Durable High Power Membrane Electrode Assembly with Low Pt Loading

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General Motors, Fuel Cell Activities

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FC156

Overview

Timeline

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

Budget

- Total Project Budget: $ 3,201,476
- Total Recipient Share: $ 640,295 (20%)
- Total Federal Share: $ 2,561,181
- Total DOE Funds Spent*: $ 0 invoiced

** As of 3/31/17, project awaiting final GM approval.*

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: *Not signed*
  - Giner
  - UT Austin
- FC-PAD
- Project lead: GM

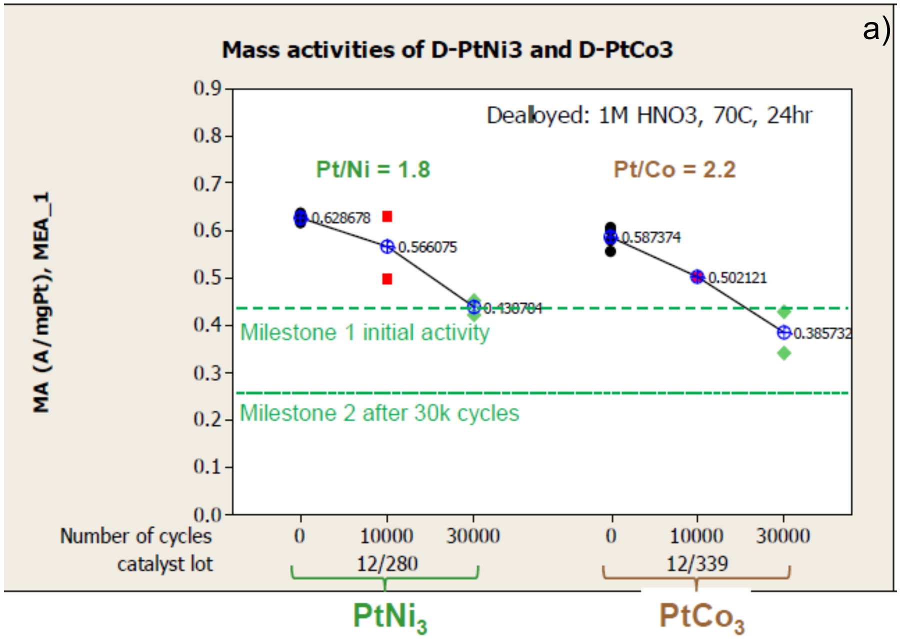
Relevance: (Objectives)

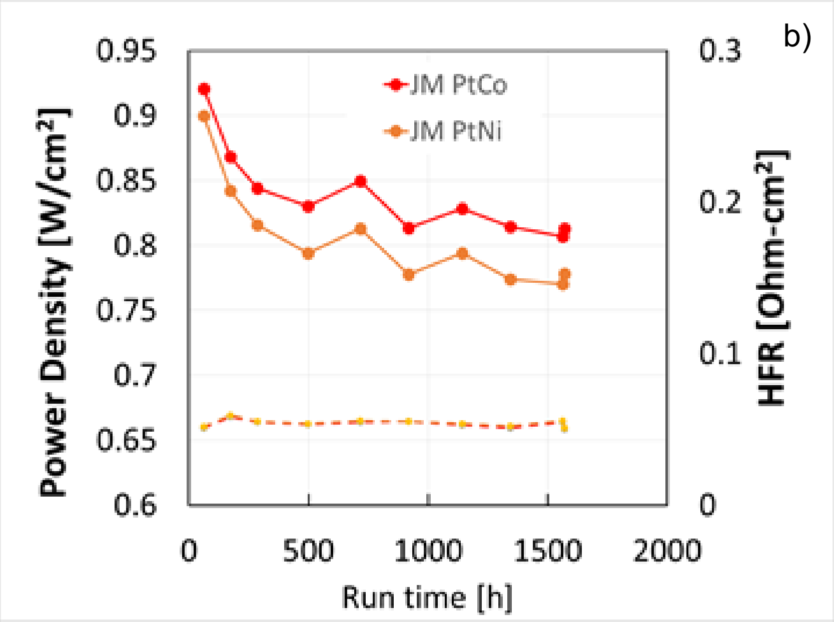
- **Relevance: DOE 2020 targets for transportation application**
  - Enable cost targets and performance targets with reduced Pt loading
  - Improve fuel cell durability
- **Objective**
  - Project goal is to improve durability of state of art (SOA) MEA by identifying and reducing the stress factors 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.

MEA - Electrode, Membrane, Catalyst Targets			
Chracteristics	units	2020 Targets	2015 status
Cost	\$/kWnet	14	17
Q/ΔT	kW/^{o}C	1.45	1.45
Performance @ 0.8 V	mA/cm^2	300	240
Performance @ rated power	mW/cm^2	1000	810
Durability w Cycling	Hours @ <10% V loss	5000	2500
Mass activity	A/mg $_{PGM}$ @ 900 mV	>0.44	>0.5
PGM Content (MEA)	g/ KW rated mg/cm^2 MEA	0.125	0.16 0.13

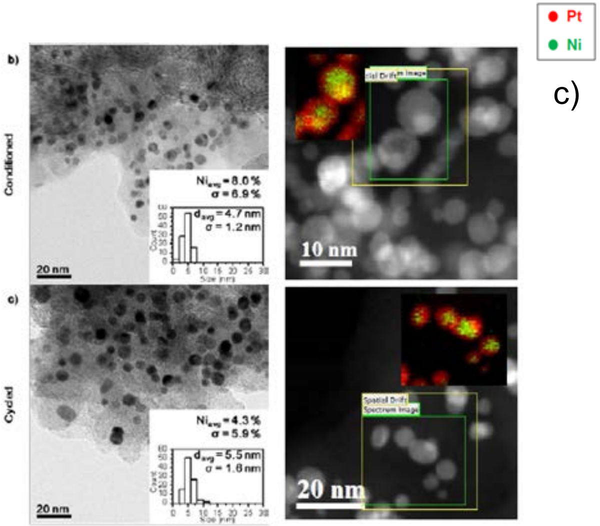
Excerpts from key DOE targets

Relevance (Challenges): Pt alloy degradation in H_2 Air



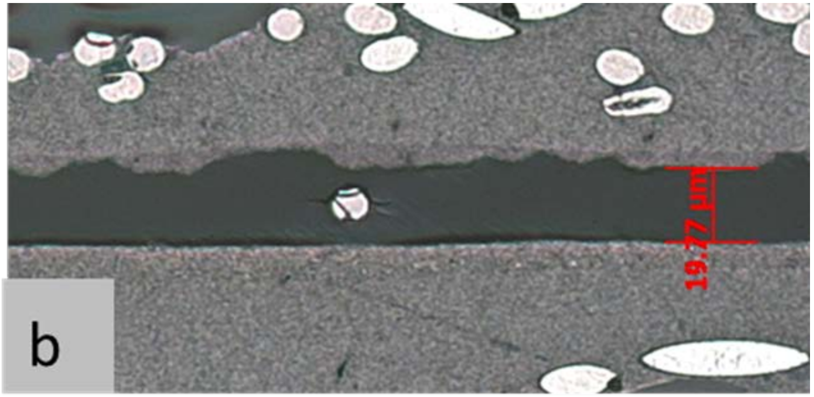


- PtNi or PtCo alloy catalyst with >0.66 A/mg_{Pt} has been demonstrated in previous de-alloyed catalyst project (FC087).
- High kinetic mass activities were also maintained post 30,000 V cycles (a).
- Power density of 0.94 W/cm^2 vs. target 1.0 W/cm^2 was achieved at BOT in a large active area stack.
  - Durability test indicated rapid decrease in high power (b).
  - Potential cause arise from both un-optimized MEA as well as complex degradation mechanisms with Pt alloy catalysts impacting MEA performance (c).

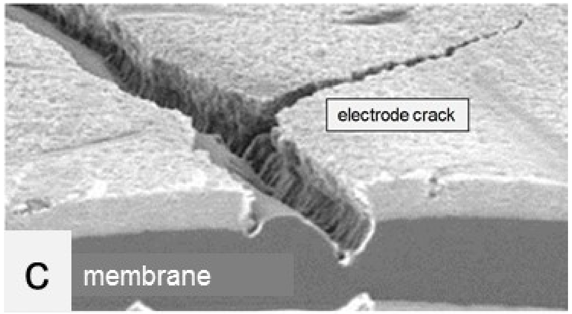


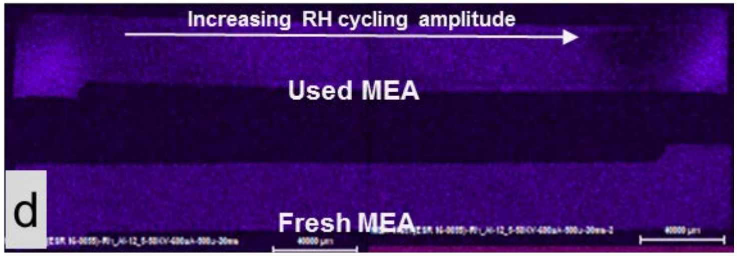
https://www.hydrogen.energy.gov/pdfs/review14/fc087_kongkanand_2014_o.pdf

Relevance (Challenges): Membrane Degradation

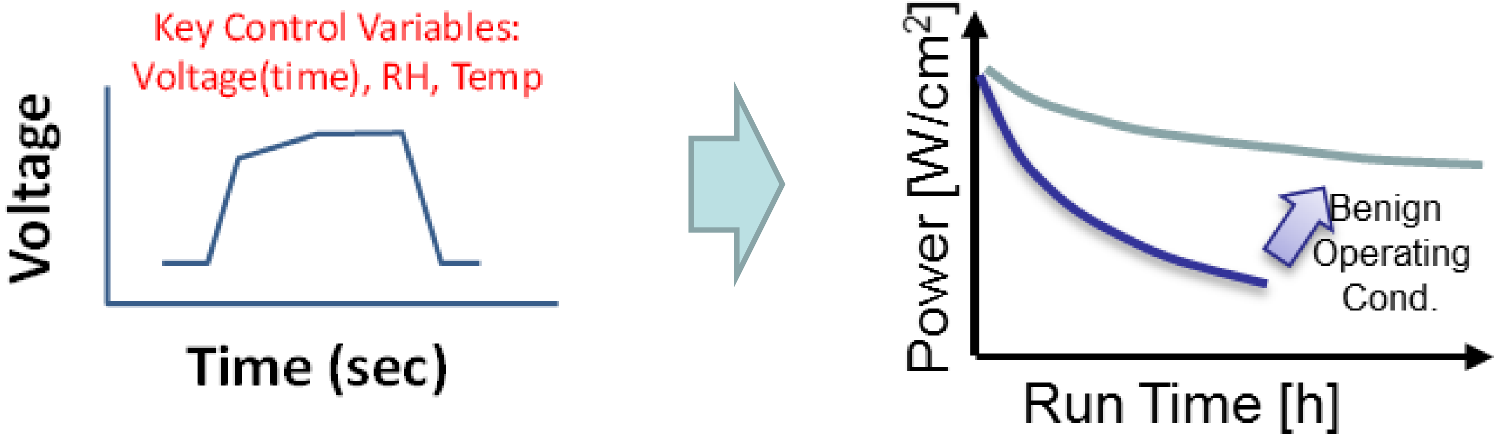


- Correlation between mechanical stress and chemical degradation not fully understood. In addition to RH cycling, mechanical failures augmented by:
    - a) Electrode defects cause high level of stress on membrane at local spots.
    - b) Fibers from GDL can puncture membrane creating a local short.
    - c) Electrode cracks tends to increase the oxidative stress.
- Chemical degradation mitigants like Ce redistribute within an MEA (d) leaving Ce depleted and Ce rich regions.

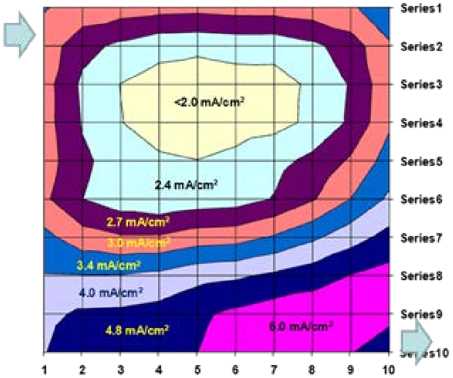




Approach



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



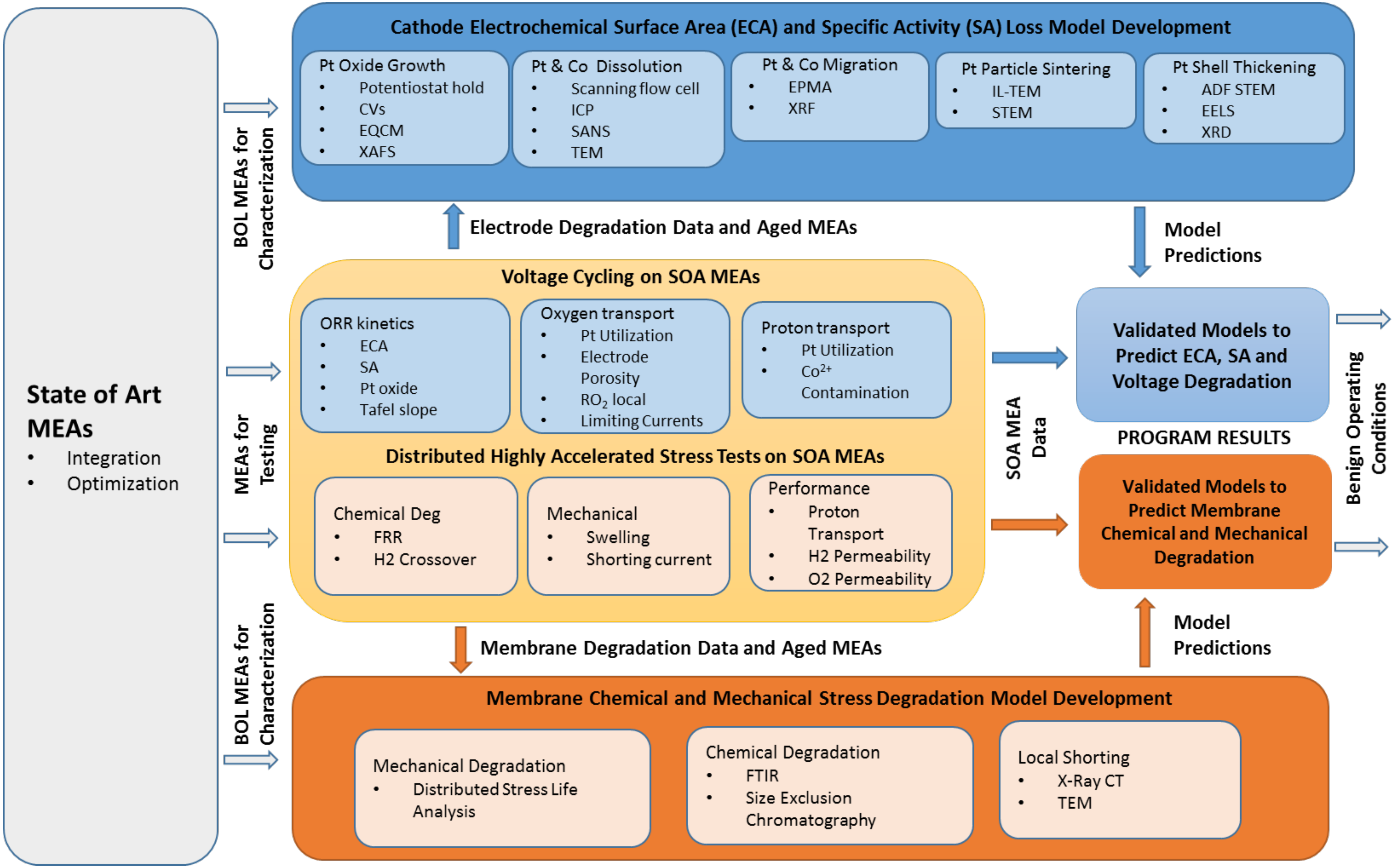
Combined Chem. and Mech. stress segmented cell test

Control Variables
RH,T, t
Mitigants
Accelerators
Local defects
GDL property

Combined chemical and mechanical Stress Model

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

Approach



State of Art MEAs
- Integration
- Optimization

BOL MEAs for Characterization

MEAs for Testing

BOL MEAs for Characterization

Cathode Electrochemical Surface Area (ECA) and Specific Activity (SA) Loss Model Development

Pt Oxide Growth
- Potentiostat hold
- CVs
- EQCM
- XAFS

Pt & Co Dissolution
- Scanning flow cell
- ICP
- SANS
- TEM

Pt & Co Migration
- EPMA
- XRF

Pt Particle Sintering
- IL-TEM
- STEM

Pt Shell Thickening
- ADF STEM
- EELS
- XRD

Electrode Degradation Data and Aged MEAs

Model Predictions

Voltage Cycling on SOA MEAs

ORR kinetics
- ECA
- SA
- Pt oxide
- Tafel slope

Oxygen transport
- Pt Utilization
- Electrode Porosity
- RO_2 local
- Limiting Currents

Proton transport
- Pt Utilization
- Co^{2+} Contamination

Distributed Highly Accelerated Stress Tests on SOA MEAs

Chemical Deg
- FRR
- H2 Crossover

Mechanical
- Swelling
- Shorting current

Performance
- Proton Transport
- H2 Permeability
- O2 Permeability

SOA MEA Data

Validated Models to Predict ECA, SA and Voltage Degradation

PROGRAM RESULTS

Validated Models to Predict Membrane Chemical and Mechanical Degradation

Benign Operating Conditions

Membrane Degradation Data and Aged MEAs

Model Predictions

Membrane Chemical and Mechanical Stress Degradation Model Development

Mechanical Degradation
- Distributed Stress Life Analysis

Chemical Degradation
- FTIR
- Size Exclusion Chromatography

Local Shorting
- X-Ray CT
- TEM

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 Op 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.

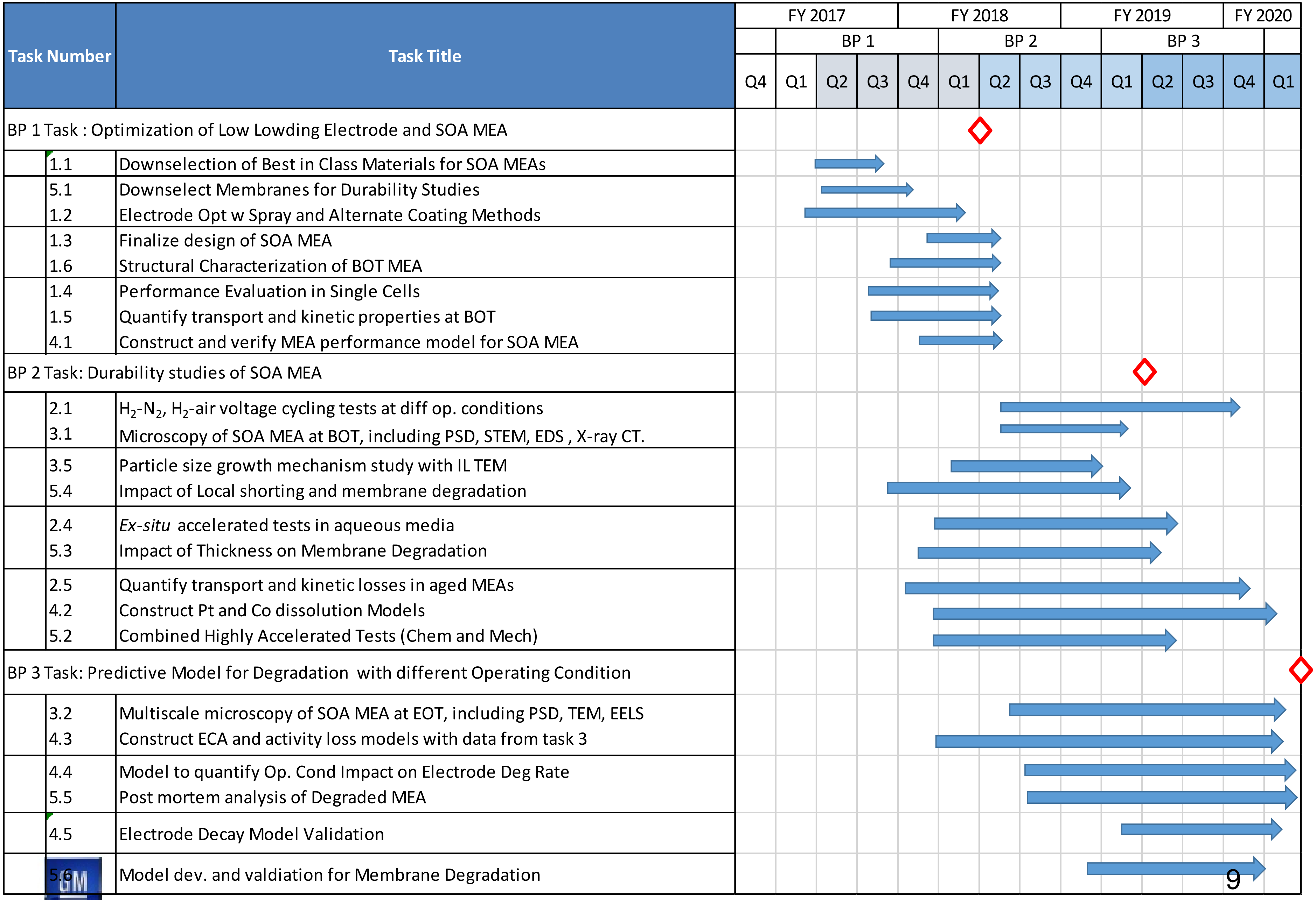
Go/No Go: Demonstrate operating conditions can provide at least 35% reduction in ECSA and performance loss.

Budget Period 3 Task: Predictive Model 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 Deg 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.

Schedule



Task Number	Task Title
BP 1 Task : Optimization of Low Lowding Electrode and SOA MEA	
1.1	Downselection of Best in Class Materials for SOA MEAs
5.1	Downselect Membranes for Durability Studies
1.2	Electrode Opt w Spray and Alternate Coating Methods
1.3	Finalize design of SOA MEA
1.6	Structural Characterization of BOT MEA
1.4	Performance Evaluation in Single Cells
1.5	Quantify transport and kinetic properties at BOT
4.1	Construct and verify MEA performance model for SOA MEA
BP 2 Task: Durability studies of SOA MEA	
2.1	H_2-N_2, H_2-air voltage cycling tests at diff op. conditions
3.1	Microscopy of SOA MEA at BOT, including PSD, STEM, EDS , X-ray CT.
3.5	Particle size growth mechanism study with IL TEM
5.4	Impact of Local shorting and membrane degradation
2.4	*Ex-situ* accelerated tests in aqueous media
5.3	Impact of Thickness on Membrane Degradation
2.5	Quantify transport and kinetic losses in aged MEAs
4.2	Construct Pt and Co dissolution Models
5.2	Combined Highly Accelerated Tests (Chem and Mech)
BP 3 Task: Predictive Model for Degradation with different Operating Condition	
3.2	Multiscale microscopy of SOA MEA at EOT, including PSD, TEM, EELS
4.3	Construct ECA and activity loss models with data from task 3
4.4	Model to quantify Op. Cond Impact on Electrode Deg Rate
5.5	Post mortem analysis of Degraded MEA
4.5	Electrode Decay Model Validation
5.6	Model dev. and valdiation for Membrane Degradation

◇ Go/No Go / Milestones

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)
  - Membrane mechanical stress model, X-ray CT
- Los Alamos National Lab (Dr. Mukund Rangachary and Dr. Rod Borup)
  - Voltage cycling tests (TBD), Accelerated stress tests
- National Renewable Energy Lab (Dr. Shyam Kocha)
  - 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. Paulo Ferreira) (University)
  - Identical location TEM, PSD measurements
- Giner (Dr. Cortney Mittelsteadt) (Industry)
  - Membrane degradation studies

Responses to Last Year AMR Reviewers' Comments

- New Project: This project was not reviewed last year.

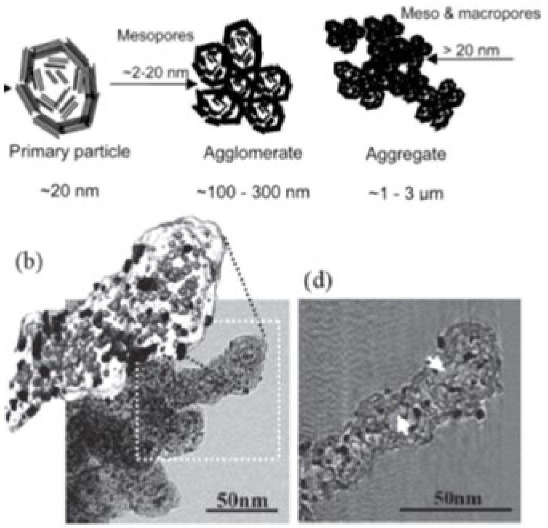
Technical (budget period 1)

Integration and Optimization of State of the Art MEAs

Objectives for Year 1

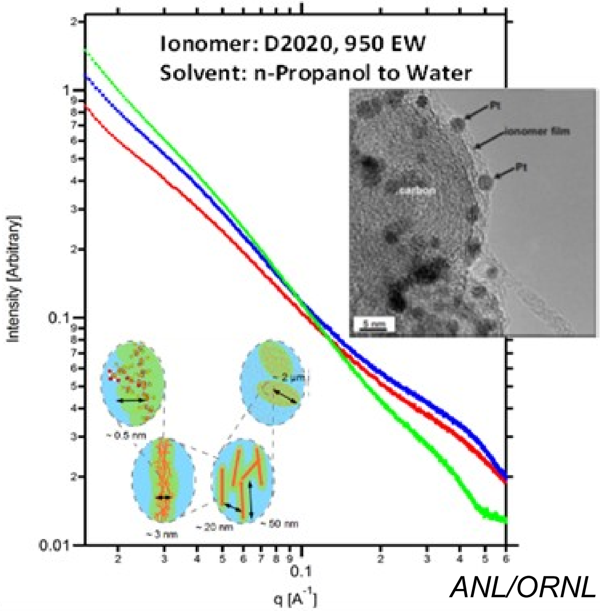
1) Deliver a state of the art MEA via systematic study of catalyst layer with best-in-class catalysts, ionomers, membranes and GDLs
2) Gain fundamental mechanistic understanding of the catalyst layer microstructure-performance relationship across the entire polarization region

- **Catalyst Microstructure**
- **Catalyst Ink Colloidal Properties**



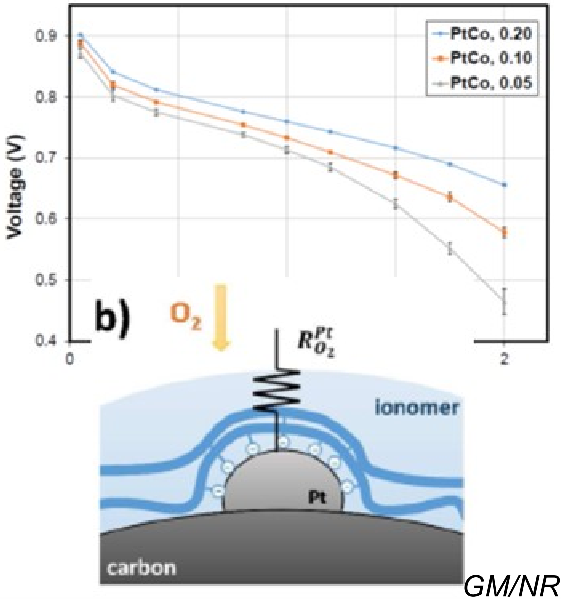
ORNL/ UTA

- **Ionomer Colloidal Structure**
- **Ionomer Distribution**



ANL/ORNL

- **MEA Performance**
- **Electrochemical Diagnostics**



GM/NREL

Soboleva. T ACS Applied Materials 2010 2 (2) 375-384
Ito.T Electrochemistry 2011 79(5) 374
More. K ECS Transactions 2006 3 717-733

Technical (budget period 1)

Integration and Optimization of State of the Art MEAs

Prospective Composition of the MEA to be Delivered

Component	Description of Potential Candidates
Anode GDL	GDL with optimized water transport properties and minimized membrane shorting probability
Anode Catalyst	Monometallic Pt nanoparticles dispersed on graphitized moderate surface area carbon supports at 0.025 mg_{Pt}/cm^2
Anode Ionomer	Moderate EW (~950) ionomer for optimal dry/wet performance
Membrane	i. GM's thin (< 15 μm) low EW reinforced PFSA ii. 3M's perfluroro Imide or Ionene based ionomers iii. Giner's hydrocarbon ionomeric membrane
Cathode Ionomer	Ionomer screening for optimal Dry - Wet performance
Cathode Catalyst	Highly active Pt-alloy (Ni or Co) nanoparticle catalyst supported on high surface area carbon at 0.1 mg_{Pt}/cm^2 or lower.
Cathode GDL	GDL with optimized water transport properties and minimized membrane shorting probability

General Motors
- Design of Experiments
- Effect of catalyst ink solvent system
- Catalyst ink rheological properties
- Ionomer colloidal properties

Oakridge National Lab
- Ionomer /catalyst interaction

UT Austin
- Catalyst layer characterizations

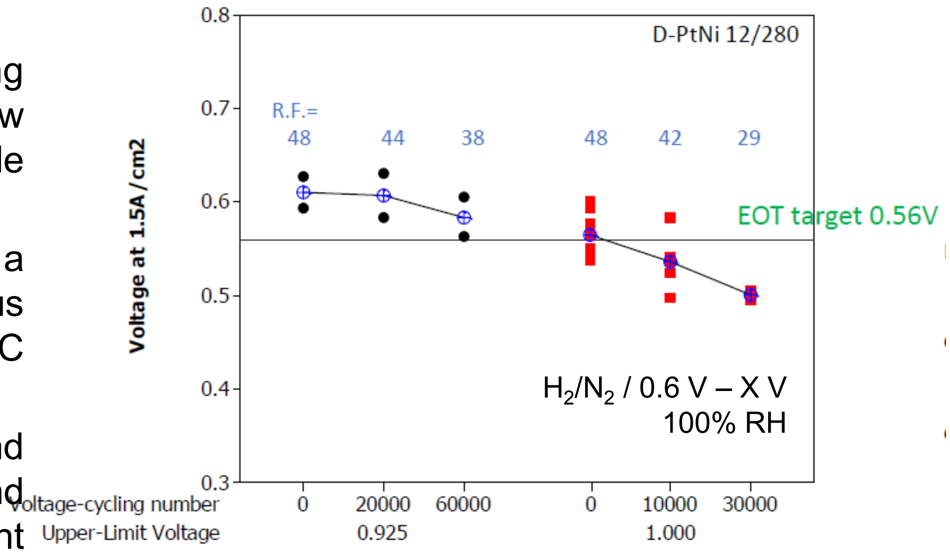
National Renewable Lab
- Differential cell performance
- Kinetic measurements
- Transport (H^+/O_2) properties

Argonne National Lab
- Ionomer and catalyst ink Characterization
- X-ray scattering measurements

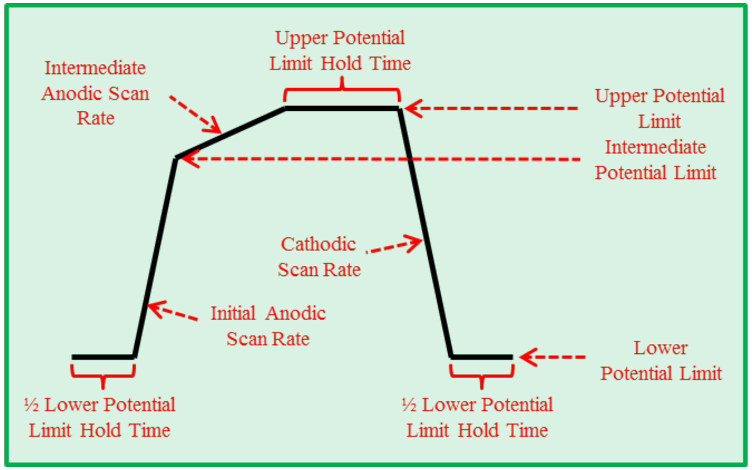
Giner
- Membrane durability studies

Technical/ Future Work

- ☐ **Electrode Durability**
  - ☐ Few studies available in literature studying the effect of peak potential and few waveforms such as square wave, triangle wave etc.
  - ☐ Peak potential is known to have a significant effect as shown in numerous studies as well as GM’s earlier project FC 087.
  - ☐ The current work envisions systematic and detailed voltage cycling tests in H_2-Air and H_2/N_2 to be conducted at different operating conditions on SOA MEA.
  - ☐ Studies to be performed as a design of experiment to limit test articles.



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

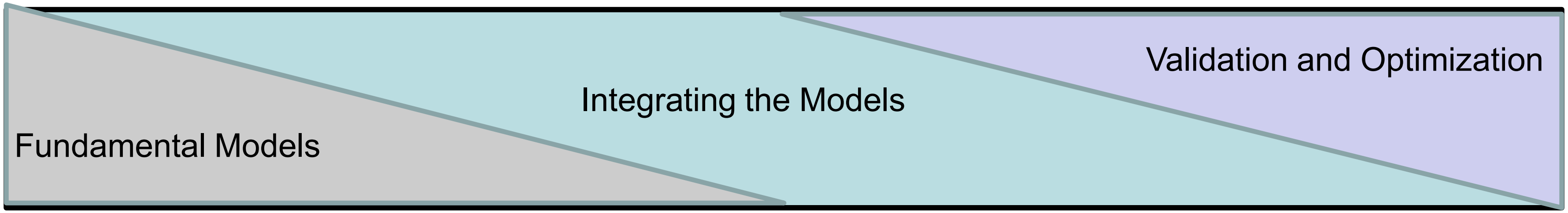


Levels	Factors					
	Cell Temp (°C)	RH (%)	Upper potential (mV)	upper potential hold time (s)	Test Stand	Lower Potential (mV)
-3						100
-1	55	50	870	1	A	300
0	75	75	900	4	B	
1	95	100	930	7	C	600
3						800
3						800

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

Technical/ Future Work

Electrode Durability Model



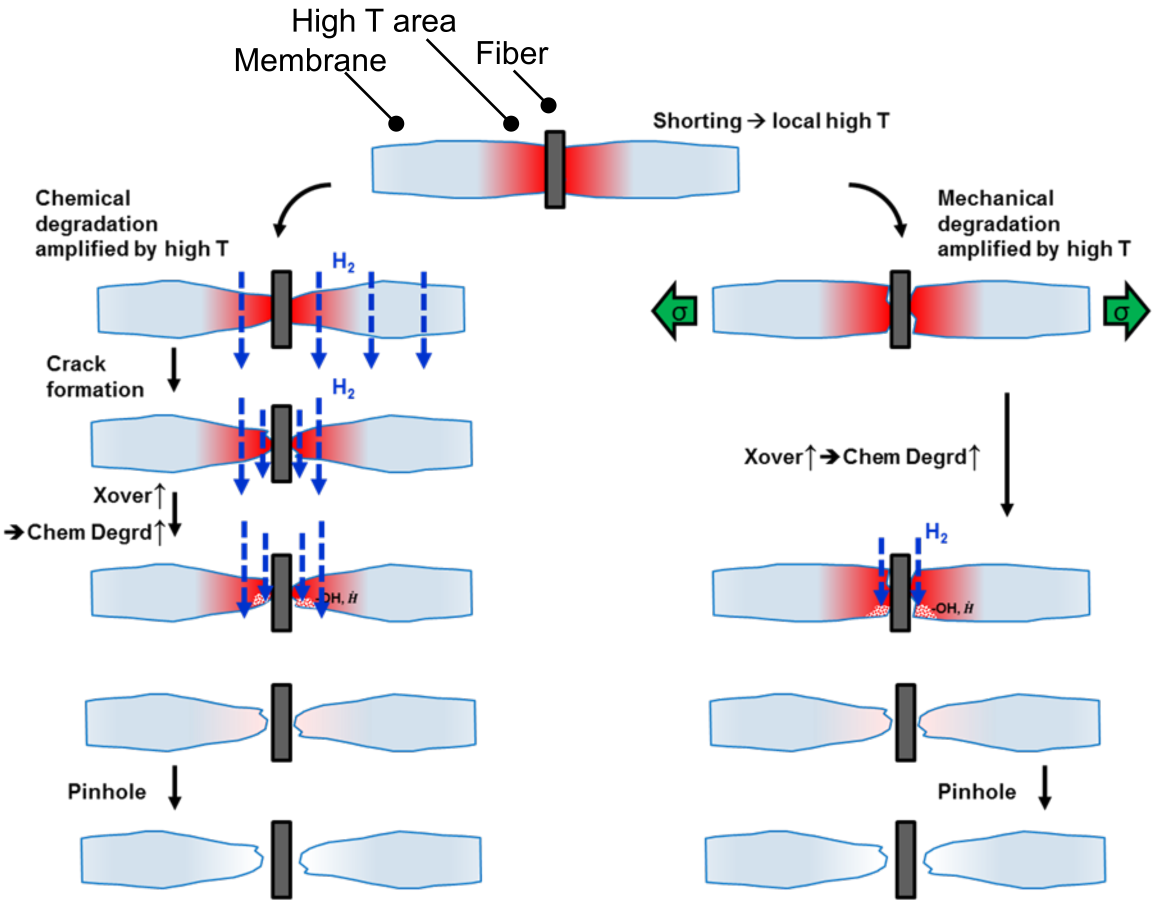
Approach	Fundamental Models	Correlations	Validation	Prediction/Optimization
Task	Match models to ex-situ diagnostic data	Correlations quantifying catalyst degradation	Possible fine tuning and successful validation of the models	Determine rate determining steps at different operating conditions
Experiments	Ex-situ dissolution of Pt & Co, Oxide charge, EPMA, TEM, ASAXS, XRF, EELS, XRD	ECA, SA, HAD, CO stripping, R_{O2} local, Limiting Current, EPMA, TEM	Pol curves, ECA, SA, HAD, CO stripping measured on MEAs used in Design of Experiments	Confirmation Runs
Models	Models for PtO growth, Pt & Co dissolution, Pt & Co transport, Pt shell thickness	Correlations quantifying Pt particle coalescence, changes in specific activity, Pt utilization, $RO_{2,\ local}$	Integrating the fundamental models with correlations to estimate voltage degradation rates	Optimization routines that minimize degradation rates

☐ Develop predictive model based on the experimental data with the fundamental understanding of degradation mechanisms

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

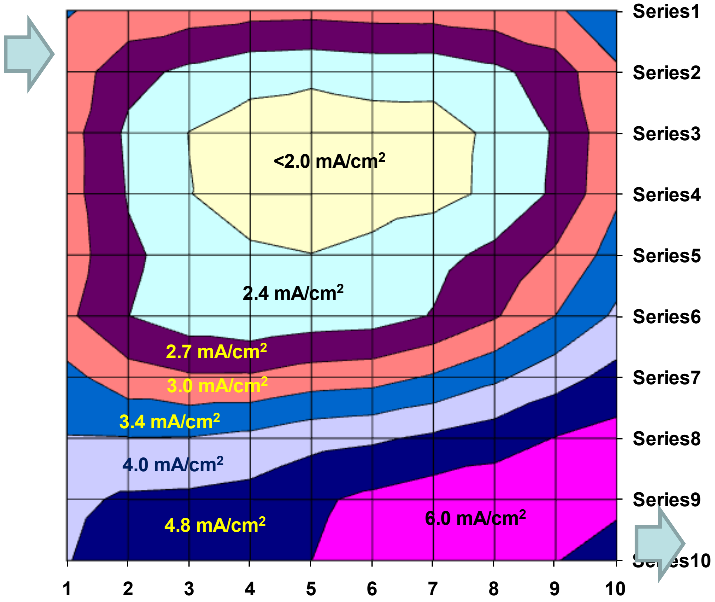
Technical/ Future Work

Shorting effect on Membrane Durability



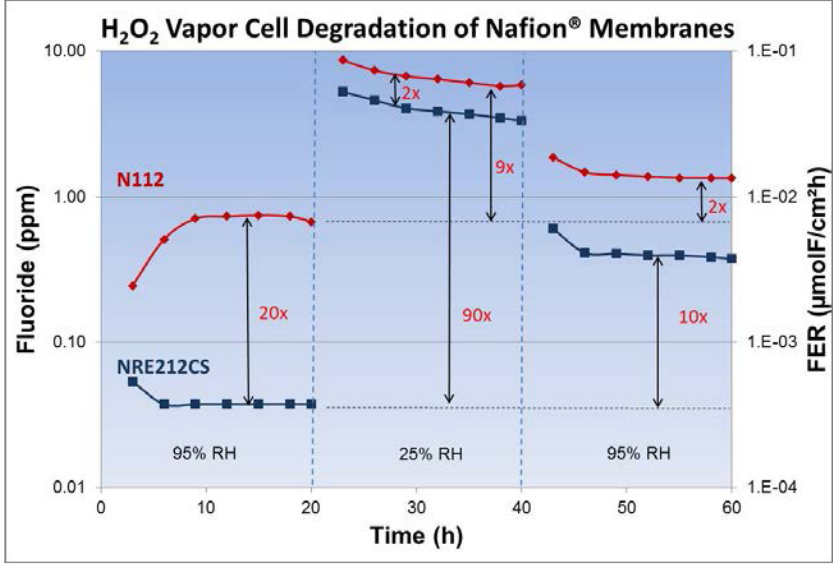
- Use advanced postmortem analysis (X-ray micro-CT, micro-IR) to look for root cause of failure

- Run accelerated single and combined stressor durability tests (OCV, RH cycling) with MEAs with intentional defects and different GDL structures
- Use segmented cell to track high resolution, *in-situ* shorting and convective & diffusive crossover current over time

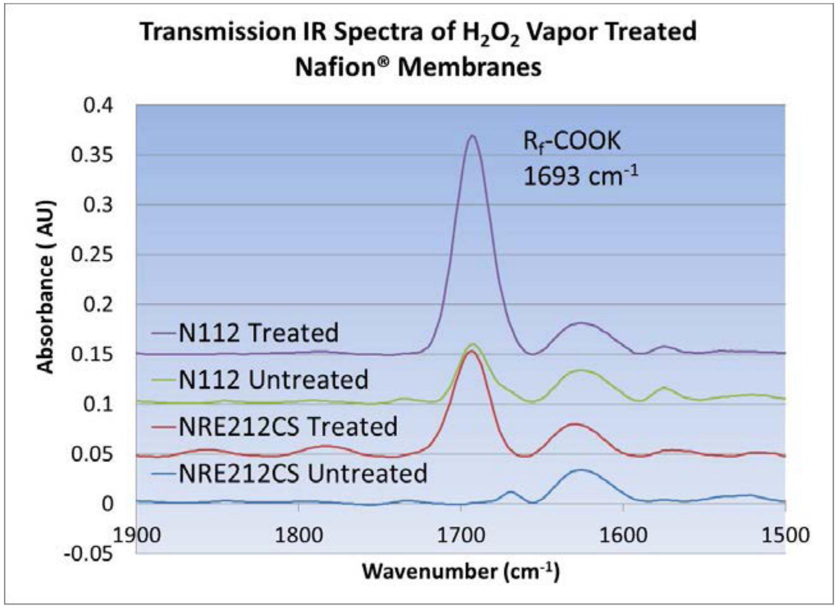


Technical/ Future Work

- **Membrane Chemical Durability**
  - GM & Giner developed peroxide vapor cell test to probe the degradation mechanism and rate of PFSA membranes.
  - Temp, RH, H_2O_2 content in vapor stream can be adjusted to provide a range of reaction conditions.
  - Fluoride emission rates combined with FTIR measurements will be used to determine degradation mechanism (unzipping vs. scission) and reaction orders and rate constants.
  - Increasing fluoride emission rate (FER) of with time suggests that new carboxylic acid end group are being created by scission processes. Steady FER indicates an unzipping mechanism
  - Impact of membrane thickness, end group fluorination and GDL structure on PEM degradation rate and mechanism will be studied.



Three Step H_2O_2 Vapor Degradation Test @ GINER

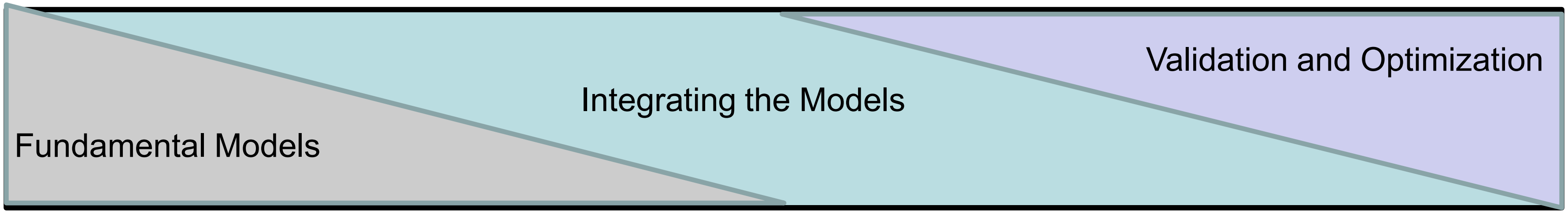


FTIR measurement on degraded MEA
Increase in R_fCOOK peal at 1693cm-1 after H2O2 test indicate PFSA chain scissions occurs at 90ºC, 25% RH (Dry Condition)

*F. D. Coms, ECS Transactions, **16 (2)**, 235-255 (2008).*
H. Xu, C. Mittelstaedt, T. McCallum, F. D. Coms, 220th ECS Meeting, Boston, MA, Oct 13, 2011

Technical/ Future Work

Membrane Degradation Model



Validation and Optimization

Integrating the Models

Fundamental Models

Approach	Fundamental Models	Correlations	Validation	Prediction/Optimization
Task	Match models to ex-situ diagnostic data	Quantifying membrane state of health	Possible fine tuning and successful validation of the models	Determine rate determining steps at different operating conditions
Experiments	OCV tests, RH cycling, HAST, Combined OCV & RH cycling test, Segmented cell.	FTIR, FRR, molecular weight, cross- over current, XRF (Ce)	Cross over, shorting resistance, FRR, pinhole, Residual thickness	Confirmation Runs (segmented HAST)
Models	Mechanical stress model, chemical stress model, cerium distribution model	Quantify stress life coefficients (T, RH to FRR)	Combined chemical and mechanical stress model to predict membrane degradation.	Optimization routines that minimize degradation rates

- Develop combined membrane degradation model based on experimental data with the fundamental understanding of degradation mechanisms

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

Summary

- The project addresses the key DOE 2020 targets in performance, durability and cost.

- A state of art MEA will be delivered to FC-PAD and partners to carry out durability studies before the end of budget period 1.

- Project approach is to use operating conditions as a key differentiator in improving the durability of the membrane electrode assembly.

- Project goal is to map the impact of operating conditions on state-of-art MEA and provide recommendations for MEA design and operation that will extend durability in implementable automotive conditions.

- SODW with FC-PAD partners agreed up on and support for key tasks identified.

Acknowledgements

DOE

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

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- Nagappan Ramaswamy
- Craig Gittleman
- Mark F. Mathias
- Yeh-Hung Lai
- Frank Coms
- Anusorn Kongkanand
- Balsu Lakshmanan

Giner

- Dr. Cortney Mittelsteadt (sub-PI)

Univ of Texas, Austin

- Prof. Paulo Ferreira (sub-PI)

FC-PAD

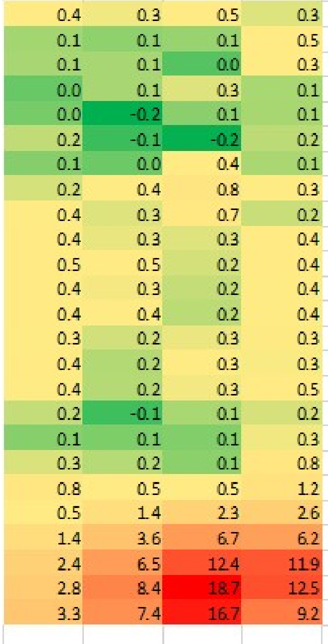
- Rod Borup
- Mukund Rangachary
- Adam Weber
- Debbie Myers
- Rajesh Ahluwalia
- Karren More
- Shyam Kocha
- KC Neyerlin

Technical Back-Up Slides

Combined Chemical and Mechanical stress – Post Durability Test

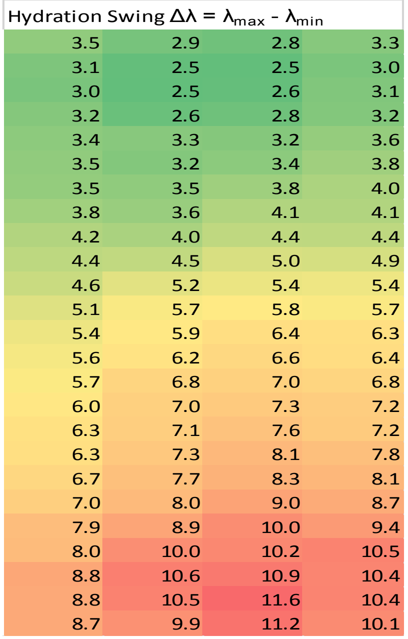
90ºC Highly Accelerated Stress Test
coflow – constant flow - 0.05 – 1.2 A/cm²

X-over current map



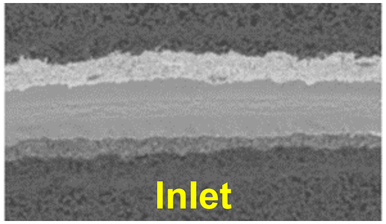
0.4	0.3	0.5	0.3
0.1	0.1	0.1	0.5
0.1	0.1	0.0	0.3
0.0	0.1	0.3	0.1
0.0	-0.2	0.1	0.1
0.2	-0.1	-0.2	0.2
0.1	0.0	0.4	0.1
0.2	0.4	0.8	0.3
0.4	0.3	0.7	0.2
0.4	0.3	0.3	0.4
0.5	0.5	0.2	0.4
0.4	0.3	0.2	0.4
0.4	0.4	0.2	0.4
0.3	0.2	0.3	0.3
0.4	0.2	0.3	0.3
0.4	0.2	0.3	0.5
0.2	-0.1	0.1	0.2
0.1	0.1	0.1	0.3
0.3	0.2	0.1	0.8
0.8	0.5	0.5	1.2
0.5	1.4	2.3	2.6
1.4	3.6	6.7	6.2
2.4	6.5	12.4	11.9
2.8	8.4	18.7	12.5
3.3	7.4	16.7	9.2

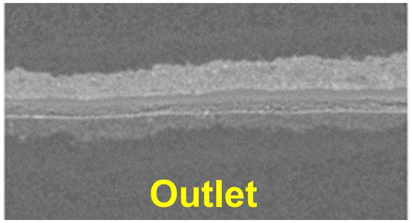
Δλ map (from HFR distr)



Hydration Swing $\Delta\lambda = \lambda_{max} - \lambda_{min}$

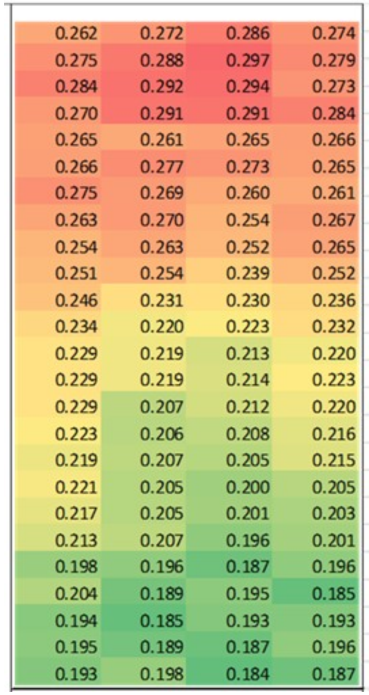
3.5	2.9	2.8	3.3
3.1	2.5	2.5	3.0
3.0	2.5	2.6	3.1
3.2	2.6	2.8	3.2
3.4	3.3	3.2	3.6
3.5	3.2	3.4	3.8
3.5	3.5	3.8	4.0
3.8	3.6	4.1	4.1
4.2	4.0	4.4	4.4
4.4	4.5	5.0	4.9
4.6	5.2	5.4	5.4
5.1	5.7	5.8	5.7
5.4	5.9	6.4	6.3
5.6	6.2	6.6	6.4
5.7	6.8	7.0	6.8
6.0	7.0	7.3	7.2
6.3	7.1	7.6	7.2
6.3	7.3	8.1	7.8
6.7	7.7	8.3	8.1
7.0	8.0	9.0	8.7
7.9	8.9	10.0	9.4
8.0	10.0	10.2	10.5
8.8	10.6	10.9	10.4
8.8	10.5	11.6	10.4
8.7	9.9	11.2	10.1





Failure Mode is membrane thinning (no mechanical damage) - Chemical Degrdation

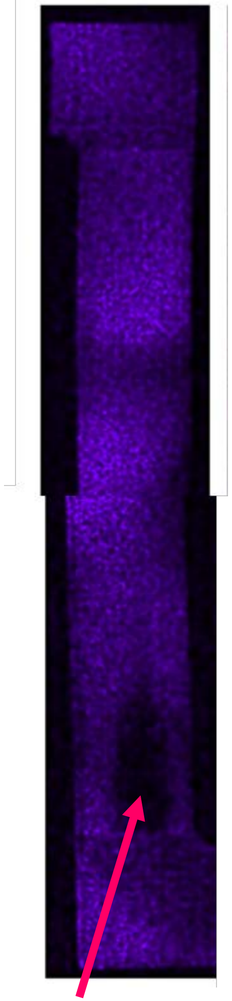
GM Chemical Damage Model predicts more damage in inlet region (lower average RH)



0.262	0.272	0.286	0.274
0.275	0.288	0.297	0.279
0.284	0.292	0.294	0.273
0.270	0.291	0.291	0.284
0.265	0.261	0.265	0.266
0.266	0.277	0.273	0.265
0.275	0.269	0.260	0.261
0.263	0.270	0.254	0.267
0.254	0.263	0.252	0.265
0.251	0.254	0.239	0.252
0.246	0.231	0.230	0.236
0.234	0.220	0.223	0.232
0.229	0.219	0.213	0.220
0.229	0.219	0.214	0.223
0.229	0.207	0.212	0.220
0.223	0.206	0.208	0.216
0.219	0.207	0.205	0.215
0.221	0.205	0.200	0.205
0.217	0.205	0.201	0.203
0.213	0.207	0.196	0.201
0.198	0.196	0.187	0.196
0.204	0.189	0.195	0.185
0.194	0.185	0.193	0.193
0.195	0.189	0.187	0.196
0.193	0.198	0.184	0.187

Failure occurs in area with largest RH swing (near outlet)
- Does mechanical stress accelerate chemical degradation?
- Does RH cycling promote Ce migration?

Ce XRF Map



Ce missing in region where there is crossover