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^2
C - Performance	ASR ≤ 0.02 Ωcm^2 max operating temp ≤120ºC and 40-80 kPa *P*(H_2O)

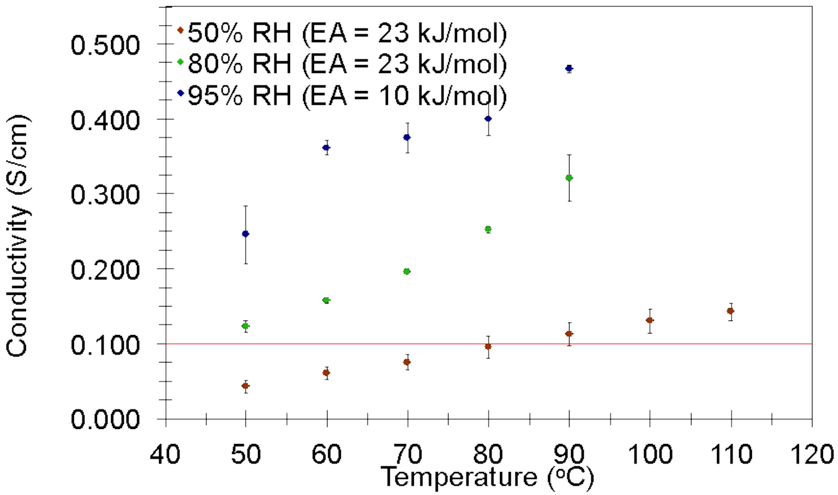
Partners

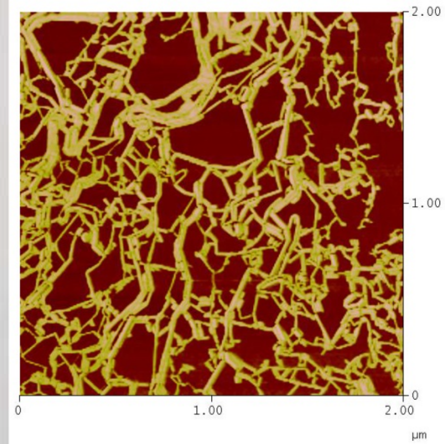
- Colorado School of Mines
- Nissan USA (sub-contractor)
- National Renewable Energy Laboratory
- 3M (in-kind partner)

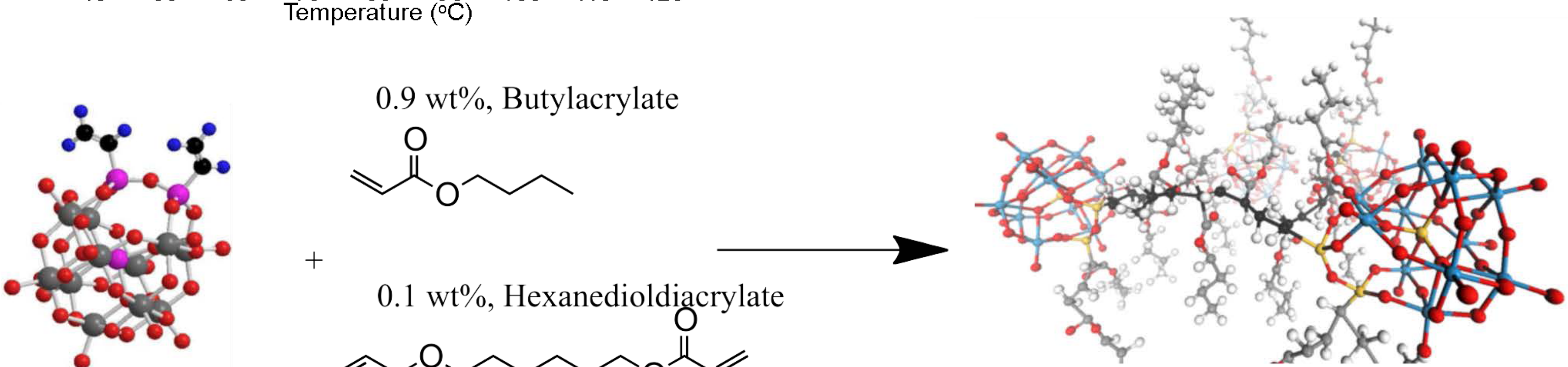
Relevance

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 – from previous funding Generation I Films – PolyPOM85v/BA







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

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^2 at 80ºC 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^2 at 80ºC and 45kPa.	50
Year 1 – Q4 Go/No Go	Demonstrate at least 1 polymer system that achieves an ASR of ≤0.02 Ohm cm^2, 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[1]

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 stroage		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%

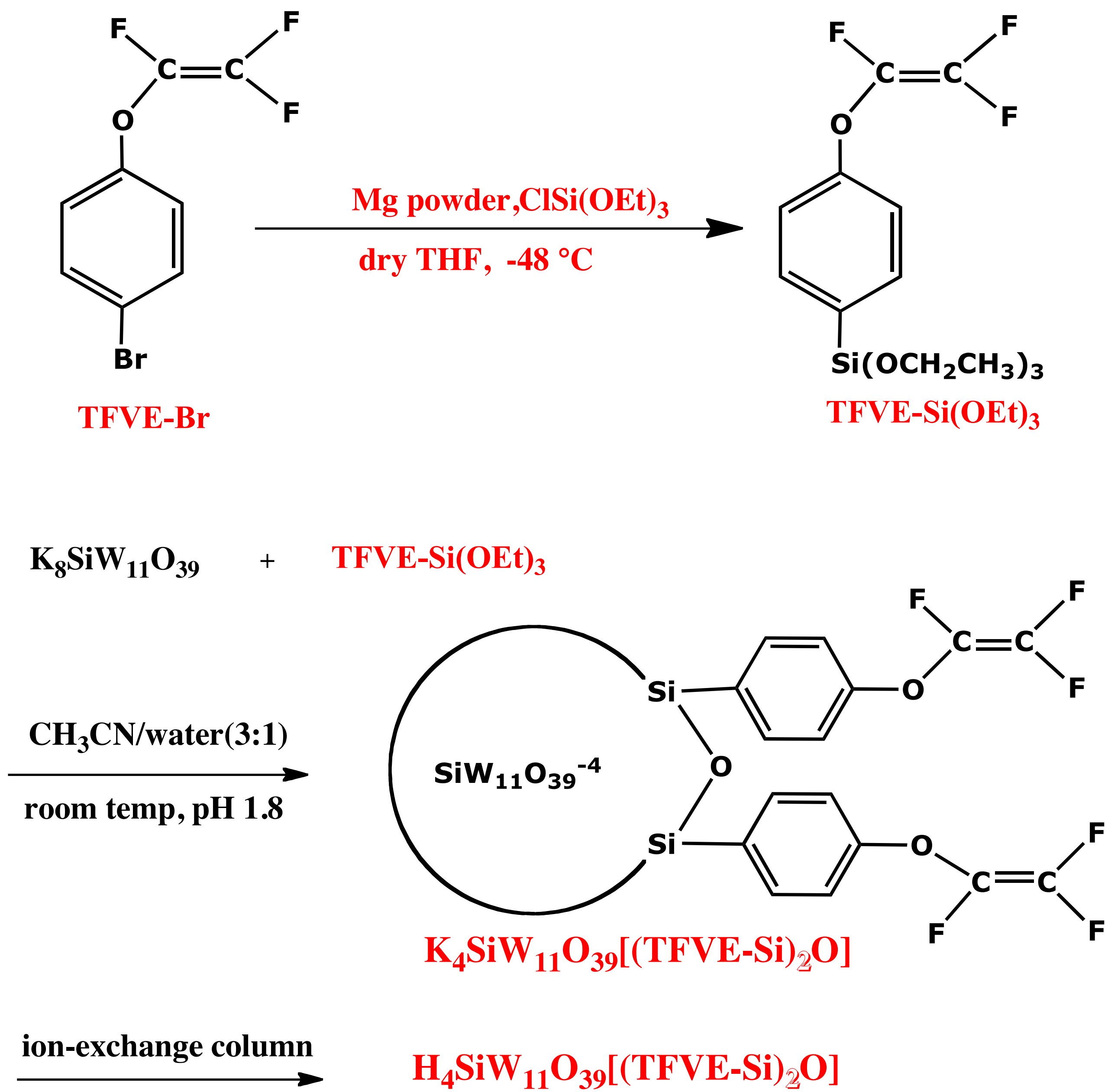
Costs as low as $40/kW could be attained at high production volumes.

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

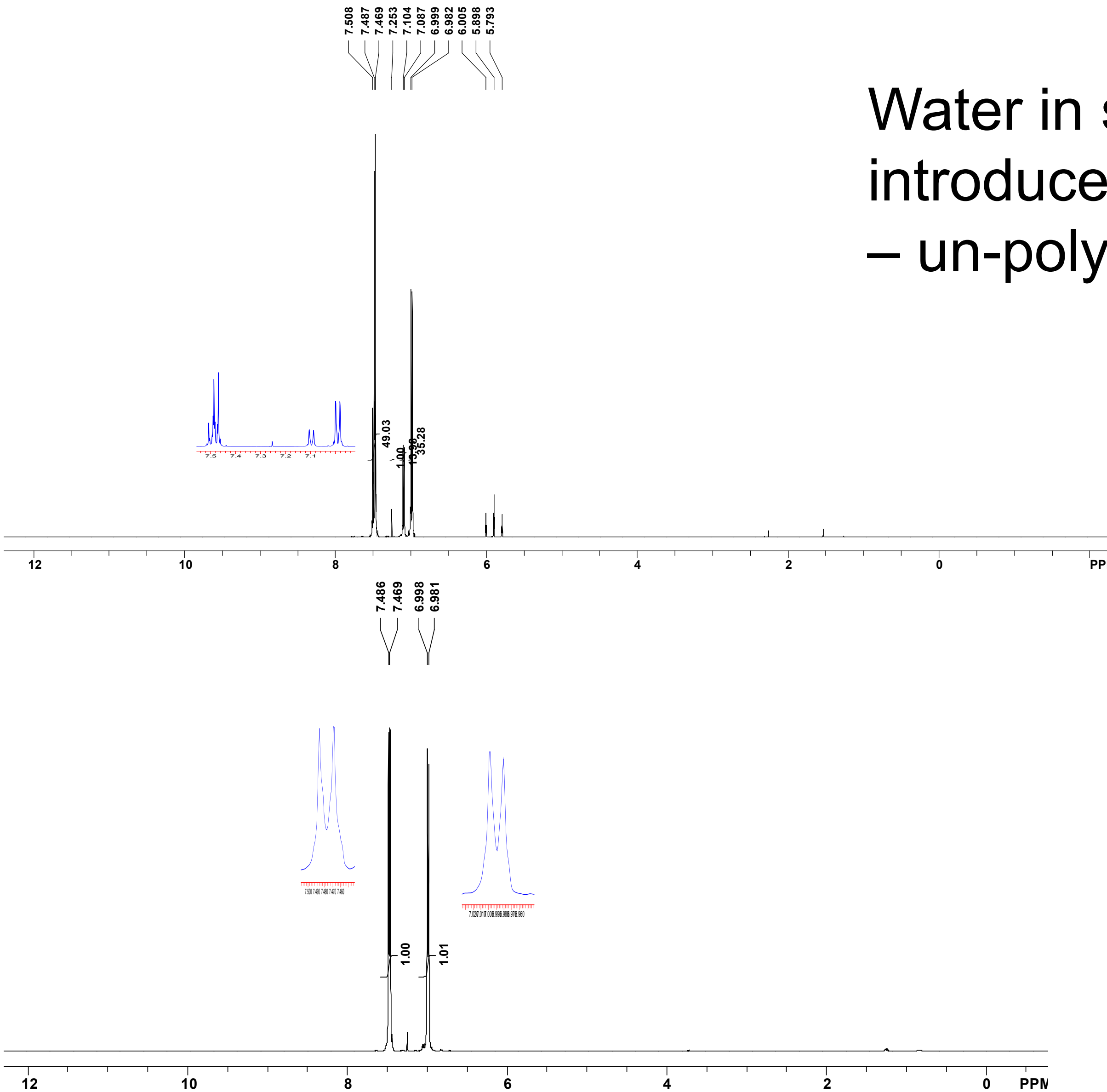
[1] Brian James, Strategic Analysis Inc. http://www1.eere.energy.gov/hydrogenandfuelcells/pdfs/sa_fc_system_cost_analysis_2012.pdf

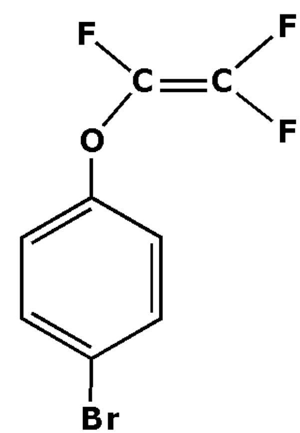
System I – TFVE-HPA Hybrid



TFVE-Br now purified

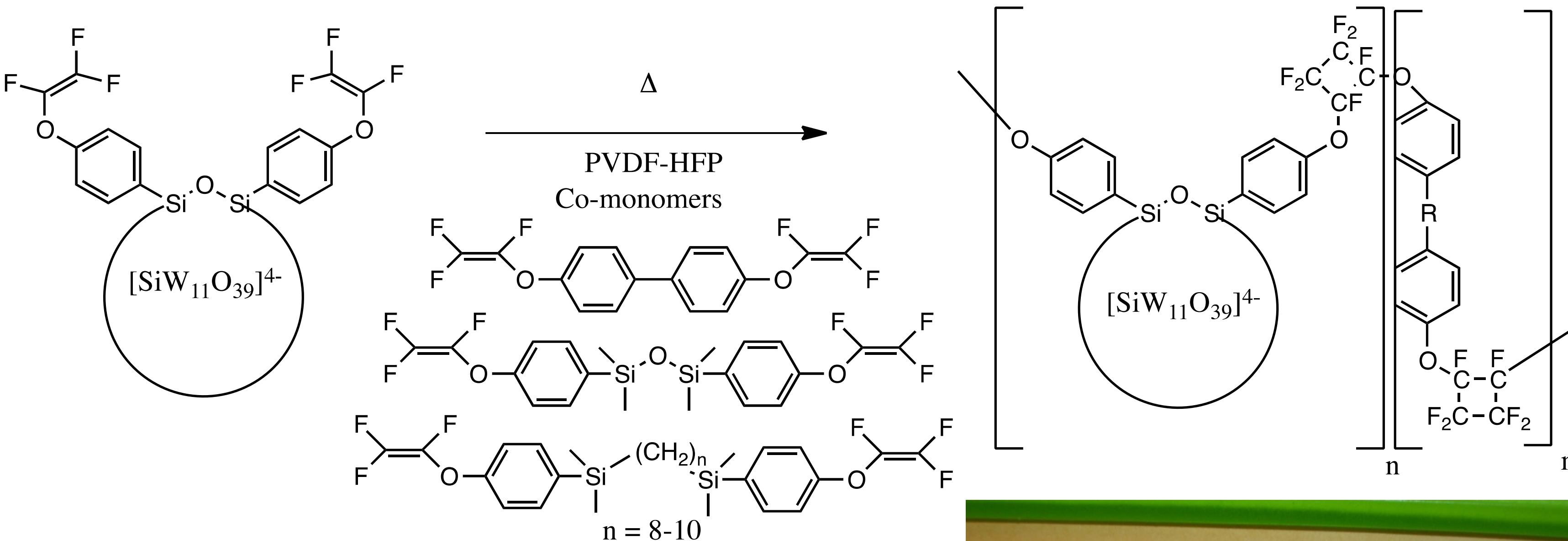
Water in system introduces hydrogen – un-polymerizable monomer



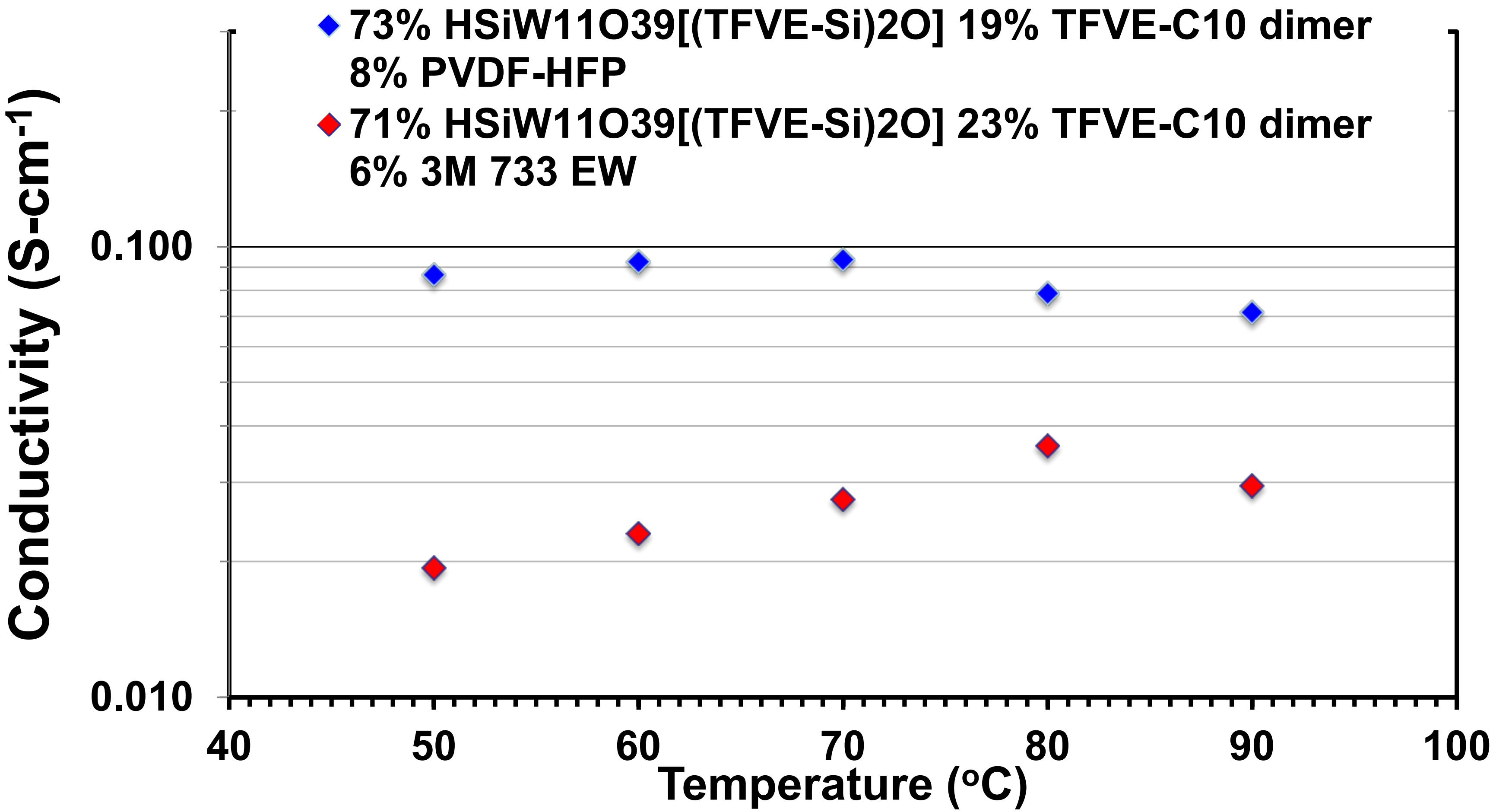


TFVE-Br

Polymerization

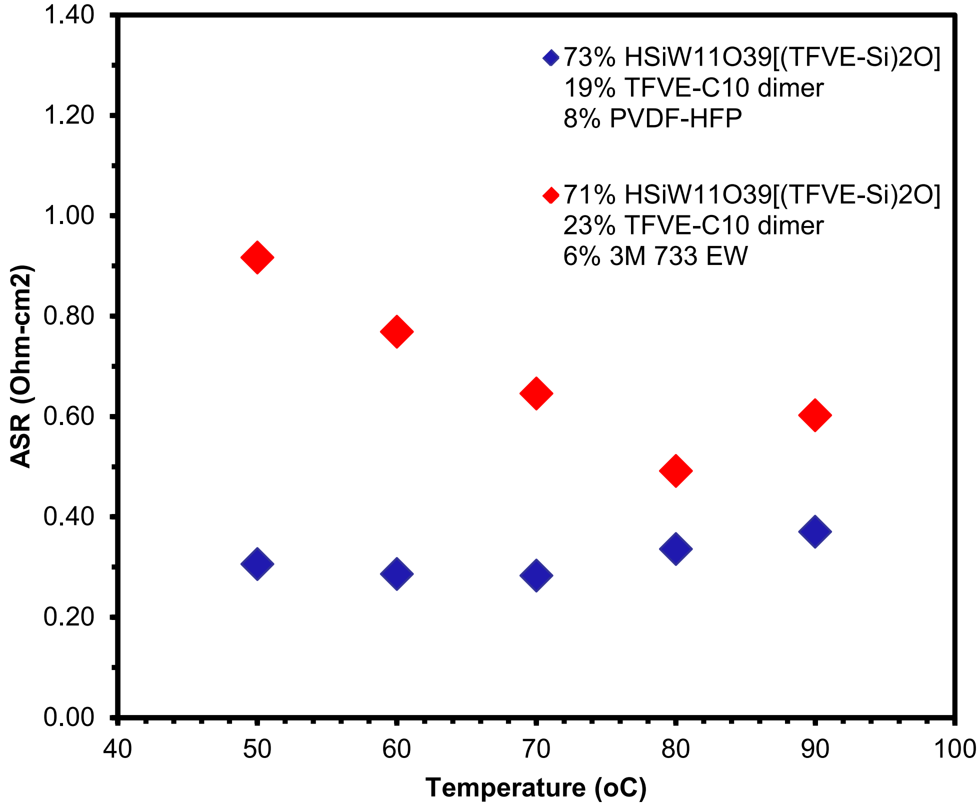


Conductivity Measurements of Best TFVE Membranes, 95% RH



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% $HSiW_{11}O_{39}[(TFVE\text{-}Si)_2O]$, 19% TFVE-C10 dimer, 8% PVDF-HFP, **189 µm**) needs to be **10 µm** thick to achieve an ASR of 0.02 Ohm-cm^2 at 70^{o}C.
- Membrane MCK-IX-90A (71% $HSiW_{11}O39[(TFVE\text{-}Si)_2O]$, 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^2 at 80^{o}C.

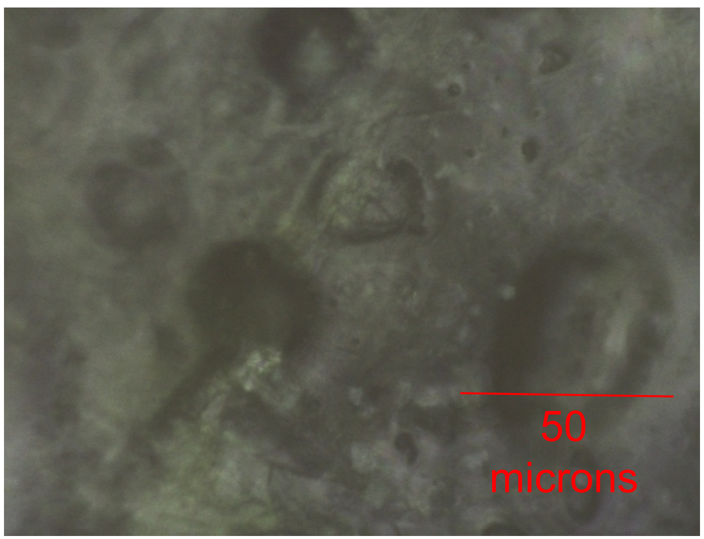
Initial TFVE membranes of new campaign, too thick, ca. 180 µm and not conductive enough, HPA loading improvements are being accomplished above old 3M achievements of 3 years ago

Film Processing Will be Key

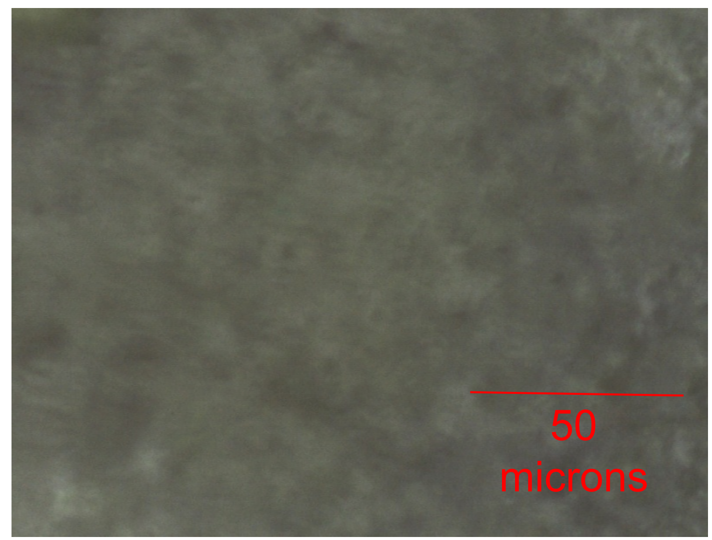
Preliminary Heat Treatment Results

Polymerization
- 73% $HSiW_{11}O_{39}[(TFVE\text{-}Si)_2O]$
- 19% TFVE-C10 Dimer
- 8% PVDF-HFP
- 120 °C

Heat Treatment
- 160 C
- 315 psi
- 3 min

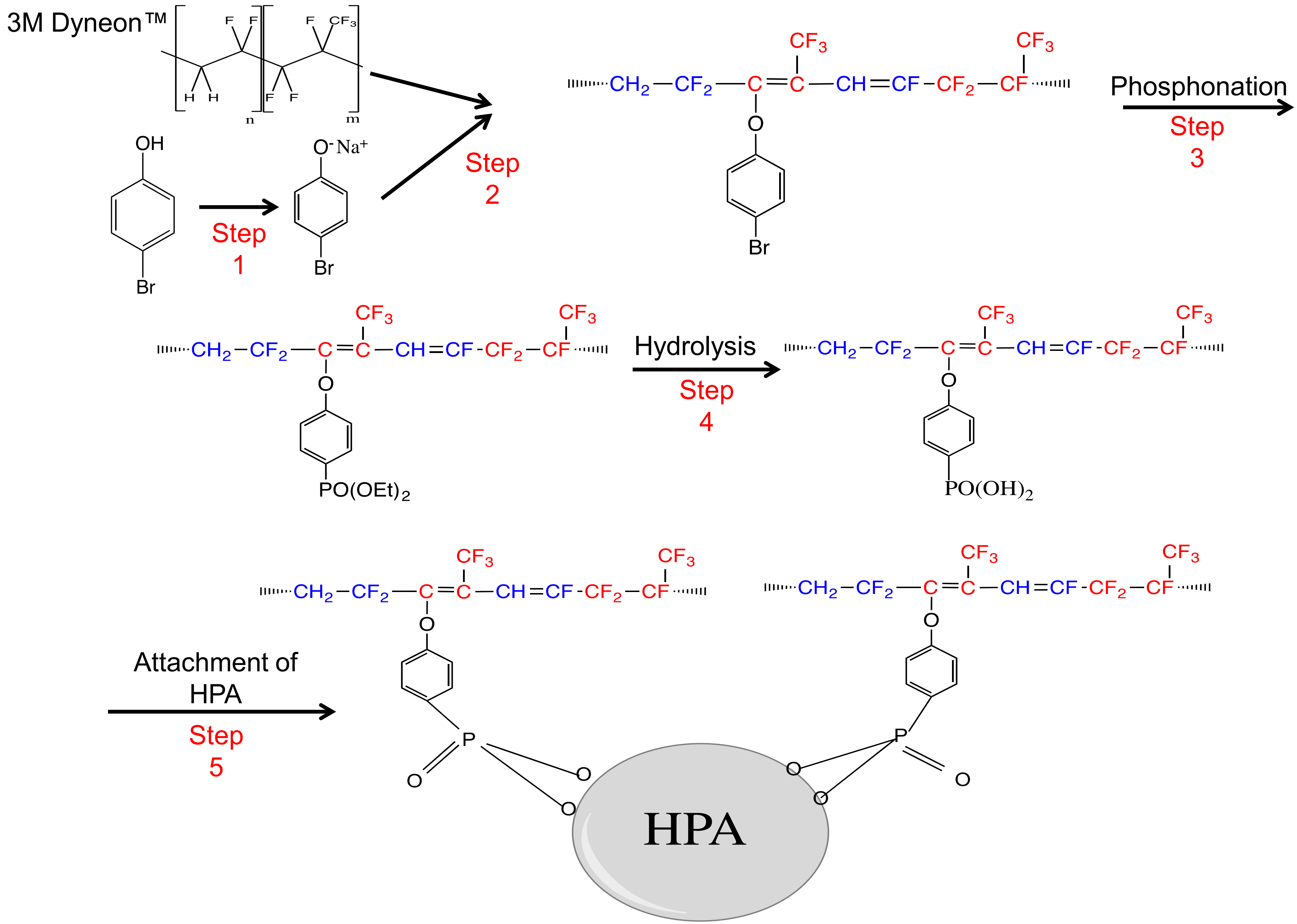


Before heat treatment,
heterogeneous, 180 μm



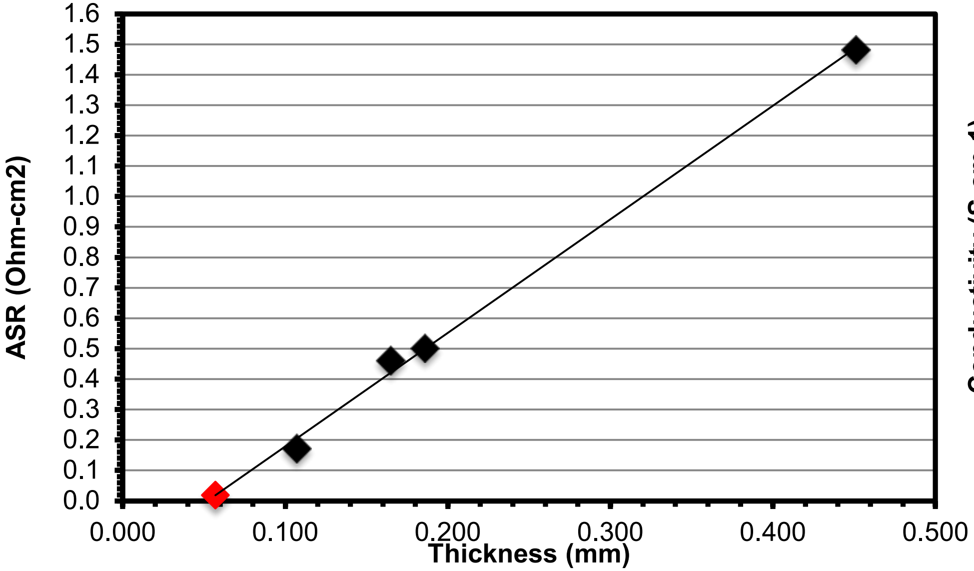
After heat treatment,
More homogeneous, 50 μm

System II – Hybrid HPA-3M Dyneon™ Ionomer

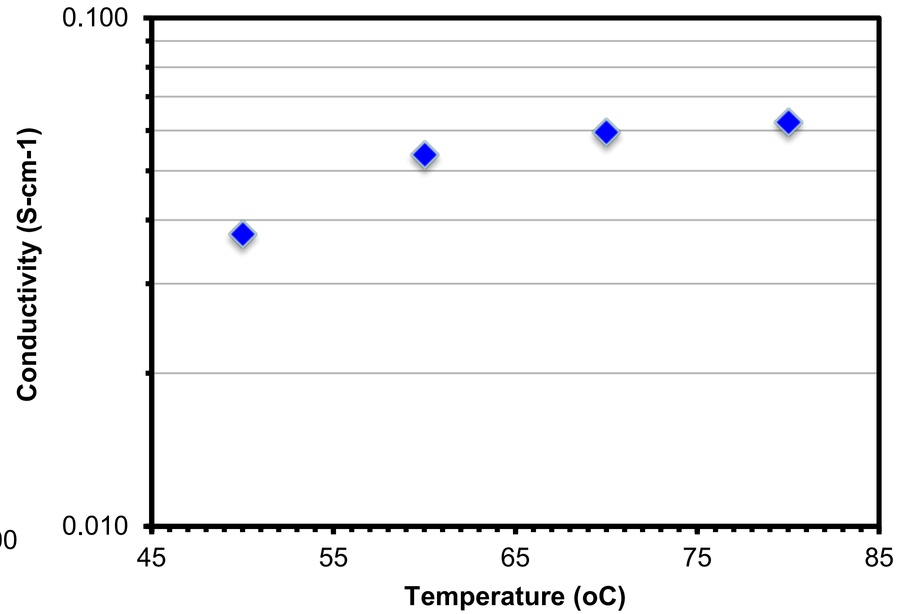


Measurements of Best Hybrid HPA- 3M Dyneon™ Ionomer, 95% RH – New Campaign

HPA Loading less than 17wt%



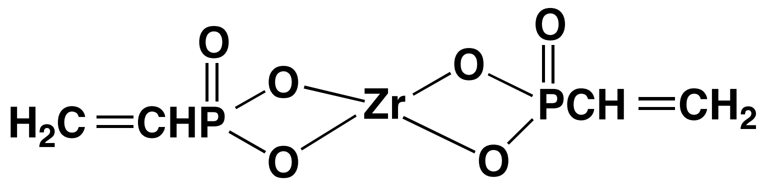
Film Thickness = 107 μm



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

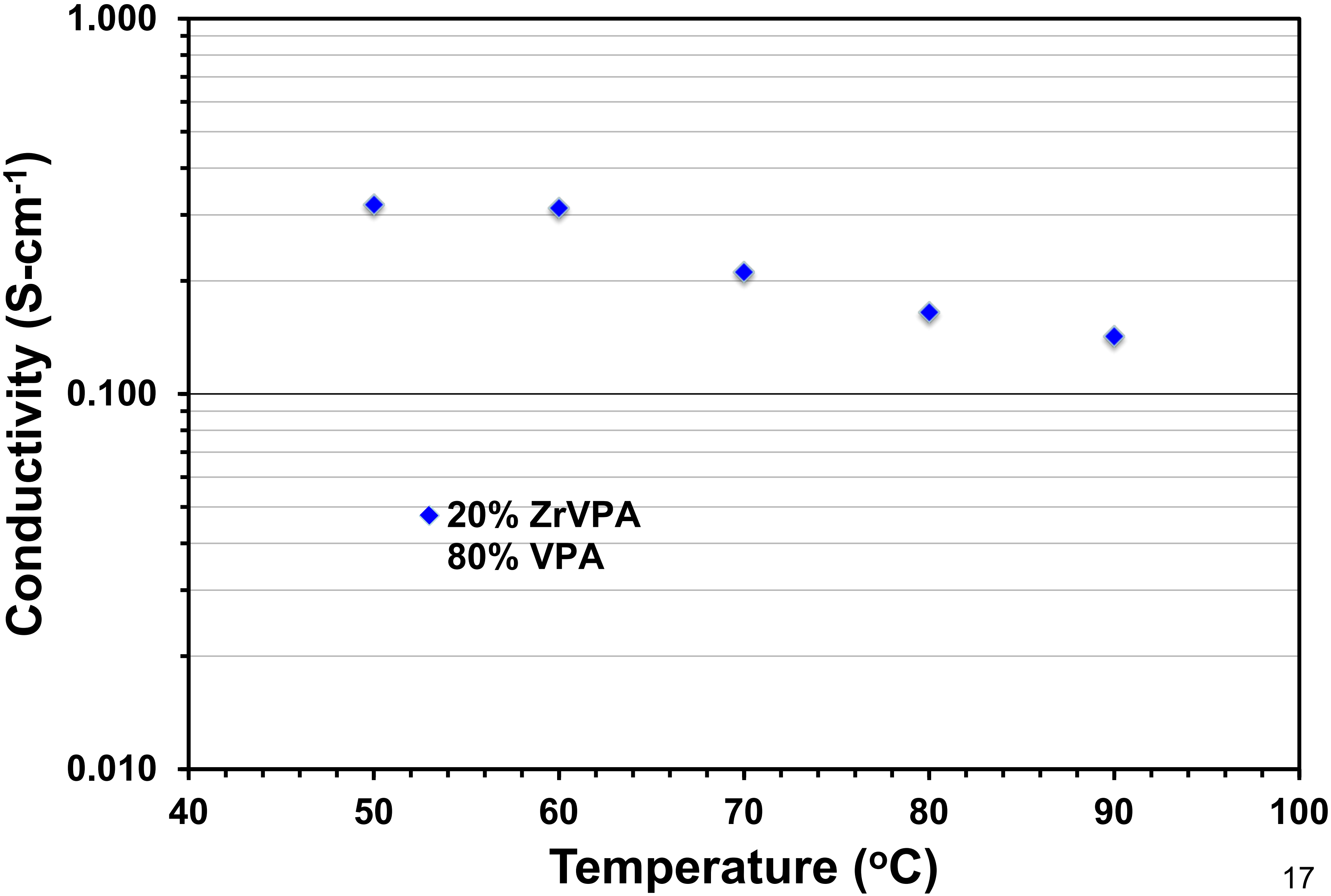
$ZrOCl_2$ + 2 CH_2=CHP(O)($OH)_2$ (VPA) —mild heating for 5 d→



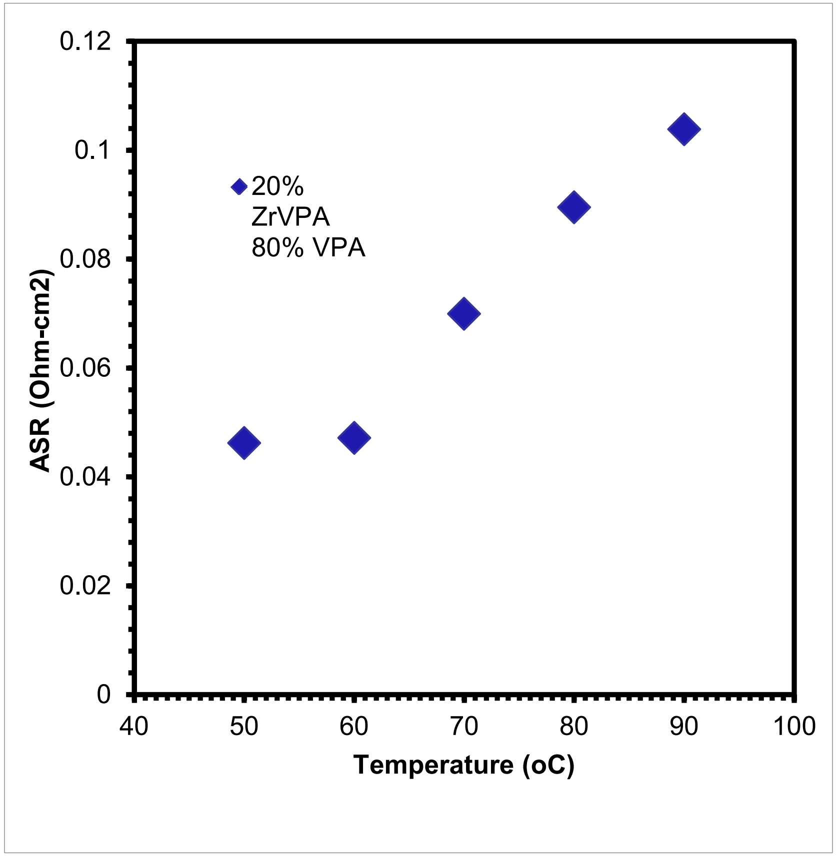
(Zirconium vinyl phosphonate-Zr-VPA)

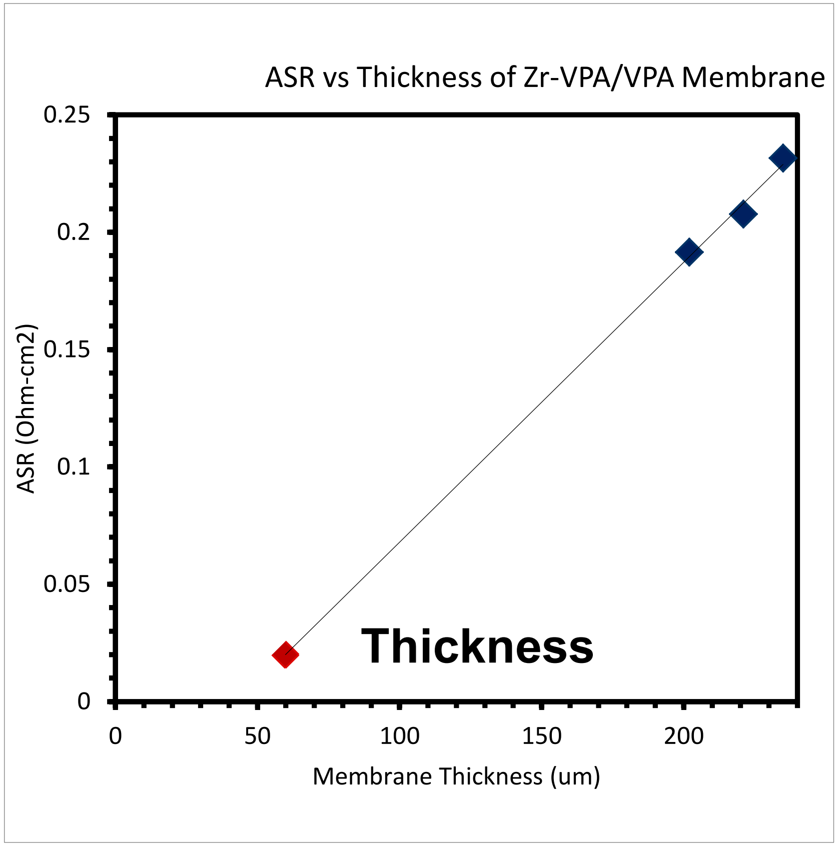
VPA + Zr-VPA —HMPP / UV curring→ polymer membrane

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

<u>Remainder of Year 1</u>

- 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

<u>Year 2</u>

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

3M NISSAN R&D AMERICAS NREL NATIONAL RENEWABLE ENERGY LABORATORY

Summary

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

	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, Dyneon-HPA	0.02	0.2	107	80ºC 95% RH
System III, ZrP/VPA	0.02	0.05	149	60ºC 95% RH