



# 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: 20%

## Budget

- Total Funding Spent as of 3/31/14:  
\$109,250.36
- Total Project Value:  
\$1,877,676
- Cost Share Percentage:  
20%

## Barriers

Barrier	2017 Target
A - Durability	Chemical: > 500 hours Mechanical: 20,000 cycles
B - Cost	\$20/m <sup>2</sup>
C - Performance	ASR $\leq 0.02 \Omega\text{cm}^2$ max operating temp $\leq 120^\circ\text{C}$ and 40-80 kPa $P(\text{H}_2\text{O})$

## Partners

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

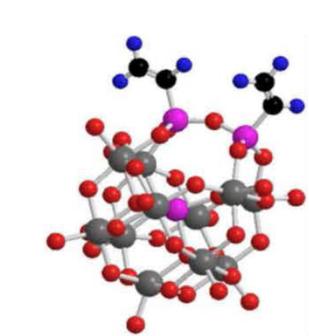
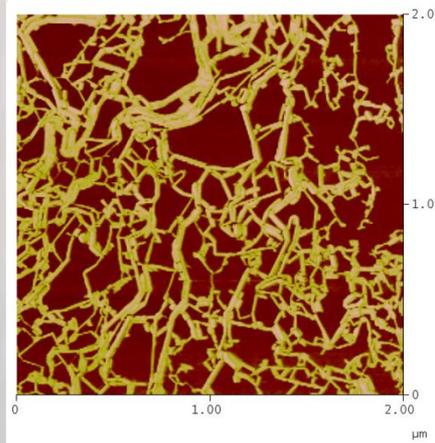
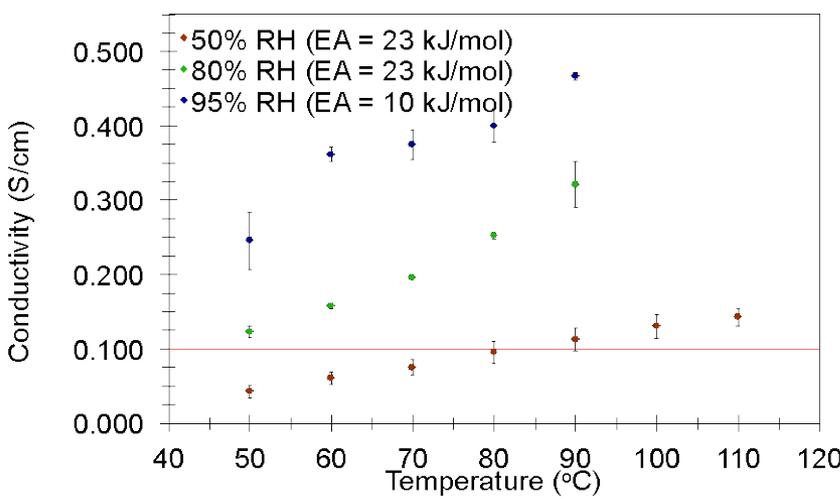


# Relevance

<b>Overall</b>	<p>Demonstrate a low cost hybrid inorganic/polymer from super-acidic inorganic functionalized monomers with:</p> <ul style="list-style-type: none"><li>• ASR &lt; 0.02 <math>\Omega</math> cm<sup>2</sup> at operating temperature of an automotive fuel cell stack (95-120°C) at low inlet RH &lt; 50%</li><li>• 50 cm<sup>2</sup> MEA with desired mechanical properties and durability</li></ul>
<b>2014</b>	<ul style="list-style-type: none"><li>• Optimize three different candidate hybrid inorganic/polymers in practical systems for low ASR, then eliminate one system</li><li>• Barrier C</li></ul>
<b>2015</b>	<ul style="list-style-type: none"><li>• Optimize two best candidate systems for low ASR, mechanical properties, oxidative stability/durability, and incorporation of electrodes, then eliminate lowest performing system</li><li>• Barrier A and C</li></ul>
<b>2016</b>	<ul style="list-style-type: none"><li>• Incorporate best hybrid polymer system into MEA, deliver 50 cm<sup>2</sup> MEA to DOE with all desired properties for third party testing</li><li>• Barrier A, B, and C</li></ul>

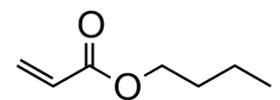


# Approach – from previous funding Generation I Films – PolyPOM85v/BA



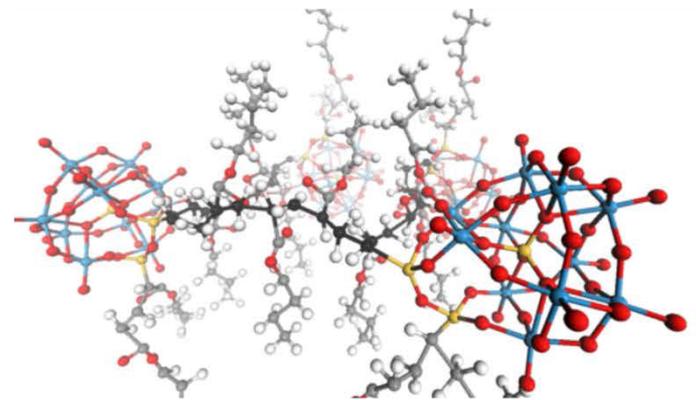
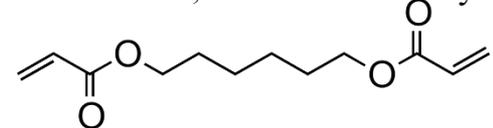
3wt%,  
 $H_4[SiW_{11}O_{40}(Si(CH=CH_2))_2]$

0.9 wt%, Butylacrylate



+

0.1 wt%, Hexanedioldiacrylate



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

Films Generally thick but ASR  $< 0.02 \Omega \text{ cm}^2$



# Approach

- Material Synthesis based on functionalized super acidic inorganic moieties, ***Generation II Films***
  - Heteropoly acid (HPA) functionalized monomer polymer system
  - Dyneon™ functionalized with HPA
  - Zirconyl phosphonate/vinyl phosphonic acid polymers
- 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 testing



# FY 2013 Milestones

Milestone	Description	% Complete
Year 1 – Q1	HPA-TVFE monomers will be synthesized of sufficient purity to allow all of the functionalized HPA to be polymerized.	100
Year 2 – Q1	An HPA functionalized Dyneon™ polymer will be synthesized where enough HPA is stable to boiling that the resultant film has an ASR of 0.02 Ohm cm <sup>2</sup> at 80°C and 45kPa.	80
Year 1 – Q3	Fabricate polyZrP films that are stable to boiling and measure that the resultant film has an ASR of 0.02 Ohm cm <sup>2</sup> at 80°C and 45kPa.	50
Year 1 – Q4 Go/No Go	Demonstrate at least 1 polymer system that achieves an ASR of $\leq 0.02$ Ohm cm <sup>2</sup> , at 80°C and 45kPa. Choose two of the three hybrid polymer systems to move forward based on lowest achievable ASR under hot and dry conditions for water stable materials.	50



# Accomplishments and Progress

## Benefit Analysis

In order to evaluate the potential gains in technology, system economics have been compared using DOE funded baseline work<sup>1</sup>

The model analysis has several assumptions:

- 1) operation up to 120°C;
- 2) the system humidification system can be removed;
- 3) catalytic gains from the increased operating temperature; and
- 4) membrane materials would be slightly (20%) more expensive than baseline materials.

Specification	UOM	Baseline	HT-PEM
Current density	A/cm2	1.456	1.456
Voltage	Vdc	0.676	0.676
Relative waste heat rejection		100%	100%
Relative stack area		100%	1
Relative fuel efficiency		100%	1.000
Relative fuel storage		100%	1.000
Stack temperature	°C	87	120
Maximum ambient temperature	°C	40	40
Maximum ambient dT	°C	47	80
Cooling system capacity		100%	59%
Number of subsystems for assembly		10	8
Total Pt loading	mgPt/cm2	0.186	0.1395
Relative membrane cost		100%	120%
Relative GDL cost		100%	100%
Relative bipolar plate cost		100%	100%

### New System

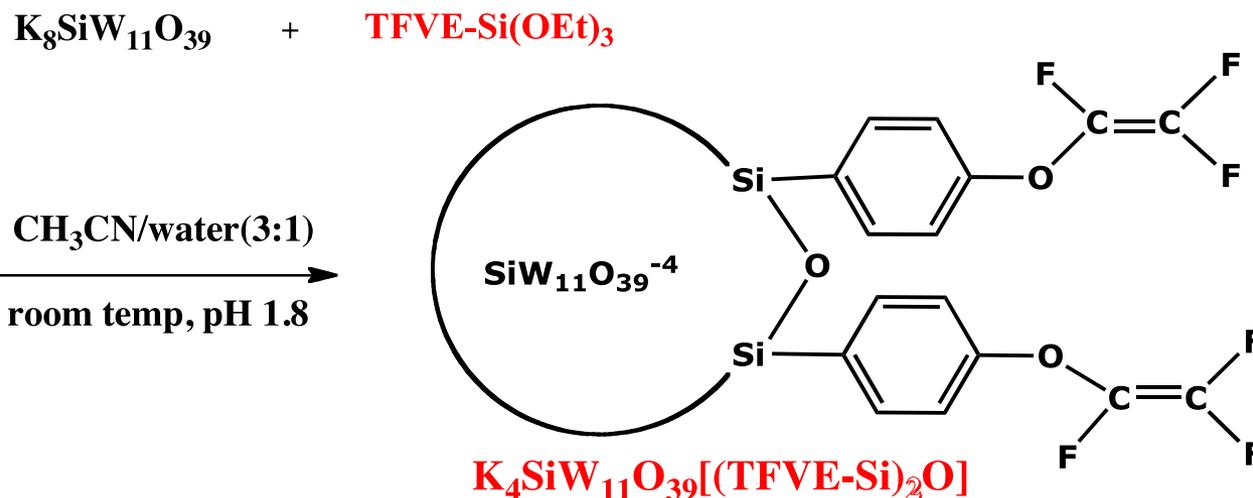
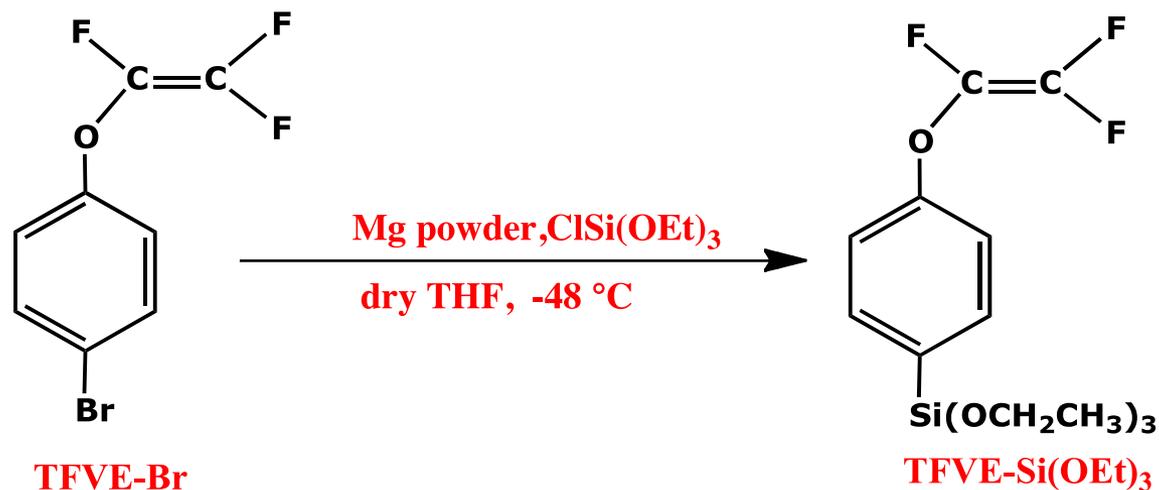
Annual Production Rate	1,000	10,000	30,000	80,000	130,000	500,000
Fuel Cell Stacks	\$12,071.60	\$3,268.45	\$2,255.57	\$1,839.60	\$1,708.45	\$1,457.64
Balance of Plant	\$4,206.48	\$2,646.99	\$2,617.95	\$2,180.89	\$2,024.35	\$1,695.69
System Assembly & Testing	\$116.10	\$80.50	\$79.12	\$78.95	\$78.59	\$78.60
Total System Cost (\$)	\$16,394.18	\$5,995.93	\$4,952.64	\$4,099.44	\$3,811.39	\$3,231.93
Total System Cost (\$/kWnet)	\$204.93	\$74.95	\$61.91	\$51.24	\$47.64	\$40.40
Total System Cost (\$/kWgross)	\$185.79	\$67.95	\$56.13	\$46.46	\$43.19	\$36.63

Costs as low as \$40/kW could be attained at high production volumes.

<sup>1</sup> Brian James, Strategic Analysis Inc. [http://www1.eere.energy.gov/hydrogenandfuelcells/pdfs/sa\\_fc\\_system\\_cost\\_analysis\\_2012.pdf](http://www1.eere.energy.gov/hydrogenandfuelcells/pdfs/sa_fc_system_cost_analysis_2012.pdf)



# System I – TFVE-HPA Hybrid

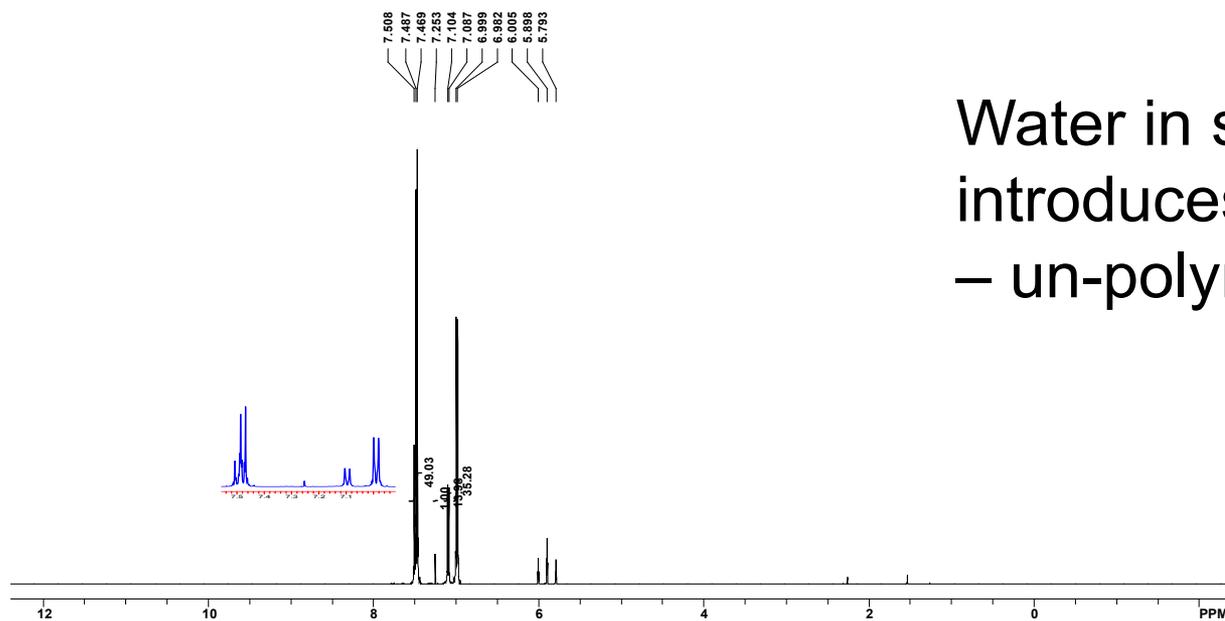


ion-exchange column

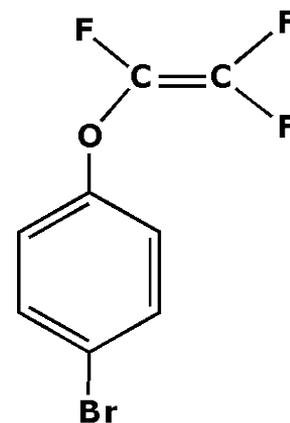
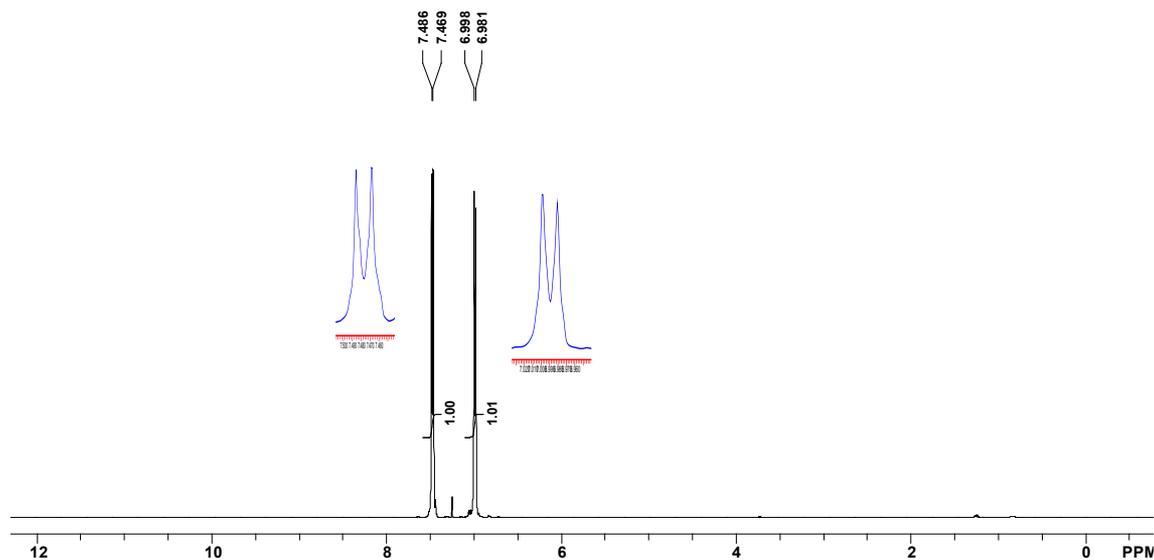




# TFVE-Br now purified



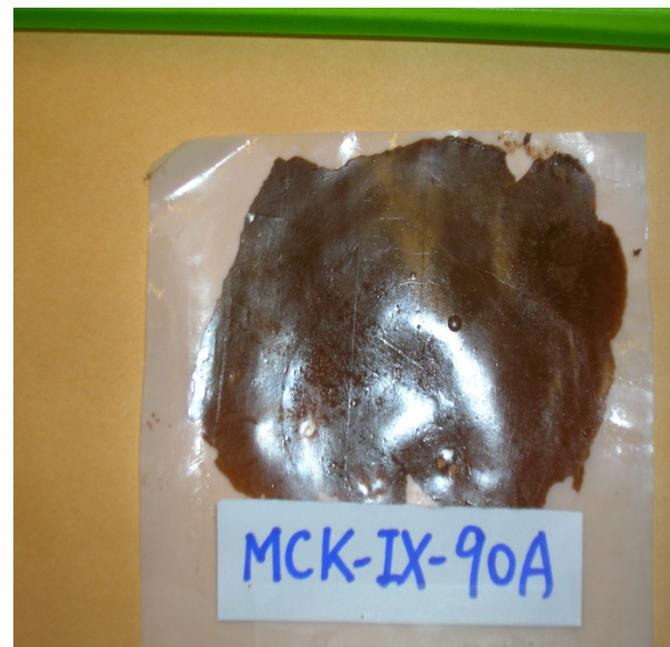
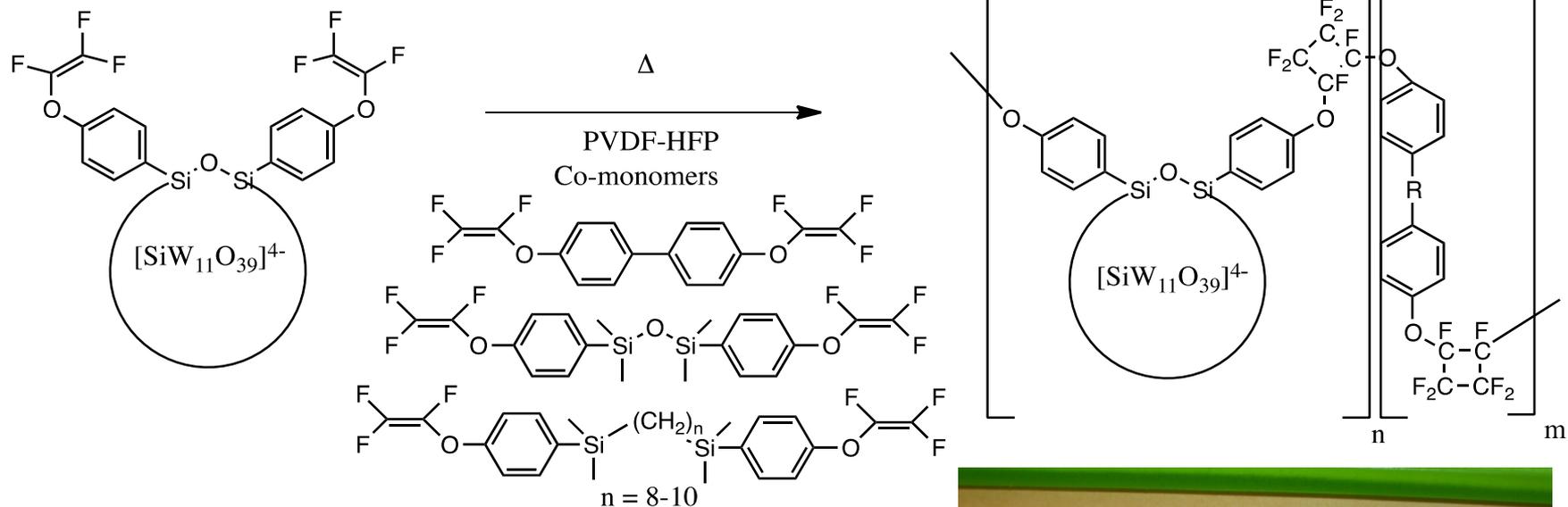
Water in system  
introduces hydrogen  
– un-polymerizable monomer



**TFVE-Br**

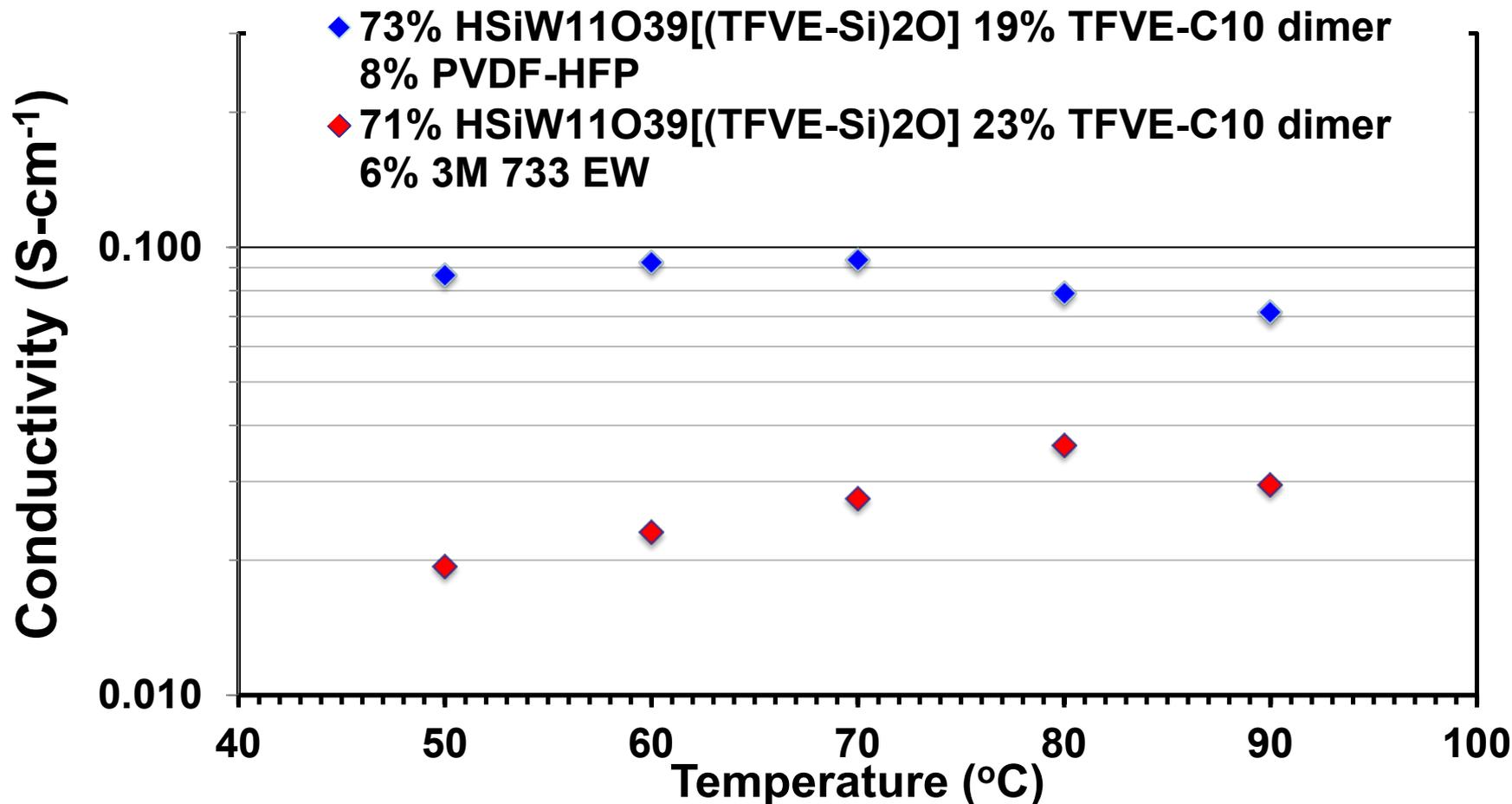


# Polymerization





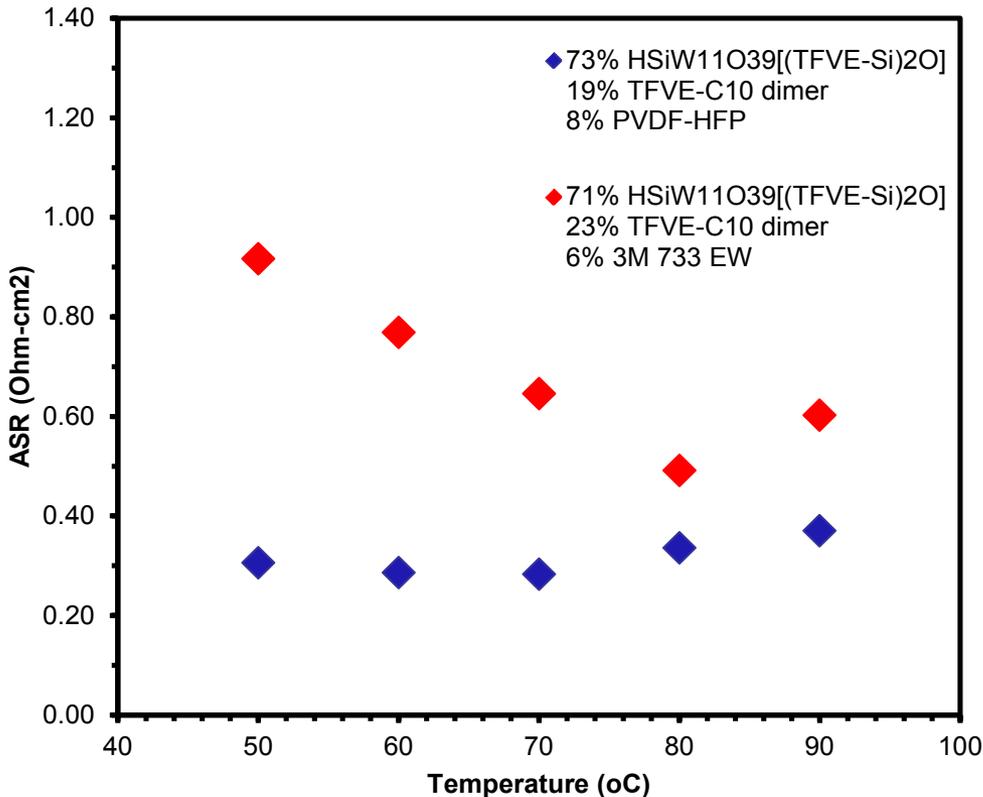
# Conductivity Measurements of Best TFVE Membranes, 95% RH



*Film formation with PVDF and recently 3M ionomer, still being optimized, clearly initial morphology is bad if 3M ionomer reduces protonic conductivity!!*



# Need Thinner Membranes



- Membrane MCK-IX-88A (73% HSiW<sub>11</sub>O<sub>39</sub>[(TFVE-Si)<sub>2</sub>O], 19% TFVE-C10 dimer, 8% PVDF-HFP, **189 μm**) needs to be **10 μm** thick to achieve an ASR of 0.02 Ohm-cm<sup>2</sup> at 70°C.
- Membrane MCK-IX-90A (71% HSiW<sub>11</sub>O<sub>39</sub>[(TFVE-Si)<sub>2</sub>O], 23% TFVE-C10 dimer, 6% 3M 733 EW, **178 μm**) needs to be **7 μm** thick to achieve an ASR of 0.02 Ohm-cm<sup>2</sup> at 80°C.

*Initial TFVE membranes of new campaign, too thick, ca. 180 μm and not conductive enough, HPA loading improvements are being accomplished above old 3M achievements of 3 years ago*



# Film Processing Will be Key

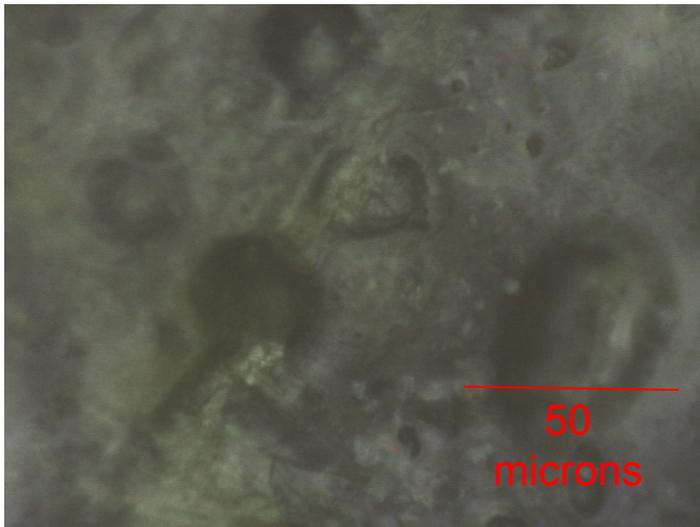
## *Preliminary Heat Treatment Results*

### Polymerization

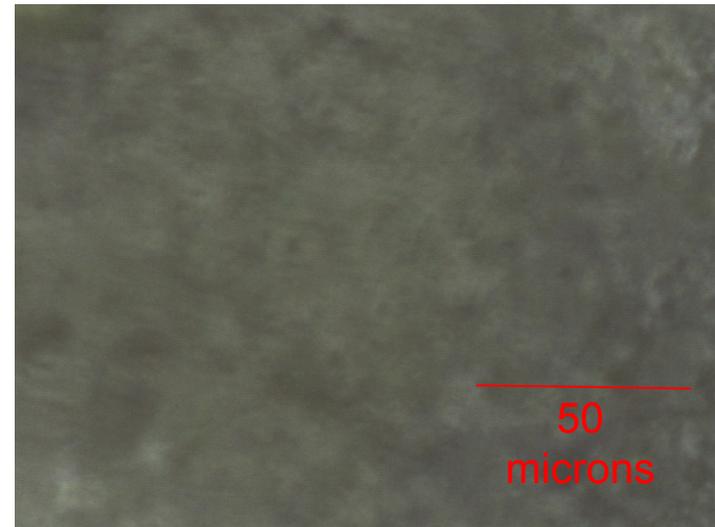
- 73% HSiW<sub>11</sub>O<sub>39</sub>[(TFVE-Si)<sub>2</sub>O]
- 19% TFVE-C10 Dimer
- 8% PVDF-HFP
- 120 °C

### Heat Treatment

- 160 C
- 315 psi
- 3 min



Before heat treatment,  
heterogeneous, 180  $\mu\text{m}$

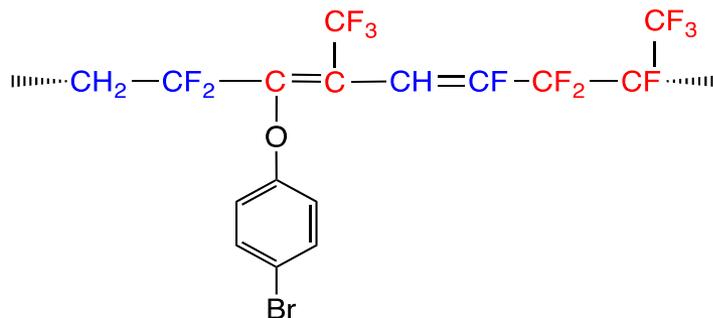
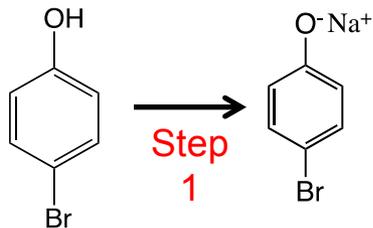
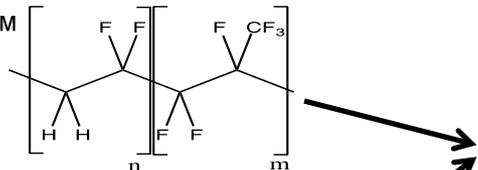


After heat treatment,  
More homogeneous, 50  $\mu\text{m}$ <sup>13</sup>

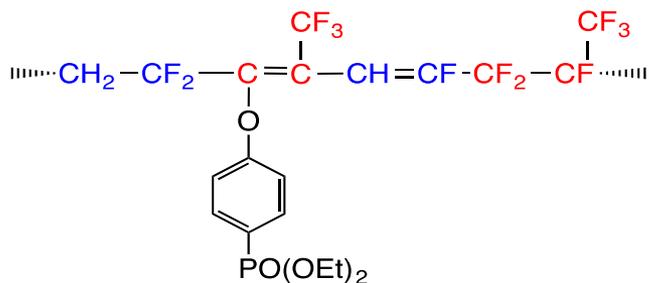


# System II – Hybrid HPA-3M Dyneon™ Ionomer

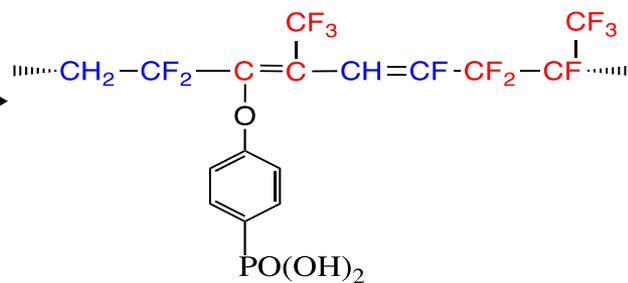
3M Dyneon™



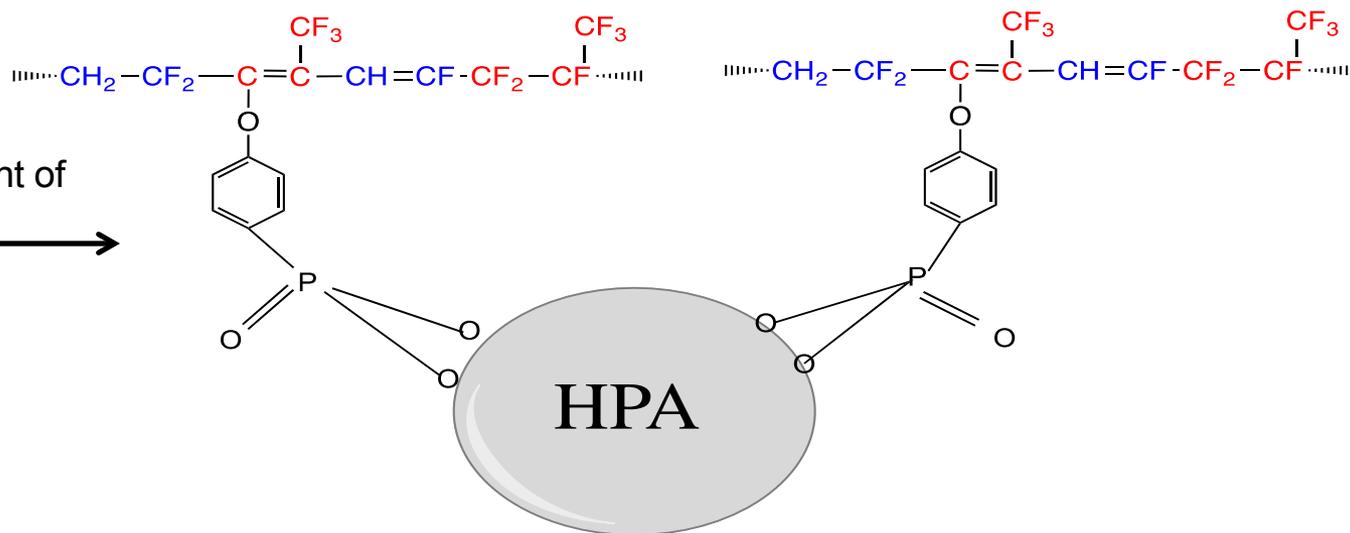
Phosphonation  
Step 3



Hydrolysis  
Step 4



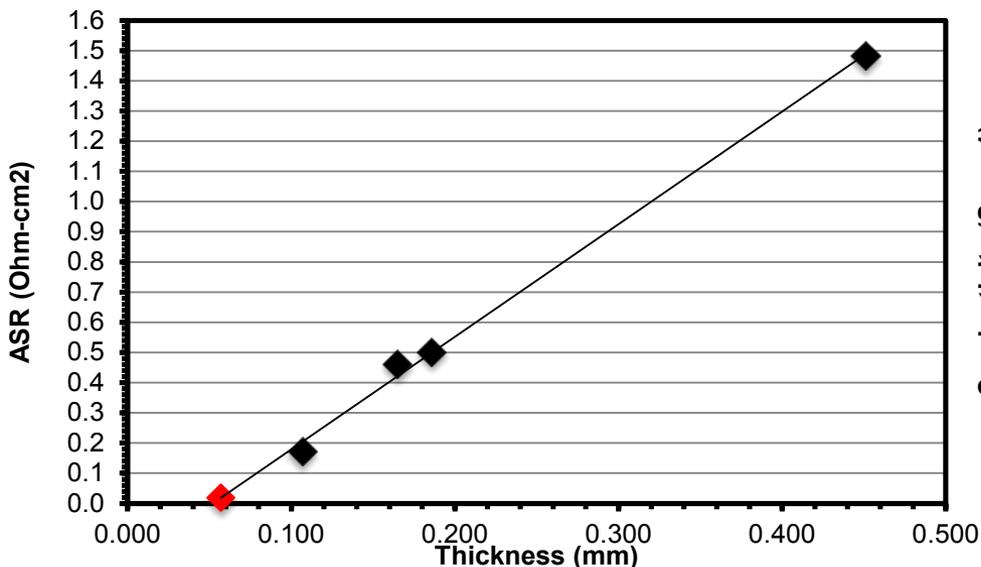
Attachment of  
HPA  
Step 5



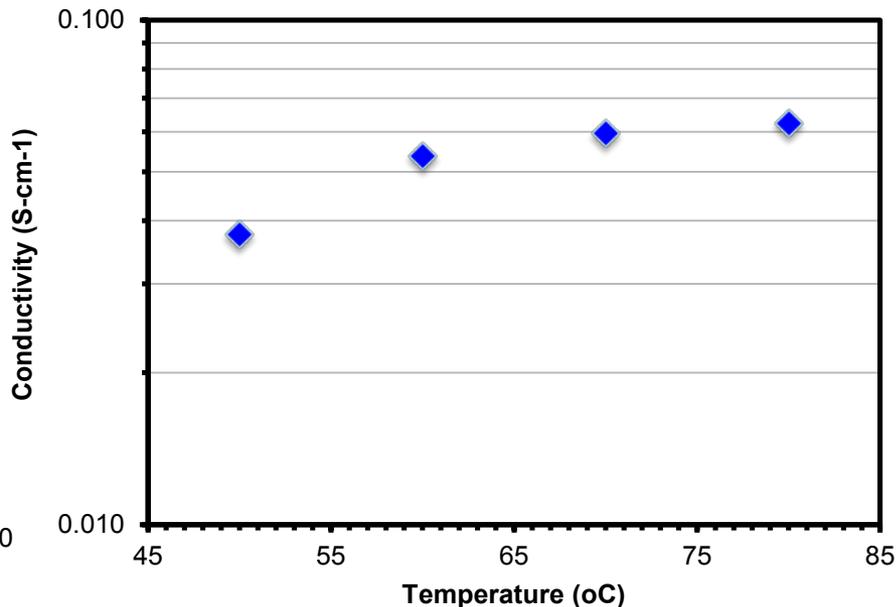


# Measurements of Best Hybrid HPA- 3M Dyneon™ Ionomer, 95% RH – New Campaign

HPA Loading less than 17wt%



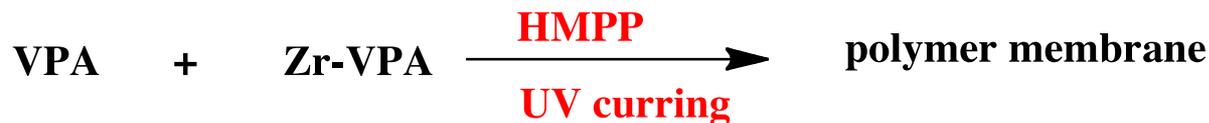
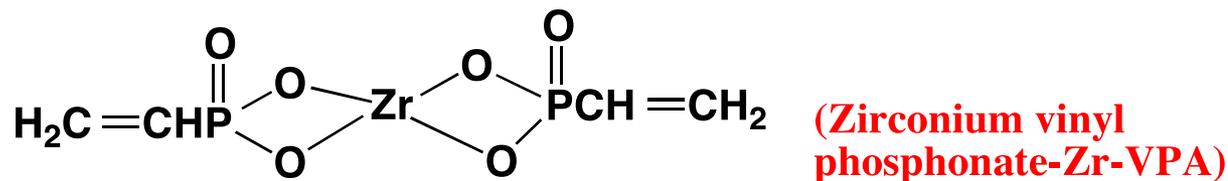
Film Thickness = 107 μm



*3M technology successfully implemented at CSM, stable HPA of >50 wt % are available, currently scaling up to allow thin film processing*

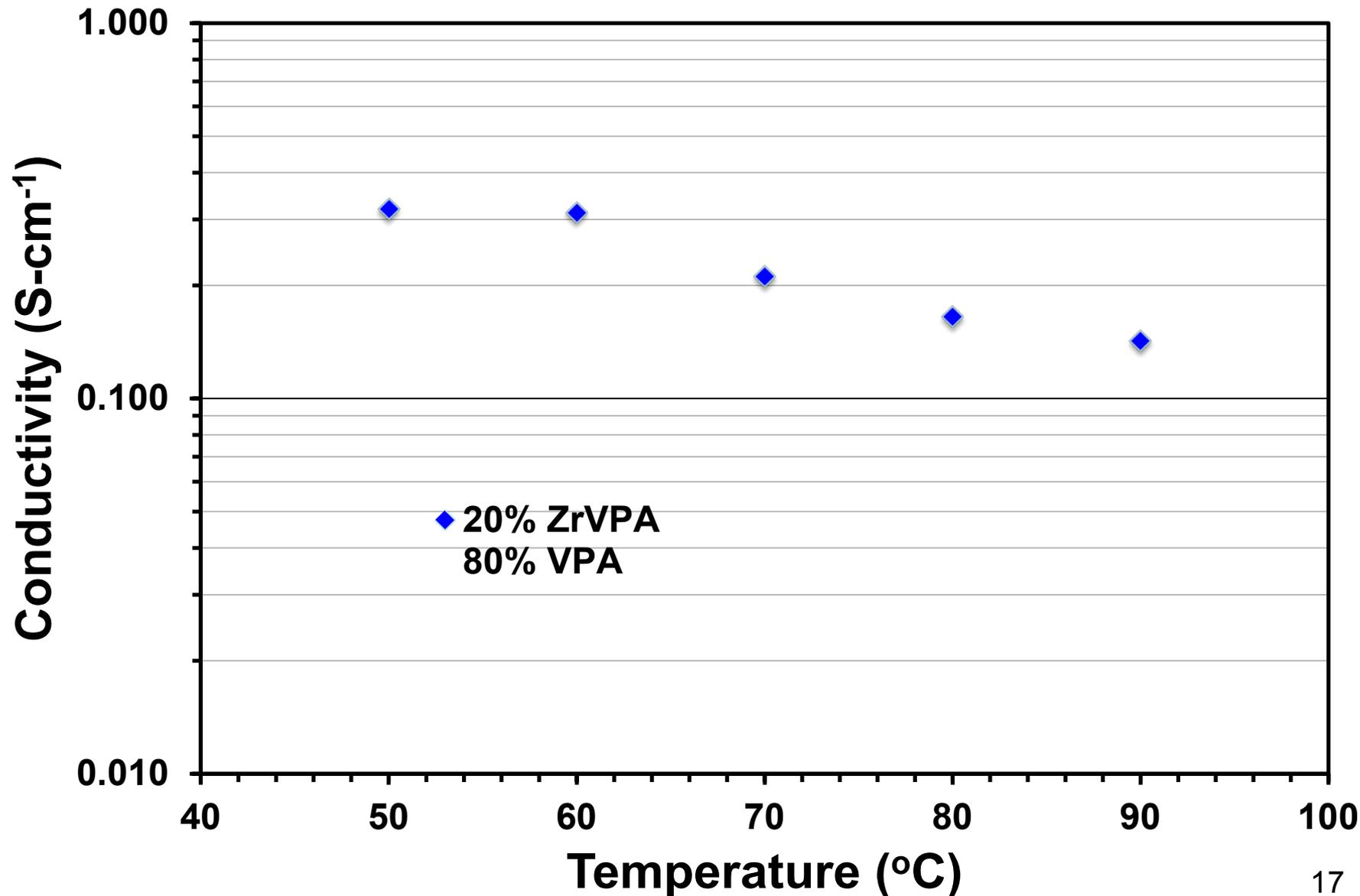


# System III – poly-Zr-VPA/VPA Membrane



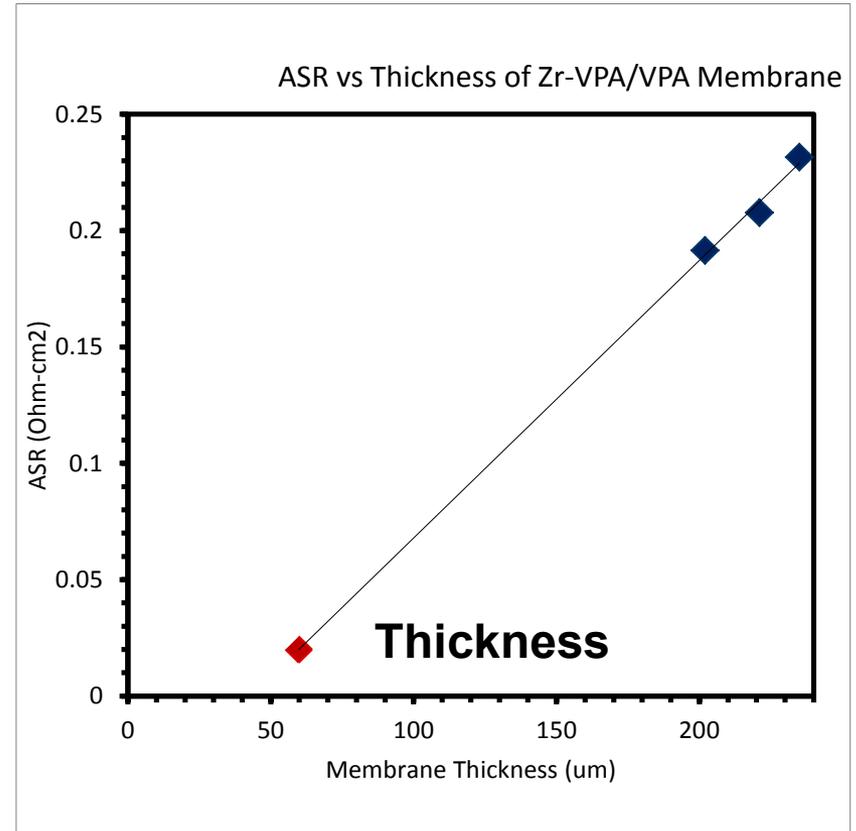
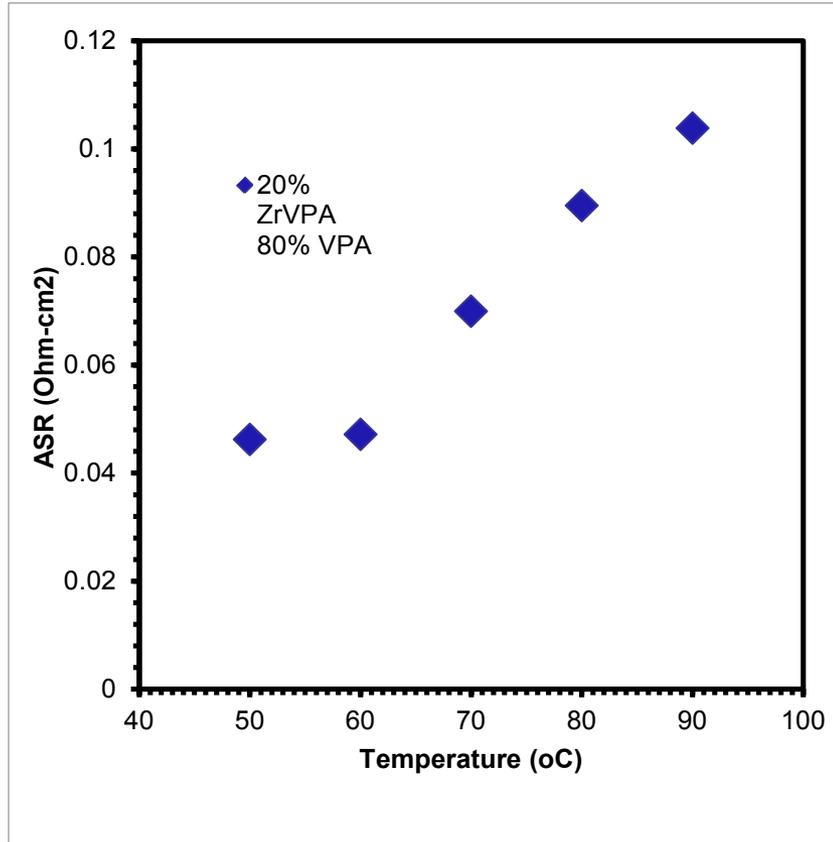


# Conductivity Measurements of best ZrVPA-VPA Membrane, 95% RH





# Need thinner membrane for 95% RH target



MCK-IX-99B: Thickness-149 μm

90°C



# Collaborations

- Prime: Colorado School of Mines – STEM University
  - Andrew Motz: Optimization of Membrane properties
  - Mei-Chen Kuo: Synthesis of System 1 and 3
  - Jim Horan: Synthesis of System 2
- Sub: Nissan R&D Americas - OEM
- National Laboratory: NREL
- Cost-Share: 3M – Component Supplier





# Remaining Challenges and Barriers

- Robust thin films with target ASRs
- Fabrication of MEAs with appropriately integrated electrodes
  - Full Fuel Cell relevant MEA testing protocol to develop membranes with durability, cost, mechanical, and performance metrics



# Future Work

## Remainder of Year 1

- Thin Films, processing CSM
  - Characterization at Nissan, NREL, 3M
- Scale Up
  - System I, optimize film forming with 3M 825 EW ionomer
  - System II, optimize HPA loading
  - System III, water stability
- Finish Pt/HPA-carbon study on heat treated Vulcan

## Year 2

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





# Summary

- Consistently High Proton Conductivity in Robust films
- 3 Film Chemistries optimized
- All will meet targets when thin

	<b>DOE Target 2017</b> $\Omega \text{ cm}^2$	<b>Result</b> $\Omega \text{ cm}^2$	<b>Thickness</b> $\mu\text{m}$	<b>Conditions</b>
System I, TFVE-HPA	0.02	0.3	180	70°C 95% RH
System II, Dyneon-HPA	0.02	0.2	107	80°C 95% RH
System III, ZrP/VPA	0.02	0.05	149	60°C 95% RH