Durable High-Power Membrane Electrode Assembly with Low Platinum Loading

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General Motors, Fuel Cell Business

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FC156

Overview

Timeline

- Project start date: 1st Jan 2017
- Project end date: 30th August 2020*
- Percent complete: <83%

Budget

- Total Project Budget: $ 3,201,476
- Total Recipient Share: $ 640,295 (20%)
- Total Federal Share: $ 2,561,181
- Total Funds Spent**: $2,129,238
  - $1,703,391 (Fed Share)
  - $425,848 (Cost Share)

***as of 03/31/2020*
**likely no cost extension to 03/31/2021*

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

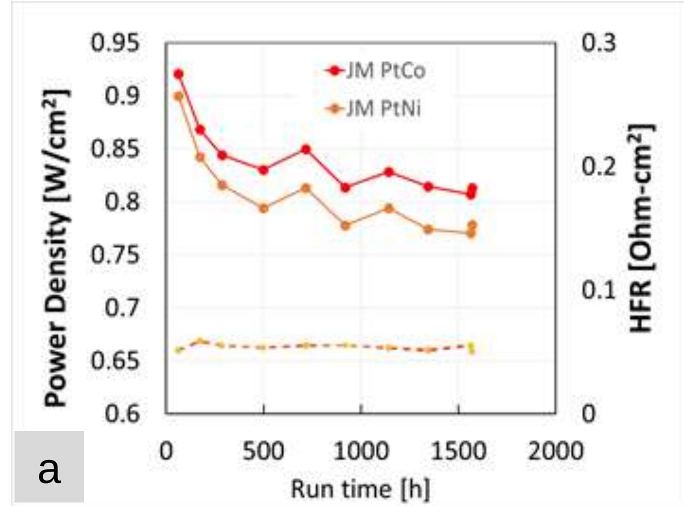
Partners

- Subcontractors:
  – Giner
  – UT Austin
- FC-PAD
- 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

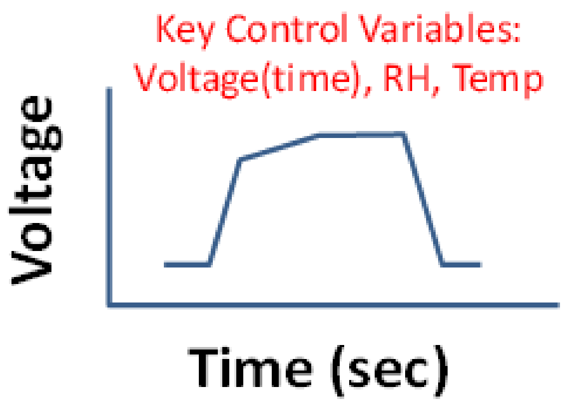


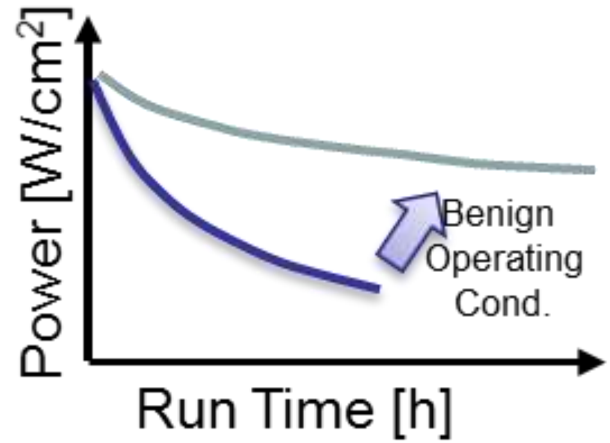
https://www.hydrogen.energy.gov/pdfs/review14/fc087_kongkanand_2014_o.pdf

Objectives

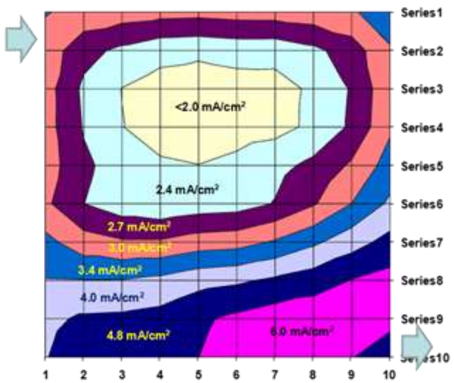
- ❑ **Project Goal**
  - ❑ Achieve DOE 2020 performance and durability target.
  - ❑ Improve durability of state of art (SOA) MEA by identifying and reducing the stress factors impacting electrode and membrane life.
- ❑ **Expected Outcome:**
  - ❑ Design and produce a state-of-art MEA with Pt loading 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 h by defining implementable benign operating conditions for fuel cell operation.

Approach





Electrode Durability : Conduct voltage cycling study on state-of-art MEA and map the 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 and Collaboration

SOA MEA

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

Chem and Mech. HAST
(Temp, RH, Voltage, dλ/dt)

State of Health Diagnostics
(FTIR, FRR, XRF, MW)

Mechanistic Studies
(Ce migration, thickness effect etc)

Advanced Characterization
(X-Ray CT)

Model Integration

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

BP 3 Milestone : Benign operating conditions from predictive model indicate >5000 h life can be achieved

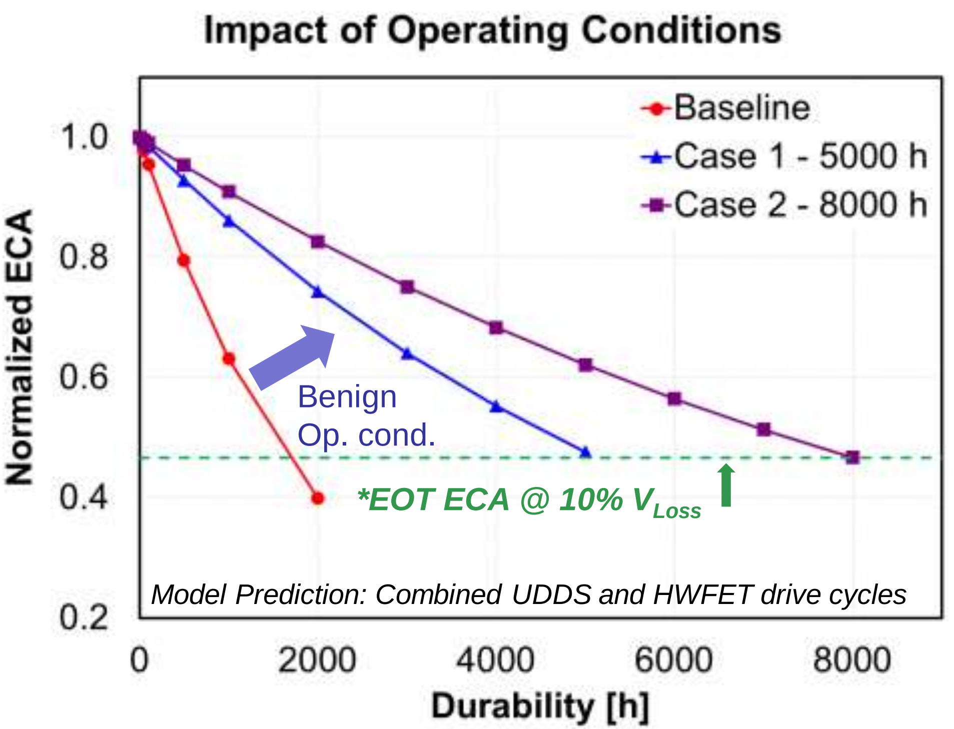
Phase 1	**Deliver 50 cm^2 SOA MEA for durability studies to FC PAD**	**Go/No-go**	**GNG1**	**Demonstrate 1 W/cm^2 @ 0.125 g/KW with 50 cm^2 SOA MEA.[b]**	**Q4**	**100%**
2.1 3.1	H_2-N_2, H_2-air voltage cycling tests at diff op. conditions Multiscale microscopy of SOA MEA at BOT, including PSD, STEM, EDS and X-ray CT.	Milestone	M2.1	Summary of VC design combinations and expected outcome using statistical approach Report on PSDs, chemical composition etc on BOT MEAs	Q5/Q8	90%
3.5 5.4	Particle size growth mechanism study with IL TEM Impact of Local shorting and membrane degradation	Milestone	M2.2	Demonstrate use of IL TEM for particle size growth mechanism with applied voltage Proof of accelerated degradation in areas induced with shorts (membrane thinning, higher X-over etc) (Go/No-go)	Q6	20% 100%
2.4 5.3	*Ex-situ* accelerated tests in aqueous media Impact of Thickness on Membrane Degradation	Milestone	M2.3	Report on dissolution rates for Pt and Co Empirical correlation between fluoride emissionrate from OCV and peroxide vapor test	Q7	70% 90%
2.5 4.2 5.2	Quantify transport and kinetic losses in aged MEAs Construct Pt and Co dissolution Models Combined Highly Accelerated Tests (Chem and Mech)	Milestone	M2.4	Plot of voltage loss terms as a funciton of operating conditions Pt and Co dissolution model for validation. Mem. stress life curves for model validation	Q8	80% 80% 100%
Phase 2	**Durability of SOA MEAs**	**Go/No-go**	**GNG2**	**Demonstrate >35% reduction in ECSA, SA and voltage degradation vs. standard DOE protocol on SOA MEA**	**Q9**	**100%**
3.2 4.3	Multiscale microscopy of SOA MEA at EOT, including PSD, TEM, EELS Construct ECA and activity loss models with data from task 3	Milestone	M3.1	Report Pt dissolution rates, Co dissolution rate, Pt shell thickening etc. Demonstrate activty and ECSA decay model to predict with in 15% of expt data.	Q10	70
4.4 5.5	Model to quantify Op. Cond Impact on Electrode Deg Rate Post mortem analysis of Degraded MEA	Milestone	M3.2	Demonstrate decay model to predict voltage loss as a function of operating conditions. Demonstrate impact of shorts on durability using X ray CT and other post mortem tests	Q11	70
4.5	Electrode Decay Model Validation	Milestone	M3.3	Validate decay model with data from task 2 and 3	Q13	30
5.6	Model dev. and valdiation for Membrane Degradation	Milestone	M3.4	Validate stress life degradation mode		
Phase 3	**Predictive model for degradation with different op. condition**	**Final Review**	**M3**	**Recommend benign operating conditions that can prolong MEA life to 5000 h**	**Q13**	**60%**

[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

Technical Accomplishment:
Target and Status

Item	Units	2020 Target	2020 Status	
			94º C 250Kpaa	80º 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	*5000-8000	2000-3600
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



*10% V$_{Loss}$, 100% RH, 250 Kpaa PC.

In this Budget Period (BP3)

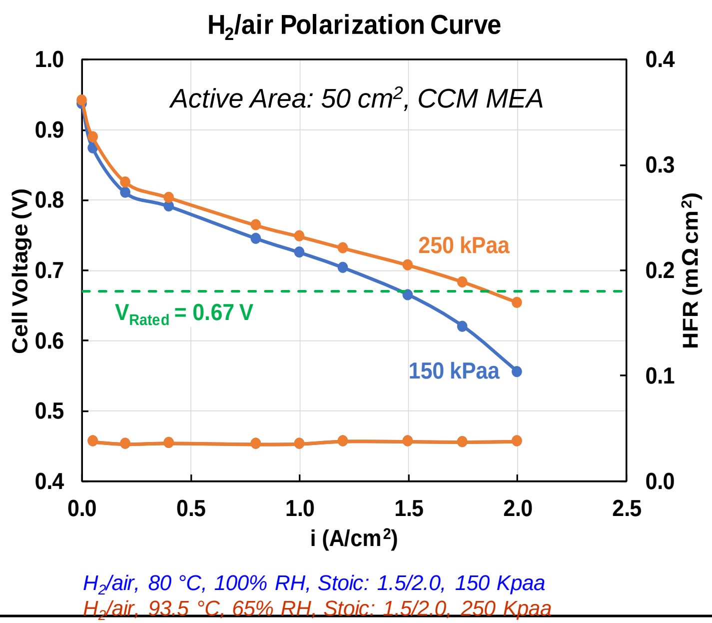
- Successful completion of H_2-N_2 voltage cycling design of experiments at various operating conditions.
- Statistical models and factors influencing degradation was estimated and ECA$_{Loss}$, V$_{Loss}$ maps generated.
- V-cycle data used to estimate parameters for ANL's predictive damage model.
- Ce^{3+} migration rates were quantified and Ce^{3+} transport model developed.

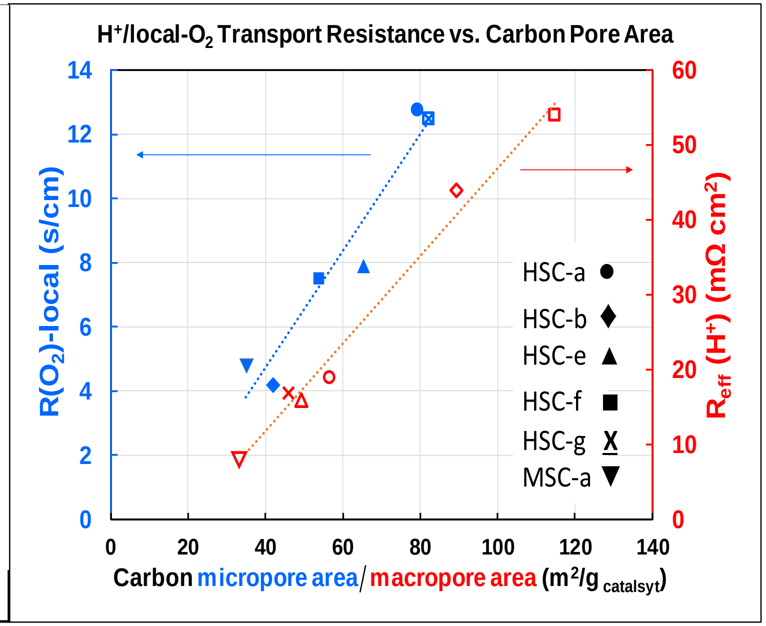
Milestone 3

- ANL's ECA damage model was used to identify operating conditions to prolong electrode life.
- Benign conditions to achieve 5000 h of durability and 8000 h of durability was identified vs. baseline durability of <2000 h.

Budget Period 1 - Recap

Technical Accomplishment:





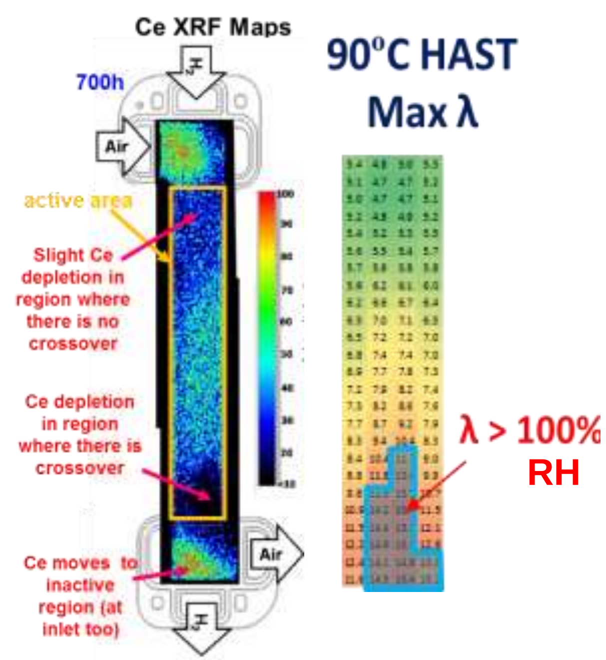
SOA MEA Design

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

- Catalysts, ionomers and membranes were down selected to generate SOA MEA that exceed DOE target.
- Impact of carbon property, ionomer EW on kinetic and transport resistances identified.
- Accelerated chemical and mechanical stress test for membrane degradation was developed.*

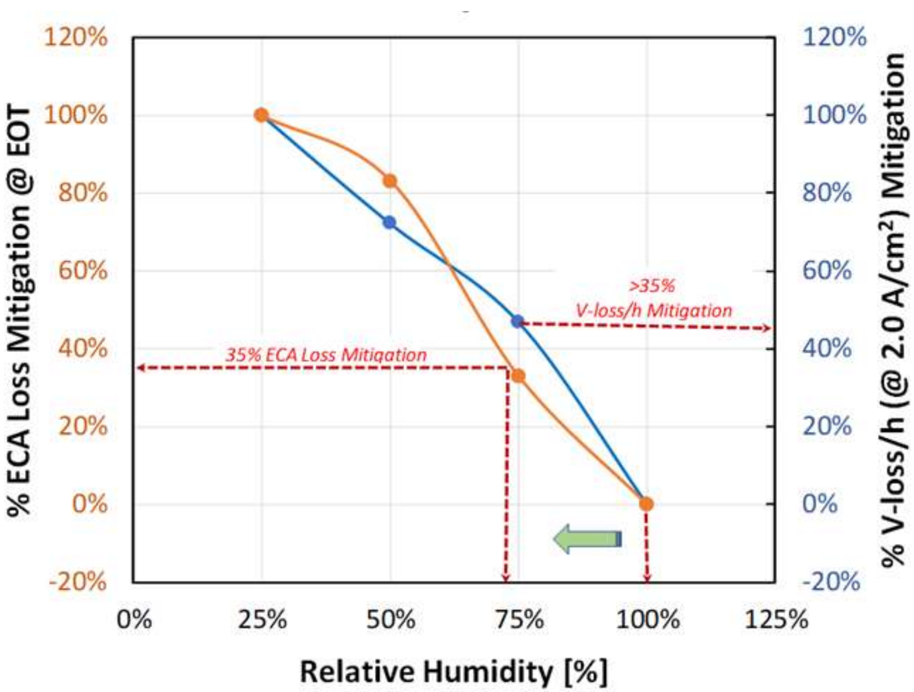
BP1 Milestone 1 / Go No Go

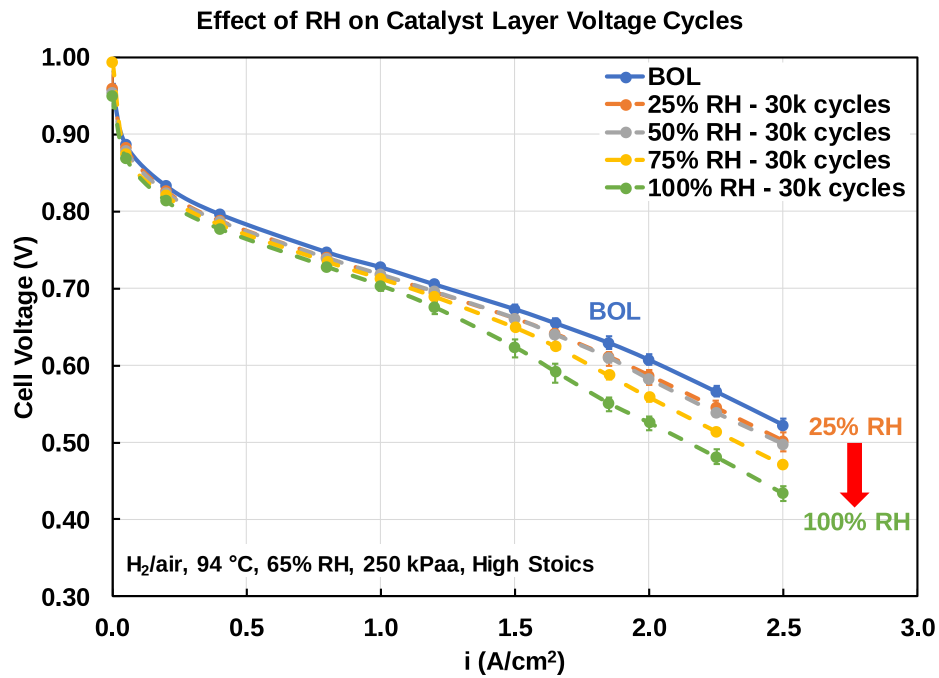
- SOA MEA exhibit > 1.2 W/cm² exceeding DOE target
  - 5 cm² and 50 cm² SOA MEAs were provided to FCPAD



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

Budget Period 2 - Recap





In this Budget Period (BP2)

- SOA MEAs developed in BP1, was verified in 3 different platforms ($5 cm^2$ differential, $10 cm^2$ common hardware and $50 cm^2$) in both GM and NREL (>1.2 W/cm^2 was confirmed in all platforms).
- H_2-N_2 Voltage cycling tests at various operating conditions were conducted on SOA MEA.
- Membrane durability studies were conducted to understand Ce migration, local shorting effect etc.

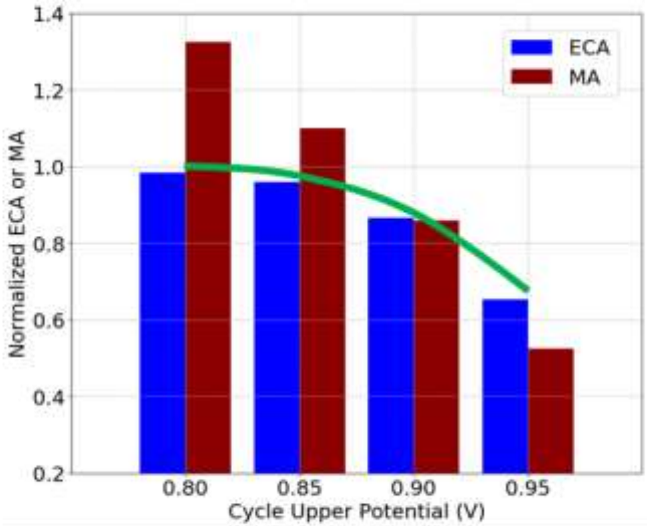
BP 2 Milestone 2/ Go No Go

- > 35% reduction in ECA loss demonstrated by changing operating condition. Example, 30% reduction in operating RH can provide > 35% reduction in ECA loss vs. 100 % RH operation.
  - Several operating factors can be optimized to achieve the same.

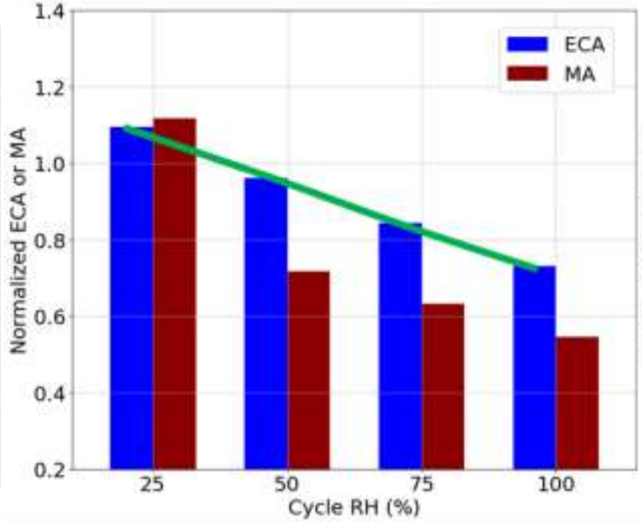
Technical Accomplishment:

Task 2. Electrode Durability and Impact of Op. Conditions

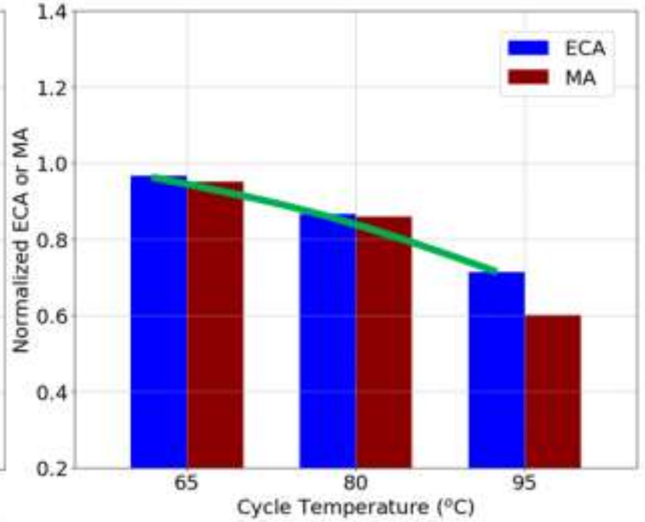
Single Factor Tests – Effect of Upper Potential, Relative Humidity and Temperature



UPL

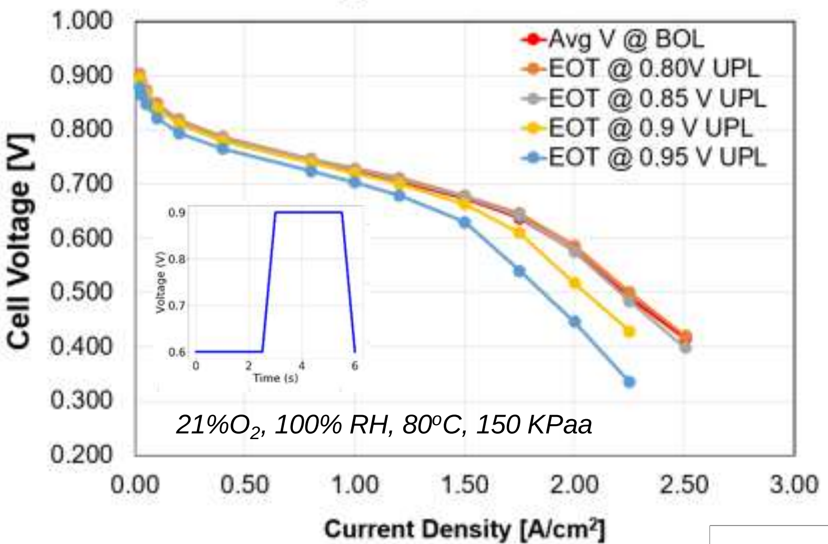


RH



Temperature

Effect of Upper Potential Limit



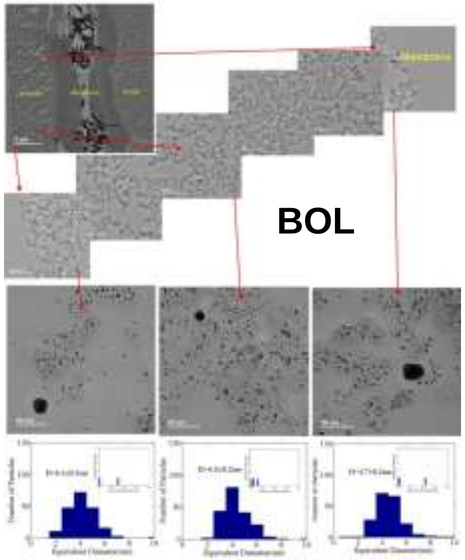
Operating Conditions:

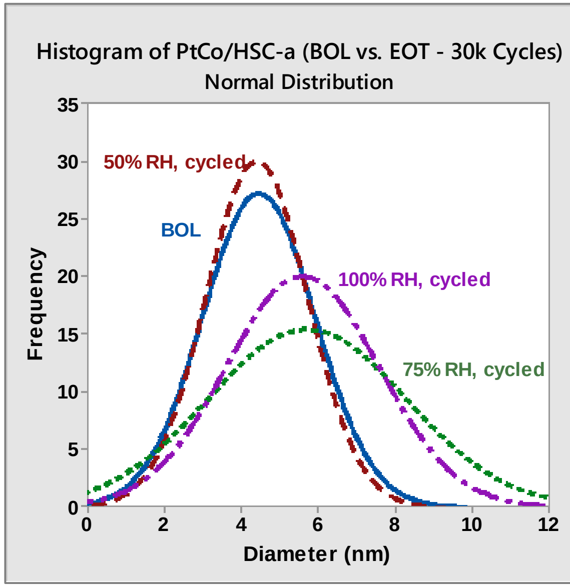
- Default when not being the variable : 80 ºC, 100% RH, 0.9 V UPL
- 2.5s hold at Upper potential and 0.60 V, 0.5s ramp, 30 K V-cycles

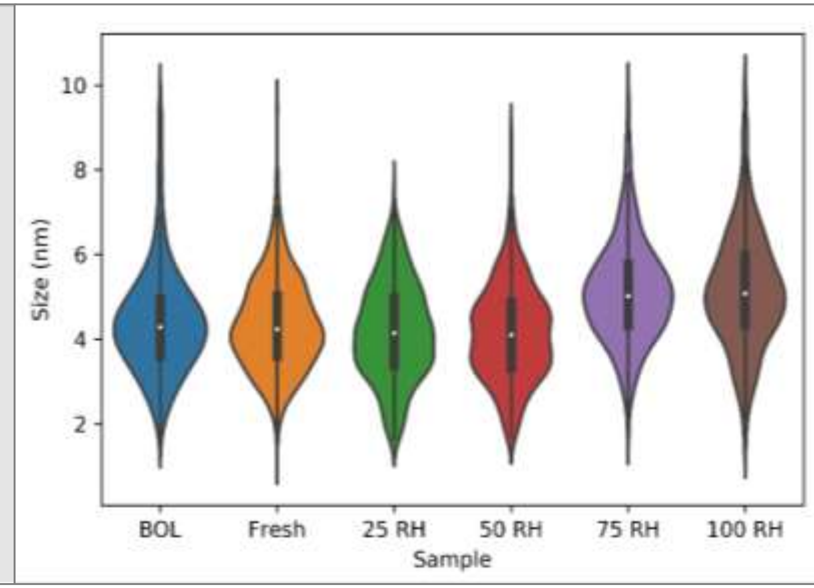
- Single factor tests to study effect of upper potential limit (UPL) of V cycle, relative humidity (RH) and temperature (T).
- Similar trends observed for all key factors studied, namely UPL, RH and T, with higher values being worse.
- Studies indicate, the degradation of ECA can be mitigated significantly when one or more of the operating conditions can be reduced.
- Some conditions like (0.8V UPL case) exhibit increase in MA or ECA, largely due the complex break in and degradation process of PtCo catalysts.

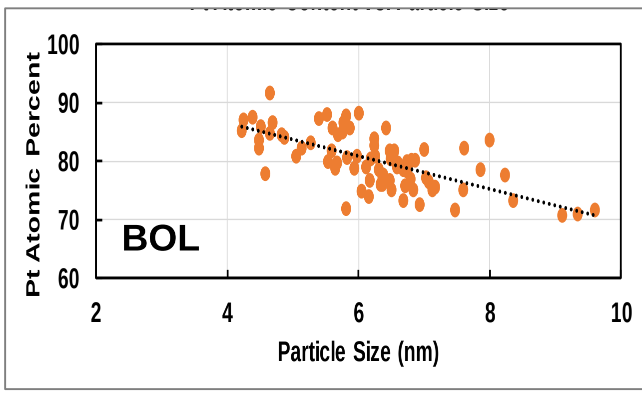
Technical Accomplishment:

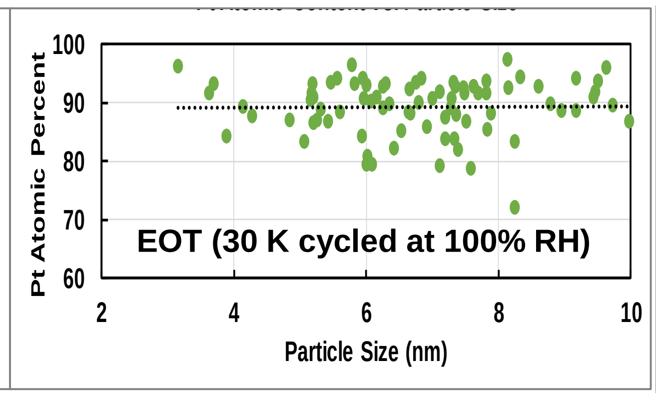
Task 3. Characterization of Voltage Cycled MEAs

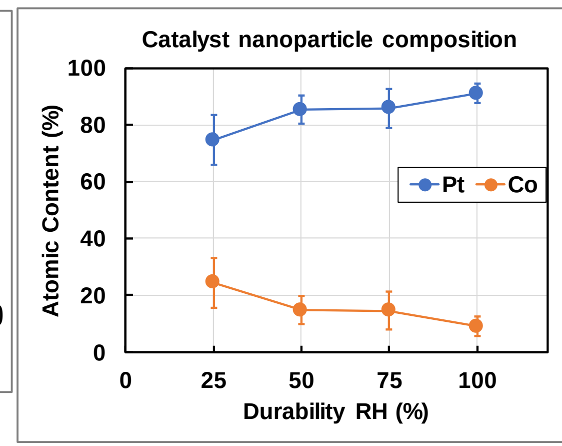












- Detailed characterization of BOL and EOT sample at UT Austin.
- As expected, (from ECA measurement's) the PSD increases with increase in operating RH.
- As PSD changes, the atomic composition of the particles also changes, more cobalt loss observed for samples cycled at higher RH.

GM TEXAS The University of Texas at Austin

BOL – Beginning of Life, EOT – End of Test

Technical Accomplishment:

Task 2.4 Ex situ tests for Pt and Co Dissolution rate

Impact of Operating Conditions

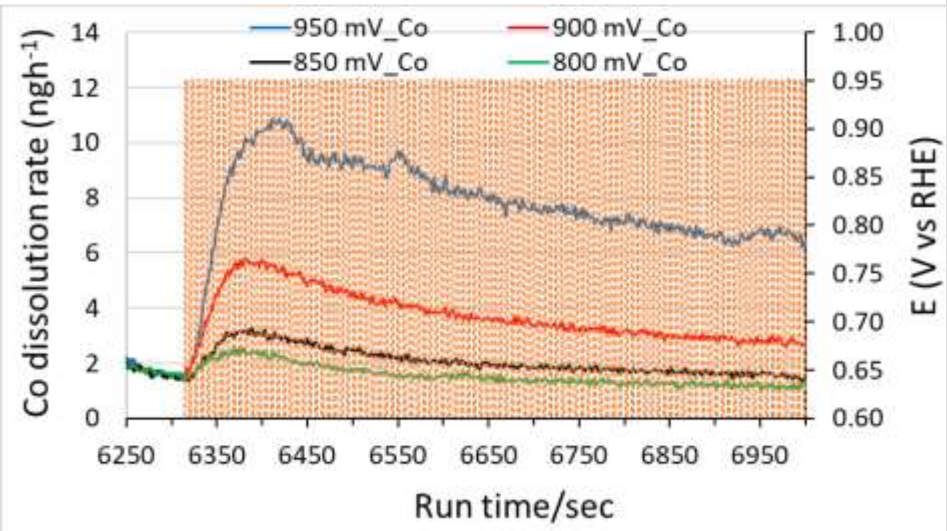
Effect of UPL During Potential Sweep-Hold Cycles

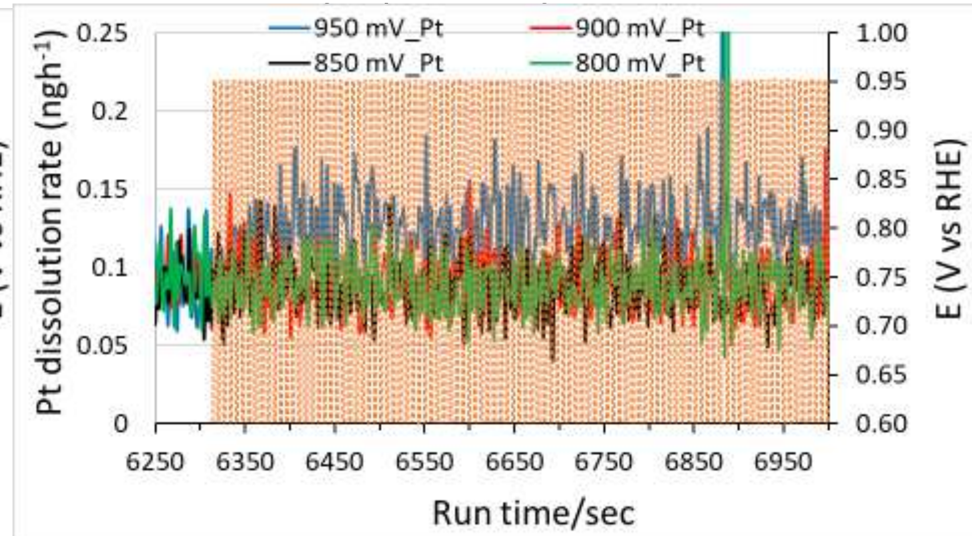
UPL (V)	LPL (V)	UPL hold time (s)	LPL Hold time (s)	An scan rate ($V.s^{-1}$)	Ca scan rate ($V.s^{-1}$)
0.95, 0.90, 0.85, 0.80	0.6	2.5	2.5	0.35	0.35

* Fresh electrode was used for each of the four UPL experiments

SOA catalyst – 30% PtCo/HSC-a, was used for all expts

- The dissolved Co increases and then decreases with increasing number of potential cycles
- Co dissolution increases with increase in UPL, scan rate, hold time (not shown)
- Very small rate of dissolved Pt observed





Electrode was held for 3 min at 0.6 V before potential sweep-hold cycling

- Co dissolution trends are similar to platinum (from earlier studies @ longer duration), the dissolution rate higher by more than an order of magnitude.
- Co dissolution factors to be used to refine the Co dissolution models.

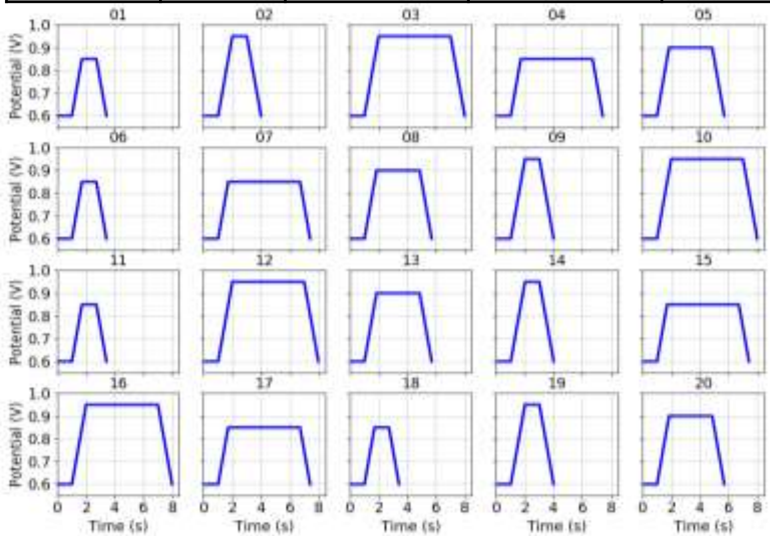
Technical Accomplishment:

Task 2 H_2-N_2 Voltage Cycling of SOA MEA

Design of Experiments (DoE) Approach

50 cm² MEA Test Matrix

Cell Temp (°C)	RH (%)	Upper potential (mV)	upper potential hold time (s)	Test Stand
55	40	850	1	A
75	70	900	3	B
95	100	950	5	C
				D



Voltage Cycling Waveforms

50 cm² MEA Test Conditions

Test Number	Cell Temp (°C)	RH (%)	Upper Potential (V)	Hold Time (s)	Stand
1	95	100.00	0.85	1	A
2	55	40.00	0.95	1	A
3	95	40.00	0.95	5	A
4	55	100.00	0.85	5	A
5	75	70.00	0.9	3	A
6	55	100.00	0.85	1	B
7	95	100.00	0.85	5	B
8	75	70.00	0.9	3	B
9	95	40.00	0.95	1	B
10	55	40.00	0.95	5	B
11	95	40.00	0.85	1	C
12	95	100.00	0.95	5	C
13	75	70.00	0.9	3	C
14	55	100.00	0.95	1	C
15	55	40.00	0.85	5	C
16	55	100.00	0.95	5	D
17	95	40.00	0.85	5	D
18	55	40.00	0.85	1	D
19	95	100.00	0.95	1	D
20	75	70.00	0.9	3	D

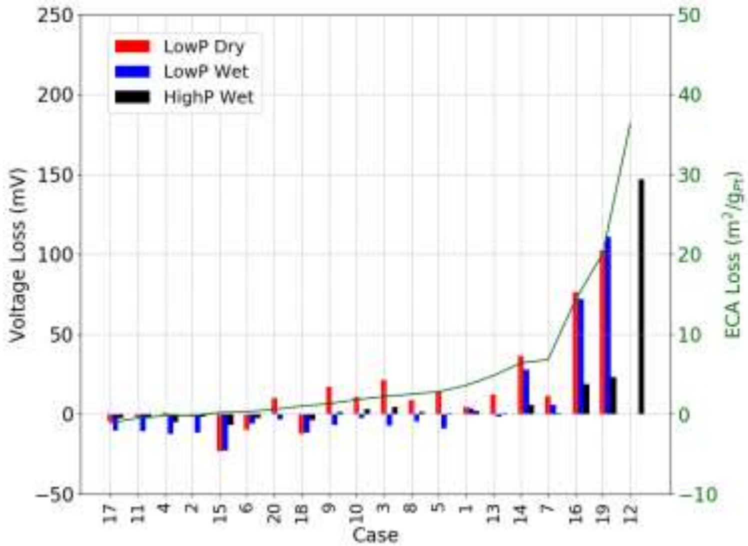
- Initial multifactor DoE studies using 5 cm² single cell (shown in 2019 AMR) had to be abandoned due to high variability of uncontrolled factors. (MEA Pt loading, test stand variation, several diagnostic tests leading to repeated test shutdowns etc).
- Learnings were incorporated in this modified DOE to minimize variation (reduced factors, levels, 50 cm² MEA, reduced Pt loading tolerance etc).

SOA MEA // CA– 0.1 mg_{Pt}/cm^2, 30% PtCo/HSC-a

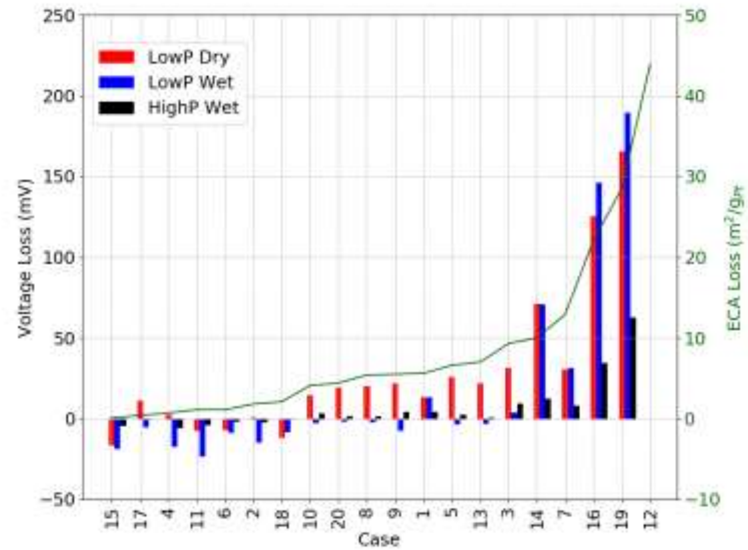
Technical Accomplishment:

Task 2 H_2-N_2 Voltage Cycling of SOA MEA

Impact of Operating Conditions



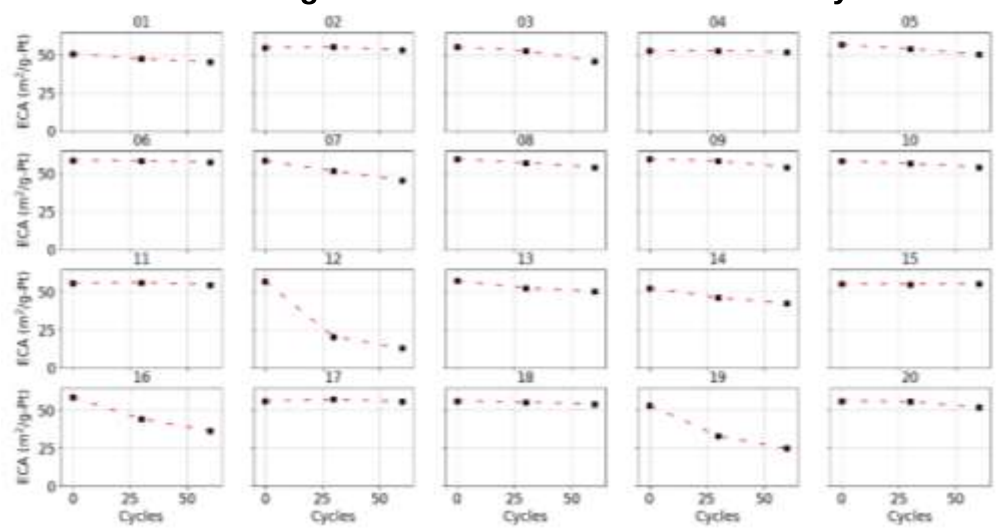
Voltage Loss and ECSA Loss after 30k cycles



Voltage Loss and ECSA Loss after 60k cycles

- ECA degradation and cell voltage loss is significantly lower for many conditions.
- Negative V-loss observed in some cases is largely due to the complex break in and PtCo degradation process.
- Conditions that involve both higher potential and RH show significant degradation.

Low P Dry - 21% O_2, 80ºC, 65% RH, 150 KPaa
Low P Wet - 21% O_2, 80ºC, 100% RH, 150 KPaa
Low P Wet - 21% O_2, 80ºC, 100% RH, 250 KPaa



ECA Measurements

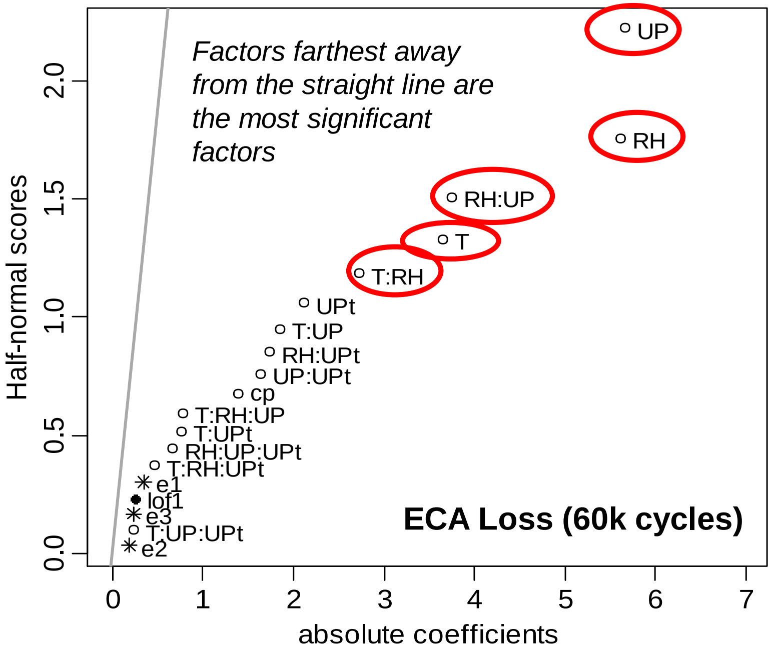
SOA MEA // CA– 0.1 mg_{Pt}/cm^2, 30% PtCo/HSC-a

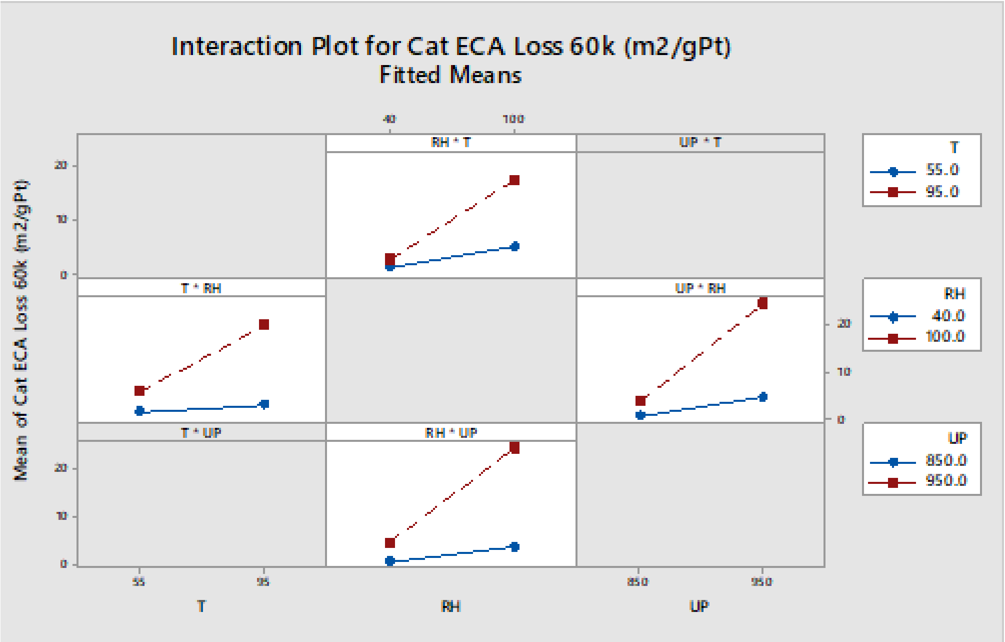
GM NREL NATIONAL RENEWABLE ENERGY LABORATORY

Technical Accomplishment:

Task 2.1 H_2-N_2 Voltage Cycling of SOA MEA

Statistical Analysis





$$ECA\ Loss = (-0.0138T - 0.2666RH + 2.171UP + 0.0006489\,(T*RH) + 0.2779\,(RH*UP) - 0.6979)^2$$

$$Voltage\ Loss = exp(-0.01459T - 0.21813RH - 4.18264UP + 0.000394\,(T*RH) + 0.236053\,(RH*UP) - 2.649229) - 0.5$$

- Statistical analysis indicate Upper potential limit, RH, T and its interactions namely RH: UP and T: RH are the most significant factors impacting degradation.
- Interaction plot show that, the dominant effect of high upper potential limit can be minimized by operating at lower RH. Similarly, the dominant effect of high RH can be minimized by lowering the operating temperature.
- A statistical model to predict ECA and Voltage loss as function of operating conditions (significant factors) is generated.

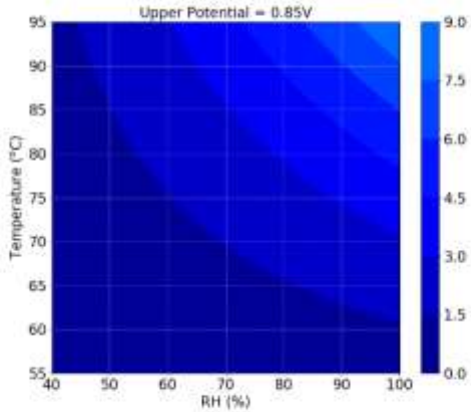
SOA MEA // CA– 0.1 mg_{Pt}/cm^2, 30% PtCo/HSC-a

Technical Accomplishment:

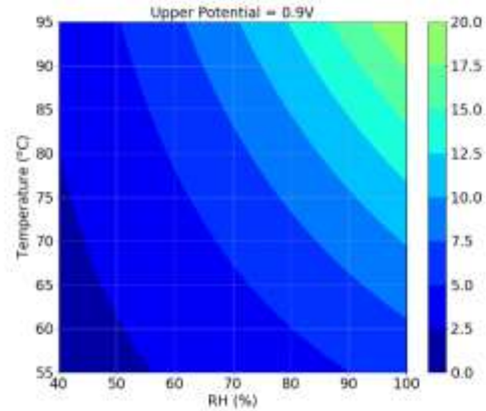
Task 2.1 H_2-N_2 Voltage Cycling of SOA MEA

Effect of Operating Conditions

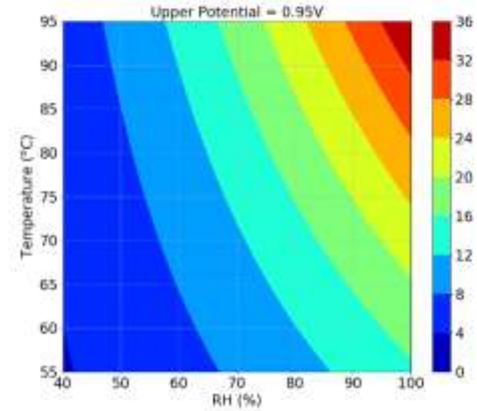
ECA Loss Maps (60 K cycles)



UPL = 0.85V

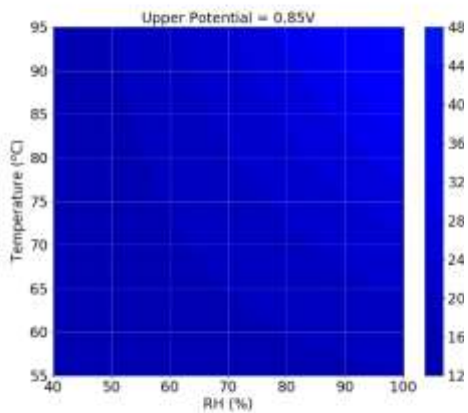


UPL = 0.90V

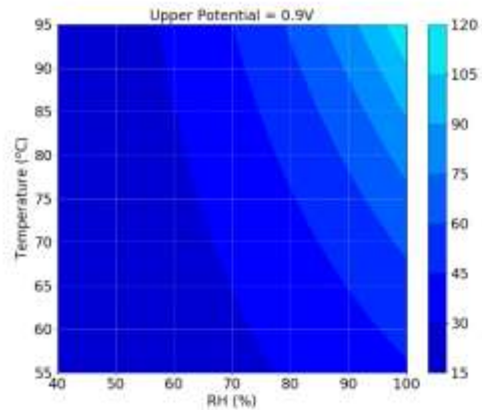


UPL = 0.95V

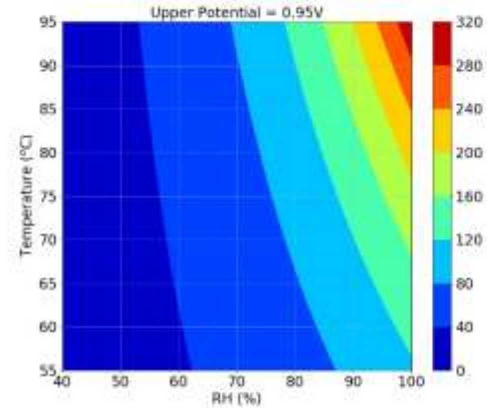
V Loss Maps (60 K cycles)



UPL = 0.85V



UPL = 0.90V



UPL = 0.95V

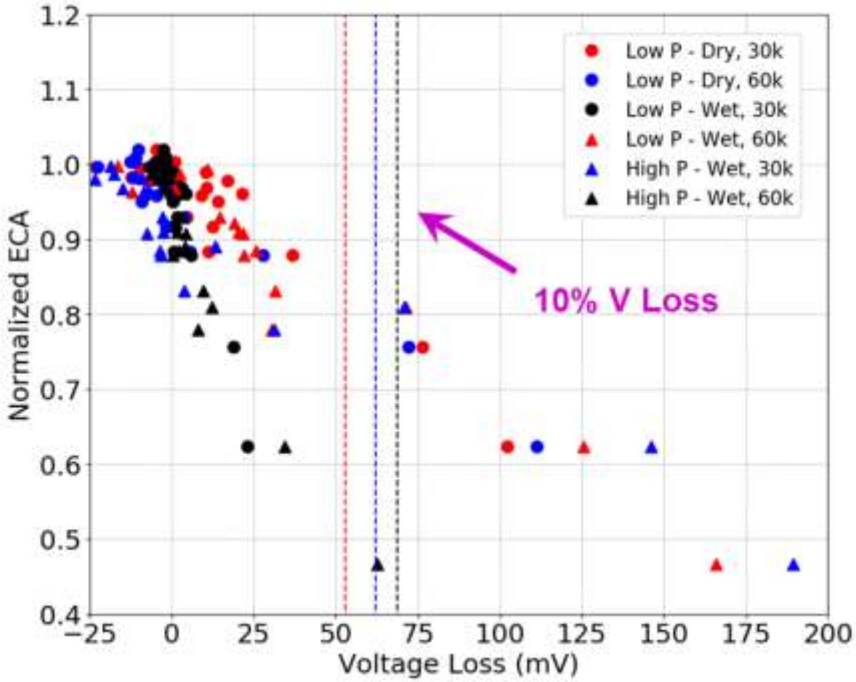
- Contour plots of predicted ECA loss and voltage loss obtained from the statistical model.
- Mapping the impact of operating conditions enables us to identify the benign operating window of operation. Supports trade off studies to prolong life.

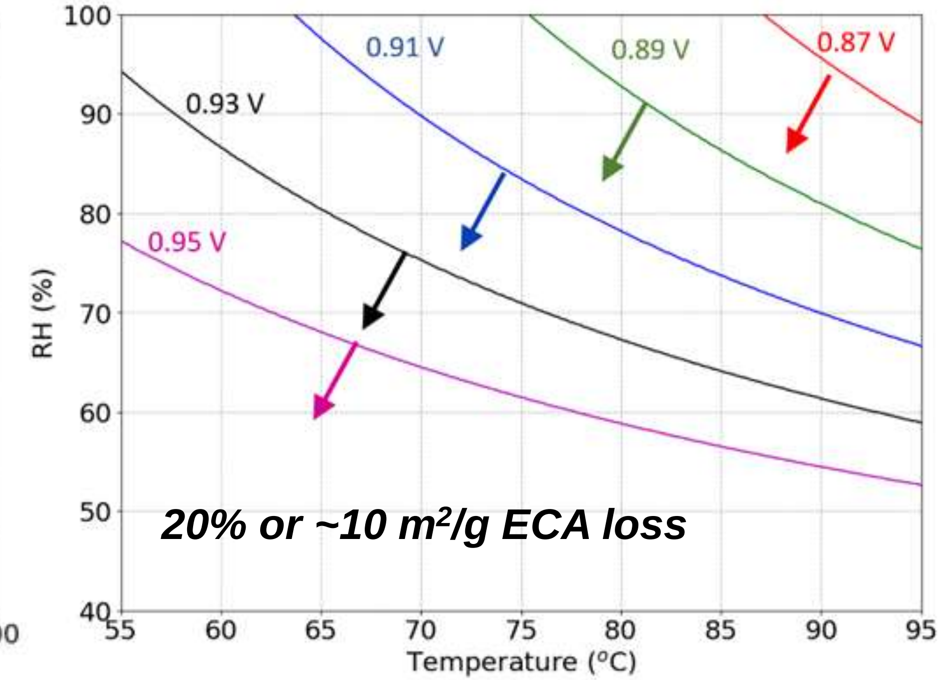
V_{loss} – 1.5 A/cm^2, 21% O_2, 80°C, 100% RH, 150 KPaa

Technical Accomplishment:

Task 2.1 H_2-N_2 Voltage Cycling of SOA MEA

Operating Condition Prediction





- Based on both ECA $_{Loss}$ vs. V $_{Loss}$ data from this DOE and performance model.
  - To achieve target 10% V $_{Loss}$ or lower (@ 150 KPaa condition), less than 20% ECA $_{Loss}$ should be maintained at end of test (EOT)
  - For 10% V_{Loss} @ 250 KPaa condition, less than ~ 55% ECA loss should be maintained at EOT.
- Operating condition maps presents a high level indication of average operating conditions that a system should be designed to prolong the MEA life.
- The current analysis is for a 60 K V cycle test and illustrates the profound impact operating conditions on electrode degradation.
- Actual drive cycle test would involve more complex waveforms and up to million V cycles.

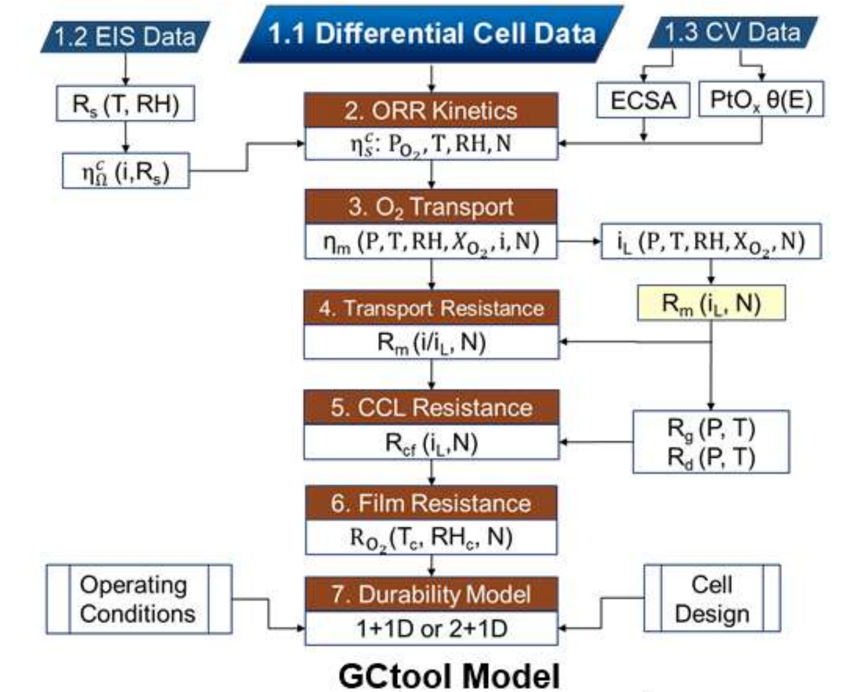
GM

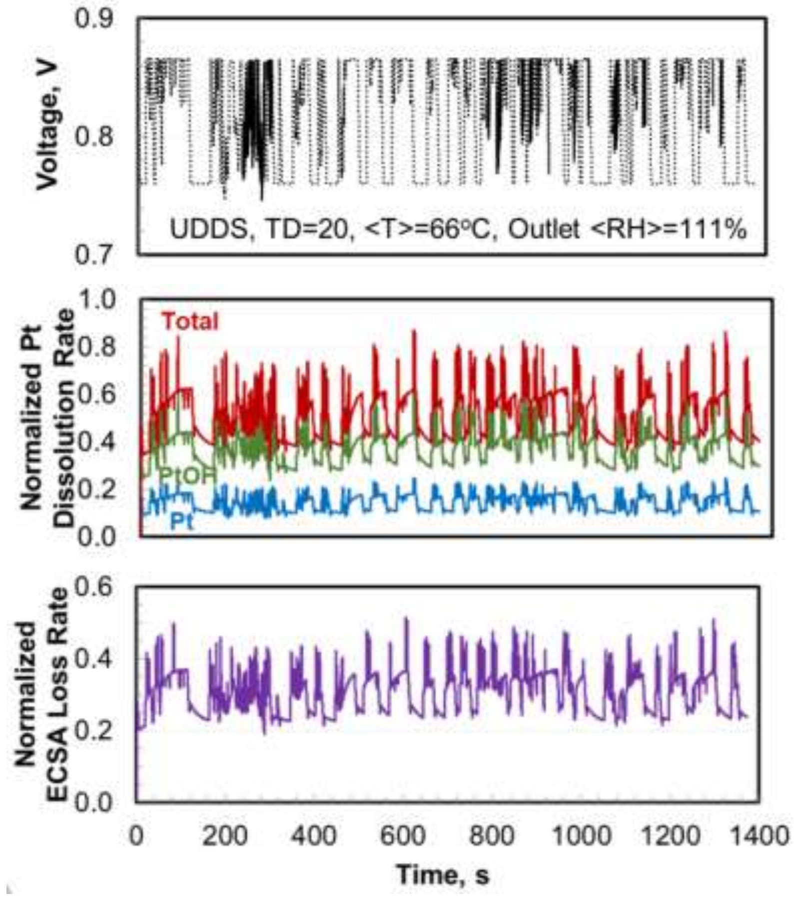
SOA MEA // CA– 0.1 mg_{Pt}/cm^2, 30% PtCo/HSC-a

Technical Accomplishment:

Task 4. Construct Pt and Co Dissolution Models

Modelling Durability Drive Cycle Protocol





- Fundamental models developed at ANL (Rajesh Ahluwalia) FC017 was used.
- Data from both Single factor and multifactor DOE studies was used to estimate all fitted parameters required for the model.
- Good fit observed between model and data (See FC017)

- ANL model used to simulate ECA degradation for EPA UDDS and HWFET drive cycle.
- Pt dissolution and ECA loss rates are estimated from the voltage profile at a given operating conditions.
- Operating conditions tuned to evaluate time to ECA loss.

FC017
R. Ahluwalia, X.Wang, J. Peng

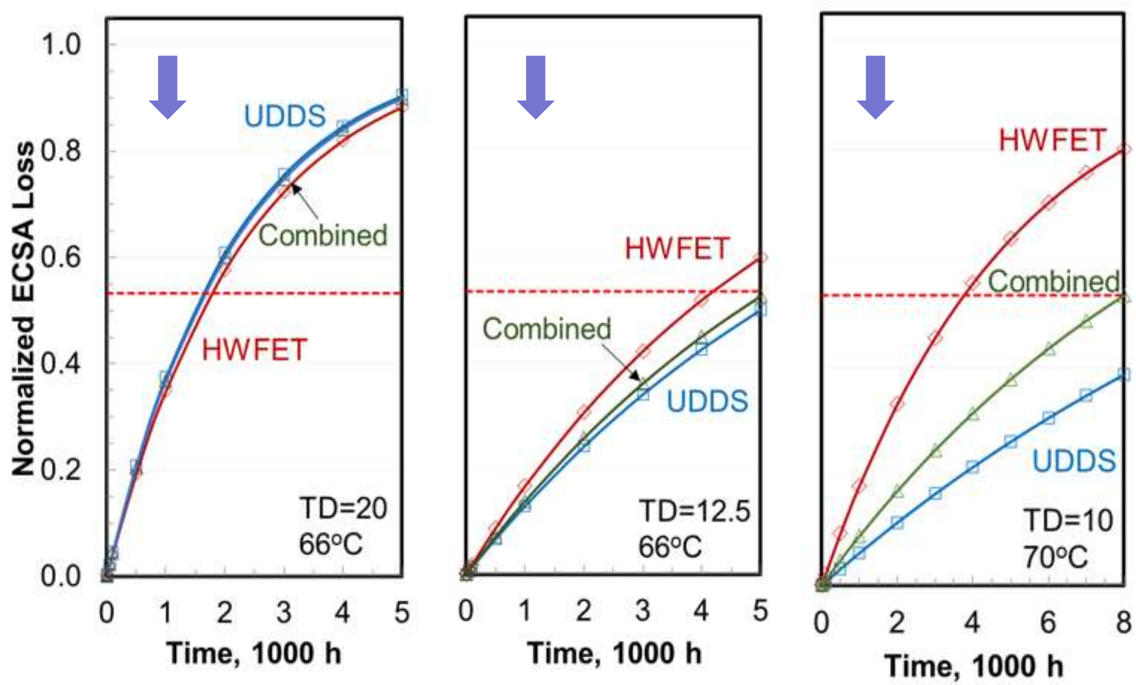
Technical Accomplishment:

Task 4. Pathways to Achieve 5000 h Electrode Lifetime.

Model Prediction – Effect of Operating Condition

	Baseline		Mitigation -Case 1 (5000 h)		Mitigation - Case 2 (8000 h)	
Load Cycles	UDDS	HWFET	UDDS	HWFET	UDDS	HWFET
CEM Turndown	20		12		10	
Average Outlet T	66°C		66°C		70°C	
Average Outlet RH	111%	116%	90%	102%	56%	83%
Cell Voltage	760-866 mV		760-850 mV		760-825 mV	
ECSA Loss	50%	60%	50%	60%	40%	80%
Combined ECSA Loss	55.30%		55.30%		55.30%	
Predicted Durability Hours	1800 h		5000 h		8000 h	

- Preliminary estimates indicate 5000h and 8000h electrode life can be achieved with modified benign operating conditions (mitigating upper potential limit and reducing relative humidity etc).
- The impact of these benign conditions (case 2) on other properties like membrane durability as well as viable overall system needs to be ascertained.

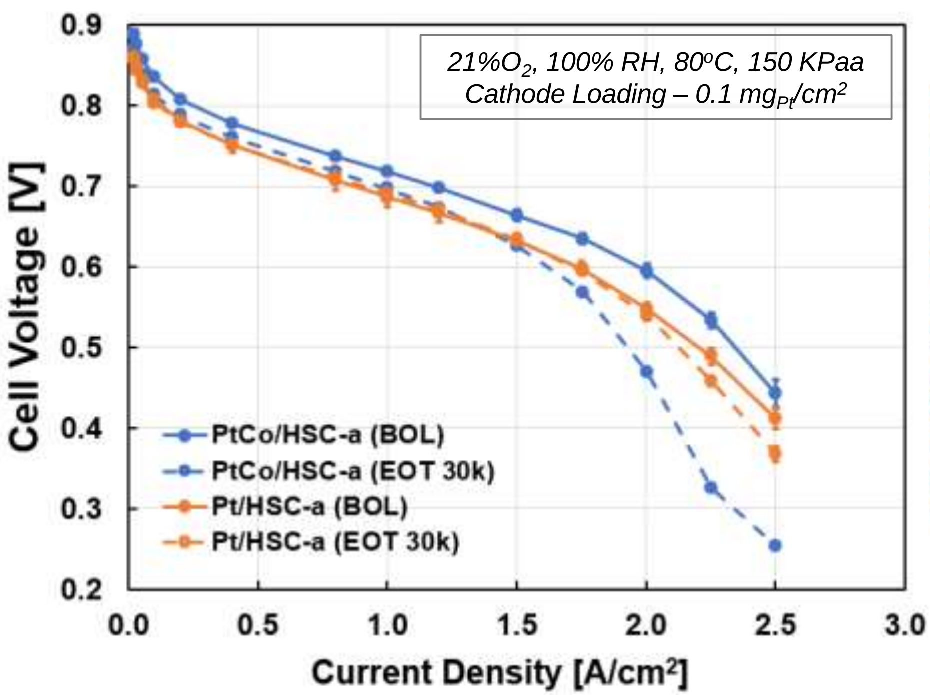


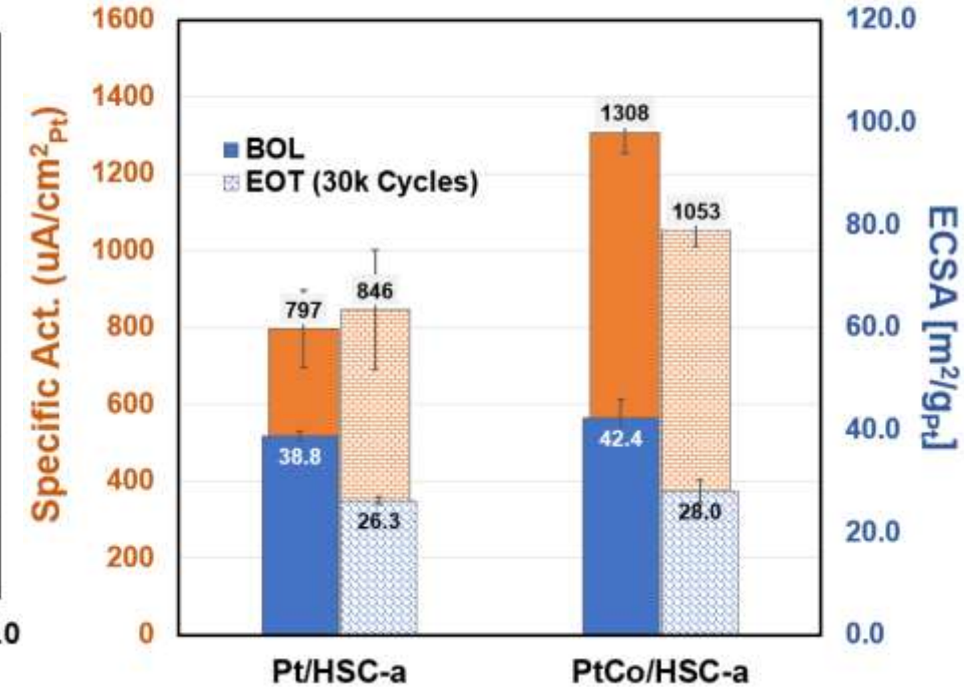
SOA MEA
CA– 0.1 mg_{Pt}/cm^2, 30% PtCo/HSC-a

Task 3. Stability of PtCo Nanoparticle.

Pt vs. PtCo (HSC-a)

0.60 to 0.95 V, 80 °C, 100% RH
30k AST cycles, TZW waveform
5 cm^2 CCM MEA – Differential Cell Cond.





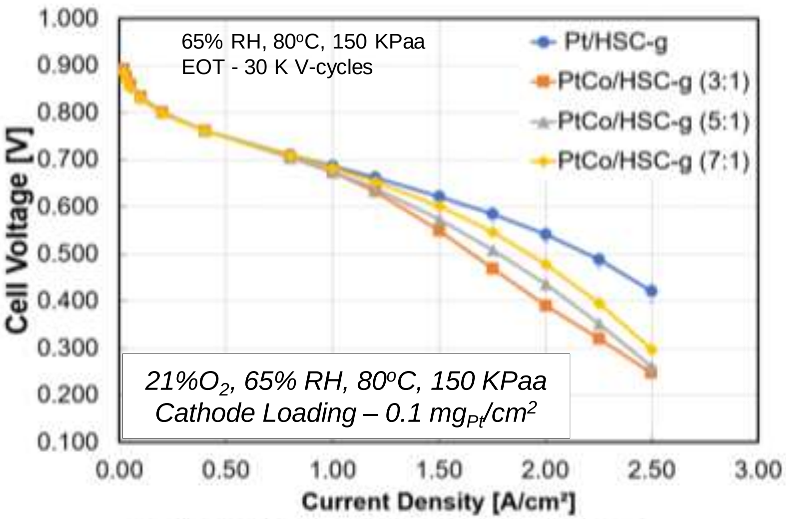
- PtCo/HSC a shows significant cell voltage losses compared to Pt/HSC a of similar particle size, specifically at > 1.5 A/cm^2.
- Similar ECSA losses between Pt/HSC a and PtCo/HSC a, indicates Co dissolution does not indicate a measurable increase in Pt dissolution and Pt particle size growth.
- Specific activity (SA) remains stable for Pt/HSC a, as all Pt catalyst, SA increases with increase in particle size. SA decrease for PtCo, likely from Co dissolution.

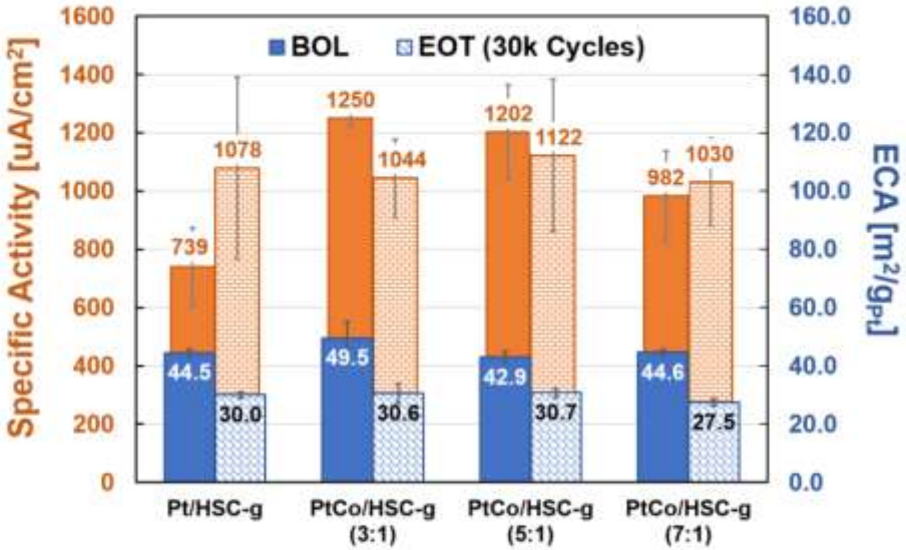
Technical Accomplishment:

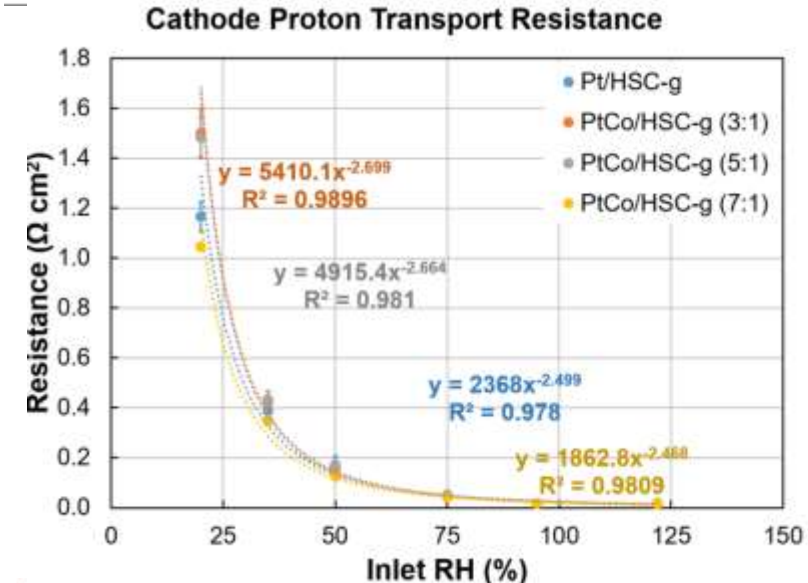
Task 3. Stability of PtCo Nanoparticle.

Impact of dissolved Co on Electrode Performance

0.60 to 0.95 V, 80 °C, 100% RH
30k AST cycles, TZW waveform
5 cm^2 CCM MEA – Differential Cell Cond.





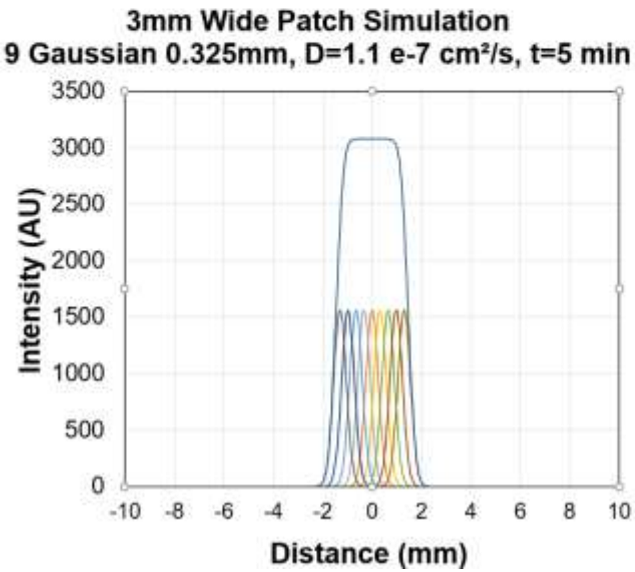


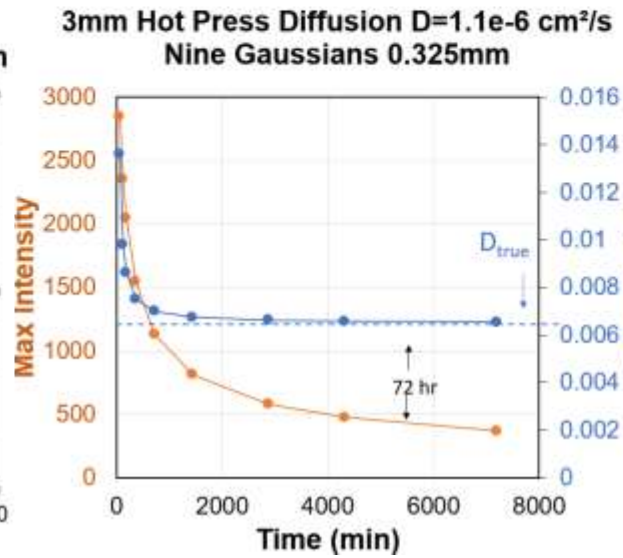
- Separate study with PtCo/HSC g catalysts at different Pt:Co (3:1, 5:1, 7:1) demonstrate a similar trend.
- After 30 K V cycles, increasing cell voltage loss with increase in Co content observed.
- Comparable ECA and specific activity at EOT indicate potential V_{Loss} at high current could be due to transport losses created by dissolved Co^{2+}
- Marginal increase in bulk proton transport resistance observed for Pt:Co, (3:1) and 5:1 samples.

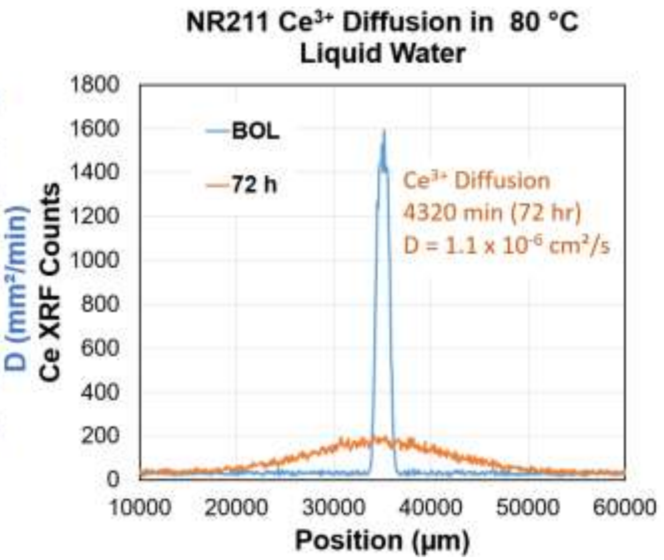
Technical Accomplishment:

Ce Transport Measurement

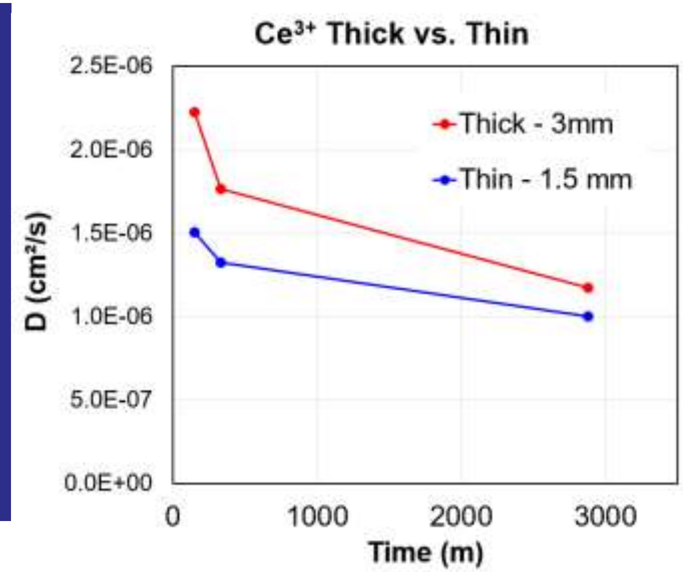
Improved Diffusion Coefficient Measurement and Fidelity







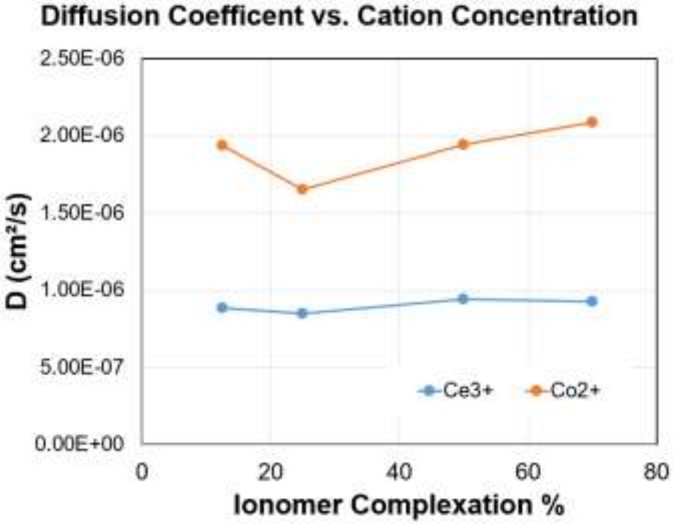
- Factor impacting diffusion measurements were identified and improved to achieve accurate measurements.
- Non delta function t=0 cation deposits simulated by summed gaussians
- True diffusion coefficients can be extracted using simple 1 d diffusion model with long diffusion times
- Long diffusion time employed to determine accurate diffusion coefficients of cations in NRE 211
- Thin t=0 cation deposits produce more accurate diffusion at all diffusion times.

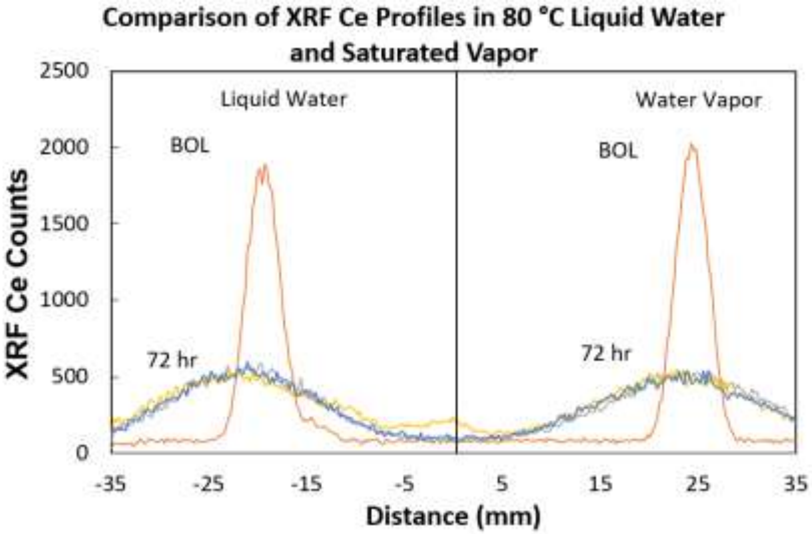


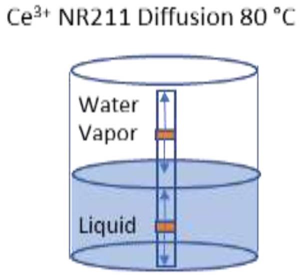
Technical Accomplishment:

Ce Transport Measurement

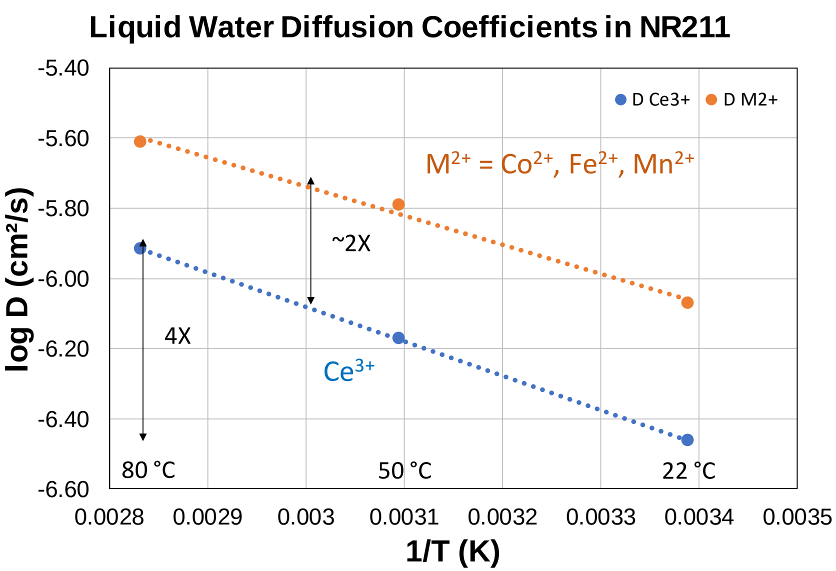
Improved Diffusion Coefficient Measurement and Fidelity





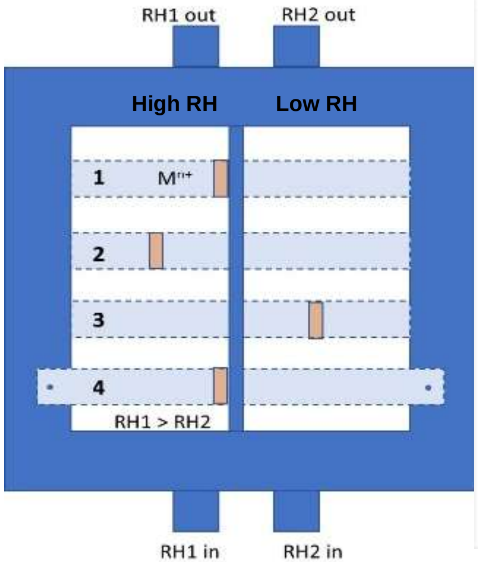


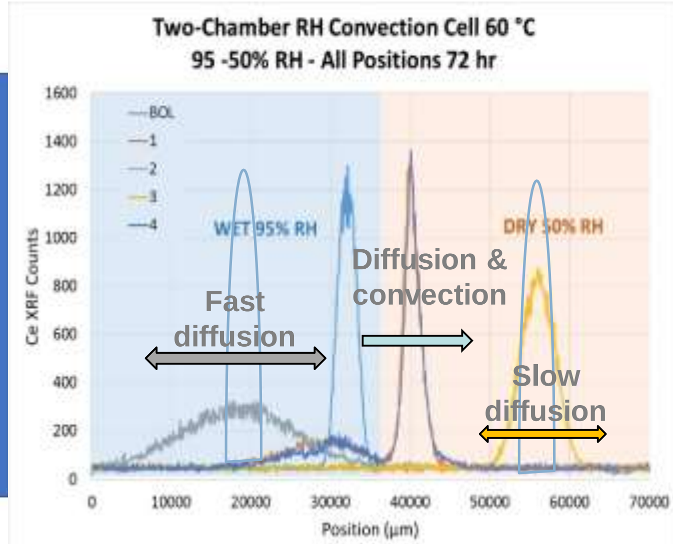
- Diffusion coefficients independent of initial cation concentration (80ºC, liquid water).
- Ce^{3+} deposits in NR211 produce identical diffusion coefficients at 80ºC, whether submerged in liquid water or with in saturated water vapor.
- Transition metal di cations have very similar diffusion coefficients that are consistently two time greater than Ce $^{3+}$.
- Fidelity of diffusion coefficient measurements significantly improved and can be utilized for Ce transport models.

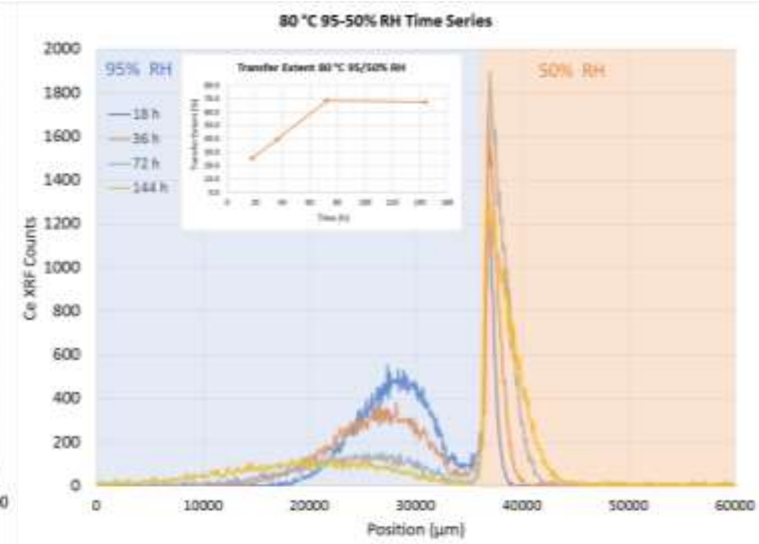


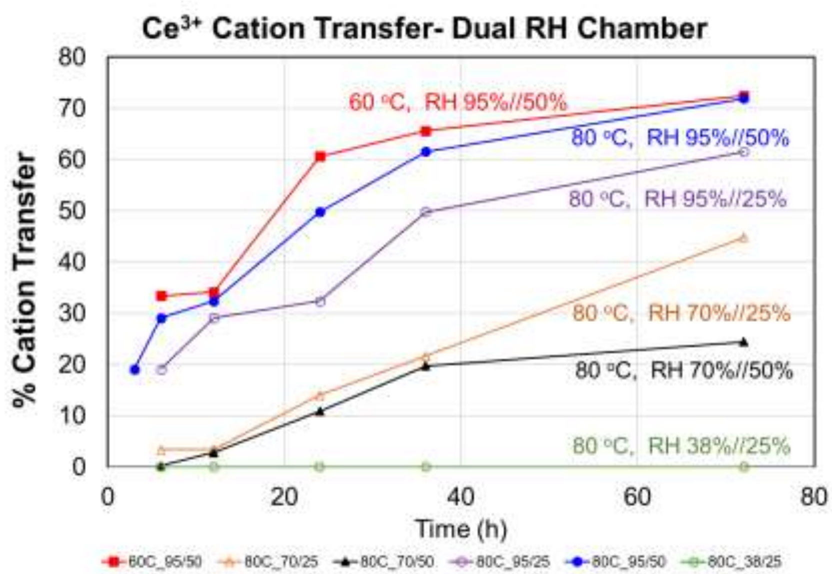
Technical Accomplishment:

Ce Transport Measurement









- Transfer of Ce^{3+} deposits from the wet to low RH chamber is governed largely by the RH value in the high RH chamber
- Transfer % are greatest when RH1=95% as this produces movement toward the dry chamber and independent on RH2 level (RH gradient)
- The transferred cation deposits are "trapped" in low RH chamber as mobility decreases
- As RH1 value decreases (70%) transfer extent decreases and may be affected by gradient
- Transfer is effectively arrested at RH1=37.5%

Technical Accomplishment:

Ce Transport Model

1-D Transient Model

(Conservation of Ce)

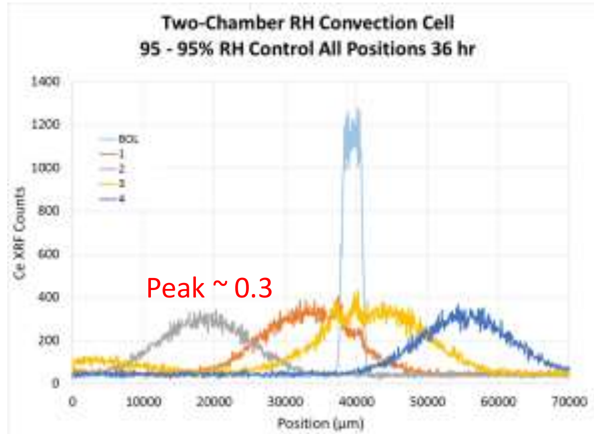
$$\frac{dc}{dt} + \nabla \cdot j = 0,$$

$$j = -D\nabla c + \mathbf{v}\cdot c - uc\nabla\phi$$

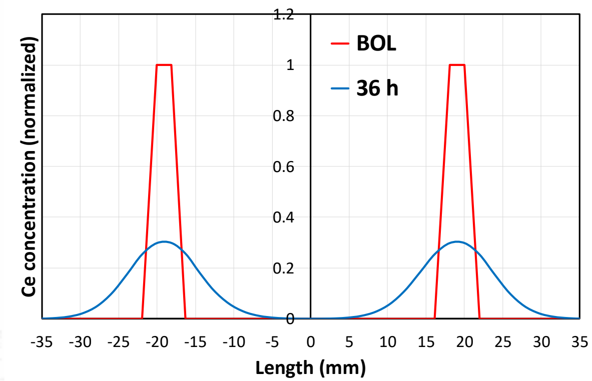
Diffusion Convection Migration

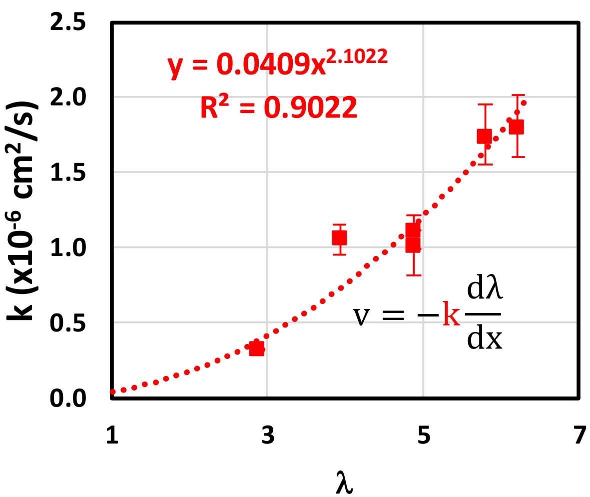
$$\mathbf{v} = -k\nabla\lambda$$

Diffusion Only // 95% RH – 95% RH // Good Agreement

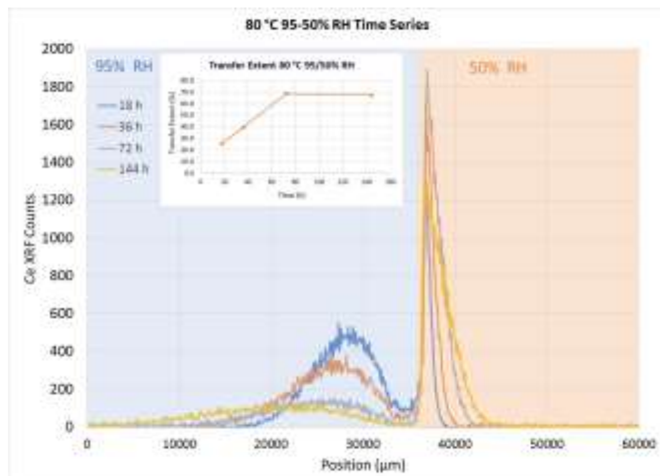


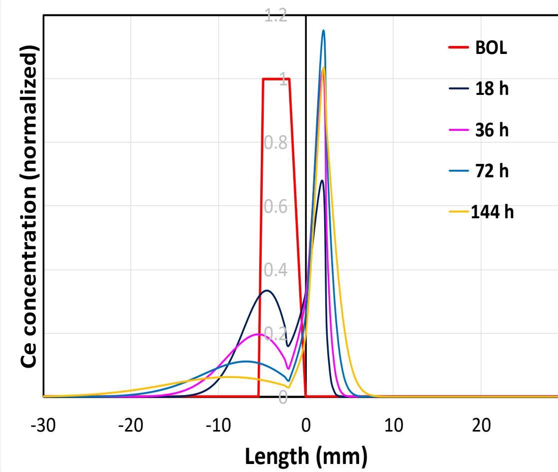
Modeled with the measured Ce diffusivity





Diffusion& Convection // 95% RH – 50% RH // Good Agreement

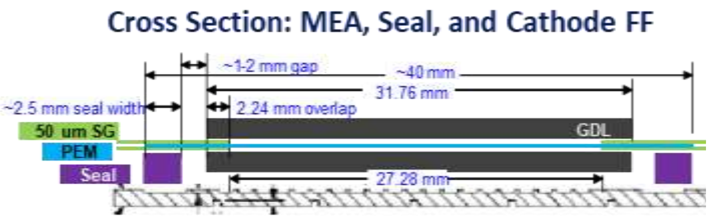




- Convection Coefficient k, dependent on membrane water content , is used to simulate Ce migration over large area
- Good agreement with data for both cases

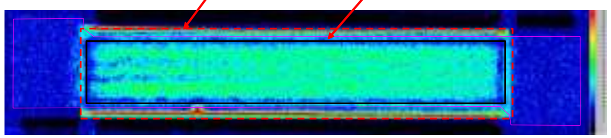
Technical Accomplishment:

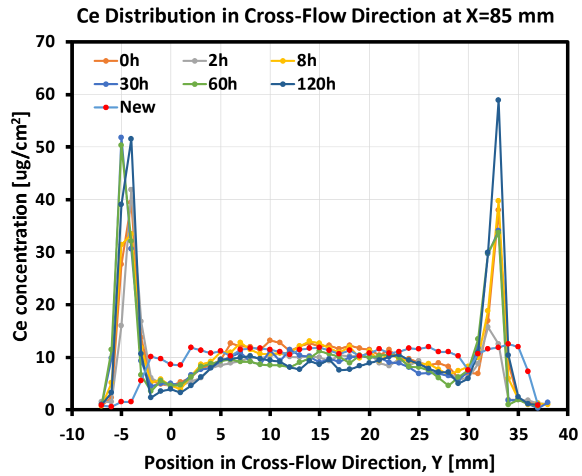
Ce Transport Model (DOE 50 cm² Segmented Cell*)

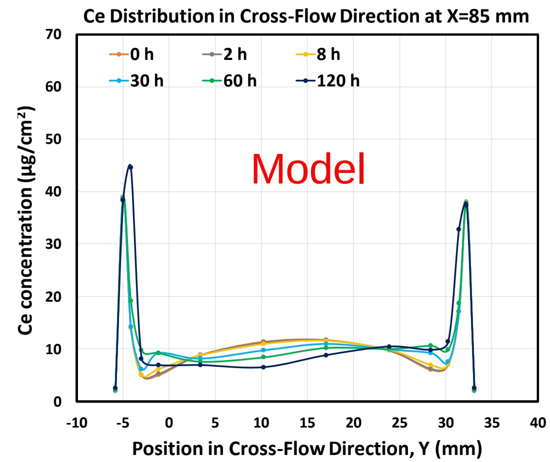


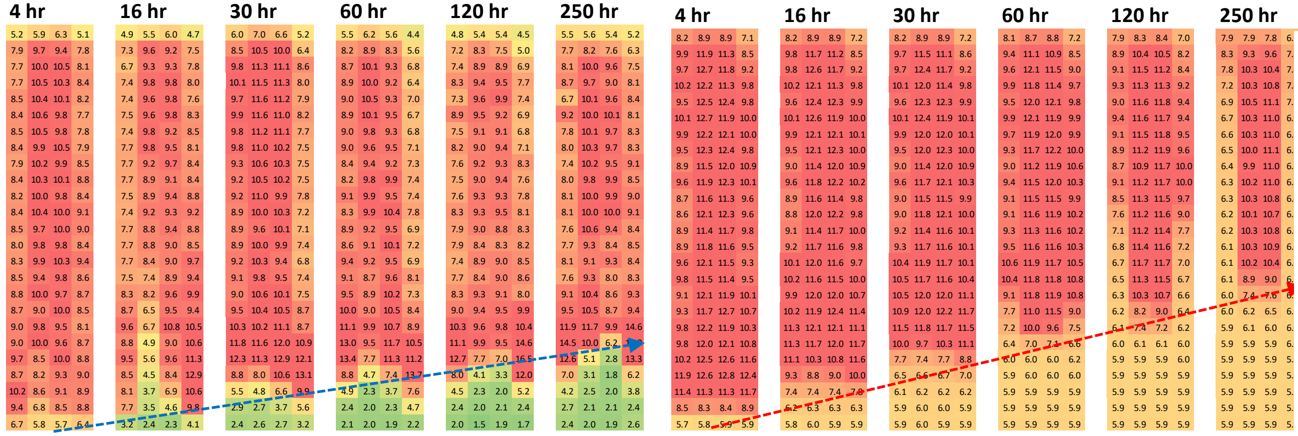
Membrane
(39.76x189 mm2)

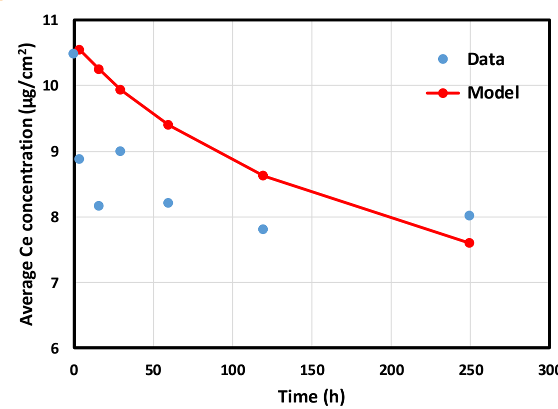
AA
(27.28x183 mm²)











- Qualitative agreement between the distributed cell measurement and model observed.
- Key trends like Ce depletion at the cathode out where RH cycling is dominant is noted. Area under Ce depletion also increases with time.
- Accumulation of Ce in the non active region observed experimentally and is captured in the model assuming no water uptake.

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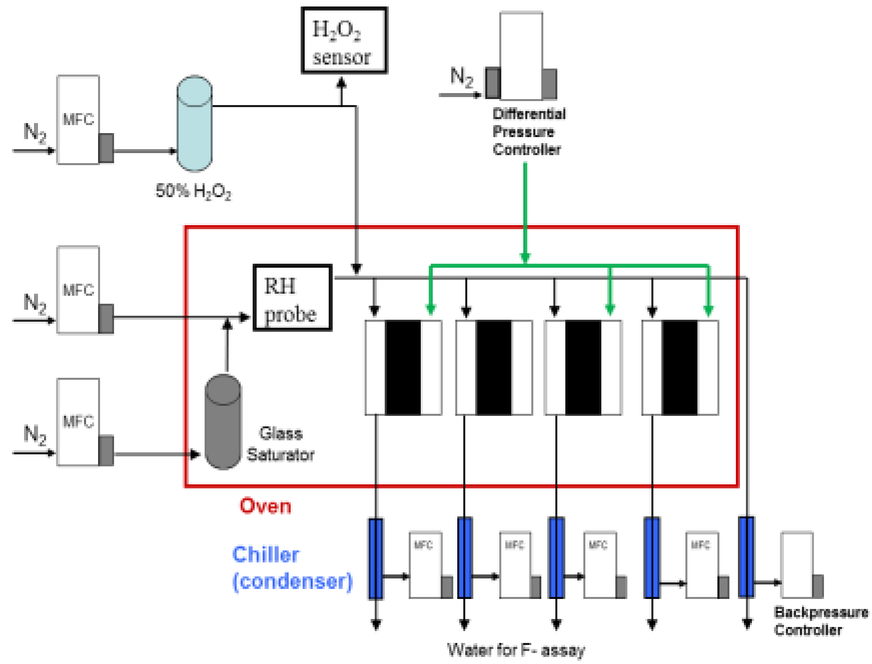
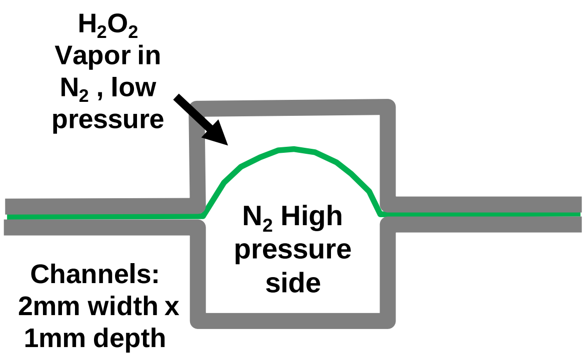
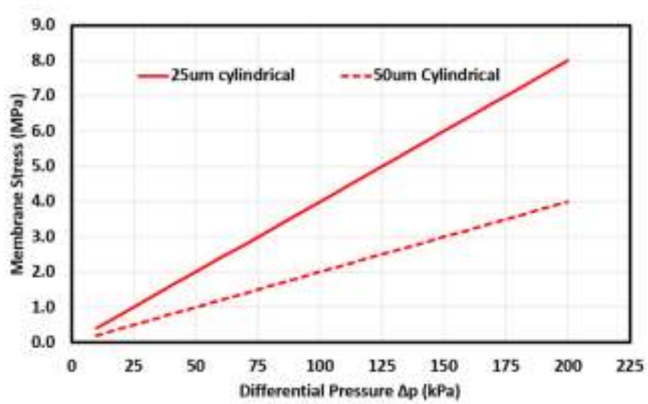
Technical Accomplishment:

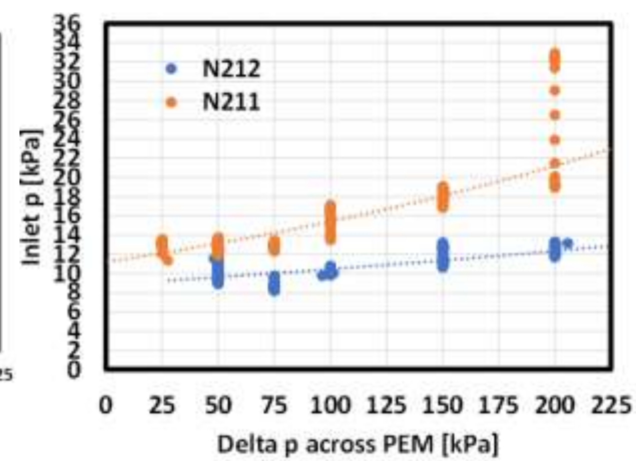
Impact of Mechanical Stress on Chemical Degradation

- Ce doped membrane show increased degradation at high mechanical stress region (cathode outlet), coupled with Ce depletion.*
- Ce-free membrane exhibit higher X-over, but no change in Mw, thickness etc at cathode outlet**.
- To understand impact of mechanical stress on chemical degradation, the H_2O_2 vapor cell test set up at Giner was used to assess chemical degradation at higher mechanical stress created by differential pressure.







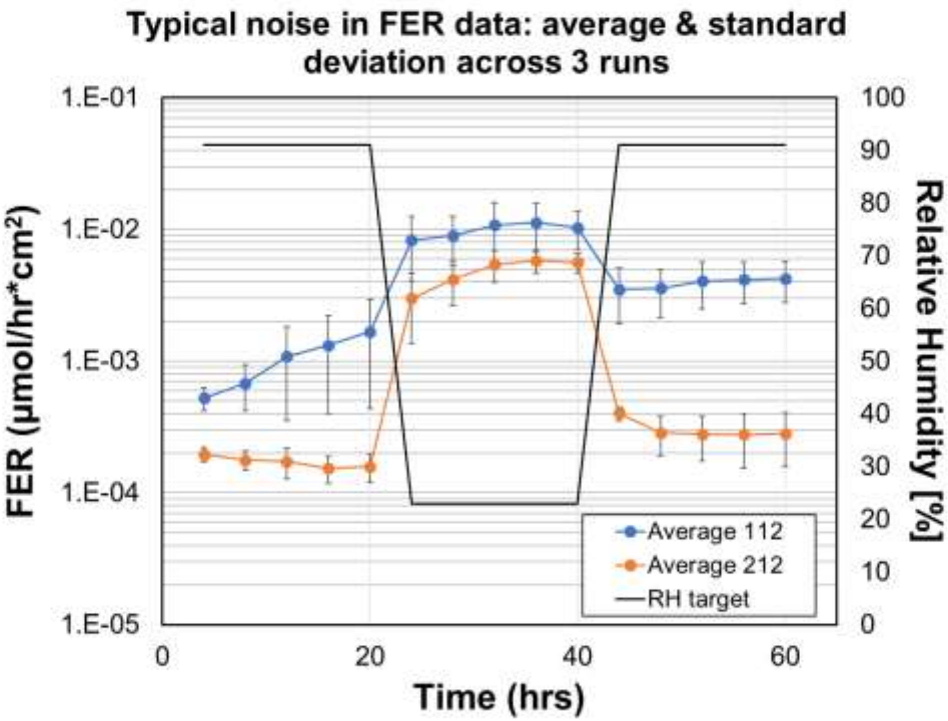


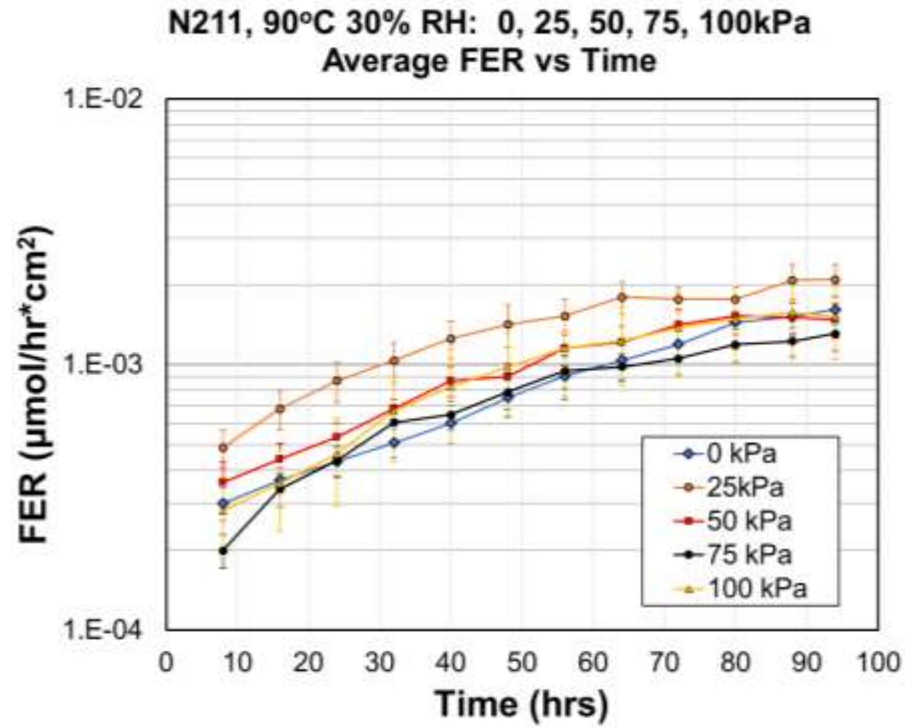
Journal of The Electrochemical Society*, **165 (6) F3217-F3229 (2018)

*** S. Kumaraguru, FC156 2019 AMR slides*

Technical Accomplishment:

Impact of Mechanical Stress on Chemical Degradation





- Relatively low noise in constant RH tests compared to the traditional wet/dry/wet baseline.
- Excluding the 25 kPa test, FRR results for tests with increasing ΔP are mostly within one standard deviation of each other.
- The preliminary results so far indicate no correlation between mechanical stress and fluoride release rate (FRR).
- Plan is to repeat tests with the SOA membrane.

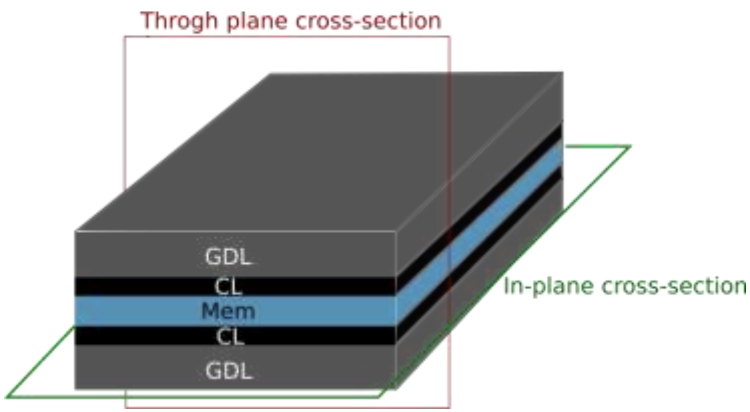
Journal of The Electrochemical Society, **165** (6) F3217-F3229 (2018)

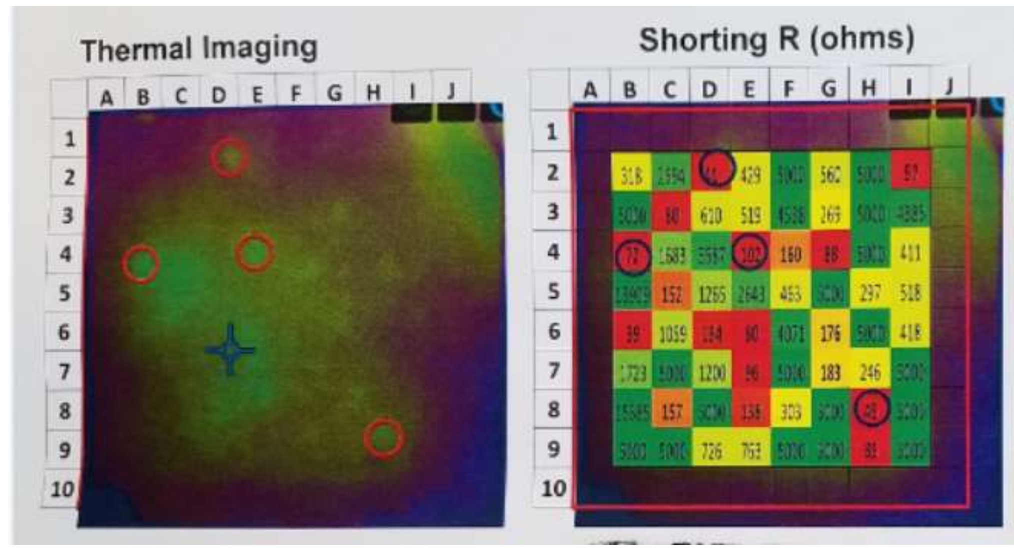
Technical Accomplishment:

Task 5.3: Impact of Local Shorting on Membrane Degradation

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

- Pre-shorted MEAs sent to LBNL





- Each location (circled) was divided in 6 segments and each segment was imaged separately

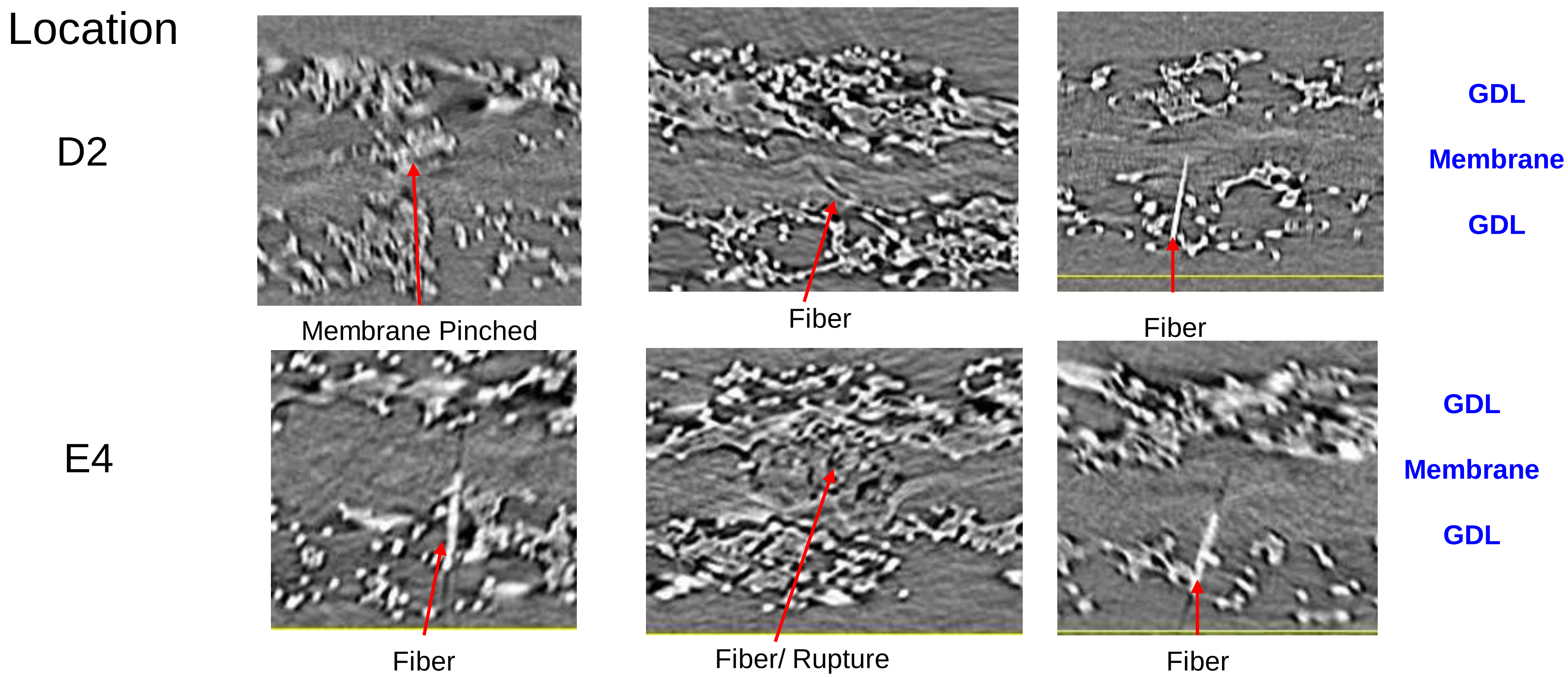
- **Imaging conditions:**
  - 25 keV monochromatic light, 700ms exposure time, 5x zoom objective
  - Resolution for 5x objective- 1.3µm/pixel

- **Image processing nomenclature**
  - Through plane images are useful for assessing the propagation depth of cracks/pinholes
  - In-plane images are useful to see the shape of cracks

Lalit Pant and Ahmet Kusoglu

Technical Accomplishment:

Task 5.3: Impact of Local Shorting on Membrane Degradation



- Visual demonstration (non destructive method) of membrane shorting created by GDL fibers piercing through the membrane.
- Very difficult technique, resistance does not always correlate with shorting points. In few cases a single prominent short can be created via shorting with a fiber. In others multiple shorting points noted, but resistance remain high.
- Next ambitious step is to re image the same location after subjecting the part to chemical degradation test.

Lalit Pant and Ahmet Kusoglu

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. Predict MEA life.
- Lawrence Berkeley National Lab (Dr. Adam Weber and Dr. Ahmet Kusoglu))
  - Advanced characterization X-ray CT, GI-SAXS
- Los Alamos National Lab (Dr. Mukund Rangachary and Dr. Rod Borup)
  - Accelerated stress tests (TBD)
- 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)
  - Identical location TEM, PSD measurements
- Giner (Dr. Cortney Mittelsteadt) (Industry)
  - Membrane degradation studies

Responses to Last Year AMR Reviewers' Comments

- *"Design of Expt (DoE) approach makes it difficult to assess emerging trends".*
  - ❑ Agree, but DoE approach is needed to look at multifactor interactions. Single factors while being easy to interpret tend to overlook the interactions. Full factorial design are out of scope for any team"
- *"RH trends and Models aren't new"*
  - ❑ "Good thing is some single factor studies exist. But this data was never complete, especially for PtCo alloy materials as well as interaction effects of operating conditions. We are focused on addressing gaps, mapping out relationship between durability and operating conditions. Same with model, we are utilizing and supporting ANL's models and focusing on gaps like Ce transport models etc"
- *"The project team should look at different carbons—for example, high surface-area carbon versus Vulcan®—as porosity can affect particle sintering and dissolution"*
  - ❑ In BP1, we have already shown that Vulcan is not the best candidate for both activity and durability. Especially for alloy catalysts Vulcan is not a good candidate. Some of these studies were also done in GM's other project FC144"
- *"It is unclear whether degradation modes and benign operating conditions identified for this best performance GM proprietary MEAs will be transferable".*
  - ❑ These are representative state of art materials and we believe the underlying physics and fundamental trends will translate very well. Again the core objective of the project is to demonstrate that we can prolong the life of the MEA by using operating conditions as the key differentiator. Especially, with heavy duty trucks durability requirements being 3X- 5X, these studies help us to assess the feasibility of design and operation that can meet such requirements.
  - ❑ BP1 work clearly indicate the type of materials used in this project and the design of the MEA as well as why we chose these to make the SOA MEA.

Future Work

- Continue degradation studies with PtCo and Pt to understand impact of dissolved Co^{2+}.
- Conduct H_2-N_2 vs. H_2- Air Voltage cycling tests.
  - Quantify differences (if any) in ECA_{Loss} and V_{Loss}
- Continue refinement of ANL's predictive degradation model.
- Model verification followed by demonstration of durability improvement in DOE durability protocol.
- Update Ce transport model to quantitatively match Ce profiles.
- Impact of membrane thickness and reactant partial pressure on chemical degradation.
- 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.
  - 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.
  - Highly accelerated stress test for chemical and mechanical degradation developed.
- In BP2, the SOA MEA was subjected to H_2-N_2 voltage cycling tests across various operating conditions. Both multi factor DOE and single factor DOE conducted.
  - Certain conditions like low RH (25%) operation demonstrate 100% reduction in ECA loss.
  - Operation conditions that can provide > 35% reduction in ECA loss demonstrated.
  - Ce diffusivity and convective measurements were performed.
- In BP3, operating conditions that would prolong electrode life were identified.
  - Single and multifactor design of experiments were used to map the impact of operating conditions were completed. Statistical model was developed and predictive equations for ECA and voltage loss was created.
  - ANL's predictive model was refined with H_2-N_2 V-cycle data. Operating conditions that can prolong electrode durability to 5000h and 8000 h was identified. The baseline durability hours being < 2000 h. 4X improvement in electrode durability possible.
  - Detailed nanoparticle characterization (UT Austin) and Pt vs. PtCo studies were performed to understand PtCo degradation.
  - Ce diffusivity and convective measurement methods were refined to improve fidelity of estimated parameters. Ce transport model was developed and the Ce distribution pattern in DOE single cell was demonstrated.
  - Modified vapor cell test with pressure gradient was used to study impact of mechanical stress.
  - X-ray CT measurements at LBNL was used to visualize shorts.

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