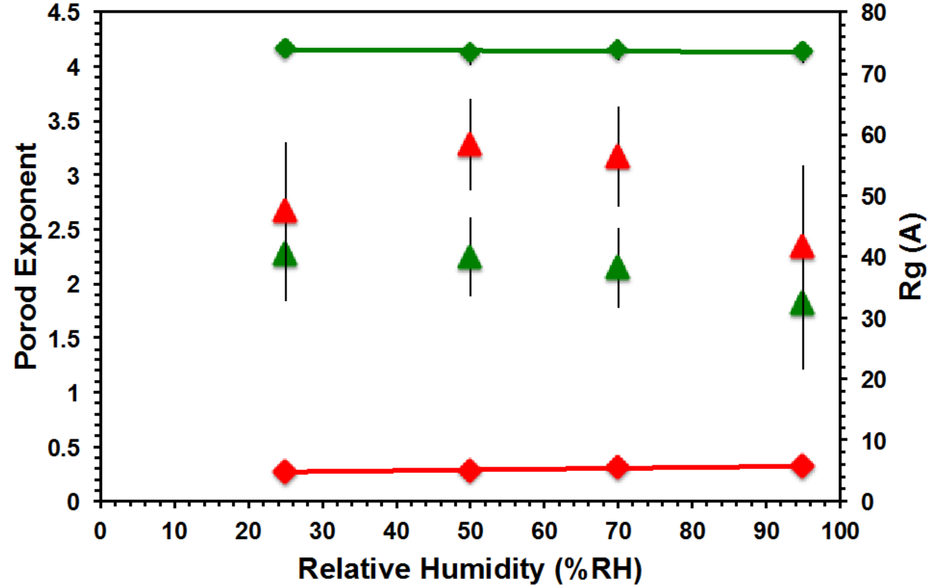


Demonstration that immobilized HPA work in Fuel cell

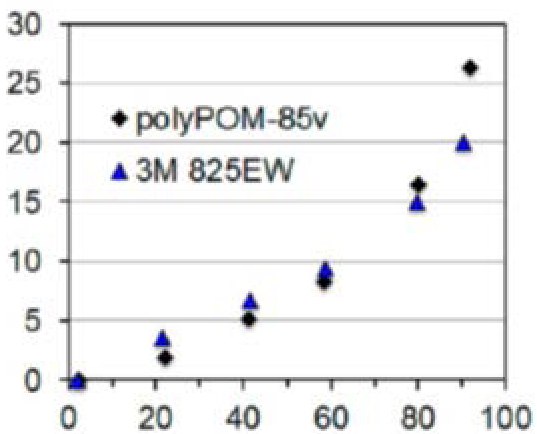
- ASR 0.1 μΩ cm^2
- Polarization curve for maximum performance of an MEA constructed from a 150 μm thick P(SiW1175V-*co*-BA-*co*-HDDA) film. H_2/Air 800/1800sccm 70 ºC, 75% RH Ambient Outlet Pressure.

SAXS polyPOM-85v, variable RH





Relative Humidity (%)	Level 1 R_g (Å)
25	4.8
50	5.1
75	5.4
95	5.8



Demonstration that λ similar to PFSAs but water goes to HPA and does not uncontrollably swell film

J.L. Horan, A. Genupur, H. Ren, S. Sachdeva, Y. Yang, L.F. Greenlee, S. Seifert, M.A. Yandrasits, S.J. Hamrock, M.H. Frey, S.F. Dec, M.-C. Kuo, A.M. Herring,* *J. Phys. Chem. C*, **2014**, *118*, 135.