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

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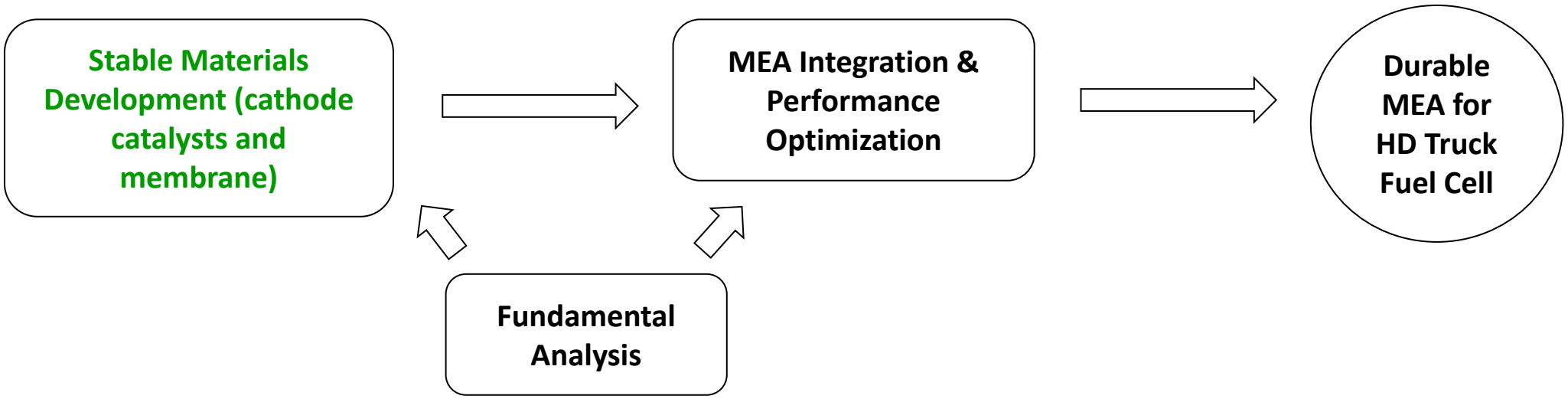
AMR Project ID: fc323

Project Goal

Vision, Goals and Outcomes

Project Goal: *Develop highly stable catalysts and membrane materials* for use in direct-H_2 fed PEM fuel cell MEA in medium-duty (MD) and heavy-duty (HD) truck applications featuring

- **low cost** – cathode PGM loading of ≤ 0.2 mg_{Pt}/cm^2
- **high efficiency** – fuel efficiency of >65%
- **high durability** – less than 10% degradation in power density after 30,000 hours of operation
  (a lifetime of 1 Million miles, ~3X compared to light-duty (LD) vehicles)



Outcome: if successful, this project will deliver highly durable MEA for PEMFC applications to enable heavy-duty truck applications and elucidate the fundamental degradation mechanisms.

Overview

Timeline, Budget, Barriers, Partners

Timeline

- Project start date: 1 Oct 2019
- Project end date: 31 May 2023
- Percent complete: 95%

Budget

- Total Project Budget: $2.73M
  - Total DOE Share: $2.0M
  - Total Cost Share: $0.73M (26.8%)
- Total Funding Spent: $2.6M*
  - DOE Billable: $1.9M
  - Participants Cost Share Funds Spent: $0.7M

* As of 03/31/2023 (amount by billings)

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

Partners

- General Motors LLC (Project lead)
- Subcontractors:
  - 3M Company (sub)
  - Pajarito Powder LLC (sub)
  - Colorado School of Mines (sub)
  - Cornell University (sub)
- M^2FCT Consortium

Relevance/Impact
Targets and Status

- **Objective:** develop highly stable catalyst and membrane materials to be integrated into an MEA for heavy-duty truck applications that meet or exceed technical targets in terms of **cost, performance, durability & efficiency**

CATALYST

Metric	Units	DOE/Project Target	Status of Proposed approach: 50% Pt/HSC-a	Status of Proposed approach: Pajarito 50% Pt/Zr-ECS3701
PGM loading (total)	mg_{PGM}/cm^2	< 0.25	0.25	0.25
Mass activity (MA) [a]	A/mg_{PGM}	> 0.44	0.29	0.54
Loss in initial catalytic activity (post-30k catalyst cycles) [b]	% MA loss	< 40	62%	40%
Performance at rated power (250 kPaabs, 94 °C)	W/cm^2	> 1.3	1.05	1.05
HD Combined Target (at 0.7 V, post-90k catalyst cycles)[d]	kW/g_{PGM}	2.5	2.3	**3.3**

MEMBRANE

Metric	Units	DOE/Project Target	Status of Proposed Approach: PFSA ($CeNO_3$)	Status of Proposed Approach: PFSA w/ 8% $CeZrO_x$	Status of Proposed Approach: PFSA blend with HPA
Membrane thickness	µm	n/a	12	12	12
H_2 crossover	mA/cm^2	< 2	1.2	1.0	1.0
H^+ area specific resistance	$\Omega\ cm^2$	<0.02	0.02	0.02	0.02
Electrical resistance	$\Omega\ cm^2$	> 1000	> 3000	9000	6000
OCV Chemical durability	hours	> 500	**> 500**	**> 306**	**671**
Combined chemical & mechanical durability	hours	n/a	**> 450**	**> 450**	150

Focal points:

- Catalyst AST – 90 ˚C, 100% RH, 0.6 to 0.95 V, 4 s/cycle
- Cost < 0.25 mg_{total}/cm^2
- HD combined durability and efficiency target achieved ~3.3 kW/g_{PGM} at EOT
- membrane chemical durability of 300 to 600 hours with immobilized additives

- **Impact:** Project has delivered a cost-effective and durable MEA for heavy-duty applications
  - catalysts with better ECSA retention
  - membrane with longer lifetime

Approach
Milestones and go/no-go decisions

TASK 1: Materials Development – Catalysts and Membranes 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) ✓

	Progress
❑ Develop anchored Pt-M/MO_x nanocluster catalysts supported on GMC	100%
❑ PFSA synthesis and HPA functionalization	100%
❑ $Ce_xZr_yO_4$ nanofiber dispersed PFSA membrane development	100%
❑ Fuel cell MEA performance and diagnostics	100%

TASK 2: Integration – Highly Durable Catalysts and Membranes into MEAs ✓

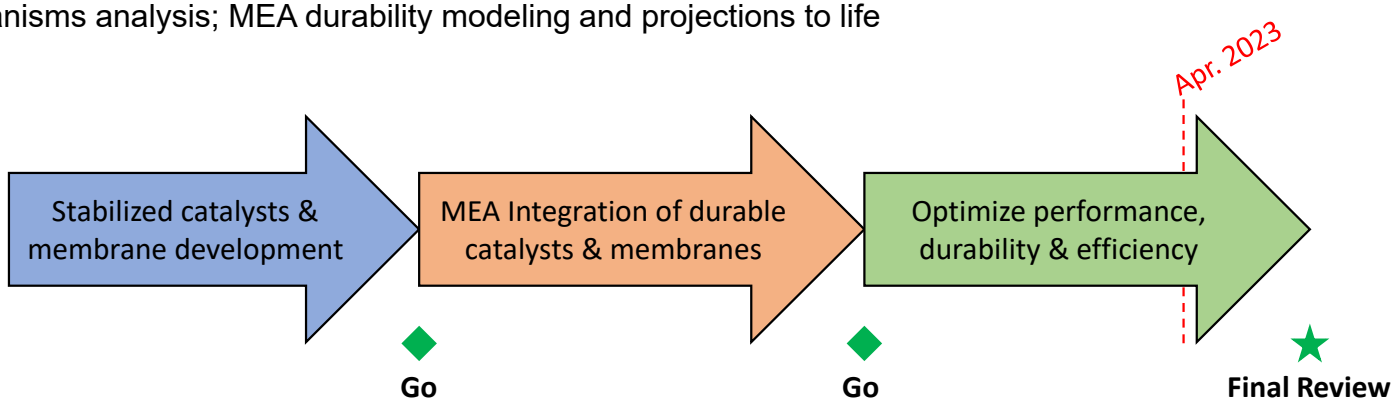
Go/No-go criteria : Anchored Pt catalyst with <30 mV loss at 0.8 A/cm^2 (60k LDV AST MEA) and membrane that meets all DOE Technical Targets (gas crossovers, ASR, chemical and mechanical durability)

❑ Optimization of down-selected anchored GMC catalyst	100%
❑ ePTFE supported membrane development	100%
❑ Fuel cell MEA performance and durability (AST)	100%
❑ Advanced characterizations of catalysts and membranes	100%

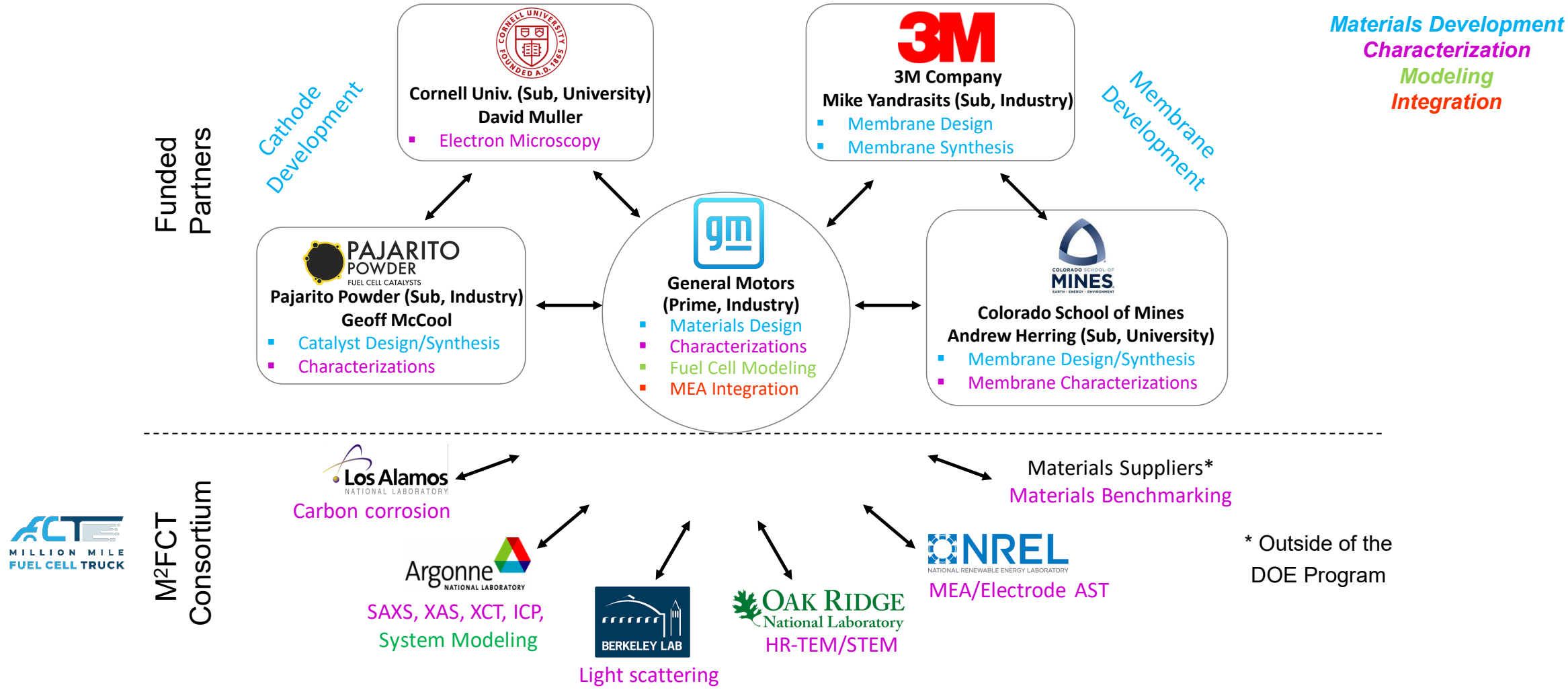
TASK 3: Optimization – Focus on High Performance, Efficiency and Durability

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

❑ Deliver MEA with state-of-the-art durable catalyst and membranes with high performance, efficiency and durability	80%
❑ Ordered intermetallic PtCo catalyst development on down-selected anchored GMC support	80%
❑ Optimization for durability of membranes with chemical stabilizers	80%
❑ MEA degradation mechanisms analysis; MEA durability modeling and projections to life	80%



Collaborations and Coordination



- 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

Approaches – Cathode and Membrane Durability

Catalyst Durability - mitigate Pt surface area loss:

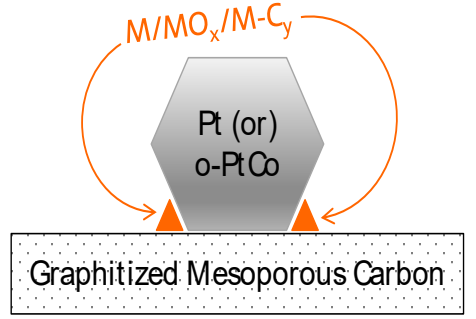
Approach 1: Pt-Carbon interface modification (anchored Pt/C catalysts)

- Zr/ZrO_x additives to stabilize Pt against surface area loss

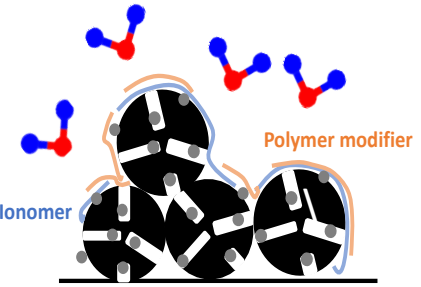
Approach 2: Pt-ionomer interface modification (advanced polymer additives)

- Hyflon® and Fluorolink® additives to stabilize Pt/C catalyst layer

1) anchoring agents on carbon to stabilize Pt catalyst nanoparticles



2) polymers to stabilize Pt/C-ionomer/water interface



Membrane Durability – mitigate Ce^{3+} migration:

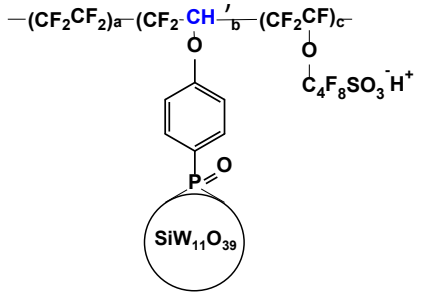
Approach 3: Covalent tethering of heteropoly acid (HPA) anti-oxidant

- Silicotungstic acid as an immobilized radical scavenger for membrane durability

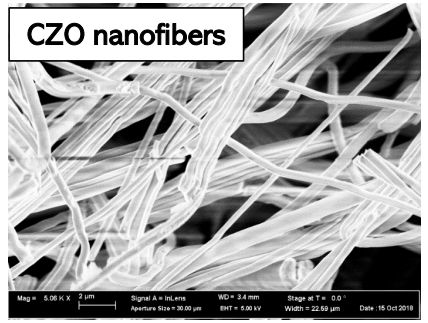
Approach 4: Dispersed $CeZrO_x$ (CZO) nanofibers for membrane stabilization

- Demonstration of improved chemical durability with CZO additive

3) PFSA with covalently tethered HPA antioxidant



4) $CeZrO_x$ nanofibers for reduced Ce migration

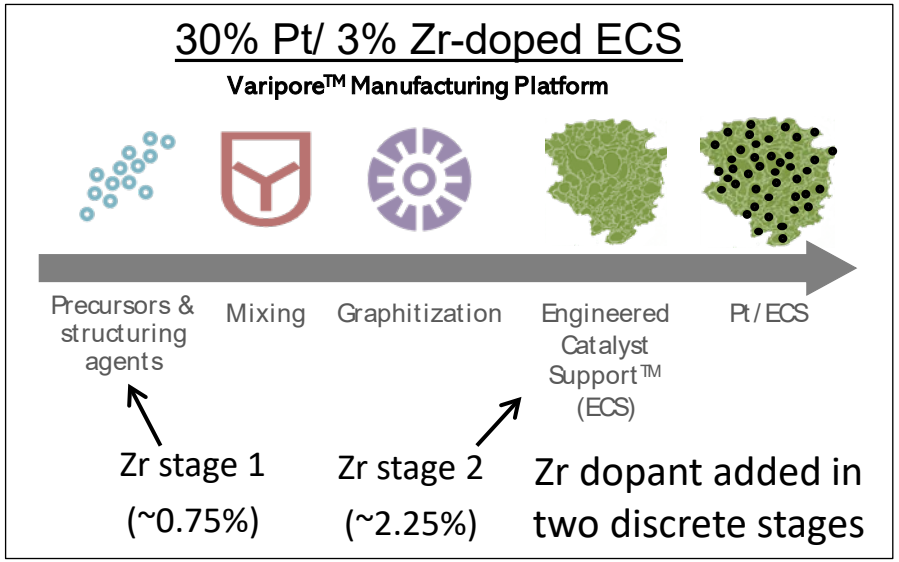


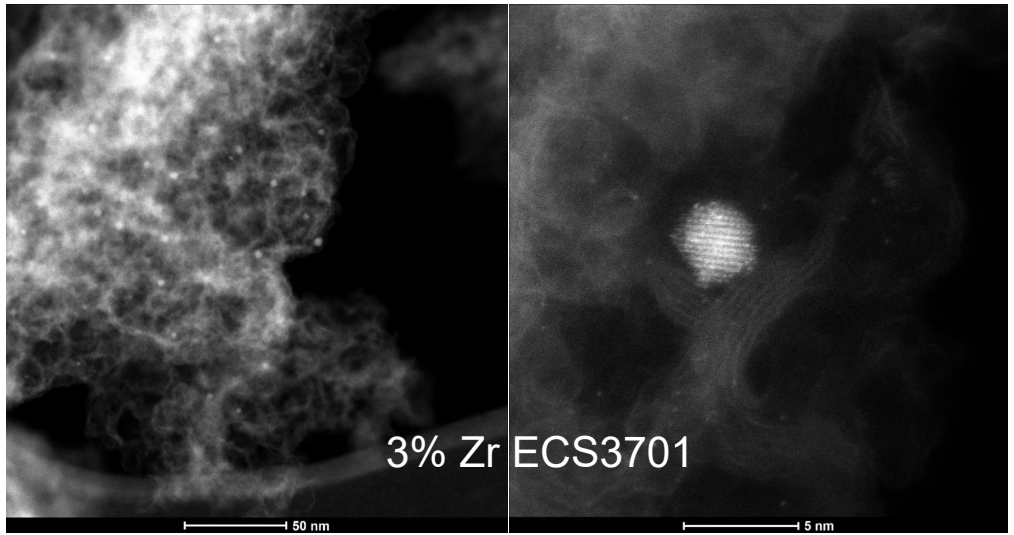
Outcome: *Durable fuel cell MEA for heavy-duty application consisting of catalyst with improved resistance towards surface area loss and/or Co-dissolution, and membranes that meet 30,000 hours of lifetime requirement.*

Engineered carbon support (ECS) – synthesis and key features

Pajarito's Varipore™ manufacturing platform used to develop catalysts with three focal points:

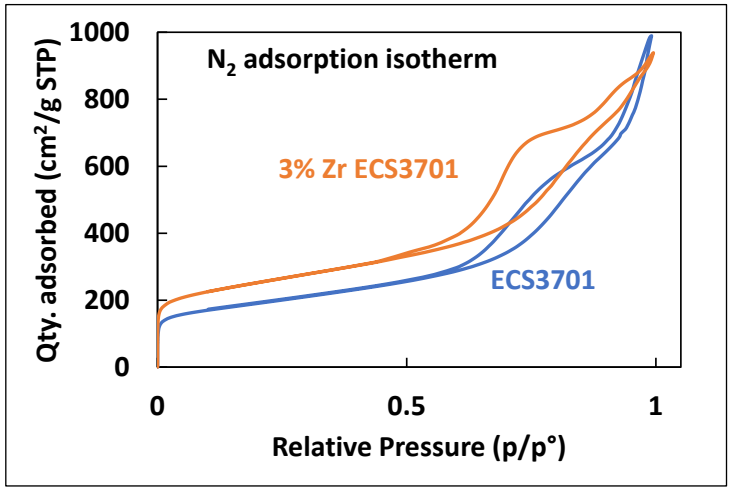
- *Mesoporosity* (~8 & ~40 nm) for Pt dispersion, accessibility & transport
- *Graphitization* (300 to 800 m^2/g) for carbon stability
- *Metal dopants* (ex: zirconium) for Pt stability

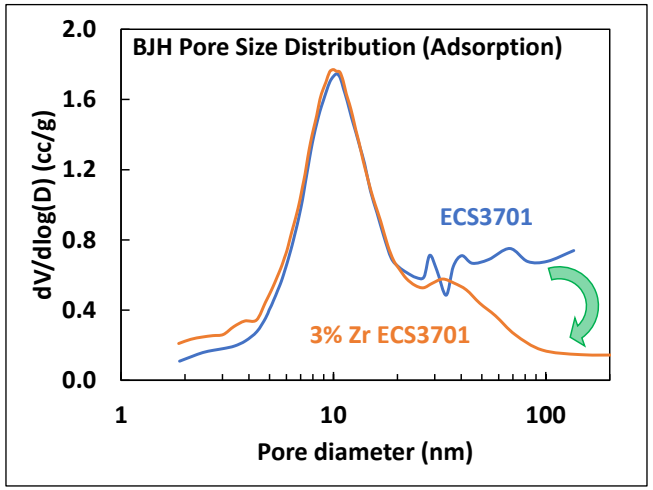


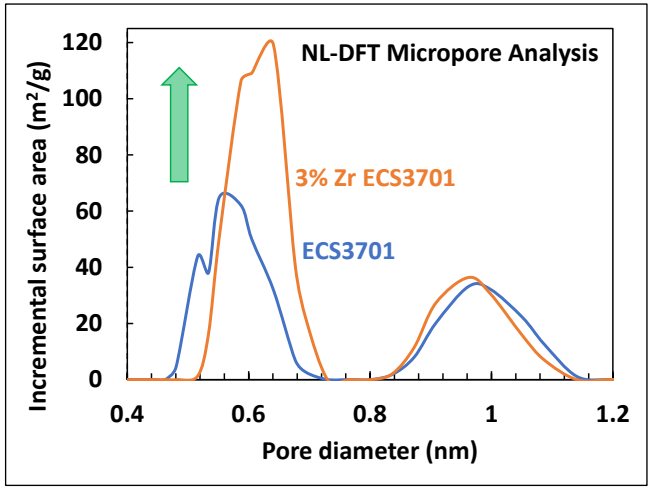


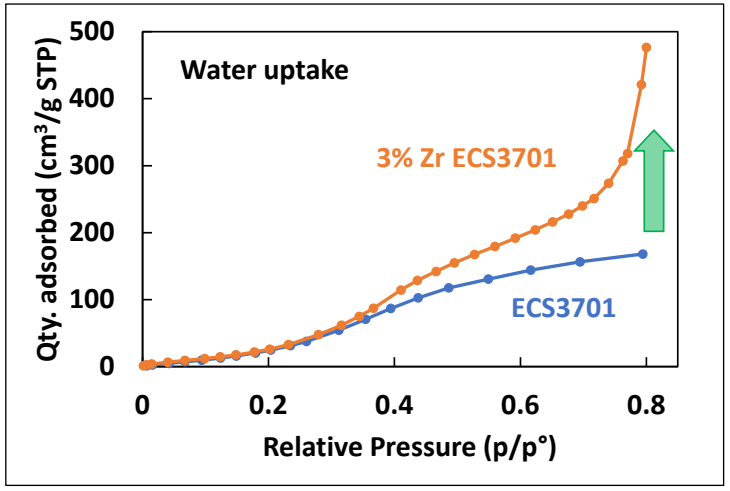
Features of the Engineered Carbon Support (ECS)

Interconnected, built-in, open mesopores with better Pt accessibility & durability



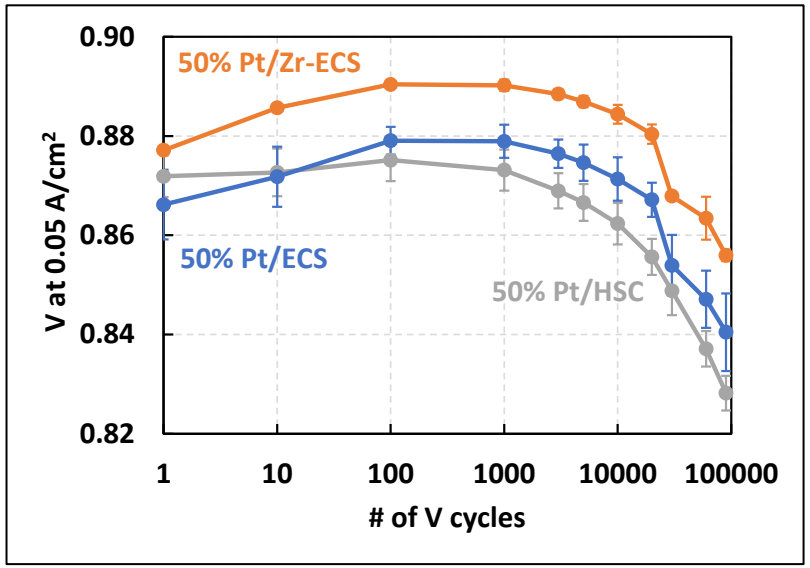


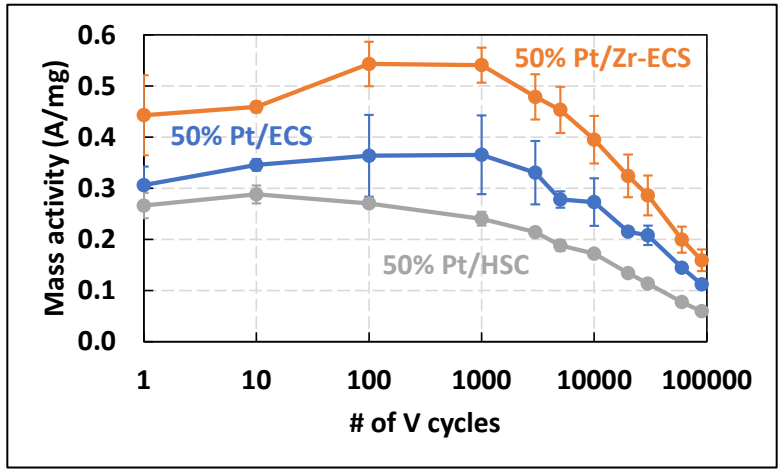


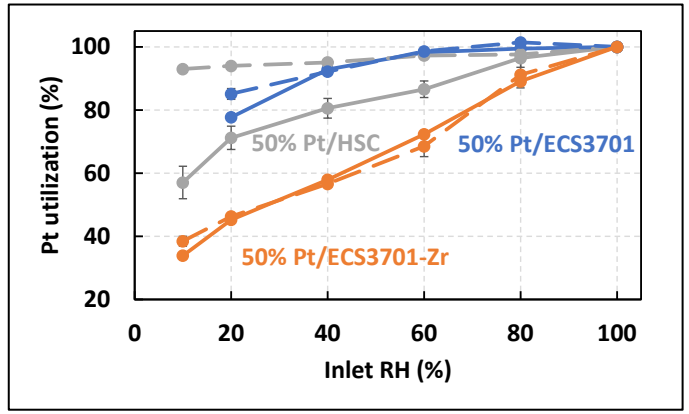


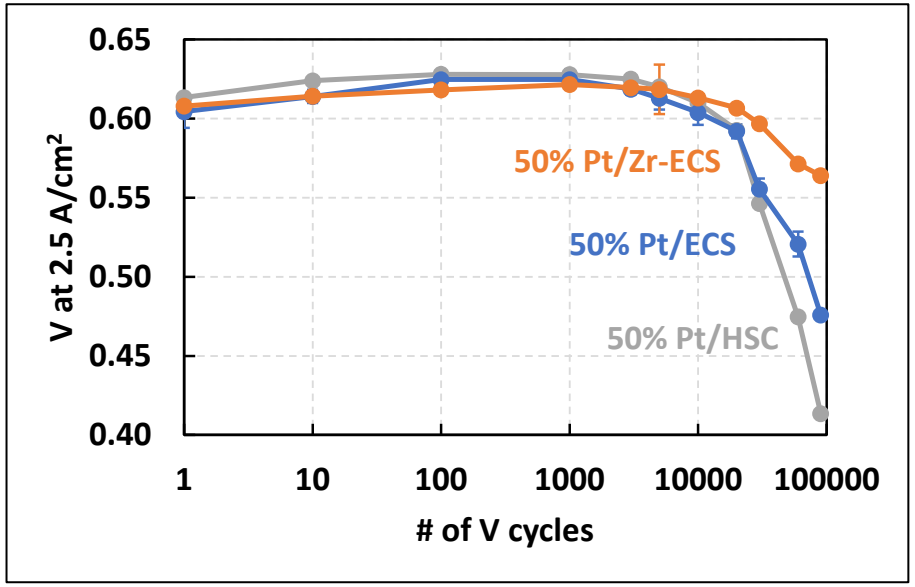
Durability of the anchored cathode catalyst

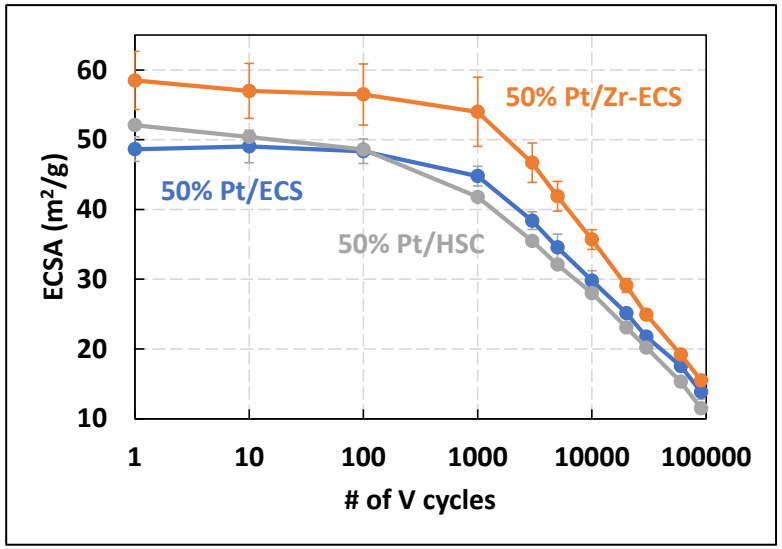
ZrO_2 doped 30% Pt/ECS catalyst is more durable that the non-doped catalyst





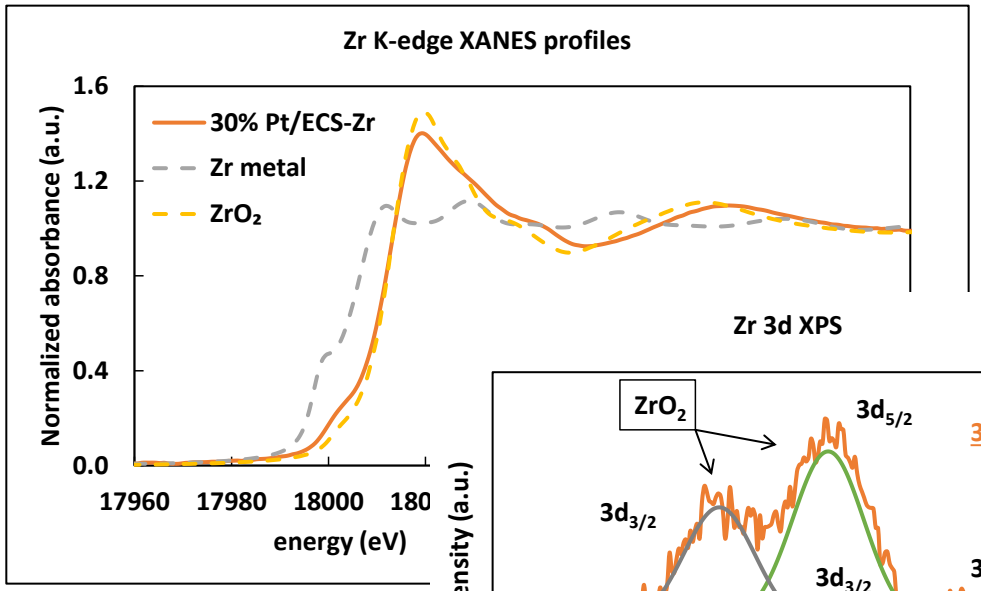


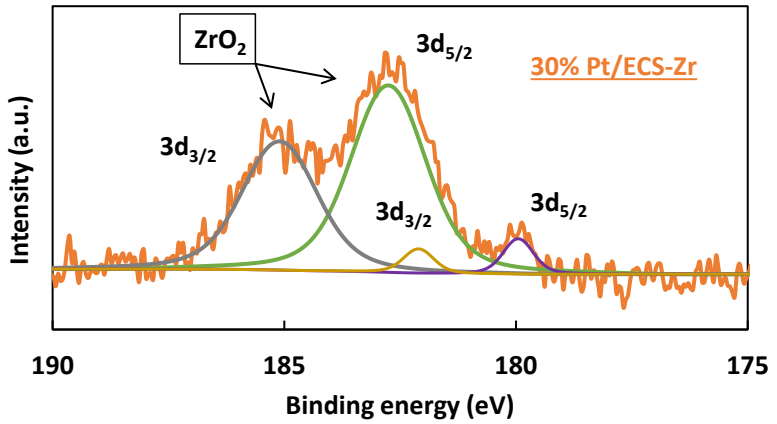




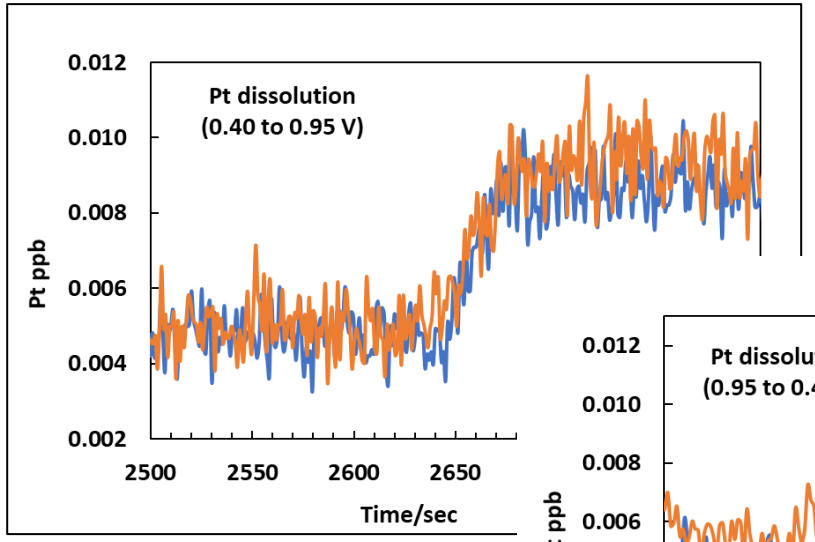
- Pt/ECS-ZrO_2 enables improvement in mass activity due to more Pt present inside the pores and hence improves voltage at low current densities
- Pt/ECS-ZrO_2 shows improvement in stability of ECSA and hence in cell voltage at high current densities

Durability of the anchored cathode catalyst

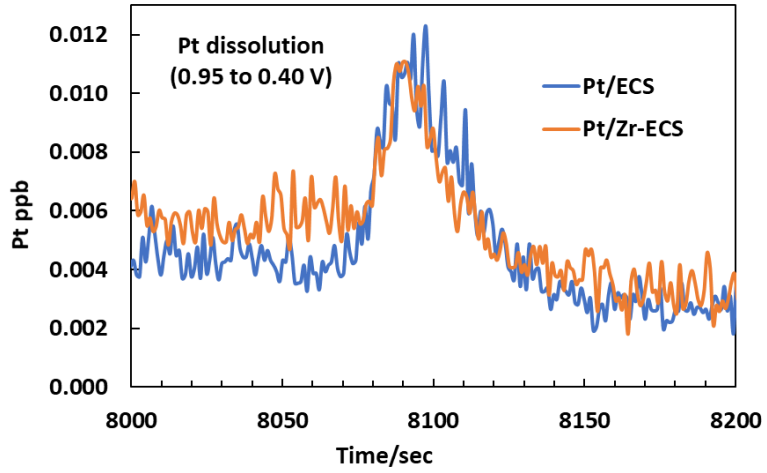




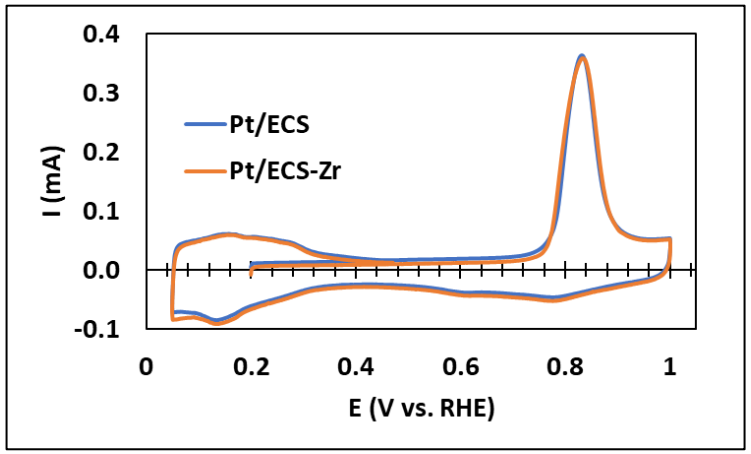
- Zr is largely present as ZrO_2 from both XPS and XANES



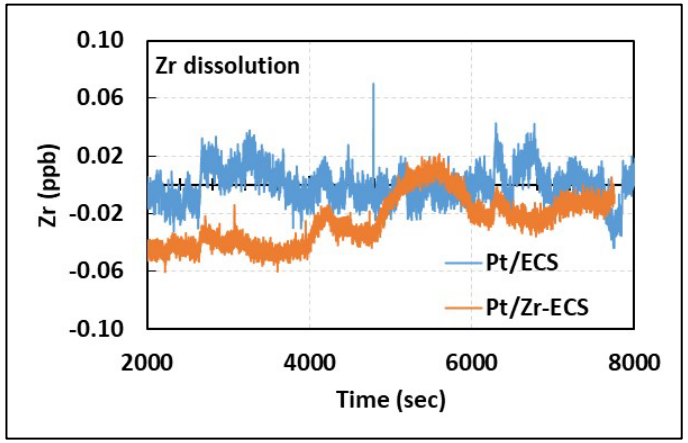
Pt dissolution in parts per billion from *in situ* flow cell electrochemical ICP



- No difference in Pt dissolution behavior with and without Zr

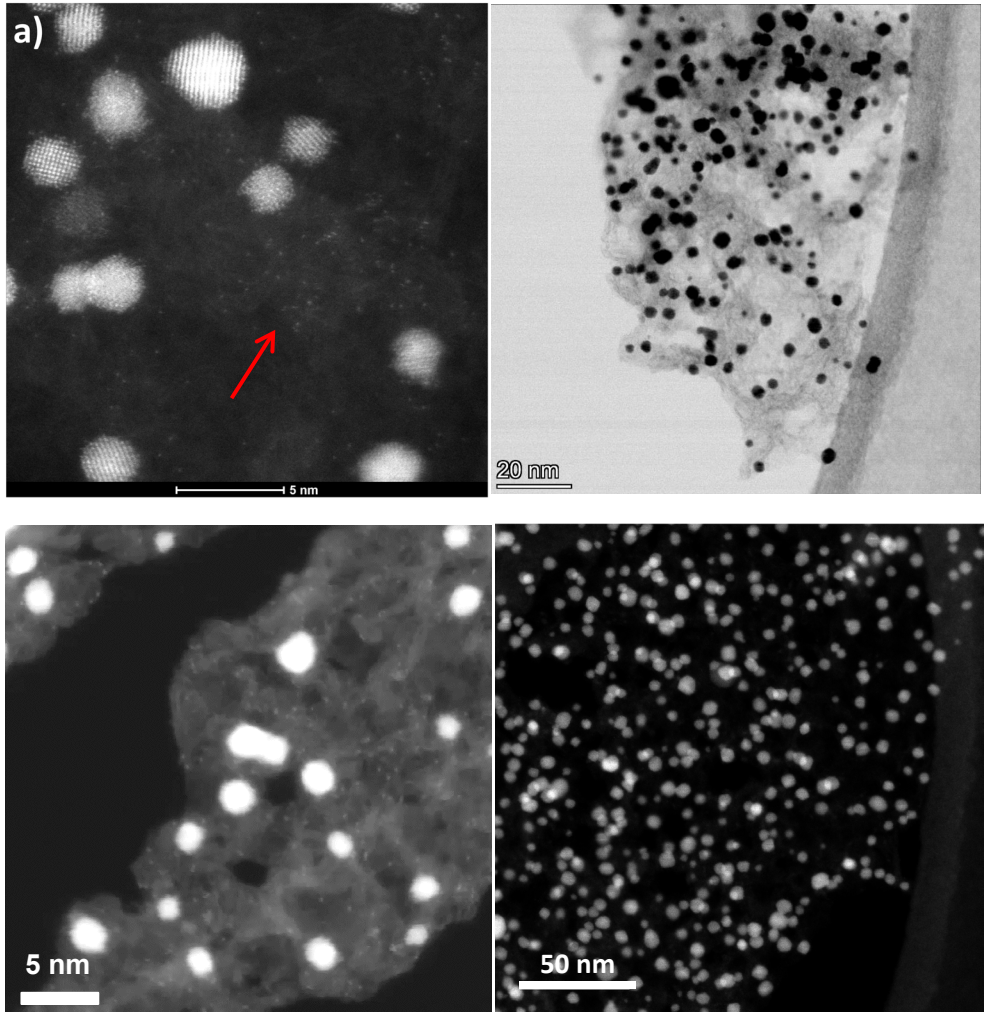


- ZrO_2 does not appear to interact chemically with Pt based on CO_{ads} stripping
- ZrO_2 dissolution below detection limit

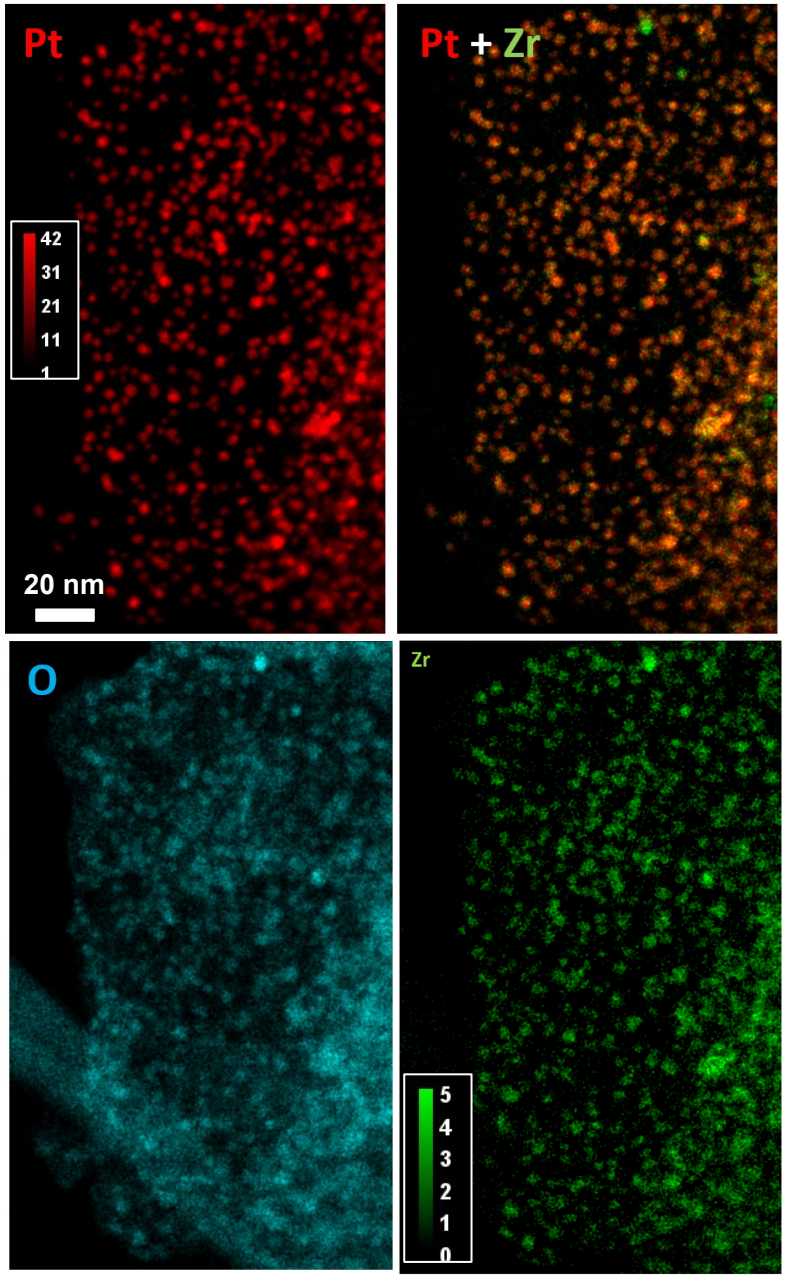


Characterization of Zr-doped Engineered Carbon Support

STEM-EDS of **BOL Pt/ECS-ZrO_2** catalyst sample



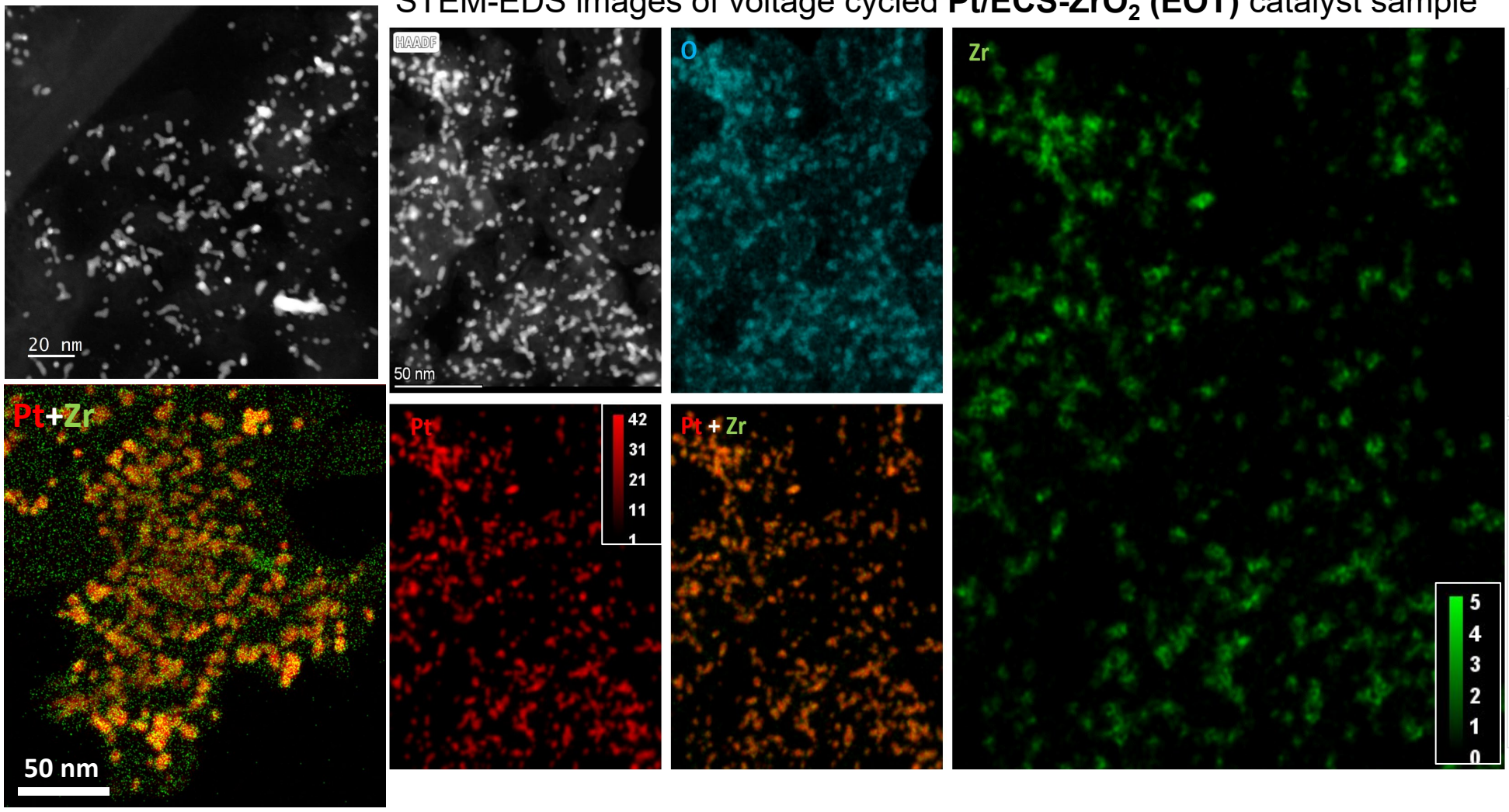
Atomically dispersed Zr single atoms and Pt nanoparticles dispersed on carbon



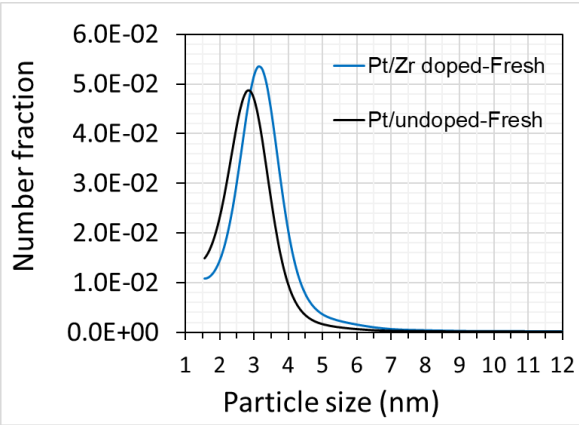
- Presence of both 1) atomically dispersed Zr single atoms on the carbon support and 2) non-uniform, porous shells of ZrO_2 around Pt nanoparticles
- ZrO_2 shells around Pt nanoparticles appear to be under sub-monolayer coverage
- Zr single atoms and/or ZrO_2 shell sterically prevents migration and coalescence of Pt nanoparticles

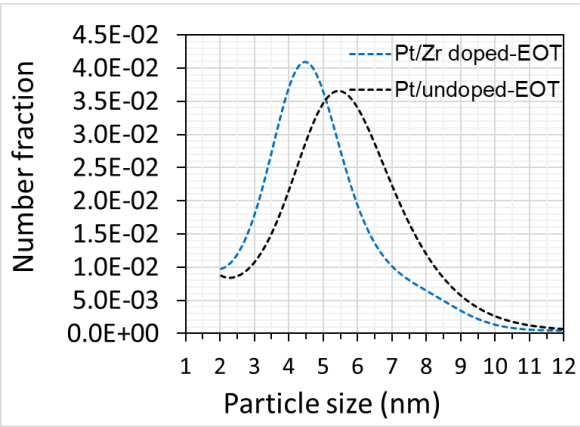
Characterization of Zr-doped Engineered Carbon Support

STEM-EDS images of voltage cycled **Pt/ECS-ZrO_2 (EOT)** catalyst sample



SAXS Pt PSD





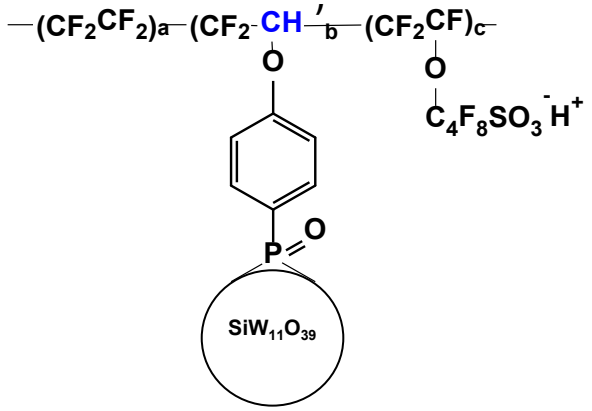
- Pt nanoparticles appear elongated and coarsened after 30k cycles but with a lower average particle size for the Zr-doped catalyst
  - agrees with the higher ECSA for Zr-doped catalyst at EOT
- ZrO_2 shell moves along with Pt nanoparticles on the carbon support

Fabrication and characterization of membrane with anchored heteropoly acid (HPA)

Accomplishments:

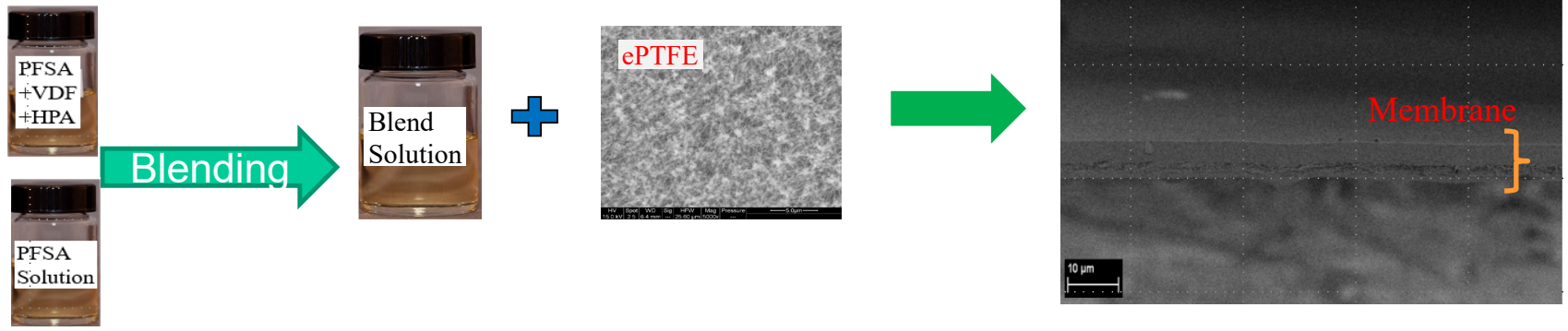
- Fabricated 12 µm thick ePTFE reinforced HPA blended membrane

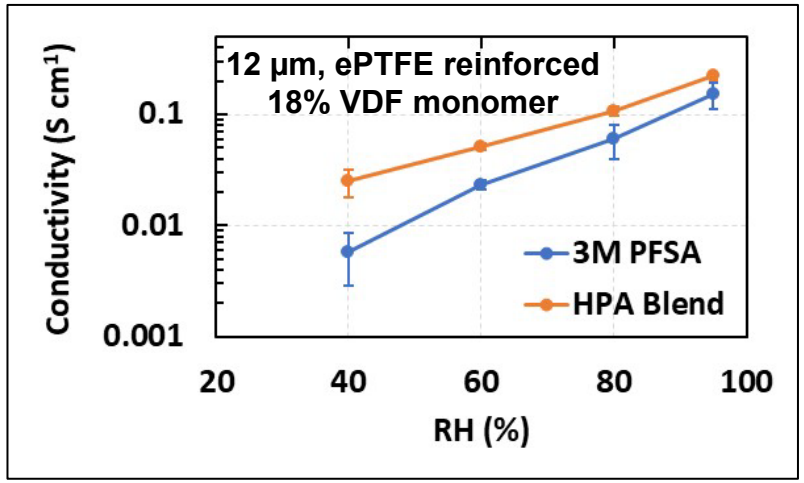
PFSA w/ tethered HPA ($SiW_{11}O_{39}$)

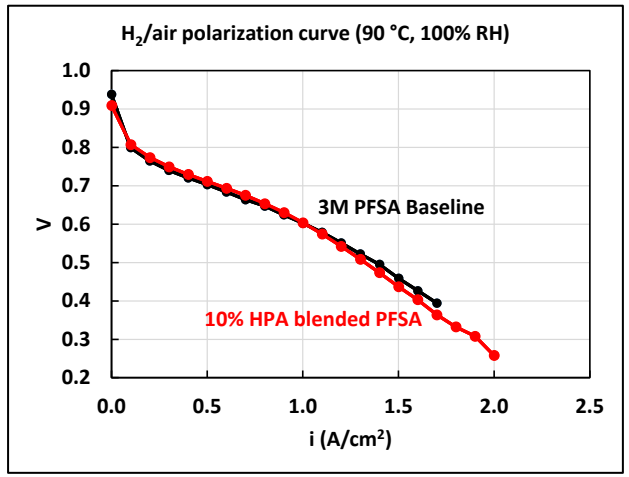


- Vinylidene fluoride (VDF) monomer (-CF_2-CH_2-) acts as an anchor point to covalently tether anti-oxidant to PFSA backbone
- Vary VDF monomer ratio to optimize performance & durability (5 to 23%)

Blended membrane (90% PFSA + 10% ionomer with tethered HPA)

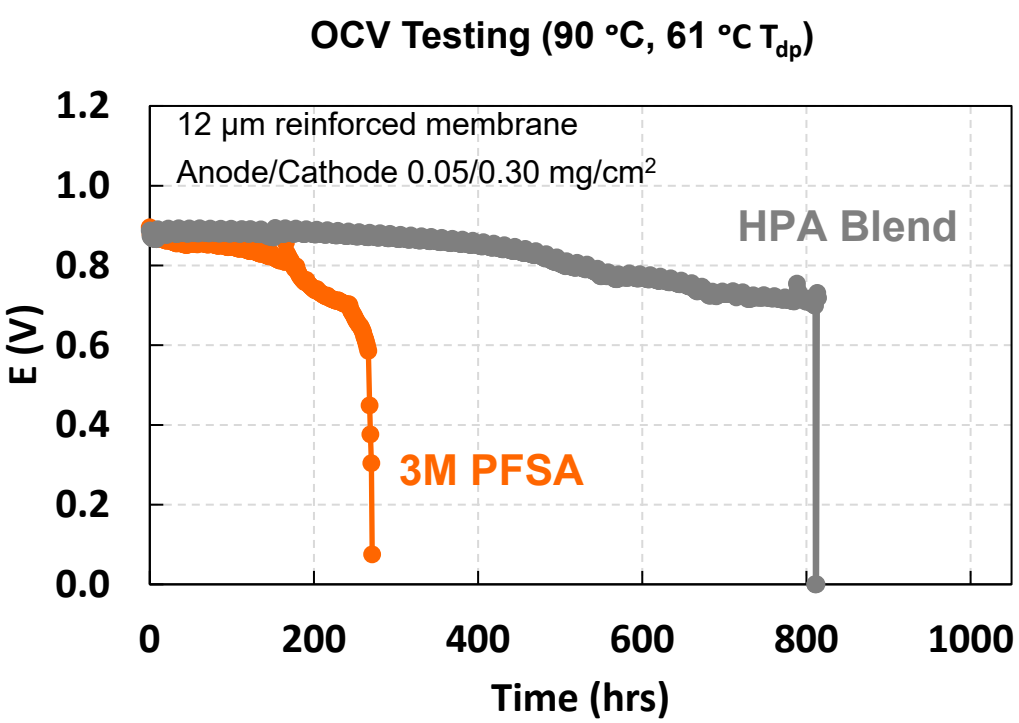


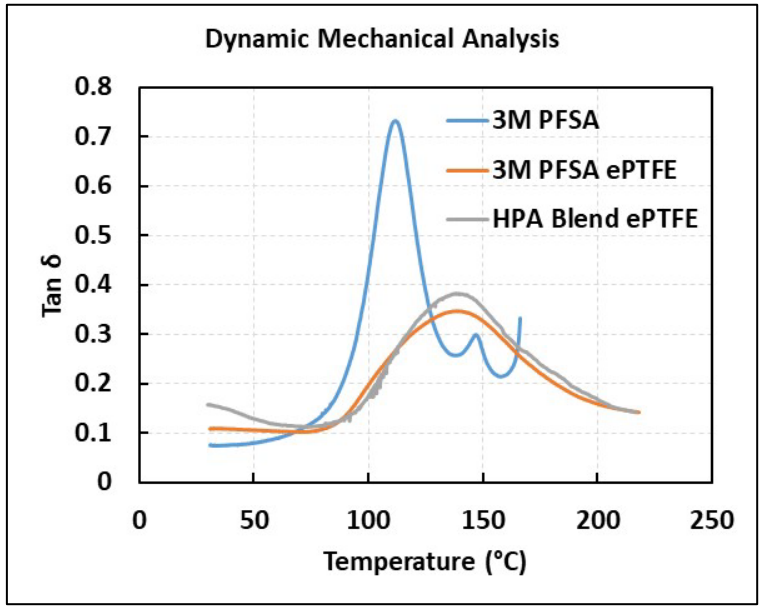


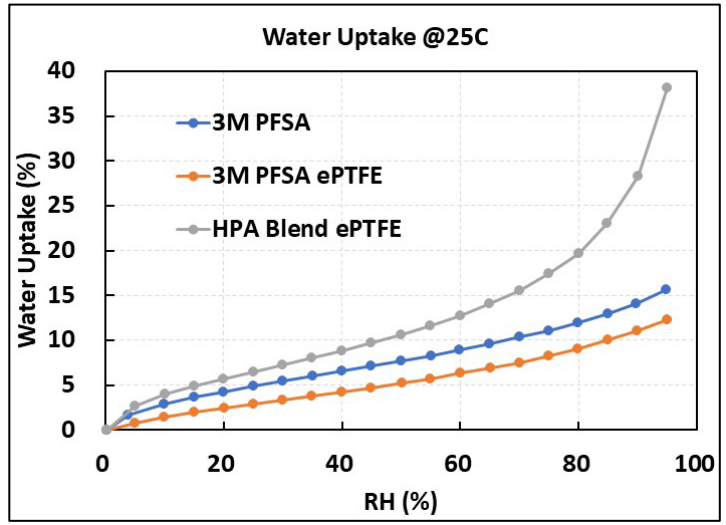


- Blended membrane fabricated with 90% PFSA + 10% HPA anchored membrane
- Minor loss in conductivity for the blended membrane
- Negligible difference in H_2/air polarization behavior

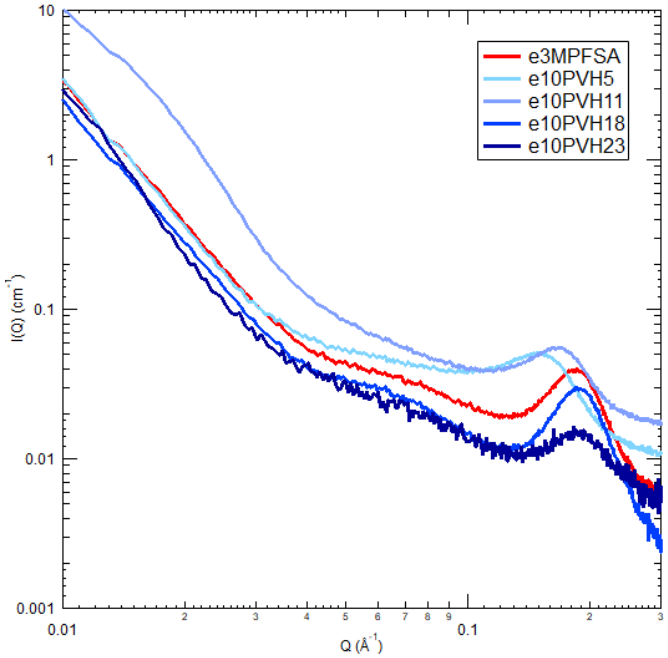
Characterization of PFSA-PFSA/HPA Blends







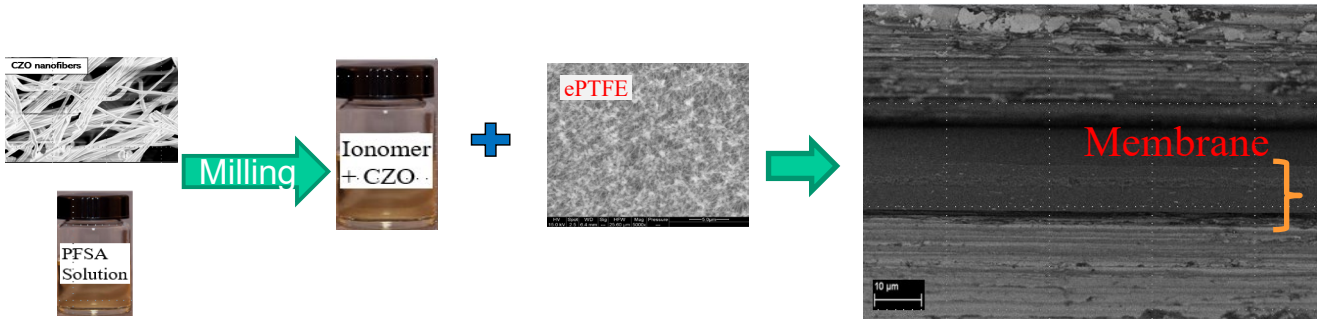
SAXS profile as a function of RH



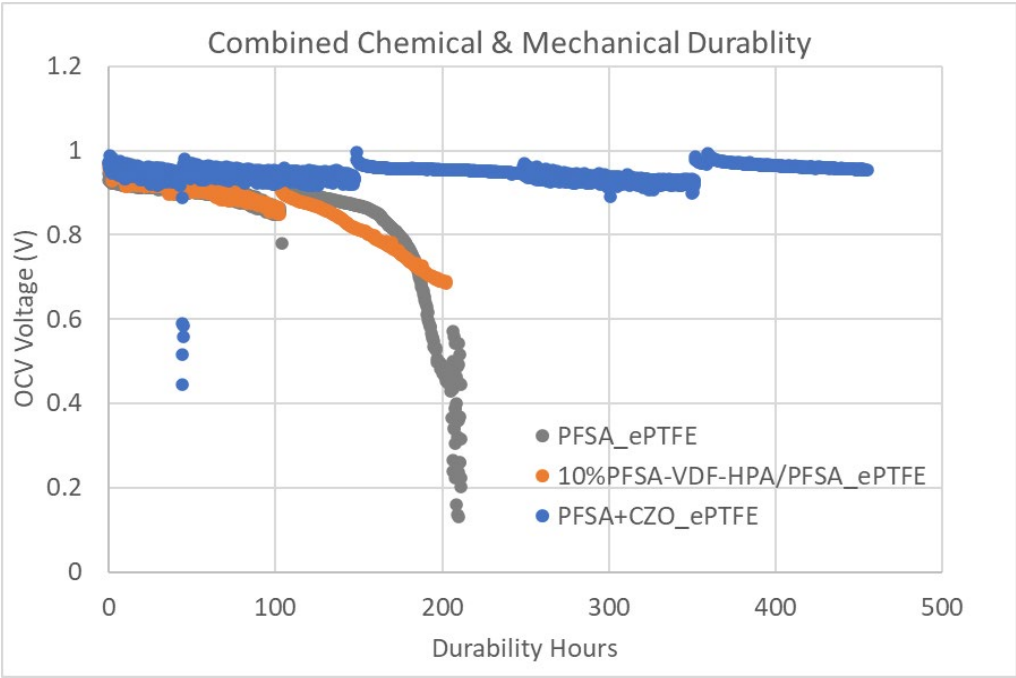
- Longer lifetimes achieved for HPA blended membranes
- Even with increased crystallinity due to e-PTFE reinforcement, 10 wt.% blended membranes had higher water uptake
  - Synergistic effect of sulfonic acid and HPA
- SAXS corroborates successful covalent binding of HPA to anchoring group and morphological ordering induced by HPA (Randomly distributed rods to lamellae)
- e-PTFE reinforcement dominates mechanical property, tensile strength increased 2X

Design of Combined Mechanical & Chemical (M&C) Durability

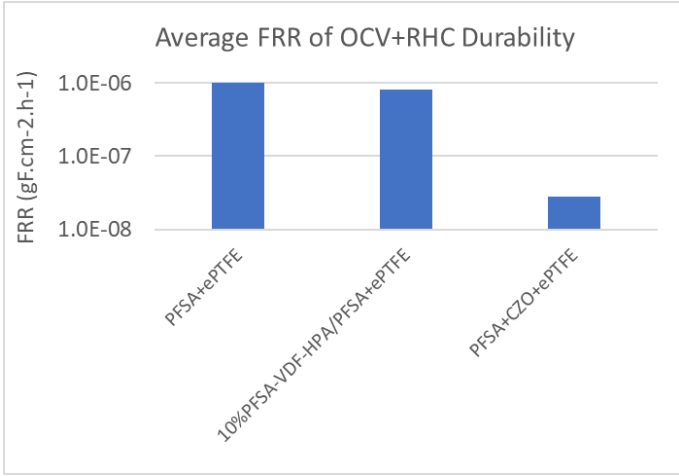
- ePTFE reinforced CZO doped membranes were fabricated
- Integrated MEAs were tested for durability with combined chemical and mechanical stressors



Step#	Description	Stress	Duration
1	RH cycling under OCV, H_2/Air. 90°C, 0-120%RH	M+C	100hr
2	OCV, H_2/Air 110°C, 25%RH	C	100hr



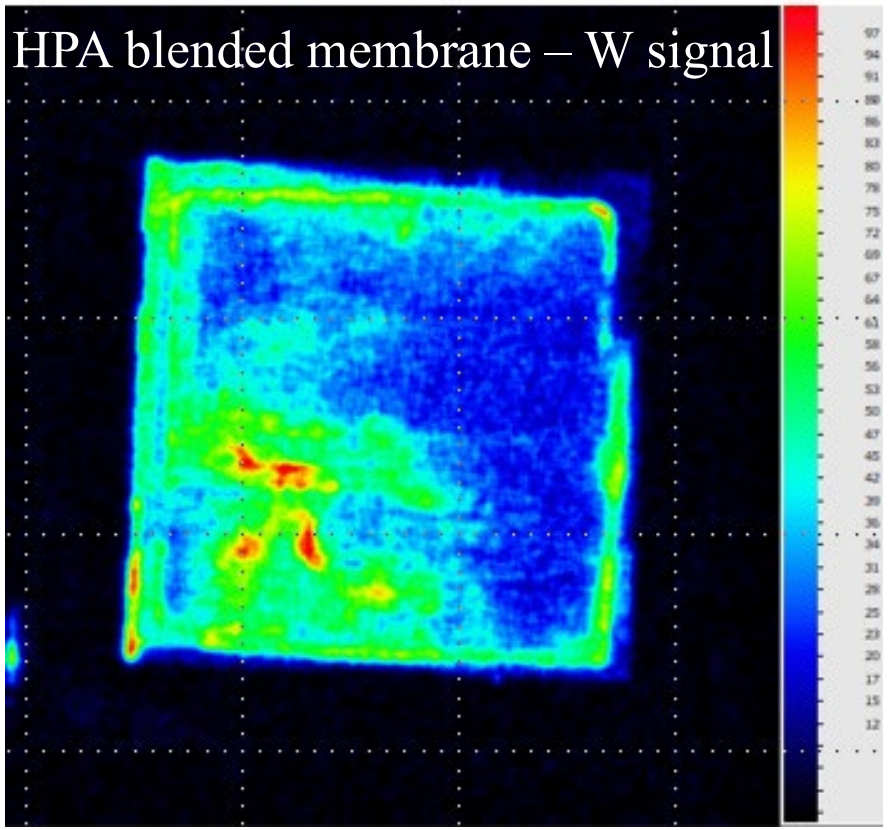
- An/Ca loading of 0.05/0.2 mg_{Pt}/cm^2.
- All membranes have ePTFE reinforcement.

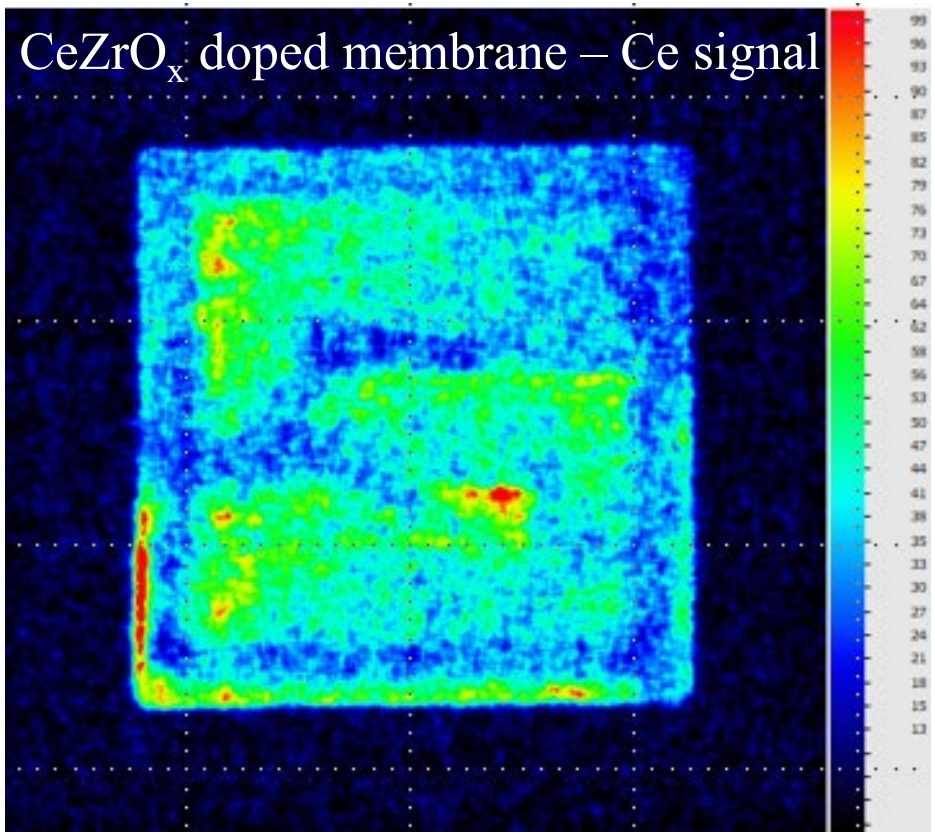


- OCV durability of membranes with CZO show stable OCV voltage, low FRR over ~450 durability hours.
- HPA blended membrane showed lower stability in the combined protocol

XRF of EOT MEA modified with CZO or HPA

- Integrated MEAs were tested by element specific X-ray fluorescence (XRF) after combined chemical & mechanical durability tests
- In HPA blended membranes, tungsten (W) XRF was imaged as a signal from the silicoitungstic acid
  - W redistribution was observed in XRF for MEA with 10% PFSA+HPA-PFSA membrane.
- In the CZO doped ePTFE reinforced membrane, Ce XRF was imaged
  - Ce redistribution was observed in XRF for MEA with PFSA+CZO_ePTFE membrane
  - $CeZrO_x$ nanofiber possibly acts a buffer for slow but continuous dissolution of $Ce^{3+/4+}$ active species into the membrane





Responses to Last Year (2021) AMR Reviewers' Comments

1) Not all major decay mechanisms will be addressed by this project. For example, it is not focused on carbon corrosion… – carbon corrosion (specifically, at > 1.0V) is out of scope of our project as it can be addressed using well-known system level mitigation strategies. There are some concerns about carbon corrosion during load cycling (< 0.95 V). We plan to track it/quantify during the project, but not necessarily directly address it. Primary objective is to mitigate ECSA losses.

2) This project is focused on critical barriers, but it seems like two completely separate work streams. – we have two separate teams each focusing on catalyst and membrane durability approaches, respectively. We believe this will lead to a durable MEA upon integration of the various concepts.

3) In terms of measuring catalyst performance, the focus on electrochemical surface area as an indicator of performance is questionable when it does not correlate well with EOL and BOL performance (slides 9 and 12). – for pure Pt catalysts, % loss in ECSA is the best indicator of catalyst durability particularly at i > 1.5 A/cm^2 as frequently demonstrated in the slides. While developing PtCo, we will include the loss in kinetic activity and Co^{2+} cation contamination aspects as well.

4) This project is taking on high-risk research, and it is great that DOE is supporting it. These concepts are very difficult to characterize and validate without a large amount of durability data. The project team seems a bit aggressive with its timeline, given the status presented. MEA integration and interpretation of fuel cell results will be difficult without a fundamental understanding of these prototype materials and the critical formulation parameters. – we agree that the timeline is quite aggressive, and it will take a significant amount of work to gain a fundamental understanding of the prototype materials, specifically post-mortem analysis of the optimized integrated MEA. However, this will not affect the materials integration in Phase 3 of the project, and we will be able to deliver a representative durable integrated MEA as originally planned.

Responses to Last Year (2021) AMR Reviewers' Comments (continued…)

5) …it is not clear that the project will contribute directly to the other major HD vehicle goal, which is higher efficiency. – our ultimate focus is to deliver an *o*-PtCo catalyst on stabilized catalyst support. This will enable a higher efficiency over the lifetime of operation by enabling better ECSA and mass activity throughout its lifetime.

6) Given that annealed Pt is identified as a promising path on slide 21, this should be addressed in the scope of future work. – annealed Pt has been demonstrated to be very durable primarily due to its large initial particle size, but there is no plan to study this further as it is reasonably well understood. Annealed Pt enables better ECSA retention but low initial activity which is not good for efficiency. So, our objective is to stabilize smaller Pt particles on durable supports thereby enabling higher efficiency and durability.

7) The team should consider trying to combine multiple approaches at the end of the project, if possible. For example, if both Pt–carbon and Pt–ionomer interface modifications are successful, then the team should see whether they can be combined in the same catalyst layer. It would be useful to know whether the benefits are additive. Additionally, the project should make an ultimate MEA with all of the successful approaches combined and compare the durability results to each of the individual approaches. – as part of the integration activity, we plan to combine both the catalyst approaches with either one or the other membrane approaches. There is no plan to combine the two membrane approaches together since the result is not expected to be additive (both membrane approaches attempt to resolve the same membrane degradation mechanism)

8) This project would benefit from expanded parametric studies. – it is out of scope of the project although the general trends of the parametric studies have already been evaluated as part of another DOE funded project (fc156)

Proposed Future Work (Durable catalyst and membrane development)

- This is the final year of the project
- Focus is on wrapping up the publications in the remaining month
- Pajarito to scale up ECS3701-ZrO_2 carbon, Pt/ECS3701-ZrO_2 catalyst and make it a part of product portfolio
- GM will evaluate Pajarito's catalysts on engineered carbon support with and without the Zr dopant for GM Gen 4 product program
- $CeZrO_x$ nanoparticle additive to be evaluated as an additive in GM's Gen 4 membrane design. Performance and durability effects of CZO in different components of fuel cell MEAs.
- Potential modifications for improved stability include utilizing different tethering strategies to avoid reliance on VDF in the membrane or modifying the polymerization process to substantially avoid having perfluorinated vinyl ether monomers next to VDF units.

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

Summary

- Promising new materials for both cathode catalyst and membrane durability
  - ZrO_2-doped Engineered Carbon Support enables improvement in ECSA at EOT (post-90k V cycles)
  - ZrO_2 doesn't chemical interact with Pt but mitigates the migration-coalescence of Pt
  - ZrO_2 is atomically dispersed on carbon and forms a thin shell around Pt nanoparticles
  - HPA immobilized membranes improved OCV chemical durability, but some challenges exist in the combined chemical and mechanical test
  - CZO nanofiber additive enables improved chemical durability both in OCV durability and combined chemical + mechanical durability evaluations
  - W and Ce redistribution observed in membranes doped with silicotungstic acid or $CeZrO_x$.
    - Possibly, $CeZrO_x$ nanofibers acts as a buffer for slow dissolution of active species into the membrane

- M^2FCT consortium has been engaged for materials characterizations (ANL – SAXS/XAS, electrode degradation model, LANL – carbon corrosion) & imaging (ORNL - TEM)
  - Developed a catalyst-specific electrode degradation model
  - Degradation of the Pt/ZrO_2-ECS catalyst is more dependent on the upper potential limit (UPL > T > RH)

so far: 50 different catalysts, 8 different polymer additives, 2 different membrane stabilizers, 5 conference presentations, 5 publications, 3 patent applications, 2 invited talks

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