# Durable Fuel Cell MEA through Immobilization of Catalyst Particle and Membrane Chemical Stabilizer

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General Motors LLC, Fuel Cell Business

May 19, 2020

Project ID
FC323

# Overview

## Timeline, Barriers, Budget

### Timeline

- Project start date: 1 Oct 2019
- Project end date: 28 Feb 2023
- Percent complete: < 5%

### Barriers

A. Durability

< 10% power degradation after 30,000 hrs.

B. Cost

< 0.2 $mg_{Pt}/cm^2$ cathode Pt metals loading

C. Efficiency

> 65% efficiency to decrease fuel cost

### Budget

- Total Funding Spent as of 03/31/2020: $0.05M
- Total DOE Project Value: $2.73M
- Cost Share: 26.8%

### Partners

- General Motors LLC (Project lead)
- Subcontractors: *Contracts not yet signed*
  - 3M Company (sub)
  - Pajarito Powder LLC (sub)
  - Colorado School of Mines (sub)
  - Cornell University (sub)
- FCPAD Consortium

# Relevance

## Objectives and Impact

- **Objectives:** Materials-approach to develop, integrate and demonstrate a direct-$H_2$ fed PEM fuel cell MEA for medium-duty (MD) and heavy-duty (HD) applications featuring
  - **low cost** - cathode PGM loading of < 0.2 $mg_{Pt}/cm^2$
  - **high efficiency** - fuel efficiency of >65%
  - **high durability** - < 10% degradation in power density after 30,000 hours of operation (a lifetime of 1 Million miles, ~3X compared to light-duty (LD) vehicles)

| Metric | Units | DOE Target | End of Project Target | Status of Proposed Approach (PtCo) | Status of Proposed Approach (Pt annealed) |
|---|---|---|---|---|---|
| PGM loading (total) | $mg_{PGM}/cm^2$ | 0.25 | < 0.25 | 0.25 | 0.25 |
| Mass activity (MA) [a] | $A/mg_{PGM}$ | > 0.44 | > 0.44 | 0.78 | 0.31 |
| Loss in initial catalytic activity (post-90k) [b] | % MA loss | < 40 | < 40 after 3X AST | 66% | 28% |
| Performance at 0.8 V (150 kPa, 80°C) | $A/cm^2$ | 0.3 | 0.3 | 0.4 | 0.2 |
| Performance at rated power (150 kPaabs, 94 °C) | $mW/cm^2$ | > 1.0 | > 1.0 | TBD | TBD |
| Performance at rated power (250 kPaabs, 94 °C) | $W/cm^2$ | NA | > 1.3 | 1.45 | 1.35 |
| Loss in performance at 0.8 $A/cm^2$ (90-k catalyst cycles)[b] | mV | < 30 | < 30 after 3X AST | 40 | 16 |
| Area specific $H^+$ resistance (80 °C & water partial pressures from 25-45kPa) | $\Omega\cdot cm^2$ | 0.027 | <0.02 | 0.027 | 0.027 |
| Membrane durability (Combined chemical/mechanical) [e] | Hours | 30000 | 30000 | 10000 | 10000 |

[a] Test at 80 °C, $H_2/O_2$ in MEA; fully humidified with total outlet pressure of 150 kPaa; anode/cathode stoichiometry 2/9.5;

[b] Catalyst/support durability testing performed according Tables P1/P2 in Appendix of EERE Fuel Cells MYRRDD Plan

[e] To demonstrate the ability to reach 30,000h of drive cycle durability, the goal is for the membranes developed in this project to run for <1625h in the 90ºC HAST test, which has proven to accelerate the time to failure of a state-of-the-art membrane by >15X.

# Relevance
## Major technical challenges to be overcome

1) **Electrocatalyst surface area loss**
    1) Major contributor to cell voltage loss
    2) Mechanisms:
        1) Ostwald ripening
        2) Pt particle migration and coalescence
        3) Pt-mass loss to membrane phase (“Pt-band” formation)

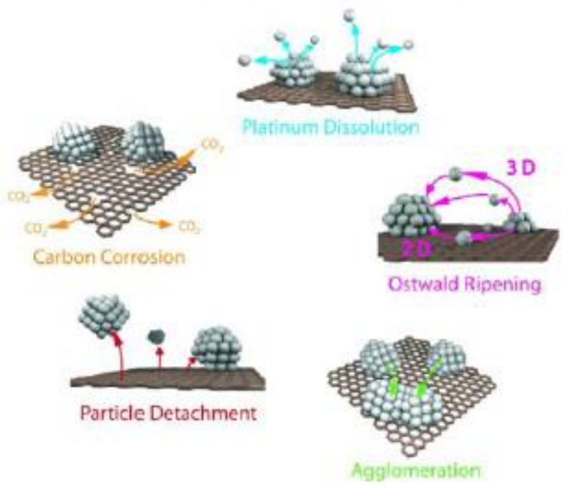
2) **Electrocatalyst specific activity loss**
    1) Pt-shell thickening (extension of Ostwald ripening)
    2) $Co^{2+}$ dissolution and contamination

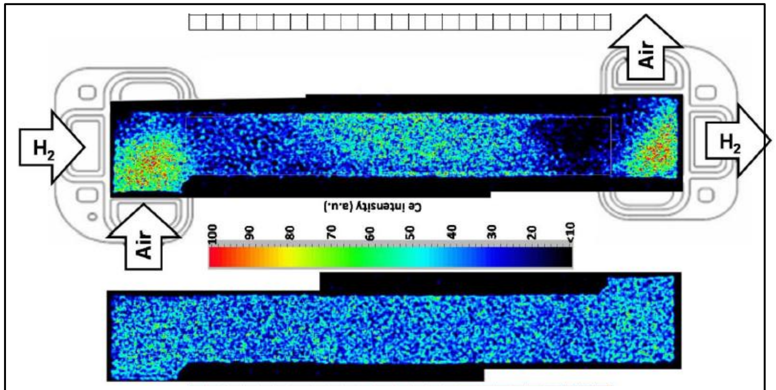
3) **Local reactant transport and HCD performance losses**
    1) Relatively a minor loss factor at BOL (≥ 0.1 $mg/cm^2$ loading)
    2) Plays a role in stack sizing (EOT performance at HCDs)
        1) Catalyst aging: ECSA loss, Pt particle location changes, Pt-ionomer interactions

4) **Carbon Support Corrosion**
    1) Idle/OCV conditions (0.90 to 0.95 V)
    2) Load cycles (0.6 to 0.95 V, ~90k cycles)
    3) Unmitigated startup/shutdown transients (> 1.0 V)

5) **Cerium migration and membrane durability limitations**
    1) Migration of $Ce^{3+}$-cation salt additive due to RH gradients
    2) Can lead to premature membrane failure
    3) Key factor to enable 25000 hours MEA durability

**Pt Surface Area Loss Mechanisms**





**$Ce^{3+}$ cation XRF images of BOL (Bottom) and EOT (Top) MEA subjected to 90 °C, 30% RH HAST test**

S. Cherevko *et al.*, *Nano Energy*, 29, 275-298, (2016)
E. Padgett *et al.*, *J. Electrochem. Soc.*, 166, 4, F198-F207, (2019)
Y.H. Lai *et al.*, *J. Electrochem. Soc.*, 165, 6, F3217-F3229, (2018)

# Overall Approach
## Durable cathode and membrane development via immobilization

1) **Develop highly-accessible, graphitized mesoporous carbon (GMC) support with anchoring agents (GM/Pajarito/Cornell)**
   1) Develop graphitized carbon supports with tuned mesoporosity
   2) Embed acid-stable and conductive metal/metal-oxide based anchoring agents to prevent catalyst surface area loss

   Expected Outcome: catalyst with higher resistance to nanoparticle sintering and carbon support corrosion

2) **Develop ordered PtCo intermetallic catalysts (GM/Pajarito/Cornell)**
   1) Develop intermetallic catalysts with ordered $Pt_3Co$ core and Pt shell that show enhanced retention of activity and HCD performance

   Expected Outcome: PtCo catalysts with ORR activity and HCD performance exceeding DOE targets and with resistance to surface area loss.

3) **Stabilization of catalyst with polymers and additives (GM)**
   1) Modify catalyst-ionomer interface, water activity, oxide formation kinetics with hydrophobic polymer additives

   Expected Outcome: Electrode with less ECSA loss via decreased Pt dissolution/redeposition

4) **Stabilize PFSA membranes via stabilizer immobilization (GM/3M/CSM)**
   1) Heteropoly acid tethered membrane
   2) Cerium zirconium oxide nanoparticles/nanofibers stabilized membrane

   Expected Outcome: Highly durable membranes that meet 30,000 hours of durability requirements

# Approach (Cathode Durability)

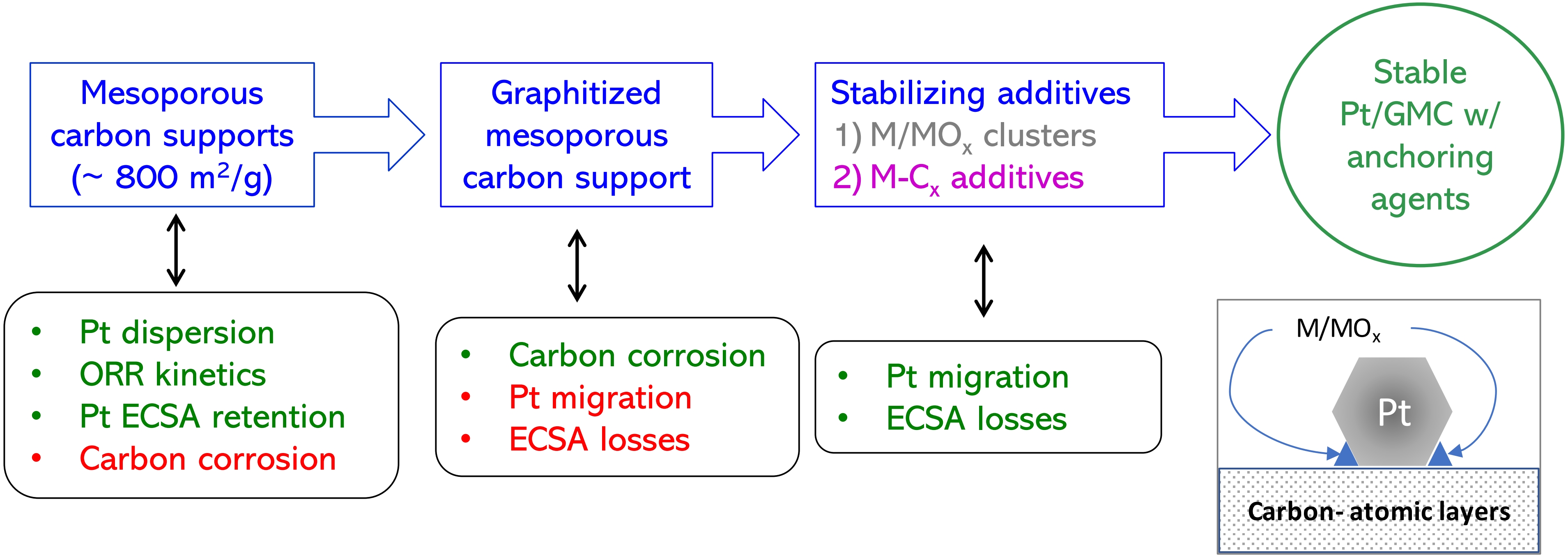
## Metal anchored catalysts

**Challenge:** Mitigate Pt surface area loss via prevention of migration/coalescence

**Approach:**

- Develop graphitized mesoporous carbon (GMC) support with tuned micro-/meso-porosity
- Modify Pt-carbon interface via use of metal anchoring agents to mitigate Pt dissolution/migration

**Path to highly durable catalyst development**



Mesoporous carbon supports (~ 800 $m^2/g$)

- Pt dispersion
- ORR kinetics
- Pt ECSA retention
- Carbon corrosion

Graphitized mesoporous carbon support

- Carbon corrosion
- Pt migration
- ECSA losses

Stabilizing additives
1) $M/MO_x$ clusters
2) $M\text{-}C_x$ additives

- Pt migration
- ECSA losses

Stable Pt/GMC w/ anchoring agents

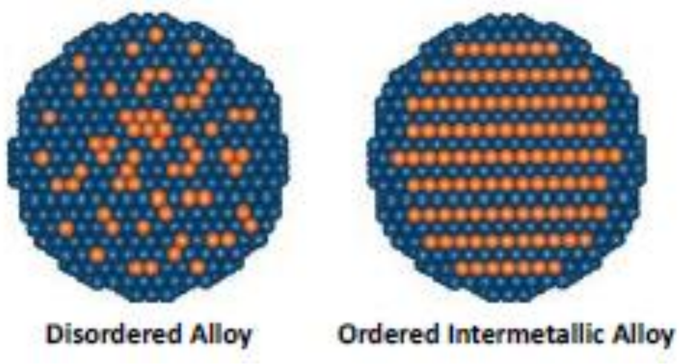
# Approach (Cathode Durability)

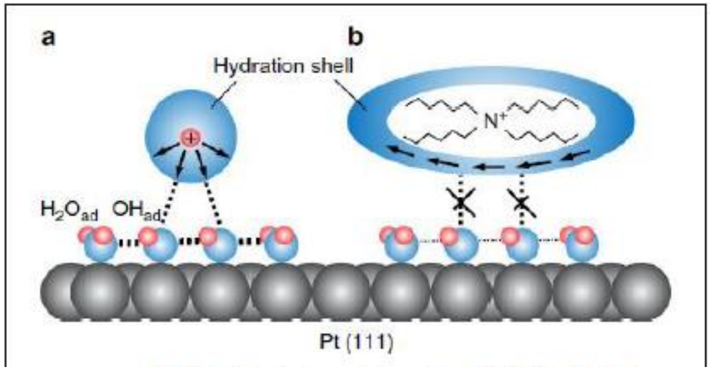
## Ordered alloy nanostructures and interfaces

**Challenge:** Mitigate surface area loss via prevention of Pt and Co dissolution

**Approach:**

- Improve catalyst nanostructure durability via use of ordered-PtCo intermetallic catalysts
- Modify Pt-ionomer interface via use of hydrophobic polymer additives





- Ordered $Pt_3Co$ catalysts enable higher ECSA, MA and cell voltage retention due to increased resistance to PtCo dissolution
- Synthesize o-$Pt_3Co$ catalysts on the anchored GMC support

- Mitigation of Pt-O(H) formation could potentially improve ORR kinetics and durability
- Evaluate the effect of commercially available hydrophobic polymer, ionic liquids and large cations

T. Kumeda et al, *Nat. Commun.*, 9 (1), 4378, **2018**

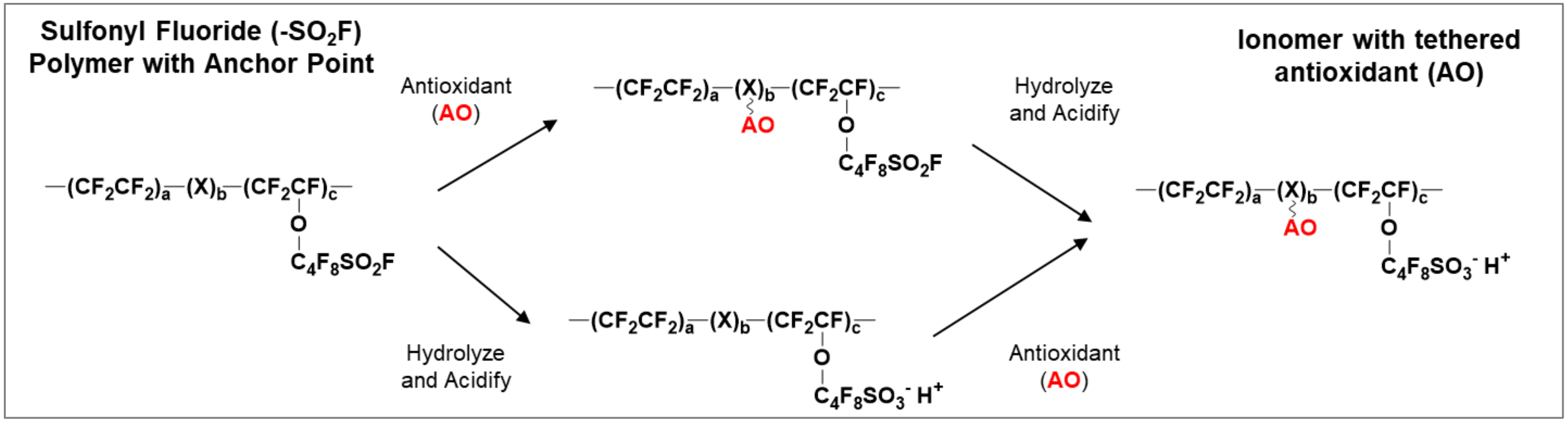
# Approach (Membrane Durability)

## Stable PFSA membrane using covalently tethered additives

**Challenge:** Covalently immobilize •OH-radical decomposition additives in the membrane

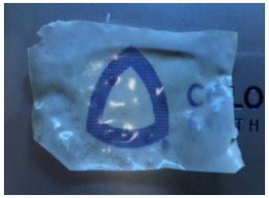
**Approach:**

- Use heteropolyacid (HPA) based antioxidants as radical decomposition catalysts covalently attached to the PFSA membrane



- Synthesize sulfonyl fluoride ($-SO_2F$) polymers with reactive anchor points (3M)
- Attach antioxidant (AO) to polymer through covalent bonds (CSM)
  - Options: Attach prior to hydrolysis and acidification or vice versa
- Vary monomer ratios a:b:c to optimize ionomer performance and durability (3M and CSM)
- Fabricate and test ePTFE supported membranes using HPA-tethered PFSA ionomers (GM)

**PFSA** + **$-SO_2F$ Polymer** + **Antioxidant** →



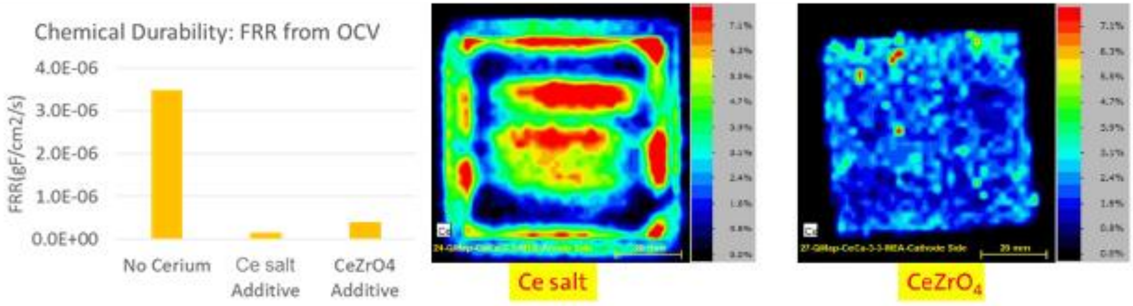
# Approach (Membrane Durability)

## Stable PFSA membrane using cerium zirconium oxide additives

**Challenge:** Mitigate the migration of $Ce^{3+}$-salt based additives via use of insoluble CZO additives

**Approach:**

- Use of cerium zirconium oxide (CZO) nanoparticles or nanofibers as additive in MEA, for:
  - Membrane chemical stability
  - Reduced Ce migration
- Apply CZO in membrane or electrode layers
- Evaluate fuel cell performance and chemical stability on MEAs with CZO
- Evaluate Ce migration profile using XRF mapping (post the highly accelerated stability test)



(Left) Fluoride release rate during 200 hrs OCV test at 95 °C and 25% RH on PFSA membranes with and without Ce stabilizers; (center) Ce XRF map of Ce salt stabilized PFSA membrane and (right) $Ce_xZe_yO_4$ nanofiber stabilized PFSA membrane after 85 hrs at 1.0 A/$cm^2$, 80 °C and 100% RH.

- CZO nanofibers may also provide enhanced mechanical durability
- Negligible local cerium redistribution within the membrane compared to mobile Ce salts

# Approach

## Milestones and go/no-go decisions

### TASK 1 – Development of Catalyst and Membrane Materials with Chemical Stabilizers

Go/No-go criteria: Anchored Pt catalyst with >60 $m^2/g_{Pt}$ at BOL and >35 $m^2/g_{Pt}$ ECSA at EOT (30k LDV AST MEA)

- ☐ Develop anchored Pt-M/$MO_x$ nanocluster catalysts supported on GMC
- ☐ PFSA synthesis and HPA functionalization
- ☐ $Ce_xZr_yO_4$ nanoparticle/nanofiber – PFSA membrane development
- ☐ Fuel cell MEA performance and diagnostics

### TASK 2 – Integration of Highly Durable Catalysts and Membranes into MEAs

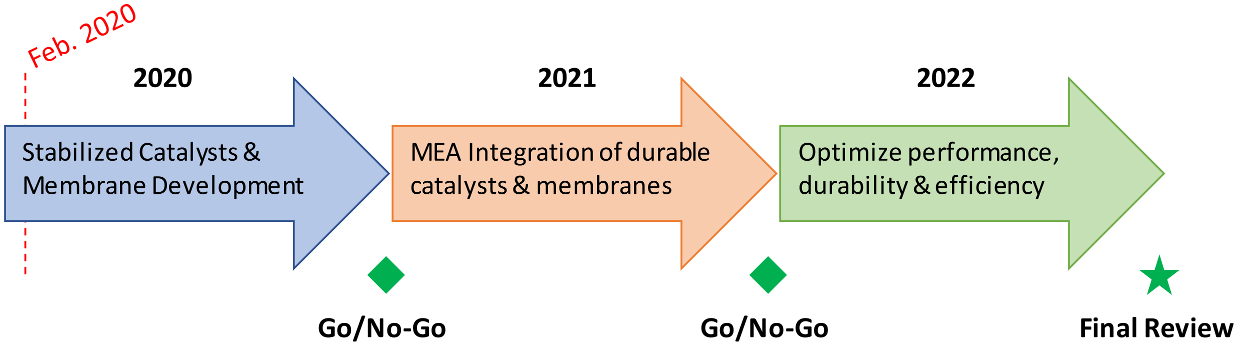
Go/No-go criteria : Anchored Pt catalyst with <30 mV loss at 0.8 A/$cm^2$ (60k LDV AST MEA) and membrane that meets all DOE Technical Targets (gas crossovers, ASR, chemical and mechanical durability)

- ☐ Optimization of down-selected anchored GMC catalyst
- ☐ ePTFE supported membrane development
- ☐ Fuel cell MEA performance and durability (AST)
- ☐ Advanced characterizations of catalysts and membranes

### TASK 3 – Optimization of High Performance, Efficiency and Durability

Milestone: Deliver MEA with <0.2 $mg_{Pt}/cm^2_{cathode}$, <40% loss in MEA, <10% loss in power after 25000 hours based on fuel cell system model lifetime projection studies

- ☐ Deliver MEA with state-of-the-art durable catalyst and membranes with high performance, efficiency and durability
- ☐ Ordered intermetallic PtCo catalyst development on down-selected anchored GMC support
- ☐ Optimization for durability of membranes with chemical stabilizers
- ☐ MEA degradation mechanisms analysis; MEA durability modeling and projections to life



Feb. 2020

2020

Stabilized Catalysts & Membrane Development

2021

MEA Integration of durable catalysts & membranes

2022

Optimize performance, durability & efficiency

Go/No-Go

Go/No-Go

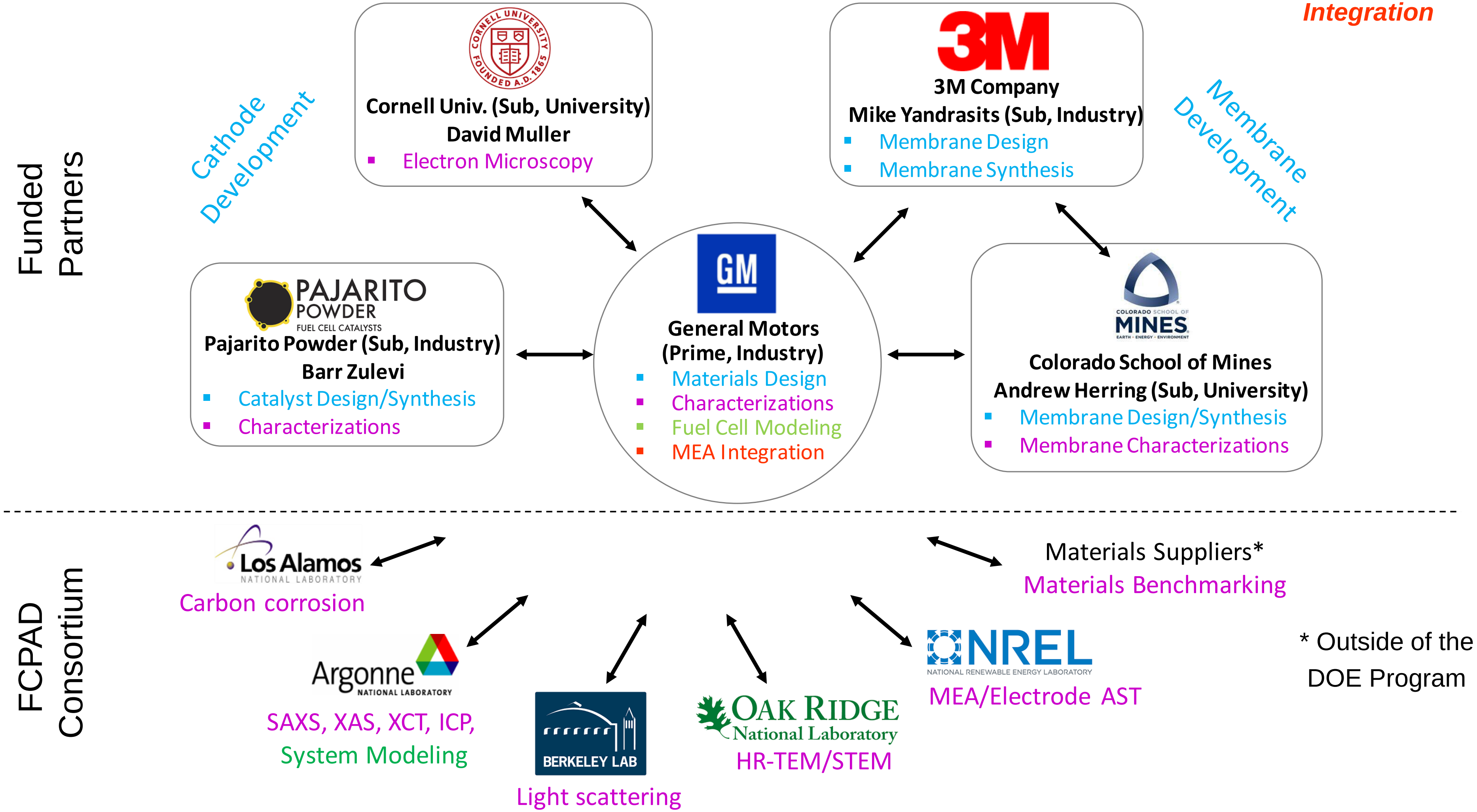
Final Review

# Collaborations and Coordination

## Project team

**Not signed**

*Materials dev't*
*Characterization*
*Modeling*
*Integration*



Funded Partners

Cathode Development

**Cornell Univ. (Sub, University)**
**David Muller**
- Electron Microscopy

**3M Company**
**Mike Yandrasits (Sub, Industry)**
- Membrane Design
- Membrane Synthesis

Membrane Development

**Pajarito Powder (Sub, Industry)**
**Barr Zulevi**
- Catalyst Design/Synthesis
- Characterizations

**General Motors**
**(Prime, Industry)**
- Materials Design
- Characterizations
- Fuel Cell Modeling
- MEA Integration

**Colorado School of Mines**
**Andrew Herring (Sub, University)**
- Membrane Design/Synthesis
- Membrane Characterizations

FCPAD Consortium

Los Alamos National Laboratory: Carbon corrosion

Argonne National Laboratory: SAXS, XAS, XCT, ICP, System Modeling

Berkeley Lab: Light scattering

Oak Ridge National Laboratory: HR-TEM/STEM

NREL National Renewable Energy Laboratory: MEA/Electrode AST

Materials Suppliers*
Materials Benchmarking

* Outside of the DOE Program

- All the partners are within of the DOE Hydrogen and Fuel Cells Program
- There is extensive collaboration between the funded partners who are experts in their fields of research and all of them play a critical role in achieving the project objectives

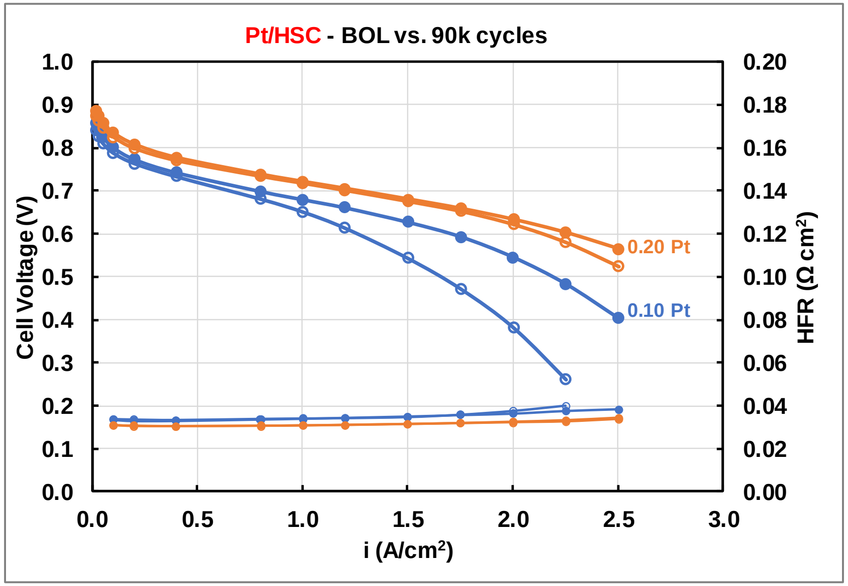
# Technical Accomplishment

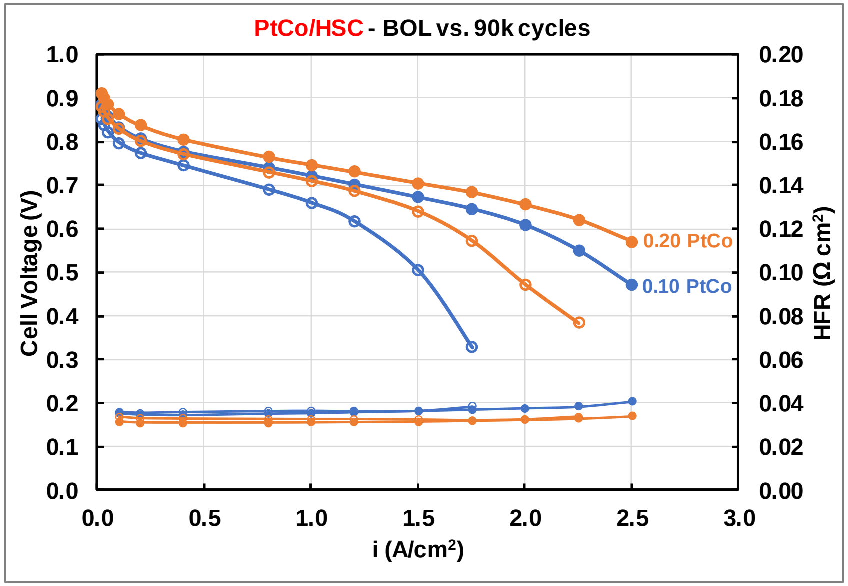
## FCPAD MEA benchmarking (Pt vs. PtCo)

- Benchmark the durability of baseline Pt/HSC and PtCo/HSC catalysts
  - Use light-duty vehicle catalyst AST protocol (90k cycles)
- Both catalysts have a BOL average particle size of ~4.5 nm

Catalyst AST protocol
Trapezoidal waveform
0.6 to 0.95 V, **90k cycles**
$H_2/N_2$, 80 °C, 100% RH

**Pol Curve Conditions: $H_2$/air, 80 °C, 100% RH, 150 kPaa, high stoics**





**Membrane: 12 µm PFSA membrane. Anode: 0.05 $mg_{Pt}/cm^2$**

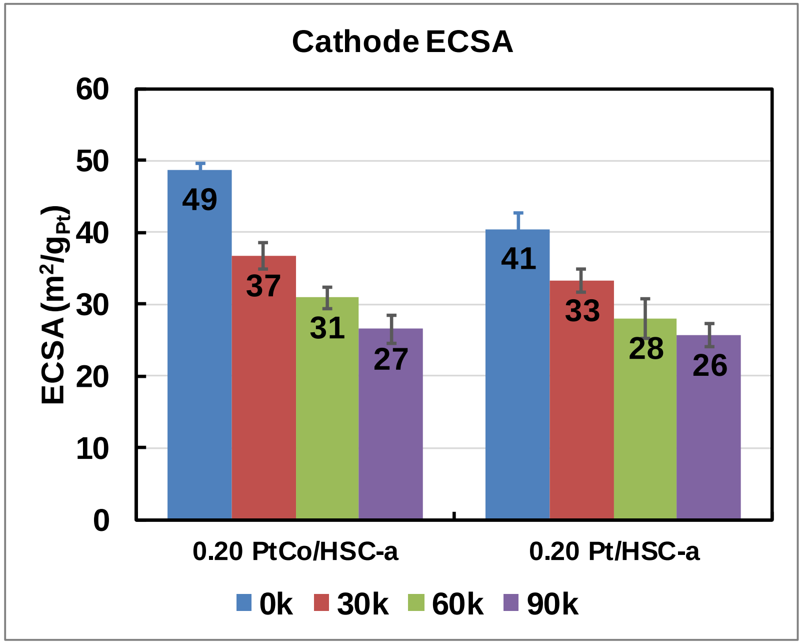
**Closed circles - BOL**
**Open circles - EOT (90k cycles)**

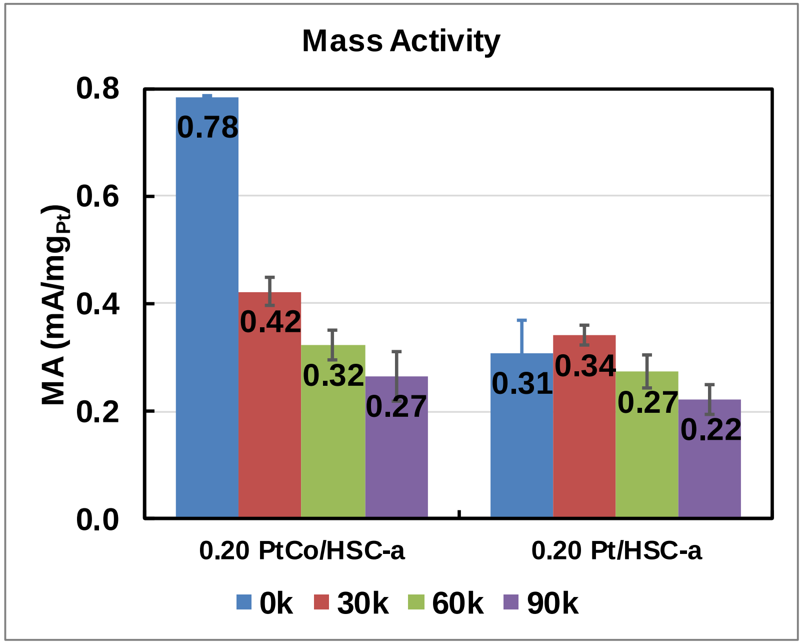
- PtCo/HSC alloy catalyst show significant loss in cell voltage post-90k voltage cycles
- Pt/HSC catalyst at 0.2 $mg_{Pt}/cm^2$ shows exceptional stability in cell voltage at EOT

# Technical Accomplishment

## FCPAD MEA benchmarking (Pt vs. PtCo)

- ECSA of the two catalysts are ~45 $m^2/g_{Pt}$ at BOL
- PtCo/HSC is ~2.5 times more active than Pt/HSC





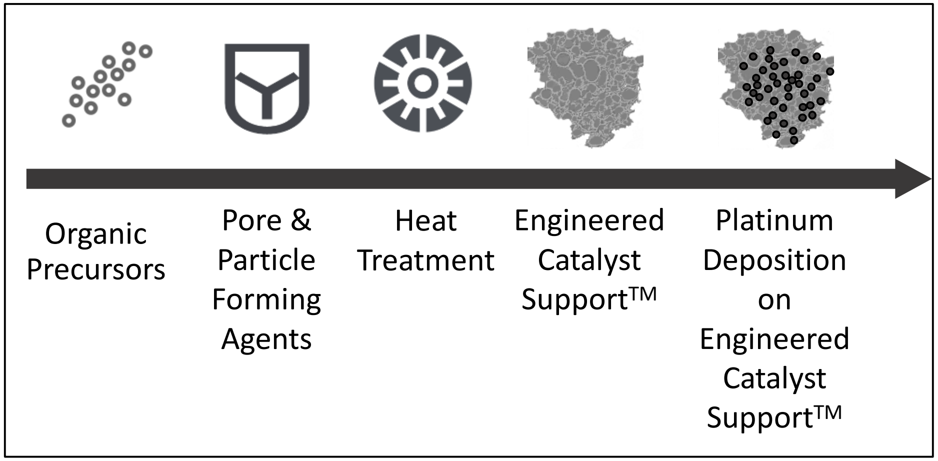
- Roughly similar ECSA loss for both Pt and PtCo (from ~45 to ~25 $m^2/g_{Pt}$ post-90k cycles)
- Mass activity loss for PtCo/HSC catalyst more than the DOE target of <40% at EOT
  - Activity benefit of PtCo over Pt is almost lost within the first 30k cycles.
- Mass activity of Pt/HSC stable in the first 30k cycles followed by a ~30% loss post-90k cycles

# Technical Accomplishment

## Development of Pt-$MO_x$/GMC immobilized catalysts

- Varipore manufacturing platform is being used to develop catalyst with three focal points
  - Mesoporosity (~6 nm and ~40 nm) for Pt accessibility and mass transport
  - Graphitization (500 to 900 $m^2/g$) for carbon stability
  - Metal dopants (ex: Niobium) for Pt stability

**Varipore Manufacturing Platform**



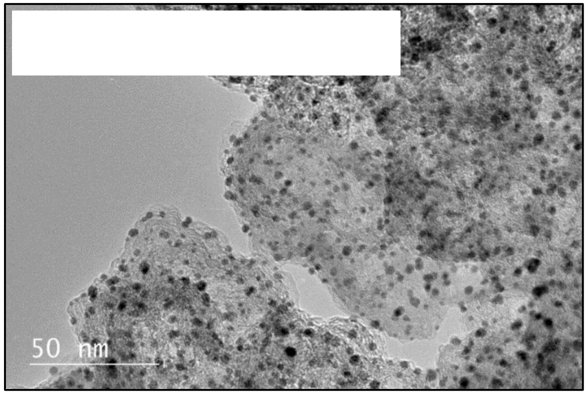
Organic Precursors

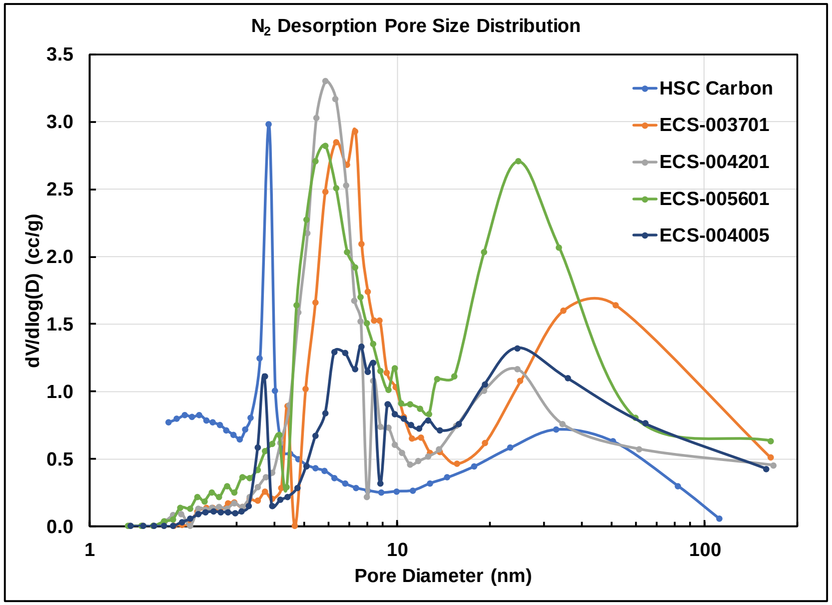
Pore & Particle Forming Agents

Heat Treatment

Engineered Catalyst Support™

Platinum Deposition on Engineered Catalyst Support™



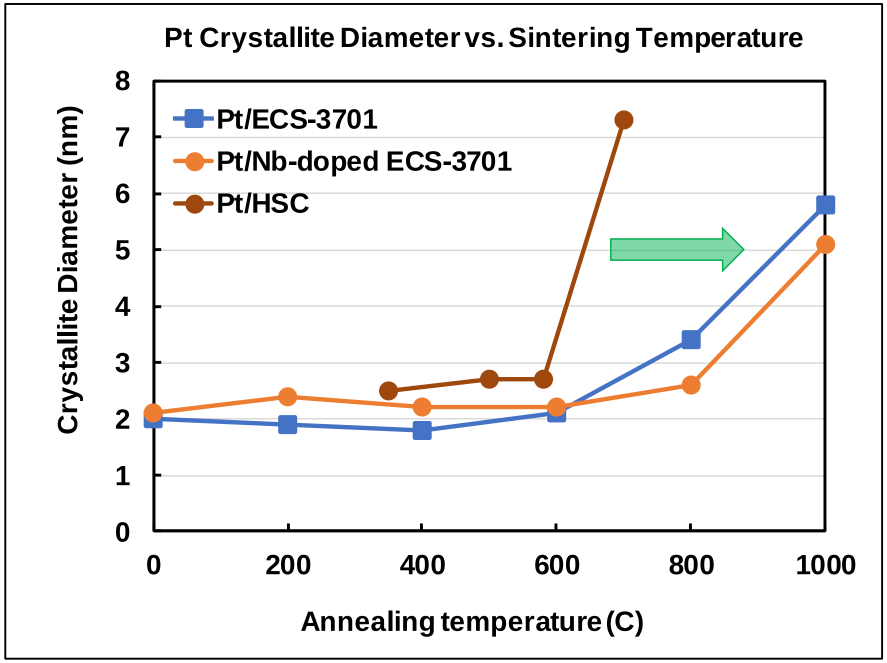


- Four ECS supports have been manufactured with varying pore size and pore volumes that will be compared to determine the optimal support shape and pore size form.

# Technical Accomplishment

## Development of Pt-$MO_x$/GMC immobilized catalysts

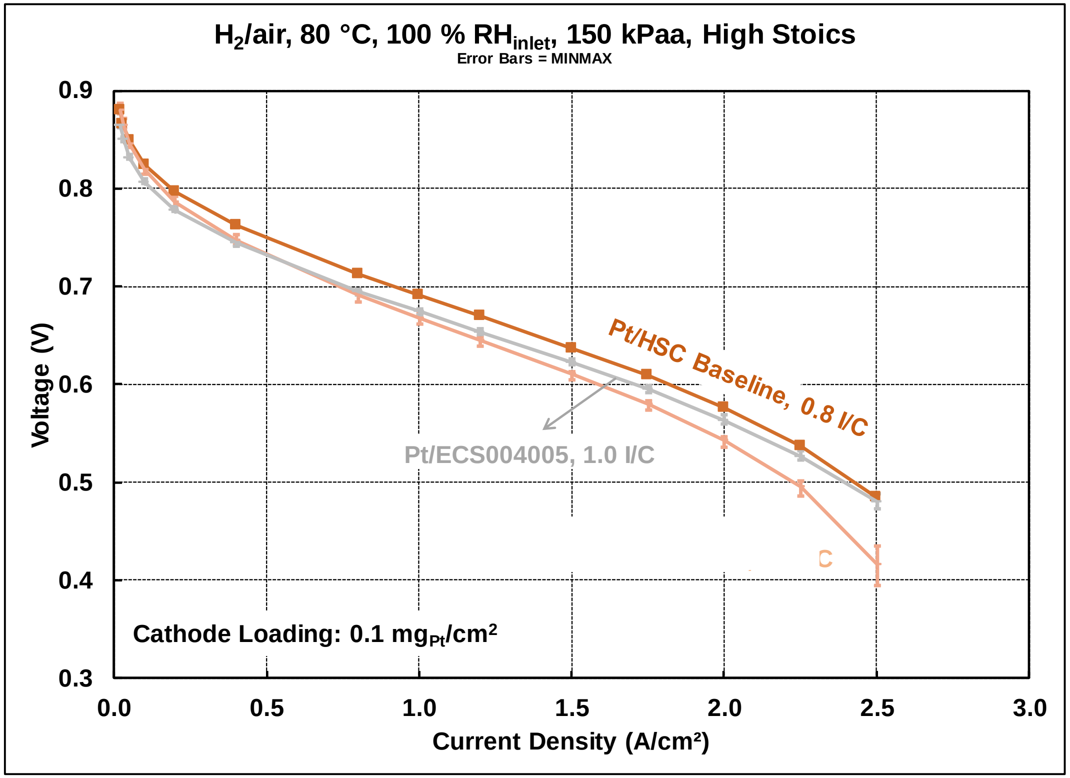
- For the anchored catalysts, the addition of metal anchoring agent on the GMC support involves two different approaches
  - a) $MO_x$ nanocluster approach
  - b) the atomically dispersed M-$C_y$ embedded approach
- Several different metal dopants (ex: Niobium) for Pt catalyst stability have been shortlisted



- *Ex situ* studies have been carried out to understand the sintering resistance of the ECS support and the metal anchoring agent.
- XRD crystallite diameter shows that the ECS support provides sintering resistance to Pt compared to KetjenBlack type conventional HSC supports
- Metal anchoring agent (ex: Nb) provides further additional resistance towards Pt sintering
- An *in situ* CO chemisorption method to quantify surface area loss via thermal sintering is also being developed

# Technical Accomplishment

## Pt/GMC catalysts with tuned porosity



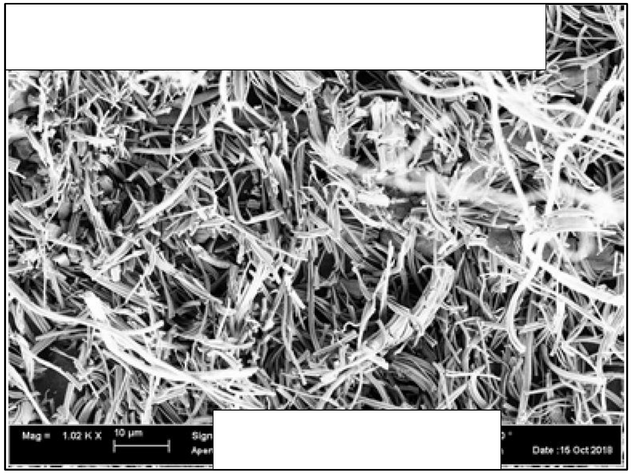
| Catalyst | $H_{UPD}$ ECSA ($m^2/g_{Pt}$) | Specific Activity ($\mu A/cm^2_{Pt}$) |
|---|---|---|
| 20% Pt/HSC Baseline | 73 ± 5 | 427 ± 16 |
| Pajarito 20% Pt/ECS003701 | 70 ± 5 | 462 ± 19 |
| Pajarito 20% Pt/ECS004005 | 65 ± 5 | 353 ± 58 |

- Promising BOL performance for Pajarito catalysts. Need more studies on ink formulation and electrode design to suit the engineered carbon supports with tuned porosity.
- Criteria used for metal dopant selection – acid stability, cost, Pt affinity, membrane compatibility, toxicity and prior literature information.
- A priority list of metal dopants has been prepared based on several criteria
  - Focus on several acid-stable elements (ex: Nb)
  - Ir and Au are precious metals that could be used in low quantities due to their high stability

# Technical Accomplishment

## CZO membrane additives - OCV durability and $H_2$/air performance

- CZO immobilized PFSA membranes were successfully fabricated
  - solution containing $Ce_xZr_yO_4$ additive and PFSA ionomer was dispersed in water/alcohol solvent followed by coating to fabricate 12 µm thick ePTFE reinforce membranes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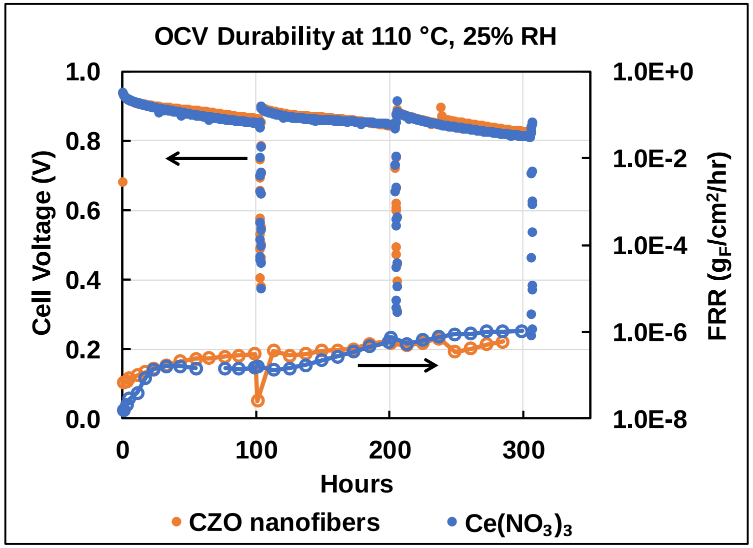
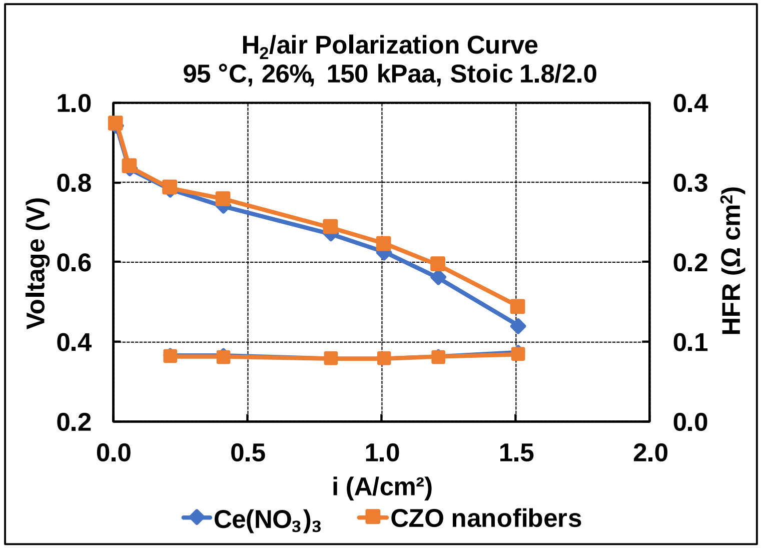




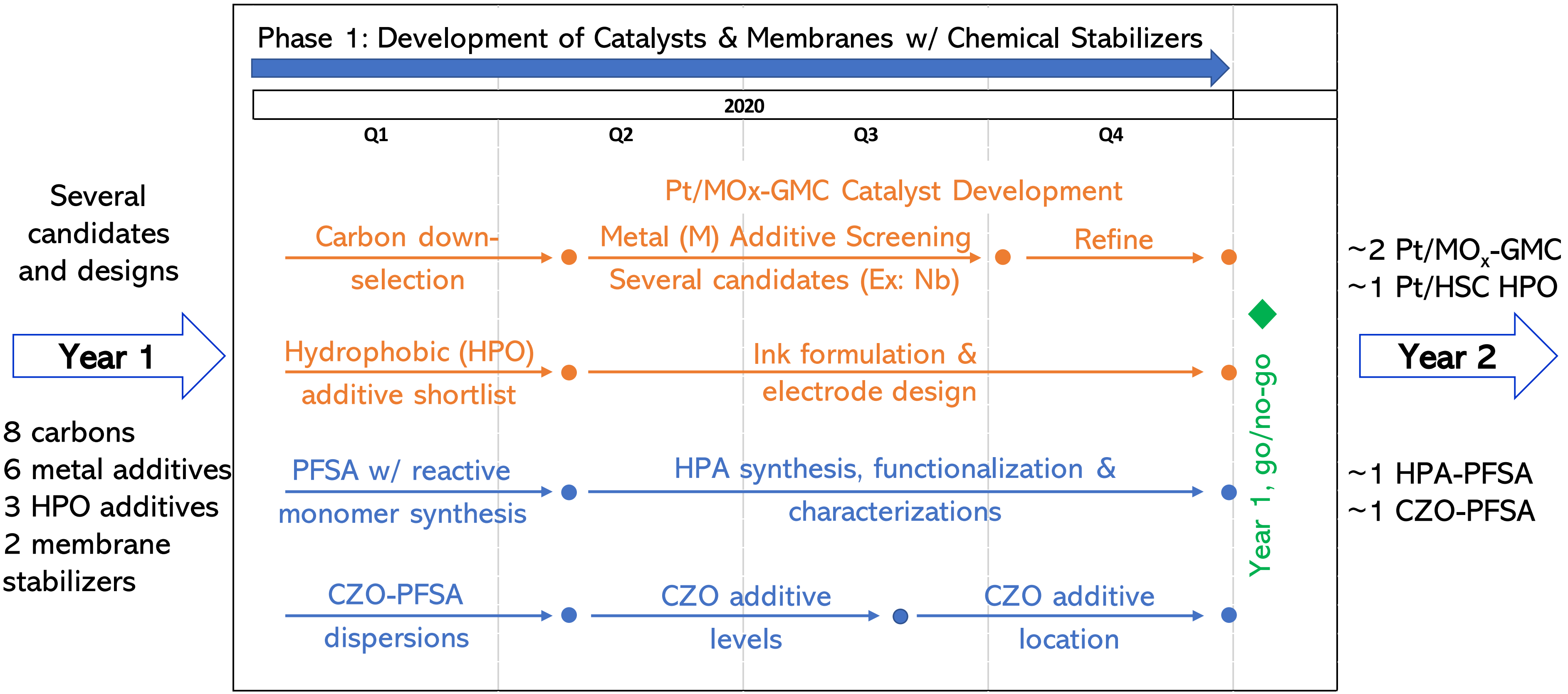
- OCV durability shows similar results between $Ce(NO_3)_3$ salt and CZO nanofiber membrane additives without compromising the fuel cell performance
- This confirms the functionality of the CZO nanofiber additive in membrane durability

# Responses to Last Year AMR Reviewers' Comments

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

# Proposed Future Work

## Materials selection: 1st year work flow



Several candidates and designs

**Year 1**

8 carbons
6 metal additives
3 HPO additives
2 membrane stabilizers

Phase 1: Development of Catalysts & Membranes w/ Chemical Stabilizers

2020

Q1 | Q2 | Q3 | Q4

Pt/MOx-GMC Catalyst Development

Carbon down-selection → Metal (M) Additive Screening, Several candidates (Ex: Nb) → Refine

Hydrophobic (HPO) additive shortlist → Ink formulation & electrode design

PFSA w/ reactive monomer synthesis → HPA synthesis, functionalization & characterizations

CZO-PFSA dispersions → CZO additive levels → CZO additive location

Year 1, go/no-go

~2 $Pt/MO_x$-GMC
~1 Pt/HSC HPO

**Year 2**

~1 HPA-PFSA
~1 CZO-PFSA

- Year 1 to focus on individual development of stabilized catalysts and membranes along with extensive materials characterizations *(in-house and FCPAD)*
- Year 2 will focus on integration of highly stable catalysts and membrane candidates while continuing to refine the synthesis of materials

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

# Proposed Future Work

## Selection methods

| Component | Sub component | Property | Method |
|---|---|---|---|
| Cathode | Carbon | Surface area, pore structure, Graphitization | $N_2$ adsorption (BET-BJH)<br>Raman Spectroscopy |
| | Metal additive ($M/MO_x$) | Acid stability, Pt affinity<br>Membrane Compatibility<br>Cost | ICP-MS, thermodynamics, Pt-M alloy heat of formation<br>$H_2$/air OCV durability |
| | HPO Additive | Dispersibility, Activity, Stability | Catalyst ink rheology, RDE activity, MEA performance and durability |
| | Catalyst (Pt, PtCo/C) | Catalyst activity, Reactant ($H^+$, $O_2$) transport | MEA $H_2/O_2$, $H_2$/air polarization<br>$H_2/N_2$ impedance, $O_2$ limiting current |
| | | Pt migration,<br>Catalyst durability<br>$Co^{2+}$ distribution | STEM imaging, *in situ* sintered CO chemisorption, DOE LDV AST (catalyst & carbon), EPMA, µ-XRF |
| Membrane | HPA-PFSA | Performance and durability | MEA $H_2$/air polarization, conductivity, OCV durability, highly accelerated stress test (HAST), Ce-XRF mapping |
| | CZO-PFSA | | |

- Many techniques were identified to use for selection although not all will be applied.
- Some techniques are solely for understanding performance (modeling).
- MEA performance will ultimately be the overriding selection criteria.

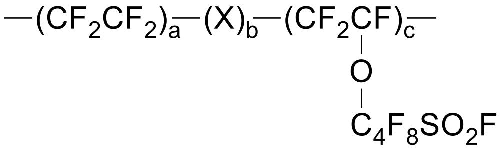
Any proposed future work is subject to change based on funding levels.

# Proposed Future Work

## Membrane future plans

<u>HPA Immobilized Membranes</u>

- First experimental terpolymer produced with reactive anchor point
- Attached antioxidant to terpolymer. First membrane sample casted. Benchmark the chemical stability of functionalized ionomer prior to antioxidant addition (BP1)
- Produce additional precursor ionomers with different comonomer ratios (a:b:c) (BP2)



$$-(\mathrm{CF_2CF_2})_a-(\mathrm{X})_b-(\mathrm{CF_2}\underset{\substack{|\\ \mathrm{O}\\ |\\ \mathrm{C_4F_8SO_2F}}}{\mathrm{CF}})_c-$$

- Fabricate mechanically reinforced membranes with tethered antioxidant
- Evaluate durability in DOE AST and GM’s Highly Accelerates Stress Test (HAST) at 90 °C which combines chemical and mechanical stressors conditions (FC156)

<u>CZO Immobilized Membranes</u>

- Conduct XRF on Ce distribution
- Test performance, OCV durability, HAST durability on MEAs with different levels of CZO in membranes or electrodes

# Proposed Future Work

## FCPAD engagement and timeline

- ❑ FCPAD consortium laboratories will be engaged strategically for achieving the overall goals of the project (electrochemical diagnostics, x-ray characterizations, analytical measurements, post-mortem experiments, fuel cell system modeling studies)

**FCPAD Engagement Timeline**

DE-FOA-0002044 (Control #2044-1551)

| | | | | 2020 | | | | 2021 | | | | 2021 | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **TASK** | **FCPAD Lab** | **Sample Type** | Q4 | Q1 | Q2 | Q3 | Q4 | Q1 | Q2 | Q3 | Q4 | Q1 | Q2 | Q3 | Q4 |
| **Year 1 - 2020** | | | | | | | | | | | | | | | |
| Light scattering and viscosity (CZO - PFSA dispersions) | LBNL | Ionomer dispersions | | ■ | ■ | ■ | ■ | | | | | | | | |
| SAXS and XCT characterizations | ANL | Electrodes | | | ■ | ■ | ■ | | | | | | | | |
| Ex situ membrane characterizations | LBNL | Membranes | | | ■ | ■ | ■ | | | | | | | | |
| Imaging of stabilizing additives in membranes | ORNL | Membranes | | | | ■ | ■ | | | | | | | | |
| Fuel cell MEA diagnostics (cathode and membrane) | NREL | MEAs | | | | ■ | ■ | | | | | | | | |
| **Year 2 - 2021** | | | | | | | | | | | | | | | |
| MEA electrochemical diagnostics | NREL | MEAs | | | | | | ■ | ■ | ■ | ■ | | | | |
| Cathode carbon corrosion (*in situ* NDIR) | LANL | MEAs | | | | | | ■ | ■ | ■ | | | | | |
| X-ray absorption spectroscopy (XAS) of catalysts | ANL | Electrodes | | | | | | ■ | ■ | ■ | | | | | |
| Electrochemical ICPMS for PtCo catalyst durability | ANL | Catalysts | | | | | | ■ | ■ | ■ | | | | | |
| Imaging of stabilizing additives in membranes | ORNL | Membranes | | | | | | ■ | ■ | ■ | | | | | |
| **Year 3 - 2022** | | | | | | | | | | | | | | | |
| MEA voltage cycling sensitivity measurements | NREL | MEAs | | | | | | | | | | ■ | ■ | ■ | ■ |
| MEA post-mortem analysis | All/FC-PAD | MEAs | | | | | | | | | | ■ | ■ | ■ | ■ |
| MEA Durability Modeling and Life-Projections | ANL | n/a | | | | | | | | | ■ | ■ | ■ | ■ | ■ |

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

# Summary

- Benchmarking of current state-of-the-art PtCo/HSC and Pt/HSC shows exceptional stability for pure-Pt compared to the alloy catalyst (90k cycles AST cycles, 0.2 $mg_{Pt}/cm^2$)
- Four GMC supports have been manufactured with varying pore size and pore volumes that will be compared to determine the optimal support shape and pore size form.
  - GMC supports with and without Nb-additive shows exceptional resistance towards Pt thermal sintering compared to conventional HSC support
  - More than six metal additives (Nb, Ta, Zr, Re, Ir, Au etc.) are being evaluated as immobilization agents for catalyst stabilization
- CZO immobilized PFSA membranes have been successfully demonstrated for mitigation of membrane degradation.
- HPA immobilized membranes have been successfully fabricated
  - Durability evaluation ongoing
- Discussions with FCPAD consortium are ongoing and plan is in place to engage the national labs once the agreements are in place.

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# Technical Back-Up Slides

# MEA Development for Medium- and Heavy-Duty Truck Applications

## Requirements from FCPAD

| S. No. | FC PAD Lab | Analytical technique/Models | Component | Comments |
|---|---|---|---|---|
| | ANL | SAXS/u-SAXS | Catalysts | Pt particle size distribution (BOT and EOT) |
| | | X-ray absorption spectroscopy | Catalysts | Metal additive oxidation state and coordination chemistry |
| | | Pt dissolution (*in situ* ICP-mass spectrometry) | Catalysts | *In situ* potential dependent studies on Pt and metal additive electrochemical dissolution characteristics |
| 4 | | X-ray computed tomography | Electrodes | Catalyst layer characterizations |
| 5 | | MEA durability modeling and projections-to-life | MEAs | Lifetime projections based on catalyst/MEA AST results |
| 6 | LANL | MEA Carbon corrosion (*in situ* ND infrared) | MEAs | Carbon corrosion in the load cycle region (0.6 to 0.95 V) – impact of catalyst layer hydrophilicity and structural changes on cell voltage loss over 3X durability cycles |
| | LBNL | Light scattering and viscosity measurements | CZO-ionomer dispersions | Ionomer dispersion characteristics; determine particle size distributions and ionomer domain sizing studies |
| 8 | | Membrane characterizations | Membranes | Impact of CZO on membrane properties |
| 9 | NREL | MEA diagnostics<br>MEA voltage cycling durability | MEAs | Impact of operating conditions, cathode catalyst layer electrochemical characterizations |
| 10 | ORNL | Microscopic imaging | Membranes<br>(HPA dispersion) | HPA and CZO distribution in the membrane |

# Publications and Presentations

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

# Milestone Summary Table

**Recipient Name:** General Motors LLC

**Project Title:** Durable Fuel Cell MEA through Immobilization of Catalyst Particle and Membrane Chemical Stabilizer

| Task Number | Task Title | Milestone Type (Milestone or Go/No-Go Decision Point) | Milestone Number* (Go/No-Go Decision Point Number) | Milestone Description (Go/No-Go Decision Criteria) | Milestone Verification Process (What, How, Who, Where) | Anticipated Quarter (Quarters from Start of the Project) |
|---|---|---|---|---|---|---|
| 1.2.1 | Catalyst characterizations | Milestone | M1.1 | Establish baseline catalysts and ex situ surface area measurement protocols | GM/Pajarito/Cornell/FC-PAD | Q1 |
| 1.1.1 | Develop Pt-MOx nanocluster catalysts supported on GMC | Milestone | M1.2 | Provide >5g of first iteration of Pt-MOx/GMC catalyst to GM | Pajarito/GM | Q2 |
| 1.1.5 | Prepare and characterize CexZryO4 nanoparticle/PFSA dispersions | Milestone | M1.3 | Prepare CexZryO4 nanofiber or nanoparticle /PFSA dispersions with at least 3 different CexZryO4 loading levels | GM/FC-PAD | Q3 |
| 1.1.3 | Polymer Synthesis | Milestone | M1.4 | Copolymers with 3 different levels of tetherable monomer delivered for functionalizing with HPA | 3M | Q4 |
| **Phase 1** | **Development of Catalysts and Membranes with Chemical Stabilizers** | **Go/No-go** | **MA1** | **Anchored supported Pt catalyst with > 60 m$^2$/g$_{Pt}$ ECSA at BOL in MEA and > 35 m$^2$/g$_{Pt}$ ECSA after 30,000 cycles of DOE LDV catalyst AST.** | **All** | **Q4** |
| 2.2.1 | MEA performance, electrochemical diagnostics and modeling | Milestone | M2.1 | Validate anchored Pt/GMC catalysts in MEAs (BOL ECSA >60 m$^2$/g) | GM/FC-PAD | Q5 |
| 2.2.2 | AST for anchored Pt/GMC catalyst durability | Milestone | M2.2 | Demonstrate durability enhancements with anchored Pt/GMC catalysts (<30% ECSA loss after 30000 cycles) | GM | Q6 |
| 2.1.2 | Prepare ePTFE supported membranes with chemical stabilizers | Milestone | M2.3 | HPA immobilized membranes that enable 200 hours of OCV at 90°c/30% RH | GM/CSM/3M | Q7 |
| 2.2.3<br>2.2.4 | 1) Quantify anchored GMC support corrosion in MEA using in situ NDIR<br>2) X-ray absorption spectroscopy of MOx anchoring site durability | Milestone | M2.4 | Report on the mitigation of carbon corrosion with GMC and the stability of MOx anchoring sites | FC-PAD | Q8 |
| **Phase 2** | **Integration of Highly Durable Catalysts and Membranes into MEAs** | **Go/No-go** | **MA2** | **1) Anchored supported Pt catalyst with < 30 mV loss at 0.8 A/cm$^2$ after 60,000 cycles of DOE LDV catalyst AST protocol.**<br>**2) Membrane with H$_2$ & O crossovers (<2mA/cm$^2$), 80°C proton ASR (<0.02 ohm cm2), electrical resistance (<1000 ohm cm2), chemical durability (>500h in AST), mechanical durability (>20,000 cycles in AST)** | **All** | **Q8** |
| 3.1.3 | Catalyst, support and membrane AST on SOA MEA | Milestone | M3.1 | Anchored Pt/GMC catalyst with <30% ECSA loss after catalyst AST. | GM | Q9 |
| 3.1.1 | Develop ordered intermetallic PtCo catalysts on down-selected support | Milestone | M3.2 | Deliver >2g of ordered catalyst with mass activity >0.44 A/mg$_{Pt}$. | Pajarito/GM/Cornell | Q10 |
| 3.1.3<br>3.2.1 | Catalyst, support and membrane AST on SOA MEA<br>MEA post-mortem analysis | Milestone | M3.3 | 1) MEA that achieves 1750h of 90 °C HAST testing<br>2) Report on the Pt nanoparticle location before and after AST | All/FC-PAD | Q11 |
| 3.3.1<br>3.3.2 | 1) MEA durability modeling and life-projections<br>2) Deliver Final MEA with High Efficiency and Durability to DOE | Milestone | M3.4 | 1) Report on the MEA life projections using durability models<br>2) Deliver six or more 50 cm2 MEAs to DOE | GM/FC-PAD | Q12 |
| **Phase 3** | **Optimization for High Performance, Efficiency and Durability** | **Final Review** | **MA3** | **Deliver MEA with < 0.2 mg$_{Pt}$/cm$^{2}_{cathode}$, < 40% loss in mass activity, < 10% loss in power after 25000 hours based on fuel cell system model lifetime projection studies. The MEA will have BOL efficiency of 65% at 10% power and a rated power of >1.2 W/cm$^2$ measured in a 50 cm$^2$ active area cell.** | **All** | **Q12** |