U.S. DEPARTMENT OF ENERGY

Office of ENERGY EFFICIENCY & RENEWABLE ENERGY

Enabling Durable High Power Membrane Electrode Assembly with Low Pt Loading

Swami Kumaraguru, General Motors

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Fuel Cell Technologies Office Webinar

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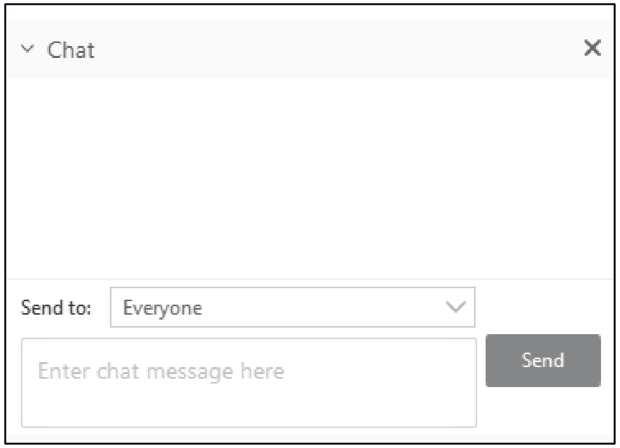
This presentation is part of the monthly webinar series provided by the U.S. Department of Energy's Fuel Cell Technologies Office (FCTO) within the Office of Energy Efficiency and Renewable Energy (EERE). Funding for research, development and innovation to accelerate progress in hydrogen and fuel cell technologies is provided by EERE FCTO.

During Q&A session:

Please type your questions to the chat box. **<u>Send to: (HOST)</u>**



General Motors – Fuel Cell Technology

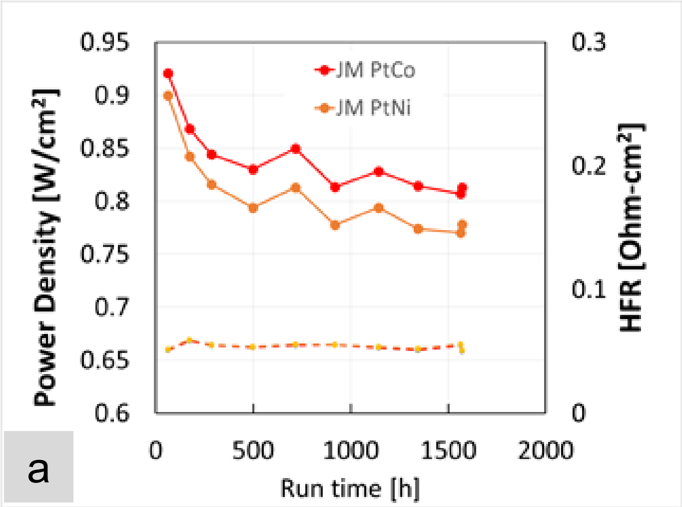
GM & Honda Announce Joint Manufacturing Venture (2017)

CONTACT US: FUELCELL@GM.COM

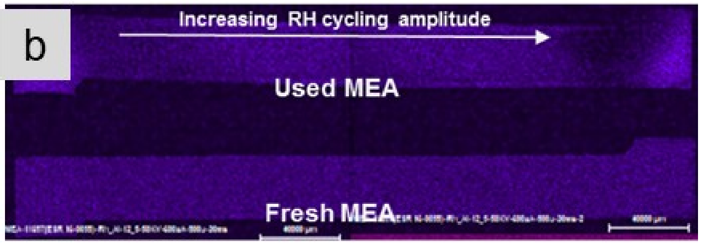
https://www.gmhydrotec.com

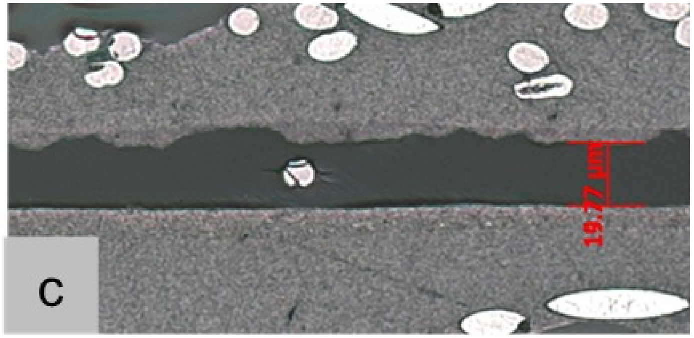
Relevance (Challenges)

- **Electrode Durability**
  - 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 Durability**
  - 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 (c) from GDL create stress points which can lead to early failure
  - Are thinner membranes inherently less durable?
- **Define State of Art MEA**
  - How do you define a best in class catalysts and properties needed.
  - What is the role of electrode ionomer and its properties
  - Role of ink formulation and its impact catalyst layer structure
  - Can current materials achieve DOE 2020 performance and durability target



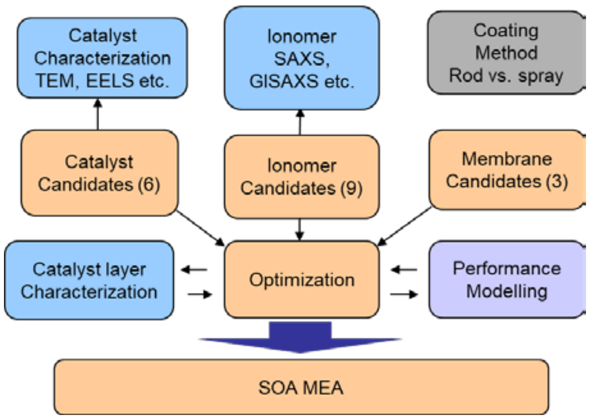
https://www.hydrogen.energy.gov/pdfs/review14/fc087_kongkanand_2014_o.pdf





Approach

Enabling SOA MEA



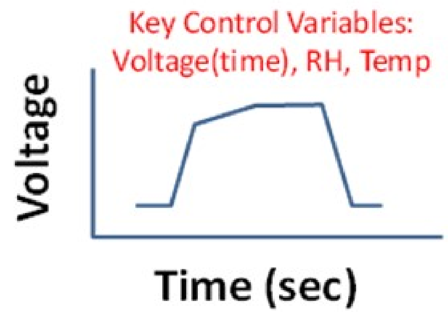
- Systematic screening of various best in class catalysts and ionomers to generate SOA.

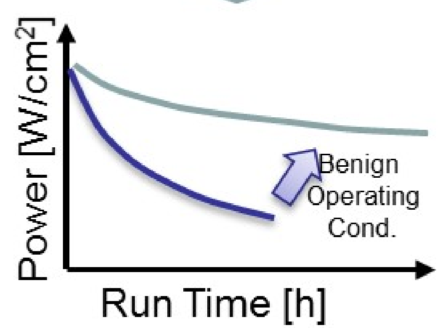
- Characterization of both components and integrated SOA MEA conducted to provide fundamental understanding of the material properties and its impact on performance.
    - Role of carbon support on activity
    - Role of carbon support on transport losses
    - Role of Ionomer properties
    - Role of Ink properties

Enabling Durability

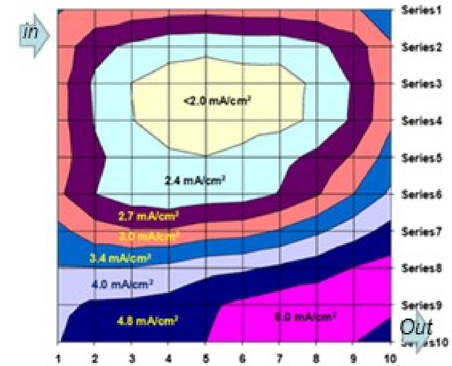
- Study effect of operating conditions on electrode and membrane durability
- Map degradation stress factors

Electrode





Membrane



Combined Chem. and Mech. stress segmented cell test

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

Develop fundamental models to predict electrode and membrane degradation

Approach and Collaboration

SOA MEA

- Electrochemical Diagnostics (R_{H+}, i_L, RO_2, MA, SA)
- Catalyst Characterization (TEM, BET, EELS)
- Ionomer Characterization (SAXS, GISAXS)
- Catalyst Layer Characterization
- Catalyst Layer Optimization

Electrode Durability

- H_2-N_2 Voltage Cycling Diagnostics (I-V, ECA, R_{H+}, i_L, RO_2, MA, SA)
- BOL & Aged MEA Characterization (TEM, XRD, EDX, SAXS, EPMA)
- Pt and Co Dissolution (Ex-situ ICP -MS)
- Construct PtCo Models
- Predict and Verify on ASTs

Membrane Durability

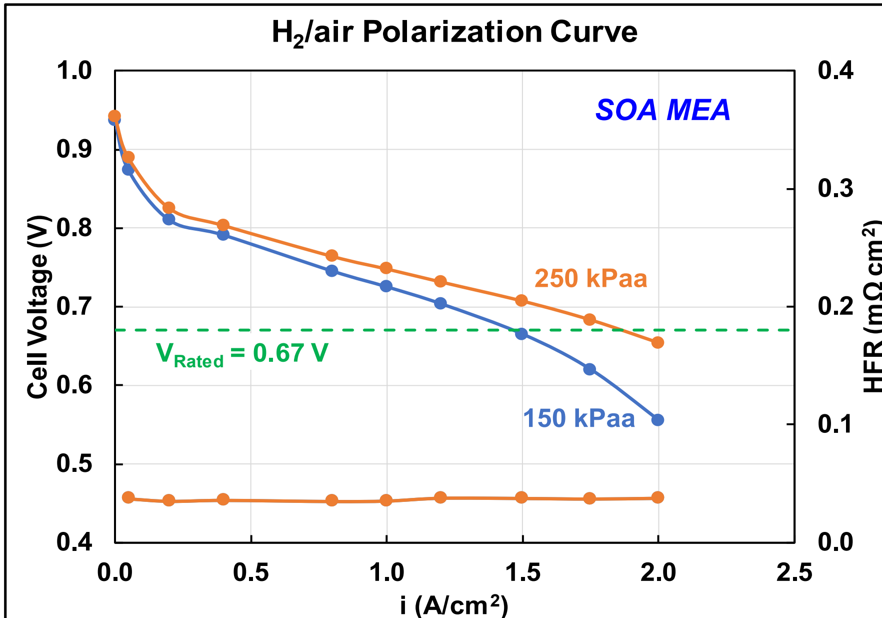
- Chem and Mech. HAST (Temp, RH, Voltage, $d\lambda/dt$)
- State of Health Diagnostics (FTIR, FRR, XRF, MW)
- Mechanistic Studies (Ce migration, thickness effect etc)
- Advanced Characterization (X-Ray CT)
- Model Integration

Technical Accomplishment:

State of Art (SOA) MEA

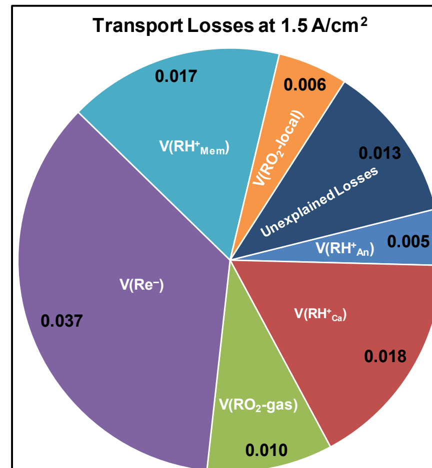
Item	Units	2020 Target	2018 Status	
			94° C 250Kpaa	80° C 150kPaa
Cost	$\$/kW_{net}$	14	-	-
Q/ΔT	kW/°C	1.45	1.45	1.94
i at 0.8 V	A/cm²	0.3	0.44	0.30
PD at 670 mV	mW/cm²	1000	**1275**	**1000**
Durability	Hours @ < 10% V loss	5000	TBD	TBD
Mass activity	A/mg_{PGM} at 0.9 V	> 0.44	0.65	0.65
PGM Content	g/kW rated mg/cm^2_{MEA}	0.125	0.10	0.125

- The generated SOA exhibit > 1000 mW/cm². Higher temperature and higher pressure polarization curve used to achieve the Q/ΔT target.
- Performance verified in FCPAD (NREL) on 5 cm², 10 cm² and 50 cm² single cells.

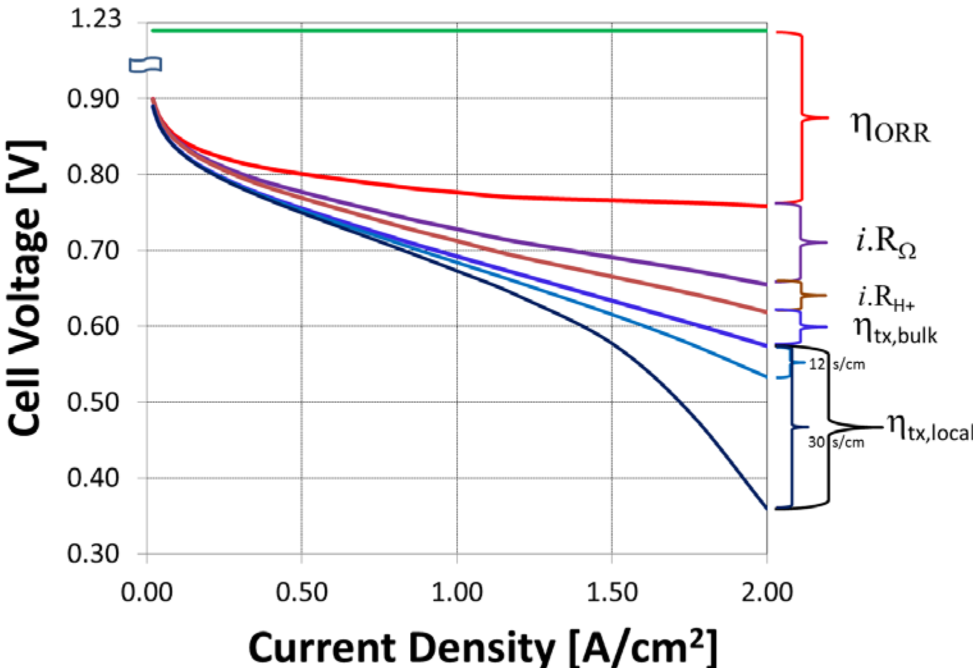


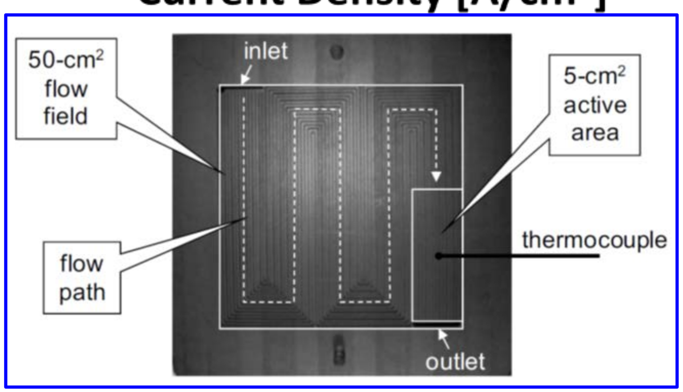
Active Area: 50 cm², CCM MEA
H_2/air, 80 °C, 100% RH, Stoic: 1.5/2.0, 150 Kpaa
H_2/air, 93.5 °C, 65% RH, Stoic: 1.5/2.0, 250 Kpaa

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



Electrochemical Testing and Diagnostics





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 Kpaa, 250 Kpaa
- Modelling Performance z
  - 1 D Model

*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)

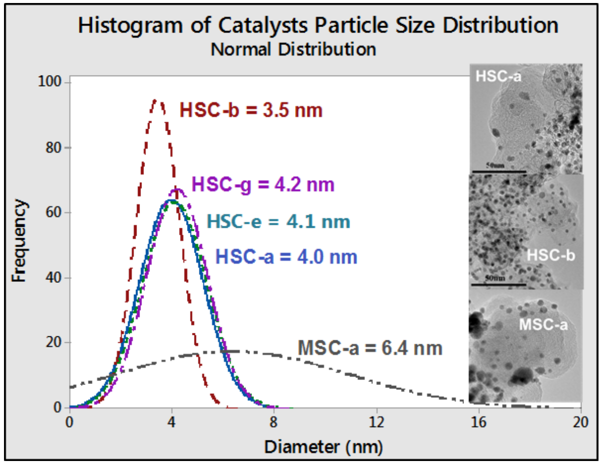
z Gu et al., *Handbook of Fuel Cells* , Vol. 6, p. 631, John Wiley & Sons (2009)

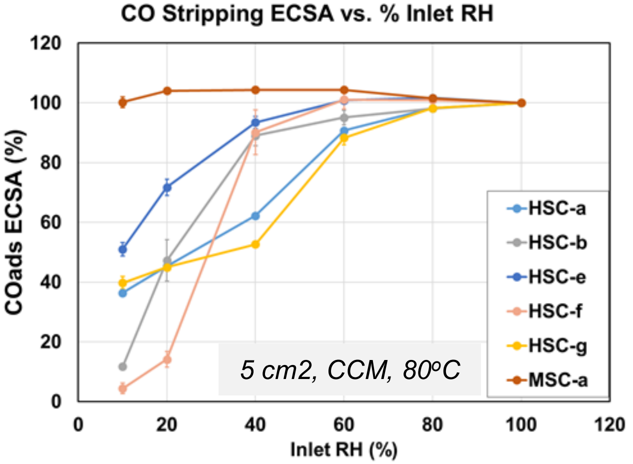
Technical Accomplishment:

Catalyst Selection

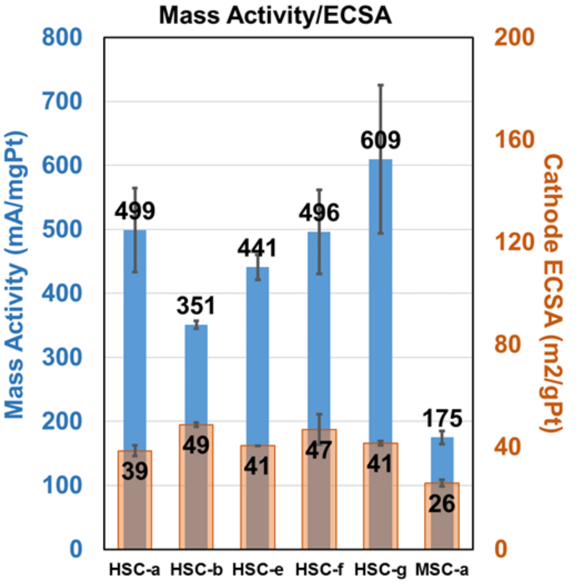
Catalyst Properties

- 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 HSC (ex. ketjen black) and MSC (ex. vulcan)
- MSC-a being solid carbon exhibit 100% Pt particles outside carbon support and lowest ECA and activity
- Modified carbon, HSC-e exhibit improved accessibility to Pt particles.
- HSC-a and HSC-g are identical in activity and carbon support properties.





Catalyst	Comments	BET Area (m^2/g_{Carbon})	Accessible Pt @ 30% RH	Pt : Co (atomic)	PtCo Size (nm)
HSC-a	High sur. area carbon	~778	57%	3.3	4.0 ± 0.2
HSC-b	High sur. area solid carbon	~797	68%	3.5	3.5 ± 0.1
HSC-e	Modified high surf. area carbon	~778	82%	3.3	4.1 ± 0.2
HSC-f	High surf. area carbon	>780	57%	3.3	TBD
HSC-g	Similar to HSC-a, alt. synthesis	~744	54%	2.7	4.2 ± 0.2
MSC-a	Medium sur. area solid carbon	~214	100%	2.3	6.4 ± 0.6



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

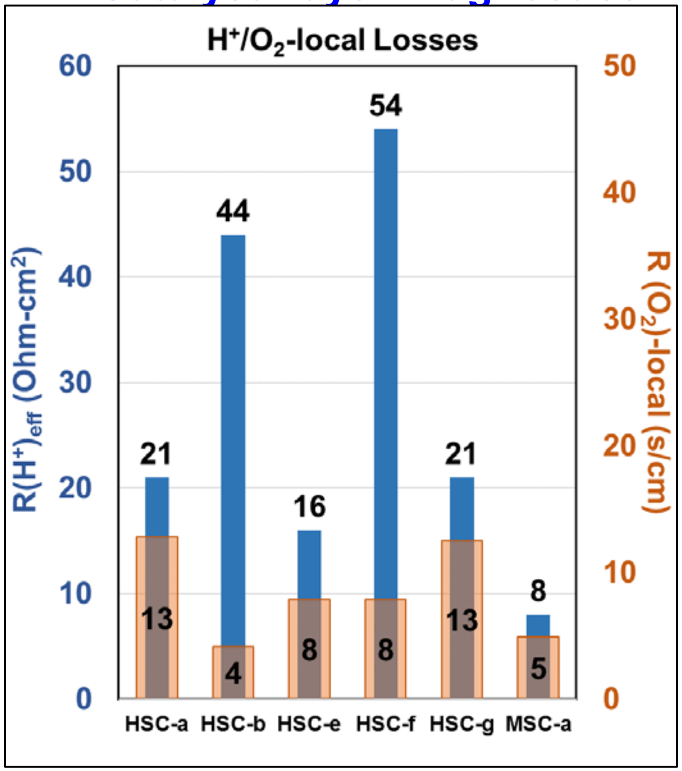
GM TEXAS The University of Texas at Austin

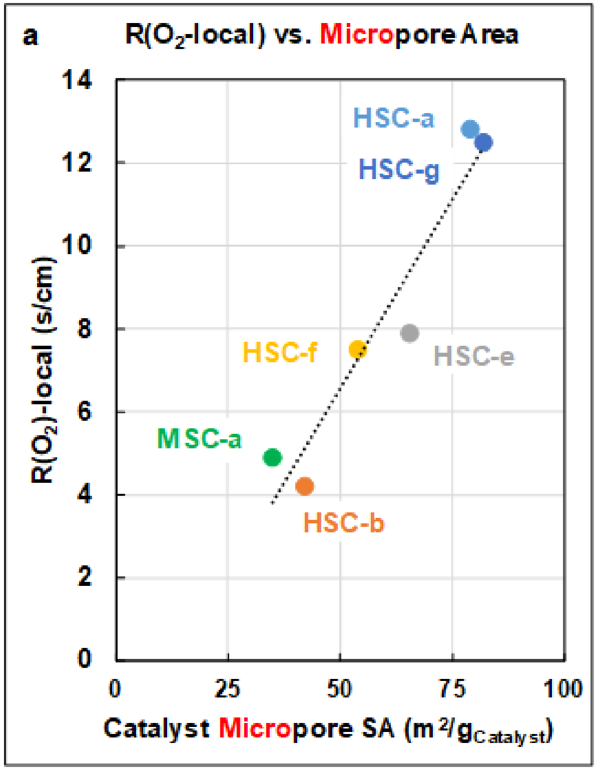
N. Ramaswamy and S. Kumaraguru, ECS Transactions, 85 (13) 835-842 (2018)

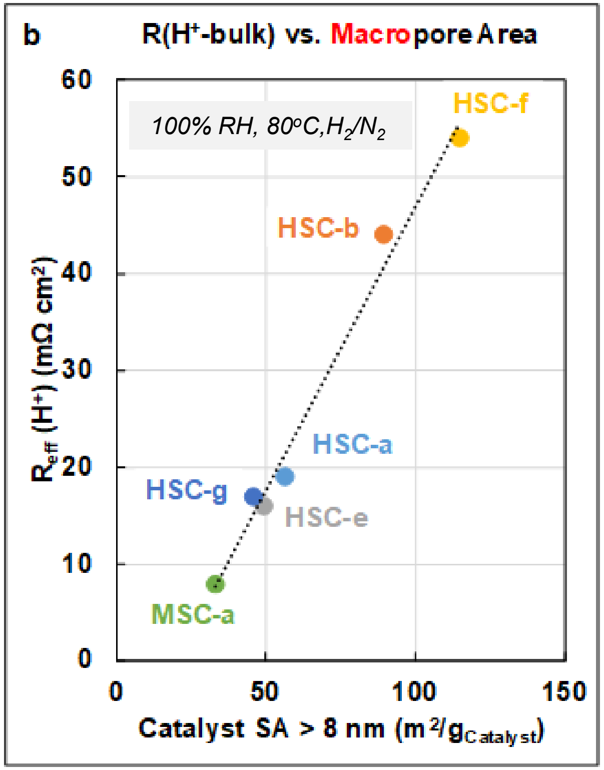
Technical Accomplishment:

Catalyst Selection

Catalyst Layer Diagnostics







- HSC-b and MSC-a exhibit low oxygen transport resistance.
  - The local oxygen transport resistance correlates well with the microporous surface area (<2nm)
  - More investigation needed to understand the impact of micropore surface area and its mechanism towards impact on local oxygen transport resistance.
- HSC-b and HSC-f exhibit higher proton transport resistance.
  - Bulk proton transport resistance correlates well with macro porous (>8 nm) carbon surface area.

N. Ramaswamy and S. Kumaraguru, ECS Transactions, 85 (13) 835-842 (2018)

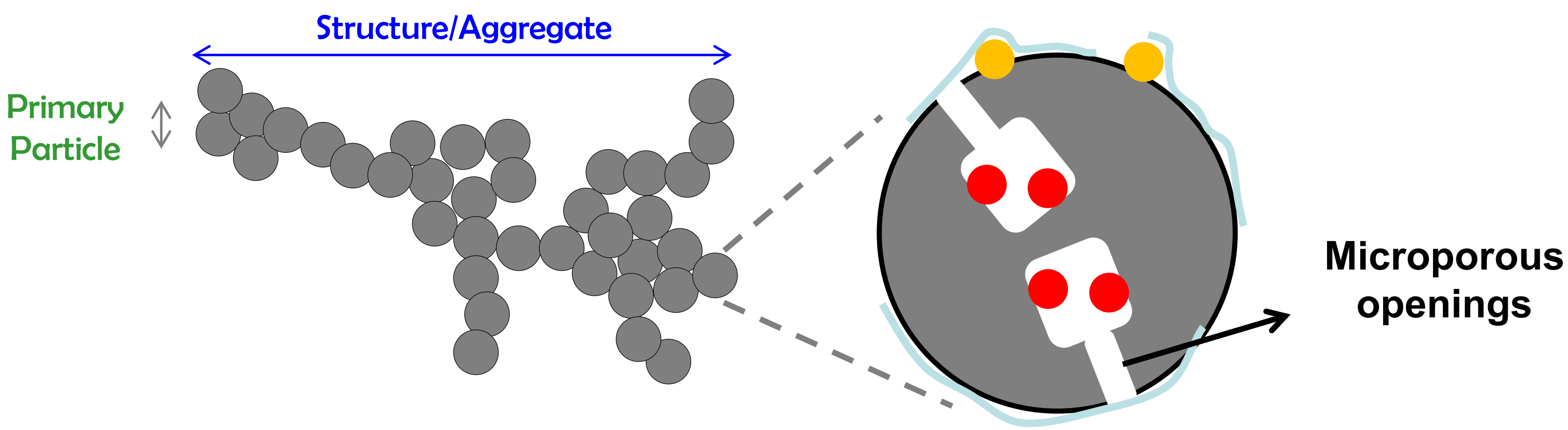
Technical Accomplishment:

Catalyst Selection

Catalyst layer O_2/H^+ transport properties and diagnostics

For a given catalyst layer

- Local-O_2 transport is dependent on the **micro**porous surface area indicating that the need for O_2 to diffuse through the micropore volume of the carbon black support is limiting cell voltage
- Bulk proton transport is dependent on the **macro**porous surface area indicating that the ionomer is distribued on the macropore surface of the carbon black support



- Direct correlation between the carbon surface/pore size distribution and the high current density transport losses have been provided
- We need a high surface area carbon with minimal micropore, maximum mesopore and optimal macropore area.

N. Ramaswamy and S. Kumaraguru, ECS Transactions, 85 (13) 835-842 (2018)

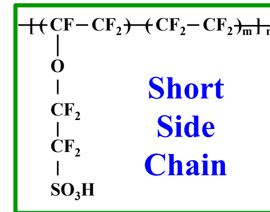
Technical Accomplishment:

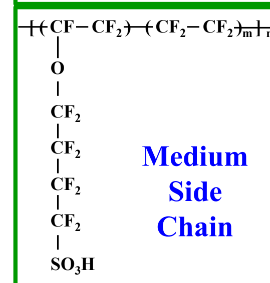
Ionomer Selection

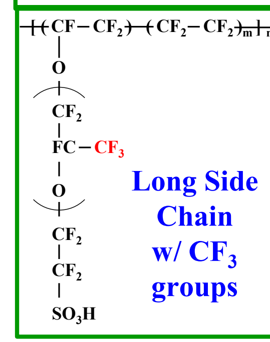
Ionomer Side Chain Length and Chemistry

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

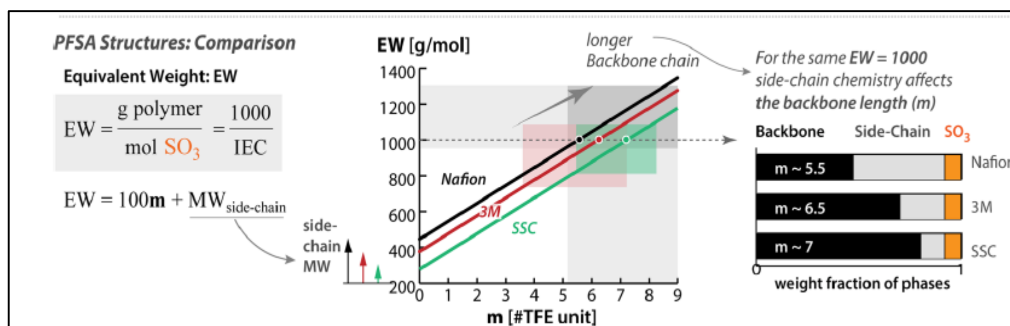
S.No	Measurement	Site
1	Viscosity	GM
2	Dynamic Light Scattering	GM
3	Small angle X-ray scattering	ANL
4	Size exclusion chromatography	GM
5	Ionomer adsorption	GM
6	Grazing Incidence SAXS	LBNL
7	Ionic conductivity	GM
8	Zeta Potential	GM
9	Particle Size Distribution	GM







- 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



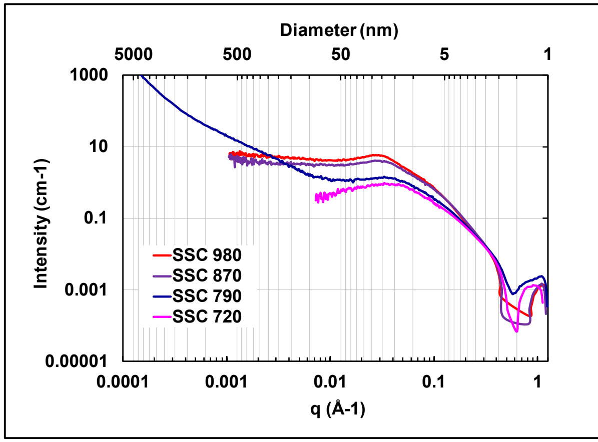
A. Kusoglu et al, *Chem. Rev.*, **2017**, 117 (3), 987-1104

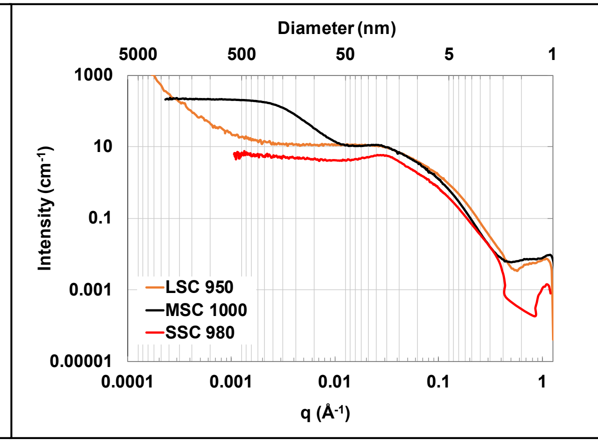
Technical Accomplishment:

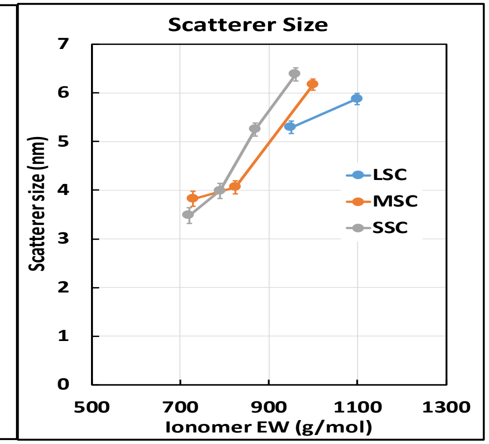
Ionomer Selection

Ionomer Characterization

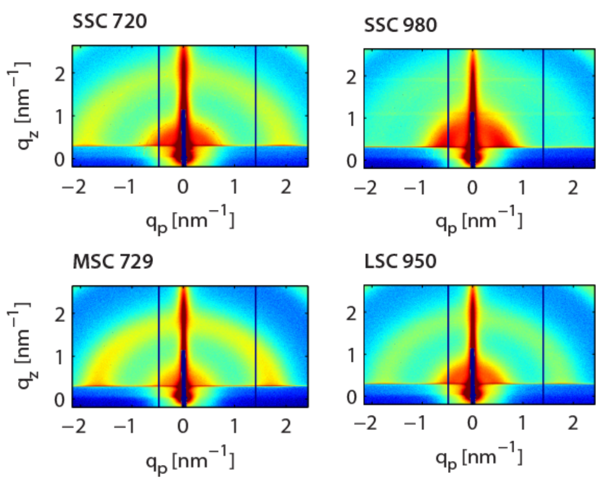
- Dilute ionomer solutions (same ionomer solids% and solvent as inks) were provided to ANL and LBNL for characterization

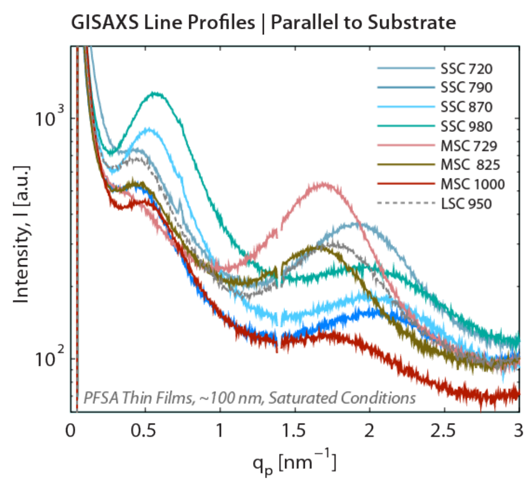


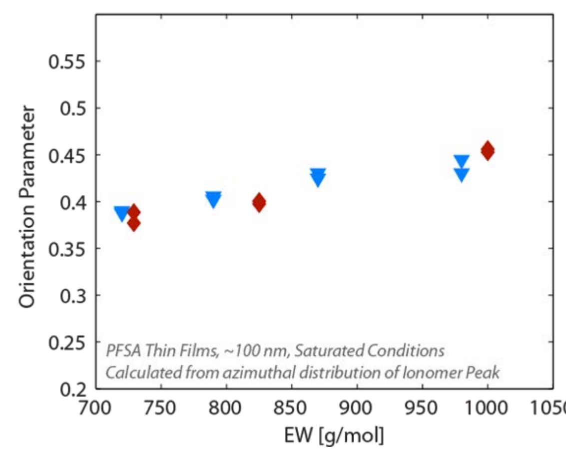




- **USAXS measurements at ANL :** Lower EW and side chain length result in smaller degree of aggregation and hence smaller rod diameters (better connectivity with more dispersed ionomer aggregates).







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

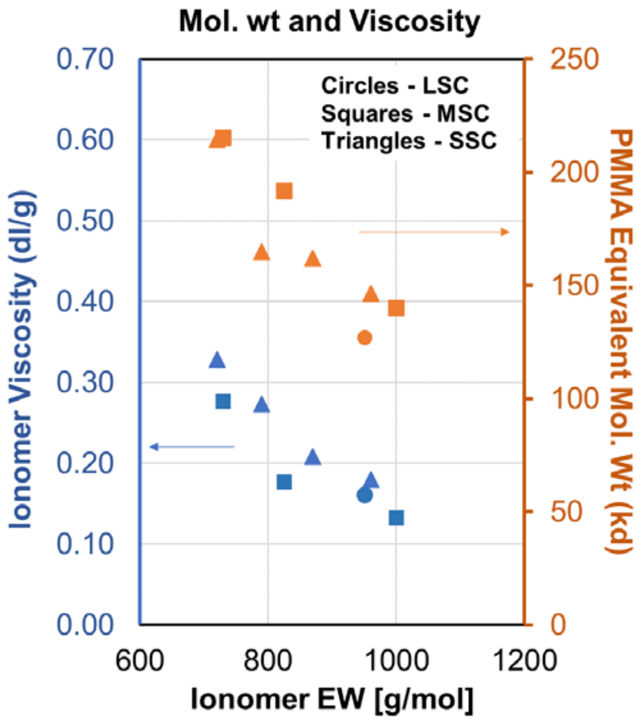
**Thin Films of 90-110 nm, spin-cast on Si substrate, annealed*

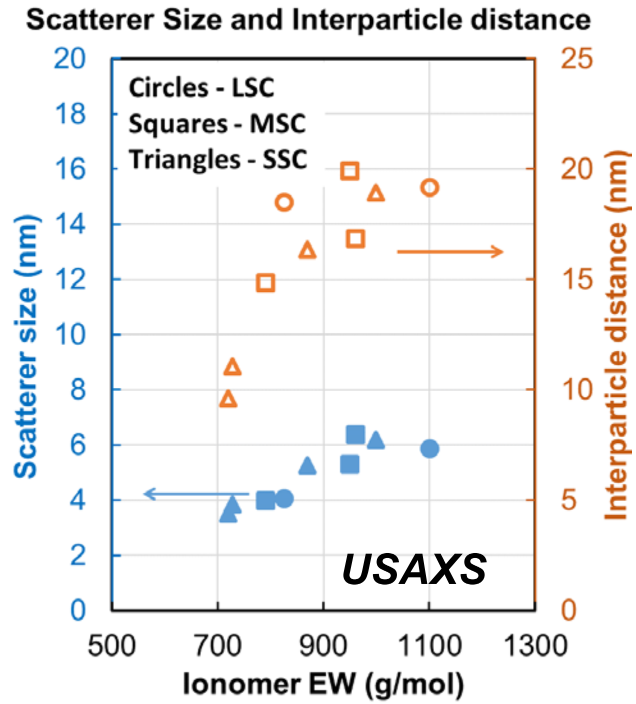
ANL: Deborah Myers, Nancy Kariuki
LBNL: Ahmet Kusoglu

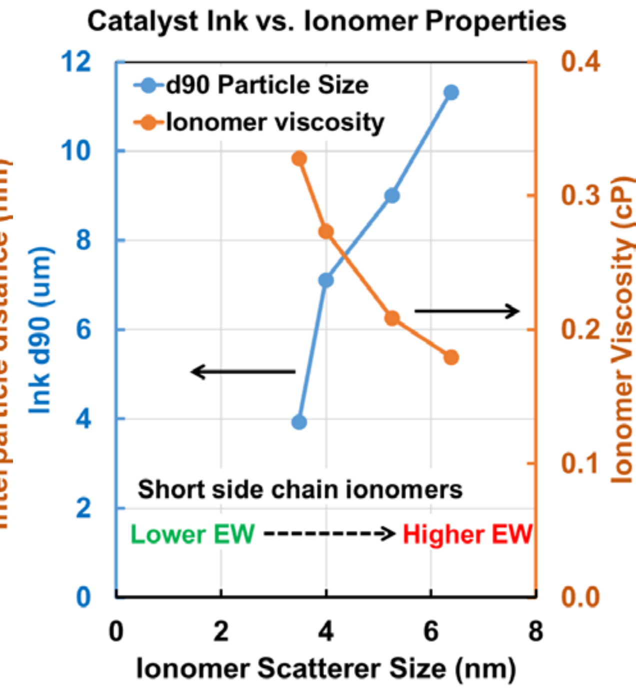
Technical Accomplishment:

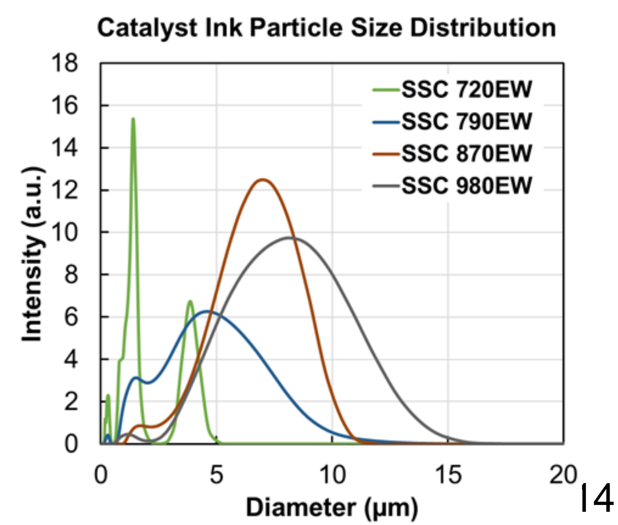
Ionomer Selection

Ink Characterization







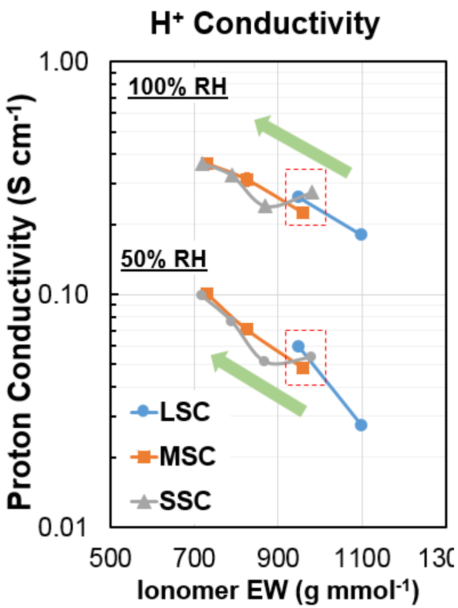


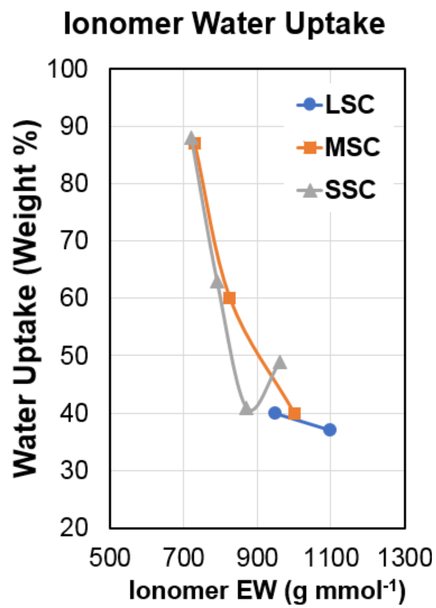
- Lower scatterer size, lower interparticle distance, higher viscosity of ionomer solution tend to break down ink agglomerates to lower values as measured by light scattering experiments.
- Does higher PSD in catalyst ink translate to differences in catalyst layer is still TBD. Samples to be assessed 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.

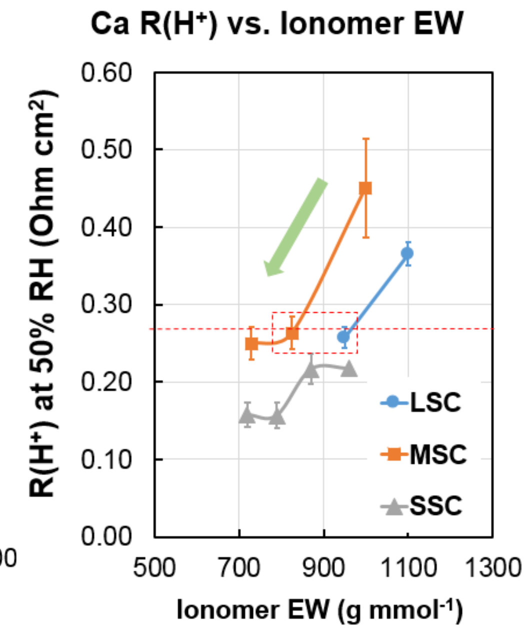
Technical Accomplishment:

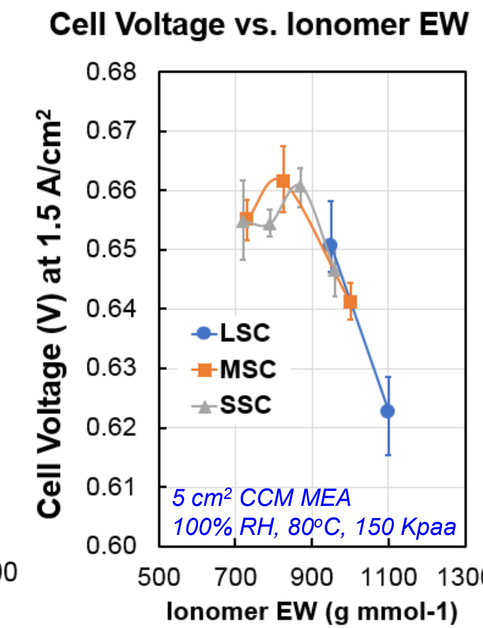
Ionomer Selection

Performance Characterization

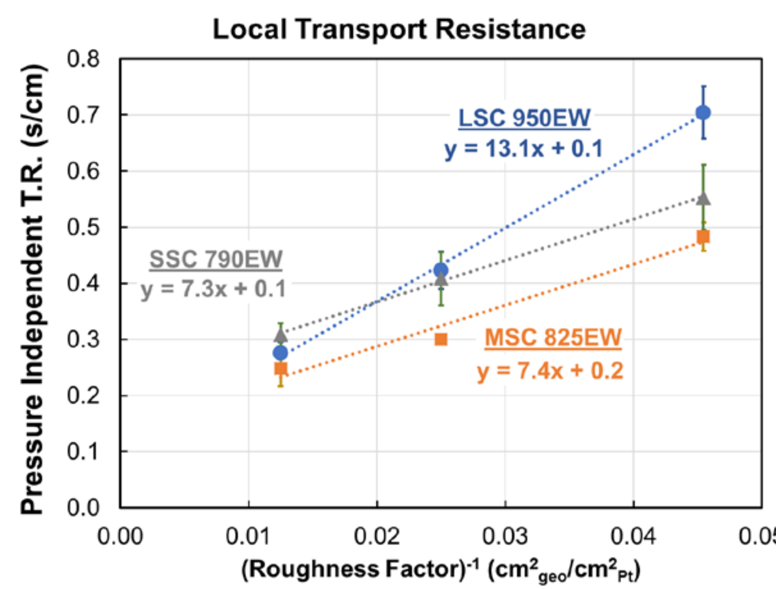






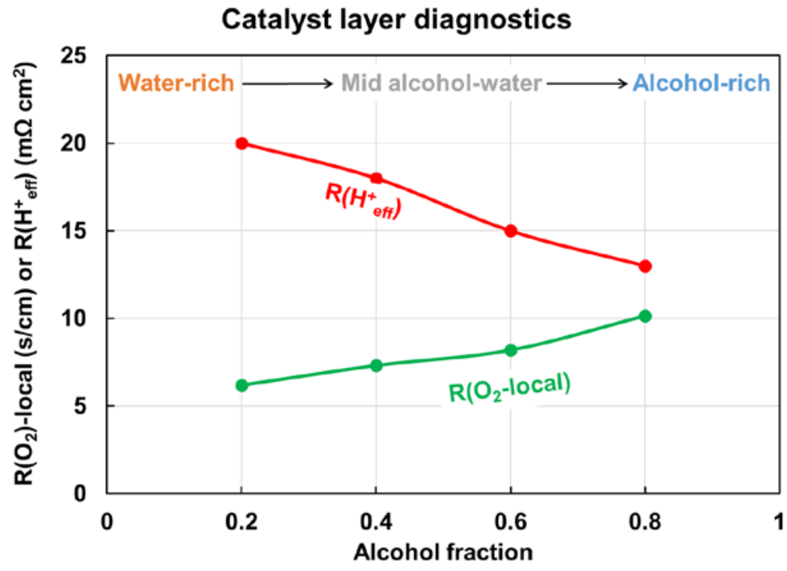


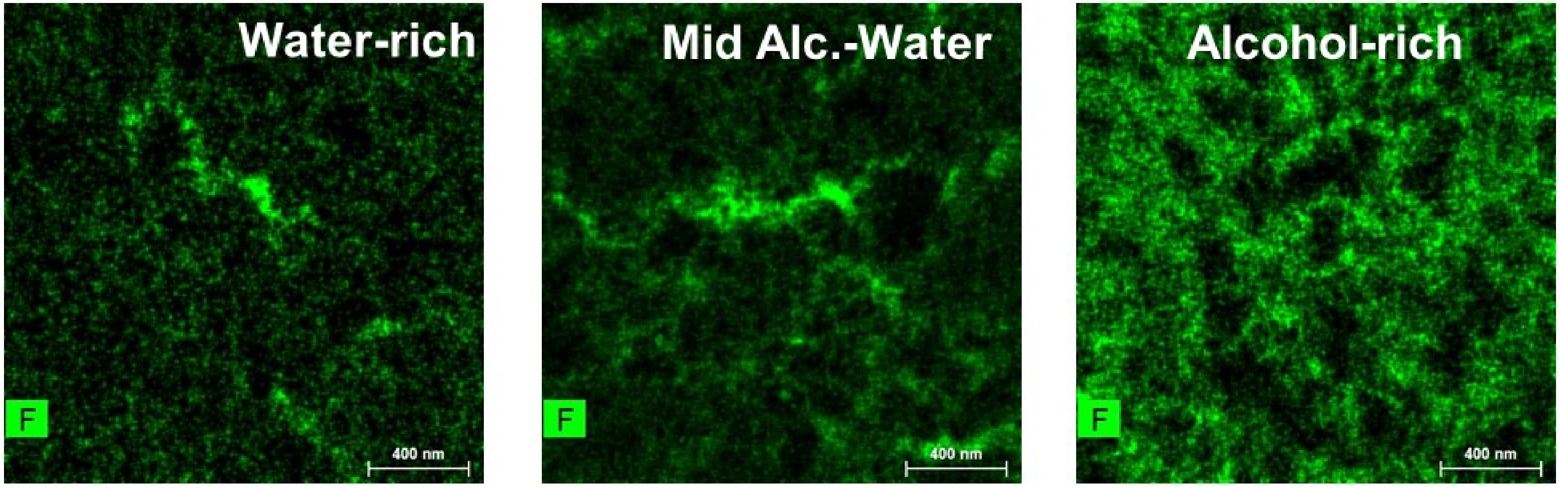
- Proton conductivity and water uptake measurements were conducted in cast films (~12 um thick)
- Cathode proton transport resistance and cell voltage measurements measured in 5 cm² MEA under differential test conditions.
- **EW has the most significant impact on cell voltage**. Decrease in proton transport resistance aids performance improvement in high current density.
  - Decrease in oxygen transport resistance also observed with lower EW ionomers.



Technical Accomplishment:
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

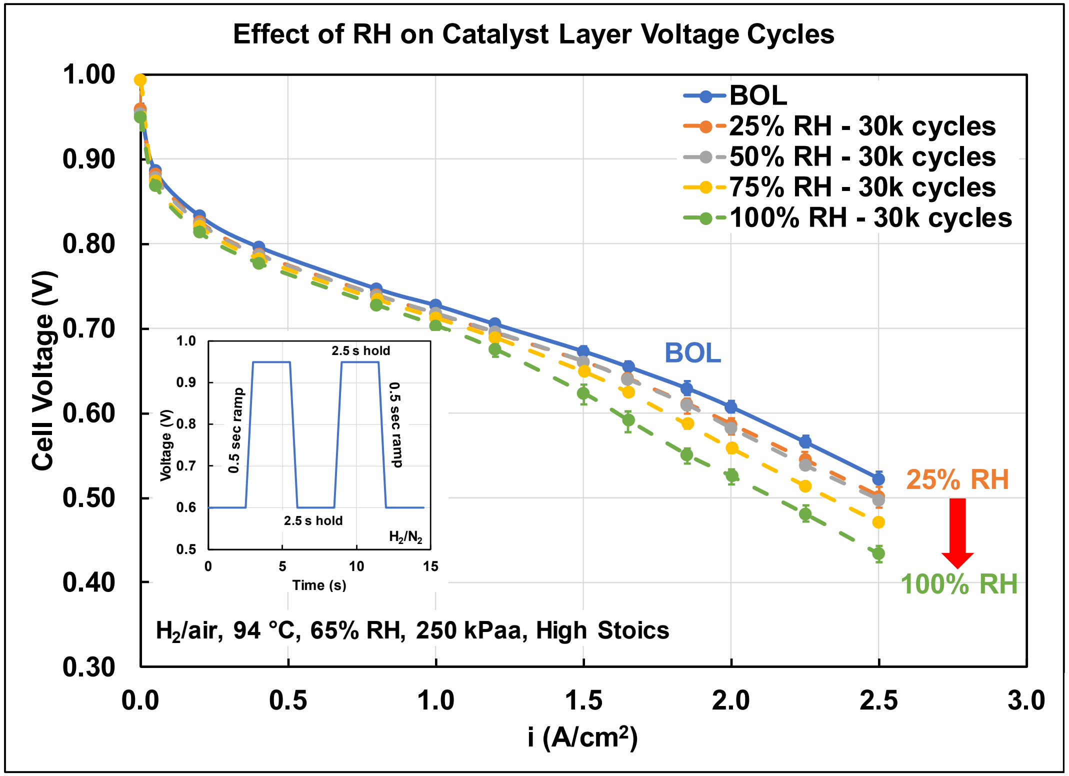
Uniform ionomer distribution with no aggregation (<20 nm)

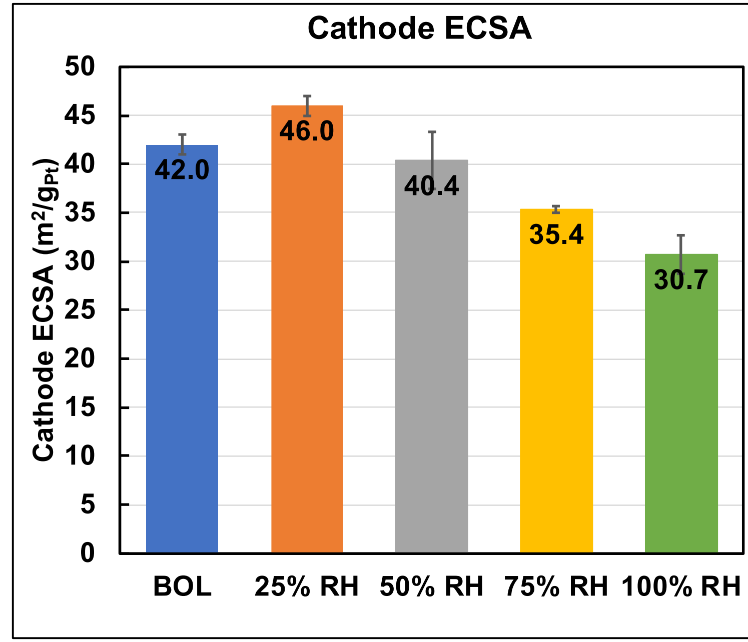
Technical Accomplishment:

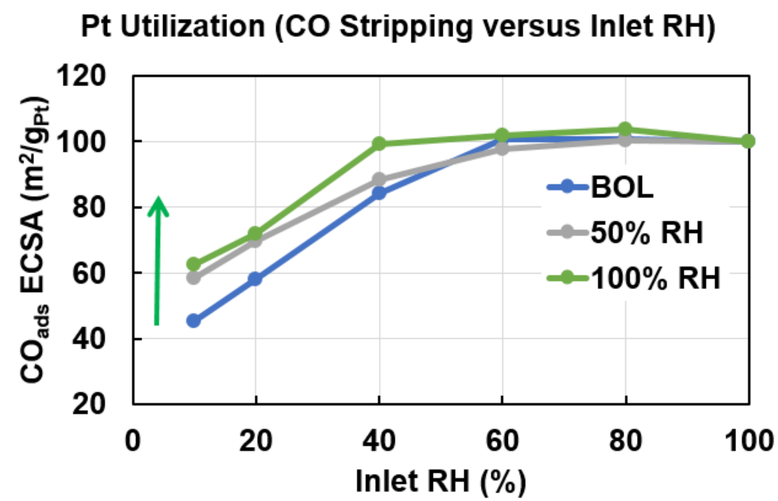
H_2-N_2 Voltage Cycling of SOA MEA

Single Factor Studies - Effect of RH

5 cm² CCM MEA (3 repeats). Differential Conditions





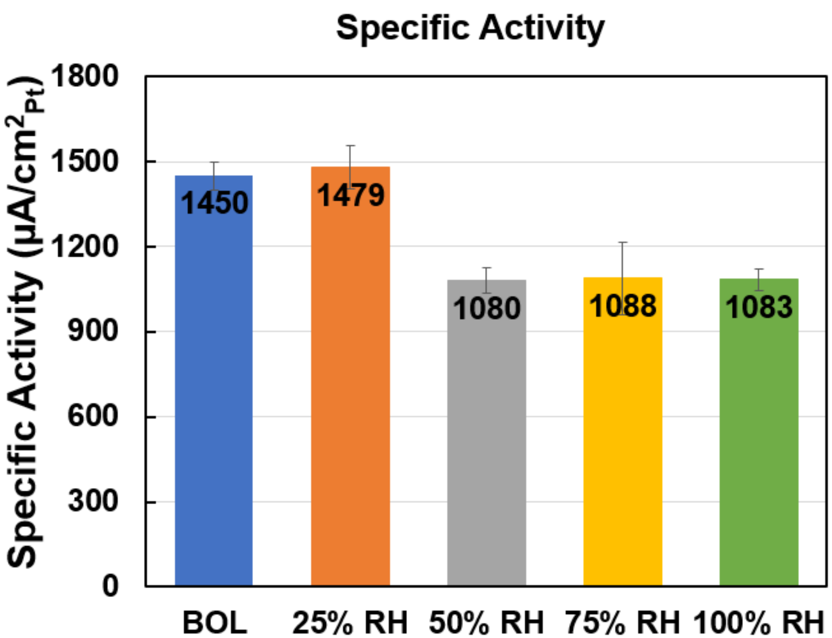


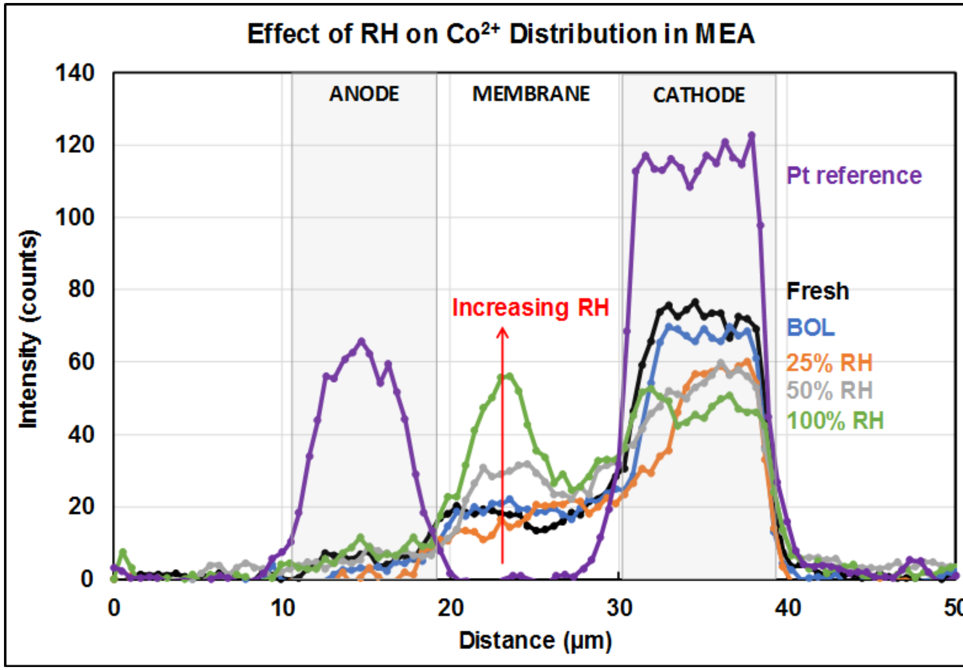
- Few single factor studies such as effect of RH was conducted.
- RH has a very strong effect on both ECSA degradation and corresponding H_2-air performance
- Wetter conditions exhibit higher electrode degradation compared to drier condition.
- Pt utilization inside pores increase with degradation.

H_2-N_2 Voltage Cycling of SOA MEA

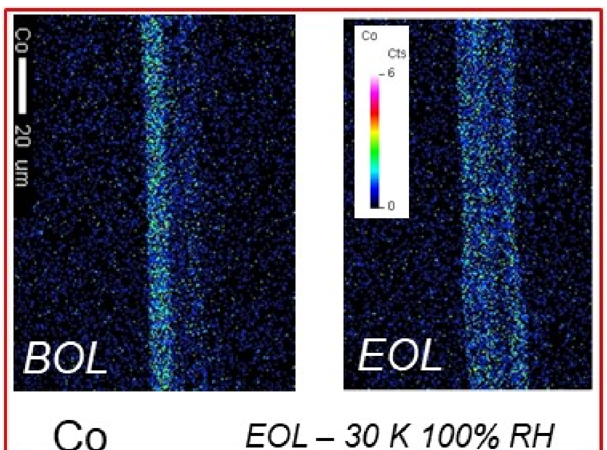
Single Factor Studies - Effect of RH

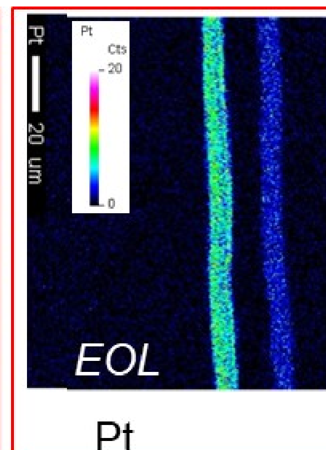
5 cm² CCM MEA (3 repeats). Differential Conditions





- Effect of RH has a strong impact on both mass activity and ECA.
- No difference in specific activity loss observed beyond 50%RH operation.
- The ECA and mass activity loss also indicate higher Co loss into MEA.
- Resolution on cobalt loss as a function of RH/ cycles - ongoing

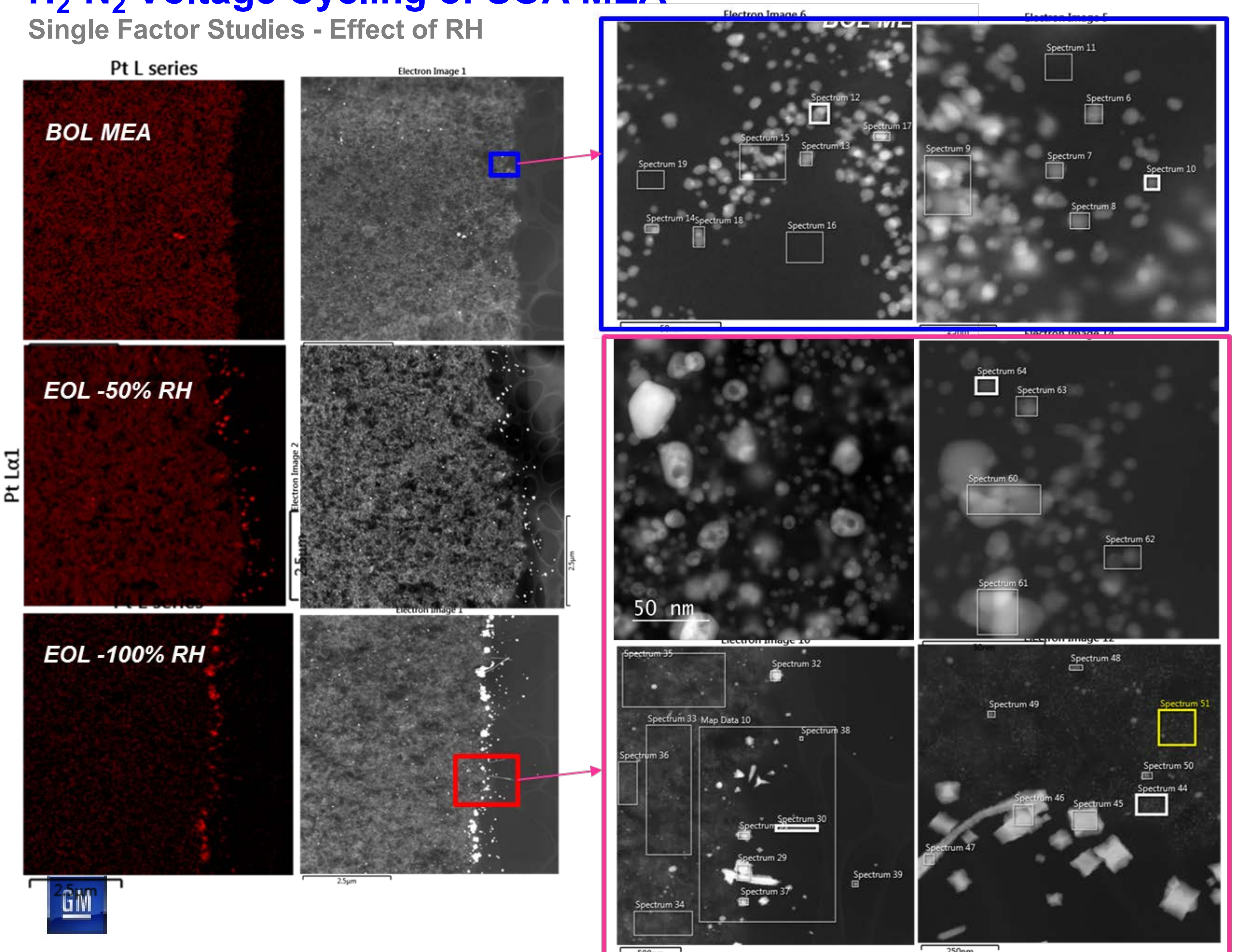




Technical Accomplishment:

H_2-N_2 Voltage Cycling of SOA MEA

Single Factor Studies - Effect of RH



Atomic%
Pt ~ 84.5
Co ~ 15.5

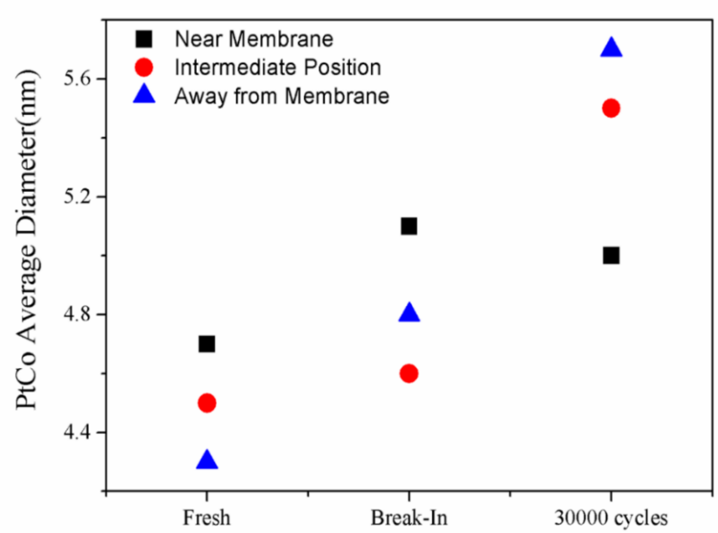
Atomic%
Pt ~ 95.1
Co ~ 4.9

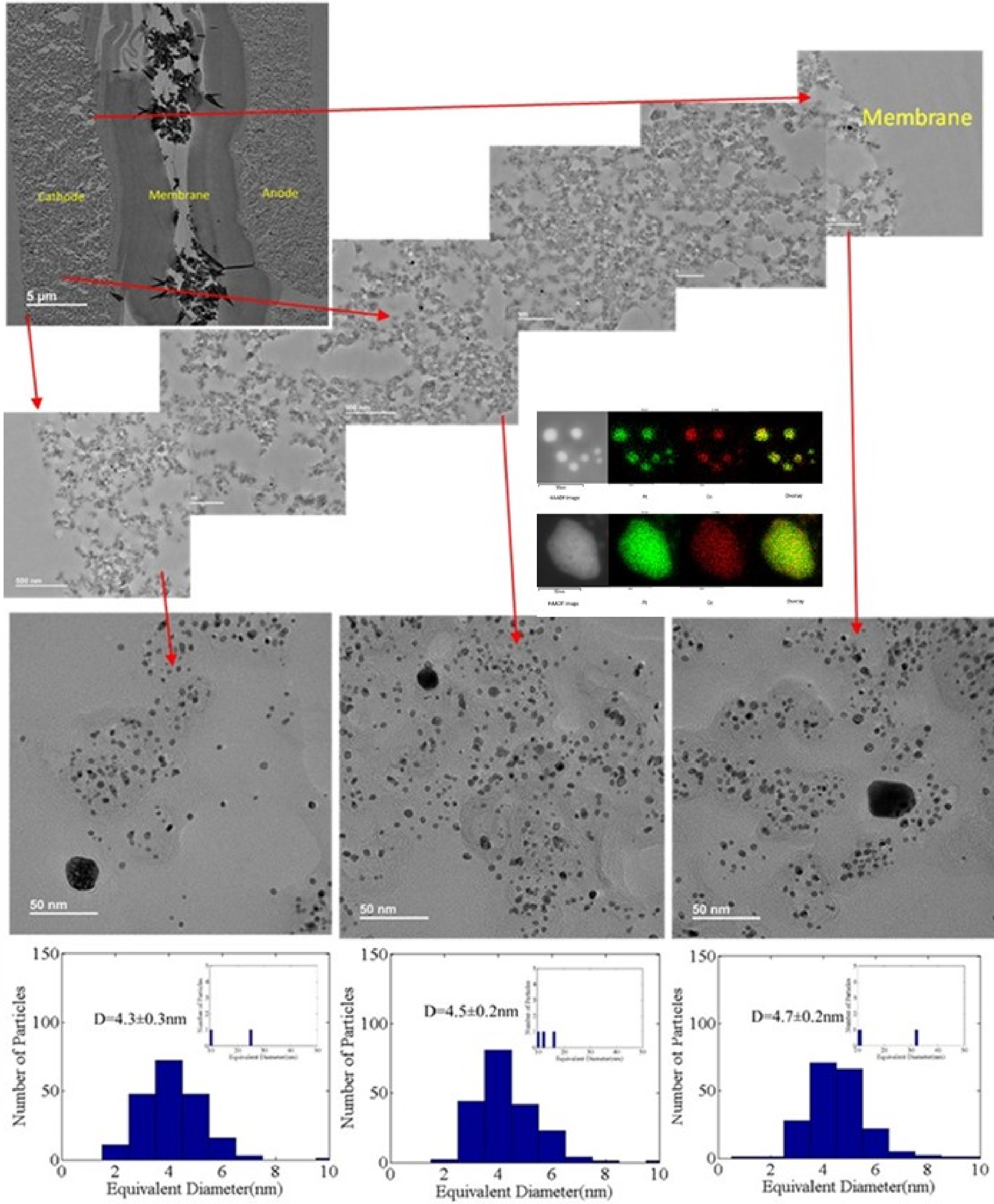
Atomic%
Pt ~ 98%

Technical Accomplishment:

Characterization of Voltage Cycled MEAs

- PSD and composition measurements are the key inputs to the model.
- PSD of a fresh electrode, electrode after break in and electrode after 30 K voltage cycles were obtained at three different locations, namely near the membrane, center of electrode and near GDL is quantified.



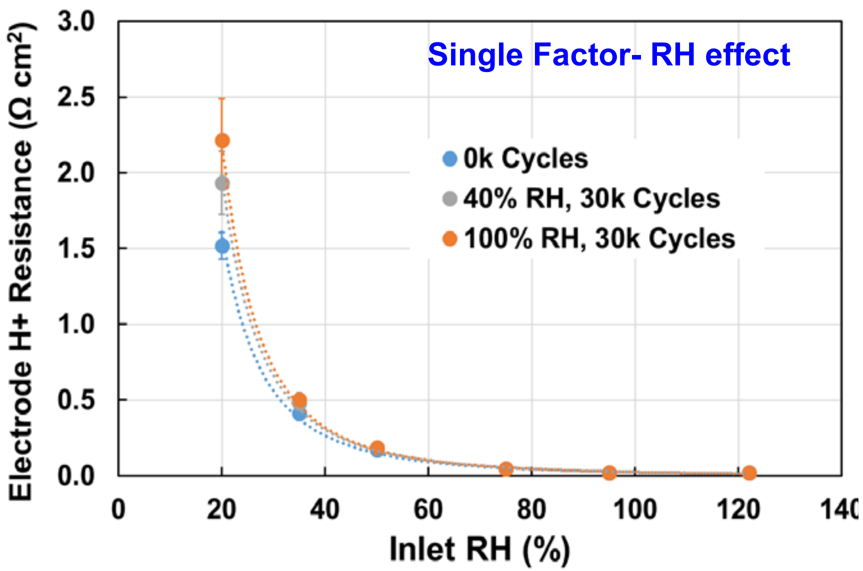


TEXAS
The University of Texas at Austin

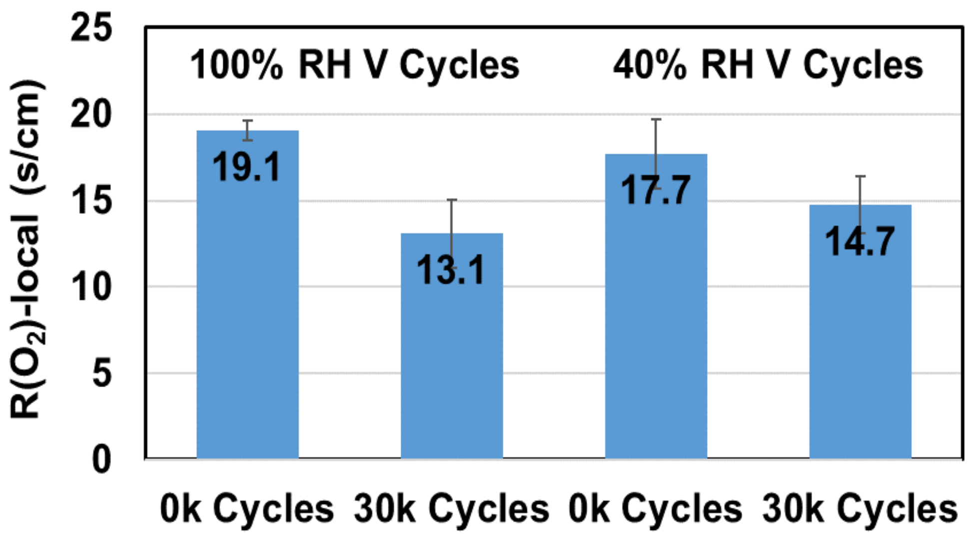
Technical Accomplishment:

Voltage Cycling of SOA MEA

Transport Losses



5 cm² CCM MEA. Differential Conditions



- Marginal increase in proton transport resistance at very dry condition observed. Possibly from leached Co^{2+}.
  - Exact quantification of proton transport during operation is still unclear. Could be higher due to higher exchange of proton conducting sites.

- Marginal decrease in RO_2 local (μ-pore) observed
  - Possible opening of pores as observed from the increased accessibility of pores in CO stripping measurements (at low RH)

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Makharia et.al, *JES*, **152** (5), A970 (2005)

Greszler et al, *JES*, **159** (12) F831 (2012)

Technical Accomplishment:

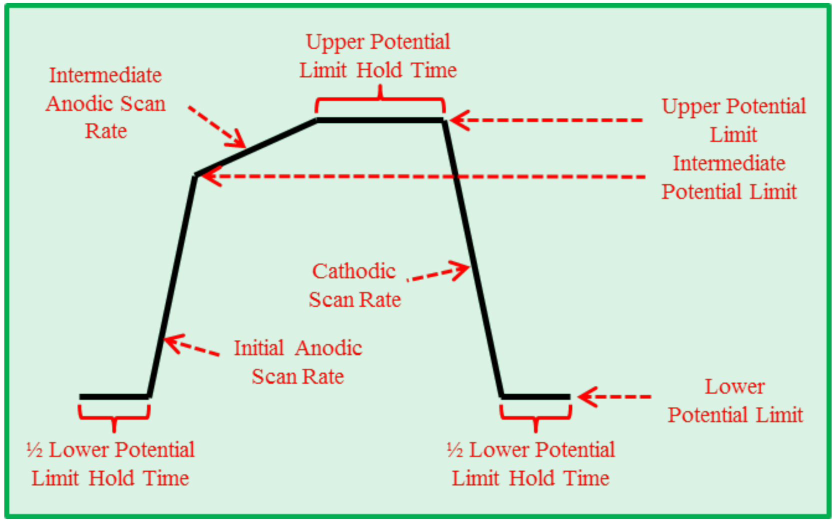
H_2-N_2 Voltage Cycling of SOA MEA

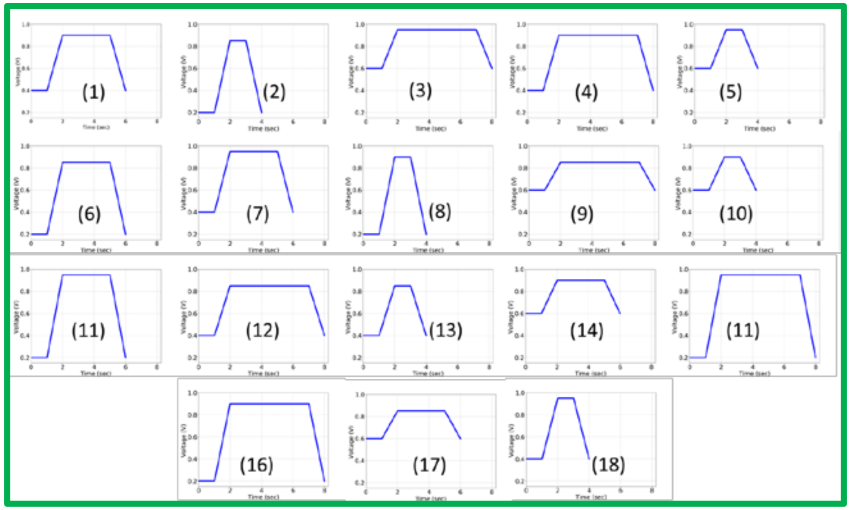
Multifactor DOE

- Single factor experiments can be misleading at times.
- Understanding of the interaction of factors is key to define operating conditions favorable for electrode and membrane degradation.
- Exploring initial design of experiments focused on temp, RH, lower and upper potential limit, upper potential hold time.
- Design of experiment approach was utilized (18 runs).

5 cm² CCM MEA. Differential Conditions

	Cell Temp (°C)	RH (%)	Upper potential (mV)	Lower Potential (mV)	upper potential hold time (s)	Test Stand
-5						A
-3						B
-1	55	40	850	200	1	C
0	75	70	900	400	3	
1	95	100	950	600	5	D
3						E
5						F





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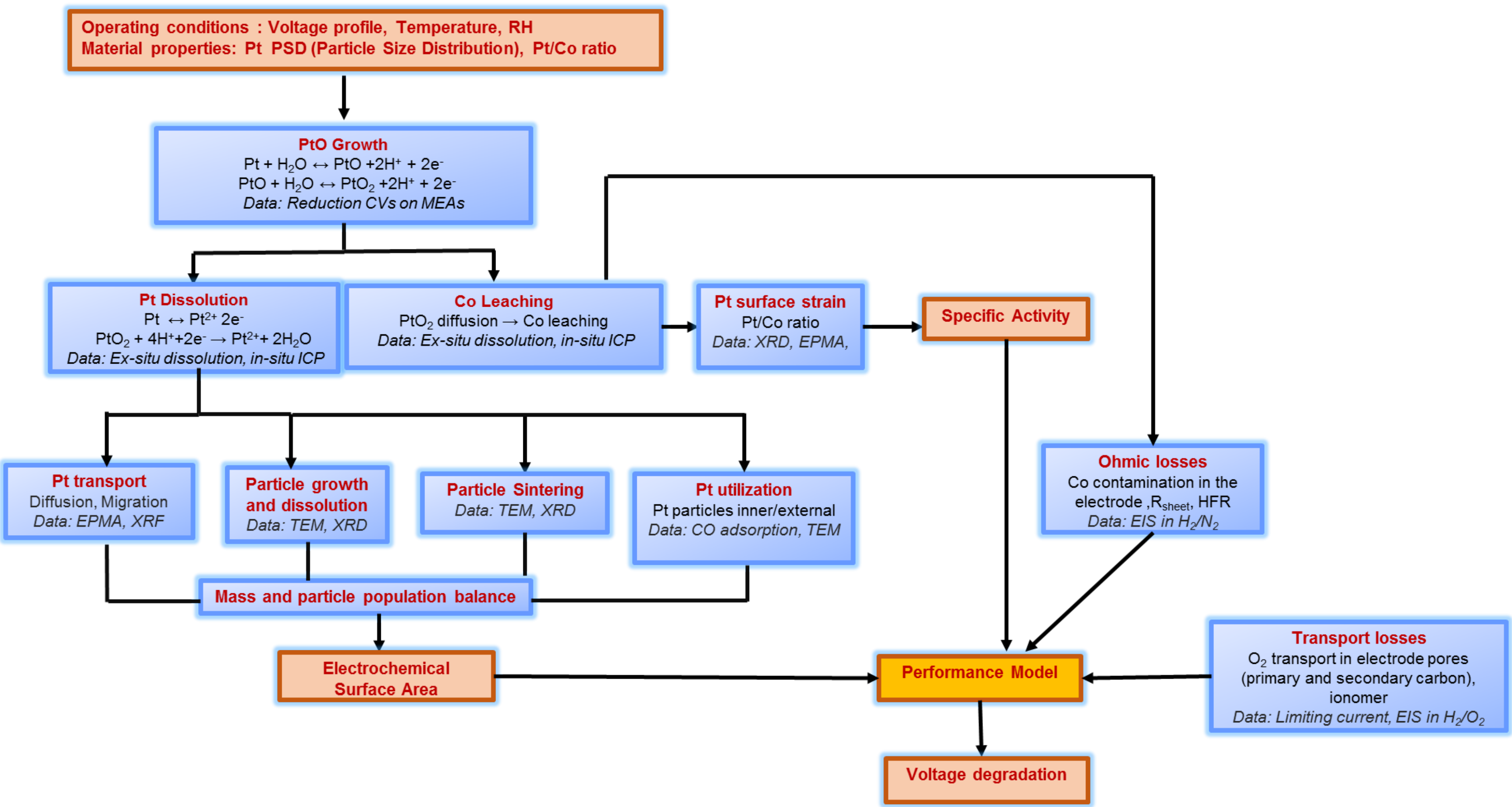
Technical Accomplishment:

Construct Pt and Co Dissolution Models

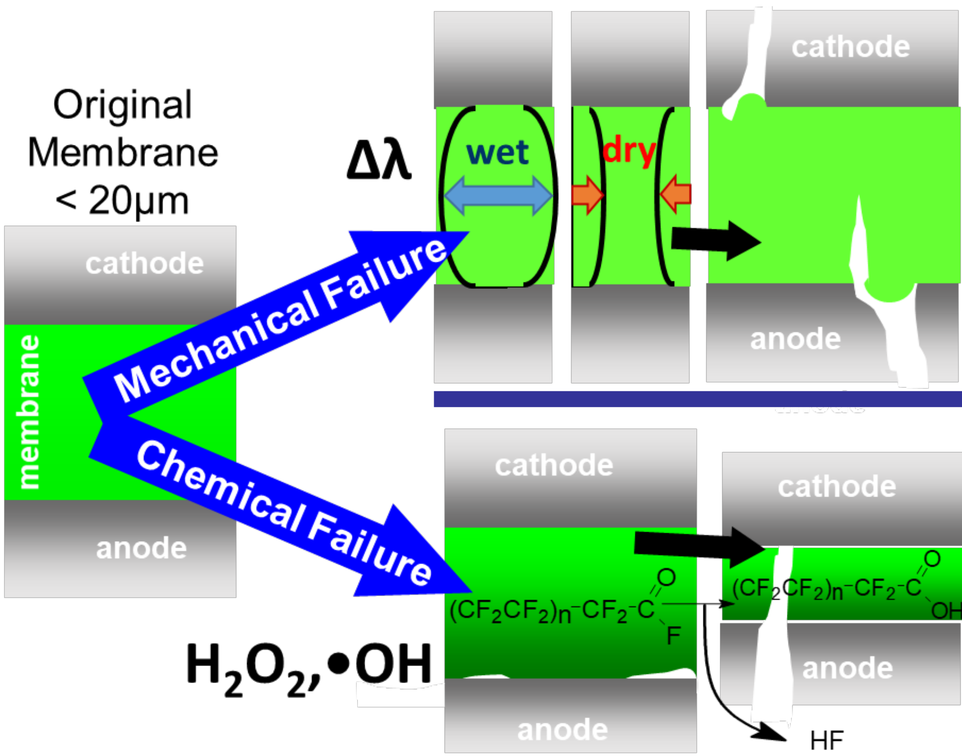
Model Framework



Technical Accomplishment:

Membrane Degradation

Single Stress Failure Modes



During humidity cycling

- Membrane swells/shrinks with changing relative humidity
- Repeated stressing of membrane leads to fatigue induced fracture

During fuel cell operation

- Peroxide & radicals generated at electrodes
- Radicals attack polymer structure of membrane
- Membrane thins, releasing HF (PFSA PEMs only)

- Factors affecting membrane degradation in real life operation that involves simultaneous chemical and mechanical stress

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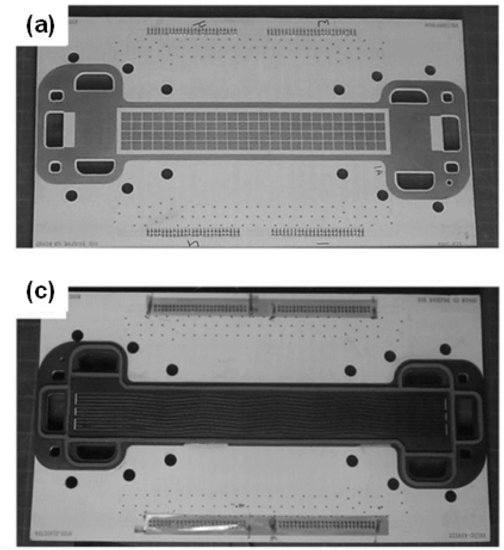
C.S. Gittleman, F.D. Coms , Y-H Lai, Modern Topics in Polymer Electrolyte Fuel Cell Degradation, Elsevier, 2011, pp. 15-88

Technical Accomplishment:

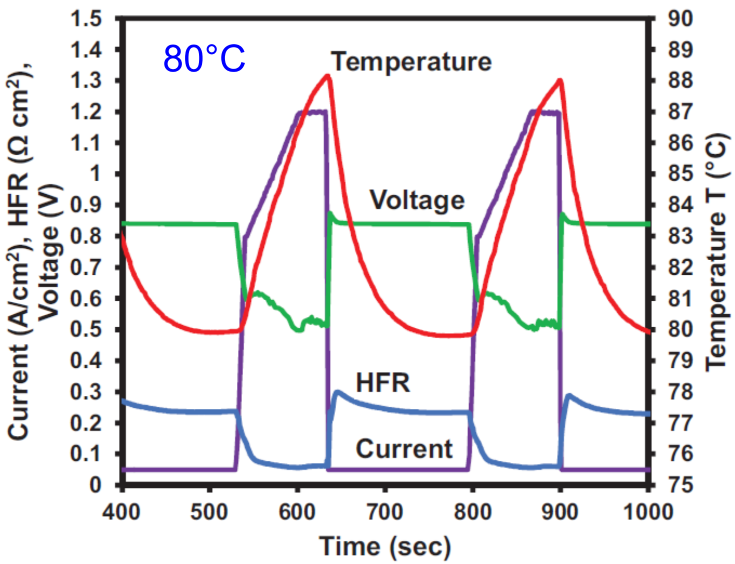
Combined Chemical-Mechanical HAST

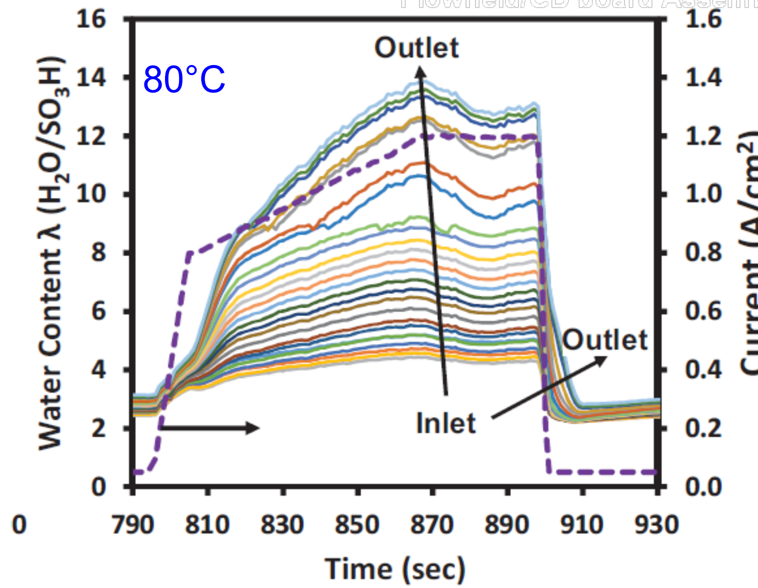
Goal: develop a highly accelerated stress test to evaluate membrane durability in a realistic fuel cell environment (no dry inlets, no OCV)

- 70, 80 & 90°C/30%Rh_{in}, 0.05 – 1.2 A/cm^2 , (distributed measurements)
- Constant flow, Co-flow
- Current an Temp Distribution tool used to measure local environment
  - Collect 100 membrane T & HFR profiles vs. time
- 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**



Flowfield/CD board Assembly

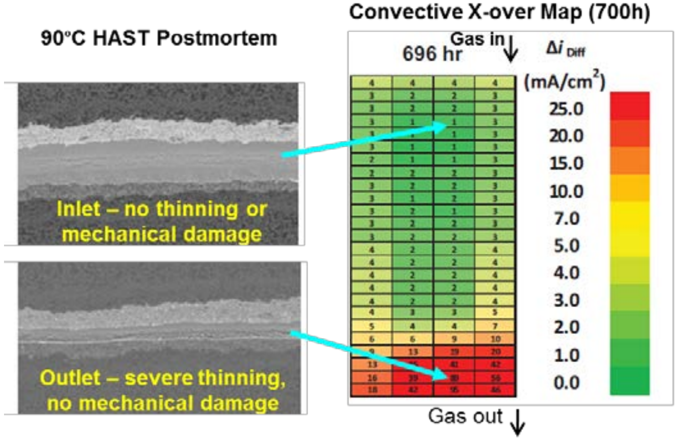


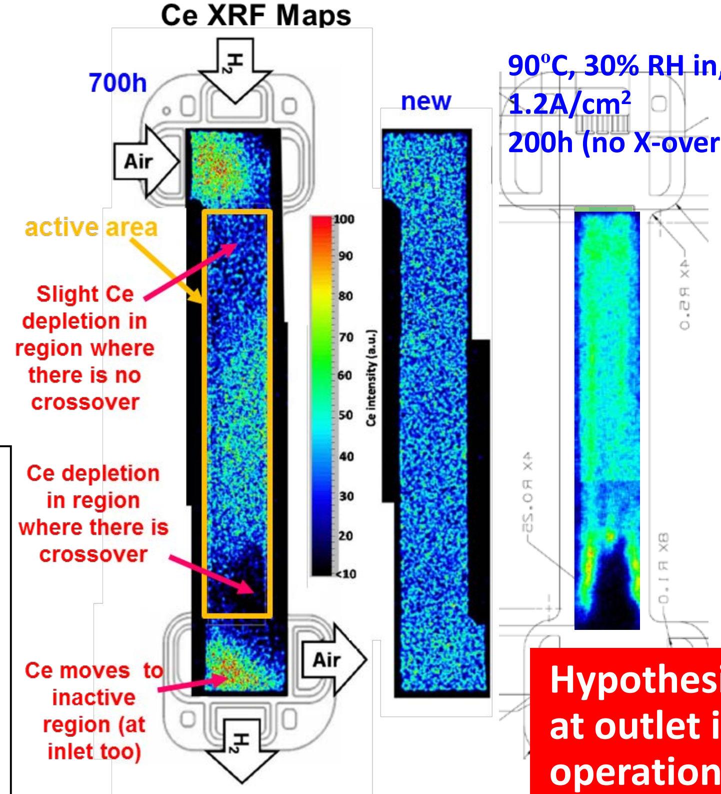


Y.H. Lai, Journal of The Electrochemical Society, **165** (6) F3217-F3229 (2018)

Technical Accomplishment:

Combined Chemical-Mechanical HAST





90°C HAST Max λ

5.4	4.8	5.0	5.3
5.1	4.7	4.7	5.2
5.0	4.7	4.7	5.1
5.2	4.8	4.9	5.2
5.4	5.2	5.3	5.5
5.6	5.5	5.4	5.7
5.7	5.9	5.8	5.8
5.9	6.2	6.1	6.0
6.2	6.6	6.7	6.4
6.5	7.0	7.1	6.5
6.5	7.2	7.2	7.0
6.8	7.4	7.4	7.0
6.9	7.7	7.8	7.3
7.2	7.9	8.2	7.4
7.3	8.2	8.6	7.6
7.7	8.7	9.2	7.9
8.3	9.4	10.4	8.3
8.4	10.4	11.7	9.0
8.8	11.8	13.4	9.9
9.8	12.5	13.7	10.7
10.9	14.2	[illegible]	11.5
11.5	14.4	[illegible]	12.1
12.2	14.9	[illegible]	12.6
12.4	14.1	14.8	[illegible]
11.6	14.5	15.4	[illegible]

λ > 100%RH

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 (just underway)

Hypothesis: Ce depletion at outlet is caused by wet operation, and is not solely a result on ionomer loss

- What happens when we run a HAST test w/o Ce stabilizer?

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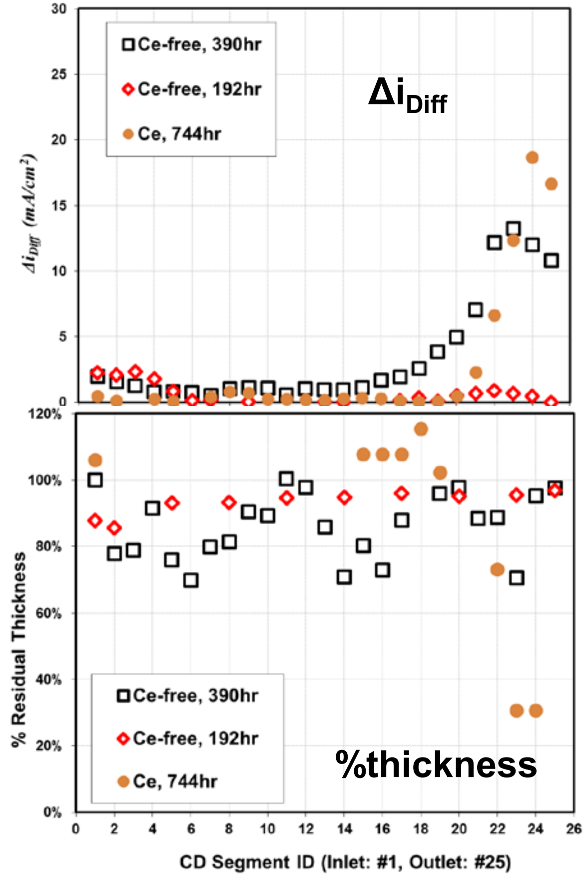
Y.H. Lai, *Journal of The Electrochemical Society*, **165** (6) F3217-F3229 (2018)

Technical Accomplishment:

Combined Chemical-Mechanical HAST – Ce Effect

90°C HAST Diffusive X-over

	w/ Ce X-over 750h				No Ce 390h			
R1	0	0	0	0	1	1	2	2
R2	0	0	0	0	1	1	2	1
R3	0	0		0	1	1	1	1
R4		0	0	0	1	1	1	1
R5				0	1	1	1	1
R6	0			0	1	1	1	1
R7			0	0	1	1	1	1
R8	0	0	1	0	2	1	1	1
R9	0	0	1	0	2	1	1	1
R10	0	0	0	0	2	1	1	1
R11	0	0	0	0	2	1	1	1
R12	0	0	0	0	1	1	1	1
R13	0	0	0	0	2	1	1	1
R14	0	0	0	0	1	1	1	1
R15	0	0	0	0	2	1	1	2
R16	0	0	0	0	2	2	2	2
R17	0		0	0	3	2	2	2
R18				0	4	4	3	2
R19	0	0		1	8	7	4	3
R20	1	0	0	1	10	7	5	4
R21	0	1	2	3	6	6	7	7
R22	1	4	7	6	5	8	12	10
R23	2	7	12	12	5	8	13	12
R24	3	8	19	13	7	9	12	13
R25	3	7	17	9	6	7	11	11



- MEA w/ Ce lasts 2X longer than Ce free MEA in HAST tests
- In automotive drive cycle, MEA w/ Ce last 10X longer than Ce-free MEA

- Both w/ & w/o Ce failure crossover first observed in outlet region with high RH cycling
- Crossover occurs in half the time w/o Ce
- **While Ce depletion may contribute to earlier failure in outlet region, it is not the only reason → some other mechanism is at play**

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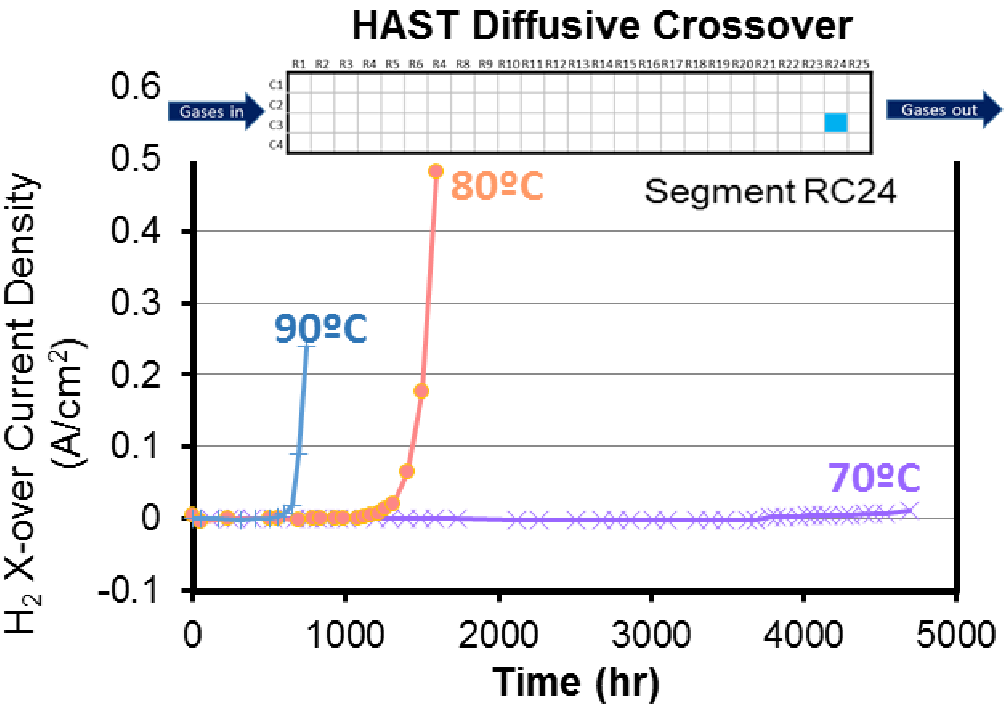
Technical Accomplishment:

Combined Chemical-Mechanical HAST

Effect of Operating Temperature



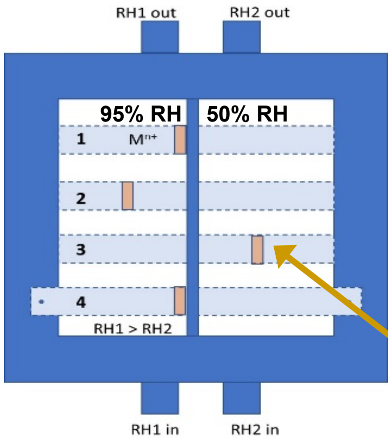
Diffusive X-over Maps

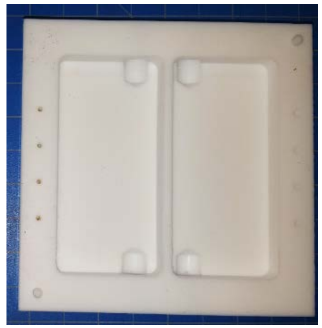
90°C 650h				80°C 1200h				70°C 4500h			
0.4	0.3	0.5	0.3	2.3	1.1	0.8	0.8	0.6	0.7	0.9	0.8
0.1	0.1	0.1	0.5	0.8	0.2	0.7	0.6	0.6	0.5	0.6	0.6
0.1	0.1	0.0	0.3	0.5	0.7	0.4	0.6	0.4	0.2	0.6	0.5
0.0	0.1	0.3	0.1	0.5	0.5	0.5	0.6	0.1	0.3	0.3	0.7
0.0	-0.2	0.1	0.1	0.6	0.5	0.5	0.5	0.1	0.1	0.1	0.2
0.2	-0.1	-0.2	0.2	0.5	0.5	0.7	0.6	-0.2	-0.2	-0.2	-0.1
0.1	0.0	0.4	0.1	0.6	0.6	0.7	0.6	-0.2	-0.3	-0.5	-0.3
0.2	0.4	0.8	0.3	0.5	0.5	0.4	0.3	-0.1	0.3	-0.1	-0.3
0.4	0.3	0.7	0.2	0.6	0.6	0.3	0.5	-0.2	0.0	-0.1	-0.1
0.4	0.3	0.3	0.4	0.4	0.5	0.2	0.3	0.1	0.0	-0.2	-0.1
0.5	0.5	0.2	0.4	0.3	0.4	0.5	0.5	0.0	-0.3	-0.2	0.1
0.4	0.3	0.2	0.4	0.4	0.5	0.2	0.4	-0.2	-0.1	0.2	0.2
0.4	0.4	0.2	0.4	0.7	0.1	0.3	0.5	0.0	-0.1	0.2	0.1
0.3	0.2	0.3	0.3	0.4	0.3	0.1	0.4	0.1	-0.1	0.4	0.8
0.4	0.2	0.3	0.3	0.5	0.5	0.4	0.3	0.1	0.3	0.8	1.2
0.4	0.2	0.3	0.5	0.7	0.4	0.3	0.6	0.1	0.4	0.4	1.1
0.2	-0.1	0.1	0.2	0.5	0.1	0.5	0.6	0.0	0.2	0.5	1.3
0.1	0.1	0.1	0.3	0.6	0.7	0.7	0.8	0.1	0.1	1.0	3.1
0.3	0.2	0.1	0.8	0.8	1.1	0.9	1.4	0.2	0.6	1.9	4.0
0.8	0.5	0.5	1.2	1.3	2.1	3.2	1.9	2.2	1.6	3.0	6.8
0.5	1.4	2.3	2.6	2.3	4.4	6.3	4.0	4.3	2.5	4.0	11.1
1.4	3.6	6.7	6.2	3.5	10.1	17.6	5.5	4.9	3.8	4.3	9.3
2.4	6.5	12.4	11.9	4.1	9.6	10.0	4.2	8.2	4.3	4.1	5.3
2.8	8.4	18.7	12.5	4.3	7.4	7.4	3.9	7.1	3.6	3.0	4.1
3.3	7.4	16.7	9.2	4.4	4.5	5.1	3.4	4.5	2.8	2.7	3.2

- Temperature is the key accelerating factor for membrane degradation. Almost 8X difference in time to failure noticed with 20°C reduction in temperature.
- Even though time to failure is strongly dependent on temperature, the failure location (outlet) and failure mode (thinning or diffusive crossover) is similar at all temperatures.

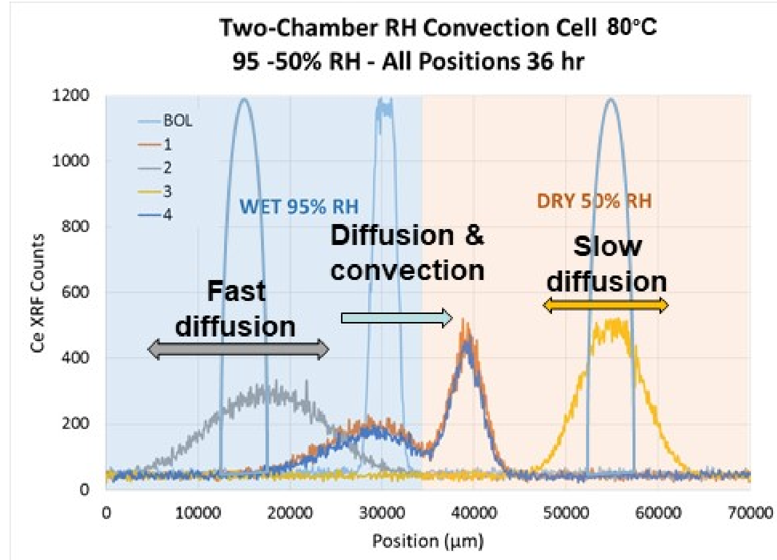
Technical Accomplishment:

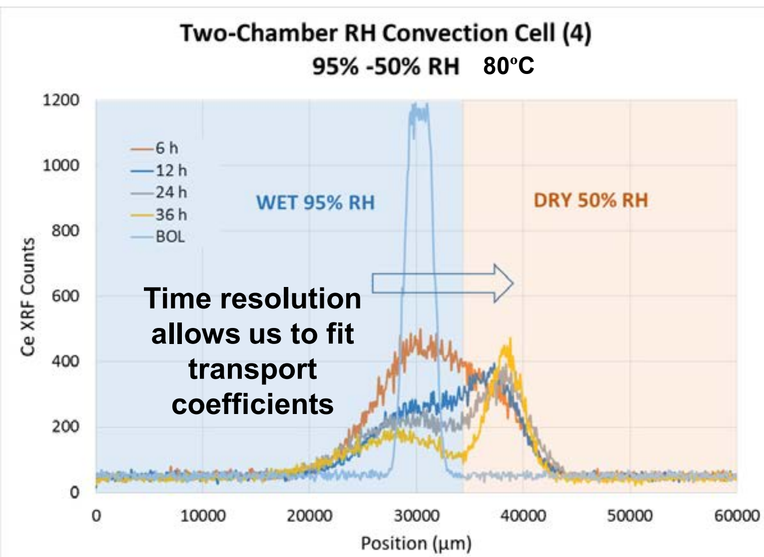
Ce Transport Measurement

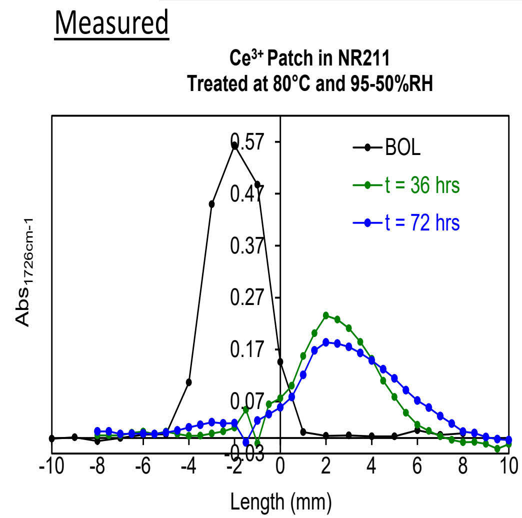


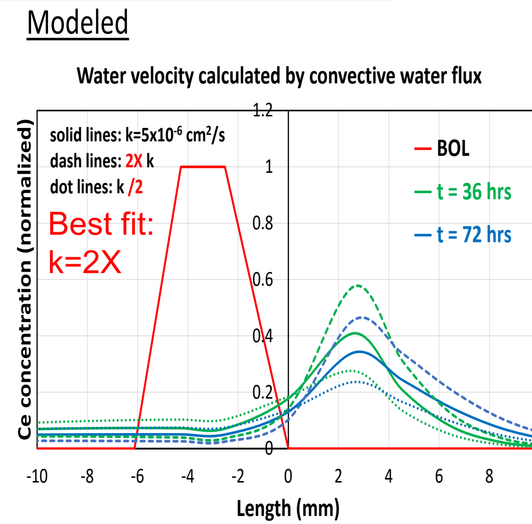


Ce patches doped locally on membrane strips









- Relatively rapid movement of samples 1 and 4 (nearest gradient) from high to low RH
- Diffusion of samples 3 and 4 are consistent with RH values of the respective chambers
- Data fit to determine convection coefficient (k) as f(t, RH) - see next slide

F.D. Coms and A.B. McQuarters, ECS Transactions, 86 (13) 395-405 (2018)

Technical Accomplishment:

Ce Transport Model

1-D Transient Model (Conservation of Ce)

$$\frac{dc}{dt} + \frac{dj}{dx} = 0$$

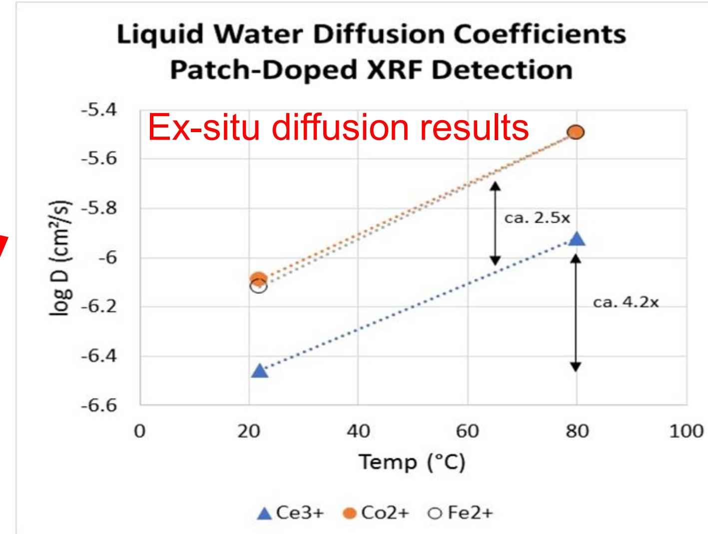
$$j = -uc\frac{d\phi}{dx} + v \cdot c - D\frac{dc}{dx}$$

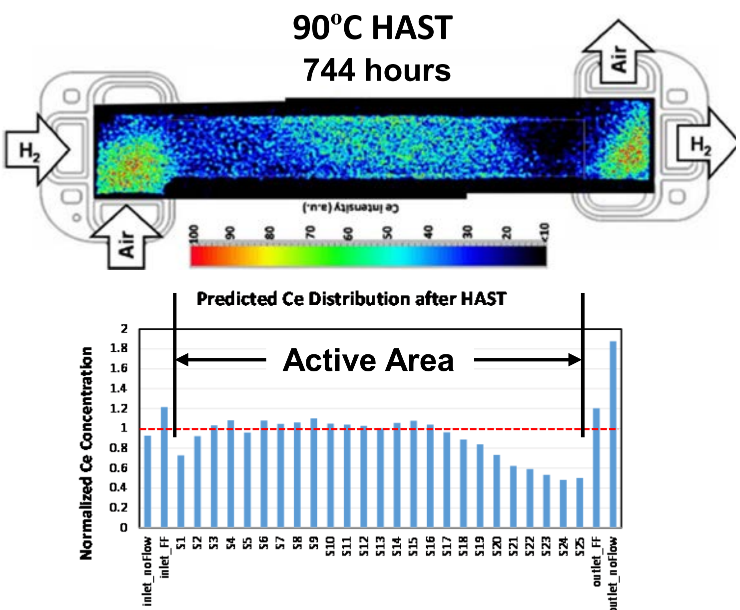
conduction convection diffusion

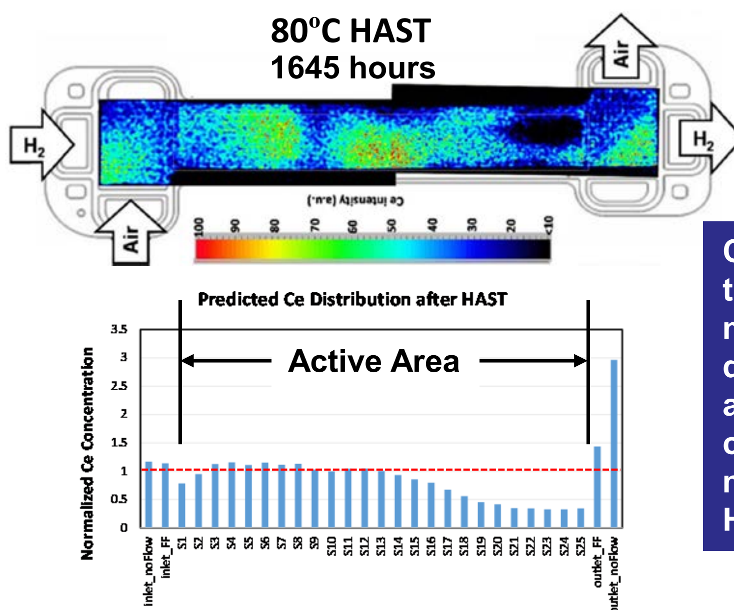
Nernst-Einstein for Ce^{3+}, z = 3

$$u = \frac{zFD}{RT}$$

$$v = -k\frac{d\lambda}{dx}$$





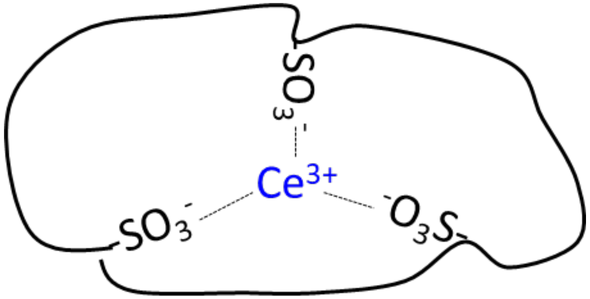


Ce migration model that accounts for mechanisms of diffusion, convection, and conduction can capture the Ce migration behavior of HAST test

Technical Accomplishment:

Ce Migration

Does Ce^{3+} Leave the Cell?



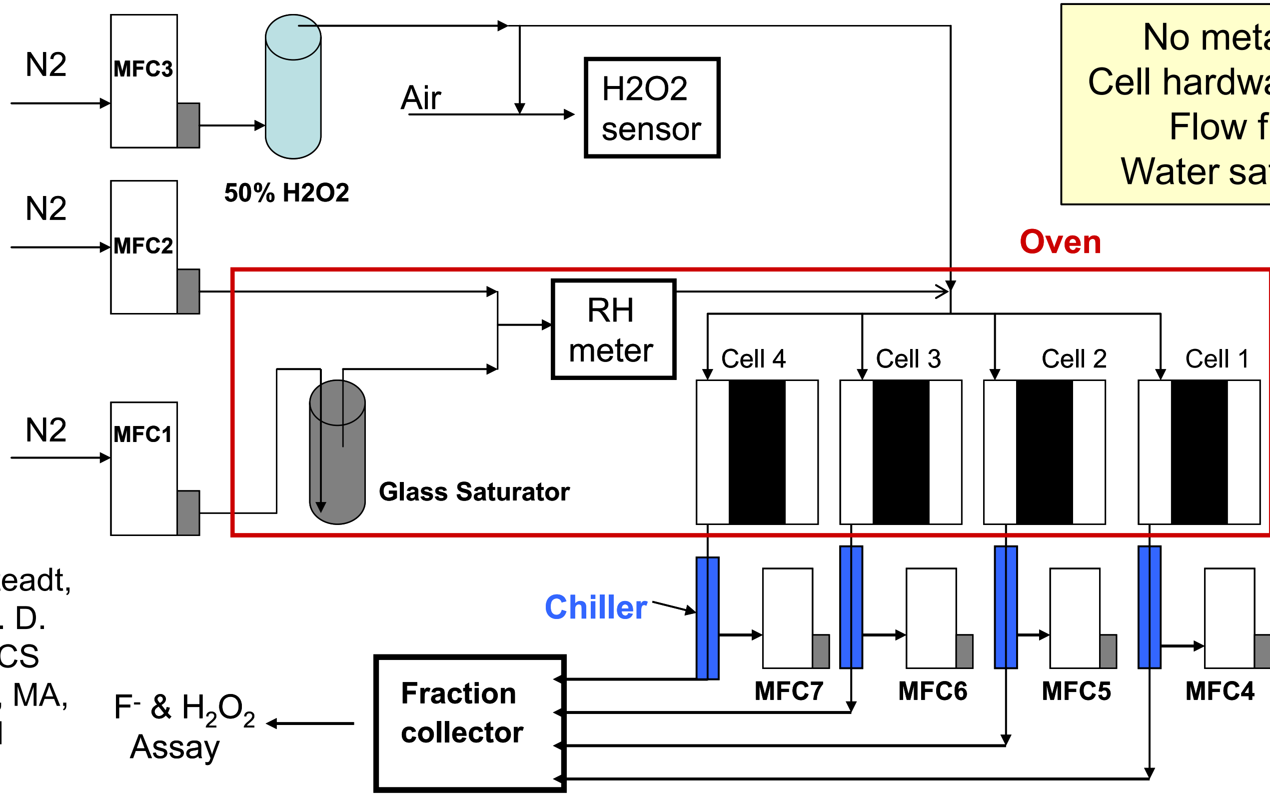
- Clearly Ce^{3+} is highly mobile, but can it leave the cell?
- Ce^{3+} is tightly ion paired to the polymer sulfonate groups and cannot leave the ionomeric phase unless accompanied by an anion (or three). F^- is already spoken for as it leaves as H-F or ion pair
  - Exhaust pH correlates with FRR. High FRR → decreased exhaust pH
- ICP analysis of exhaust water finds no traces of Ce^{3+} to the detection limit of 50 ppt!
- In cases of gross chemical degradation where sulfonate fragments are leaving the membrane (i.e. Fe contamination), Ce^{3+} could leave the cell. By then, the battle is already lost. Ce^{3+} loss is the effect, not the cause and the MEA is probably already dead.

Impact of Thickness on Membrane Chemical Degradation

Relative humidity of the H_2O_2 vapor stream can be readily adjusted to provide a range of reaction conditions

H_2O_2 Vapor Cell Test Set-up

No metal in test unit
Cell hardware: polysulfone
Flow field: Telfon
Water saturator: glass

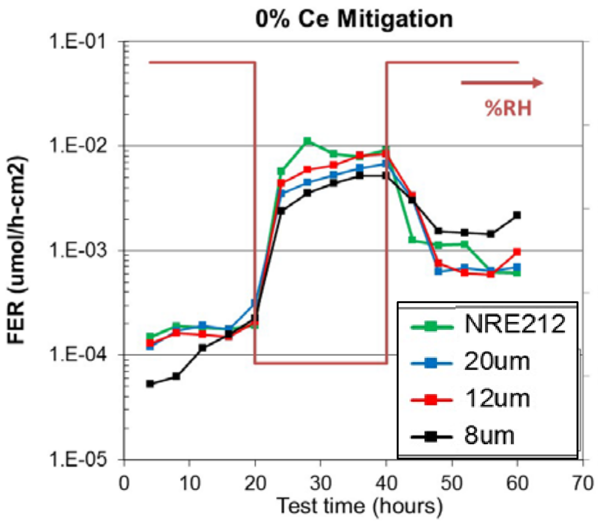


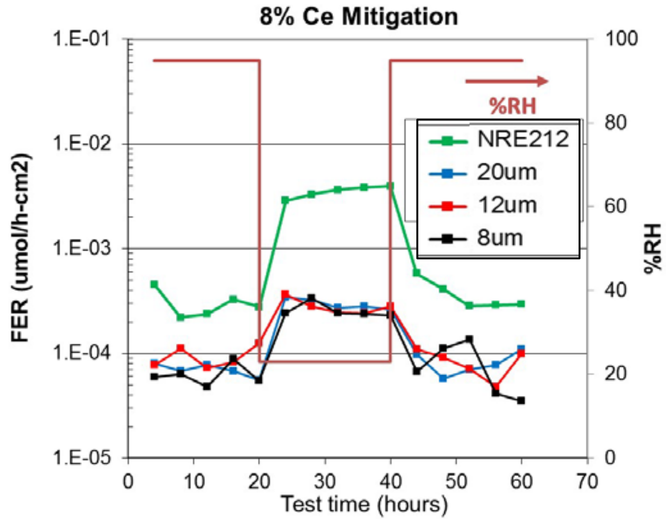
H. Xu, C. Mittelsteadt, T. McCallum, F. D. Coms, 220th ECS Meeting, Boston, MA, Oct 13, 2011

Technical Accomplishment:

Impact of Thickness on Membrane Chemical Degradation

- Both ex-situ and in-situ tests are being conducted to assess impact of membrane thickness and gas crossover on durability
- Ex-Situ H_2O_2 vapor tests of membranes of varying thickness and Ce^{3+} content (Giner)
    - H_2O_2 vapor test do not address gas crossover impact – intrinsic impact of thickness only
- In-Situ chemical durability (OCV) tests
    - Addresses impact of gas crossover & thickness





- 90°C, 30ppm H_2O_2 vapor cells tests
- No significant thickness impact when crossover is not considered
- Significant suppression of FRR at dry conditions with Ce

We have started a design of experiments using single cell OCV tests at 90°C (fixed Ce loading of 2%)

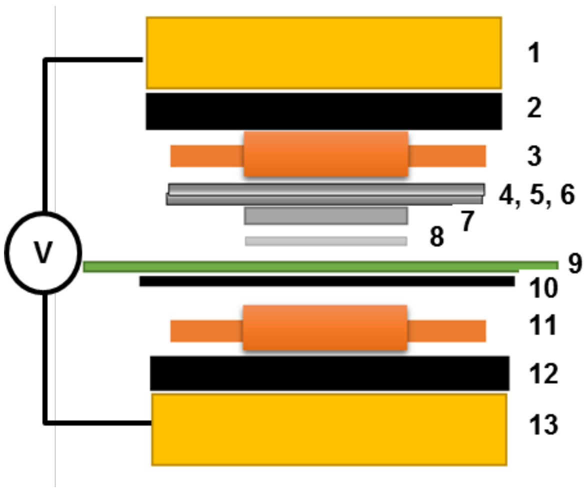
- DOE will isolate the impact of gas crossover of degradation rate
- Measuring Fluoride release, MW loss & carboxylate increase to isolate unzipping & chain scission mechanisms

Thickness (µm)	RH	Cathode P (kPa)	ΔP (kPa)
8	30%	150	-20
12	60%	200	20
20	90%	250	60

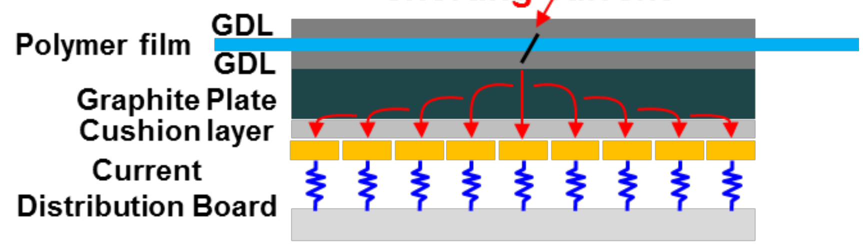
Technical Accomplishment:

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

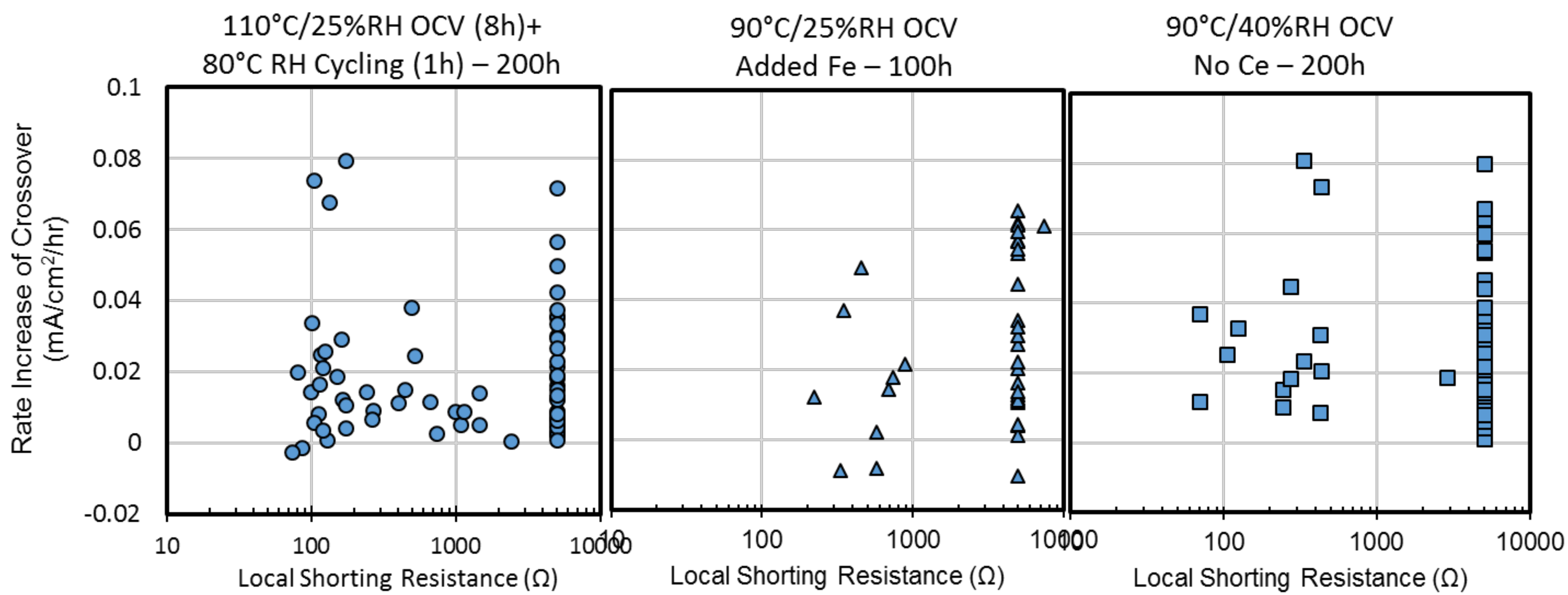
De-convoluted Shorting Resistance (Ω)

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:

Impact of Local Shorting on Membrane Degradation

- 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
- Run accelerated membrane durability tests to see if local shorts accelerate rate of local degradation
  - Use segmented cell to track progression of local shorting and gas crossover



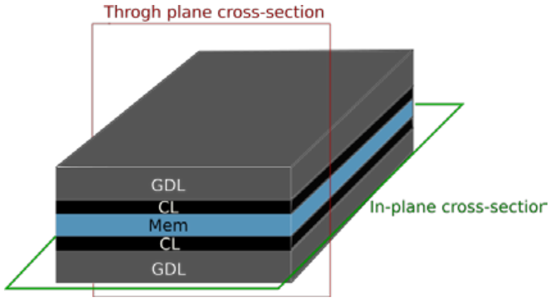
- There is no clear correlation between local shorting and increase in crossover.
  - Lack of correlation unexpected based on high modelled local temperature
- Plan to repeat tests while running to failure

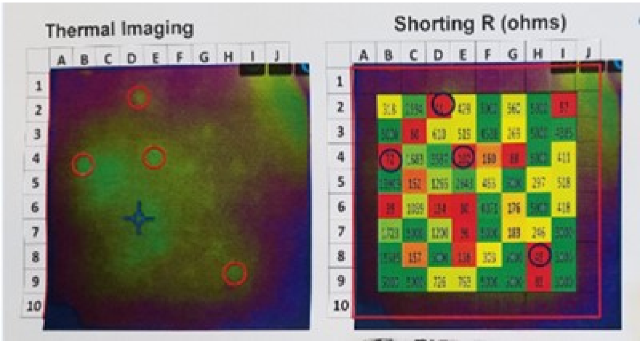
Technical Accomplishment:

Impact of Local Shorting on Membrane Degradation

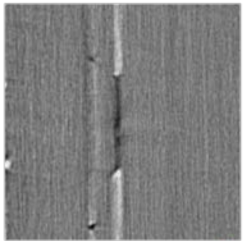
Goal: Develop a non-destructive method to image shorting location in an MEA

- Pre-shorted MEAs sent to LBNL instead
- Location of short is identified by the distributed resistance measurement as well as thermal imaging.

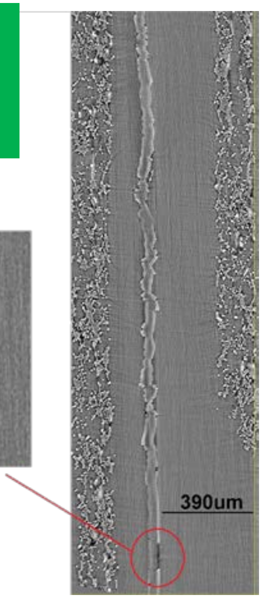




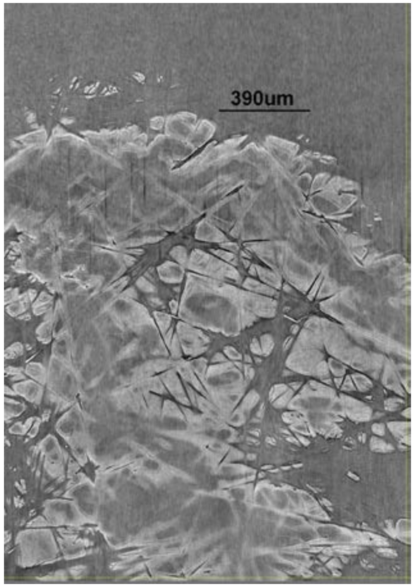
Imaged segments with low shorting resistance



Through-plane



In-plane at CL location



CL cracks observed

- Initial study indicate, X-ray CT resolution good enough to visualize shorts
- X-ray CT measurement of current sample complete, analysis in progress.
- If results look good, plan is to run HAST like test on the pre-shorted MEA, followed by imaging again.

Summary

SOA MEA

- SOA MEA exceeding (1.25 W/cm^2) DOE targets achieved by systematic selection of catalyst, ionomers and membrane
- Oxygen transport resistance is dependent on micropore surface area (<2 nm)
- Proton transport resistance is dependent on macropore surface area (>8 nm)
- Performance impact dominated by equivalent weight of the ionomer.

Electrode Durability

- ECSA loss decreases with decrease in operating RH
- > 35% reduction in ECA loss demonstrated with reduction in RH from 100% to 70%.

Membrane Durability

- Combined chemical/mechanical highly accelerated stress (HAST) was developed.
- Deep RH cycling at outlet results in increased crossover for both Ce containing and Ce free MEAs
- Ce^{3+} migration studies indicate Ce^{3+} movement via convection is the most dominant. Corresponding model was drafted.
- Method developed to generate and quantify local resistance of membrane shorts.

Future Work

- Execute Multifactor operating conditions DOE using H_2N_2 Voltage cycling.
  - 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).
- Predictive model based on the experimental data with the fundamental understanding of degradation mechanisms.
- Continue 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
  - Accelerated stress tests of SOA and pre-shorted MEAs in segmented cells combined with visualization techniques such as XRF & X-ray CT (LBNL).
  - Effect of membrane thickness and gas crossover using single cell OCV tests at 90^{o}C. (Giner)
- Refine 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.

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Technical Accomplishment:

Catalyst / Ionomer Interaction

Electrode Optimization

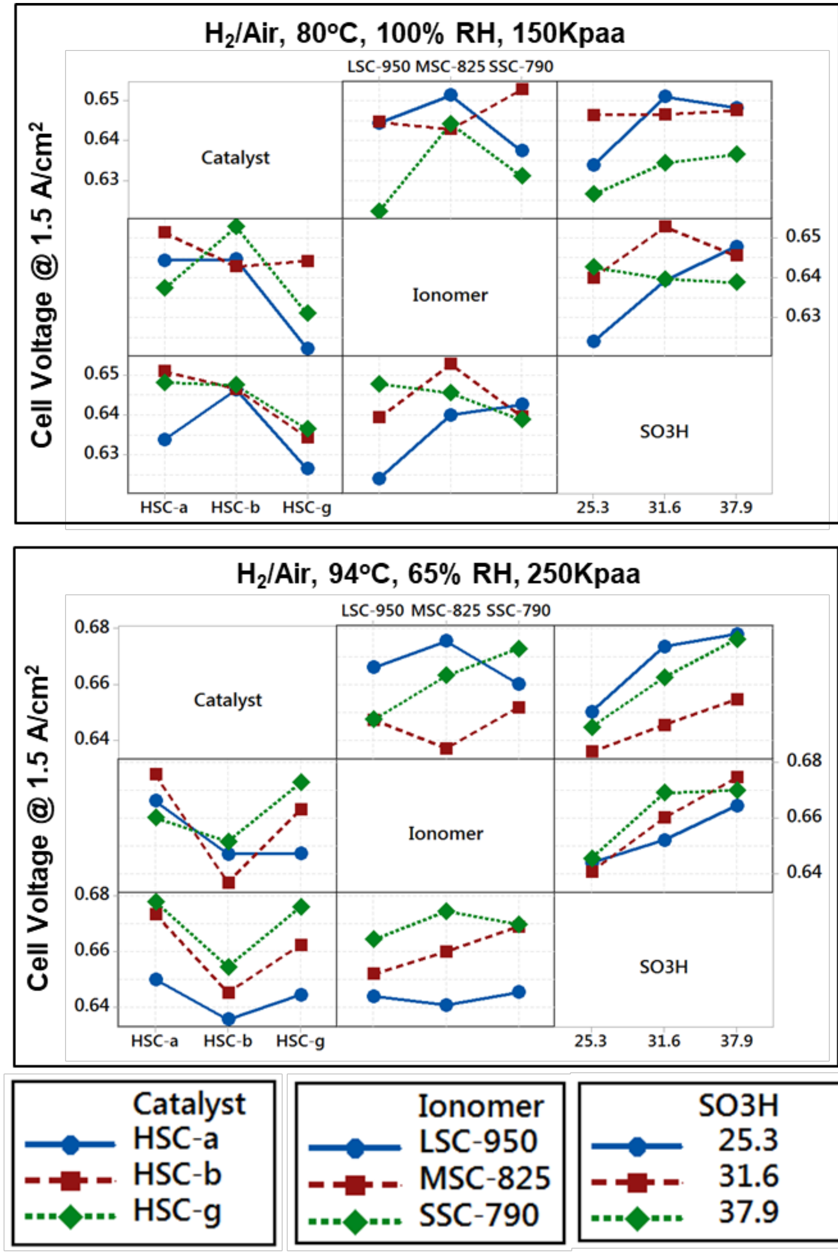
- 3 Catalysts and 3 Ionomers have been down-selected based on the catalyst and ionomer screening experiments

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

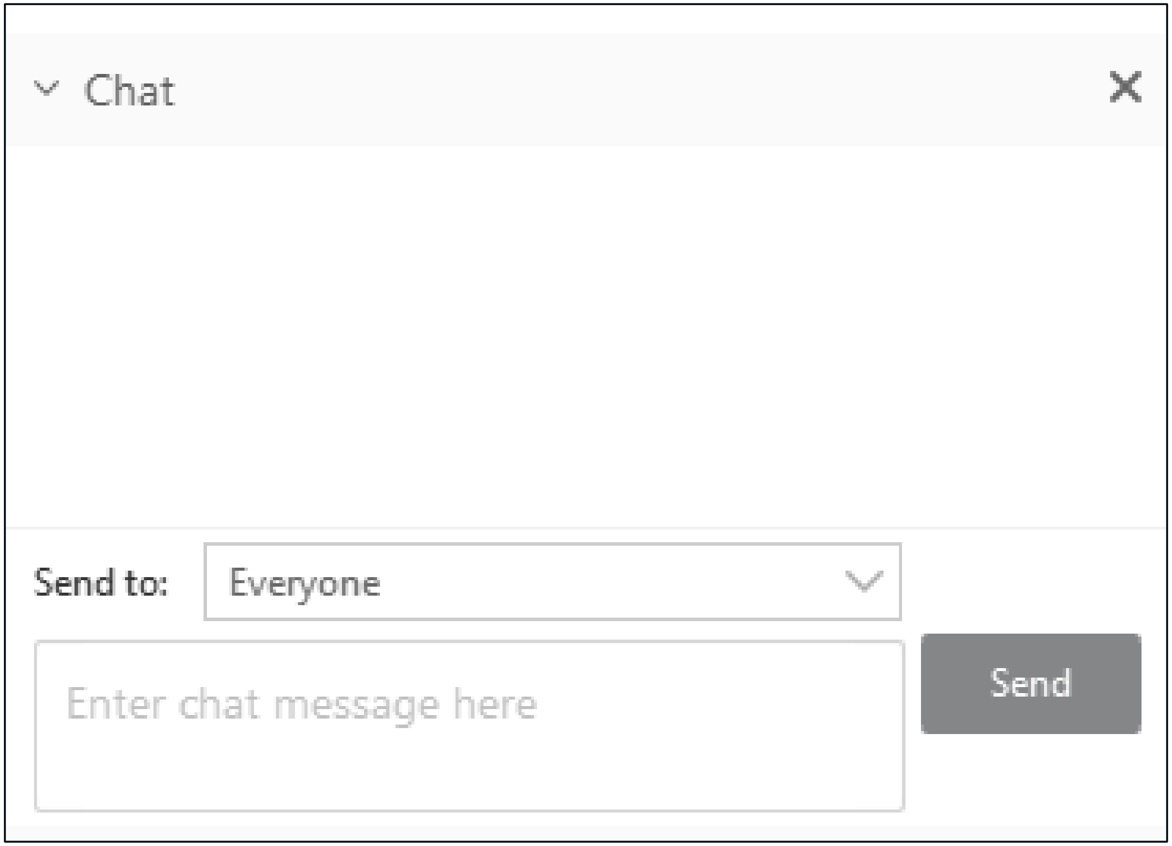
- **Combination of HSC-a with MSC ionomer provides the most robust combination across various operating conditions.** HSC-a also exhibit higher activity retention (from FC144)
- HSC-b cathode with SSC ionomer combination provides benefits under low pressure and wet conditions but severely falls below 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 cm² CCM MEA (3 repeats). Differential Conditions



Question and Answer

- Please type your questions to the chat box. **<u>Send to: (HOST)</u>**



Thank you

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