COLORADO SCHOOL OF MINES
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Advanced Hybrid Membranes for Next Generation PEMFC Automotive Applications

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06/7/2017

FC110

Overview

Timeline

- Project start date: 10/1/13
- Project end date: 7/31/17
- Percent complete: 90%

Budget

- Total Funding Spent as of 6/7/17: $1,700,000
- 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 Group of North America (sub-contractor)
- National Renewable Energy Laboratory
- 3M (in-kind partner)
- Steven Hamrock Consultant (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
2015/16	• 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 FC-PAD with all desired properties for third party testing • Barrier A, B, and C

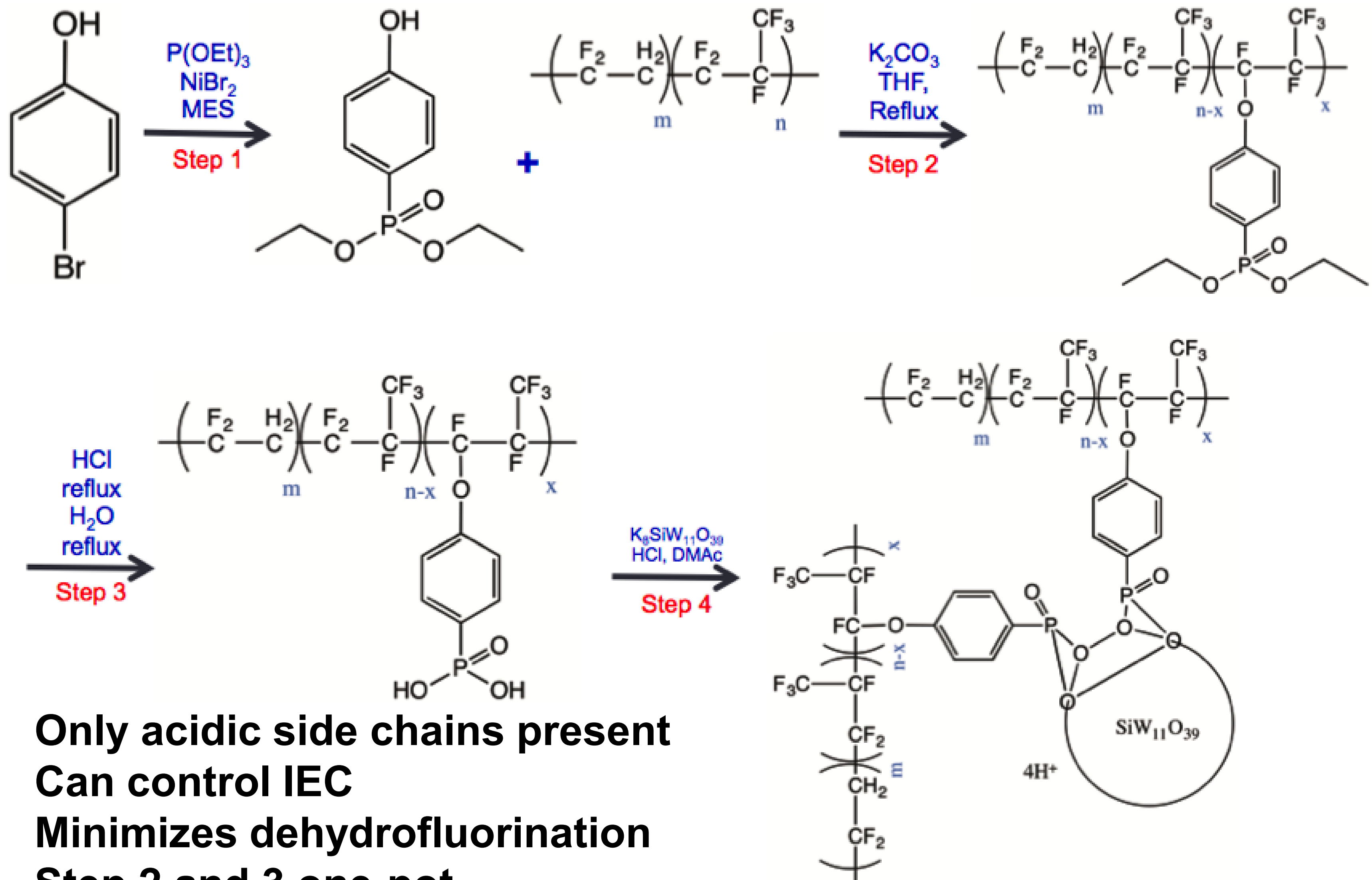
Approach

- Material Synthesis based on functionalized super acidic inorganic moieties, ***Generation II Films (Chemically stable)***
  - FC-2178 functionalized with heteropoly acid HPA (Looking extremely promising)
- The chemistry is mature
- Current and future innovation is in film processing
- This system has tunable properties (type and loading of HPA)
- Industry and National lab partners for scale up and MEA fabrication and testing

FY 2017 Milestones

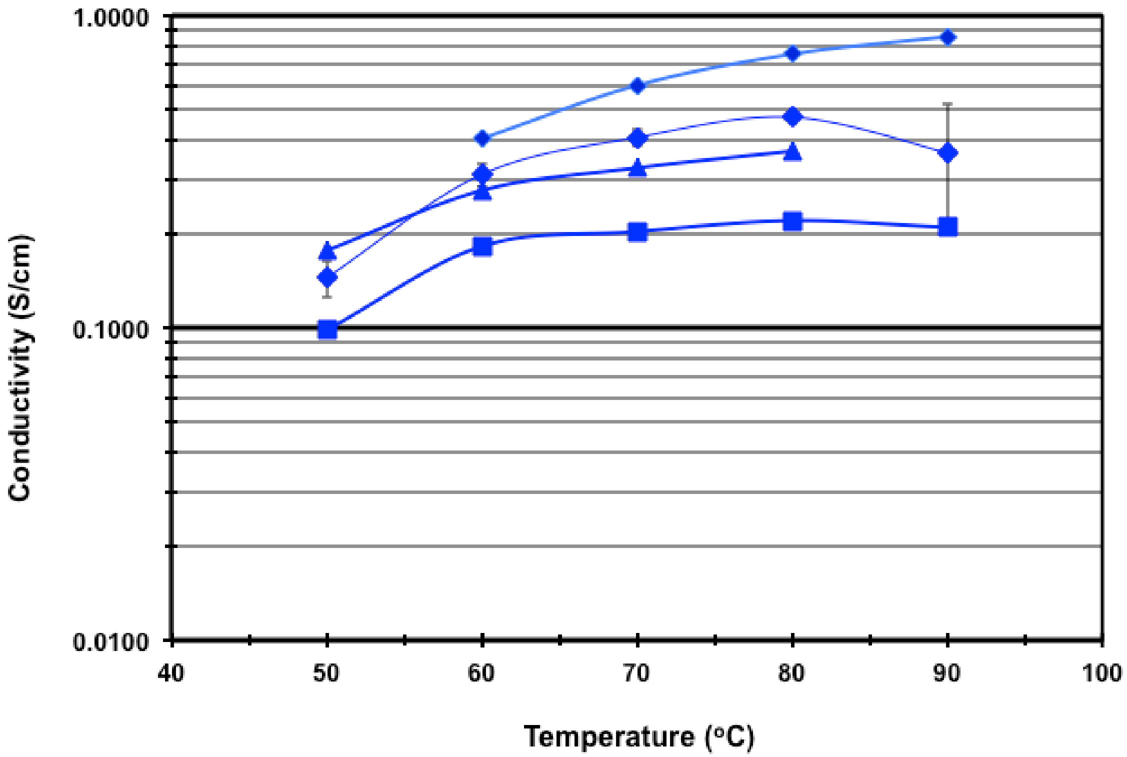
Milestone	Description	% Complete
Milestone 9 (FY17-Q1)	Demonstrate <2 mA cm^2 crossover for both H_2 and O_2 in a sub-scale MEA (5 cm^2)	100
Milestone 10 (FY17-Q2)	Demonstrate 500 hours stability for an MEA with HPA or ZrP membrane using the chemical stability test from Table D3 from Appendix D of the FOA DE-FOA-0000360. This test will be run concurrently at all four partners so that optimization and result duplication can be achieved	90
Milestone 11 (FY17-Q3)	Demonstrate mechanical stability over ≥20, 000 cycles using DOE's test protocol from Table D4 of the FOA DE-FOA-0000360. This test will also be run by our automotive partner using their own protocol so that optimization and result duplication can be achieved.	100
Milestone 12 (FY17-Q4)	Deliver 50 cm^2 MEA with a hybrid inorganic/polymer membrane with an ASR of ≤0.02 Ω cm^2 at 80ºC and 120ºC and inlet water partial pressure of <80 kPa with crossover of ≤2 mA cm^{-2} for hydrogen and oxygen and a minimum electrical resistance of 1,000 Ω cm^2. In addition, the MEA and membrane will survive the durability tests described in tables D-3 and D-4 in Appendix D of the FOA DE-FOA-0000360 (20,000 cycles of the DOE mechanical test and >500 hours of the chemical crossover test) DOE target table specifies 40-80 kPa	50

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



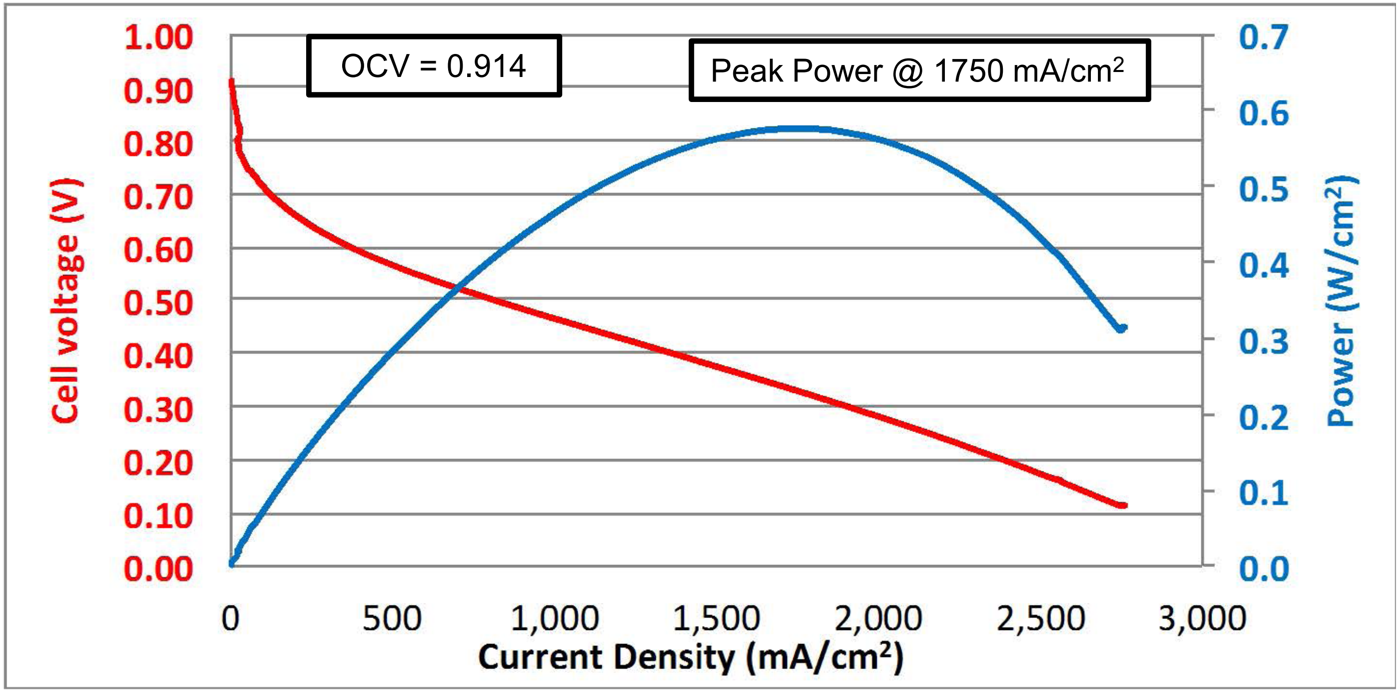
- **Only acidic side chains present**
- **Can control IEC**
- **Minimizes dehydrofluorination**
- **Step 2 and 3 one-pot**
- **Can be scaled up further**

Preliminary Processing study: High annealing temperature and lower HPA loading (60%)



- **Conductivity of >800 mS/cm at 90ºC / 95%RH**
- **Processing shows variation in conductivity, but poor mechanicals of highly conductive films**
- **Morphology and HPA loading is a major factor in conductivity**

First attempt at MEA in Fuel Cell used GDE as support



Directly deposited film, 70% HPA, 10 μm

Active area: 4 cm^2

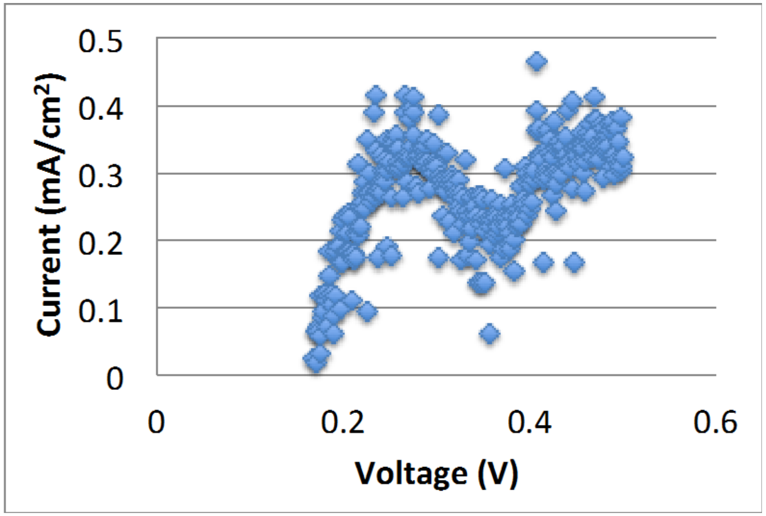
H_2 / O_2: No back pressure

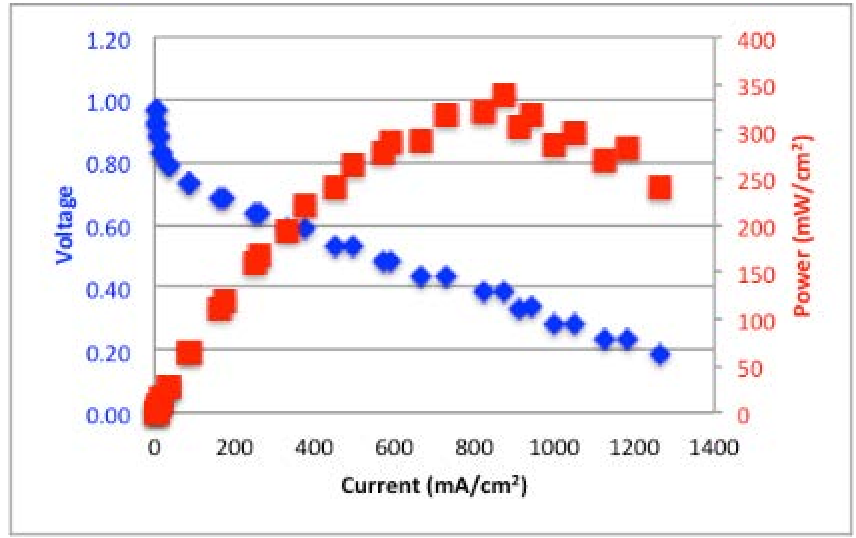
Cell Temp: 60° C

Humidifier Temp: 55° C (75%RH)

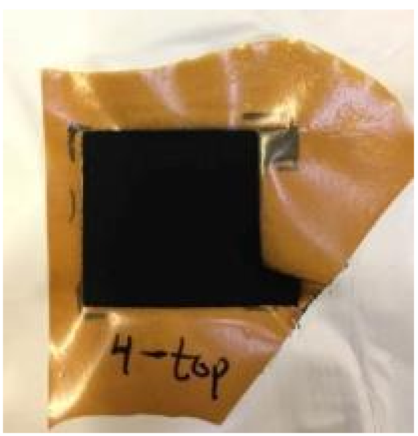
Nafion® Ionomer

Baseline Mechanical AST Accomplishments (NREL) – preliminary benchmark film – 70% HPA 80μm film





H_2 cross-over



Stand alone film after 20,000 wet/dry cycles, accelerated stress test.

Active area: $5cm^2$

H_2 / Air : 1atm

Cell Temp: 80° C

Humidifier Temp: 80° C (100%RH)

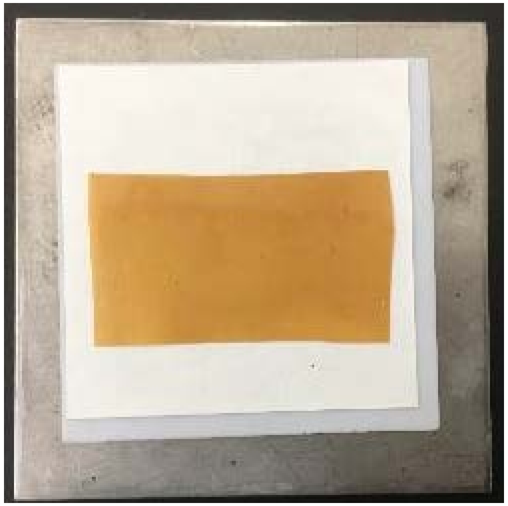
H_2 Cross-over <$1mA/cm^2$ (target <15 mA/cm^2)

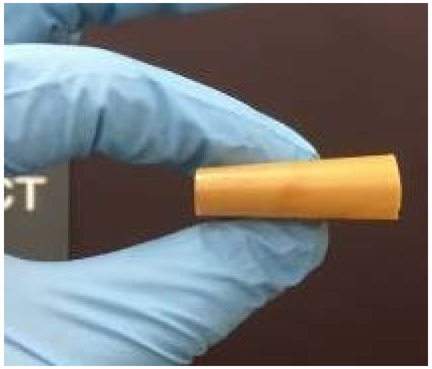
Evaluation of baseline 80 µm film

- In all the evaluations, membrane sample was first hot-pressed to make it more uniform. An MEA (5 cm x 2 cm) was fabricated using JM Pt/C/PFSA Ionomer GDEs on both anode and cathode, and hot-press method.
- H_2 crossover, EIS, Water Vapor Transport, and Chemical Durability under OCV Hold Test were evaluated.

Hot-press
130^0C, 2MPa
10 minutes

Hot-pressed Sample

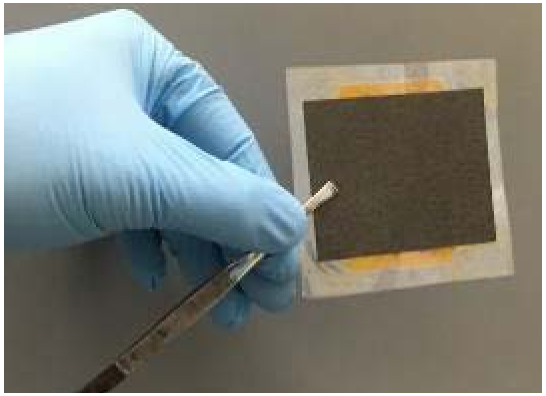




Hot-pressed membrane with sub-gasket

Hot-press with JM Pt/C/PFSA Ionomer GDEs

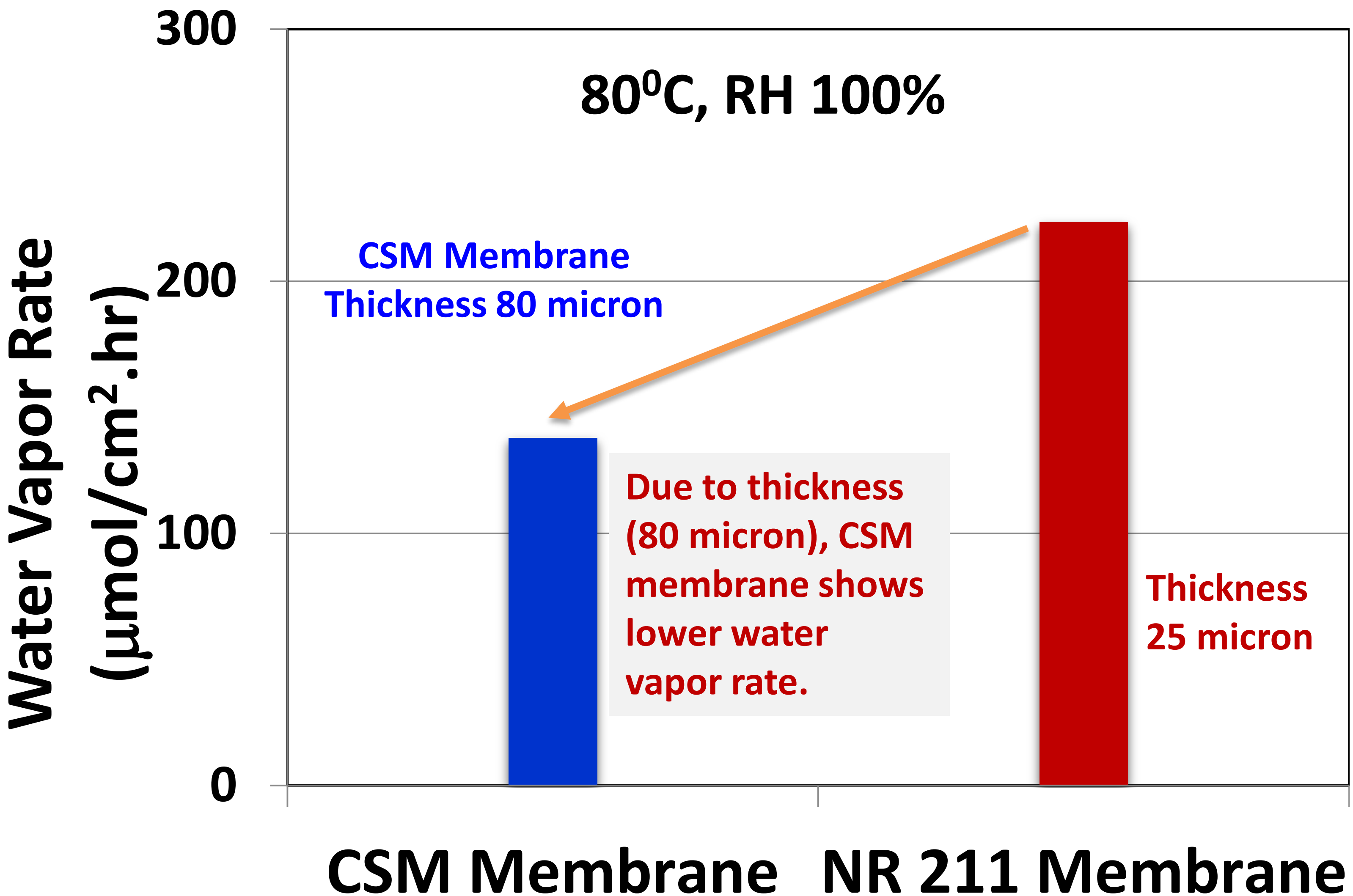
130^0C, 2 MPa, 10 minutes



Active Area: 10 cm^2 (5 cm x 2 cm)

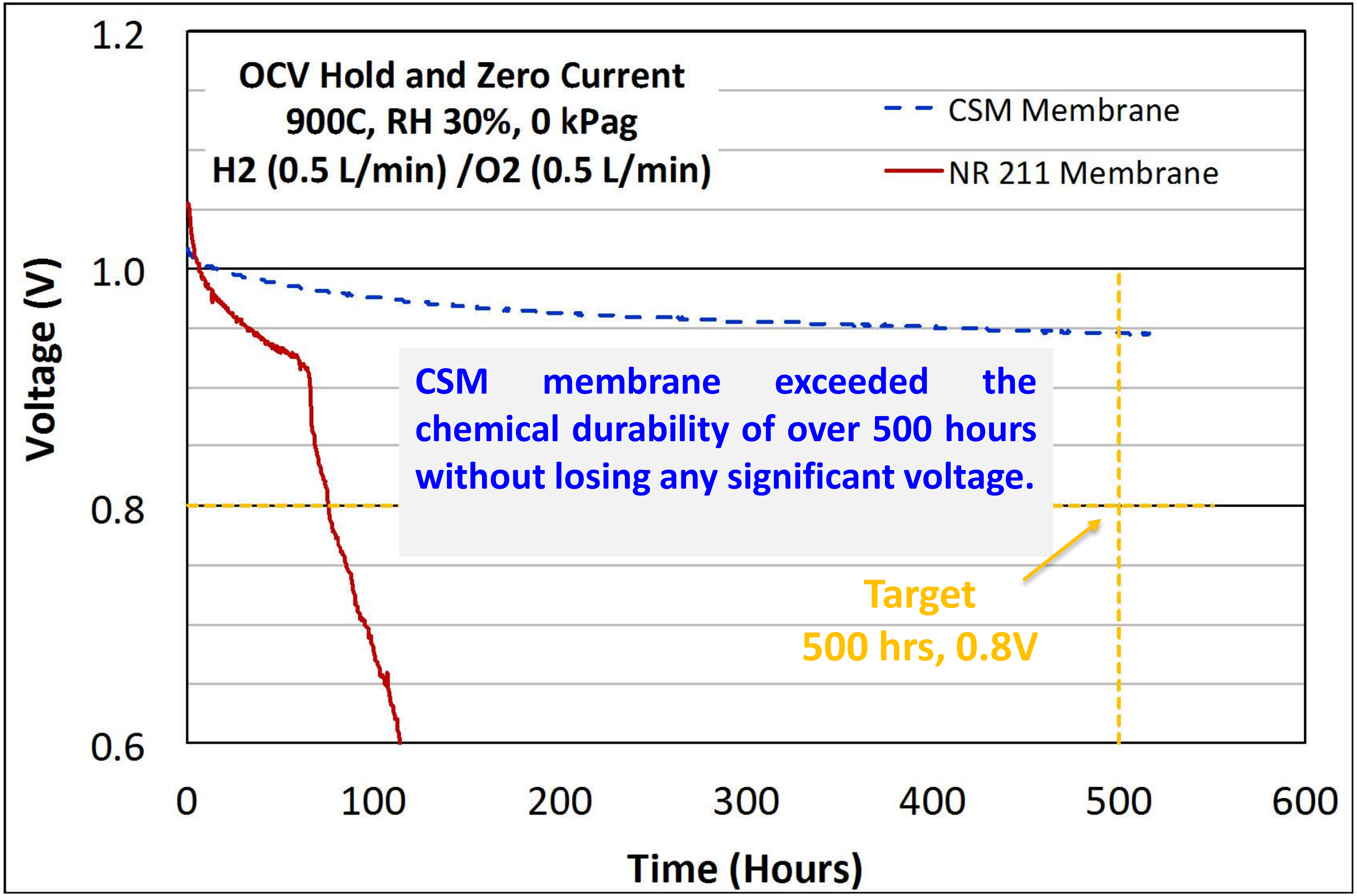
Water Vapor Rate in MEA

- In-situ Water Vapor Rate was measured to learn about the water transport ability of membrane.



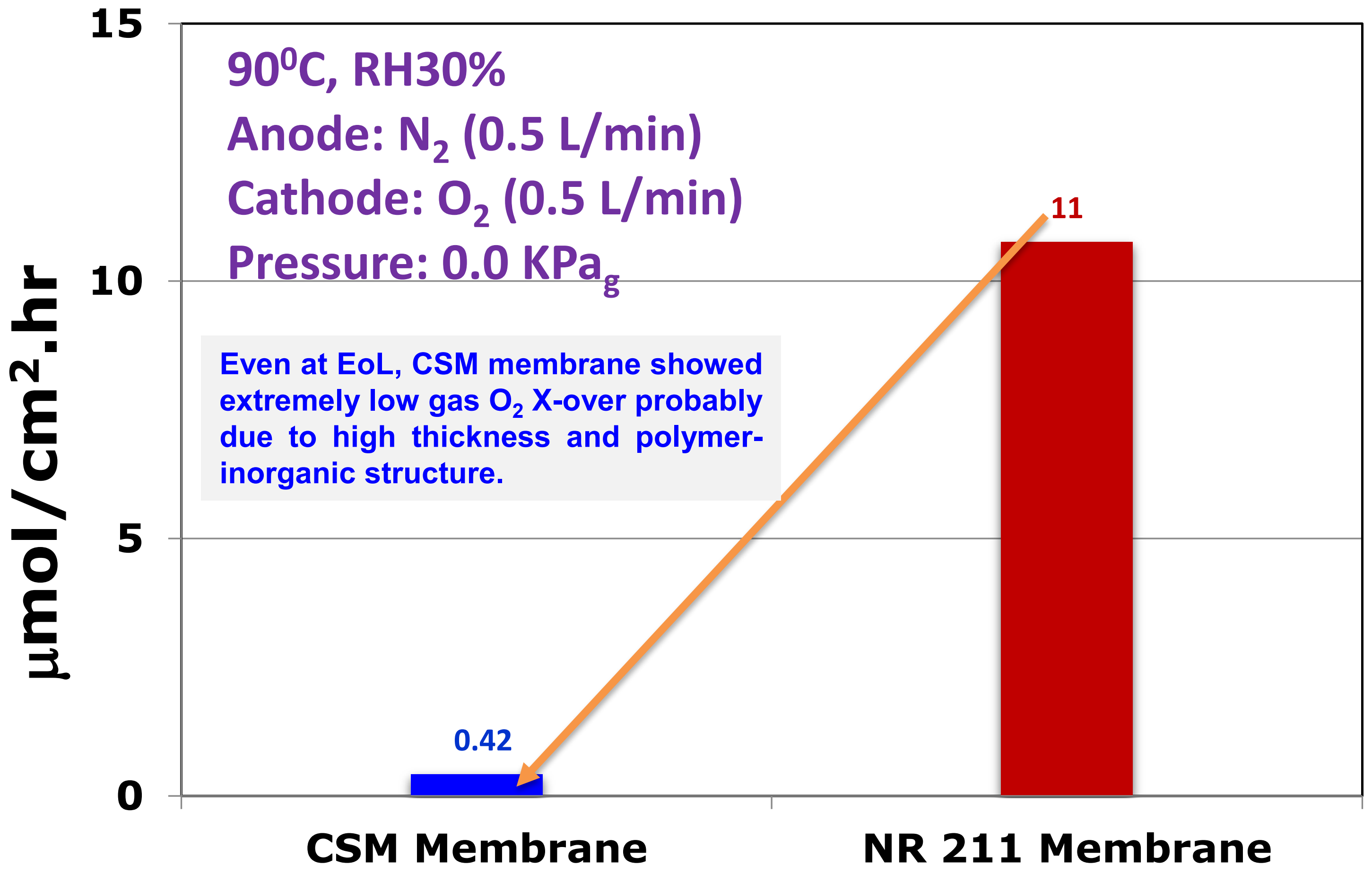
Chemical Durability Accomplishments

- **Chemical durability was evaluated under most aggressive OCV hold test in which anode was fed with 100% H_2, and cathode was fed with 100% O_2 instead of air without drawing any current.**



End of Life In-situ O_2 crossover

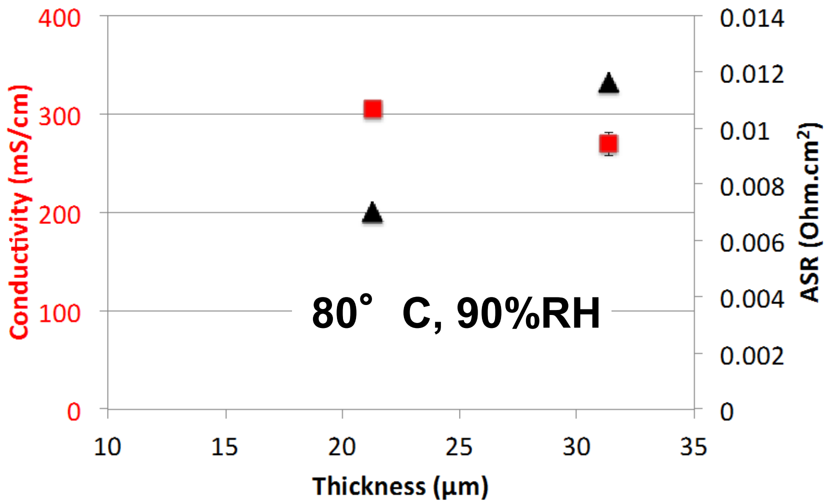
- In-situ O_2 crossover was measured after End of Life (EoL) across the MEA (CSM 80 micron membrane) that was evaluated in OCV hold test.
- This measurement was done using NTCNA's proprietary O_2 measurement set-up.



Nissan Summary for 10 cm^2 membrane

- The CSM membrane showed reasonable and comparable ionic conductivity in liquid water.
- It showed extremely low H_2 gas crossover. This is expected due to polymer chemistry/inorganic nature of the membrane.
- Water Vapor Rate of CSM membrane is found to be lower than that in NR 211 membrane. This could be due to high thickness of 80 micron. It is expected that a thinner membrane of ~25 micron thickness can have comparable water vapor rate.
- The in-situ ohmic resistance and ASR are quite high in CSM membrane. It is believed that high HPA loading and reduction in thickness can help reduce the ASR.
- This membrane has exceeded the chemical durability of 500 hrs without any significant loss in voltage, especially under one of the most aggressive OCV hold tests.

Significant Improvement in Film Properties by Varying Processing Conditions

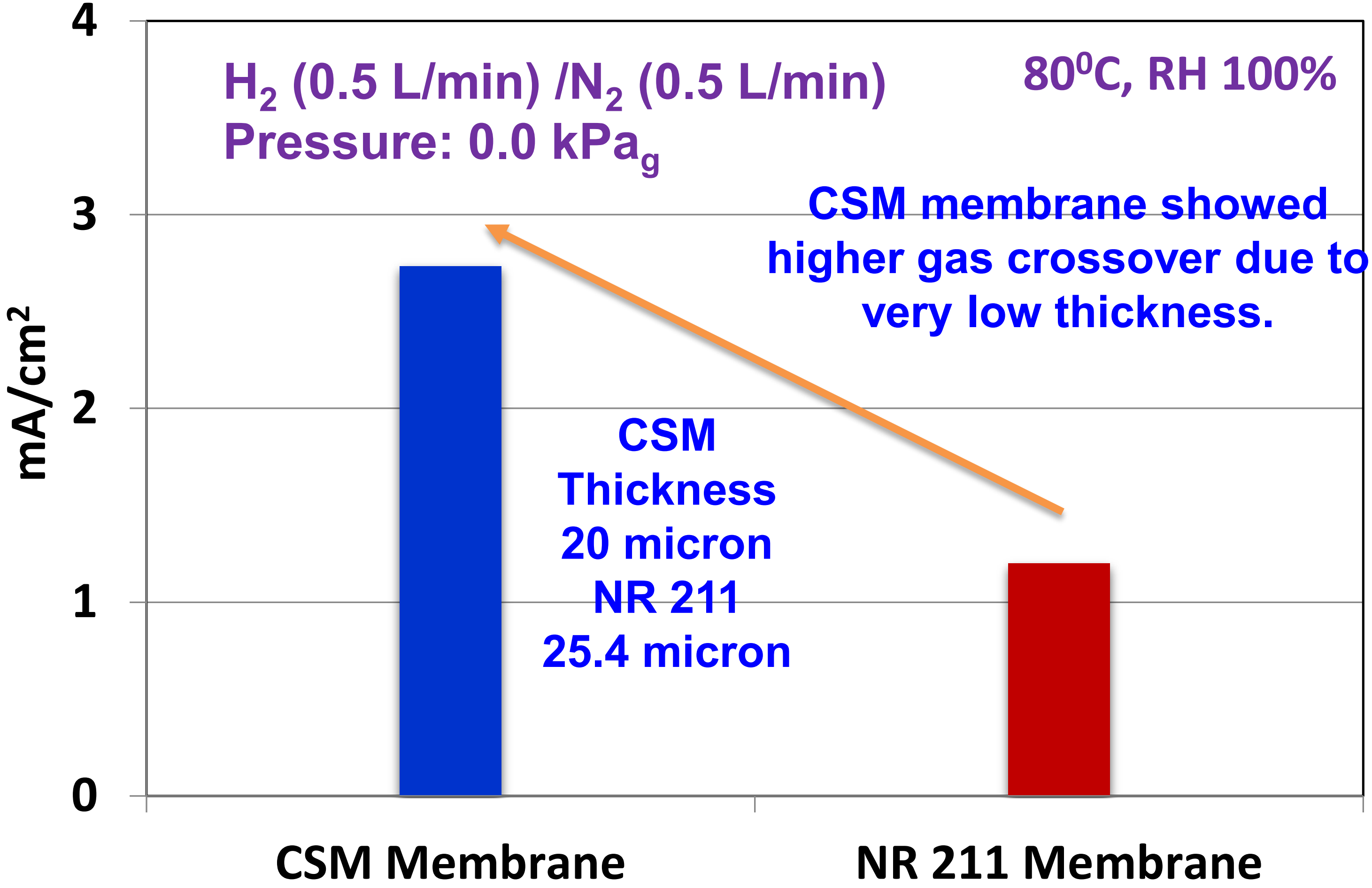


Processing conditions	Results
180° C, 95 psig , 10 min	Very brittle, fragments
180° C, 95 psig , 5 min	Less Brittle
170° C, 95 psig , 10 min	Less Brittle yet intact
170° C, 95 psig , 5 min	swelling, intact
180° C, 3 days	Brittle when dry, intact when wet
180° C, 6000 psi, 20 min	Too stiff, brittle
180° C, 6000 psi, 10 min	stiff, less brittle
180° C, 6000 psi, 5 min	**Flexible, transparent, strong**

- 10 µm uniform and stand alone membrane
- ASR <0.02 Ohm. cm^2 at 90%RH
- Processing affects the thickness and conductivity

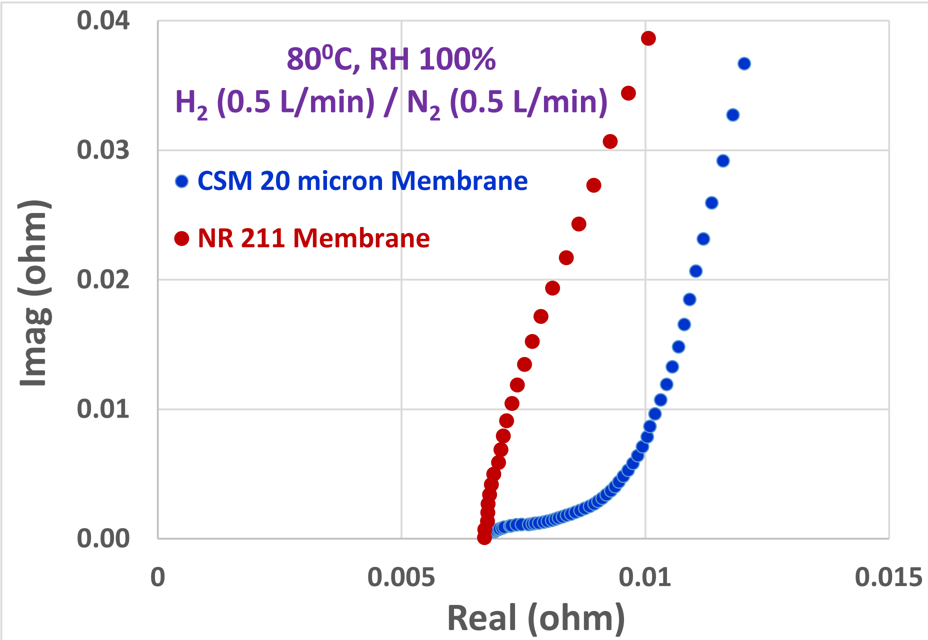
H_2 crossover – 20 µm film

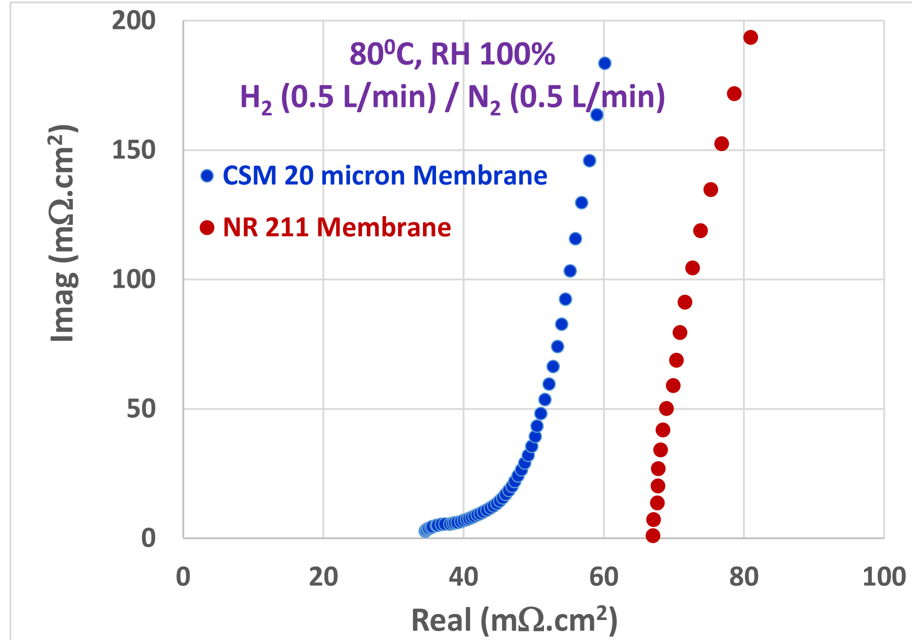
- In-situ crossover across the MEA was measured using an electrochemical method (LSV). This film also had micron sized defects due to incorrect handling of KCl by-product.



Accomplishment: In-situ EIS–20µm film

- In-situ EIS was measured to learn about ohmic resistance of the membrane.



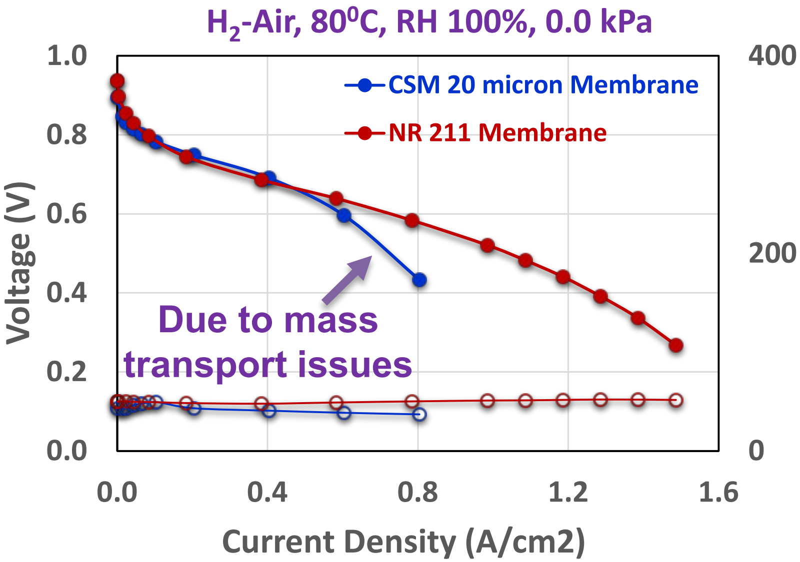


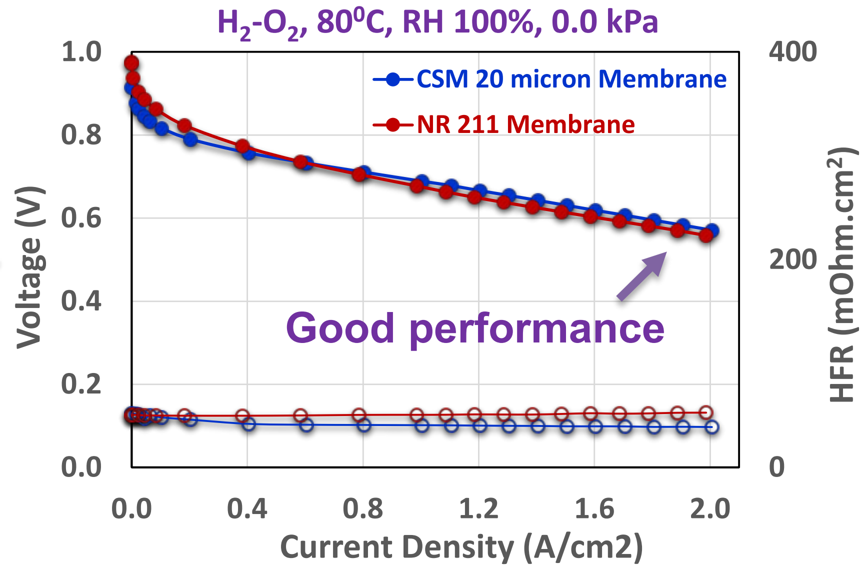
	ASR (mΩ.cm²)
CSM (5 cm² MEA)	35
NR 211 (10 cm² MEA)	67

- CSM membrane showed lower ASR at RH 100% due to low thickness and 70 wt% HPA loading in the membrane.

Accomplishment: Remarkable IV Performance with un-optimized ionomer/electrode

IV performance of CSM 20 micron membrane based MEA (5 cm^2) was evaluated using H_2-Air and H_2-O_2. Initially, the MEAs were leak-tested and conditioned using NTCNA's standard protocols.





- **CSM MEA showed remarkable IV performance, produced ~0.6 V at 2 A/cm^2 under H_2-O_2 condition**
- **However, CSM membrane based MEA needs to be optimized to improve performance under H_2-Air system, a common theme here is that electrode/ionomer research is needed to realize full potential of these materials**
- **CSM 20 micron membrane also showed comparable ASR.**

CSM 20 micron Membrane MEA	Both anode and cathode based on JM GDEs. Pt/C, Loading 0.35 mg/cm2. Flow Rates: Anode 2.0 L/min, Cathode 4.0 L/min.
NR 211 Membrane/catalyst coated membrane (CCM)	Anode: TEC 10EA-30E, Pt/C, 0.055 mg/cm2 Cathode: TEC 10E-50E-HT, Pt/C, 0.355 mg/cm2 Flow Rates: Anode 4.0 L/min, Cathode 8.0 L/min.

Reviewers Comments

However, given how much work the PI has already performed on HPA-based membranes without demonstration of a membrane that can actually be incorporated into an MEA, this approach does not seem promising.

The project was structured to first develop a membrane in the first two years and then incorporate it into an MEA for testing in the final year, there were no resources to divert from membrane fabrication to MEA testing before now, therefore the lack of previous fuel cell data said nothing about the suitability of the material. As was shown above these materials perform very well as MEAs (even with unoptimized electrodes) and have enormous potential to solve current issues in durability and performance.

The approach of attaching HPA groups to fluoroelastomers seems sensible, though the fluoroelastomer stability may need to be studied to understand how it compares to other materials in response to fuel-cell-like challenges.

The material outperforms many other solutions in a chemical stability test, this is not surprising considering that the HPA was chosen based on its ability to enhance the performance and stability of a PFSA.

Mechanical testing will also be important at some point.

The material does extremely well in the DOEs mechanical stability test as it has minimal swelling and that the base material is used in load bearing components such as o-rings

The team should use a standard 2-mil Nafion® membrane for conductivity comparison.

As shown above we are doing this.

Conclusions

We have passed all project targets on separate films, but now we need to achieve all targets on one single film

- We have made a film that can pass the ASR in *ex-situ* testing
- We have improved the film mechanics through a new, quicker synthesis step
- The improved films were able to pass the DOE AST protocols, but they were thicker than desirable
- Hot pressing at 6000 psi and 180ºC makes flexible, strong membranes with reduced swelling
- 10 μm uniformly thick, mechanically strong large membranes can be prepared to meet the ASR target
- Through processing and optimizing HPA loading, we anticipate we can make a film that meets the end of project milestone

Collaborations

- Prime: Colorado School of Mines – STEM University
  - Andrew Motz, Jonathan Garton, Mei-Chen Kuo, Jim Horan, Tara Pandey, and Jessica Hoffman: Polymer synthesis, membrane fabrication, MEA fabrication
- Sub: Nissan Group of North America – 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

Remaining Challenges and Barriers

- Thin robust film that meets all targets simultaneously
- Fabrication of MEAs with appropriately integrated electrodes
  - Full Fuel Cell relevant MEA testing protocol to develop membranes with durability, cost, mechanical, and performance metrics
- Development of Ionomer/electrode – beyond the scope of this project

CSM Future Work

- Our approach will consist of making thinner, more flexible films with optimized HPA loading and morphology to meet the ASR targets
- The low swelling HPA films should retain the outstanding durability
- Improved processing to allow for fully scalable, manufacturable film with controlled HPA content (we have recently performed a full QA/QC exercise to identify all variable processes in the synthesis/processing sequence)
- Improving ionomer / membrane interface is still needed to optimize a device

Nissan Future Work

- NTCNA in partnership with CSM will continue to do *in*-situ evaluation of CSM membranes to meet US DOE milestones set in this project.
- NTCNA will measure the *in*-situ O_2 and H_2 crossover across the most recent CSM membrane/MEA to learn about O_2 transport in the membrane.
- NTCNA will fabricate next MEAs using thinner and flexible CSM membranes/ionomer to evaluate *in*-situ mechanical durability of MEA using US DOE protocol to meet > 20k cycles target.
- NTCNA will evaluate current-voltage polarization (IV) performance of next thinner CSM membranes/ionomer at high temperature (> 80^0C) and various RH%.
- During this IV evaluation, NTCNA will also monitor HFR and perform EIS across MEA at high temperature and at RH 50% towards meeting *in*-situ ASR target of 20 mOhm.cm^2.
- NTCNA and CSM will jointly work towards developing 50 cm^2 MEA for third party testing.

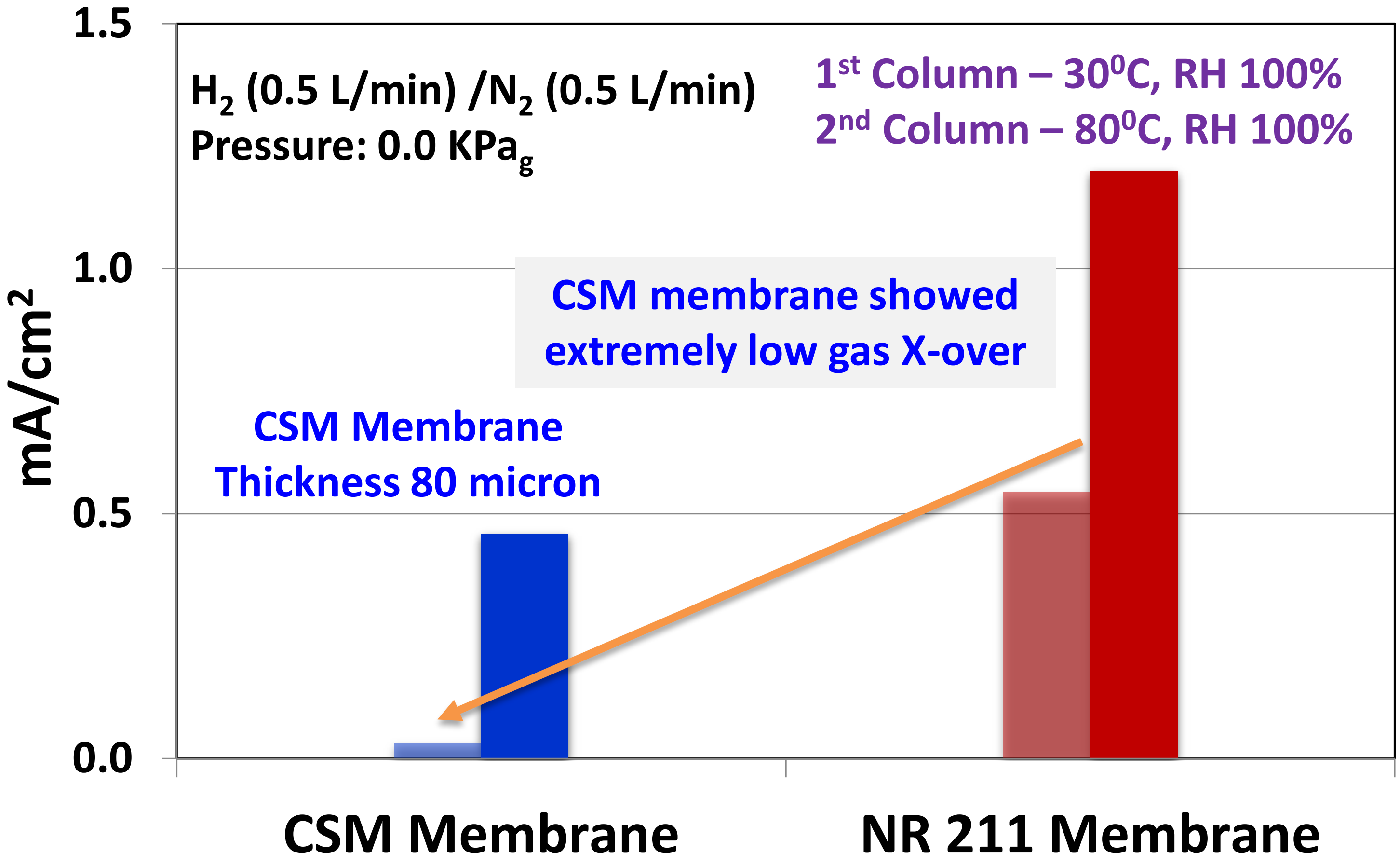
Summary

DOE Target 2020 Ω cm²	Result Ω cm²	Thickness μm	Conditions
0.02	0.015	10	110ºC 50% RH
0.02	<0.01	20	80ºC 95% RH
0.03	0.01	20	30ºC 95%RH
H_2 Cross over 2 mA/cm²	2.7 mA/cm²	20	80ºC/100%RH
Chemical Durability >20% OCV loss 500 h	<4% 500+ h	80	90ºC/30%RH/O_2 More severe than DOE test
Mechanical Durability 20,000 cycles >15 mA/cm²	H_2 Cross-over <1mA/cm²	80	20,000 wet/dry 80ºC

Technical Back-Up Slides

MEA H_2 X-over Accomplishments - 80 µm

- In-situ X-over across the MEA was measured using an electrochemical method (LSV).
- O_2 crossover below detection limits



Experiments - 20 µm

- CSM provided NTCNA a thinner membrane (20 micron) sample for in-situ evaluation.
- Two MEAs (5 cm x 1 cm) and (5 cm x 2 cm) were fabricated using JM GDEs (Pt/C) on both anode and cathode. Hot-pressing was not done to fabricate the MEAs.
- In-situ H_2 X-over, In-situ EIS, and current-voltage performance were evaluated across the 5 cm^2 MEA. Results are compared with NR 211 membrane based CCM (10 cm^2).

Sub-gasket (5 cm x 2 cm) on top of GDE

Example MEA

20 micron Membrane on top of the sub-gasket
Active Area: 10 cm^2 (5 cm x 2 cm)