COLORADO SCHOOL OF MINES
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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: 7/30/17
- Percent complete: 66%

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 $P(H_2O)$

Budget

- Total Funding Spent as of 3/31/16: $1,000,000
- Total Project Value: $1,875,300
- Cost Share Percentage: 20%

Partners

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

9 Month No-Cost Extension Requested - Vandals Caused Millions of Dollars of Damage to Labs at Colorado School of Mines, 7/4/15

- Over $214,000 spent so far to replace equipment
- 32 instruments damaged or destroyed
- No work allowed in the lab for one month after incident
- No computers until two months after incident
- Very limited work capacity for several months after flood.
- 80-90% work capacity achieved after first of the year
- Expect full capacity work environment to be restored sometime in May
- Insurance claim for over 1,100 hours lost by research group personnel for time spent dealing with flood effects

Relevance

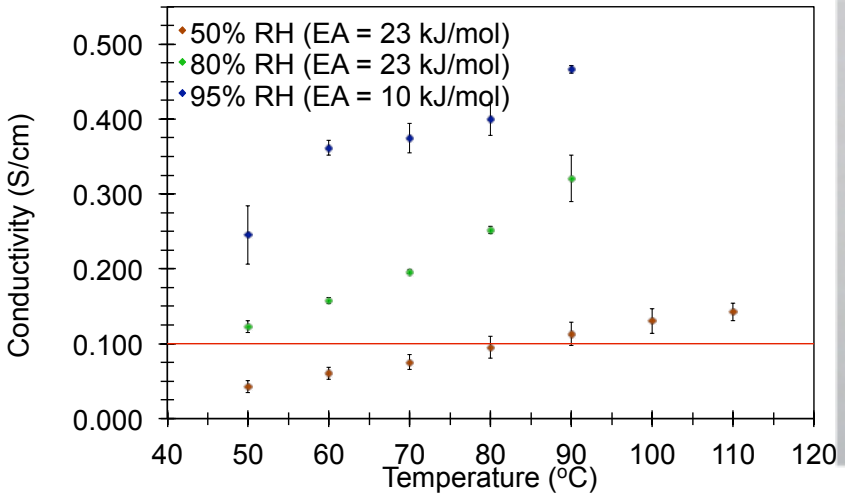
Overall	Demonstrate a low cost hybrid inorganic/polymer from super-acidic inorganic functionalized monomers with: •ASR < 0.02 Ω cm^2 at operating temperature of an automotive fuel cell stack (95-120ºC) at low inlet RH <50% •50 cm^2 MEA with desired mechanical properties and durability
2014	• Optimize three different candidate hybrid inorganic/polymers in practical systems for low ASR, then eliminate one system • Barrier C
2015/16	• 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
2016/17	• 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

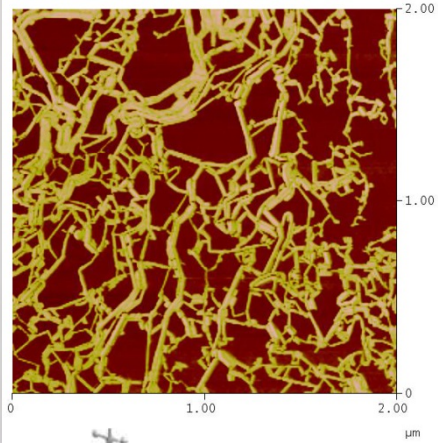
Approach

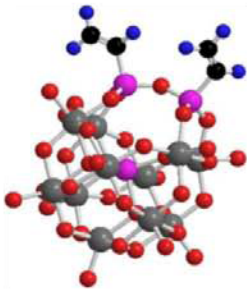
- Material Synthesis based on functionalized super acidic inorganic moieties, ***Generation II Films (Chemically stable)***
  - Heteropoly acid (HPA) functionalized monomer (TFVE) polymer system (To be phased out)
  - FC-2178 functionalized with HPA (Looking extremely promising)
- All systems have tunable 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

Approach - Learning from Generation I Films

High and dry conductivity, but ester linkage susceptible to hydrolysis

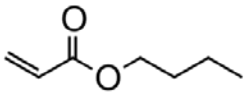






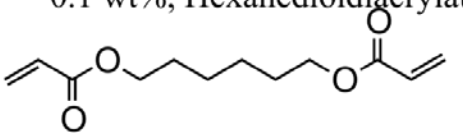
3wt%,
$H_4[SiW_{11}O_{40}(Si(CH=CH_2))_2]$

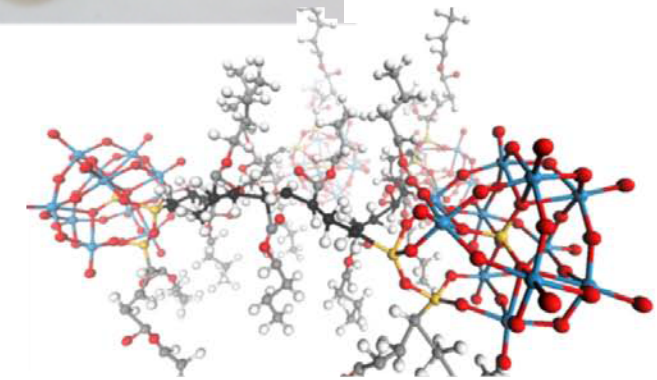
0.9 wt%, Butylacrylate



+

0.1 wt%, Hexanedioldiacrylate





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

Films generally thick but ASR <0.02 Ω cm^2

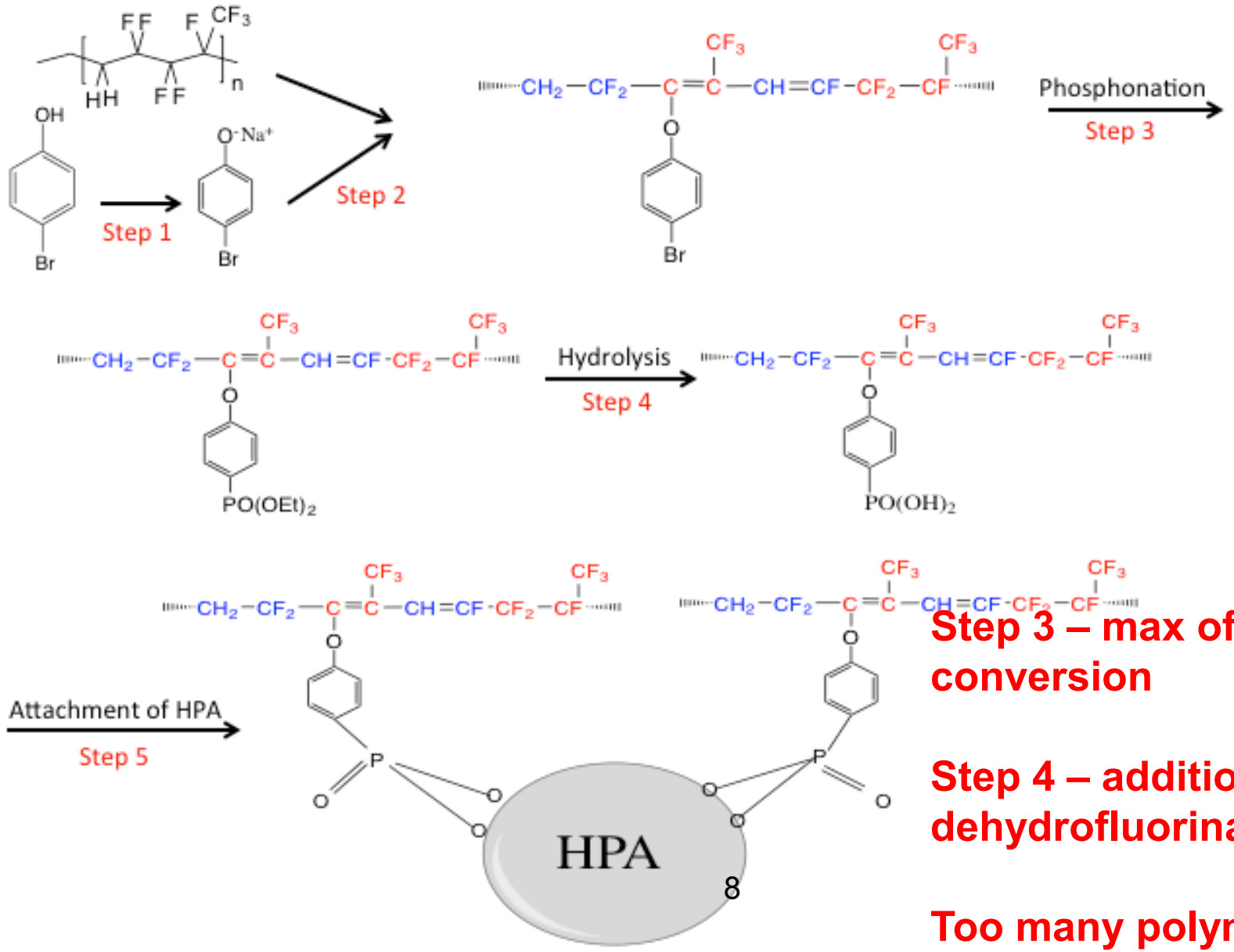
J.L. Horan, A. Genupur, L. Ren, B.J. Sikora, M.-C. Kuo, F. Meng, S.F. Dec, M.H. Frey, G.M. Haugen, M.A. Yandrasits, S.J. Hamrock, and A.M. Herring,* *Chem. Sus. Chem.*, **2009**, *2*, 226.

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.

FY 2016 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.	100
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.	90

Initial Chemical Synthesis Route

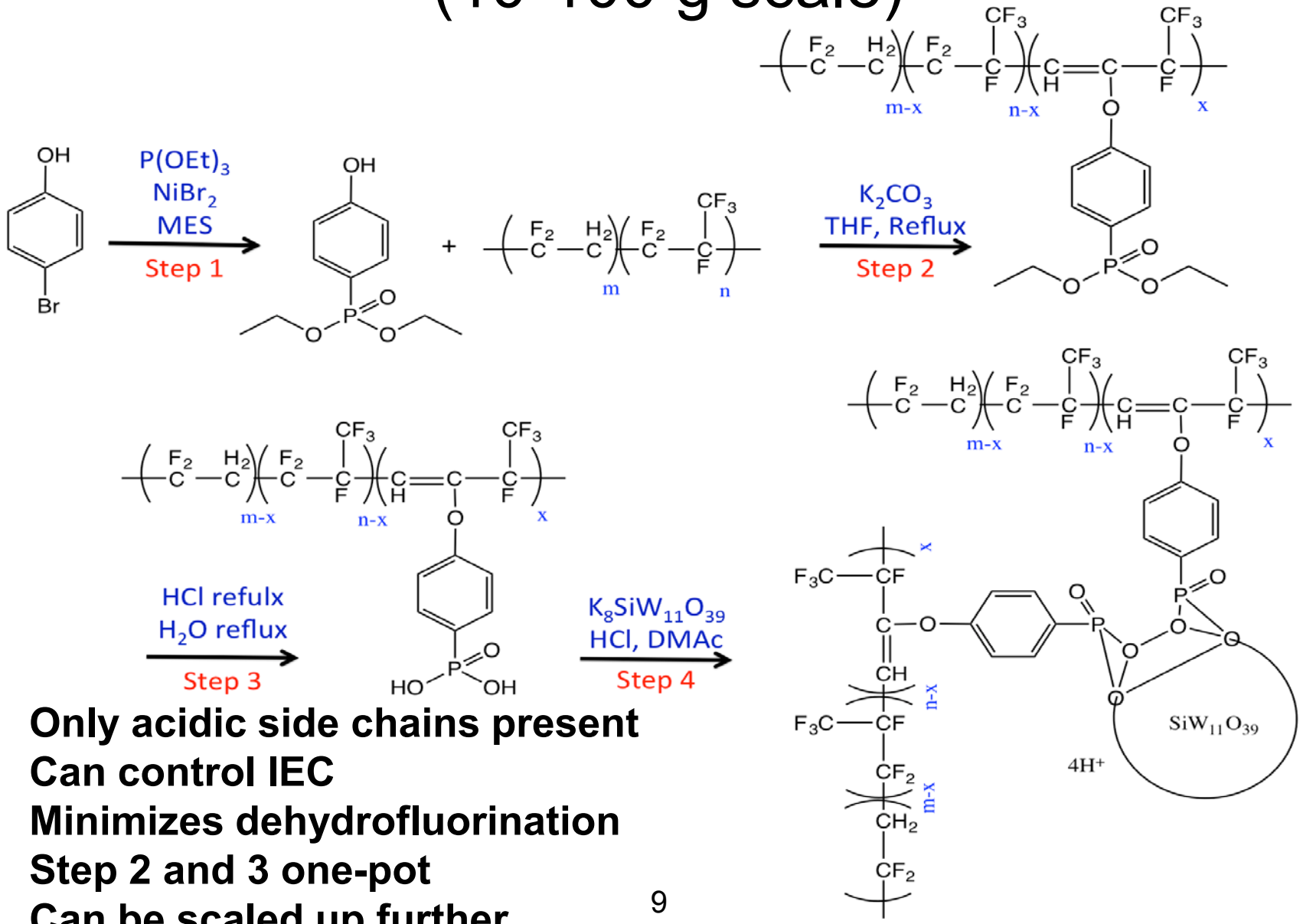


Step 3 – max of 47% conversion

Step 4 – additional dehydrofluorination

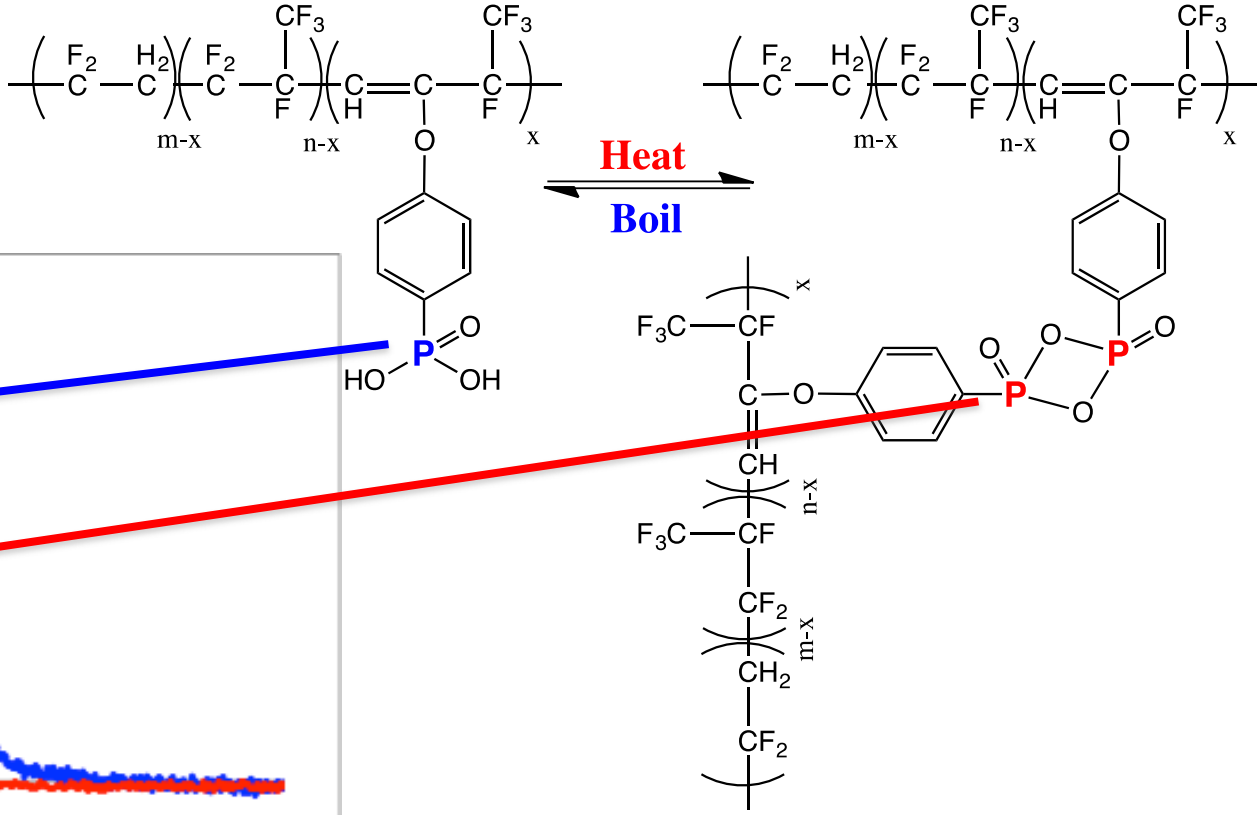
Too many polymer steps

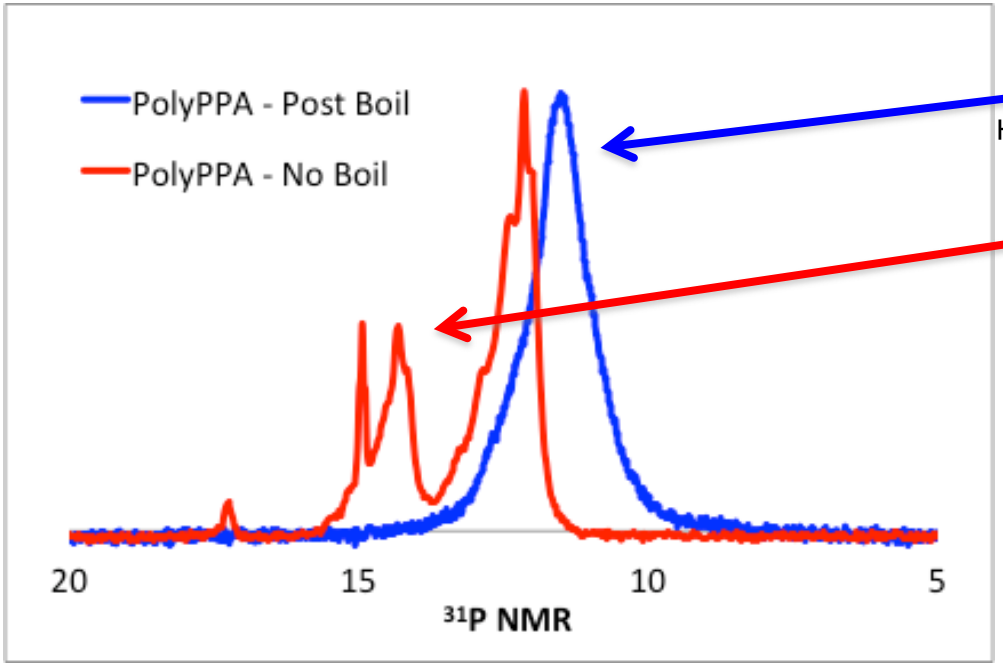
Improved, Efficient, High Yield Synthesis (10-100 g scale)



- **Only acidic side chains present**
- **Can control IEC**
- **Minimizes dehydrofluorination**
- **Step 2 and 3 one-pot**
- **Can be scaled up further**

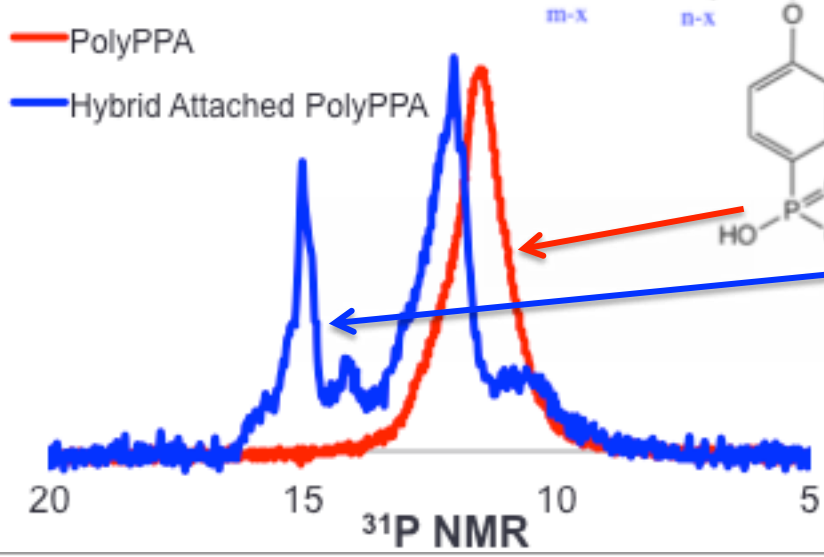
Synthesis stopped at Anhydride, however easily removed by boiling

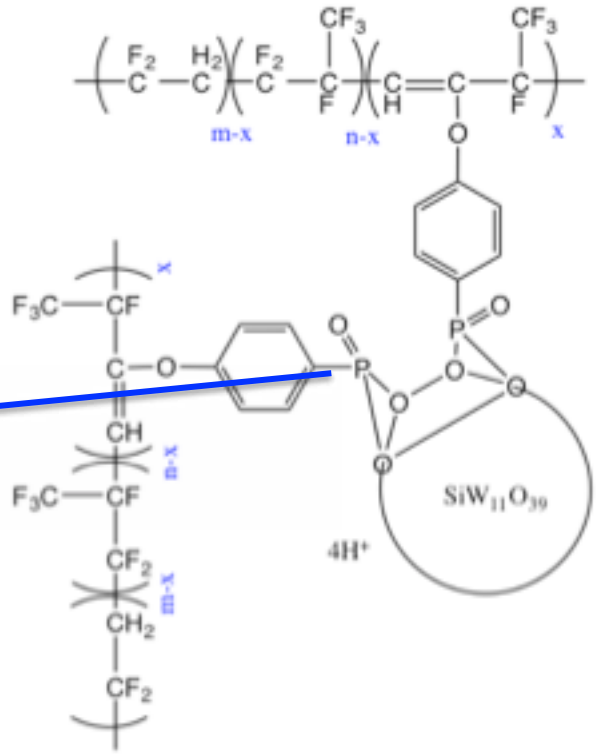


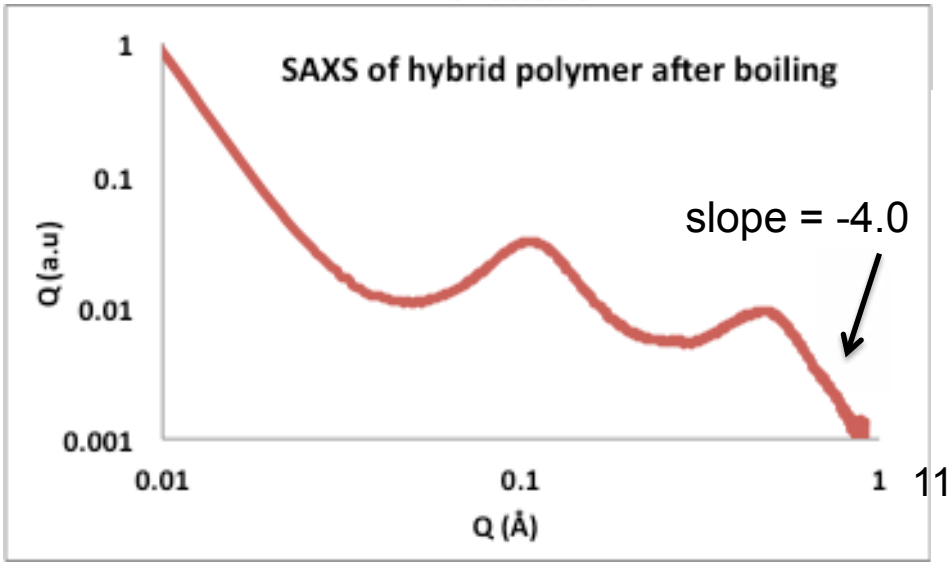


- **HCl reflux followed by water reflux results in full conversion and no further dehydrofluorination**
- **Routinely make 20 g. batches plan to scale up to 100 g.**

HPA covalently attached to polymer







- **NMR of PolyPPA and reaction solution shows covalent bonding of HPA**
- **SAXS after boiling film shows 1nm spheres indicating HPA is stable to boiling**

HPA loading

- Reaction solution was cast and dried with a target of 70wt% HPA loading

- After soaking in water and drying, the HPA loading is 60% - as we improve processing losses are decreasing

Weight Percent Waterstable HPA				
Mass of dried hybrid polymer (70% HPA)	0.2901	0.1959	0.2273	
Mass of hybrid polymer after soak in 60°C water	0.2213	0.1495	0.1719	
Mass Loss (assume all HPA)	0.0688	0.0464	0.0554	
Mass of HPA remaning	0.13427	0.09073	0.10371	Average
Weight% HPA stable to water	**60.7%**	**60.7%**	**60.3%**	**60.6±0.2 %**

IEC of new material

IEC of PolyPPA*	
Target IEC	4.0
IEC from yield	4.1
IEC from ^{31}P NMR	3.8±0.4

* Only half of protons are dissociable, causing large error in titrations

$$IEC_{Hybrid}(x) = \frac{4\ mmol\ H^+}{1\ g\ PolyPPA + x\ grams\ HPA}$$

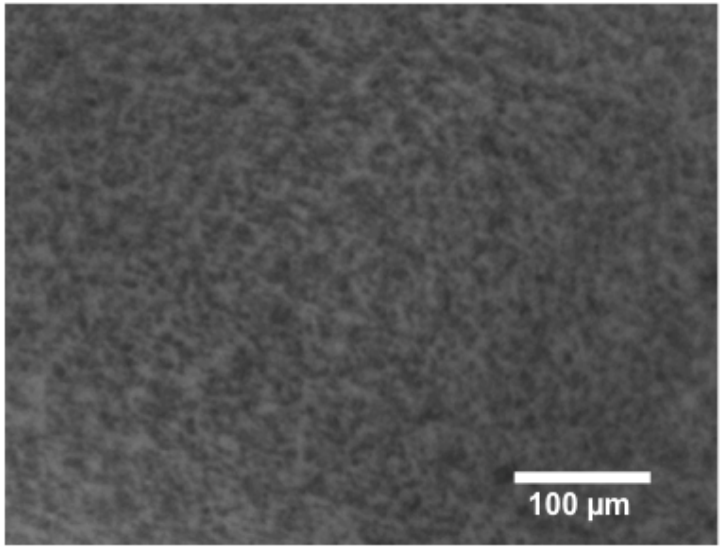
Wt% HPA	Total Hybrid IEC
50%	2.0
60%	1.6
70%	1.2
80%	0.8

IEC will go down with addition of HPA because mass increases and amount of H^+ remains constant, however volumetrically we don't know and films behave like high IEC materials

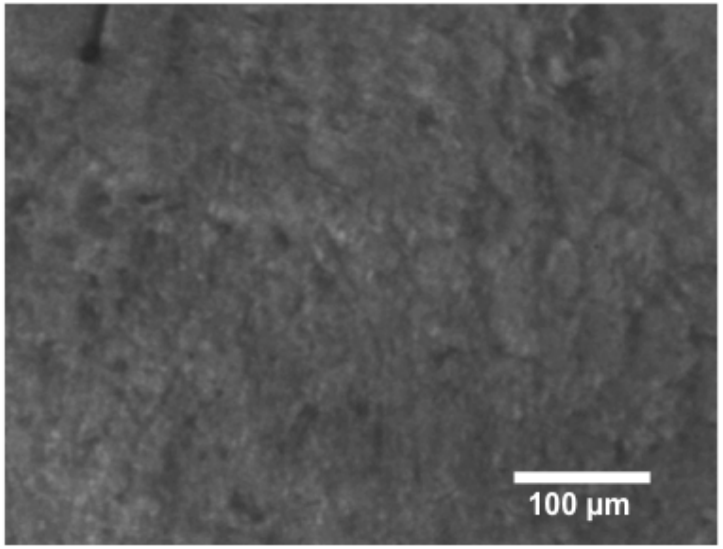
Swelling reduction with processing

	Water uptake (mass%)			
	Film 1	Film 2	Film 3	Average
Unprocessed film	118%	107%	108%	111±5 %
Processed film	56%	40%	39%	45±7 %

Pre annealed film



Annealed film

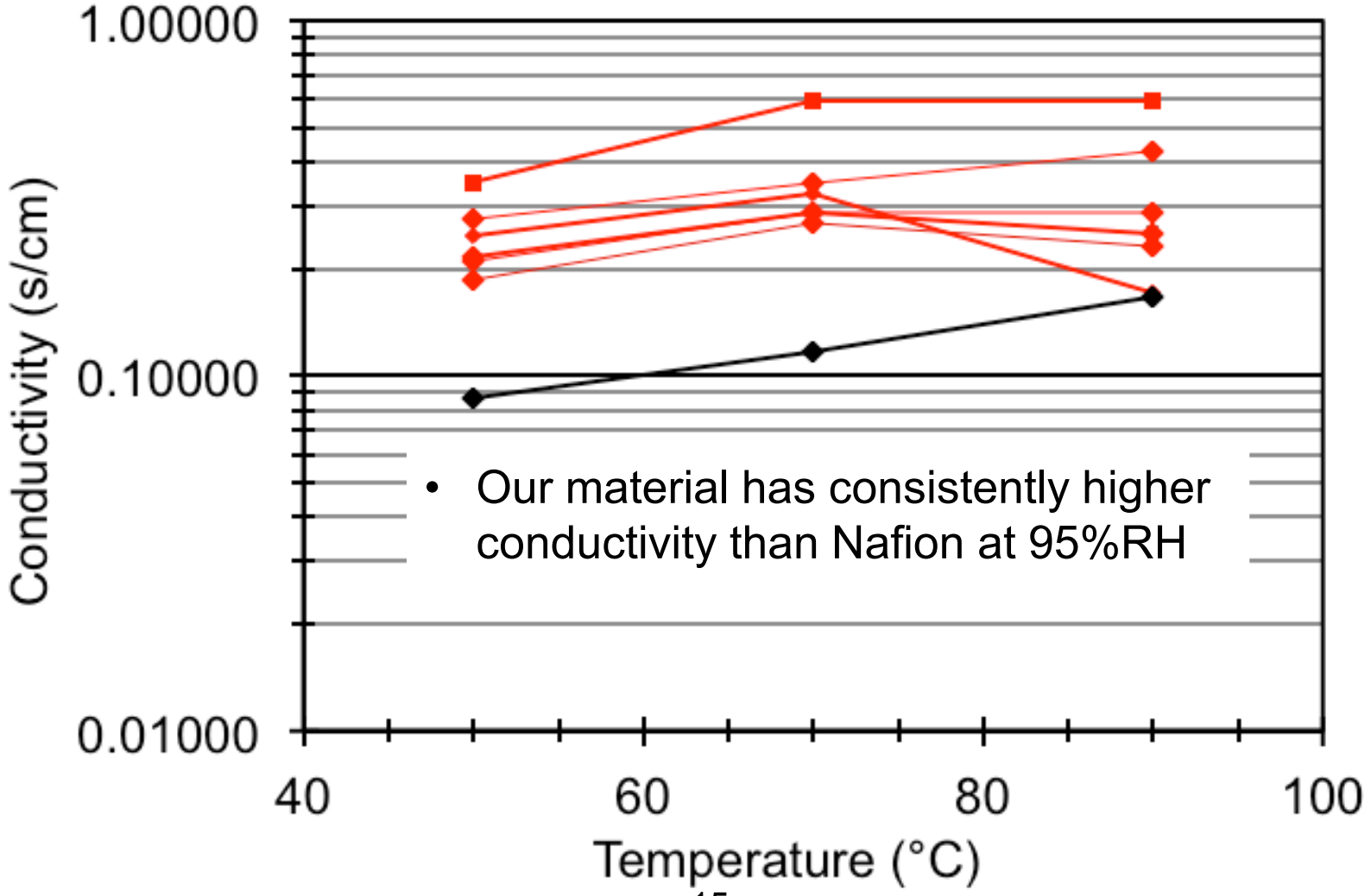


- **Improving crosslinking process may greatly reduce swelling**

Conductivity @ 95%RH

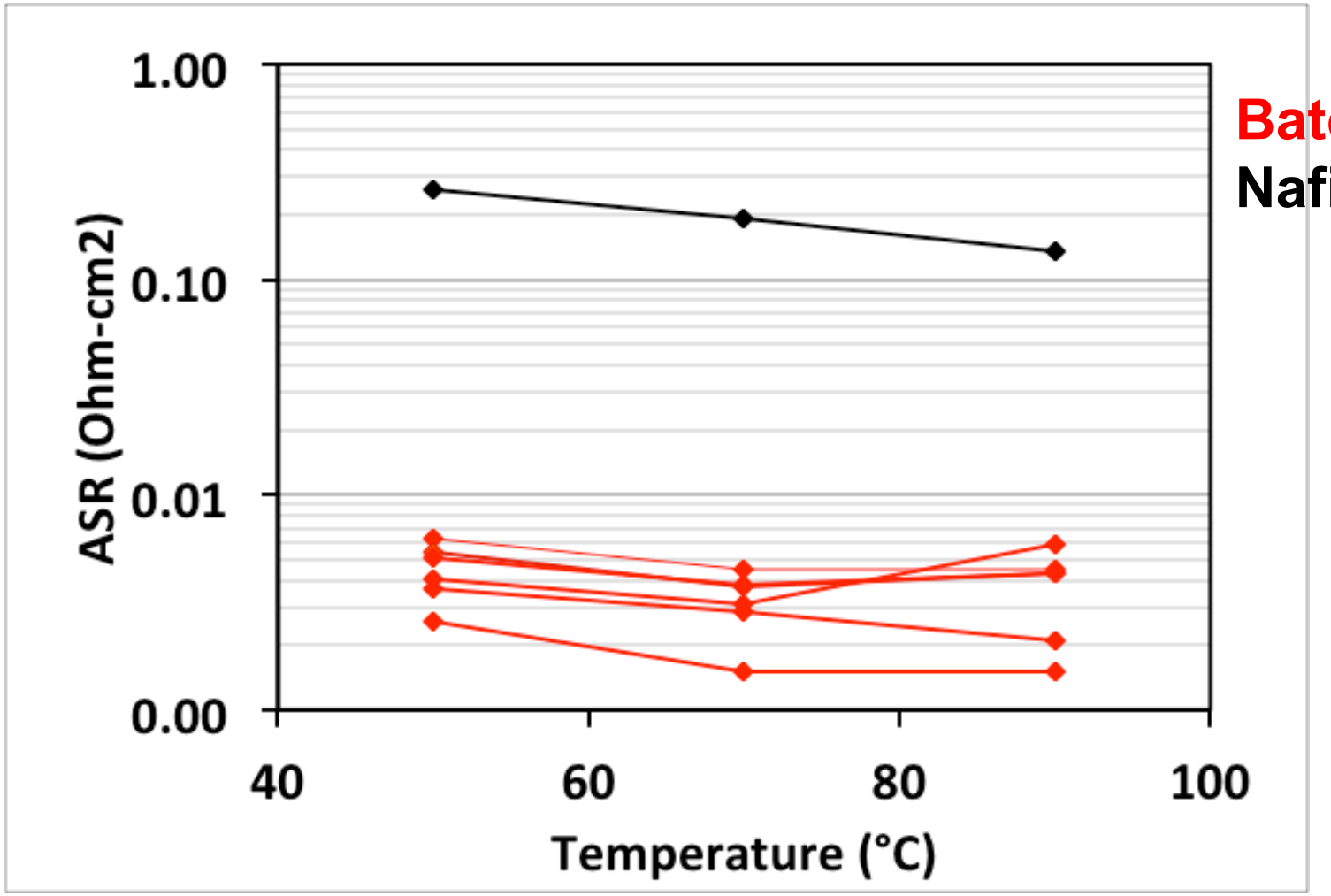
Batch1 – 70%HPA

Nafion 117



- Our material has consistently higher conductivity than Nafion at 95%RH

ASR @ 95%RH

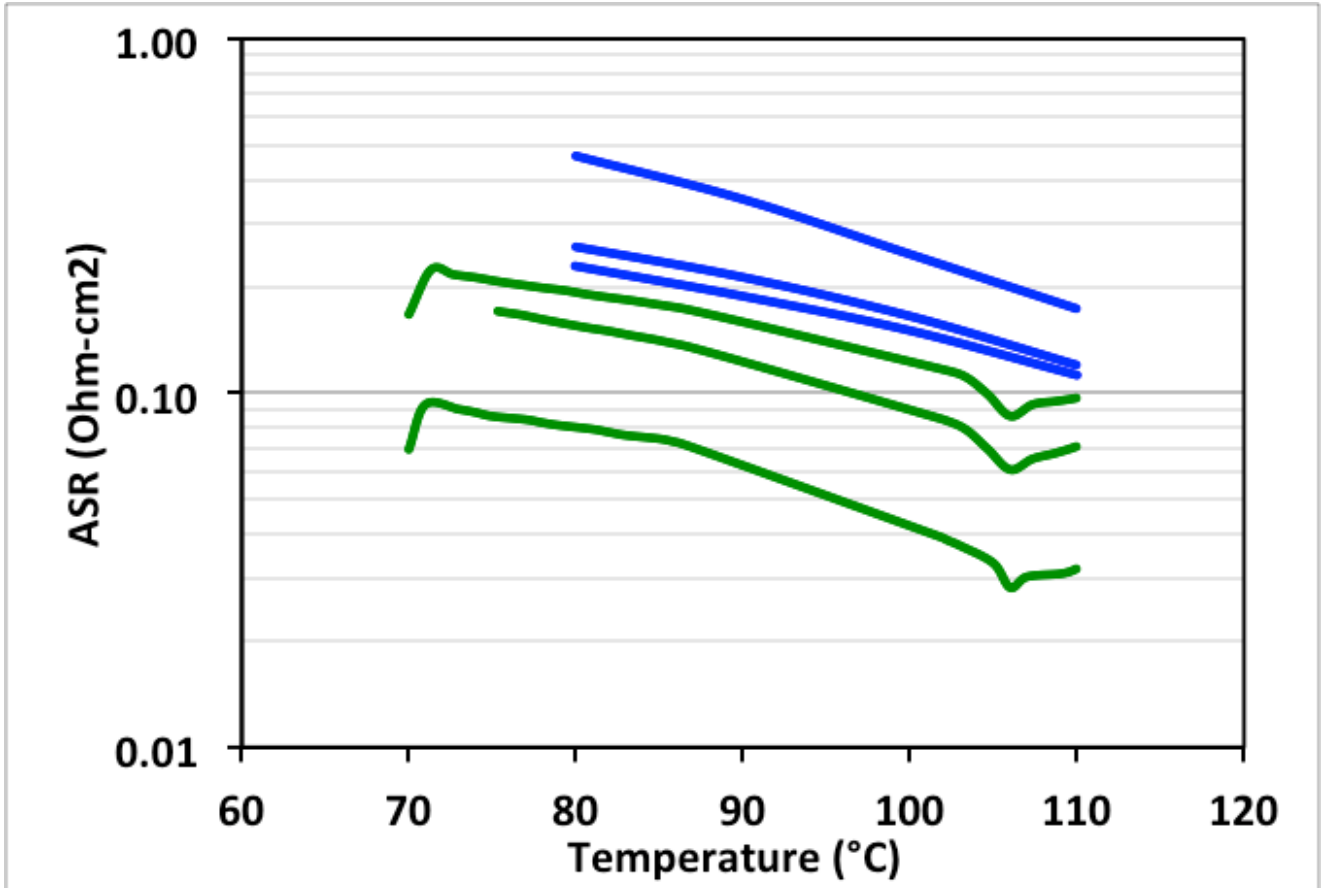


In full temperature sweeps,30° C ASR target easily met

ASR @ 50%RH – thin films

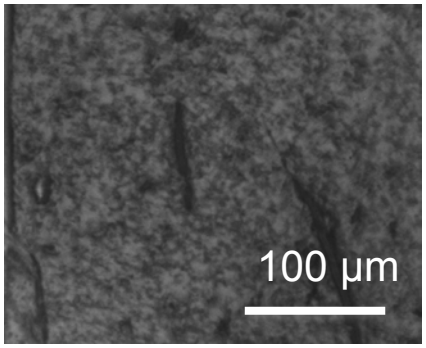
Batch1 – 70%HPA

Batch2 – 80%HPA

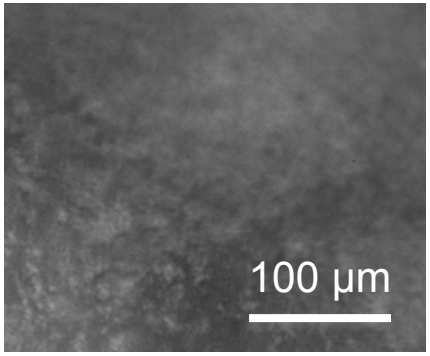


- Higher HPA loading, quality control, and better annealing process are showing progress

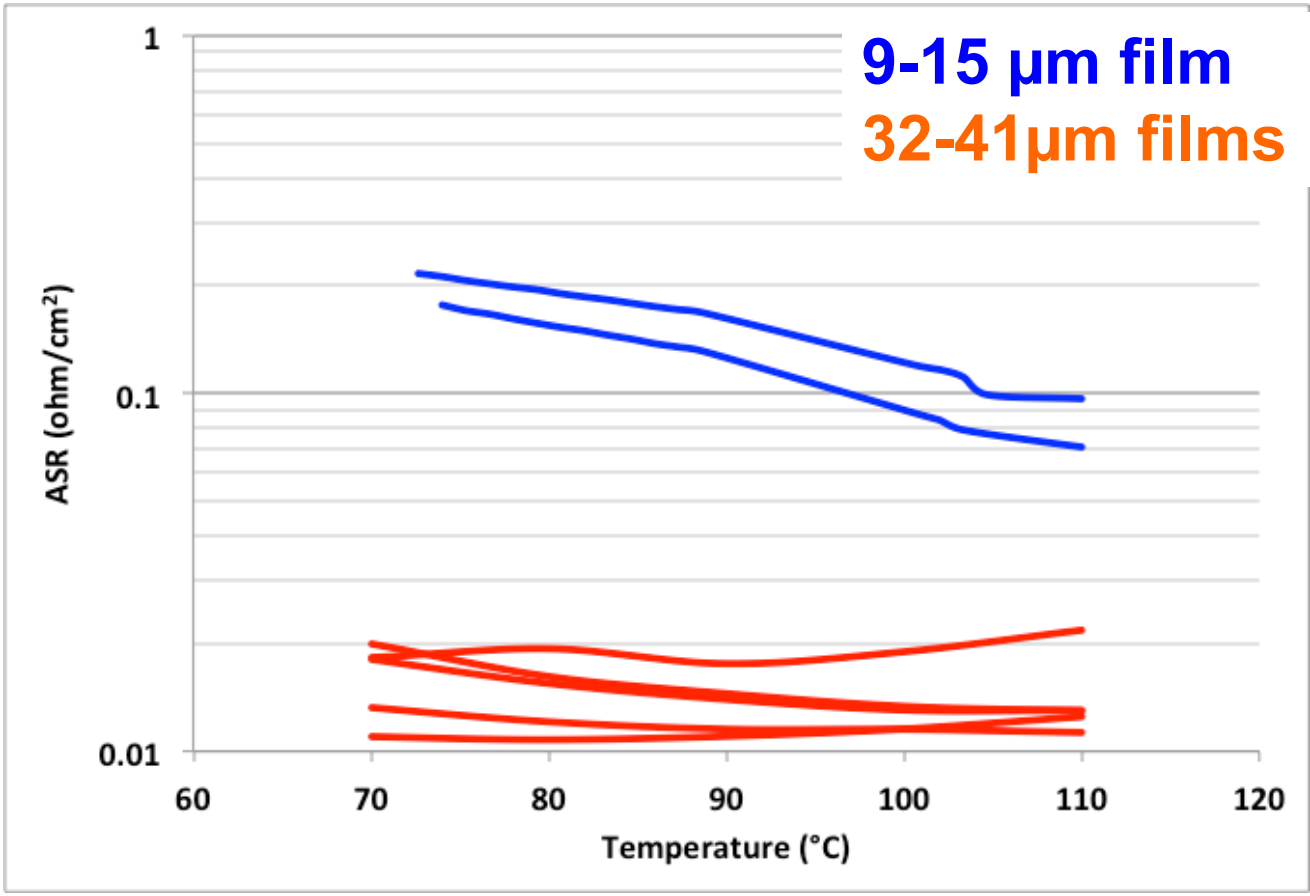
ASR at 50%RH - Thicker Films



10µm thick film

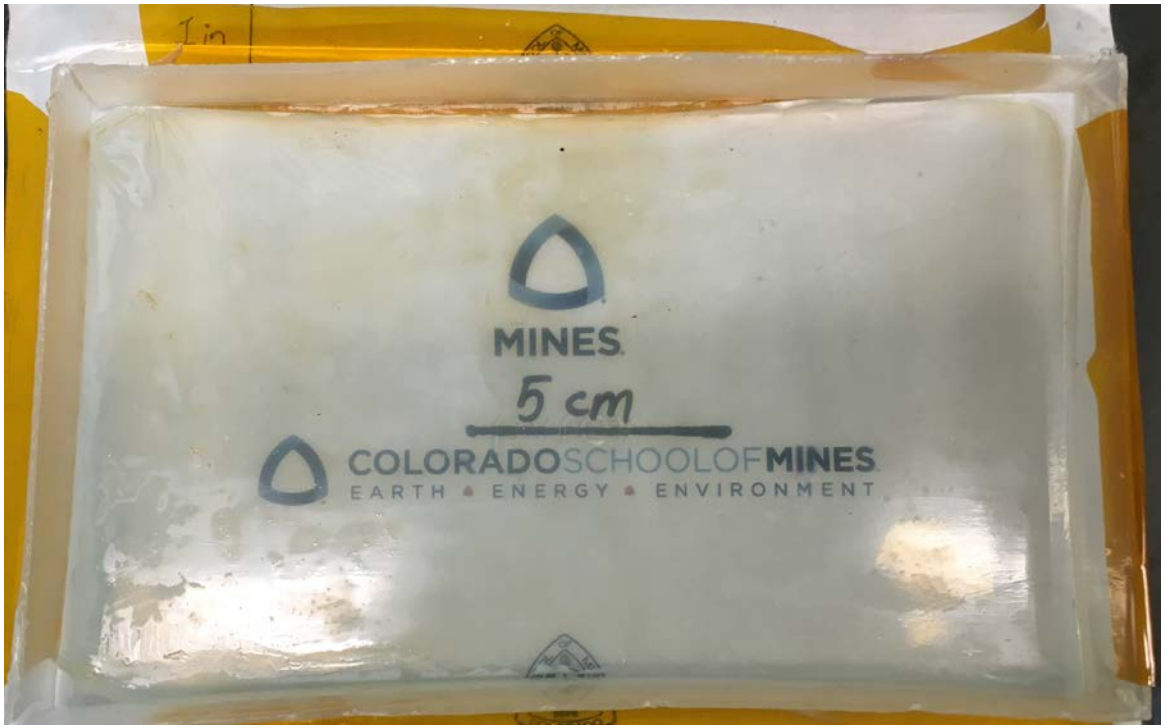


40µm thick film



Thicker, fracture free films with 80wt% HPA had lower ASR due to greatly increased conductivity (in-plane)

Work on supporting the films



- **Currently working on supporting material with ePTFE and blending with PVDF-HFP**
- **10 µm films are feasible**

Collaborations

- Prime: Colorado School of Mines – STEM University
  - Andrew Motz, Jonathan Garton, 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
  - Michael Yandrasits
    Chemicals, polymer consulting, testing
- Cost-Share: Steven Hamrock, consultant

NISSAN
R&D AMERICAS

3M

NREL
NATIONAL RENEWABLE ENERGY LABORATORY

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

In general criticisms were leveled at the synthetic claims of the team, the lack of proof that the other targets could be met, and the under utilization of the partners

As can be seen above a highly efficient synthetic route has been developed that over comes all the issues of the original method. We can control IEC and are close to full immobilization of HPA. We can scale up the synthesis. These efforts took more time than was originally anticipated.

Data is now provided at 50% RH.

Cost cannot be disclosed as 3M does publically release cost of materials, we can only say that the cost of the membrane would be similar to other fluoro-elastomers when mass produced and would be competitive.

We showed previously that the membranes where not electrically conductive.

Many of the other properties require a stronger film to be measured, and we are confident that high performance supported films will be produced for testing at Nissan, NREL, and 3M.

We are anticipate that the materials will be chemically stable in fuel cells, 3M demonstrated that the sulfonated version was more stable than a PFSA (see back up sloes) and 3M and CSM demonstrated that HPAs in PFSAs dramatically enhanced stability (previously published data)

3M has been extremely involved in terms of consultation with Dr. Steven Hamrock (on a bi-weekly basis) and Steve is still involved as an independent consultant since retiring 12/31/15. 3M supplies all the base polymer and additional materials to enable the synthesis of these polymers.

NREL and Nissan have been under utilized as they require fuel cell ready materials, however now that the synthesis is robust and we can make supported films these activities will be rapidly ramped up.

FC-2178 – Conclusion

- Improved chemistry to allow for fully scalable manufacturable film with controlled HPA content
- Most HPA retained in boiled films.
- DOE targets for ASR are easily met or are close with a viable route to meet them.
- Thin films are viable on Kapton, and the material can be supported on e-PTFE or blended with PVDF
- Films to be sent to partners for testing

Future Work

Remainder of Year 2 ½

- Testing
  - 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
  - study IEC property trade offs , optimize HPA loading, supported films (in collaboration with 3M)

Year 3

- 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 water stable films
- 1 Film Chemistry under full development
- Supported Films in Preparation

DOE Target 2020 Ω cm^2	**Result** Ω cm^2	**Thickness** μm	**Conditions**
0.02	<0.02	40	110ºC 50% RH
0.02	<0.01	20	80ºC 95% RH
0.03	0.01	20	30ºC 95%RH

Technical Back-Up Slides

Fenton test from US patent #6423784 from 3M

- A is perfluorinated sulfonic acid film
- B is sulfonated FC-2145 chemistry
- C is typical hydrocarbon film