Durable High Power Membrane Electrode Assembly with Low Pt Loading

Swami Kumaraguru (PI)

General Motors, Fuel Cell Activities

June 14th 2018

FC156

This presentation does not contain any proprietary, confidential, or otherwise restricted information

Overview

Timeline

- Project start date: 1st Jan 2017
- Project end date: 31st Dec 2019
- Percent complete: <28%

Budget

- Total Project Budget: $ 3,201,476
- Total Recipient Share: $ 640,295 (20%)
- Total Federal Share: $ 2,561,181
- Total Funds Spent*: $461,786
  - $369,429 (Fed Share)
  - $92,357 (Cost Share)

as of 2/28/2018

Barriers

- B. Cost
  - Decrease amount of precious metals.
- A. Durability
  - Reduce degradation via operating conditions
- C. Performance
  - Achieve and maintain high current densities at acceptably-high voltages

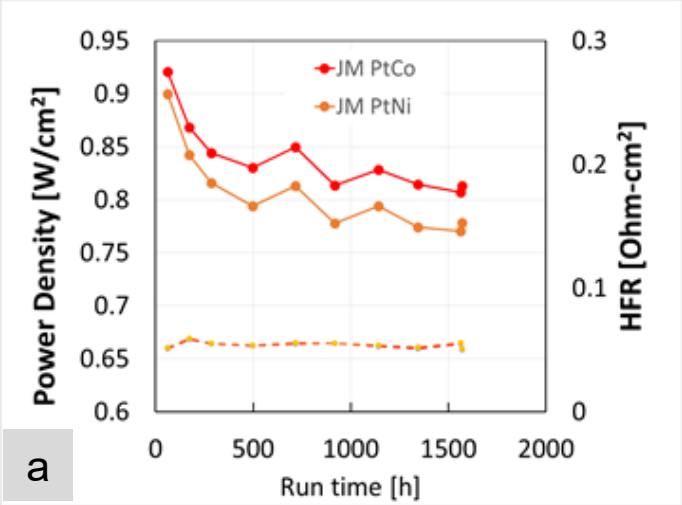
Partners

- Subcontractors: *Signed*
  - Giner
  - UT Austin
- FC-PAD *NDA pending*
- Project lead: GM

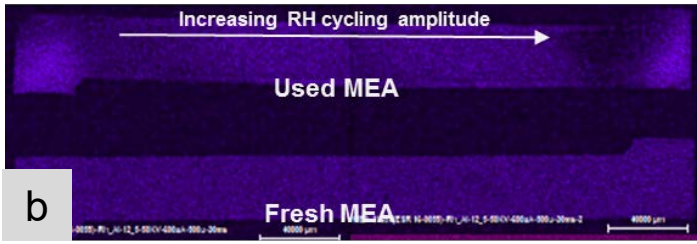
Relevance

Challenges

- **Electrode :**
  - Higher than expected degradation of Pt-alloy catalysts at high power(a). Poorly understood, complex degradation mechanisms of platinum alloy catalysts and their impact on high power.
- **Membrane:**
  - Higher than expected membrane degradation with combined chemical & mechanical stresses. Ce re-distribution during operation can affect membrane life (b).
  - MEA defects such as electrode cracks & fibers from GDL create stress points which can lead to early failure



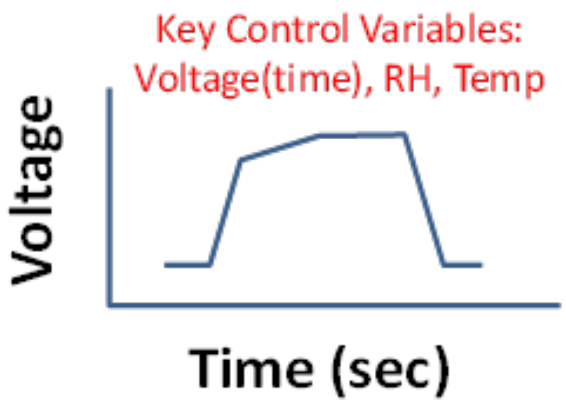
https://www.hydrogen.energy.gov/pdfs/review14/fc087_kongkanand_2014_o.pdf

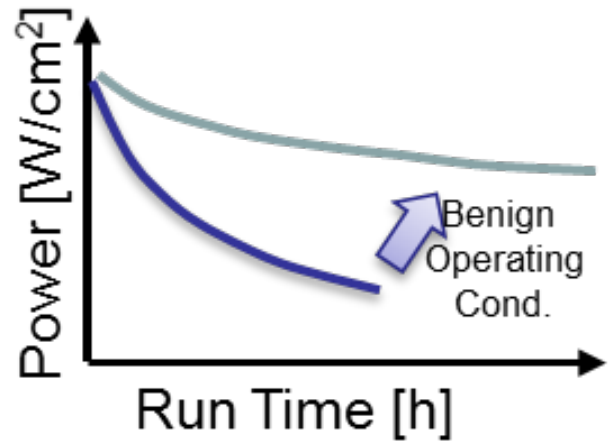


Objectives

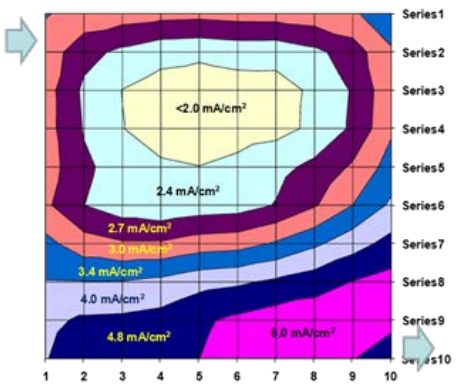
- **Project Goal**
  - Achieve DOE 2020 performance and durability target.
  - Improve durability of state of art (SOA) MEA by identifying and reducing the stress factors impacting electrode and membrane life.
- **Expected Outcome:**
  - Design and produce a state-of-art MEA with Pt loading of 0.125 mg_{Pt}/cm^2 or less and an MEA cost meeting the 2020 DOE Target of $14/$kW_{net}$ or less, and
  - Demonstrate a pathway to cathode (10% power loss) and membrane life of > 5000 hr by defining implementable benign operating conditions for fuel cell operation.

Approach





Electrode Durability : Conduct voltage cycling study on state-of-art MEA and define benign operating conditions to minimize power degradation rate.



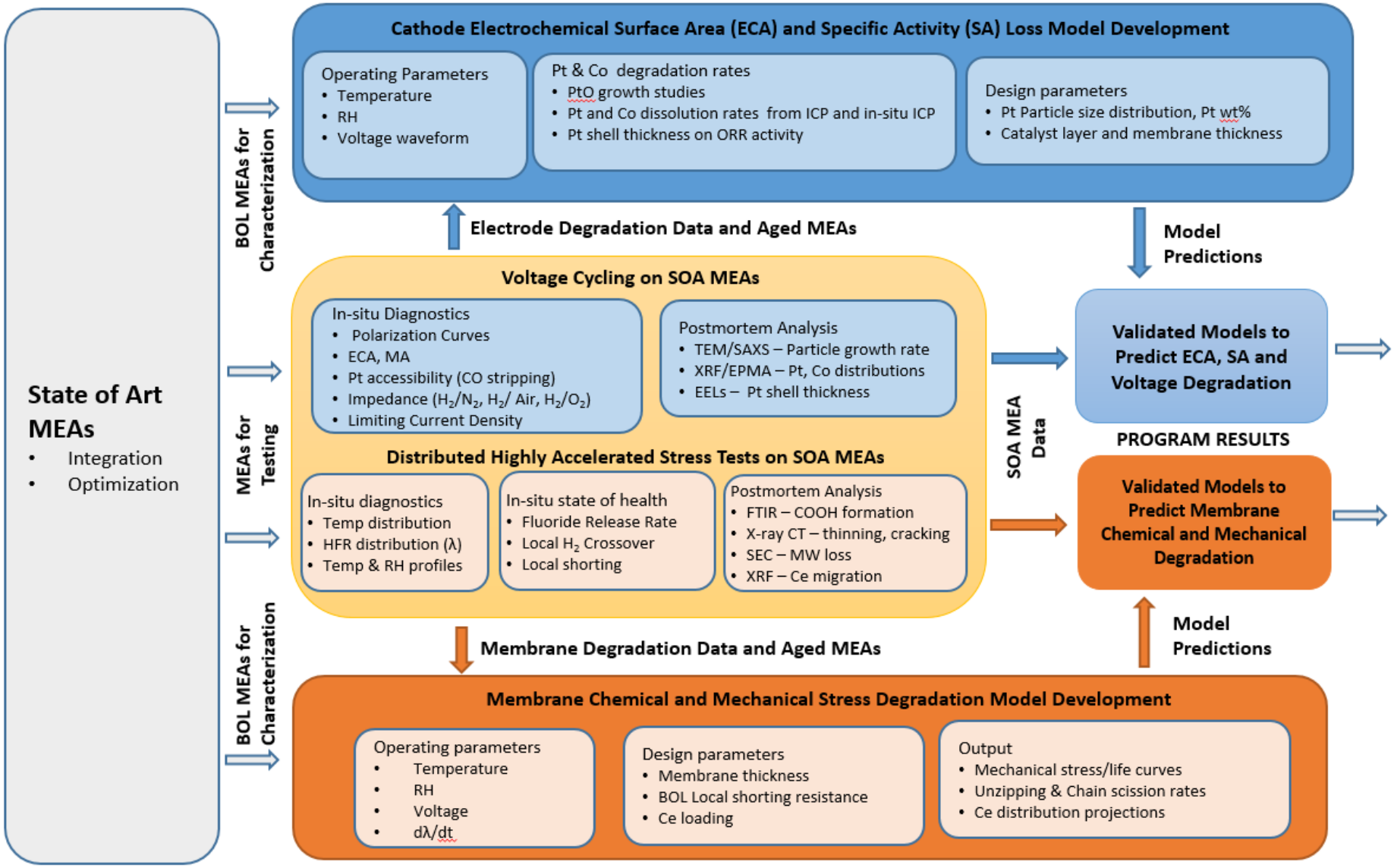
Combined Chem. and Mech. stress segmented cell test

Control Variables
RH,T, t, V
Mitigants
Accelerators
Local defects
GDL properties

Combined Chemical and Mechanical Stress Model

Membrane Durability : Develop fundamental models of mechanical stress, chemical degradation and Ce migration in the membrane and combine them to create a unified predictive degradation model.

Approach



Project framework for electrode and membrane degradation studies. Yellow box represents MEA degradation testing, blue boxes support electrode degradation models, and orange boxes support membrane degradation models.

Approach/ Milestones and Go/No Go

Budget Period 1 Task : Optimization of Low Loading Electrode and SOA MEA

- Down-select MEA components such as catalyst, GDL, membrane etc.
- 2 -3 rounds of design of experiments to optimize electrode performance to generate SOA MEA
  - Optimized perf. for both beginning and end of test (accelerated tests).
- Ink, catalyst layer characterization and correlation with performance and electrochemical diagnostics
- Combined mechanical and chemical accelerated stress tests for membrane

Go/No Go: 50 cm^2 SOA MEA that meets DOE target performance requirements – 1 W/cm^2 @ 0.125 $g/Kw_{rated.}$ (250 $Kpa,_{abs}$). Provide 50 cm^2 MEAs to FC-PAD.

Budget Period 2 Task: Durability Studies of SOA MEA

- H_2-air and H_2-N_2 voltage cycling tests on SOA MEA at different operating conditions
- Analytical characterization (PSD, EELS mapping, TEM etc) of BOT and EOT MEAS
- Model development, studies to evaluate model parameters, such as dissolution rates etc.
- Membrane durability studies, chemical degradation mechanism shorting propagation studies.

Go/No Go: Demonstrate operating conditions can provide at least 35% reduction in ECSA and performance loss.

Budget Period 3 Task: Predictive Models for Degradation with different Operating Condition

- Continue H_2-air and H_2-N_2 voltage cycling tests on SOA MEA
- Analytical characterization (PSD, EELS mapping, TEM etc.) of EOT MEAs
- Model Development (ECSA, SA degradation models) and validation
- Membrane Durability – post mortem studies and membrane degradation model validation

Final Milestone: Predictive model for both electrode and membrane durability. Recommend benign operating conditions to prolong the MEA durability to >5000 h.

Milestones and Go/No Go

Budget Period 1 Task : Optimization of Low Loading Electrode and SOA MEA

Go/No Go: 50 cm^2 SOA MEA that meets DOE target performance requirements – 1 W/cm^2 @ 0.125 $g/Kw_{rated.}$ (250 $Kpa,_{abs}$). Provide 50 cm^2 MEAs to FC-PAD.

Milestone Summary Table

Task Number	Task Title	Milestone Number*	Milestone Description (Go/No-Go Decision Criteria)	Anticipated Quarter	Progress
1.1	Downselection of Best in Class Materials for SOA MEAs Catalsyt Selection Ionomer Selection	M1.1	Report on downselection process. Catalysts to demonstrate >0.6 A/mg in MEA at BOT. [a]	Q1	100%
5.1 1.2	Downselect Membranes for Durability Studies Electrode Opt w Spray and Alternate Coating Methods	M1.2	Membrane to pass single stressor durability test. ASR of $0.02\Omega\cdot cm^2$ at 95°C Finalize coating method, solvent system to generate $1W/cm^2$ BOT performance at HCD.	Q2	100% 100%
1.3 1.6	Finalize design of SOA MEA Structural Characterization of BOT MEA	M1.3	Report BOT performance and corrleation with electrode structure properties	Q3	60%
1.4 1.5 4.1	Performance Evaluation in Single Cells Quantify transport and kinetic properties at BOT Construct and verify MEA perf. model for SOA MEA	M1.4	Demonstrate BOT performance of 1 W/cm^2 Demonstrate less than 20 mV delta between model and experimental data	Q4	100%
Phase 1	**Deliver 50 cm^2 SOA MEA for durability studies to FC PAD**	**GNG1**	**Demonstrate 1 W/cm^2 @ 0.125 g/KW with 50 cm^2 SOA MEA.** [b]	**Q4**	**95%**
5.4	Impact of Local shorting and membrane degradation	M2.2	Proof of accelerated degradation in areas induced with shorts (membrane thinning, higher X-over etc) (Go/No-go)	Q6	15%
5.2	Combined Highly Accelerated Tests (Chem and Mech)	M2.4	Mem. stress life curves for model validation (from atleast 2 GDLS)	Q8	35%

[a] Mass activity tested under DOE - specified condition

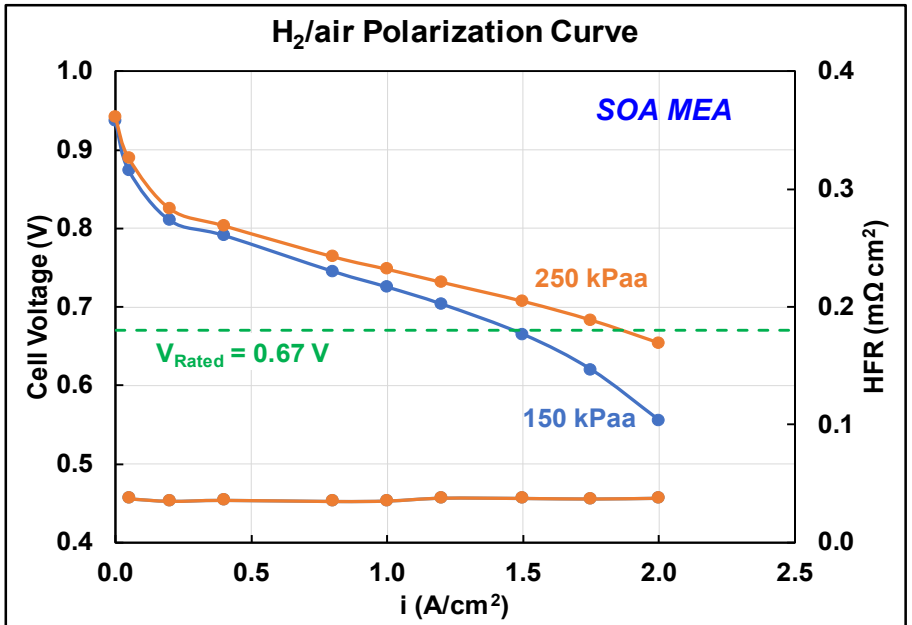
[b] Measured under anode/cathode: H_2/air, 94°C, 250/250 kPa, $_{abs, out}$, 65%/65% RH_{in}, st=1.5/2. Uncorrected cell voltage must be lower than Q/Delta T of 1.45

Target and Status

Item	Units	2020 Target	2018 Status	
			94° C 250Kpaa	80° C 150kPaa
Cost	$/kW$_{net}$	14	-	-
Q/ΔT	kW/°C	1.45	1.45	1.94
i at 0.8 V	A/cm^2	0.3	0.44	0.30
PD at 670 mV	mW/cm^2	1000	1275	1000
Durability	Hours @ < 10% V loss	5000	TBD	TBD
Mass activity	A/mg$_{PGM}$ at 0.9 V	> 0.44	0.65	0.65
PGM Content	g/kW rated mg/cm$^2_{MEA}$	0.125	0.10	0.125

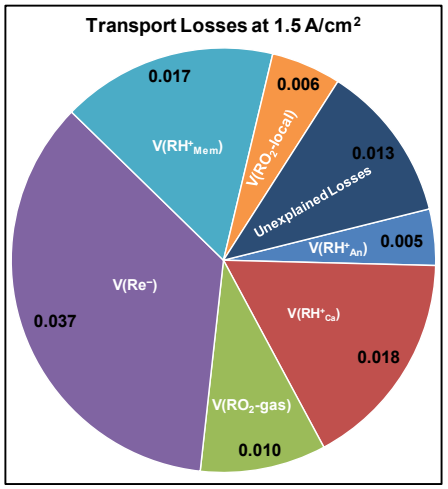
- Systematic screening of various best in class catalysts, ionomers and membranes were conducted to generate SOA.
- The generated SOA exhibit > 1000 mW/cm^2. Higher temperature and higher pressure polarization curve used to achieve the Q/ΔT target.
- 50 cm^2 MEAs provided to FC-PAD for verification studies.

Technical Accomplishment:



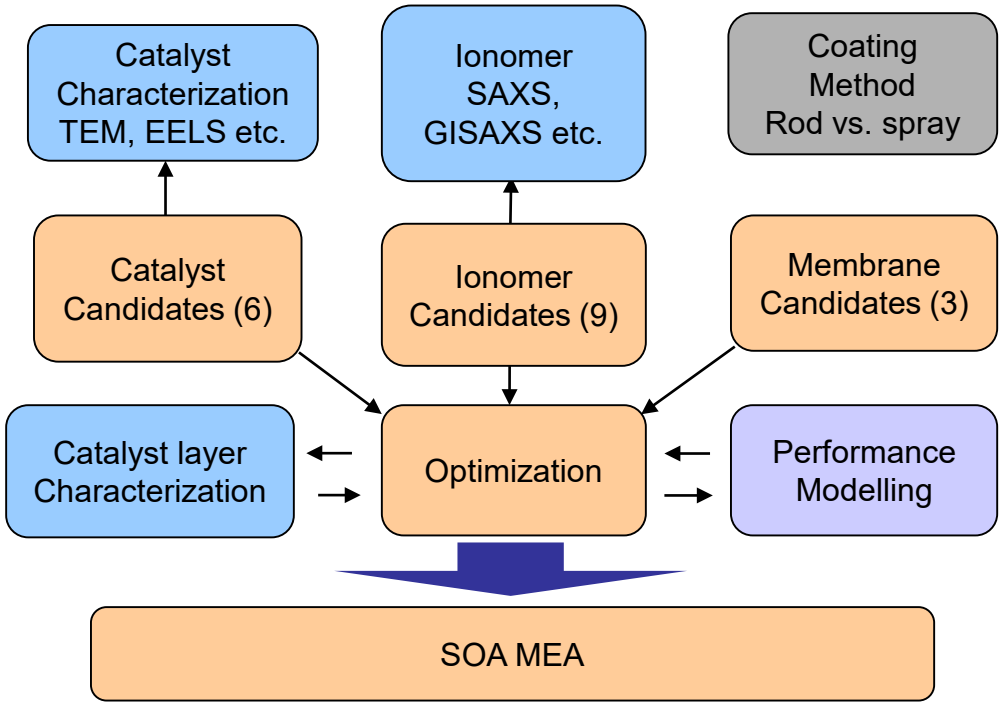
Active Area: 50 cm^2, CCM MEA
H_2/air, 80 °C, 100% RH, Stoic: 1.5/2.0, 150 Kpaa
H_2/air, 93.5 °C, 65% RH, Stoic: 1.5/2.0, 250 Kpaa

Item	Description
Cathode catalyst	30% PtCo/HSC-a 0.1 mg$_{Pt}$/cm^2
Cathode ionomer	Mid side chain 0.9 I/C (EW825)
Membrane	12 µm PFSA
Anode catalyst	10% Pt/C 0.025 mg$_{Pt}$/cm^2
GDL thickness	235 µm



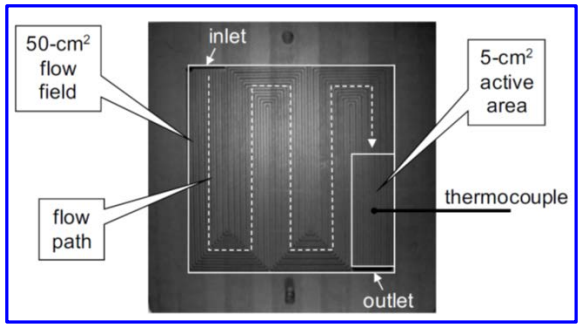
Technical Accomplishment:

Generating SOA MEA



- Systematic screening of various best in class catalysts and ionomers were conducted to generate SOA. (~200 MEAs tested)
- Characterization of both components and integrated SOA MEA conducted to provide fundamental understanding of the material properties and its impact on performance.

*Garrick et al, *JES.* **164** (2), F55 (2017)
Padgett et.al, *JES.* **165 (3) F173 (2018)
† Makharia et.al, *JES*, **152** (5), A970 (2005)
†† Greszler et al, *JES*, **159** (12) F831 (2012)



Performance and electrochemical diagnostics were conducted in 5 cm² MEA in differential test conditions. (all measurements in 5 cm² CCM differential cell (3 repeats), unless noted)

Key Measurements (for electrode)

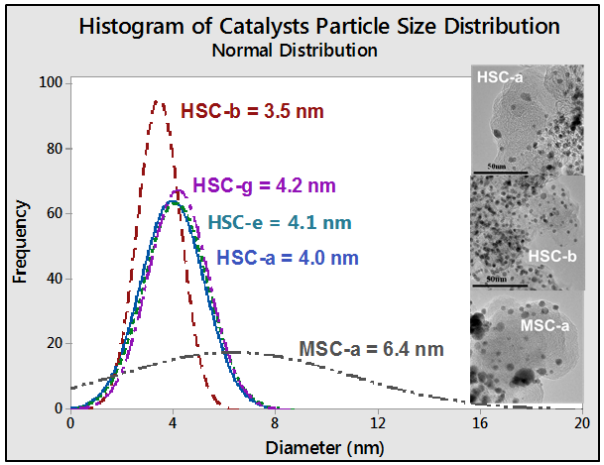
- ECA Measurement (H_2/N_2 CV, CO stripping*)
- Pt particle accessibility
  - CO stripping at different RH**
- Mass activity and Specific Activity
  - I-V curves : 100% O_2 and 100% RH
- Proton transport resistance measurement
  - H_2/N_2 impedance, 80°C †
- Bulk and local O_2 transport resistance
  - Limiting current at different Pt loading ††
- H_2/Air Performance
  - I-V curves : 100% RH, 65% RH, 150 Kpa, 250 Kpaa
- Modelling Performance ᶻ
  - 1 D Model

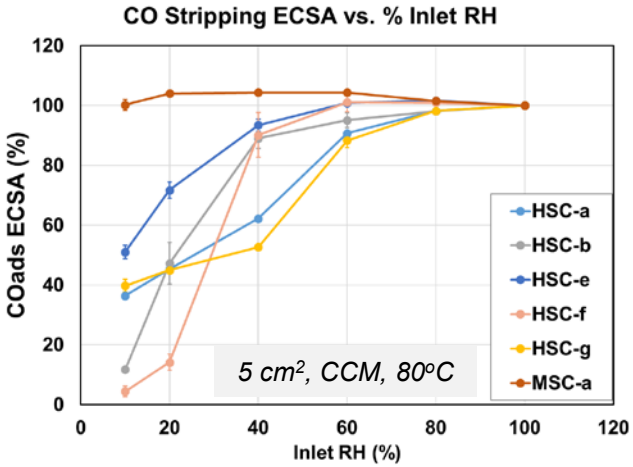
ᶻ Gu et al., *Handbook of Fuel Cells* , Vol. 6, p. 631, John Wiley & Sons (2009)

Task 1.1 Catalyst Selection

Catalyst Properties

- Several PtCo catalysts (Pt:Co ~ 3:1) supported on various carbon supports were tested for activity and performance.
- MSC-a being solid carbon exhibits 100% Pt particles outside carbon support.
- HSC-a and HSC-g are nearly identical in carbon support properties.
- Modified HSC carbon HSC-e exhibits improved accessibility to Pt particles.





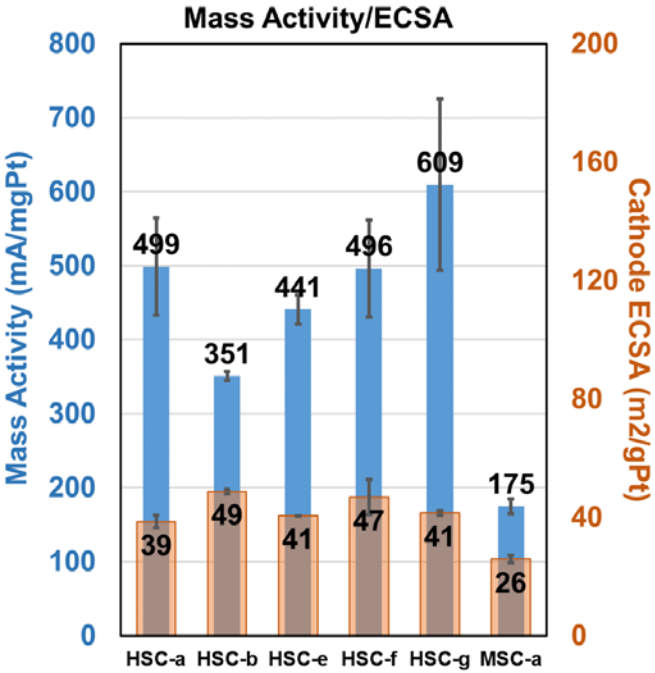
Catalyst	Comments	BET Area (m^2/g_{Carbon})	Area ($m^2/g_{Catalyst}$)		Accessible Pt @ 30% RH	Pt : Co	PtCo Size (nm)
			Micropore (< 2 nm)	Macropore (> 5 nm)			
HSC-a	High surface area carbon	~778	79	85	57%	3.3	4.0 ± 0.2
HSC-b	High surface area (less porous)	~797	42	123	68%	3.5	3.5 ± 0.1
HSC-e	High surface area carbon	~778	65	77	82%	3.3	4.1 ± 0.2
HSC-f	High surface area carbon	>780	54	183	57%	3.3	TBD
HSC-g	Similar to HSC-a, alternate synthesis	~744	82	72	54%	2.7	4.2 ± 0.2
MSC-a	Medium surface area solid carbon	~214	35	44	100%	2.3	6.4 ± 0.6

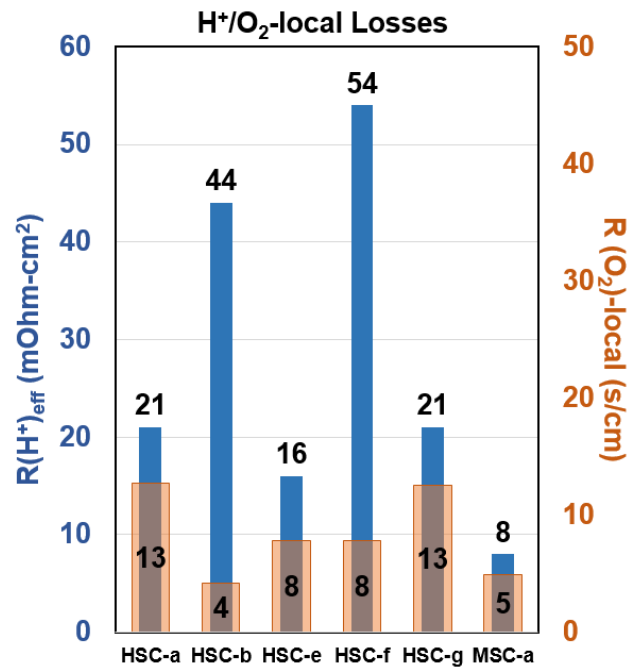
In-depth characterization of some of the above catalysts can be found in FC144

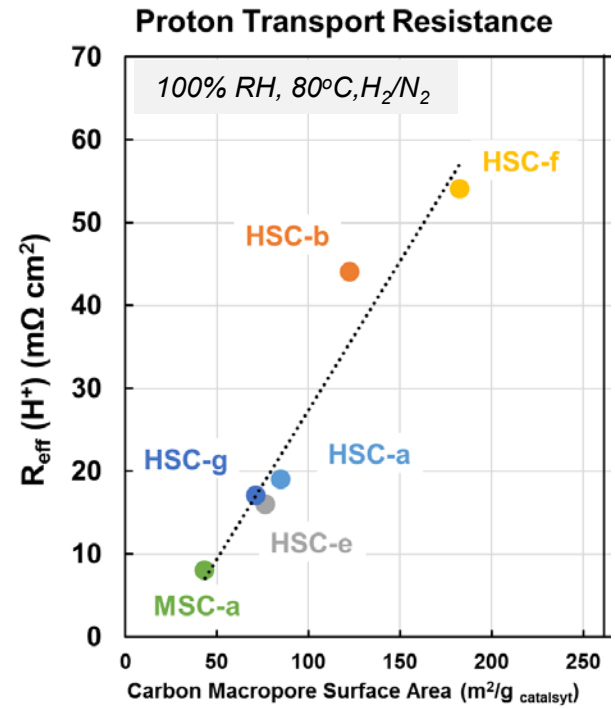
Technical Accomplishment:

Task 1.1 Catalyst Selection

Catalyst Layer Diagnostics





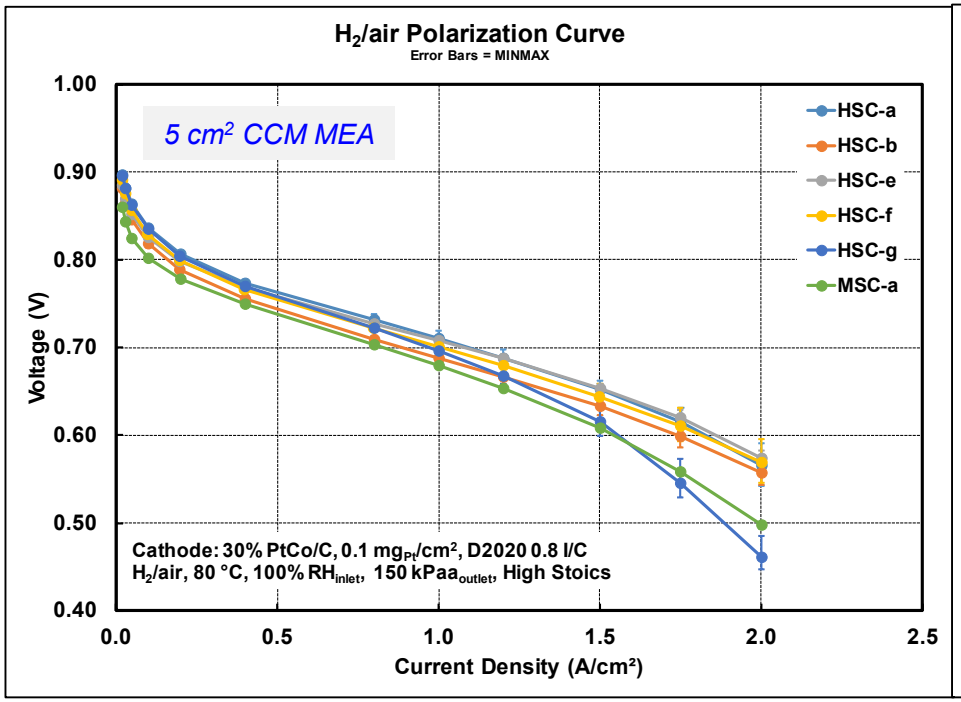


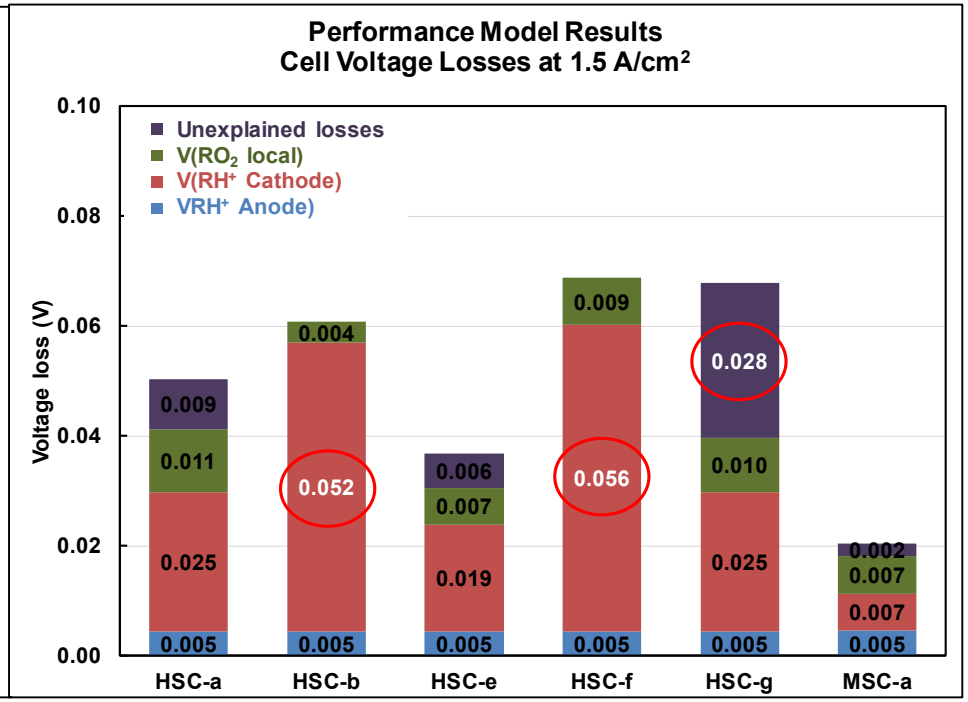
- Mass activity as high as 0.6 A/mg Pt achieved for PtCo on high surface area carbon supports
- Clear separation in mass activity and ECA between high surface area carbons and medium surface area carbons such as vulcan.
- HSC-b and HSC-f exhibit higher proton transport resistance.
  - Bulk proton transport resistance correlates well with macro porous carbon surface area.
- HSC-b and MSC-a exhibit low oxygen transport resistance. HSC-a and HSC-g are identical.
- **Carbon support has a strong influence of PtCo nanoparticle structure and catalyst layer properties**.

Technical Accomplishment:

Task 1.1 Catalyst Selection

Performance and Modelling



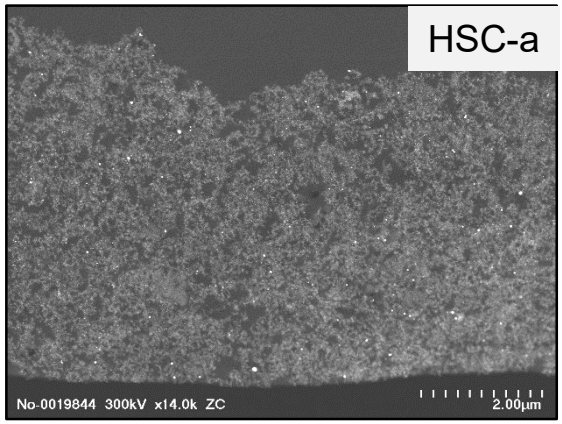


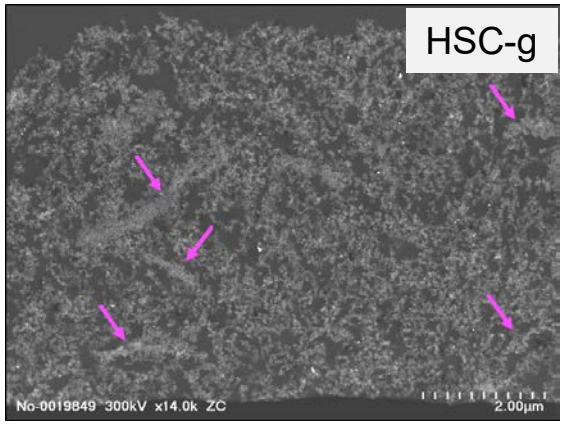
- 1-D model was used to assess the H_2-air performance measured at various conditions.
- Initial performance screening of catalyst provide the following performance order at 1.5 A/cm^2.
  - HSC-a $\geq$ HSC-e $\geq$HSC-f >HSC-b > HSC-g and MSC-a
- Transport losses in HSC-b and HSC-f are dominated by proton transport resistance.
- Being solid carbon, MSC-a exhibits significantly lower transport losses (both proton and oxygen). The HCD performance is limited due to poor dispersion.
- HSC-g exhibits drop in performance at high current density despite identical properties with HSC-a.

Technical Accomplishment:

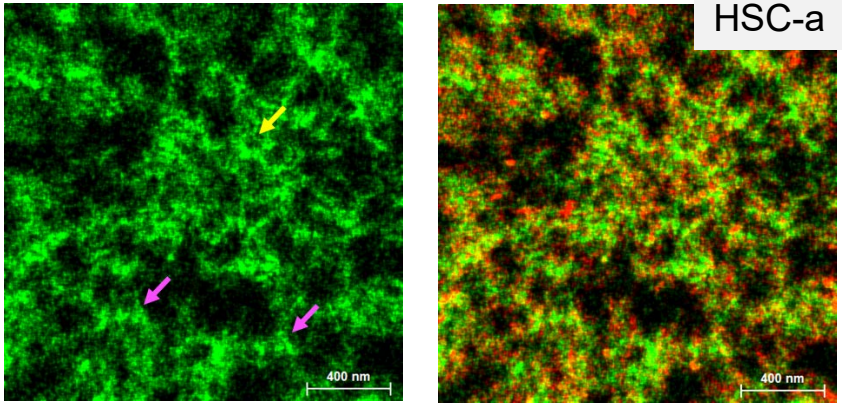
Task 1. 3 Catalyst / Ionomer Interaction

Carbon support /catalyst layer structure (HSC-a vs. HSC-g)

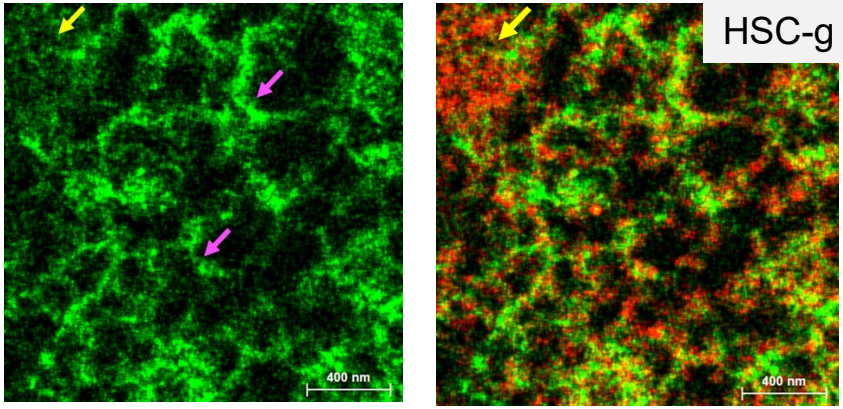




- Despite similarity in electrode diagnostic measurements and activity measurements (HSC-a vs. HSC-g), differences observed in catalyst layer microstructure.
- HSC-g tends to have larger secondary pore and local densification or "banding" (magenta arrows) observed with in catalyst layer.
- Some differences in ionomer aggregates and distribution observed (see below).



- No significant ionomer aggregation, ionomer aggregate sizes typically ~20nm (magenta arrows)
- Good infiltration of ionomer into PtCo/C agglomerates (yellow arrow)



- Relatively thicker films (40 -50 nm) around large secondary pore (magenta arrow)
- More significant ionomer aggregation with less infiltration in to PtCo/C dense agglomerates (yellow arrow)

Karren More

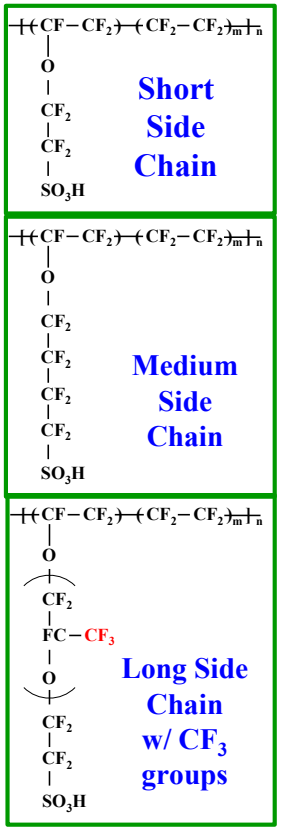
Technical Accomplishment:

Task 1.1 Ionomer Selection

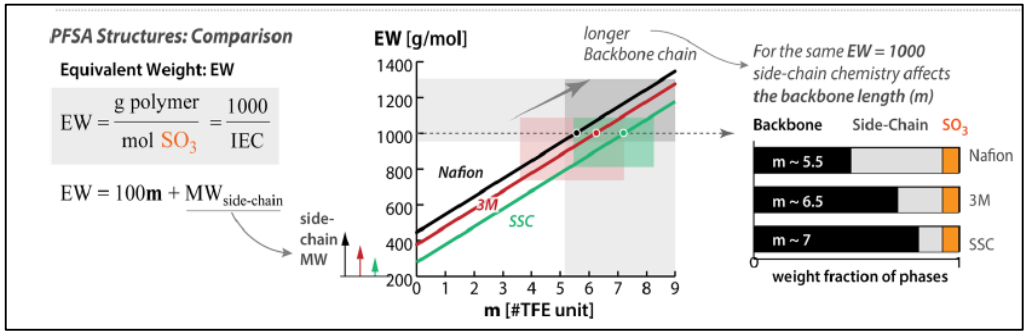
Ionomer Side Chain Length and Chemistry

Type	Ionomer	EW	A/W	I/C
1	Long Side Chain	950	3	0.90
2		1100	3	1.04
3	Medium Side Chain	729	3	0.69
4		825	3	0.78
5		1000	3	0.95
6	Short Side Chain	720	3	0.68
7		790	3	0.75
8		870	3	0.83
9		980	3	0.91

S.No	Measurement	Site
1	Viscosity	GM
2	Dynamic Light Scattering	GM
3	Small angle X-ray scattering	ANL
4	Size exclusion chromatography	GM
5	Ionomer adsorption	GM
6	Grazing Incidence SAXS	LBNL
7	Ionic conductivity	GM
8	Zeta Potential	GM
9	Particle Size Distribution	GM



- Both side-chain length and backbone length (m) affect EW and chemical structure and hence its <u>phase separation behavior</u>
- Impact of different ionomers with various sidechain chemistry and equivalent weight was tested in differential cell conditions



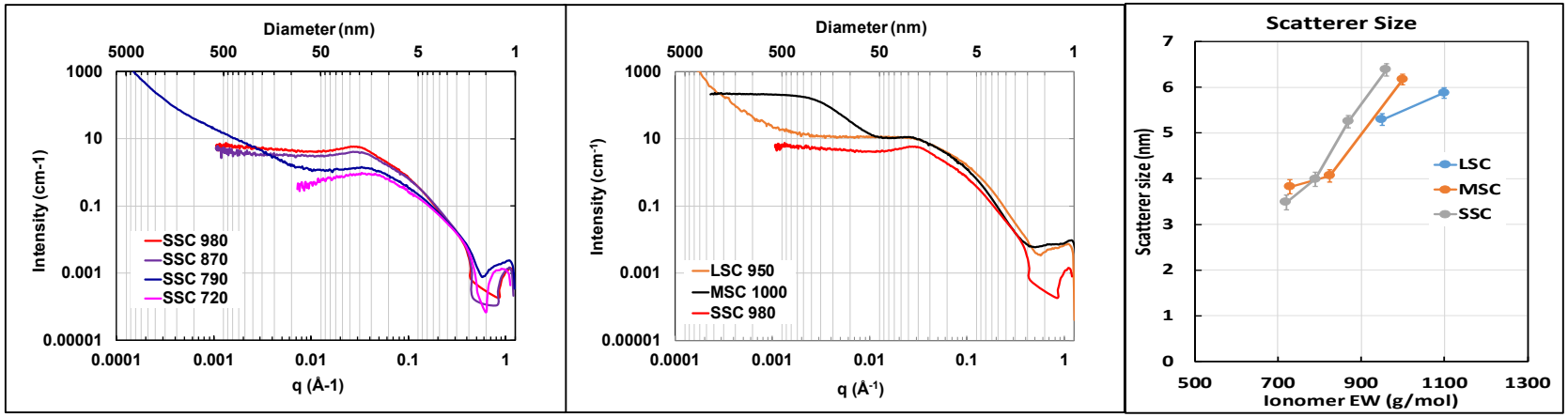
A. Kusoglu et al, *Chem. Rev.*, **2017**, 117 (3), 987-1104

Technical Accomplishment:

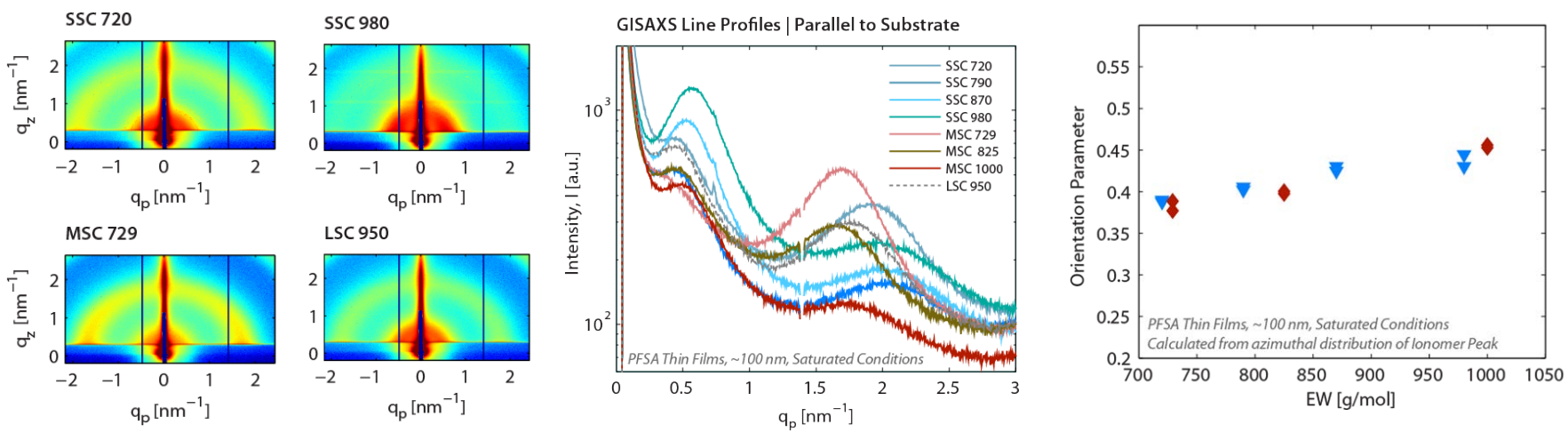
Task 1.1 Ionomer Selection

Ionomer Characterization

- Dilute ionomer solutions (same ionomer solids% and solvent as inks) were provided to ANL and LBNL for characterization



- **USAXS measurements at ANL :** Lower EW and side chain length result in smaller degree of aggregation and hence smaller rod diameters (better connectivity with more dispersed ionomer aggregates).



- **GISAXS* at LBNL** : Domain orientation and domain spacing increases with EW. For a given EW, sidechain could change distribution of ionomer domains.

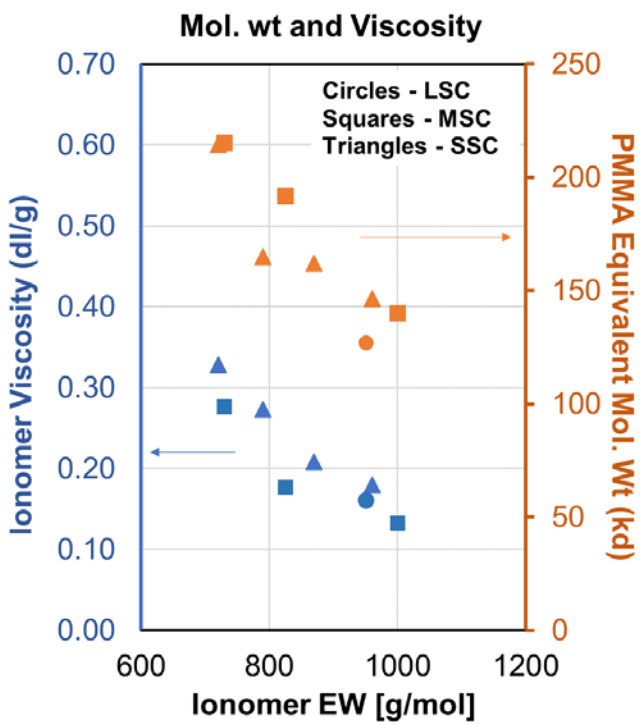
**Thin Films of 90-110 nm, spin-cast on Si substrate, annealed*

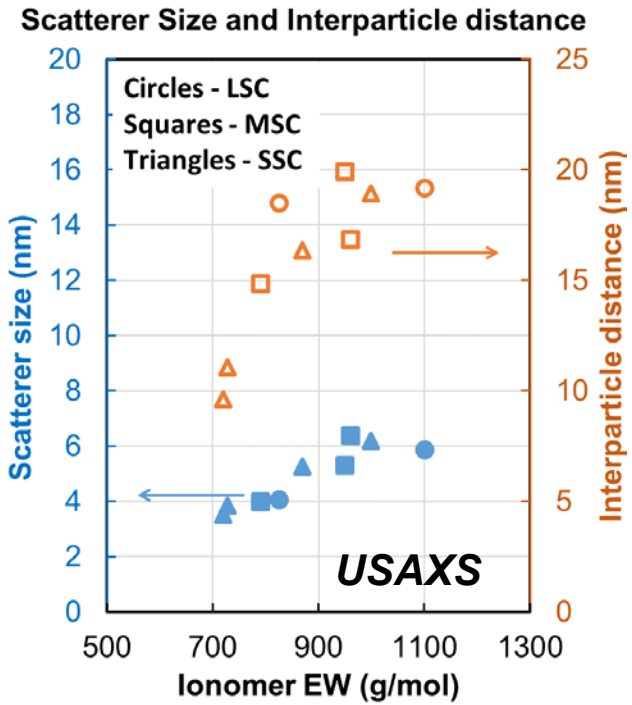
ANL: Deborah Myers, Nancy Kariuki
LBNL: Ahmet Kusoglu

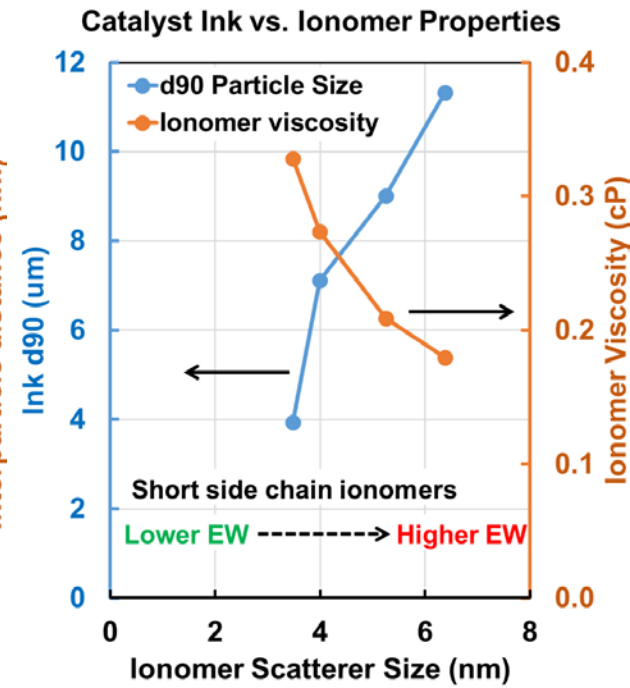
Technical Accomplishment:

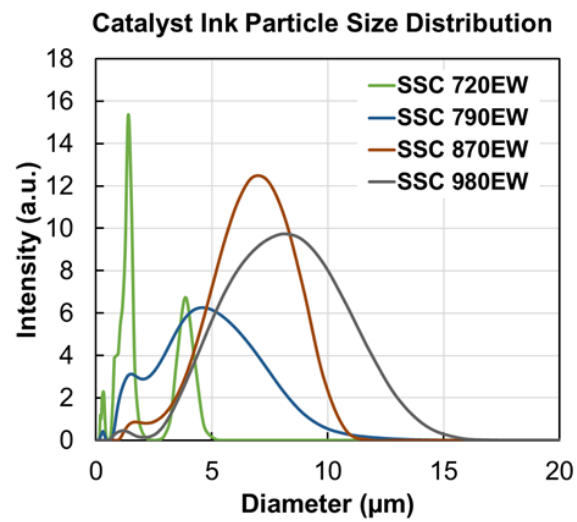
Task 1.1 Ionomer Selection

Ink Characterization







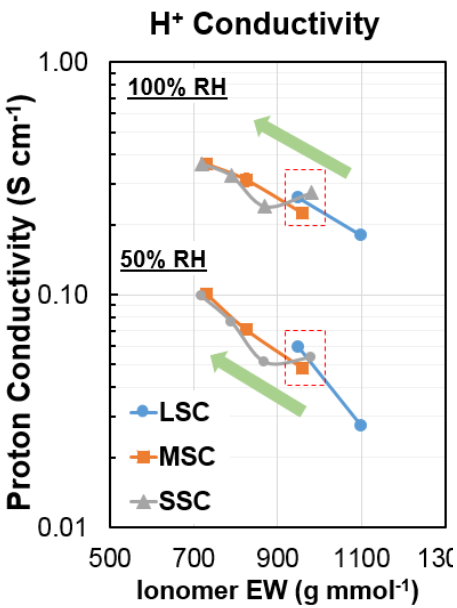


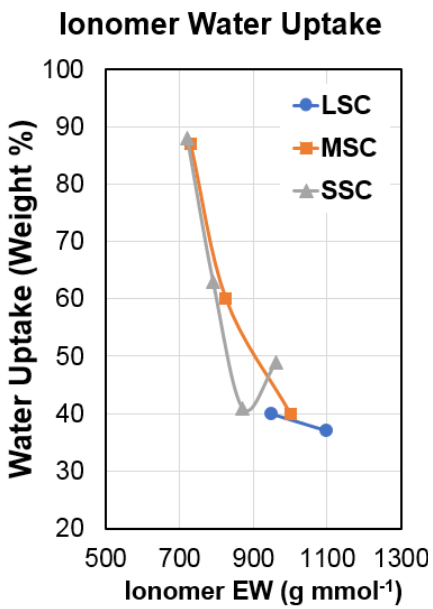
- Lower scatterer size, lower interparticle distance, higher viscosity of ionomer solution tend to break down ink agglomerates to lower values as measured by light scattering experiments.
- Does higher PSD in catalyst ink translate to differences in catalyst layer is still TBD. Samples to be assessed at ORNL.
- The current studies imply changes only to the bulk properties of ink and catalyst layer. How it impacts interfacial properties is still TBD. Needs more correlation with GISAXS measurement.

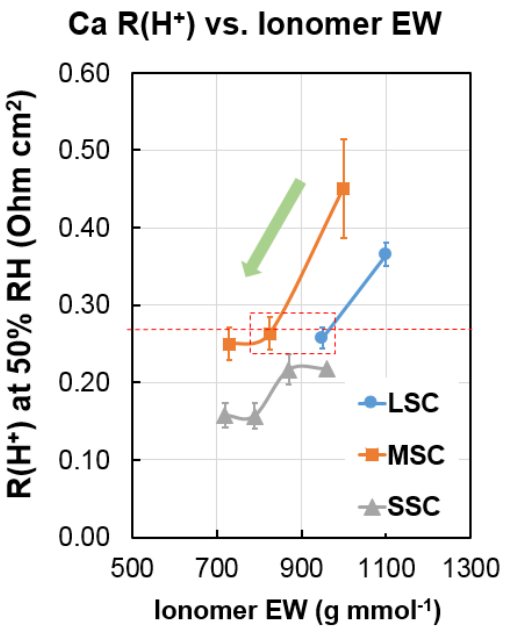
Technical Accomplishment:

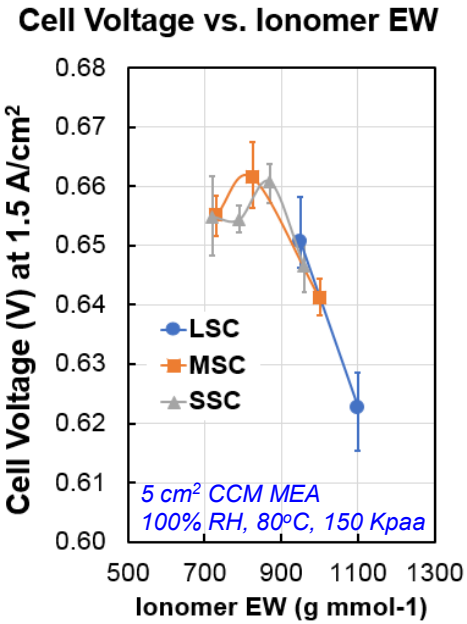
Task 1.1 Ionomer Selection

Performance Characterization

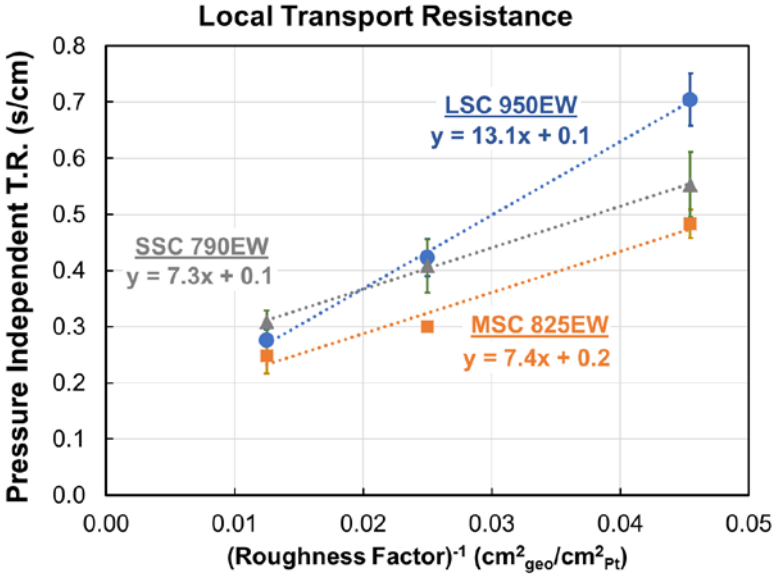








- Proton conductivity and water uptake measurements were conducted in cast films (~12 um thick)
- Cathode proton transport resistance and cell voltage measurements measured in 5 cm^2 MEA under differential test conditions.
- **EW has the most significant impact on cell voltage**. Decrease in proton transport resistance aids performance improvement in high current density.
  - Decrease in oxygen transport resistance also observed with lower EW ionomers.

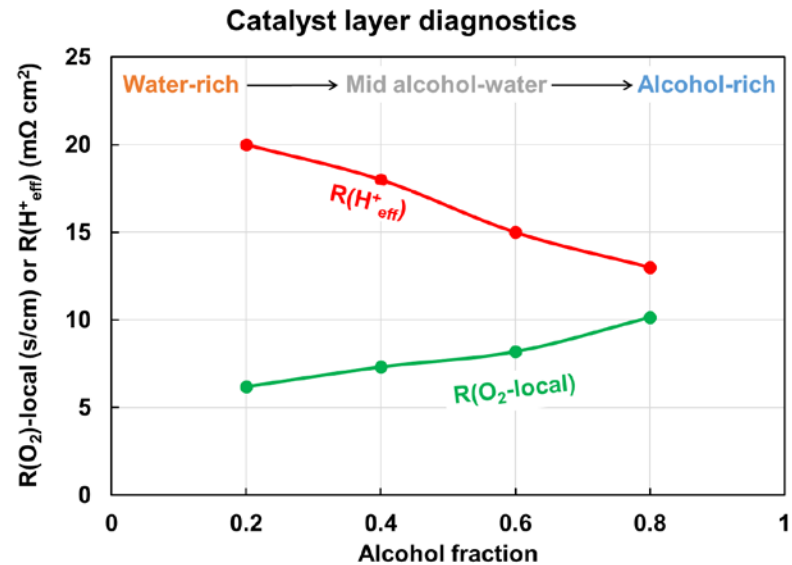


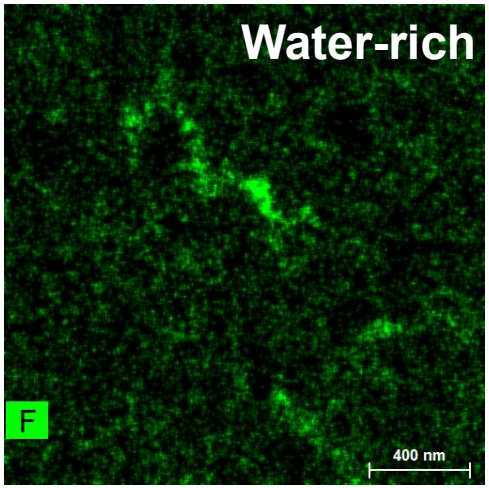
Technical Accomplishment:

Task 1. 3 Catalyst / Ionomer Interaction

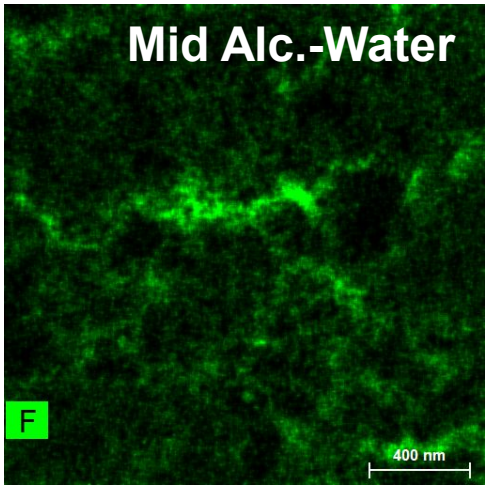
Ink solvent Effect

- Factors like alcohol to water ratio exhibit a significant impact on catalyst layer structure and measured electrode diagnostics.
- Water-rich catalyst layers enable a lower $R(O_2)$-local but with trade-off of a higher H^+-transport resistance in the catalyst layer
- Alcohol-rich inks enable a uniform ionomer distribution whereas either ionomer bands or aggregates are observed with increasing water content

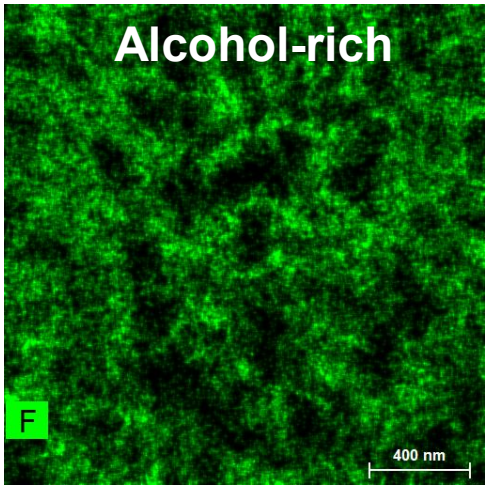




Ionomer aggregates (20-100 nm) associated with secondary pores



Ionomer bands (20-100 nm) running parallel to substrate



Uniform ionomer distribution with no aggregation (<20 nm)

Karren More

Technical Accomplishment:

Task 1. 3 Catalyst / Ionomer Interaction

Electrode Optimization

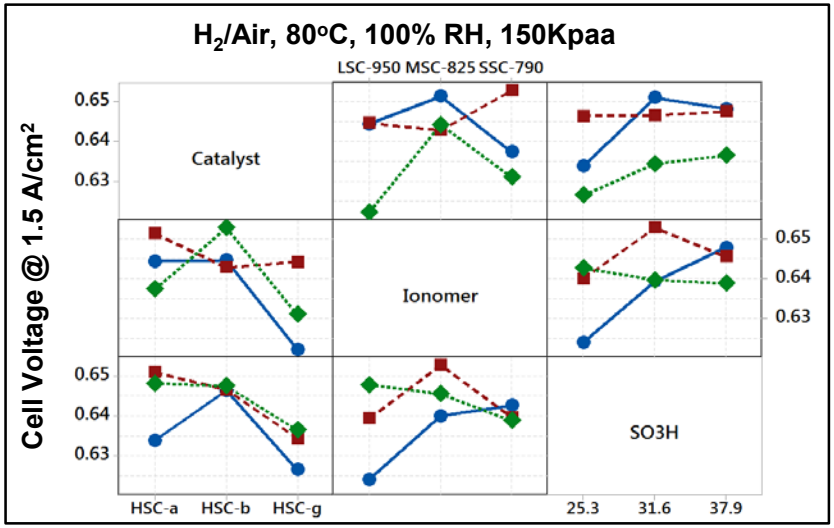
- 3 Catalysts and 3 Ionomers have been down-selected based on the catalyst and ionomer screening experiments

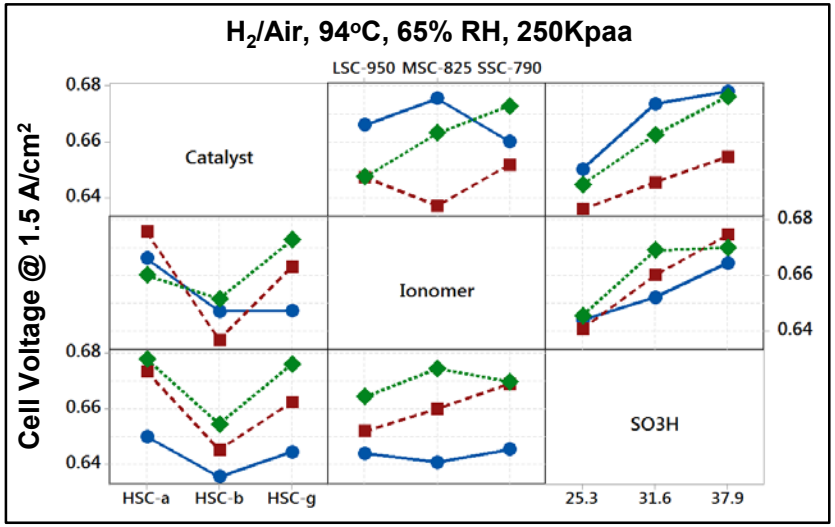
DoE with three factors (3^1)(3^1)(3^1)

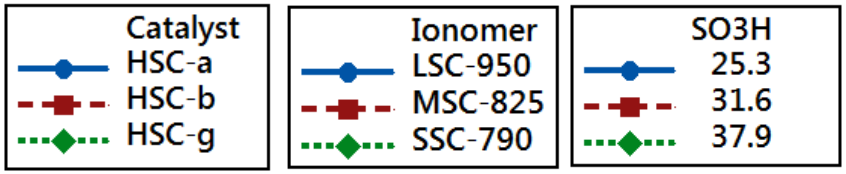
Catalysts (3)	Ionomers (3)	SO_3H Molality (mmol kg^{-1}) (3)
HSC-a	LSC EW950	25.3
HSC-b	MSC EW825	31.6
HSC-g	SSC EW790	37.9

- **Combination of HSC-a with MSC ionomer provides the most robust combination across various operating conditions.** HSC-a also exhibit higher activity retention (from FC144)
- HSC-b cathode with SSC ionomer combination provides benefits under low pressure and wet conditions but severely falls below target at dry operating conditions evens with a highly conductive ionomer
- HSC-g does show improvements under high pressure in combination with low EW SSC ionomers but severely falls short at other conditions

5 cm^2 CCM MEA (3 repeats). Differential Conditions







Technical Accomplishment:

Task 5.1 Membrane Selection

Membrane Selection

- Various membrane candidates with different ionomer chemistry and supports were studied for use in SOA MEA.

Key Requirements

- Membrane to pass single stressor durability test.
- ASR of 0.02Ω·cm^2 at 95ºC (requirement for 95ºC system with humidifier.)

Key Results

- GM PFSA has passed automotive durability cycle target (>5000h) and meets ASR requirement.
- 3M PFIA-S failed DOE automotive drive cycle durability test in 800h (target = 5000h) (see fc109_yandrasits_2017).
- Giner/RPI BP-ArF4 w/o support → ASR is higher than GM supported PFSA
  - Non-supported membrane is brittle upon handling → did not run durability ASTs

✓ **Moving ahead with Durability studies using GM PFSA membrane**

Mem.	Ionomer	Support	Thickness
GM	PFSA	ePTFE	12µm
3M	Perfluoro imide acid (PFIA)	Fluoropolymer nanofiber	10µm
Giner (RPI)	Biphenyl Perfluoroalkyl sulfonate Polymer (BP-ArF4)	DSM (dimensionally stable membrane)	12µm

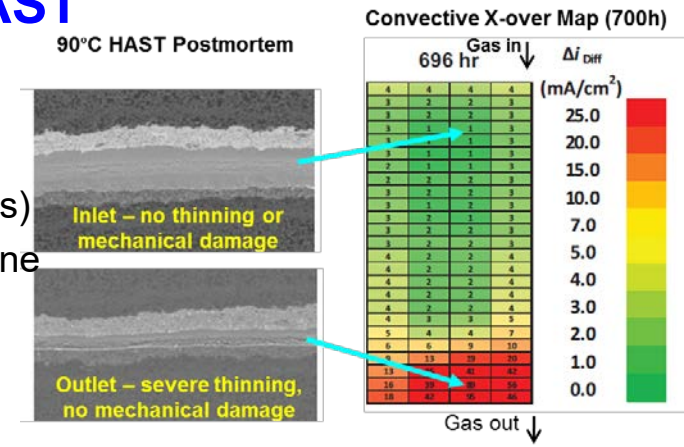
Characteristic	Units	2020 Targets	GM ePTFE-PFSA	PFIA-S (10 um)	Giner BP-ArF4 non-supported
Maximum O_2 cross-over	mA/cm^2	2	2.4	0.6[a], 3.5[b]	
Maximum H_2 cross-over	mA/cm^2	2	1.5	1.9[c]	0.6
ASR at 120°C, P_{H2O} 40 kPa	Ωcm^2	0.02	0.120	0.054	0.147
ASR at 120°C P_{H2O} 80 kPa	Ωcm^2	0.02	0.037	0.019	0.042
ASR at 95°C P_{H2O} 40 kPa	Ωcm^2	0.02	0.017	0.012	0.019
ASR at 80°C P_{H2O} 25 kPa	Ωcm^2	0.02	0.031	0.020	0.035
ASR at 80°C P_{H2O} 45 kPa	Ωcm^2	0.02	0.014	0.008	0.016
ASR at 30°C P_{H2O} 4 kPa	Ωcm^2	0.03	0.021	0.018	0.024
ASR at -20°C	Ωcm^2	0.2		0.2[d]	
Min electrical resistance	Ωcm^2	1,000	>3000	1,635[e]	4700
Mechanical Durability (80ºC RH cycling)	RH Cycles	20,000	>40,000	>24,000	
Chemical Durability (OCV, 90ºC, 30%RH)	hrs	>500	>500	614	

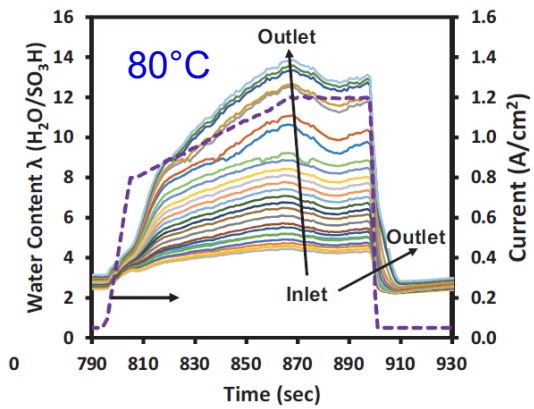
Technical Accomplishment:

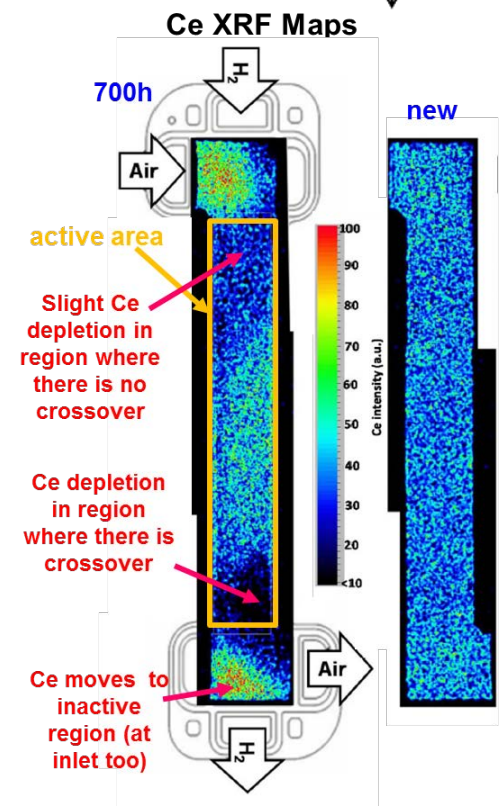
Task 5.2: Combined Chemical-Mechanical HAST

Goal: develop a highly accelerated stress test to evaluate membrane durability in a realistic fuel cell environment (no dry inlets, no OCV)

- 70, 80 & 90°C/30%Rh_{in}, 0.05 – 1.2 A/cm^2 , (distributed measurements)
- In-situ diagnostics: Shorting resistance, diffusive crossover (membrane thinning), and convective crossover (pinhole formation) mapping
- **Deep RH cycling at the outlet → High Mechanical Stress**
- **Inlet stays relatively dry throughout → High Chemical Stress**







Membrane fails by chemical degradation in the area with highest mechanical stress (deep RH cycling) but lowest chemical stress.

- Ce moves from active to inactive region
- Result led to two new work streams
  - Development of model for Ce transport during operation
    - Diffusion (slow), Convection (faster) & Conduction (fastest)
  - Ex-situ measurement of impact of mechanical stress on chemical degradation (future work)

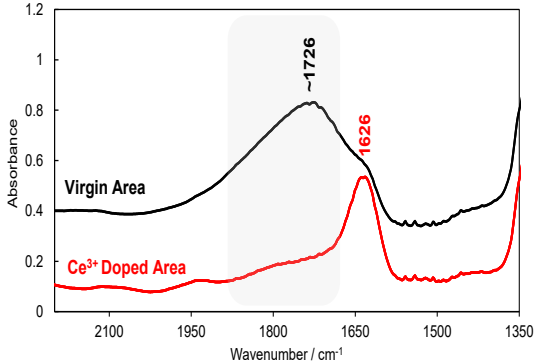
Journal of The Electrochemical Society, **165** (6) F3217-F3229 (2018)

Technical Accomplishment:

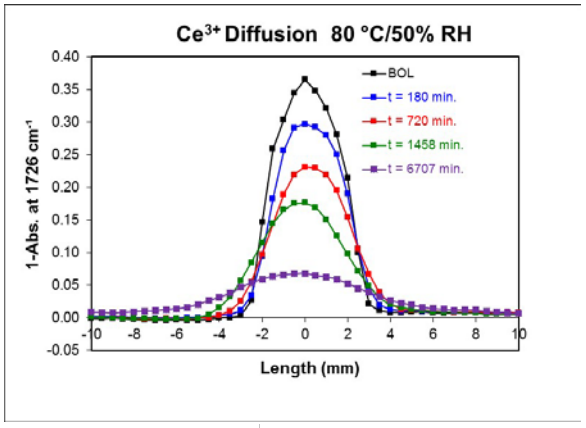
Ce Diffusion Measurement

Test: introduce a spot of Ce^{3+} in a membrane and watch it move with time

FTIR indirectly measures cations as cations modulate membrane water content and exclude H_2O

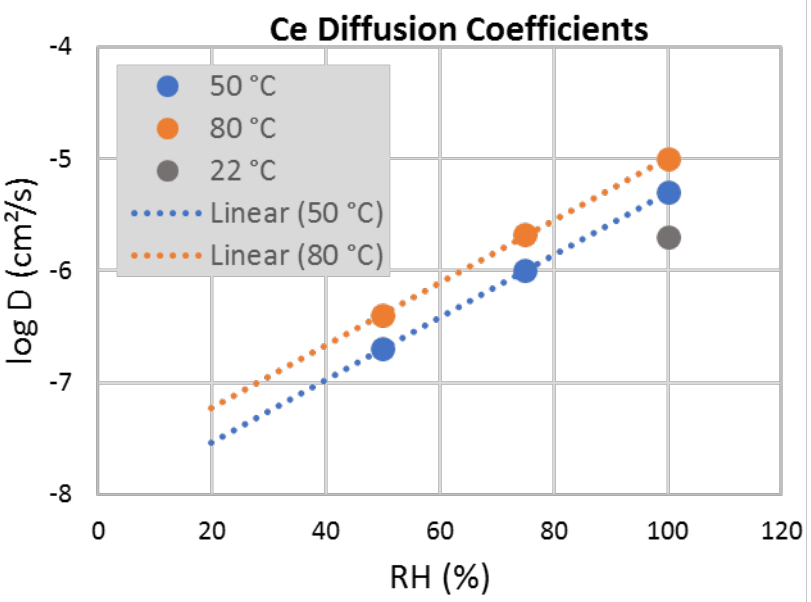


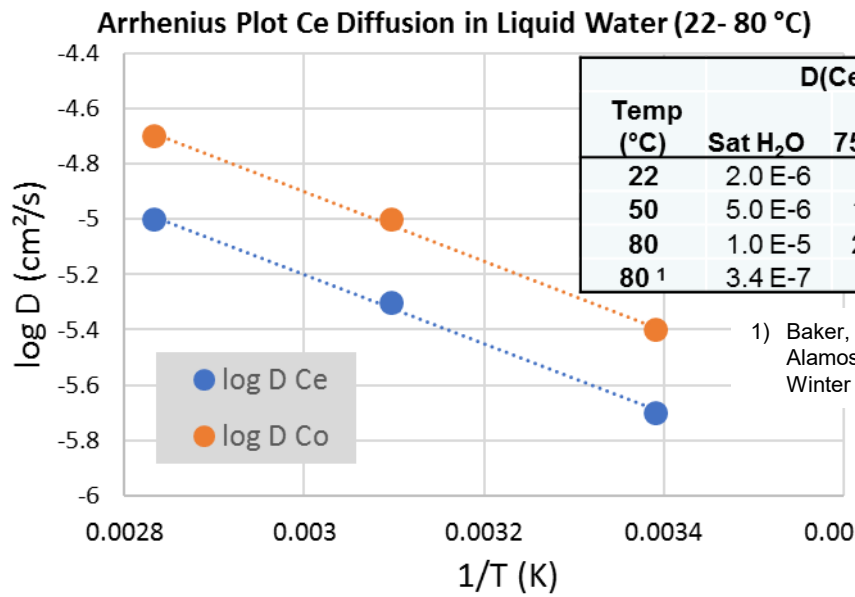
FTIR Spectrum of H_2O Bending Region



- Dilute-solution theory holds

  $C(x,t) = B/2(\pi Dt)^{1/2} * \exp(-x^2/4Dt)$
- Diffusivity is exponentially dependent on RH
- Co^{2+} about twice as mobile as Ce^{3+} in liquid water
- GM measurements >10X higher than LANL measurements



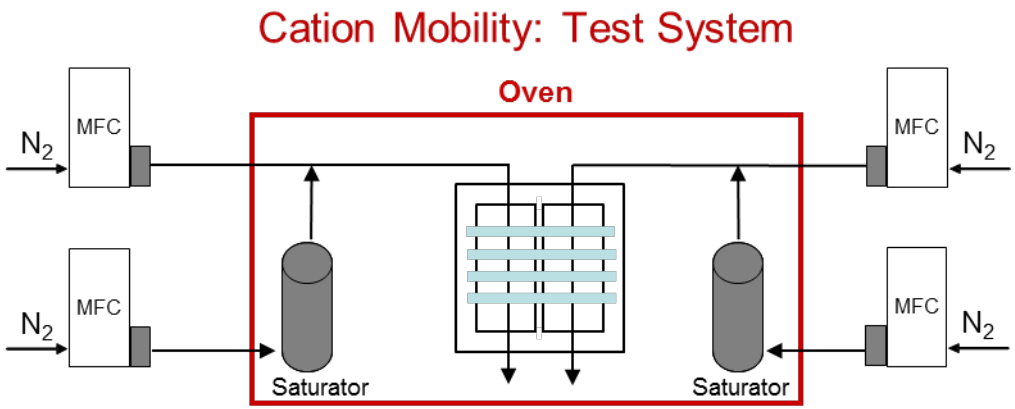


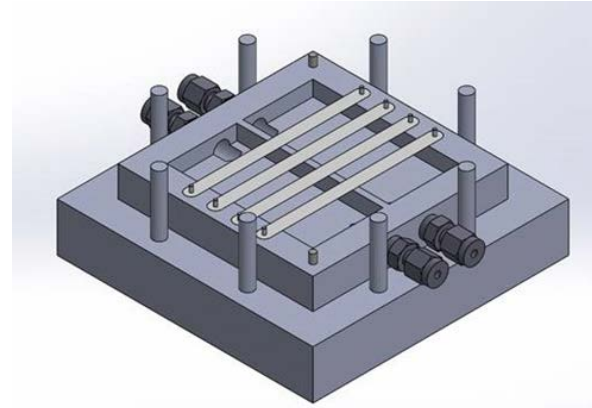
Temp (°C)	D(Ce^{3+}) (cm²/s) Sat H_2O	75% RH	50% RH
22	2.0 E-6		
50	5.0 E-6	1.0 E-6	2.0.E-7
80	1.0 E-5	2.0 E-6	4.0 E-7
80 [1]	3.4 E-7		2.8 E-8

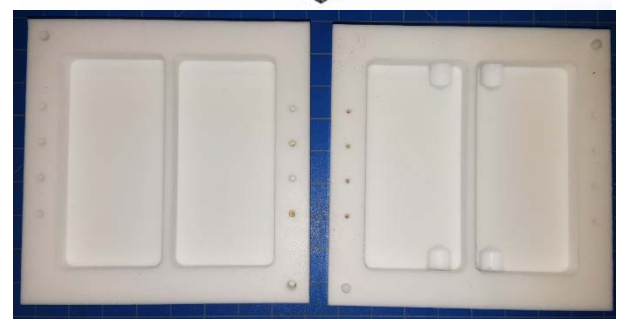
1) Baker, et. al, Los Alamos, 2017-FCPAD Winter Meeting

Technical Accomplishment:

Ce Convection Measurement

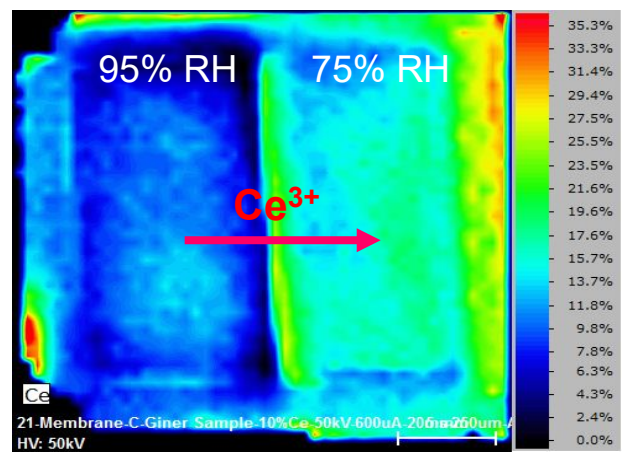






- 2 discreet chambers with independent RH control
- Can test 4 samples (i.e., different cations or concentrations) simultaneously
- Migration will be investigated as a functions of Δ RH, Δ [M^+], Temperature, Time

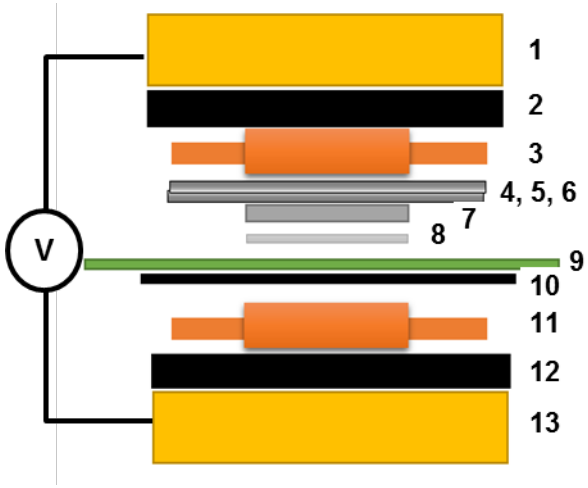
Initial testing underway
- Single sheet of 10% Ce^{3+}- exchanged N211
- 80° C, 95% RH → 75% RH
- XRF used to measure Ce distribution after 72h
- Ce moves from wet to dry region
- **Fairly uniform Ce distribution in each chamber indicates convection dominates over diffusion**
- Model of quantitative maps to be used to determine convective mass transfer coefficients as f(T, RH)



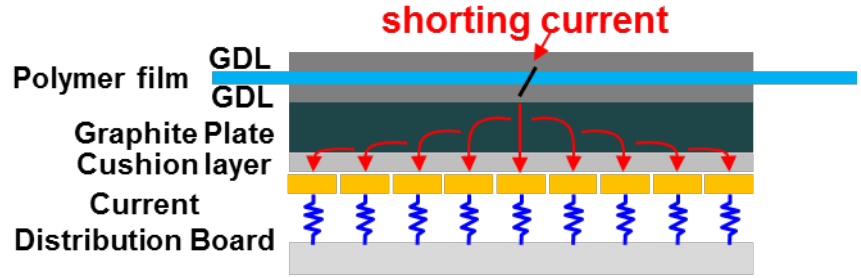
Technical Accomplishment:

Task 5.3: Impact of Local Shorting on Membrane Degradation

- Method developed to create and measure soft shorts
  - Induce shorts by incrementally increasing cell compression (95°C, ambient RH)
  - Use current distribution board to maximize spatial resolution, and sensitivity
    - In a single cell we can get multiple shorts with a range of resistances
- **GOAL: Create multiple shorts <200 Ω in different regions of the MEA**



1	Copper end plate
2	Carbon paper pack
3	Steel compression plate
4	Sample: GDL
5	Sample: Polymer film
6	Sample: GDL
7	Graphite plate
8	Carbon paper cushion
9	Current distribution board
10	Carbon paper cushion
11	Steel compression plate
12	Carbon paper pack
13	Copper end plate



- Graphite plate and GDL allows the shorting current to spillover to multiple distribution segments
- The circuit board measures a smeared current density map
- Deconvolution scheme used to recover the current from the individual shorts and convert to resistance

Shorting Current Density (A/cm2)

0.0005	0.0003	0.0002	0.0002	0.0001	0.0001	0.0001	-0.0004
0.0008	0.0004	0.0003	0.0002	0.0002	0.0002	0.0001	0.0002
0.0005	0.0004	0.0004	0.0004	0.0004	0.0003	0.0002	0.0003
0.0003	0.0005	0.0007	0.0009	0.0007	0.0005	0.0004	0.0004
0.0003	0.0005	0.0010	0.0021	0.0013	0.0008	0.0007	0.0007
0.0002	0.0004	0.0008	0.0016	0.0014	0.0013	0.0013	0.0012
0.0002	0.0003	0.0005	0.0008	0.0012	0.0021	0.0026	0.0021
0.0001	0.0002	0.0004	0.0007	0.0013	0.0027	0.0048	0.0030

De-convoluted Shorting Resistance (Ω)

159748	15963	10145	26213	11699	2042	479	312
330	2711	2216	7601	7073	1554	6535	606
5475	2042	47876	2121	1675	4608	1664	9613
2947	1799	4768	46524	6002	2635	862	67857
2269	2790	21831	92	1619	975	479	5076
2141	2103	1223	237	6866	6017	935	872
11220	2551	1116	2395	1078	175	2599	5817
1950	6010	3075	4387	5878	1251	57	2957

Technical Accomplishment:

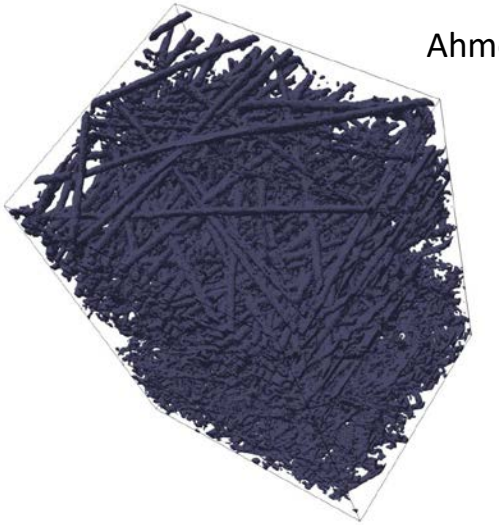
Task 5.3: Impact of Local Shorting on Membrane Degradation

Goal: develop a non-destructive method to image shorting location in an MEA

- Advanced Lights Source, beamline 8.3.2 at LBNL

Lens	Resolution	FOV
10x	0.65 µm/pixel	1.7 mm

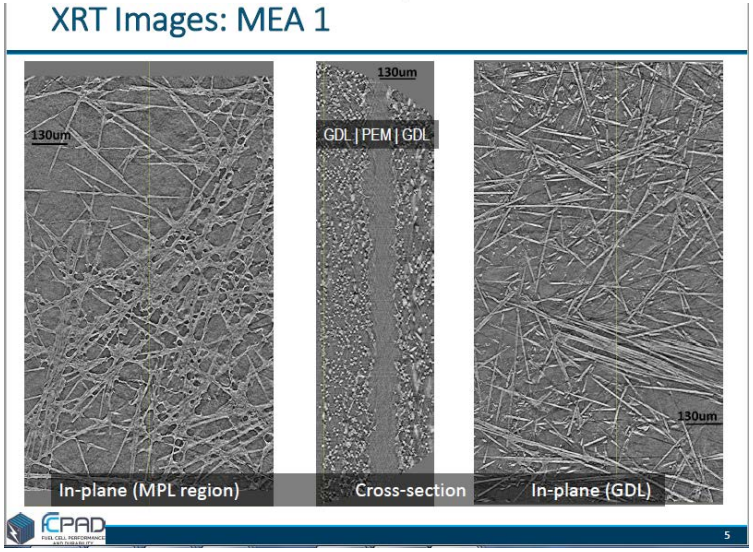
- Typical exposure time of 400ms at 20keV exposure.
- Total scan time 10-15 minutes for 2560 projections
- Full 50cm^2 MEA fits in instrument → non destructive



Ahmet Kusoglu,
Lalit Pant

LBNL X-Ray CT 3-D construction of MEA

- Top/bottom sections are GDL fibers with the membrane in between (blank space)
- Can see the 10-15µm GDL fibers in detail
- Once we have MTA executed we will send pre-shorted MEA with segmented shorting map so LBNL knows where to look → We hope to be able to see fibers puncturing across membrane



Next Steps

- Run accelerated durability tests with CD board to monitor changes in shorting and diffusive and convective crossover at shorting sites.
- Re-image same locations with X-ray CT after durability tests to isolate degradation mechanisms (thermal, chemical, mechanical)

Collaborations

- **General Motors (industry) : Prime**
  - Overall project guidance, MEA integration, durability, model development

FC-PAD (National Labs)

- Argonne National Lab (Dr. Debbie Myers and Dr. Rajesh Ahluwalia)
  - Ink characterization and Pt, Co dissolution studies
  - Electrode degradation model.
- Lawrence Berkeley National Lab (Dr. Adam Weber and Dr. Ahmet Kusoglu))
  - Membrane mechanical stress model, X-ray CT, GI-SAXS
- Los Alamos National Lab (Dr. Mukund Rangachary and Dr. Rod Borup)
  - Voltage cycling tests (TBD), Accelerated stress tests
- National Renewable Energy Lab (Dr. Kenneth Neyerlin)
  - Electrochemical diagnostics, H_2-N_2 Voltage cycling tests
- Oakridge National Lab (Dr. Karren More)
  - Catalyst layer characterization, Ionomer catalyst interaction

Sub Contractors

- University of Texas Austin (Prof. Yuanyue Liu and Prof. Paulo Ferreira) (University)
  - Identical location TEM, PSD measurements
- Giner (Dr. Cortney Mittelsteadt) (Industry)
  - Membrane degradation studies

Responses to Last Year AMR Reviewers' Comments

- *"The objective of establishing benign operating conditions does not seem particularly valuable, as operating conditions are very application-, component-, and system-dependent"*
  - ❑ Yes operating conditions can be system specific. The output of the project maps out conditions to avoid and conditions to adopt for prolonged durability. It will serve as a toolkit for system engineers to craft their systems. This knowledge was never complete and is lacking for recent advanced materials.

- *"Electrode durability model ….will be based on empirical design of experimental data. Need fundamental mechanistic model"*
  - ❑ It is not a purely empirical model. The well-understood physics (thermodynamics, kinetics, and transport) that are impacted by catalyst degradation mechanisms will be simulated using physics-based models. Models for Pt and Co transport will be fundamentally modeled, however the rate parameters for Pt and Co leaching will be empirically estimated. Given the knowledge base in the timeframe of this program, we think this is the best approach.

- *"All of ….Feedback from the work in year two to further optimize the MEA should be added.*
  - ❑ We are confident the SOA MEA at end of BP1 is rightly optimized. But if promising insights are made both in this project or relevant DOE projects in BP2, follow up studies will be conducted in BP3 as needed.

- *"It is unclear how well, if at all, project results will be translatable to the field as a whole if the project is using GM-proprietary materials exclusively".*
  - ❑ These are representative state of art materials and fundamental trends will translate very well. We are indeed providing these MEAs to FCPAD partners.

GM

Future Work

- Execute voltage cycling experiments to map the impact of operating conditions.
  - ECA, SA, CO stripping, RO_2-local (limiting current), V loss etc.(NREL)
  - MEA characterization including EPMA, TEM, EELS mapping etc. (ORNL, UT Austin).
- Obtain ex-situ dissolution rates of Pt, Co and elucidate growth mechanisms (ANL/NREL).
- Develop predictive model based on the experimental data with the fundamental understanding of degradation mechanisms.
  - Models for PtO growth, Pt & Co dissolution, Pt & Co transport, Pt shell thickness
  - Correlations quantifying Pt particle coalescence, changes in specific activity, Pt utilization, RO_2 – local.
- Fundamental studies to isolate impact of stress factors on membrane degradation.
  - Develop ex-situ method to quantify the impact of mechanical stress on chemical degradation
  - Determine Ce convective transport coefficients
  - Accelerated stress tests of SOA and pre-shorted MEAs in segmented cells combined with visualization techniques such as XRF & X-ray CT (LBNL).
  - Determine degradation reaction orders and rate constants for ionomer chain scission & unzipping using OCV and vapor cell tests on membranes of varying thickness
- Develop model for in-plane Ce migration during transient fuel cell operation
- Develop combined chemical/mechanical membrane degradation model based on experimental data and the fundamental understanding of degradation mechanisms.

Any proposed future work is subject to change based on funding levels.

Summary

- In the BP1, best in class MEA subcomponents such as catalyst, ionomer and membranes were studied to generate a state of art MEA.
  - High surface area carbon is key to achieve better dispersion and higher activity.
  - EW is likely the most important property dictating performance and ink properties of the ionomer.
  - Design of experiments with various ionomer chemistry indicated HSC-a with MSC ionomer provided the best combination for maximum performance.
- The generated SOA MEA exhibited > 1 W/cm^2. The performance was demonstrated in both 5 cm^2 and 50 cm^2 single cell MEAs.
- Combined chemical/mechanical highly accelerated stress (HAST) was developed Deep RH cycling at outlet and dry inlets were combined to induce mechanical and chemical stress in different regions of the cell.
  - Chemical degradation observed in region of highest mechanical stress
  - Significant in-plane Ce migration observed during operation
- Ce diffusivity and convective measurements were performed. Results indicate Ce^{3+} movement via convection is the most dominant.
- Method developed to generate and quantify local resistance of membrane shorts
- Pre-work to start voltage cycling design of experiments was completed.

Acknowledgements

DOE

- Greg Kleen (Technology Manager)
- Donna Ho (Technology Manager)

General Motors

- Srikanth Arisetty
- Nagappan Ramaswamy
- Vinaykumar Konduru
- Craig Gittleman
- Mark F. Mathias
- Yeh-Hung Lai
- Frank Coms
- Anusorn Kongkanand
- Ruichun Jiang
- Ken Rahmoeller
- Ashley McQuarters
- Tim Fuller
- Mehul Vora
- Balsu Lakshmanan
- Wenbin Gu
- Ratandeep Kukreja
- Joe Ziegelbauer
- Mohammed Atwan

Giner

- Cortney Mittelsteadt (sub-PI)
- Hiu Xu
- Zach Green

Univ of Texas, Austin

- Prof. Yuanyue Liu (sub- PI)
- Prof. Paulo Ferreira

FC-PAD

- Rod Borup
- Mukund Rangachary
- Adam Weber
- Ahmet Kusoglu
- Lalit Pant
- Deborah Myers
- Nancy Kariuki
- Rajesh Ahluwalia
- Joshua Wang
- Karren More
- KC Neyerlin