Durable High Power Membrane Electrode Assembly with Low Pt 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: 31st April 2020
- Percent complete: <55%

Budget

- Total Project Budget: $ 3,201,476
- Total Recipient Share: $ 640,295 (20%)
- Total Federal Share: $ 2,561,181
- Total Funds Spent*: $962,174
    - $769,739 (Fed Share)
    - $192,435 (Cost Share)

**as of 12/31/2018*

Barriers

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

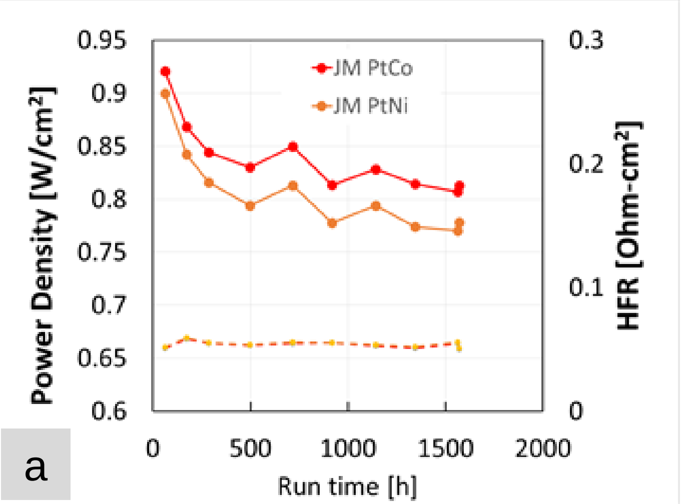
Partners

- Subcontractors:
    - 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



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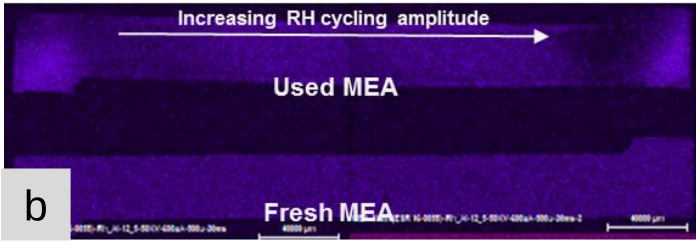
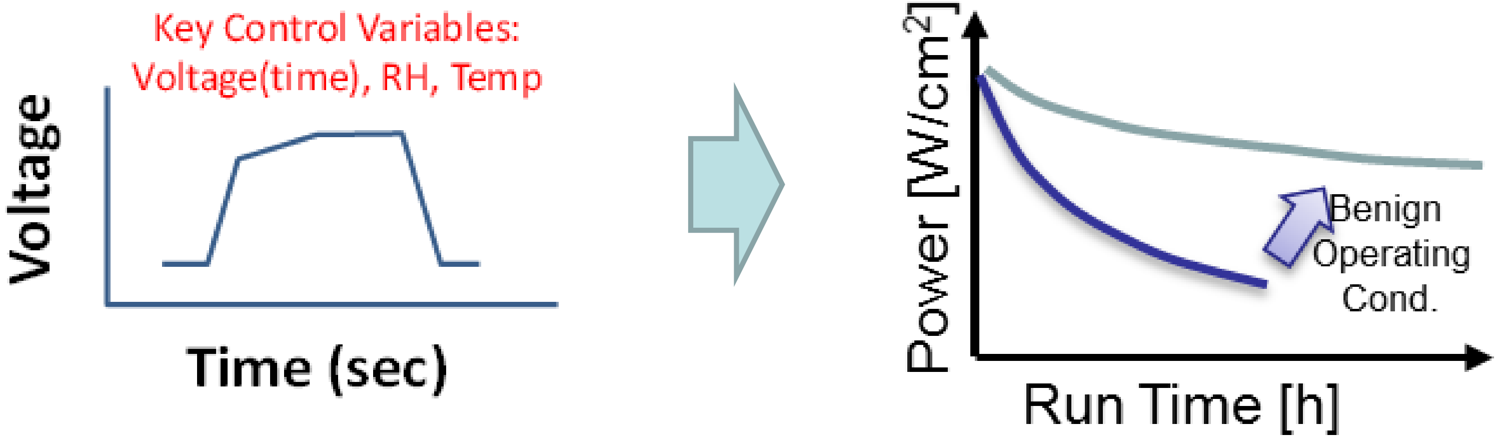


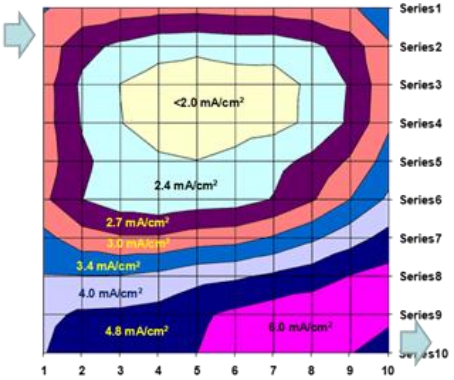
Objectives

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

Approach



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



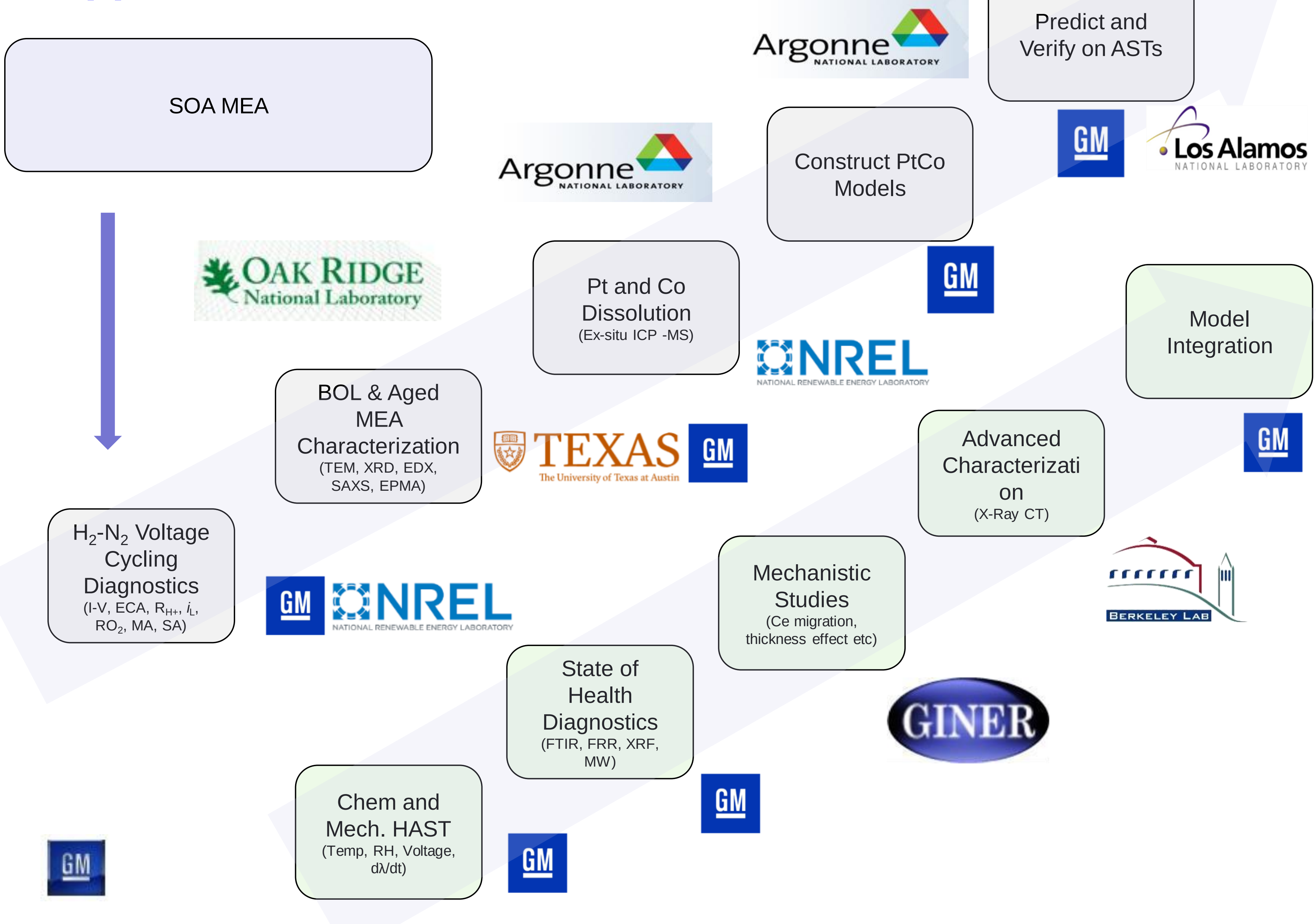
Combined Chem. and Mech. stress segmented cell test

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)

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

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

BOL & Aged MEA Characterization
(TEM, XRD, EDX, SAXS, EPMA)

Pt and Co Dissolution
(Ex-situ ICP -MS)

Mechanistic Studies
(Ce migration, thickness effect etc)

Advanced Characterization
(X-Ray CT)

Construct PtCo Models

Model Integration

Predict and Verify on ASTs

Approach/ Milestones and Go/No Go

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

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

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

Budget Period 2 Task: Durability Studies of SOA MEA

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

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

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

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

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

Milestones and Go/No Go

Budget Period 1 Task : Durability of SOA MEAs

Go/No Go: Demonstrate >35% reduction in ECSA, SA and voltage degradation SOA MEA.

Milestone Summary Table

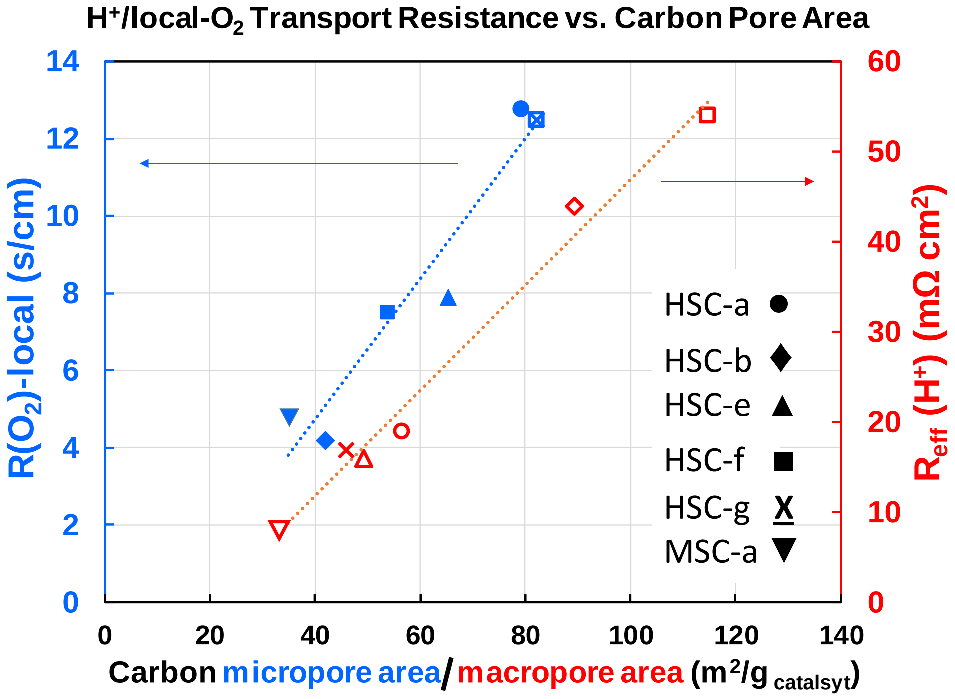
Task Number	Task Title	Milestone Type	Milestone Number*	Milestone Description (Go/No-Go Decision Criteria)	Quarter	Progress
2.1 3.1	H_2-N_2, H_2-air voltage cycling tests at diff op. conditions Multiscale microscopy of SOA MEA at BOT, including PSD, STEM, EDS and X-ray CT.	Milestone	M2.1	Summary of VC design combinations and expected outcome using statistical approach Report on PSDs, chemical composition etc on BOT MEAs	Q5	75 25
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	10 65
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	20 65
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	60 60 80
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**	**Q8**	**60**
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.	Q9	10
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	Q10	15
4.5	Electrode Decay Model Validation	Milestone	M3.3	Validate decay model with data from task 2 and 3	Q12	15
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**	**Q12**	**12**

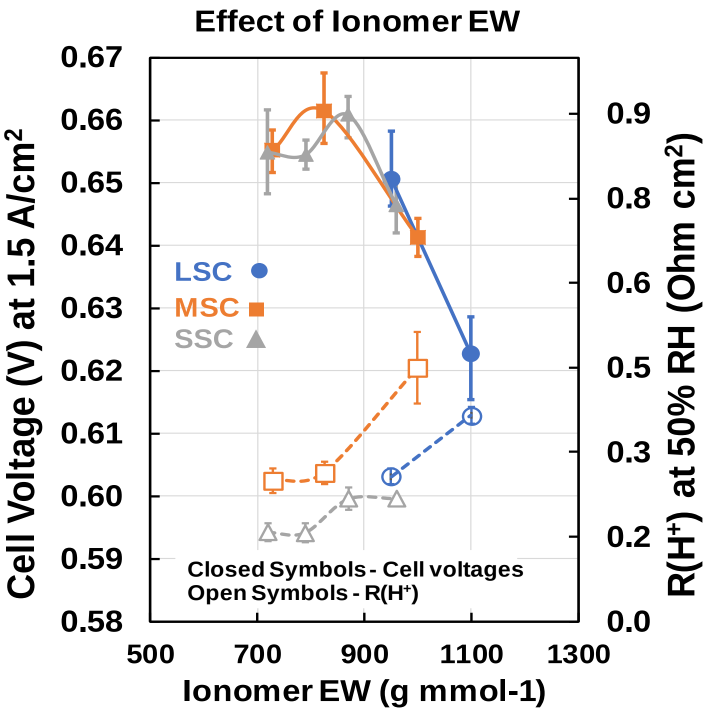
[a] Mass activity tested under DOE - specified condition

[b] Measured under anode/cathode: H_2/air, 94^{o}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:

Budget Period 1 - Recap





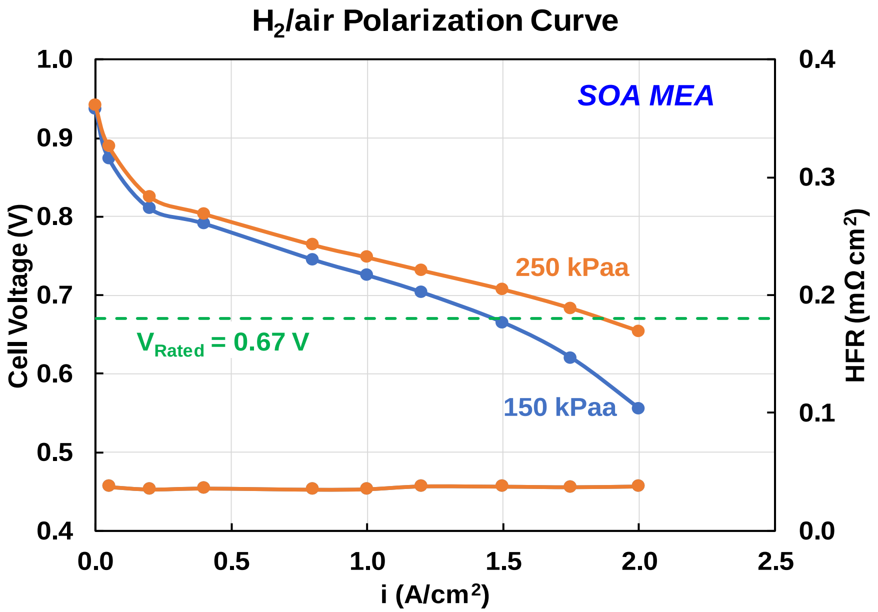
- Catalysts, ionomers and membranes were down selected to generate SOA MEA (≥1000 mW/cm^2).
- Catalyst studies indicate correlation between micropore surface area on local oxygen transport resistance and macropore surface area on proton transport resistance.
- Ionomer equivalent weight (EW) was found to be the most important property affecting performance.
- Reinforced PFSA membrane with Ce^{3+} mitigation is the most durable membrane.
- Accelerated chemical and mechanical stress test for membrane degradation.

SOA MEA	
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 Electrode	10% Pt/C, 0.025 mg$_{Pt}$/cm^2 0.6 I/C (EW900)
GDL thickness	235 µm

Technical Accomplishment:

Target and Status

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



Active Area: 50 cm^2, CCM MEA

H_2/air, 80 °C, 100% RH, Stoic: 1.5/2.0, 150 Kpaa

H_2/air, 93.5 °C, 65% RH, Stoic: 1.5/2.0, 250 Kpaa

In this Budget Period (BP2)

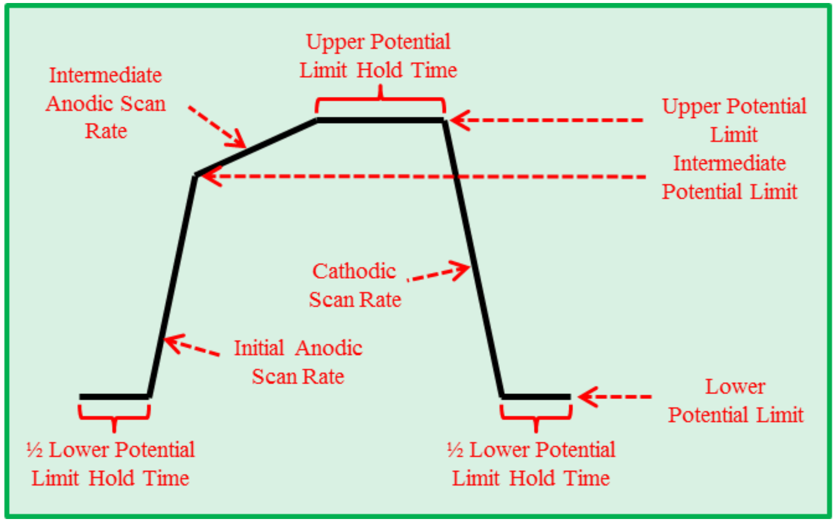
- SOA MEAs developed in BP1, was verified in 3 different platforms (5cm^2 differential, 10 cm^2 common hardware and 50 cm^2) in both GM and NREL.
- H_2-N_2 Voltage cycling tests at various operating conditions were conducted on SOA MEA.
- Membrane durability studies were conducted to understand Ce migration,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

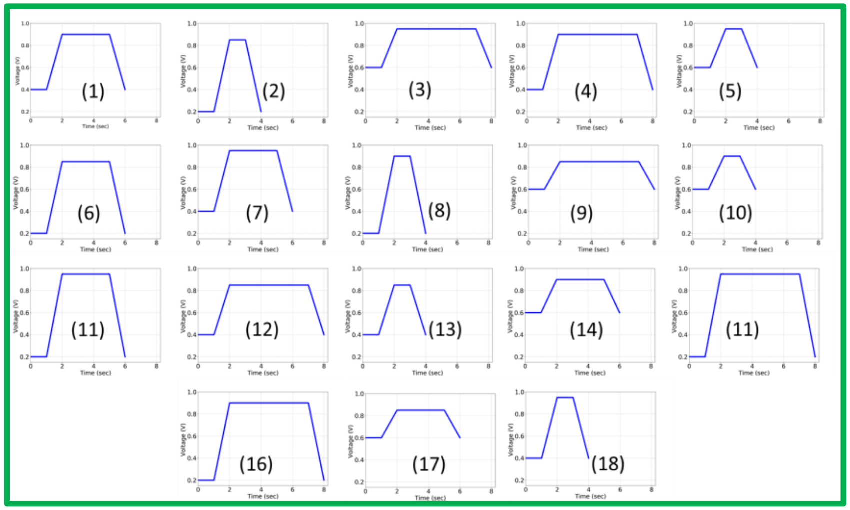
Go No Go

- > 35% reduction in ECA loss demonstrated by changing operating condition. Example, 50% 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.

Task 2. 1 H_2-N_2 Voltage Cycling of SOA MEA

Impact of Operating Conditions





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

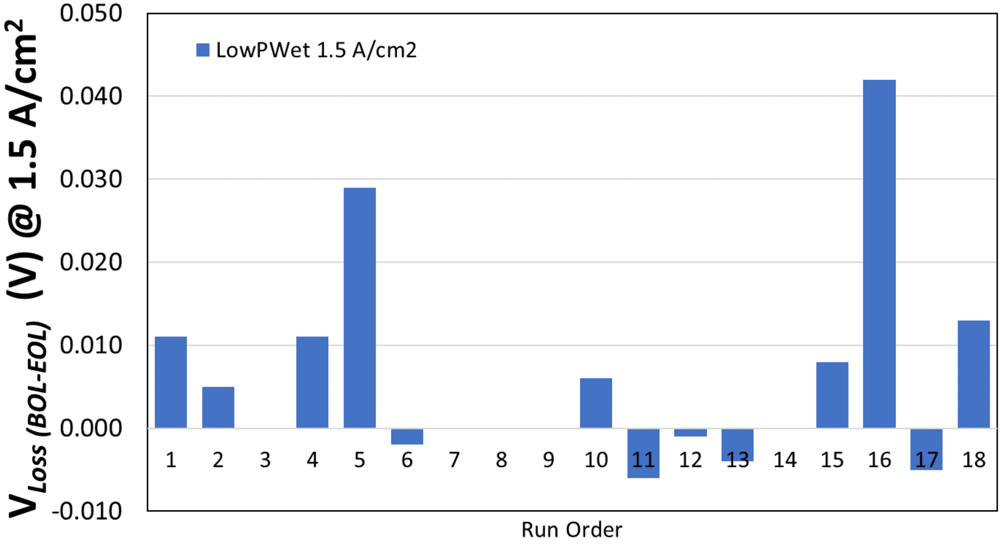
- Significant amount of time was spent in getting the test stands automated to run these durability tests.
- Exploring initial design of experiments focused on temp, RH, lower and upper potential limit, upper potential hold time.
- Design of experiment approach was utilized (18 runs). Highly fractionated DOE ($3^5 6^1$). Will run another 18 run as needed to estimate 2 factor interactions.
- Diagnostics include, polarization curves, limiting currents, H_2-N_2 impedance etc.

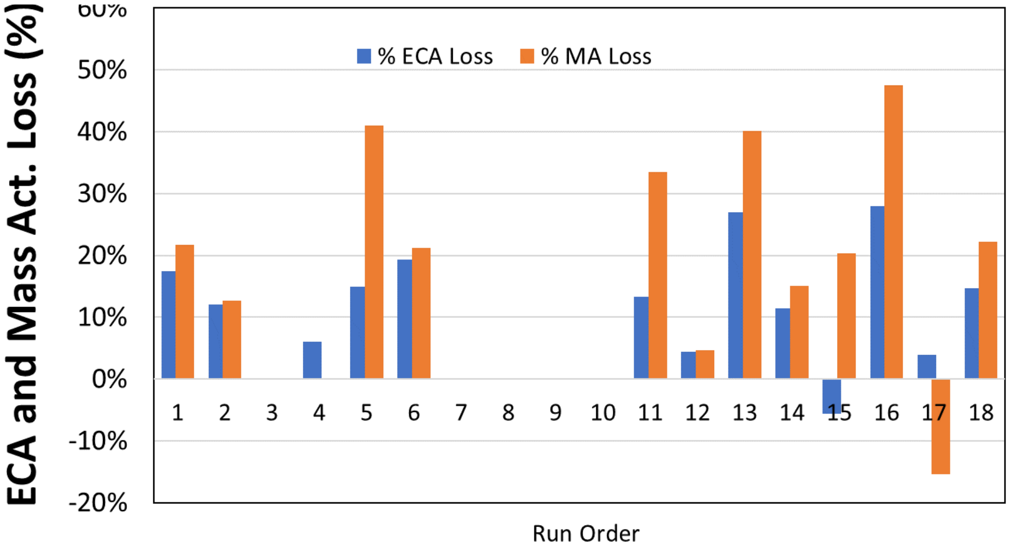
Technical Accomplishment:

Task 2. 1 H_2-N_2 Voltage Cycling of SOA MEA

Impact of Operating Conditions

5 cm^2 CCM MEA. Differential Conditions





S.No	Cell Temp (°C)	RH (%)	Upper potential (mV)	upper potential hold time (s)	Lower Potential (mV)	Scan Rate (mV/s)
1	75	70	900	3	400	500
2	55	40	850	1	200	650
3	95	100	950	5	600	350
4	55	40	900	5	400	500
5	75	70	950	1	600	350
6	95	100	850	3	200	650
7	95	40	950	3	400	550
8	75	100	900	1	200	700
9	55	70	850	5	600	250
10	95	40	900	1	600	300
11	55	70	950	3	200	750
12	75	100	850	5	400	450
13	95	70	850	1	400	450
14	55	100	900	3	600	300
15	75	40	950	5	200	750
16	95	70	900	5	200	700
17	75	40	850	3	600	250
18	55	100	950	1	400	550

- The 18 run DOE is currently in progress.
- Performance loss as high as 40 mV@ 1.5 A/cm^2 and almost 50% mass activity loss is observed for certain operating conditions.
- Few cases exhibit almost zero performance and activity loss

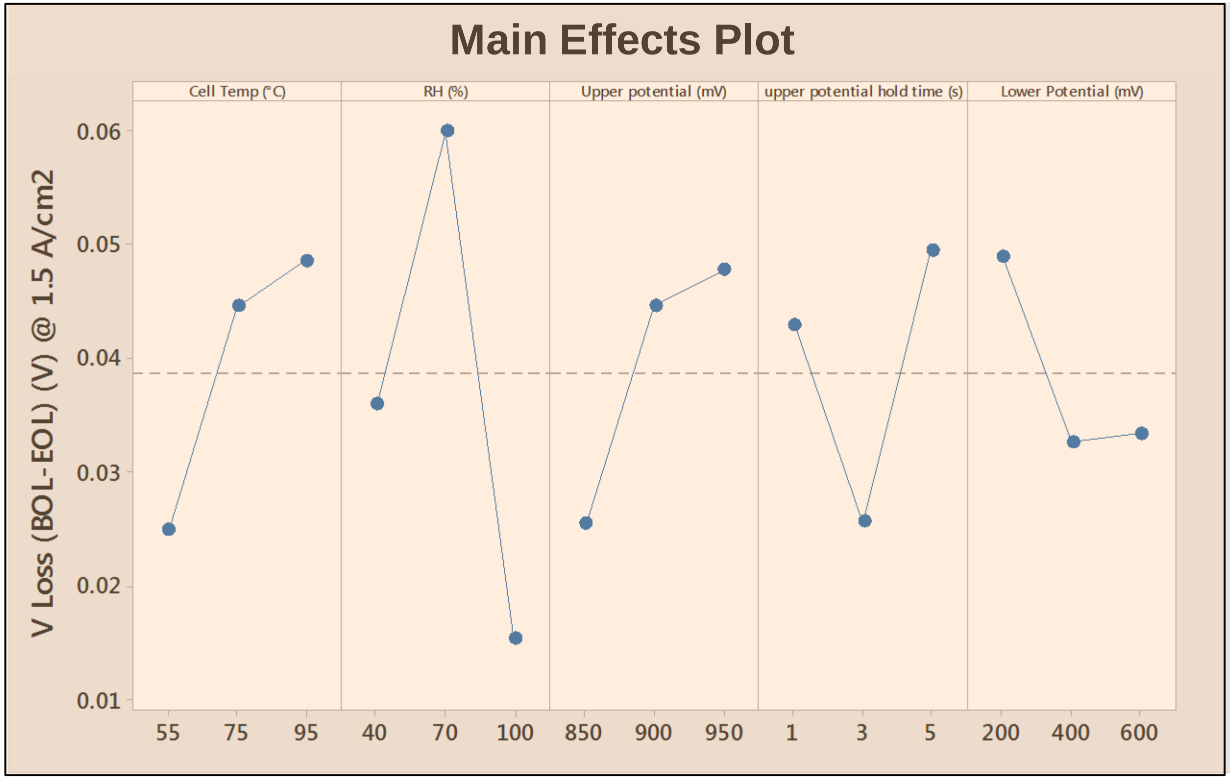
Disclaimer: Since all cells in this highly fractionated design of experiment (DOE) is not complete. The final interpretation of the data can change significantly.

Technical Accomplishment:

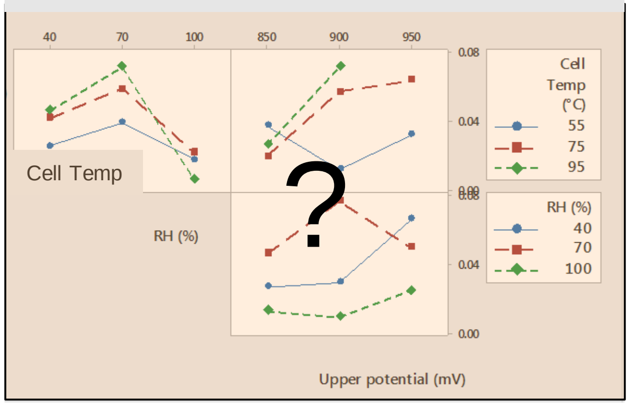
Task 2. 1 H_2-N_2 Voltage Cycling of SOA MEA

Impact of Operating Conditions

5 cm^2 CCM MEA. Differential Conditions



Interaction Plot



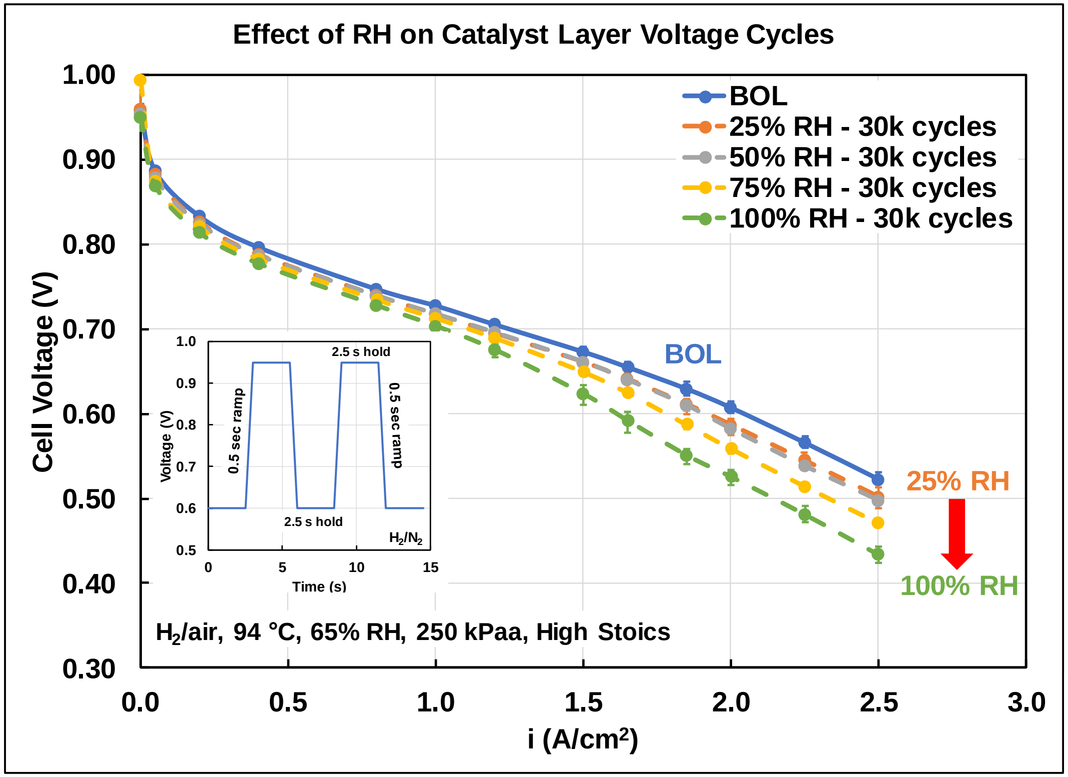
2 factor interactions are needed to map the design space that would minimize the ECA and specific activity degradation

- The initial 18 run DOE, once complete will provide the main effects of each factor. Though difficult, some 2 factor interactions can also be extracted.
- If 2 factor interactions can not be resolved. We will run an additional 18 run DOE to obtain the needed resolution.

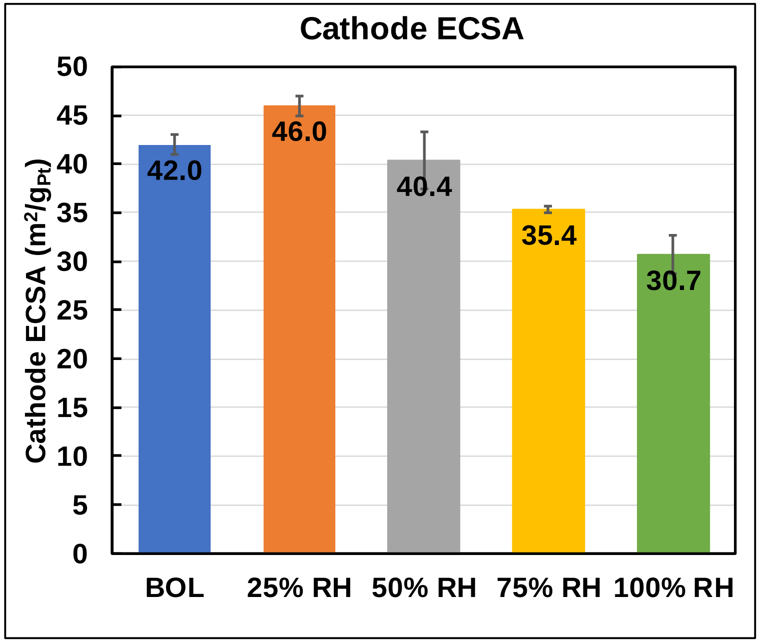
Disclaimer: Since all cells in this highly fractionated design of experiment (DOE) is not complete. The final interpretation of the data can change significantly. This slide is only to provide an image of the output.

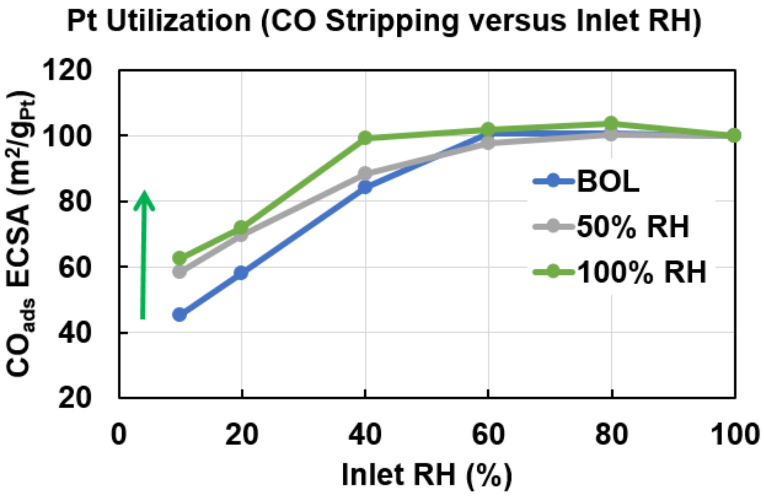
Task 2. 1 H_2-N_2 Voltage Cycling of SOA MEA

Single Factor Studies - Effect of RH



5 cm² CCM MEA (3 repeats). Differential Conditions

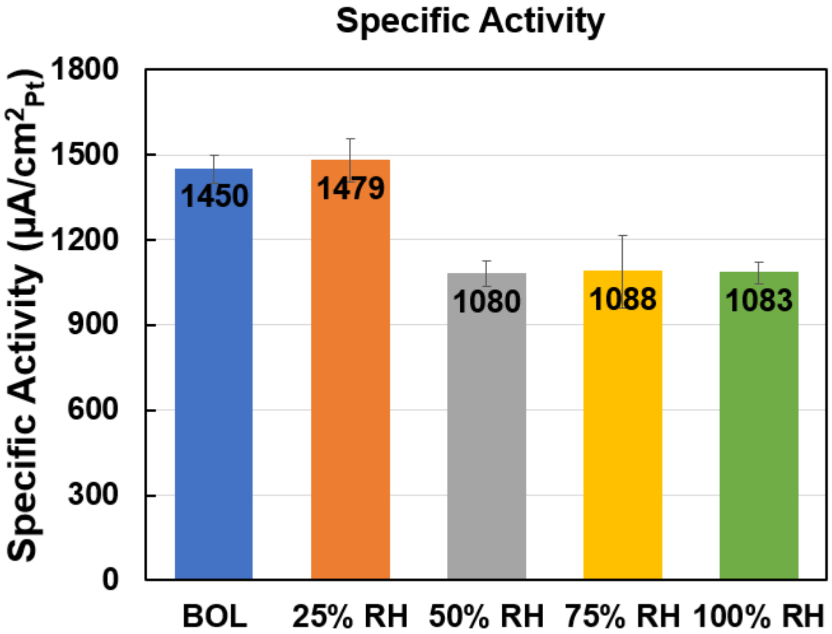




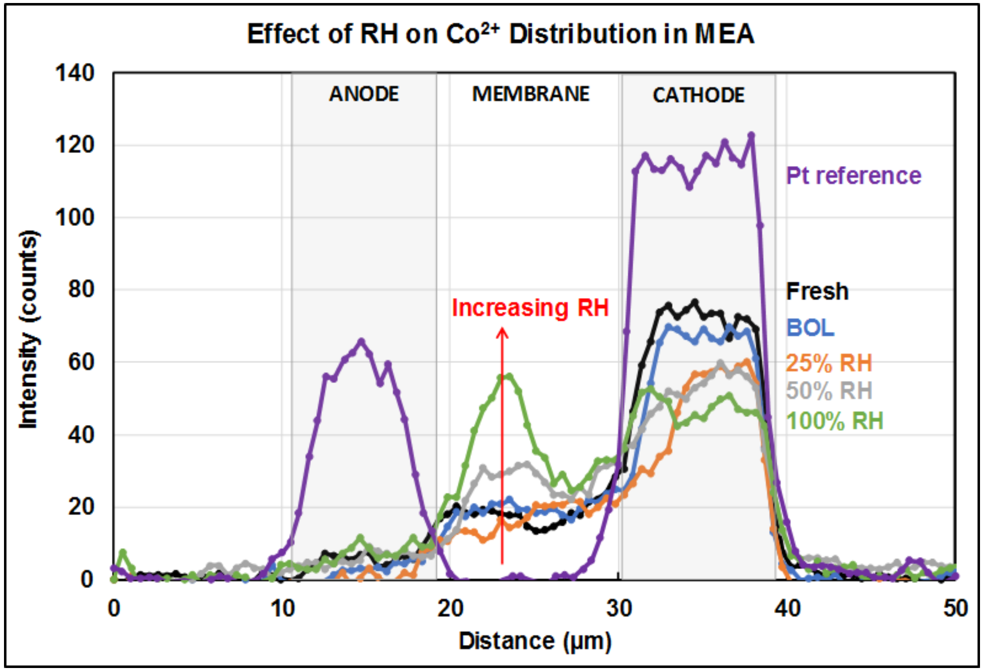
- Few single factor studies such as effect of RH was conducted.
- RH has a very strong effect on both ECSA degradation and corresponding H_2-air performance
- Wetter conditions exhibit higher electrode degradation compared to drier condition.
- Pt utilization inside pores increase with degradation.

Task 2. 1 H_2-N_2 Voltage Cycling of SOA MEA

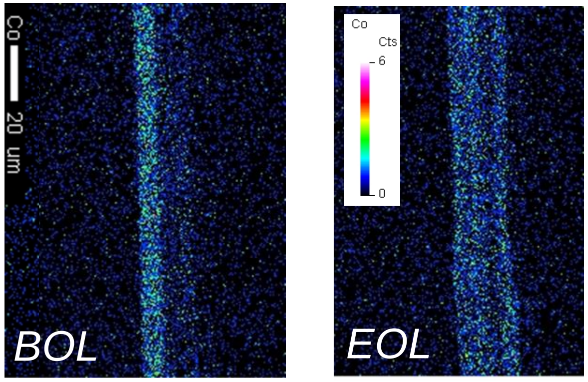
Single Factor Studies - Effect of RH



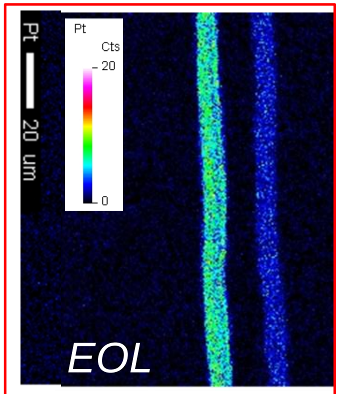
5 cm² CCM MEA (3 repeats). Differential Conditions



- 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



Co *EOL – 30 K 100% RH*

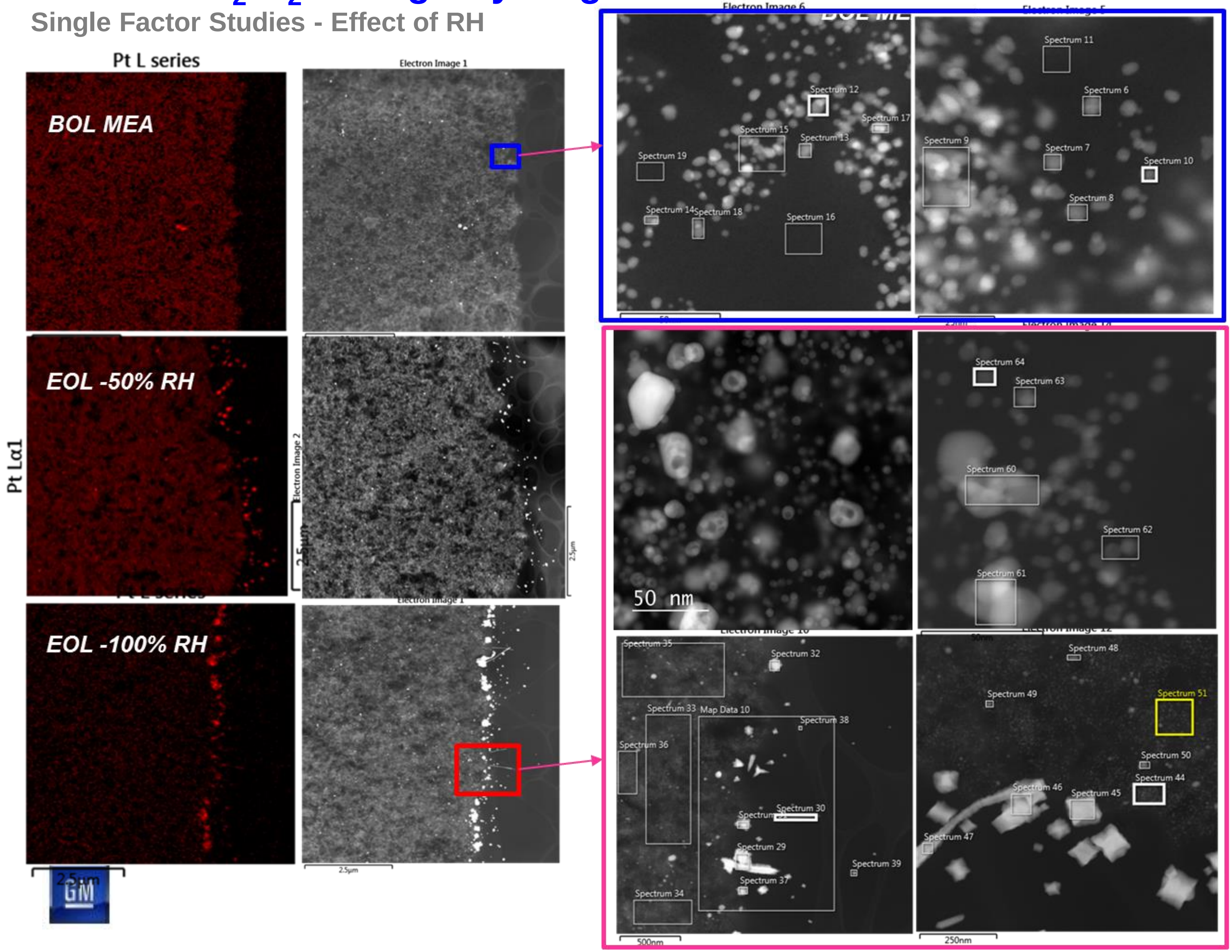


Pt

Technical Accomplishment:

Task 2. 1 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

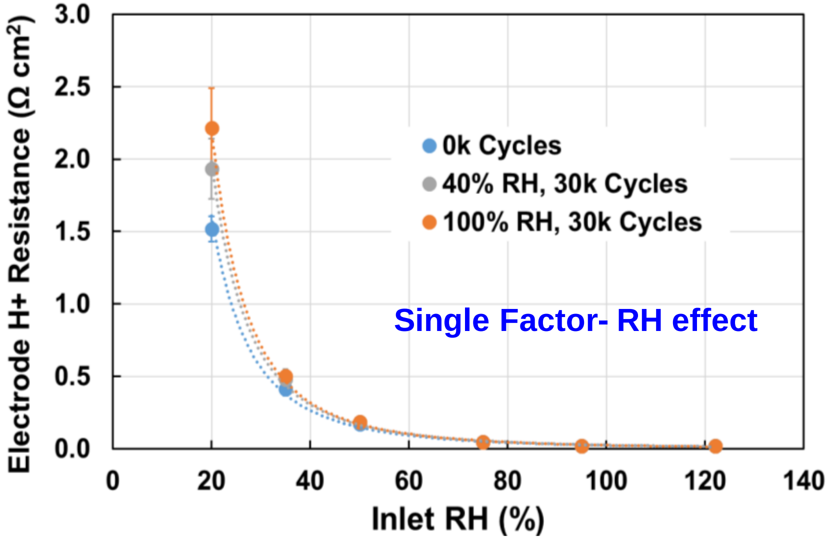
Atomic%
Pt ~ 98%

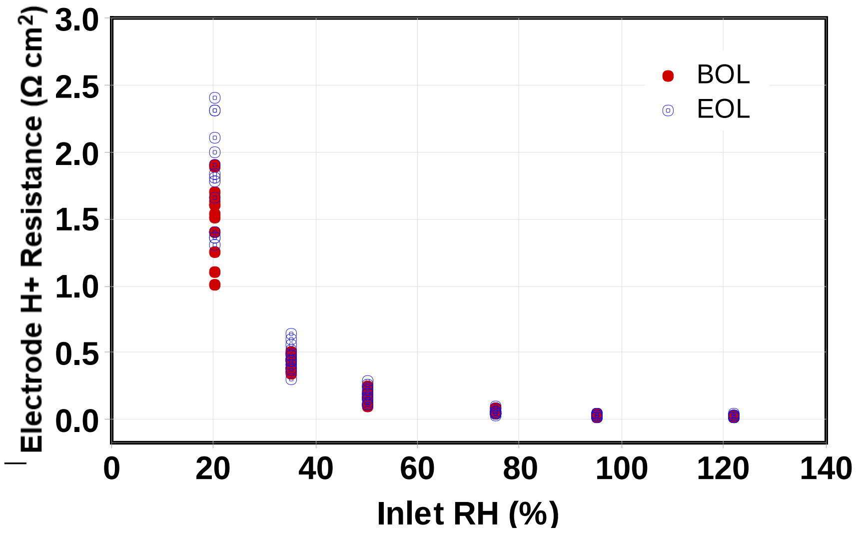
Technical Accomplishment:

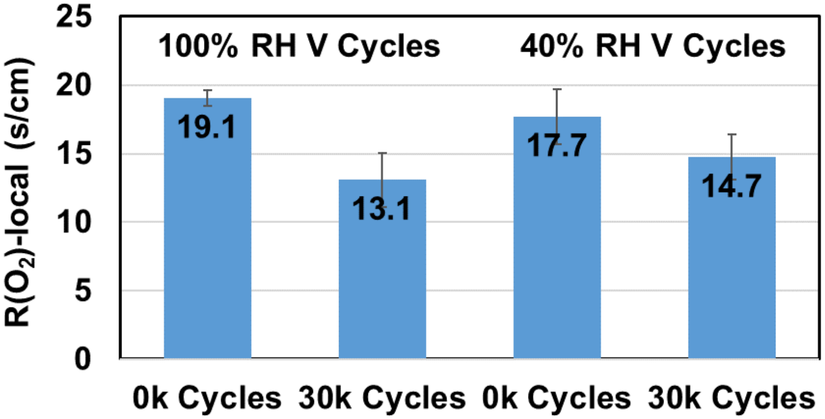
Task 2. 1 Voltage Cycling of SOA MEA

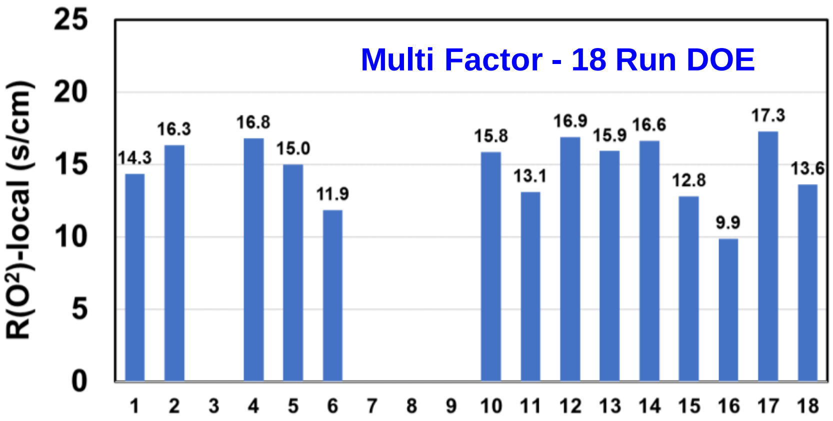
Transport Losses

5 cm² CCM MEA. Differential Conditions









- Marginal increase in proton transport resistance at very dry condition observed. Possibly from leached Co^{2+}.
- Marginal decrease in RO_2 local (μ-pore) observed (likely from more accessible pores)

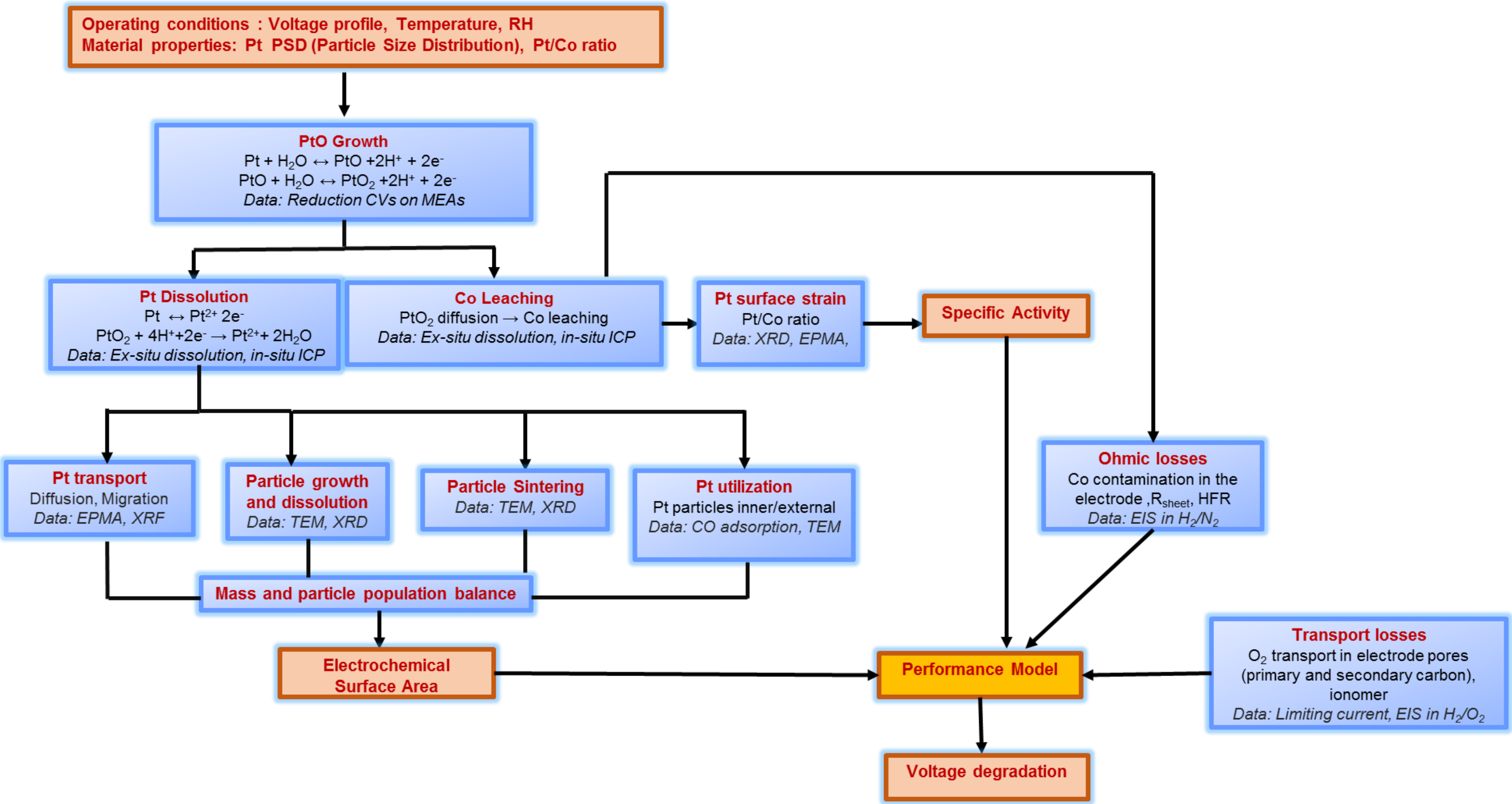
Makharia et.al, *JES*, **152** (5), A970 (2005)

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

Technical Accomplishment:

Task 4.1 Construct Pt and Co Dissolution Models

Model Framework



Operating conditions : Voltage profile, Temperature, RH
Material properties: Pt PSD (Particle Size Distribution), Pt/Co ratio

PtO Growth
$Pt + H_2O \leftrightarrow PtO + 2H^+ + 2e^-$
$PtO + H_2O \leftrightarrow PtO_2 + 2H^+ + 2e^-$
Data: Reduction CVs on MEAs

Pt Dissolution
$Pt \leftrightarrow Pt^{2+}\ 2e^-$
$PtO_2 + 4H^+ + 2e^- \rightarrow Pt^{2+} + 2H_2O$
Data: Ex-situ dissolution, in-situ ICP

Co Leaching
PtO_2 diffusion → Co leaching
Data: Ex-situ dissolution, in-situ ICP

Pt surface strain
Pt/Co ratio
Data: XRD, EPMA,

Specific Activity

Pt transport
Diffusion, Migration
Data: EPMA, XRF

Particle growth and dissolution
Data: TEM, XRD

Particle Sintering
Data: TEM, XRD

Pt utilization
Pt particles inner/external
Data: CO adsorption, TEM

Ohmic losses
Co contamination in the electrode ,R_{sheet}, HFR
Data: EIS in H_2/N_2

Mass and particle population balance

Electrochemical Surface Area

Performance Model

Transport losses
O_2 transport in electrode pores (primary and secondary carbon), ionomer
Data: Limiting current, EIS in H_2/O_2

Voltage degradation

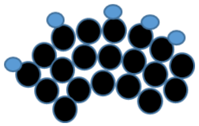
Task 4.1 Construct Pt and Co Dissolution Models

Model Framework

Pt Oxide Growth

Pt to PtO

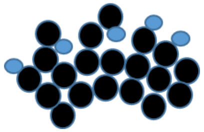
$Pt + H_2O \leftrightarrow PtO + 2H^+ + 2e^-$



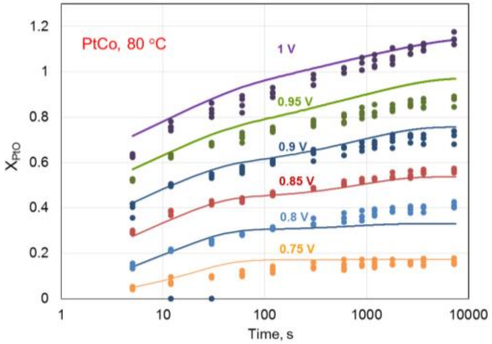
Protects Pt from dissolution

PtO to PtO$_2$

$PtO + H_2O \leftrightarrow PtO_2 + 2H^+ + 2e^-$



Destroys Pt surface exposing Cobalt



- Collected oxide growth at BOL. Plans to collect data on aged electrodes

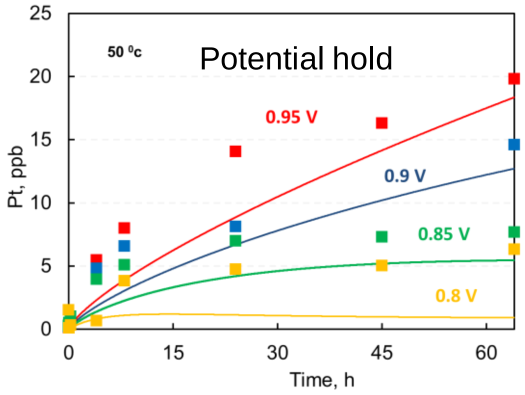
Pt Dissolution

Anodic dissolution

$Pt \leftrightarrow Pt^{2+} + 2e^-$

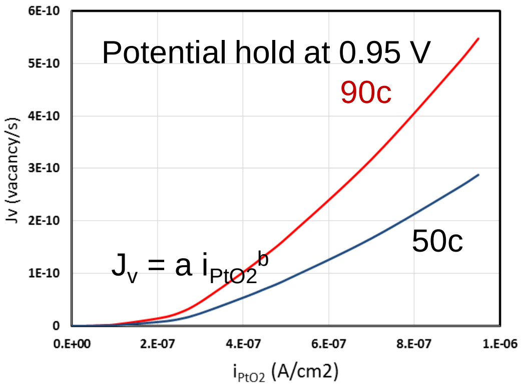
Cathodic dissolution

$PtO_2 + 4H^+ + 2e^- \leftrightarrow Pt^{2+} + 2H_2O$

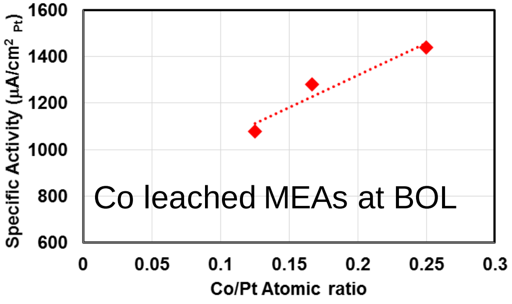


- Considered PtO_2 dissolution in the cathodic scan
- Rates of PtO_2 dissolution increases as the LPL in the cathodic scan goes below 0.85 V
- In-situ ICP measurements will be used to calibrate the kinetics with ageing
- Pt particle coalescence kinetics will also be modeled and calibrated with TEM data

Co Dissolution



- Vacancy injection into Pt particles due to Place exchanged PtO_2 from Co dissolution measurements
- Modeled Co loss due to vacancy injection



- Better correlations for SA will be obtained with data on aged MEAs

S. Arisetty, ECS Transactions, 69 17)273-289 (2015)

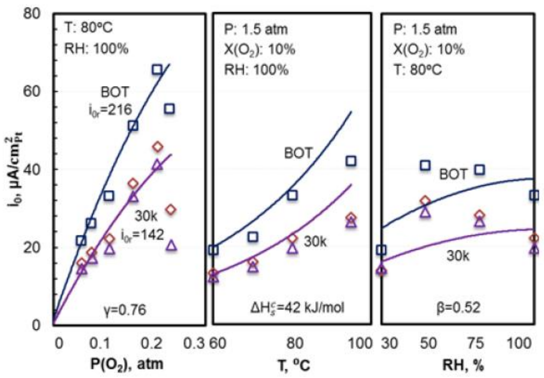
S. Arisetty, 232nd ECS meeting, National Harbor, MD

Technical Accomplishment:

Task 4.1 Construct Pt and Co Dissolution Models

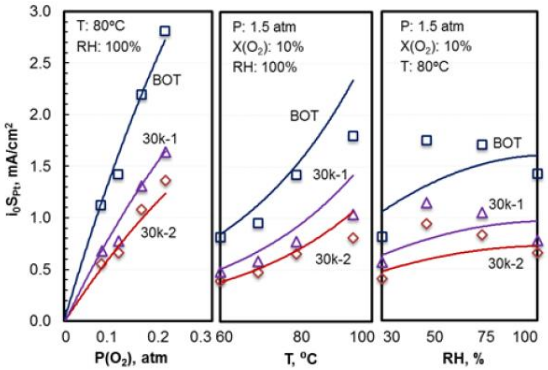
Model Framework

ORR Kinetics



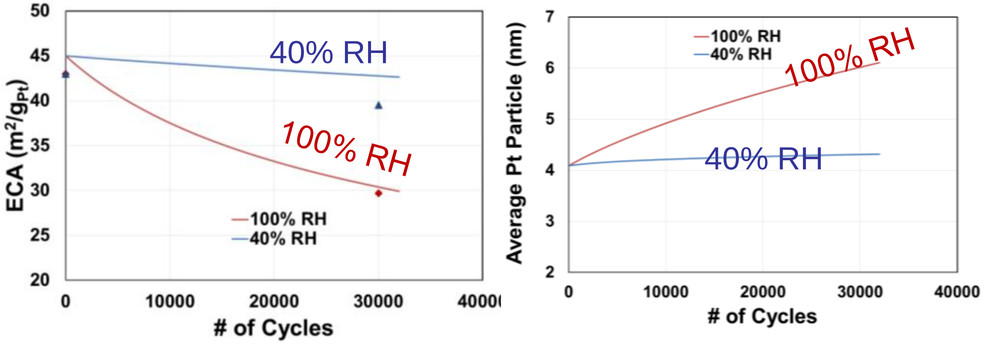
- Negligible changes in kinetic parameters with ageing
- Drop in specific activity is less sensitive to RH during the cycling

O_2 Transport



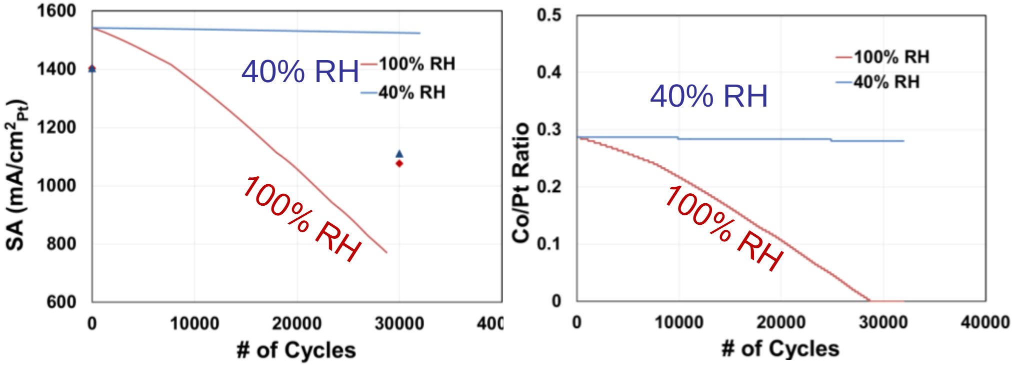
- Initial results indicate that there is a marginal increase in R_{O2} (or reduced permeability of O_2 through the ionomer)

ECA Loss



- In H_2/N_2 cycling, Pt particle growth is the main mechanism for ECA loss
- Dissolution / re-deposition kinetics and particle sintering kinetics need to be calibrated as function of operating conditions (Temperature, RH and Potential)

Specific Activity Loss



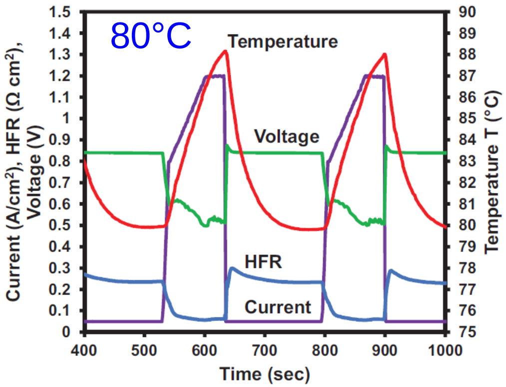
- SA Loss has been correlated to decrease in Co/Pt ratio in the electrode
- Ex-situ measurements on EOL MEAs will give a better correlation on SA degradation

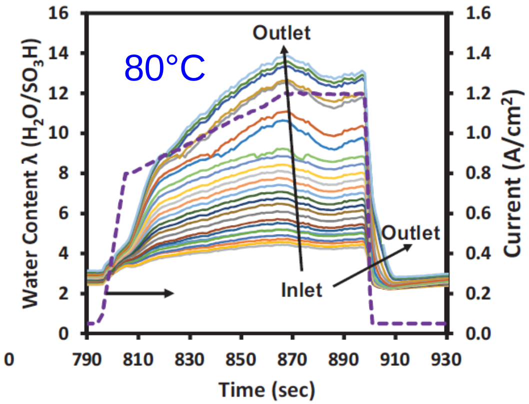
Technical Accomplishment:

Task 5.2: Combined Chemical-Mechanical HAST

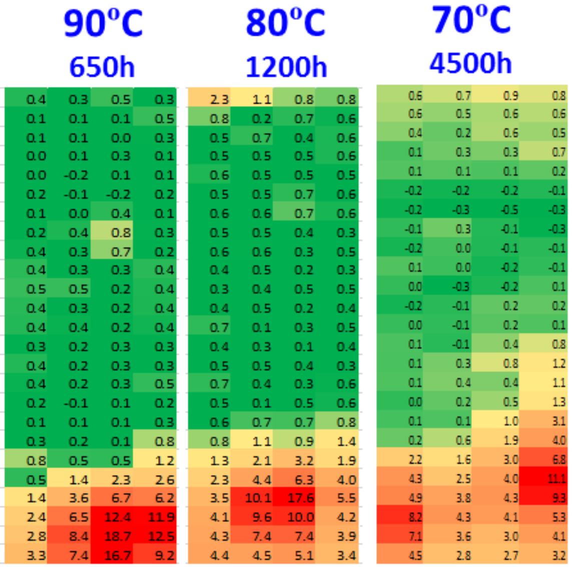
Goal: develop a highly accelerated stress test to evaluate membrane durability in a realistic fuel cell environment (no dry inlets, no OCV)

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





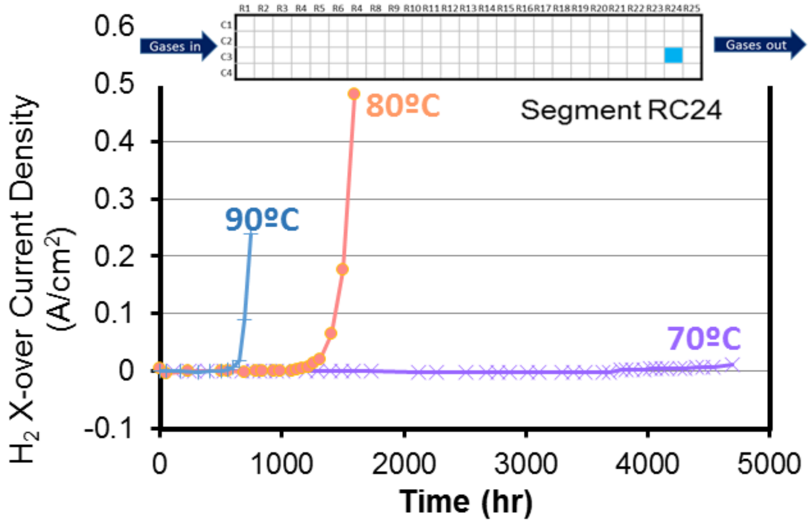
Diffusive X-over Maps



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

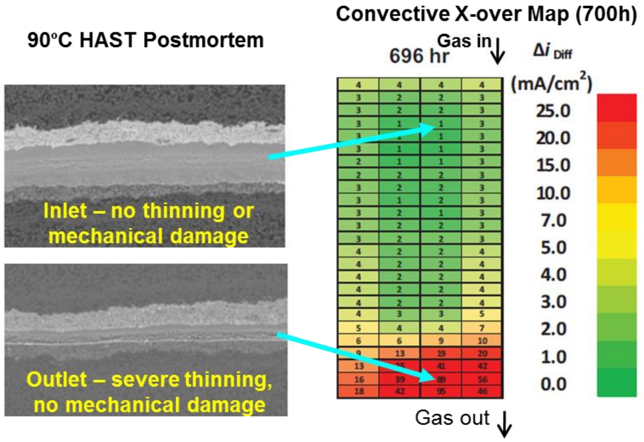
- Leaks start sooner at higher temperature
- Even though time to failure is strongly dependent on temperature, the failure location (outlet) and failure mode (thinning or diffusive crossover) is similar at all temperatures.

HAST Diffusive Crossover

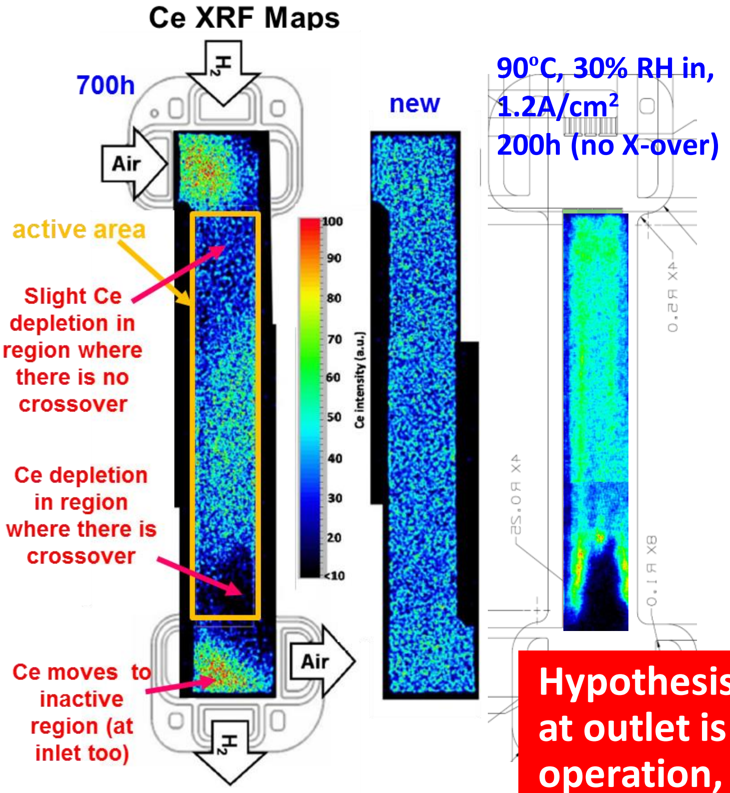


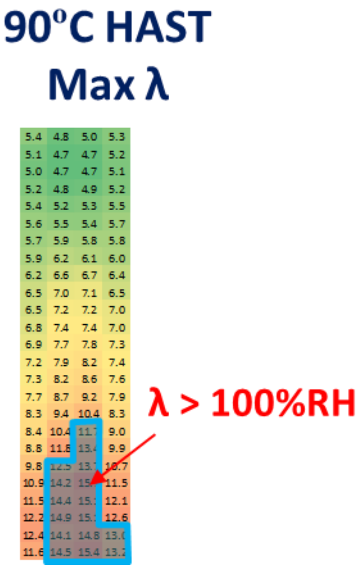
Technical Accomplishment:

Task 5.2: Combined Chemical-Mechanical HAST



4	4	4	4
3	2	2	3
3	2	2	3
3	1	1	3
3	1	1	3
3	1	1	3
2	1	1	3
2	2	2	3
3	2	2	3
3	1	2	3
3	2	1	3
3	2	2	3
3	2	2	3
4	2	2	4
4	2	2	4
4	2	2	4
4	2	2	4
4	2	2	4
4	3	3	5
5	4	4	7
6	6	9	10
9	13	19	20
13	[illegible]	41	42
16	39	89	56
18	42	95	46





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	15.	11.5
11.5	14.4	15.1	12.1
12.2	14.9	15.1	12.6
12.4	14.1	14.8	13.0
11.6	14.5	15.4	13.2

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)

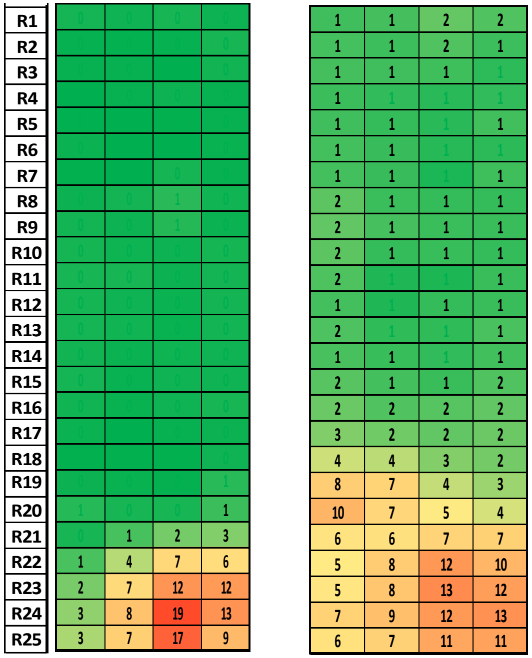
Hypothesis: Ce depletion at outlet is caused by wet operation, and is not solely a result on ionomer loss

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

Technical Accomplishment:

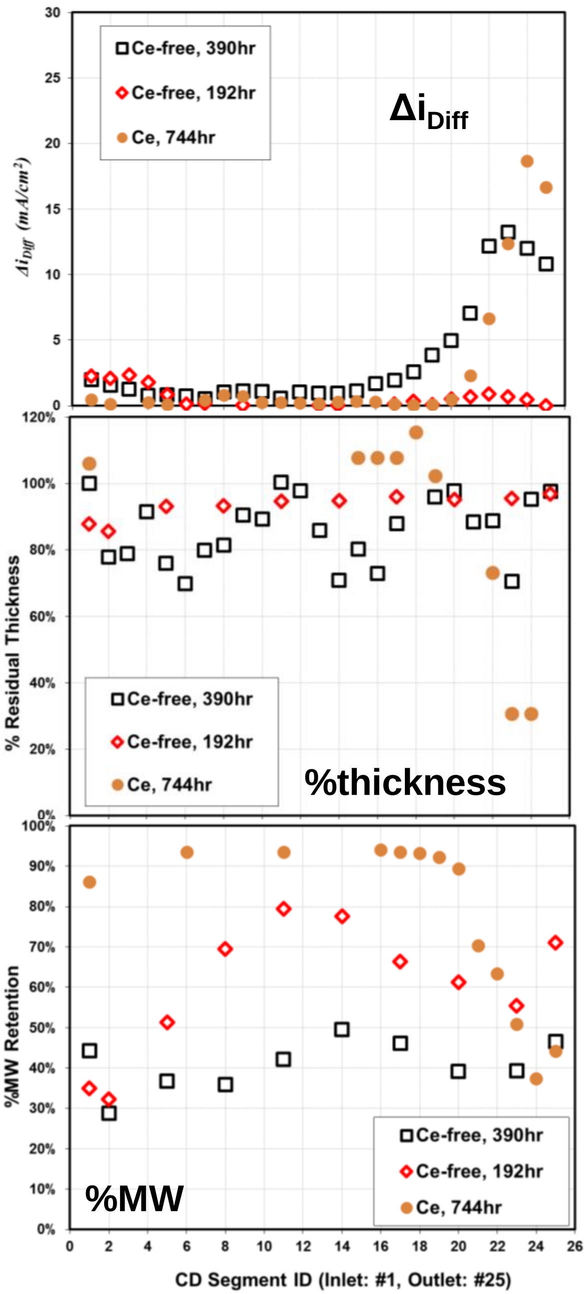
Task 5.2: Combined Chemical-Mechanical HAST – Ce Effect

90ºC 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	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



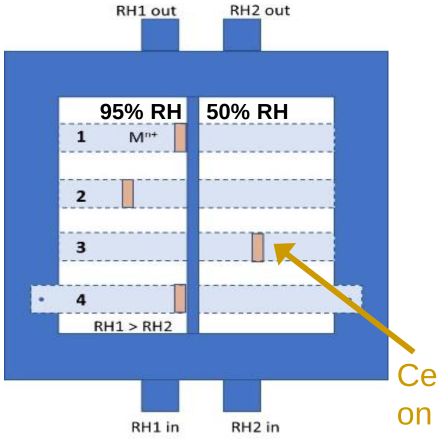
- MEA w/ Ce shows X-over near outlet only after 750h
- MEA w/o Ce shows slight increase in X-over near both inlet & outlet by 200h, by 400h, X-over increase significantly at outlet
- Significant thinning only near outlet of MEA w/ Ce after 750h
- Ce-free MEAs show more uniform thinning
- MEA w/ Ce shows significant MW loss only at outlet
- MEA w/o Ce shows MW loss throughout cell – initially more MW loss at inlet, but by 400h MW loss is uniform

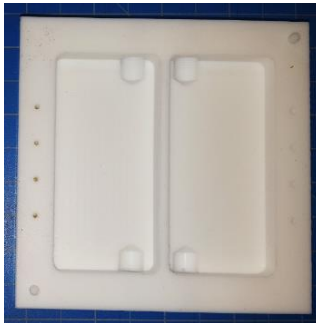
Mechanistic Hypothesis

- Ce effectively prevents MW loss and thinning at all HAST conditions
- Without Ce, degradation initiates at driest regions (inlet)
- Severe RH cycling causes Ce depletion and subsequent membrane degradation at outlet
- Even w/o Ce, RH cycling can accelerate membrane X-over

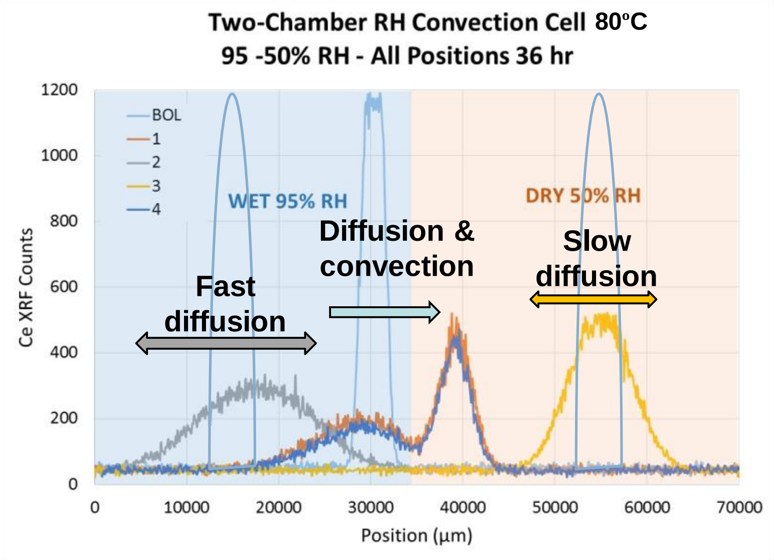
Technical Accomplishment:

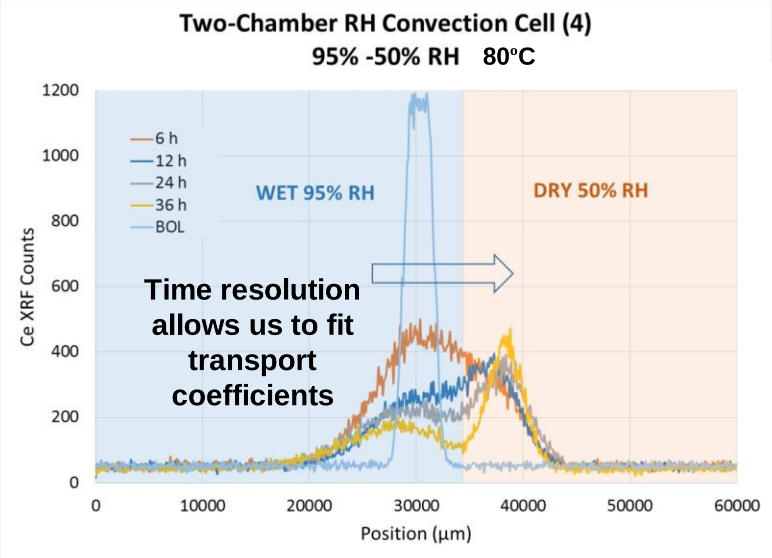
Ce Transport Measurement



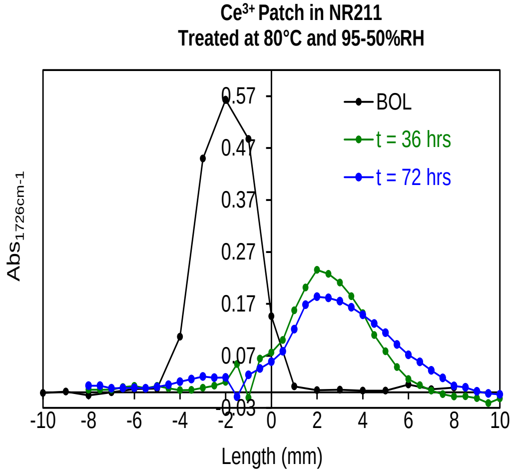


Ce patches doped locally on membrane strips

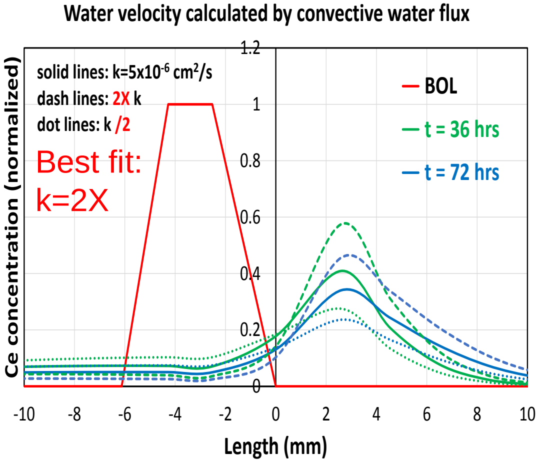




Measured



Modeled



- 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
- We are collecting data over a range of temperatures & RH gradients
- Data fit to determine convection coefficient (k) as f(t, RH) - see next slide

Technical Accomplishment:

Ce Transport Model

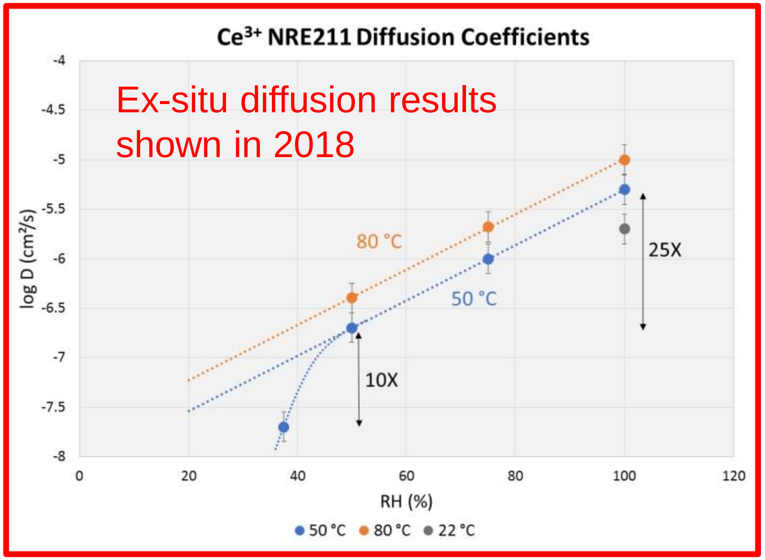
1-D Transient Model (Conservation of Ce)

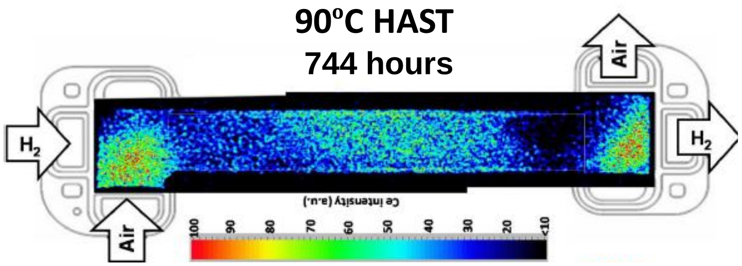
$$\frac{dc}{dt} + \frac{dj}{dx} = 0 \qquad j = -uc\frac{d\phi}{dx} + v\cdot c - D\frac{dc}{dx}$$

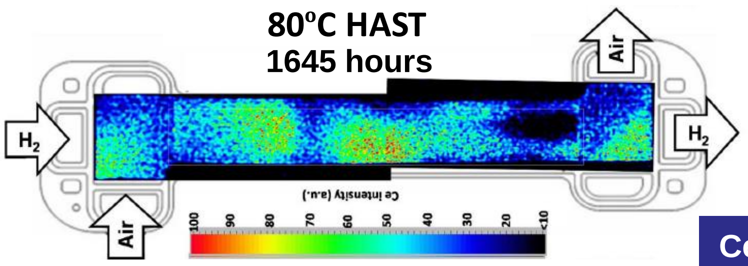
conduction convection diffusion

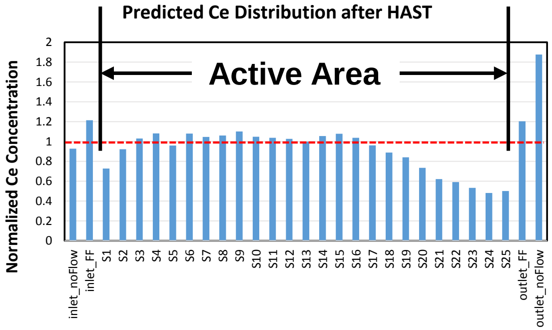
Nernst-Einstein for Ce^{3+}, z = 3

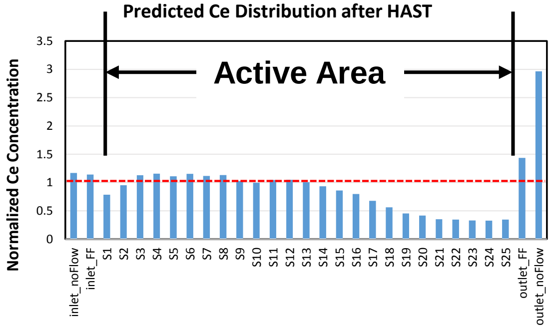
$$\boxed{u = \frac{zFD}{RT}} \qquad \boxed{v = -k\frac{d\lambda}{dx}}$$


Ex-situ diffusion results shown in 2018


90°C HAST 744 hours


80°C HAST 1645 hours



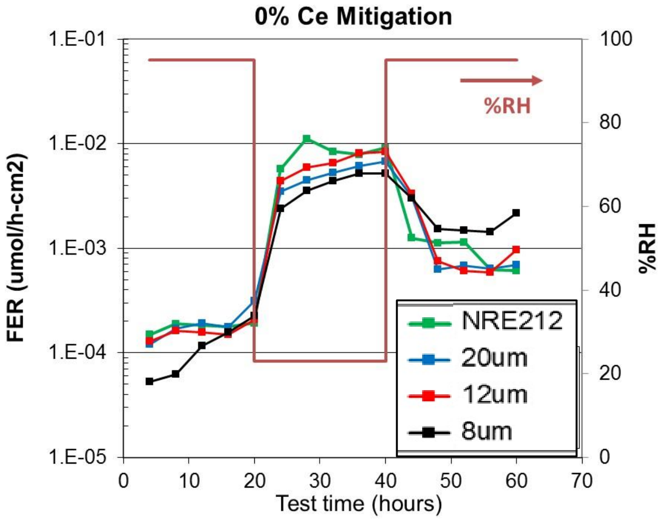


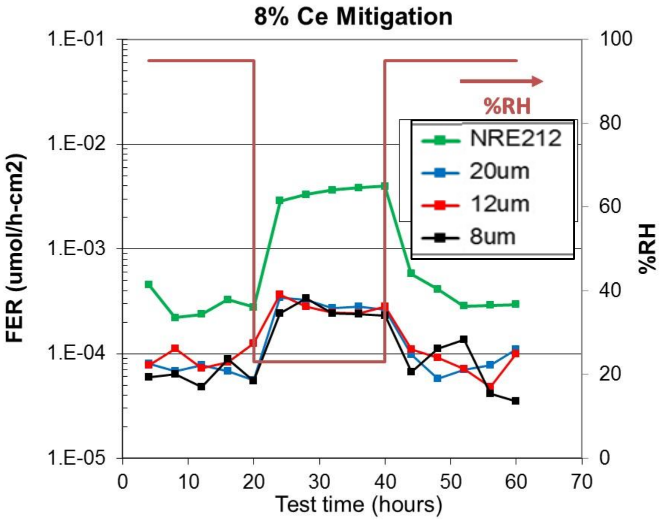
Ce migration model that accounts for mechanisms of diffusion, convection, and conduction can capture the Ce migration behavior of HAST test

Task 5.3: 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%)

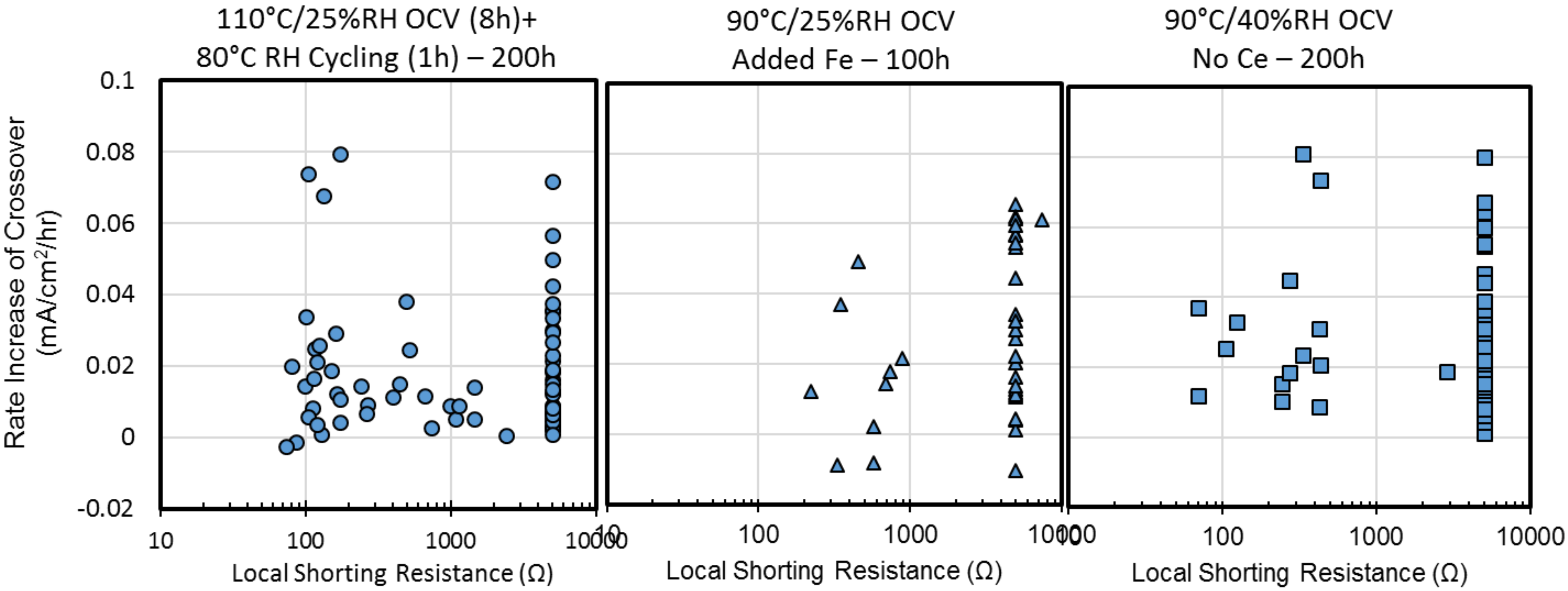
- DOE will isolate the impact of gas crossover of degradation rate
- Measuring Fluoride release, MW loss & carboxylate increase to isolate unzipping & chain scission mechanisms

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

Technical Accomplishment:

Task 5.3: 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

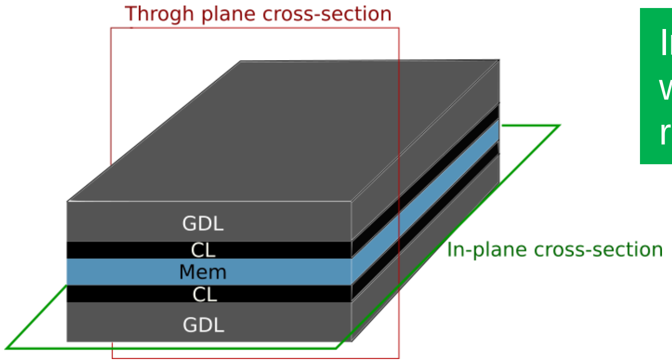


- There is no clear correlation between local shorting and increase in crossover.
  - Lack of correlation unexpected based on high modelled local temperature
- Plan to repeat tests while running to failure

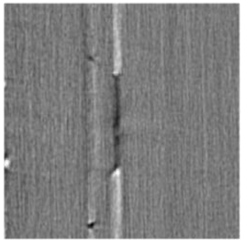
Task 5.3: Impact of Local Shorting on Membrane Degradation

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

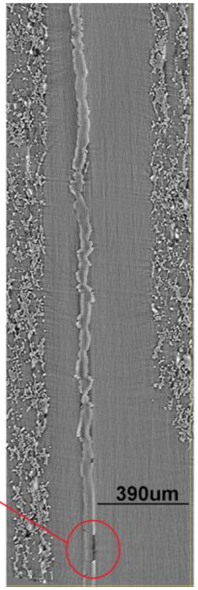
- Pre-shorted MEAs sent to LBNL instead



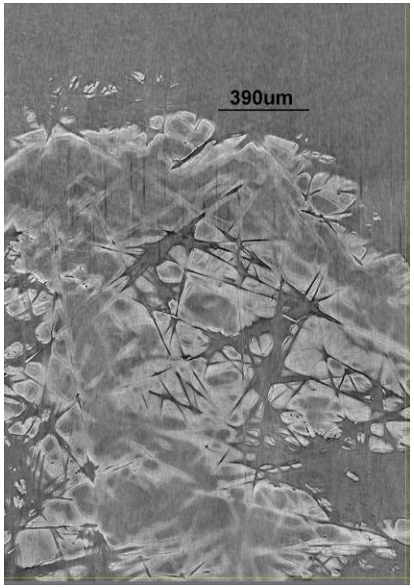
Imaged segments with low shorting resistance



Through-plane



In-plane at CL location



CL cracks observed

- The GDL detached during shipment (fixing)
- CL surface roughness can be seen in the though –plane image
- Cracks were observed in CLs
- No pinholes were observed, which was most likely due to membrane relaxation after GDL detachment
- The GDL fiber imprints show that the compression pressure was significant enough to deform the CLs & membrane
  - For compressed MEAs, the GDL fibers may penetrate through the membrane
- Developing a sample holder which can maintain the MEA compression from shorting through imaging

Next steps

- Image pre-shorted MEAs before and after durability testing

Collaborations

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

FC-PAD (National Labs)

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

Sub Contractors

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

Responses to Last Year AMR Reviewers' Comments

- *"Approach should not be to define benign operating conditions but rather map out effect of operating conditions. "*
  - Agreed and we are precisely doing the same. The output of the project is to map out conditions to avoid and conditions to adopt for prolonged durability. It will serve as a toolkit for system engineers to craft their systems. This knowledge was never complete and is lacking for recent advanced materials. To provide a quantifiable deliverable, a case study in BP3 is envisioned.

- *"Models and durability studies exist in previous DOE project as well"*
  - We are definitely not starting from ground zero. Good work by national labs and few earlier projects on both experimental and model work exist. We are focused on addressing gaps, mapping out relationship between durability and operating condition. Modelling PtCo specific activity degradation, Cerium movement etc. We are utilizing and supporting modelling activities at ANL

- *"Selection of SOA was based on BOL performance only and not durability".*
  - Probably lost in translation. When we observed some overlap in catalyst candidates, we utilized the durability studies from FC144 to make the down-selection instead of repeating expts. This was highlighted in the optimization section.

- *"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. At the end of project as needed, we will identify a couple of other catalyst/MEAs and demonstrate the same. We are providing these GM MEAs to FCPAD with NO restriction on analysis.

Future Work

- Complete the voltage cycling experiments to map the impact of operating conditions.
  - ECA, SA, CO stripping, RO_2-local (limiting current), V loss etc.(NREL)
  - MEA characterization including EPMA, TEM, EELS mapping etc. (ORNL, UT Austin).
- Obtain ex-situ dissolution rates of Pt, Co and elucidate growth mechanisms (ANL/NREL).
- Develop predictive model based on the experimental data with the fundamental understanding of degradation mechanisms.
  - Models for PtO growth, Pt & Co dissolution, Pt & Co transport, Pt shell thickness
  - Correlations quantifying Pt particle coalescence, changes in specific activity, Pt utilization, RO_2 – local.
- Model verification followed by durability improvement in AST.
- 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°C. (Giner)
  - Explore role of Fe cations in MEA degradation (LANL)
- 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.

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.
- 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.
  - Certain conditions like low RH (25%) operation demonstrate 100% reduction in ECA loss.
  - Other factors like lower temperature and lower upper potential limit also demonstrate significant reduction in ECA loss.
- Operation conditions that can provide > 35% reduction in ECA loss demonstrated.
- Combined chemical/mechanical highly accelerated stress (HAST) was developed. Deep RH cycling at outlet and dry inlets were combined to induce mechanical and chemical stress in different regions of the cell.
  - Chemical degradation observed in region of highest mechanical stress.
  - Significant in-plane Ce migration observed during operation.
  - Non Ce Cell indicate role of mechanical stress on increased gas crossover at outlet.
- Ce diffusivity and convective measurements were performed. Results 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.

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