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

Nagappan Ramaswamy
General Motors LLC, Global Fuel Cell Business

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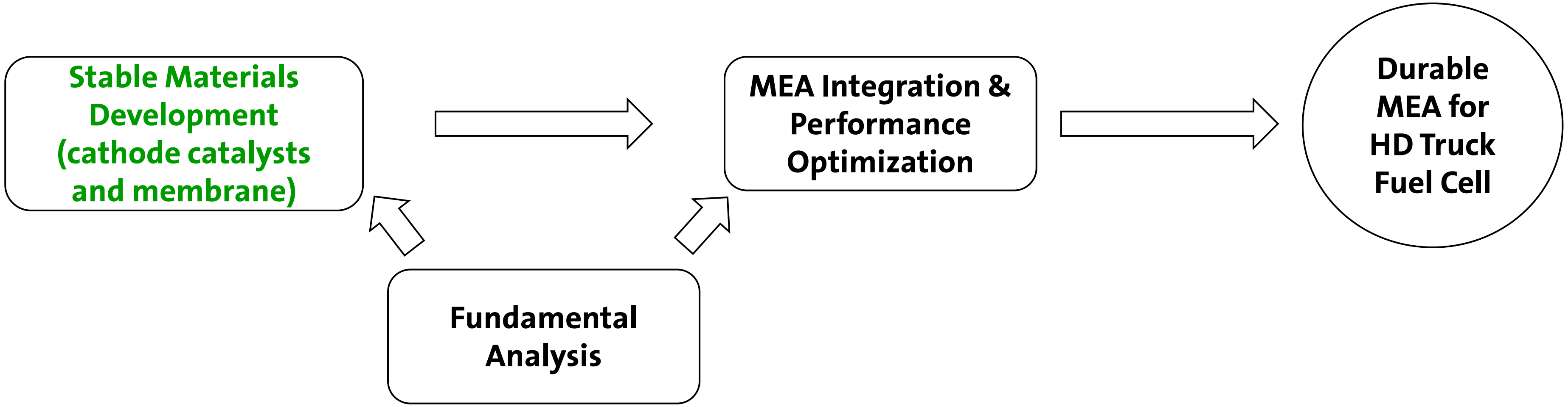
AMR Project ID: fc323

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** - < 10% degradation in power density after 30,000 hours of operation (a lifetime of 1 Million miles, ~3X compared to light-duty (LD) vehicles)


Stable Materials Development (cathode catalysts and membrane)

MEA Integration & Performance Optimization

Durable MEA for HD Truck Fuel Cell

Fundamental Analysis

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: 70%

Budget

- Total Project Budget: $2.73M
    - Total DOE Share: $2.0M
    - Total Cost Share: $0.73M (26.8%)
- Total Funding Spent: $2.1M*
    - DOE Billable: $1.5M
    - Participants Cost Share Funds Spent: $0.6M

* As of 03/31/2022 (amount by billings)

Barriers

A. Durability

< 10% power degradation after 30,000 hrs.

B. Cost

$\leq 0.2\ \mathrm{mg_{Pt}/cm^2}$ 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^{2}FCT Consortium

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	
			Pt/HSC-a	**Pajarito 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	0.68	0.49
Loss in initial catalytic activity (post-30k catalyst cycles) [b]	% MA loss	< 40	34%	**18%**
Performance at 0.8 V (150 kPa, 80°C)	A/cm^2	0.3	0.39	0.22
Performance at rated power (250 kPaabs, 94 °C)	W/cm^2	> 1.3	1.3	1.3
Loss in performance at 0.8 A/cm^2 (post-30k catalyst cycles) [b]	mV	< 30	15	**8**
HD Combined Target (at 0.7 V, post-90k catalyst cycles) [d]	kW/g_{PGM}	2.5	4.0	3.7

MEMBRANE

Metric	Units	DOE/Project Target	Status of Proposed approach		
			PFSA (no additive)	**PFSA w/ 8% $CeZrO_x$**	**PFSA blend with HPA**
Membrane thickness	µm	n/a	12	12	25 to 48
H_2 crossover	mA/cm^2	< 2	1.1	1	4.6
H^+ area specific resistance	$\Omega\ cm^2$	<0.02	0.02	0.02	0.02
Electrical resistance	$\Omega\ cm^2$	> 1000	> 3000	9000	6000
Chemical durability	hours	> 500	< 100	**306**	**671**
Membrane durability	Hours	30000	n/a	n/a	n/a

Focal points:

- Cost < 0.25 mg_{total}/cm^2
- HD combined durability and efficiency target – achieved ~ 4.0 g/kW at EOT
- membrane chemical durability of 300 to 600 hours with immobilized additives

Impact: Project is progressing towards delivering and 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 ✓

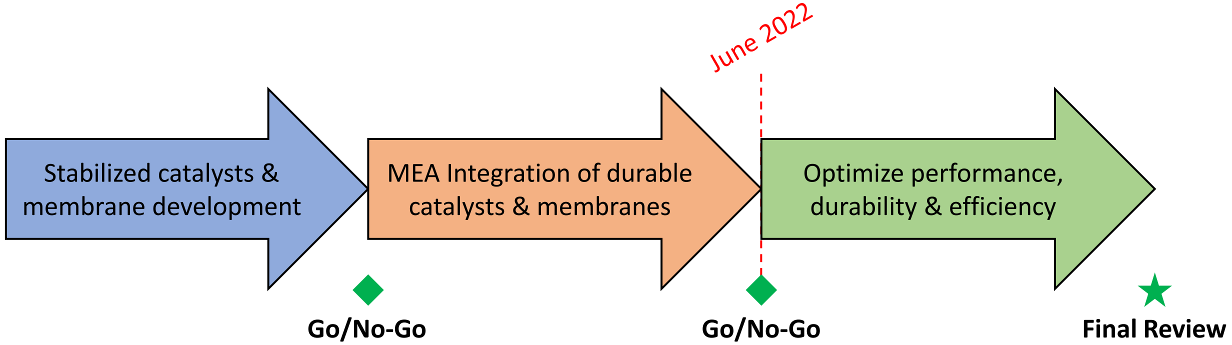
Go/No-go criteria : Anchored Pt catalyst with <30 mV loss at 0.8 A/cm^2 (60k LDV AST MEA) and membrane that meets all DOE Technical Targets (gas crossovers, ASR, chemical and mechanical durability)

	Progress
☐ Optimization of down-selected anchored GMC catalyst	80%
☐ ePTFE supported membrane development	80%
☐ Fuel cell MEA performance and durability (AST)	80%
☐ Advanced characterizations of catalysts and membranes	70%

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

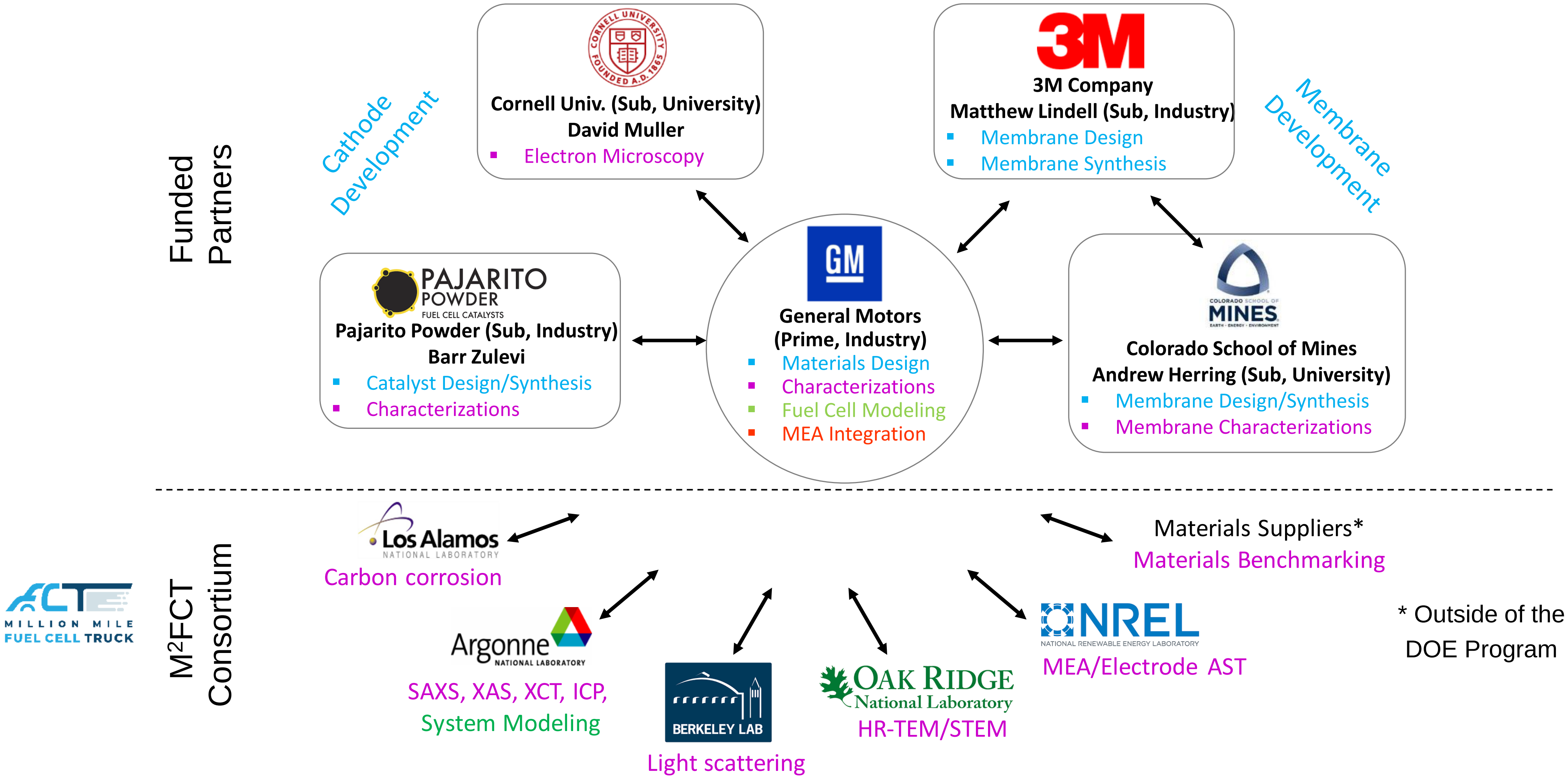
Milestone: Deliver MEA with <0.2 mg_{Pt}/cm^2 cathode, <40% MA loss in MEA, <10% loss in power after 25000 hours based on fuel cell system modeling lifetime projection studies

- ☐ Deliver MEA with state-of-the-art durable catalyst and membranes with high performance, efficiency and durability
- ☐ 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



Collaborations and Coordination

Materials dev't
Characterization
Modeling
Integration



Funded Partners

Cathode Development

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

3M Company
Matthew Lindell (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

M^{2}FCT 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: 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

Approaches – cathode and membrane durability

Catalyst durability - mitigate Pt surface area loss:

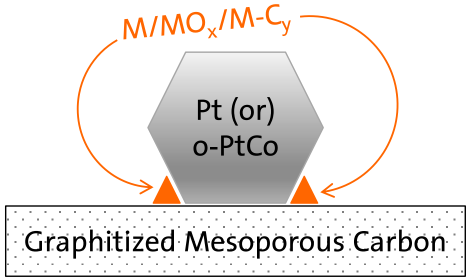
Approach 1: Pt-Carbon interface modification (anchored Pt/C catalysts)

a. Zr/ZrO$_x$ additives to stabilize Pt against surface area loss

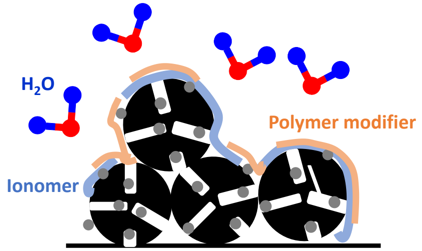
Approach 2: Pt-ionomer interface modification (advanced polymer additives)

a. 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:

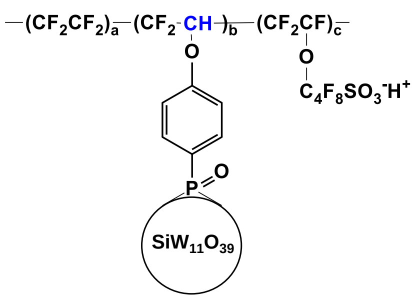
Approach 3: Covalent tethering of heteropoly acid (HPA) anti-oxidant

a. Silicotungstic acid as an immobilized radical scavenger for membrane durability

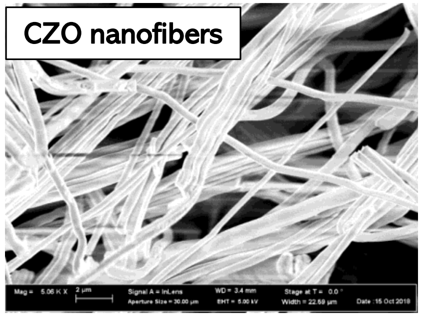
Approach 4: Dispersed CeZrO$_x$ (CZO) nanofibers for membrane stabilization

a. 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.*

Technical Accomplishment (approach 1: catalyst durability – Pt-carbon interface modification)

Engineered carbon support (ECS) – synthesis and key features

Pajarito's Varipore^{TM} 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

Demonstrated catalyst: 30% Pt/ 3% Zr-doped ECS

Varipore^{TM} Manufacturing Platform

Precursors & structuring agents

Mixing

Graphitization

Engineered Catalyst Support^{TM} (ECS)

Pt/ECS

Zr stage 1

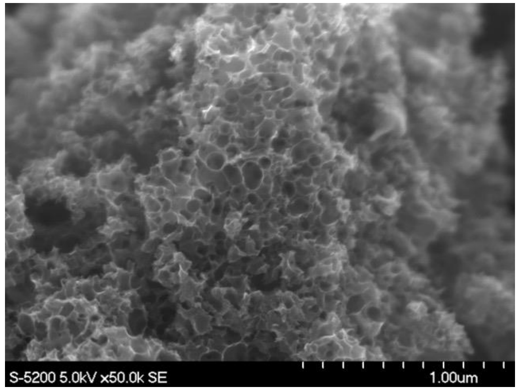
Zr stage 2

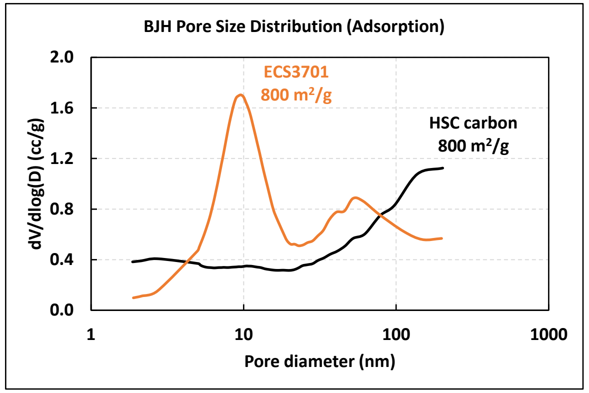
Zr dopant added in two discrete stages:

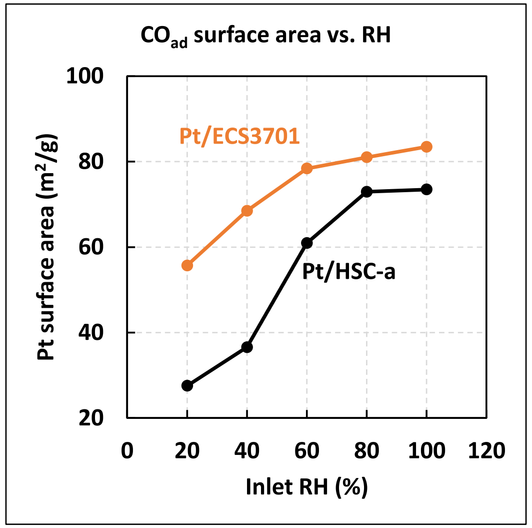
1) added to the organic carbon precursor (~0.5 wt.%)
2) added after carbon synthesis (~2.5 wt.%)

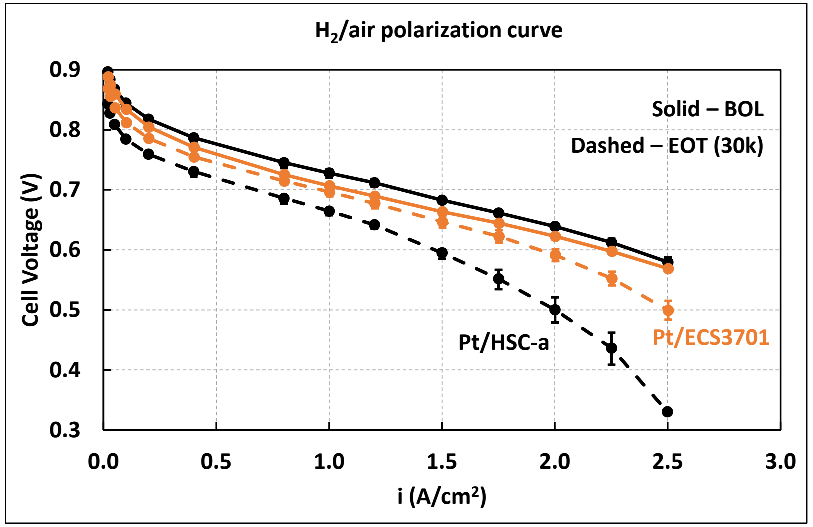
Features of the Engineered Carbon Support (ECS)

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









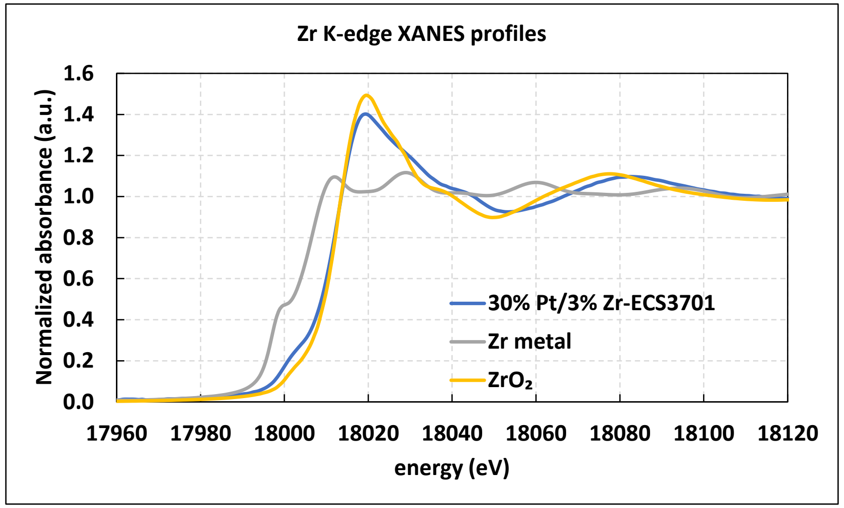
H$_2$/air, 80 °C, 100% RH, 150 kPaa (50% Pt, 0.2 mg/cm^2)

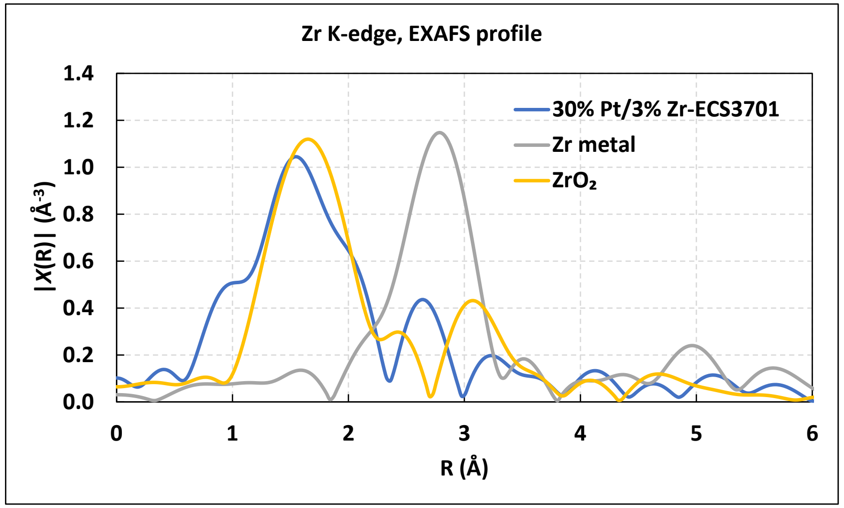
Technical Accomplishment (approach 1: catalyst durability – Pt-carbon interface modification)

Characterization of Zr-doped Engineered Carbon Support

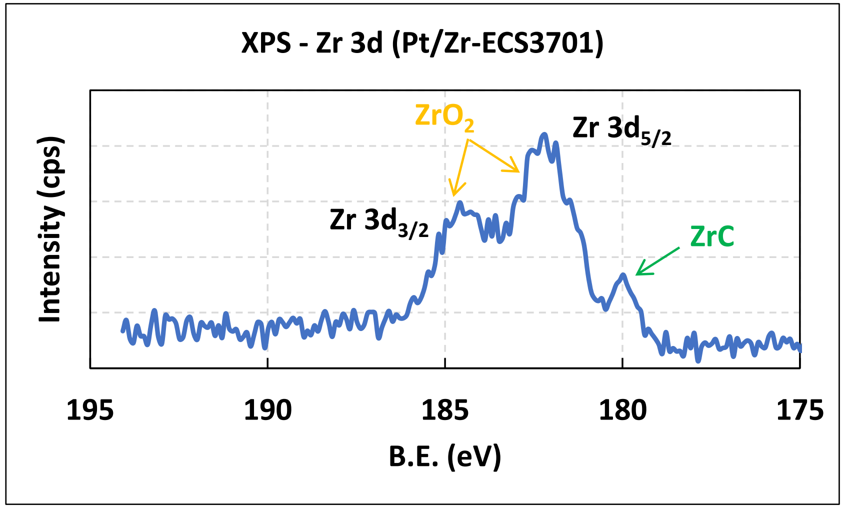
- Zr is likely dispersed as a mix of ZrC and ZrO_2 nanoclusters on the carbon support

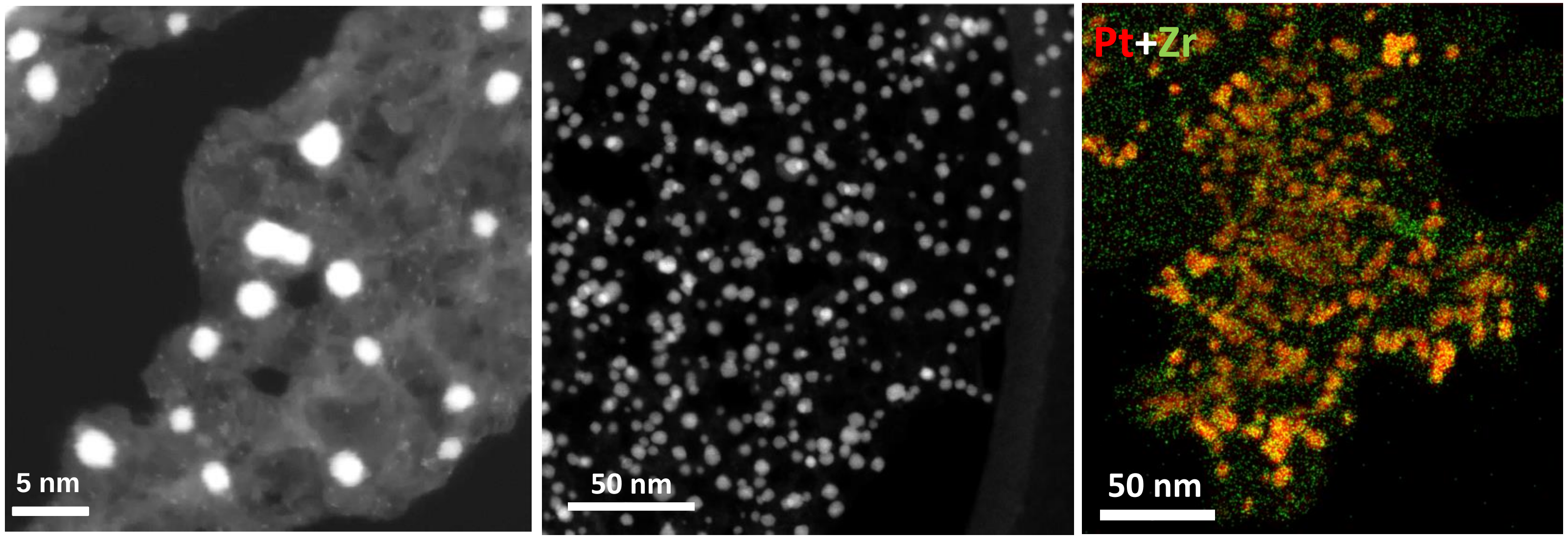
30% Pt / 3% Zr doped-ECS3701 (fresh coating)





- XAS – indicates primarily ZrO_2 feature
- XPS – suggests the presence of ZrC (possibly on the surface)
- STEM-EDS – dispersion of Pt nanoparticles along with ZrO_2





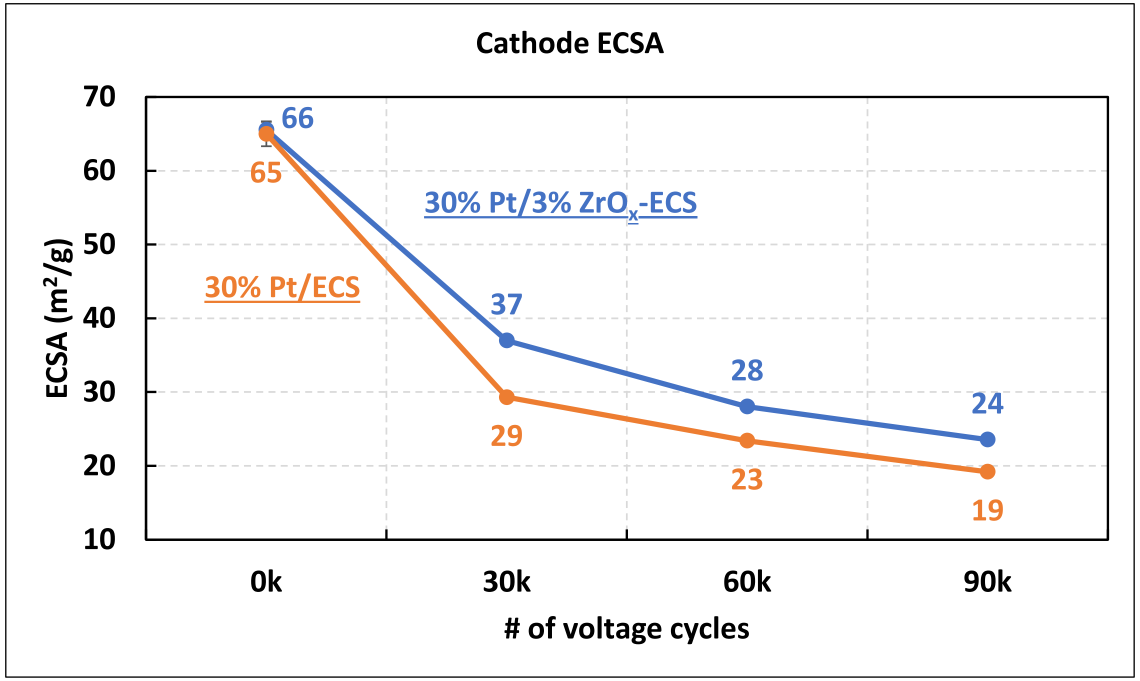
Pt distribution

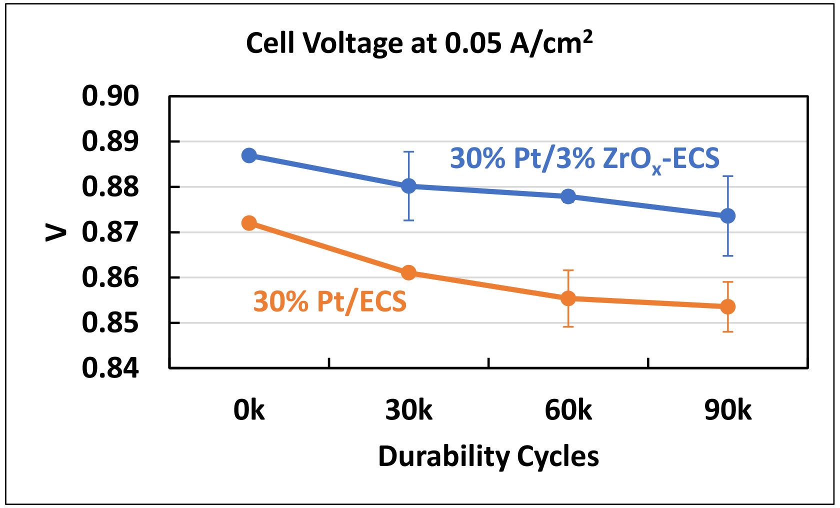
Technical Accomplishment (approach 1: catalyst durability – Pt-carbon interface modification)

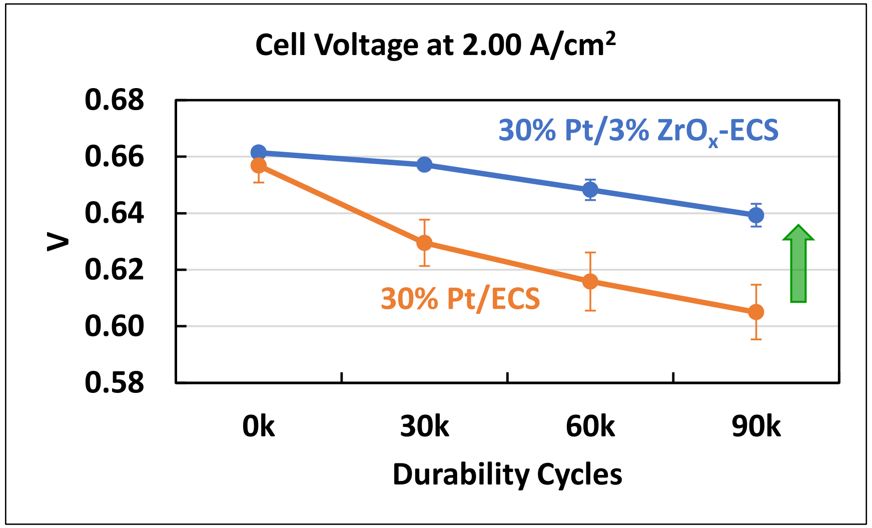
MEA durability of 30% Pt/Zr-doped ECS3701 catalyst

- Durability of 30% Pt dispersed on 3% Zr-doped carbon has been evaluated in MEA up to 90k cycles

Catalyst AST protocol
Trapezoidal waveform (H_2/N_2)
0.60 to 0.95 V, **90k cycles**
90 °C, 4s/cycle, 100% RH







Membrane: 12 µm PFSA, anode: 0.05 mg_{Pt}/cm^2

- Pt/ZrO_x-doped carbon shows 25% improvement in ECSA after extended V-cycles
    - enables ~40 mV higher cell voltage after 90k voltage cycles

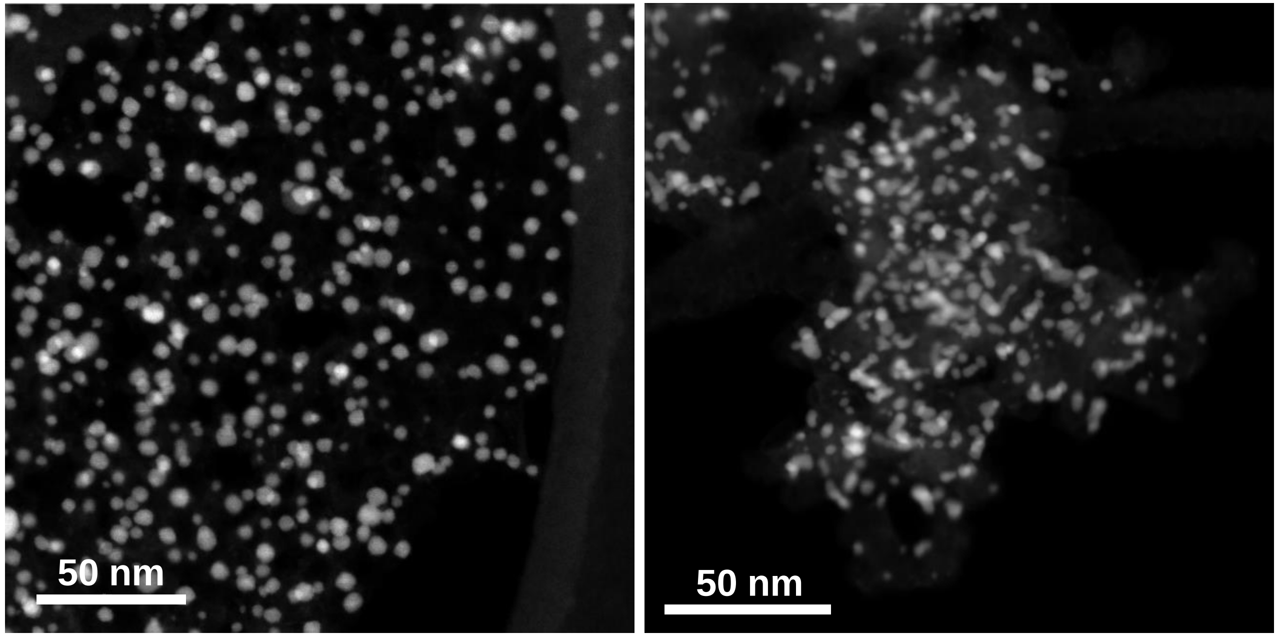
Technical Accomplishment (approach 1: catalyst durability – Pt-carbon interface modification)

Characterization of degraded Zr-doped ECS3701 catalyst

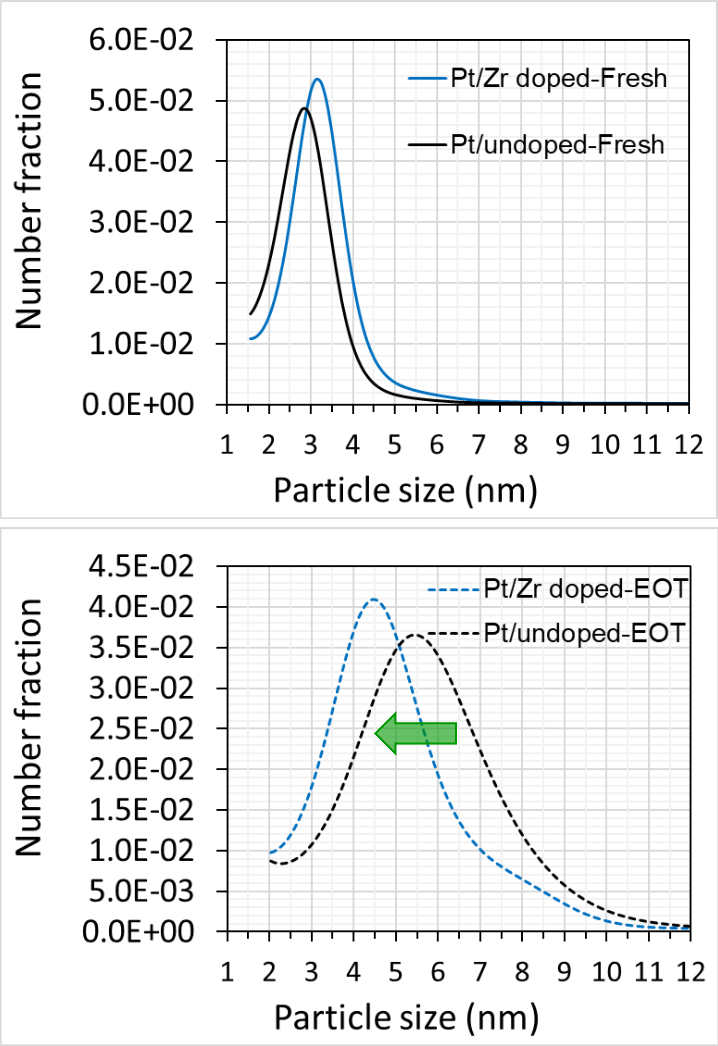
- Catalysts characterized via STEM imaging and SAXS to understand particle size growth

30% Pt / 3% Zr doped-ECS3701

BOL **EOT (30k cycled)**



SAXS Pt PSD



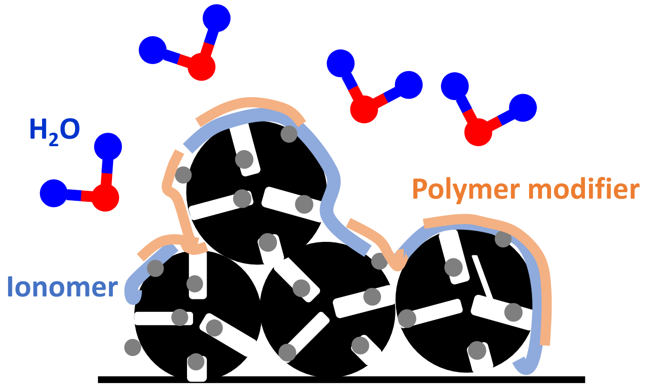
- Pt nanoparticles appear elongated and coarsened after 30k cycles but with a lower average particle size for the Zr-doped catalyst
  - agrees with the higher ECSA for Zr-doped catalyst at EOT
- Detailed STEM-EDS analysis of the cycled catalyst is ongoing

Stable catalyst layers via modification of Pt/ionomer-water interface

Technical Barrier: i) Pt surface area loss via dissolution-redeposition, and ii) dissolution of cobalt-alloying element

Approach: Pt-ionomer/water interface modification

Modify Pt/ionomer-water interface with hydrophobic polymer additives to stabilize Pt surface against Ostwald ripening mechanism



Various steps in Ostwald ripening mechanism

a. Pt oxidation (water is a reactant)

$$Pt + H_2O \rightarrow Pt\text{-}O(H) + H^+ + e^-$$

a. Pt dissolution (H_2O for solvation)

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

$$PtO + 2H^+ \rightarrow Pt^{2+} + H_2O$$

a. Pt^{z+} migration (dependent on H_2O for Pt^{z+} cation transport)

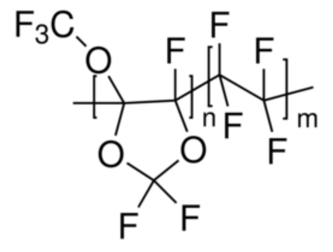
b. Pt^{z+} redeposition

- Presence of H_2O at the Pt/ionomer interface is critical for ORR kinetics & reactant transport but is also a precursor in de-stabilizing the Pt surface via the Ostwald ripening mechanism (Pt oxidation/dissolution kinetics, Pt^{z+} migration and re-deposition)
- Catalyst layer becomes more hydrophilic as it ages during voltage (load) cycles
- Also, need to stabilize Pt interface with ionomer/water against hydrophobicity changes
- This approach to evaluate the use of fluorinated polymers that need only low temperature sintering, if any

Outcome: *Durable catalyst with improved resistance towards surface area loss and Co-dissolution*

Pt-ionomer interface modification – Hyflon® polymer

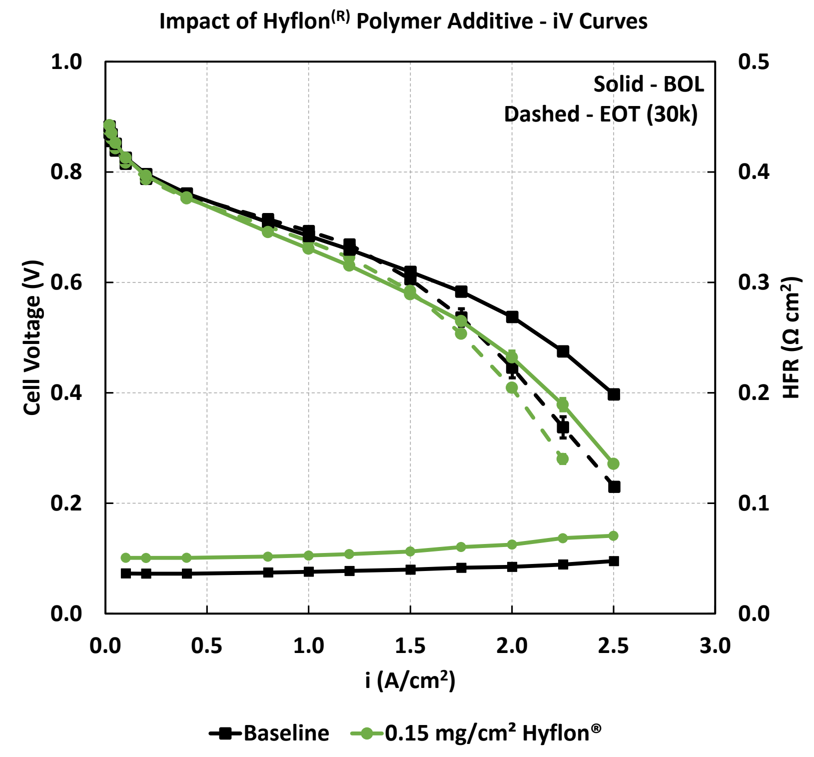
- Identified a new amorphous perfluoro-polymer with a cyclic structure for modification of the catalyst layer
  - Hyflon® - high thermal stability, hydrophobicity and chemical resistance with very low surface energy
- Added to the catalyst layer either as a topcoat, requires a thermal sintering step at 100 °C



Hyflon®

Poly(tetrafluoroethylene-co-2,2,4-trifluoro-5-trifluoromethoxy-1,3-dioxole)

P(TTD-TFE) copolymer



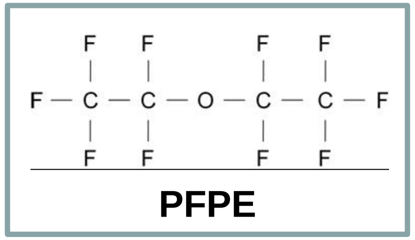
	Baseline		w/Hyflon®	
	BOL	EOT (30k)	BOL	EOT (30k)
ECSA (m^2/g)	70	30	70	37
MA (A/mg)	0.35	0.26	0.37	0.34
SA ($\mu A/cm^2$)	491	850	497	859

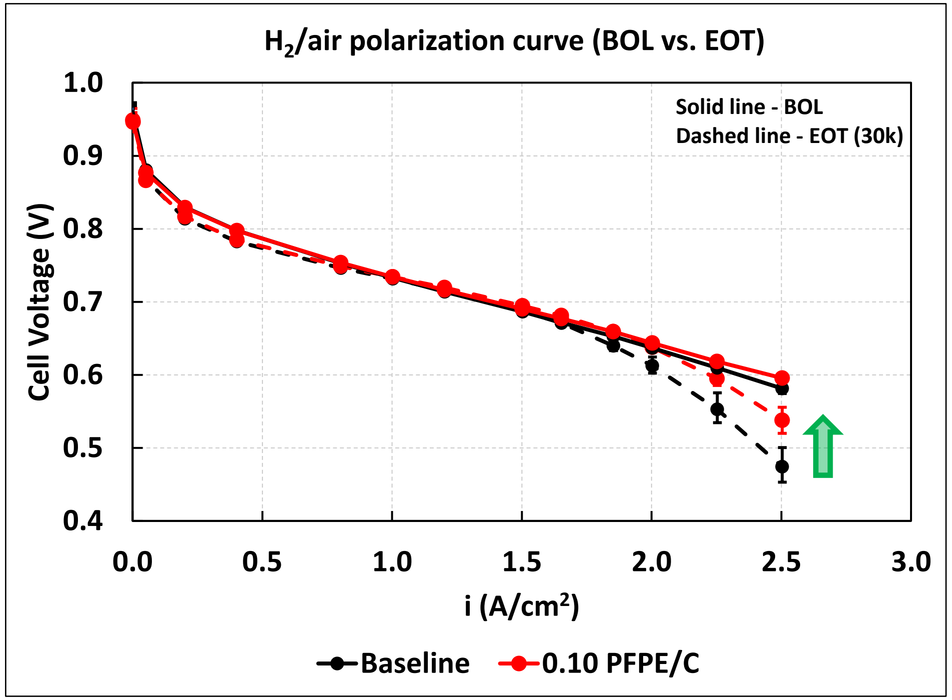
H_2/air, 80 °C, 100% RH, 150 kPaa
30% Pt/HSC-a, 0.1 mg/cm²

- Improvement in Pt surface area (~23%) and mass activity retention (<8% loss) at EOT (30k cycles) with Hyflon® additive
- Cell voltage loss after durability cycling is lower with Hyflon® additive compared to Baseline electrode
  - higher HFR with Hyflon® limits the beginning of life cell voltage

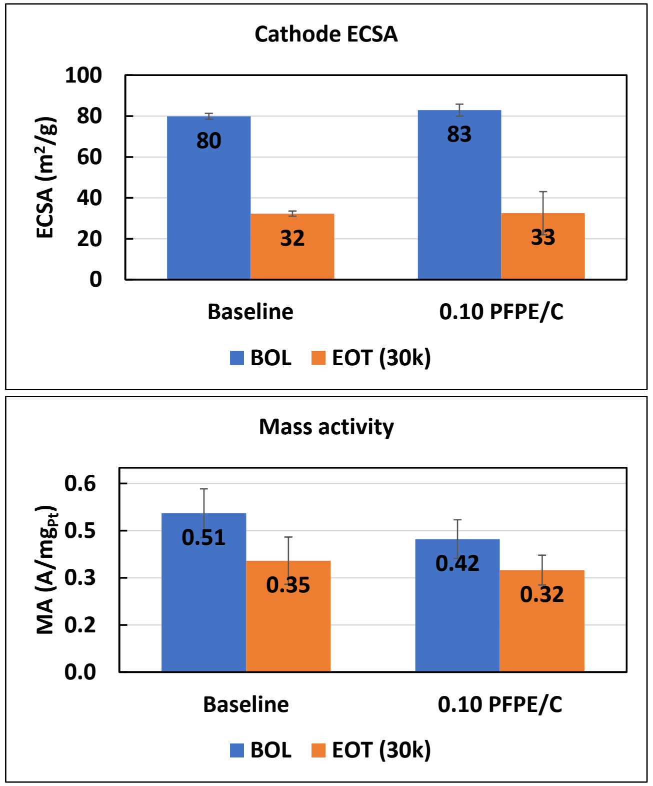
Pt-ionomer interface modification – perfluoropolyether additive

- Identified a new fluorinated perfluoropolyether (PFPE) material for modification of the catalyst layer
- Added to the catalyst layer either as a topcoat or as an additive in the ink formulation stage
- Requires a thermal sintering step at 80 °C, compatible with existing electrode fabrication procedures





H_2/air, 94 °C, 100% RH, 250 kPaa
30% Pt/HSC-a, 0.1 mg/cm^2, 0.10 PFPE/C



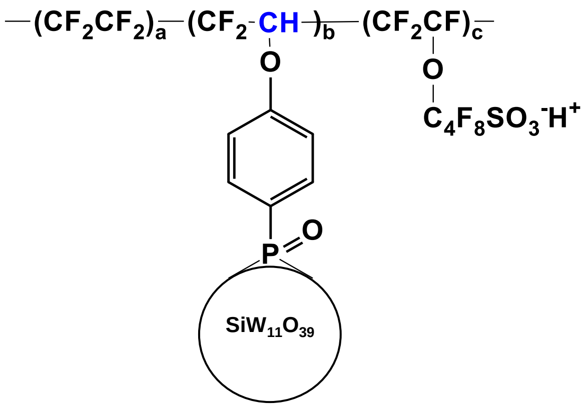
- PFPE enables improvement in cell voltage at EOT, specifically at high current densities
  - No notable durability differences in kinetic activity and ECSA parameters
- PFPE likely stabilizes the catalyst layer against hydrophobicity changes that occurs during load cycling
  - Minimal differences at dry operating conditions (data not shown)

Technical Accomplishment (approach 3: membrane durability – immobilization of HPA antioxidant

HPA immobilized membrane – synthesis and blended membrane fabrication strategy

- Use of silicotungstic acid as a representative heteropoly acid (HPA) additive with radical scavenging properties
- Developed synthesis chemistry to covalently bind silicotungstic acid to the PFSA membrane backbone

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

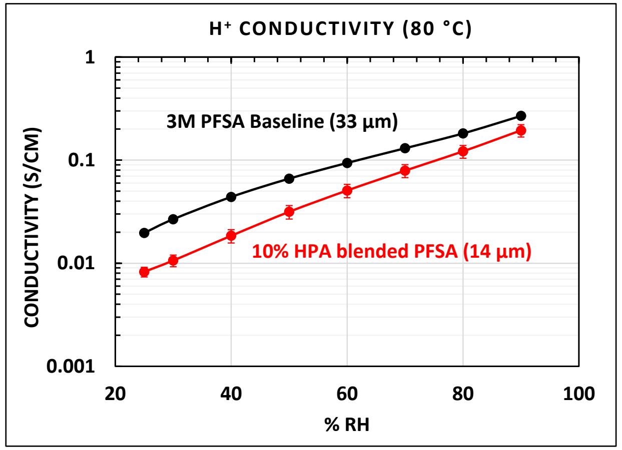


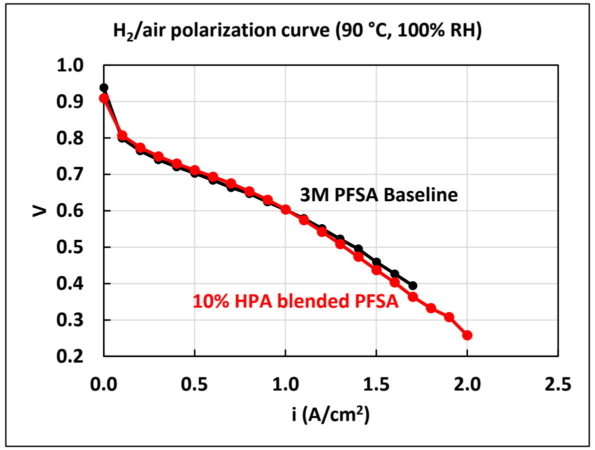
- Vinylidene fluoride (VDF) monomer ($-CF_2-CH_2-$) acts as an anchor point to covalently tether anti-oxidant to PFSA backbone
- Vary VDF monomer ratio to optimize performance and durability

Blended membrane strategy (conventional PFSA + ionomer with tethered HPA)

PFSA (80-90%) + **PFSA w/ tethered HPA (10-20%)** → **Blended Membrane**

- Successfully fabricated 25-80 µm thick membranes composed of HPA modified PFSA blended with conventional 3M PFSA



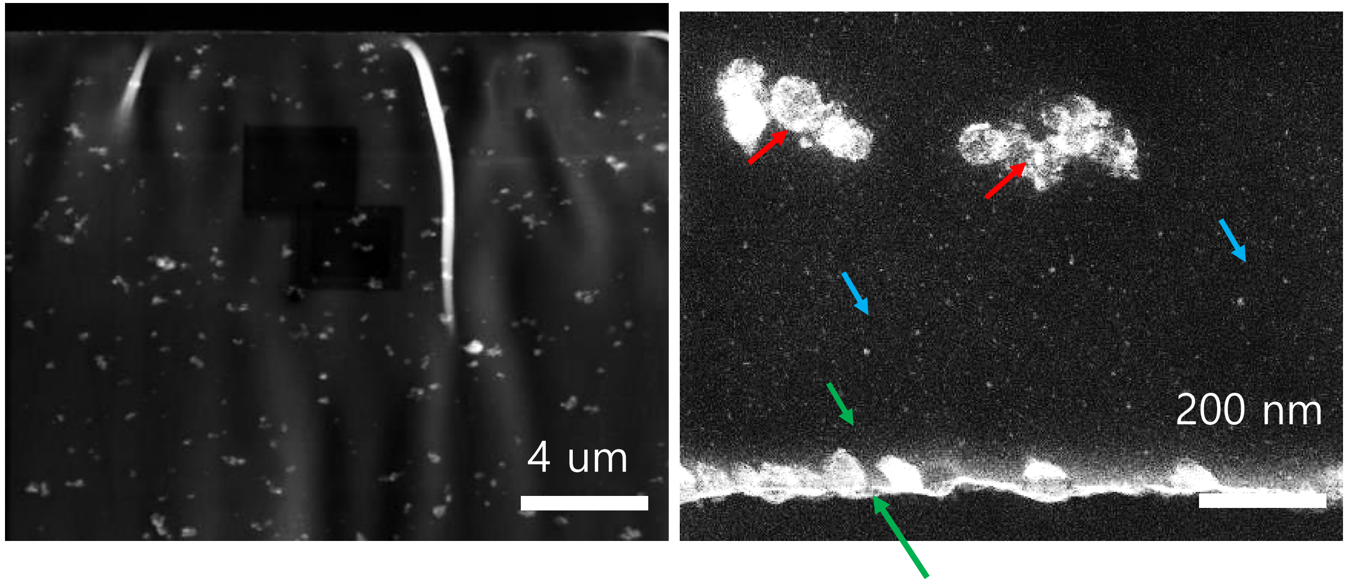


- Minor loss in conductivity for the blended membrane
- Conductivity improvement expected with better HPA dispersion
- Negligible difference in H_2/air polarization behavior

Characterization of HPA immobilized blended PFSA membrane

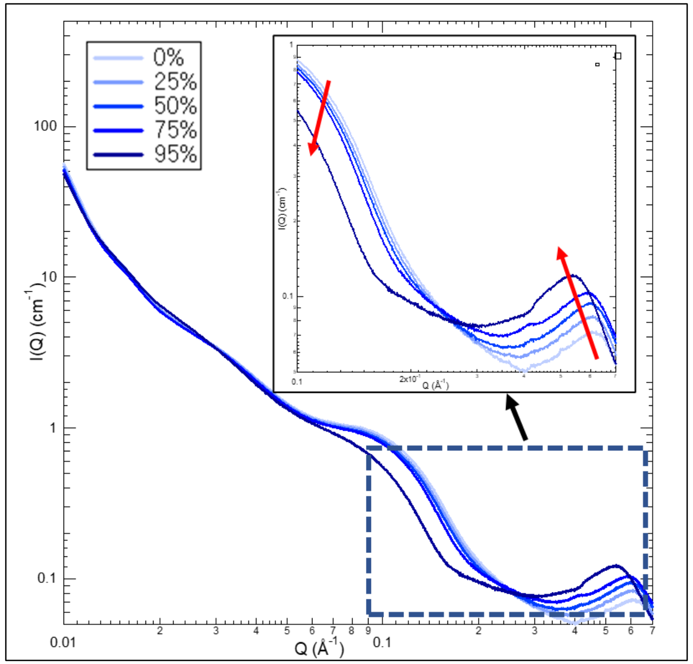
- Blended PFSA membrane with 10% HPA immobilized component was characterized using TEM imaging and SAXS
  - to understand HPA dispersion and covalent attachment to the backbone

Cross-sectional TEM images of HPA immobilized membrane



Bottom – substrate or liner side

SAXS profile as a function of RH



- TEM cross-section shows HPA dispersed as fine nm sized additives (blue arrows)
- Further, HPA is also observed as
  - 100 to 200 nm sized agglomerates that are either dispersed (red arrows)
  - or dense deposit near the substrate or liner-side of the membrane (green arrows)

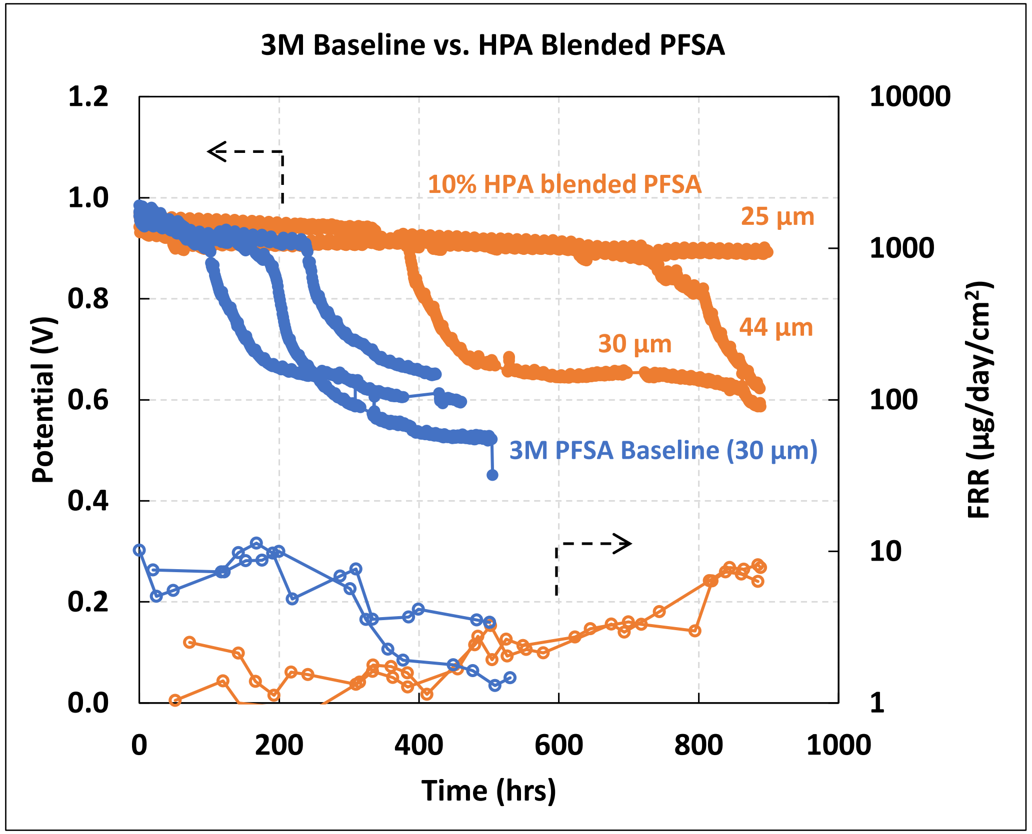
- SAXS corroborates successful covalent binding of HPA to anchoring group and morphological ordering induced by HPA
- Peak at 0.6 Å^{-1} (d-spacing of 1.0 nm)
  - water molecules favor HPA moieties
  - Enlarge d-spacing between HPAs

Technical Accomplishment (approach 3: membrane durability – immobilization of HPA antioxidant

OCV durability testing of MEAs with HPA immobilized membrane

- HPA immobilized membranes were subjected to OCV durability testing in MEAs at both GM and 3M laboratories
- Representative results are shown based on OCV testing at 3M

OCV Testing, unsupported membranes (90 °C, 38% RH)



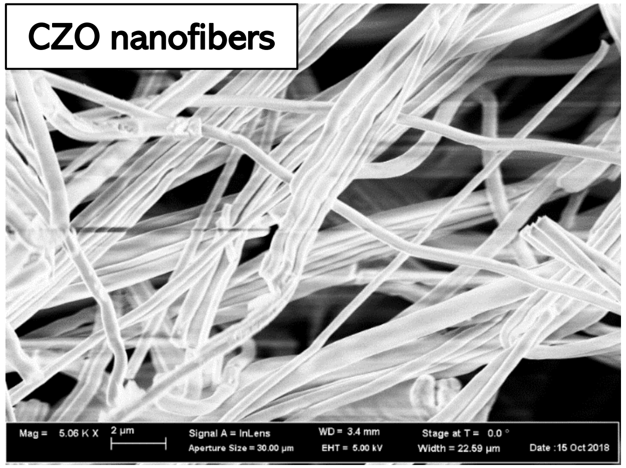
H_2/air, 90 °C, 38% RH, 696 sccm H_2, 1650 sccm air
Anode – 0.1 mg_{Pt}/cm^2
Cathode – 0.3 mg_{Pt}/cm^2

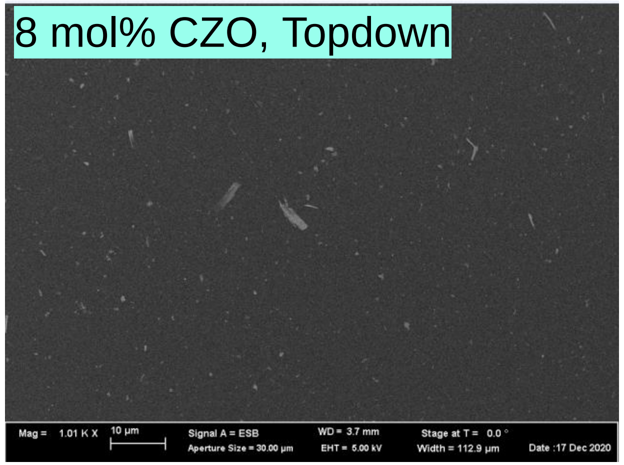
		OCV Lifetime (hrs)		Average Fluoride release rate (µg/cm²/day)	
Membrane	Samples	Mean	Stdev	Mean	Stdev
HPA-PFSA	8	671 (running)	193	3.9	0.8
3M Baseline	4	242	112	7.4	1.8

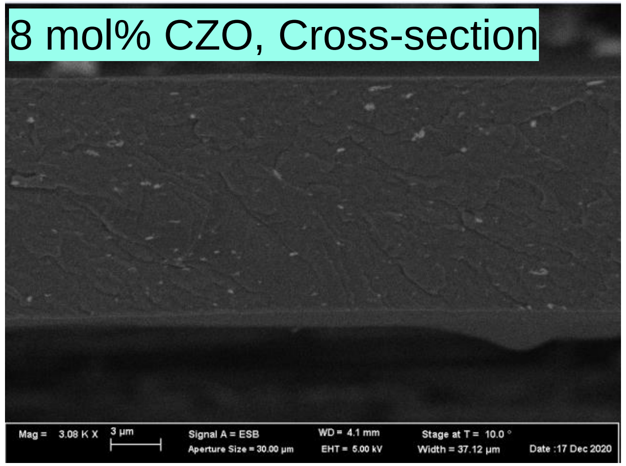
- OCV durability shows decreased voltage loss, and improved chemical durability (reduced FRR)
- Longer lifetimes achieved relative to unsupported, additive-free 3M PFSA; tests ongoing.

Technical Accomplishment (approach 4: membrane durability – dispersed CeZrO$_x$ nanofiber additives

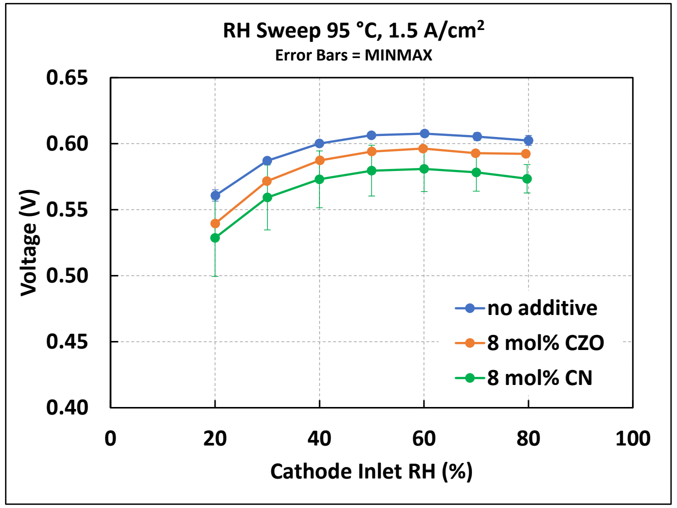
CZO membrane additives – CZO dispersion, membrane preparation and performance tests







12 µm CZO-PFSA on PEN substrate



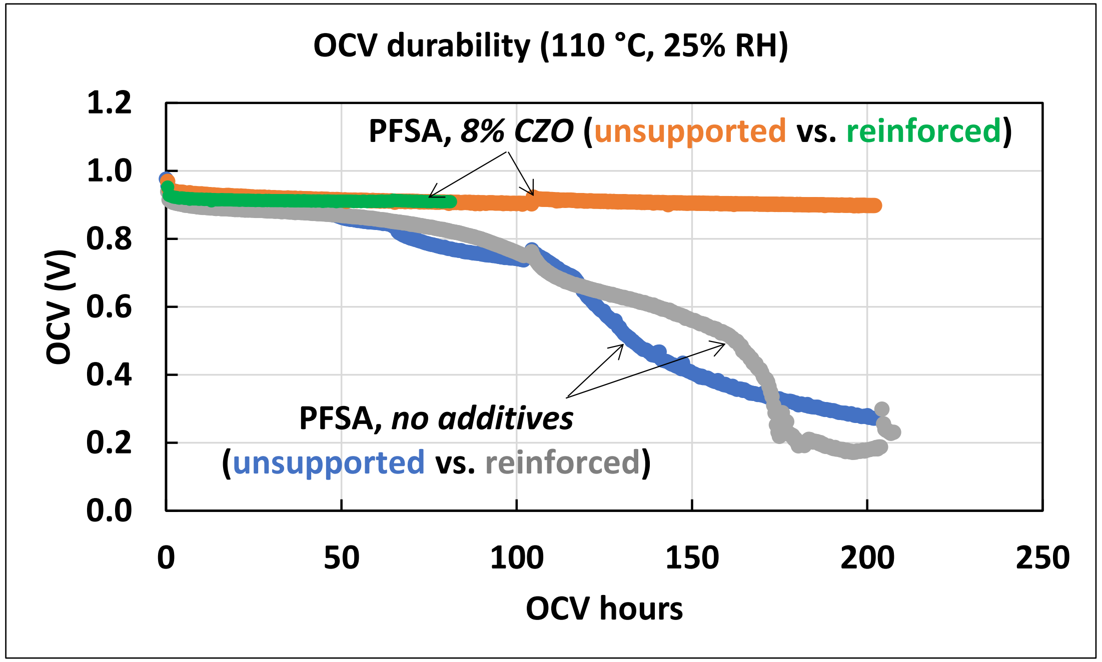
CZO – CeZrO$_x$, CN – Ce(NO$_3$)$_3$

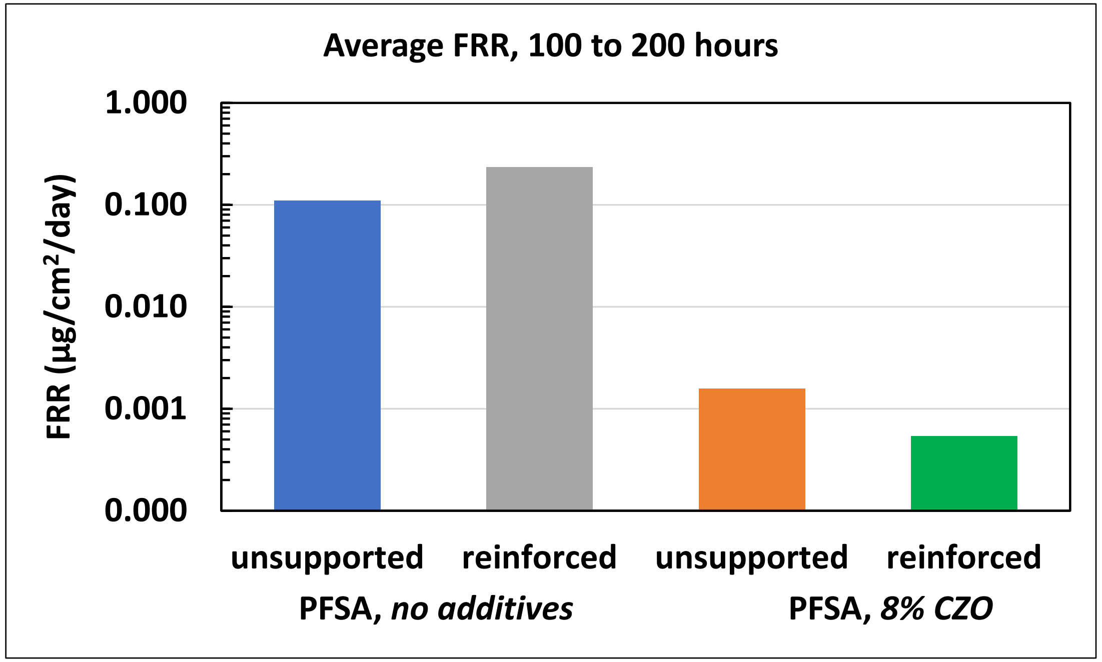
mol % - w.r.t. total MEA SO$_3$H content

- CZO nanofiber additives dispersion in ionomer solutions have been studied by beads milling with objective of obtaining homogenous coating solution. CZO particle size distribution was measured using HORIBA Laser Particle Size Analyzer, as a function of milling beads size, milling speed, additive concentrations.
- Homogeneous solution obtained and uniform additive distribution obtained within membrane.
- Fuel cell performance tests show similar performance of membrane with CZO additive to non-additive membrane.
- Preliminary data from LBNL shows membrane with CZO additive has higher water uptake than no-additive membrane.

CZO membrane additives – OCV durability and FRR

- Homogeneous membranes, and ePTFE reinforced membranes w/ and w/o CZO additives were fabricated and tested for performance and OCV chemical durability
- OCV durability of membranes with CZO show decreased OCV voltage loss, and improved chemical durability (reduced FRR)
- 500 hrs. OCV tests are scheduled for ePTFE reinforced membranes with CZO additives.
- Post OCV tests, *ex situ* analyses such as XRF and SEM cross-sections will be conducted on the MEA samples.



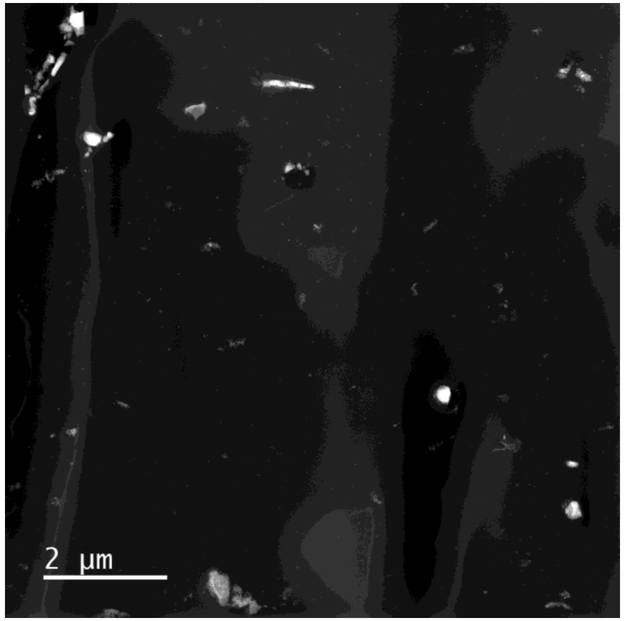


Reinforced membranes – 12 µm

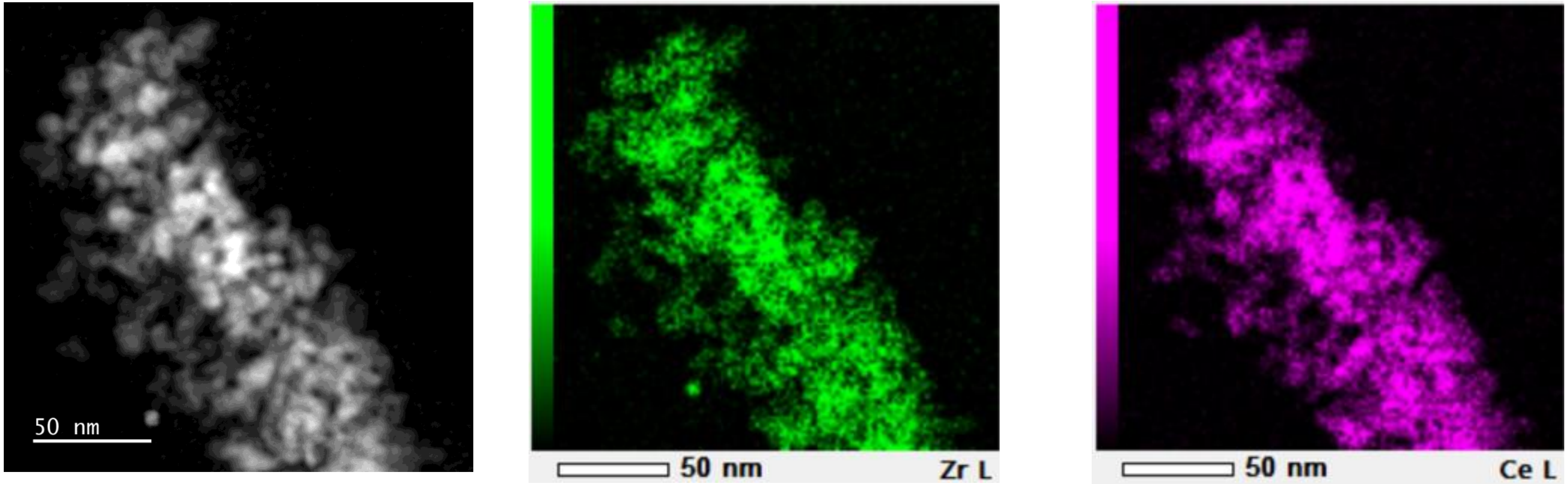
Unsupported membranes – 25 µm

Technical Accomplishment (approach 4: membrane durability – dispersed CeZrO$_x$ nanofiber additives

CZO membrane additives – End of Test (EOT) Analysis by TEM and EDX



- End of test analysis was conducted at ORNL on membrane with CZO additive after fuel cell performance and 200 hrs OCV durability tests.
- CZO nanofibers/particles still observable after fuel cell chemical degradation tests.
- EDX analysis confirmed the chemical component by detecting Ce and Zr elements in the particles.
- CZO also can be potentially used for gradually releasing Ce cation.



Proposed Future Work (durable catalysts and membrane development)

	Item	Remaining challenges	Proposed future work
Focus of Phase 3	MEA Integration	- identify concepts/approaches to integrate - durability evaluation of the integrated MEA and lifetime projection studies	- evaluate combination of the two catalyst approaches (June 2022) - perform a combinatorial study of the two catalyst approaches with membrane concepts (July – August 2022) - perform catalyst AST and combined chemical/mechanical stress tests on the integrated MEA, durability modeling for lifetime projection
Continued material optimization & post-mortem analysis	Zr-doped catalyst	- investigate the role of the Zr dopant	- characterize Zr doped ECS3701 material using STEM-EDS, XPS, XAS, *in situ* ICP, *in situ* carbon corrosion
	Polymer additives	- evaluate mechanism of improvement	- perform electrochemical diagnostics of ionomer adsorption, transport resistances & spectroscopic analysis of the polymer
	HPA tethered PFSA	- improve HPA dispersion, mechanical integrity and morphological properties of the membrane	- fabricate e-PTFE reinforced to blended HPA-PFSA membrane - XRF imaging of W to understand HPA migration, if any.
	CZO dispersed PFSA	- understand Ce redistribution from CZO	- XRF imaging of Ce to understand CZO dissolution/migration, if any.

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

Summary

- ❑ Promising new materials for both cathode catalyst and membrane durability
    - Zr-doped Engineered Carbon Support enables improvement in ECSA at EOT (post-90k V cycles)
    - Perfluoropolyether and Hyflon® additives improve cathode catalyst layer durability
    - HPA immobilized membranes enables ~400 to 800 hours of OCV durability with improved chemical stability
    - CZO nanofiber additive enables improved chemical durability based on OCV durability testing

- ❑ M^{2}FCT consortium has been engaged for materials characterizations (ANL – SAXS/XAS) & imaging (ORNL - TEM)

- ❑ Future studies will focus on
    - integration of stabilized catalysts and membranes to deliver highly durable MEA
    - execute durability tests of membranes subjected to combined chemical and mechanical stresses and the mapping of scavenger migration (in collaboration with M2FCT)
    - post-mortem analysis to understand the material structure-property relationships

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

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M^{2}FCT

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- Rajesh Ahluwalia, Xiaohua (Joshua) Wang
- Dave Cullen
- Mukund Rangachary
- Rod Borup, Adam Weber, Ahmet Kusoglu

Technical Back-Up and Additional Information

Technology Transfer Activities

Patent/Invention Submission

1. “Advanced Ionomers Based on Covalently Bound Hetero Poly Acids” Michael Yandrasits, Matthew Lindell, Arne Thaler, Andrew Herring, ChulOong Kim, Mei-Chun Kuo, Craig Gittleman, *filed January 2021* (Joint invention submission with inventors from GM, 3M, and Colorado School of Mines was filed in January of 2021 with all three partners. Independent council has been identified to draft the patent application. Provisional patent application filing will be completed before June 7th.)

2. “Fuel Cell Cathode and Fuel Cell System Including a Polymeric Additive”, Nagappan Ramaswamy, Roland Koestner, Swami Kumaraguru, filed on January 11, 2022.

Publications and Presentations

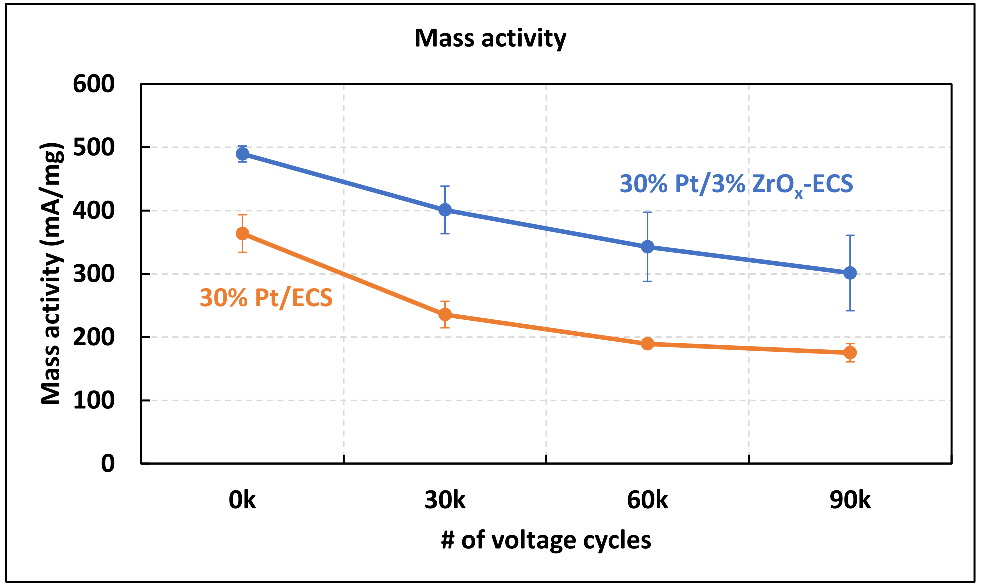
Publications

1. "High-Current Density Durability of Pt/C and PtCo/C Catalysts at Similar Particle Sizes in PEMFCs" Nagappan Ramaswamy, Swami Kumaraguru, Wenbin Gu, Ratandeep Singh Kukreja, Kang Yu, Daniel Groom and Paulo Ferreira, *J. Electrochem. Soc.* (2021) 168 (2) 024519.

Electrochemical diagnostics of Zr-doped ECS3701 catalyst

- Durability of 30% Pt dispersed on 3% Zr-doped carbon has been evaluated in MEA up to 90k cycles

Catalyst AST protocol
Trapezoidal waveform (H_2/N_2)
0.60 to 0.95 V, **90k cycles**
90 °C, 4s/cycle, 100% RH



Membrane: 12 µm PFSA, anode: 0.05 mg_{Pt}/cm^2

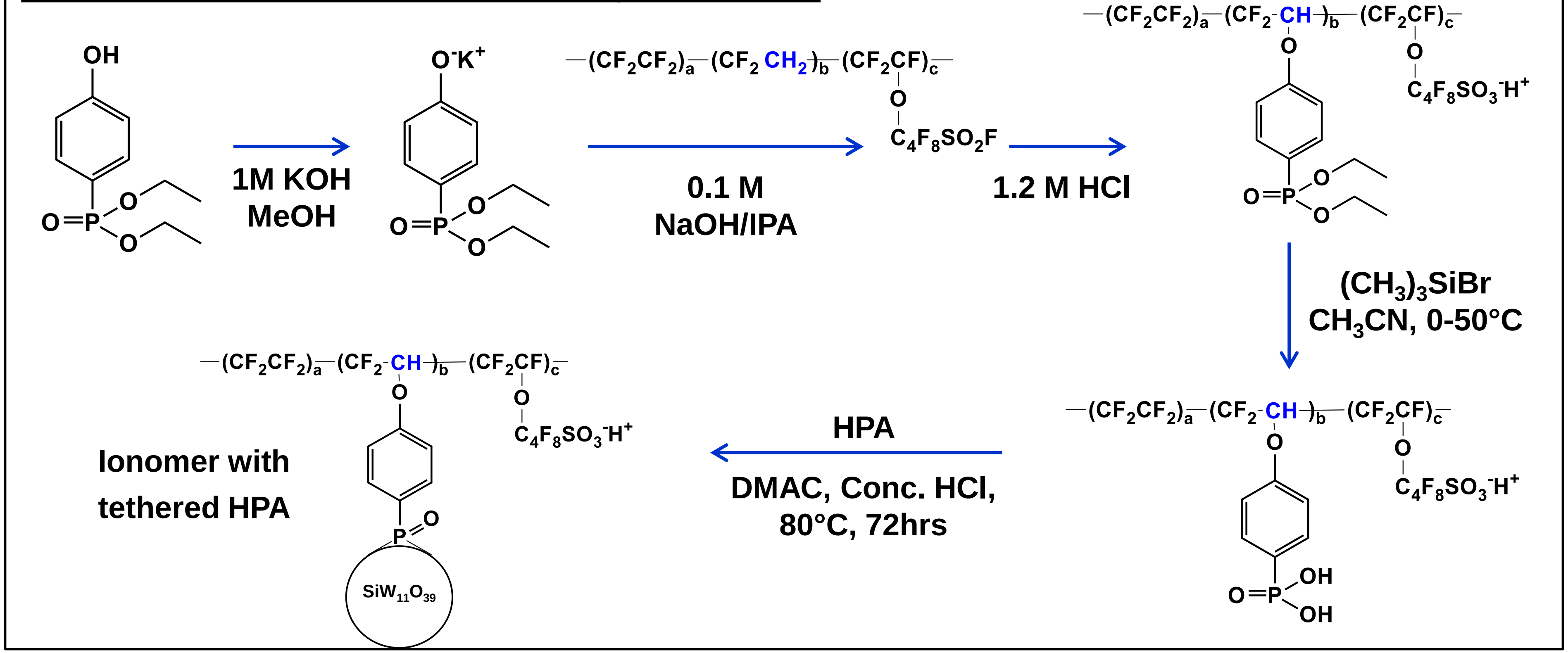
- Is direct Pt-ZrO$_x$ interaction responsible for improvement in surface area retention and cell voltages?
  - since Zr is doped into the organic carbon precursor, the possibility of better ECSA retention due to the modified carbon micro/meso-structure remains open
  - double-layer capacitance of Zr-doped ECS is reasonably higher than the non-doped carbon

Synthesis of ionomer with anchored heteropoly acid (HPA)

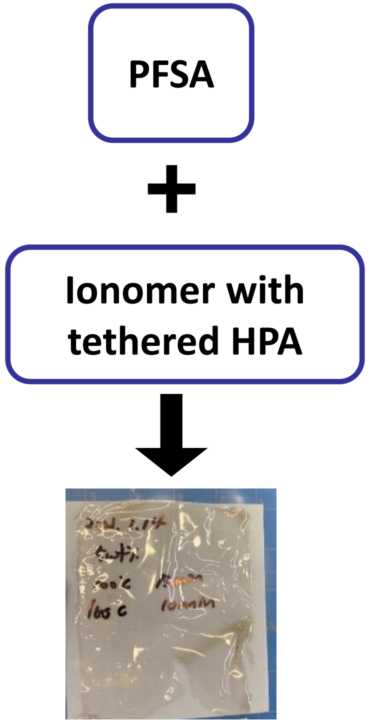
Accomplishments:

- Developed synthesis chemistry successfully to covalently bind HPA to the PFSA membrane backbone
  - Attach phosphate ester linking group before hydrolysis of SO_2F group but prior to the attachment of HPA anti-oxidant
  - Mild hydrolysis conditions developed to convert SO_2F to SO_3X

CSM route - Functionalization followed by acidification



Blended membrane strategy
(conventional PFSA +
ionomer with tethered HPA)



PFSA

+

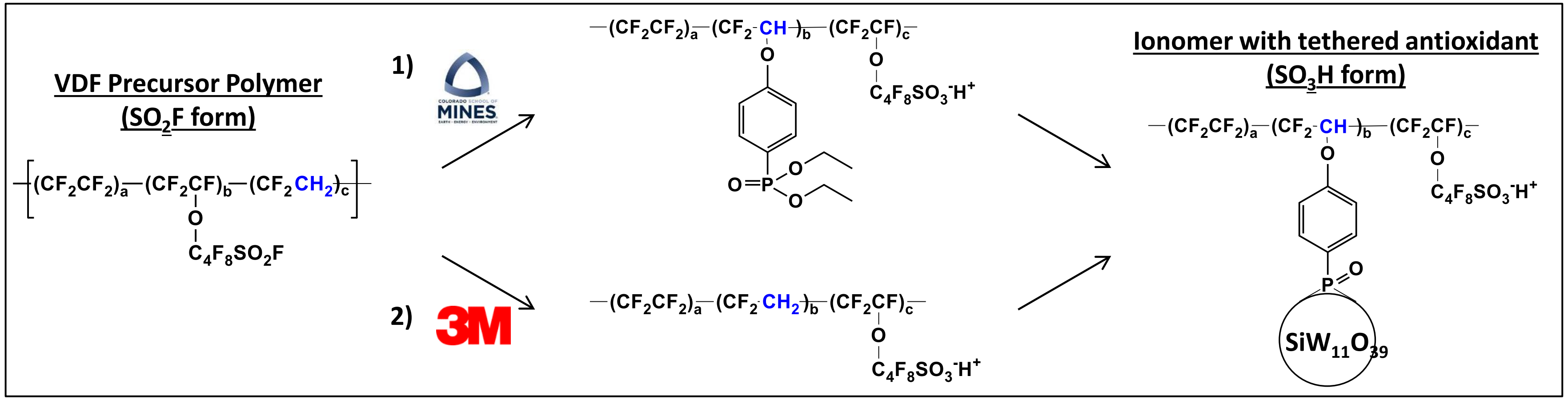
Ionomer with tethered HPA

Blended Membrane

- **Successfully fabricated 40-80 μm thick membranes composed of HPA modified PFSA blended with conventional 3M PFSA**

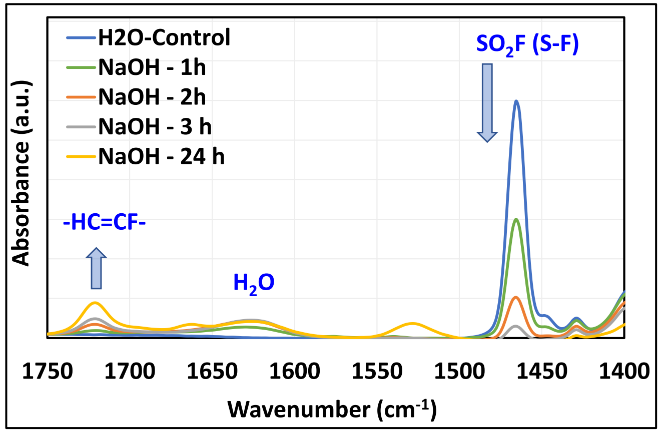
VDF Precursor Polymer Synthesis and Hydrolysis

Scheme for synthesis of PFSA ionomer with covalently tethered heteropoly acid radical scavenger additive

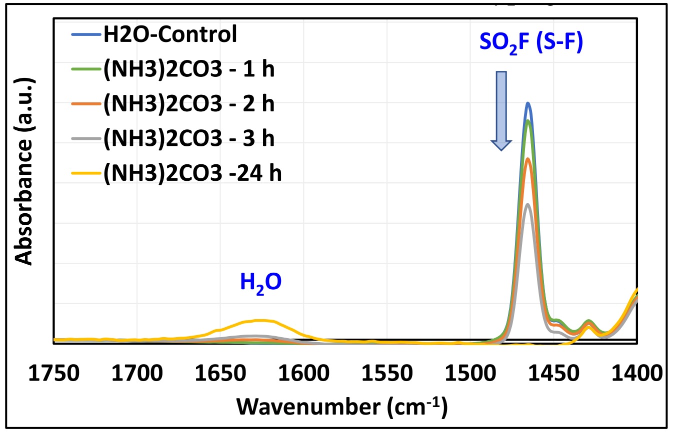


- VDF link – anchor point to tether HPA
- Two pathways
  1) Functionalize in the (~SO_2F) form
  2) Hydrolyze and acidify SO_2 to SO_3H followed by functionalization
- Optimize VDF/HPA content ratio

Hydrolysis Experiments – Harsh vs. mild hydrolysis conditions



- Harsh hydrolysis (NaOH) conditions lead to dehydrofluorination and formation of double bond in backbone ***(undesirable)***



- Mild hydrolysis ($(NH_4)_2CO_3$) shows no de-hydrofluorination Disappearance of SO_2F at 1460 cm^{-1} demonstrates successful hydrolysis ***(desirable)***

VDF Precursor Polymers Synthesized to Date

Ionomer	Synthesized	VDF (mol%)	EW* (g/mol)
Exp. Polymer -1	Nov '19	18	903
Exp. Polymer -2	Feb. '21	5	810
Exp. Polymer -3	Feb. '21	11	791
Exp. Polymer -4	Feb. '21	17	795
Exp. Polymer -5	Feb. '21	23	784

* Based on solid state NMR

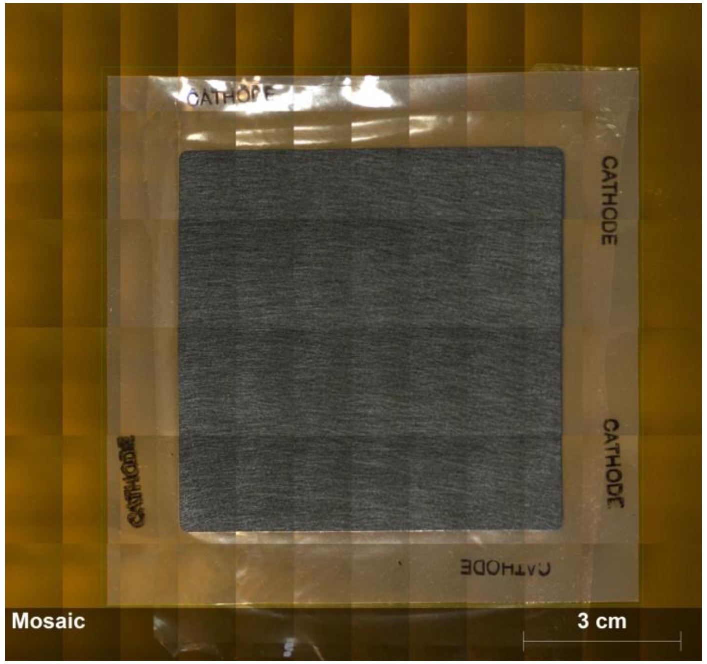
Accomplishments:

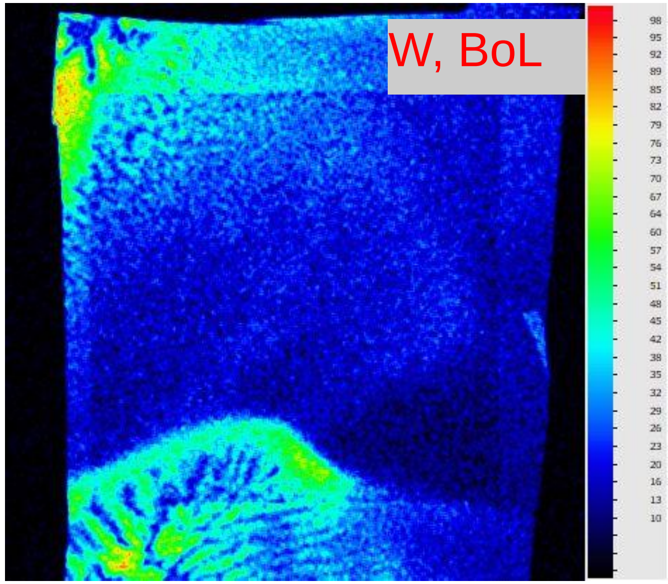
- Five precursor polymers with VDF anchor points synthesized
- Mild hydrolysis conditions identified
- Preliminary success in dispersing VDF polymer (no HPA) in alcohol/water solution which is also desirable for membrane production

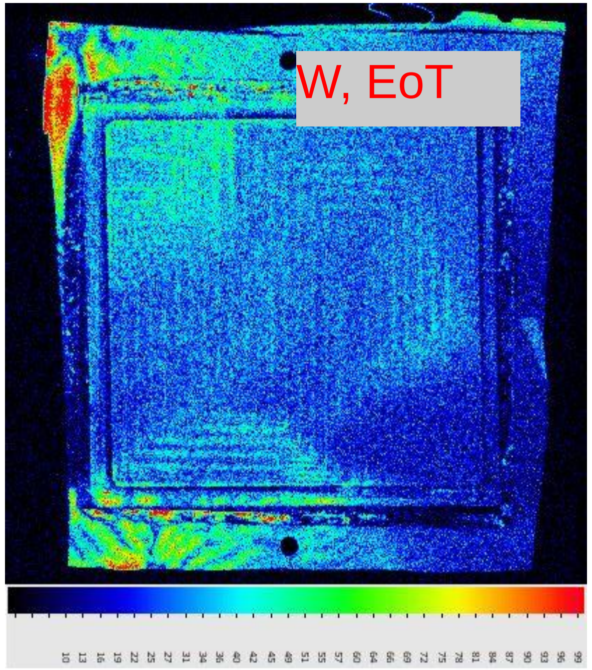
HPA tethered membrane – BOL and EOT XRF

- The BOL membrane sample has non-uniform Tungsten (W) distribution
  - will be improved by better synthesis process control in the next iteration
  - could be improved with better membrane casting conditions as well
  - improved W distribution may lead to improved durability

- Cross section analysis is on going

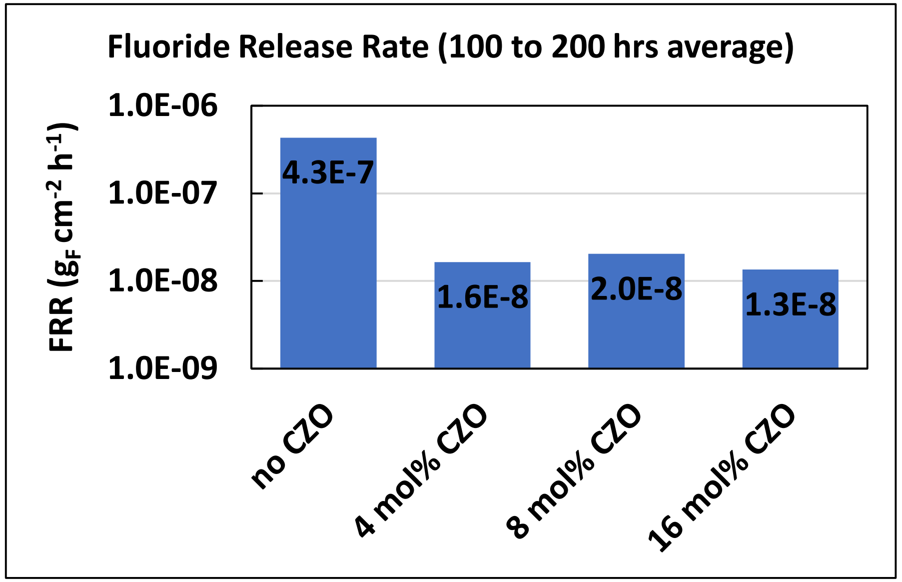


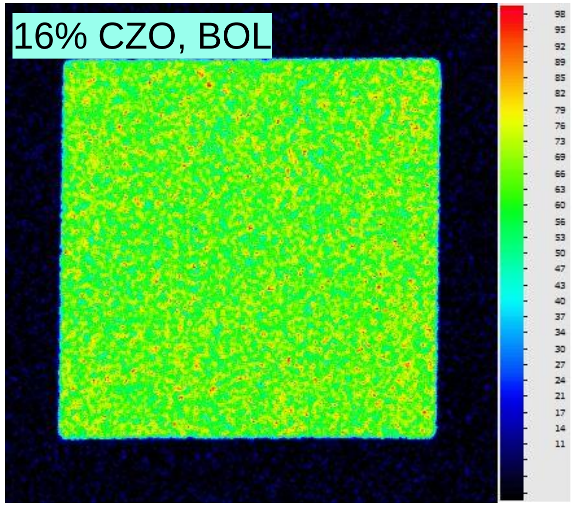


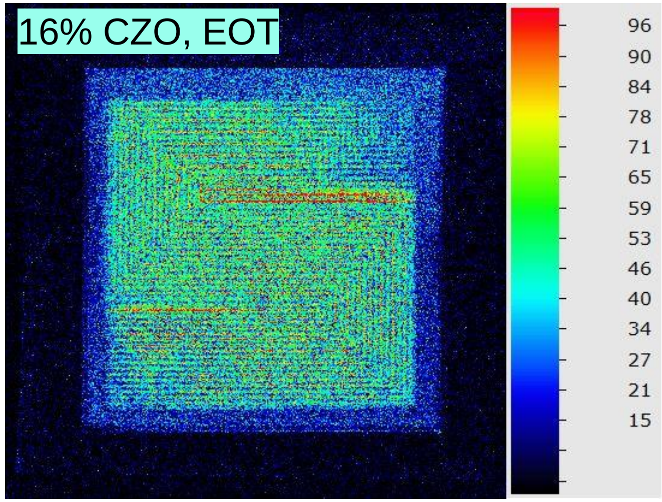


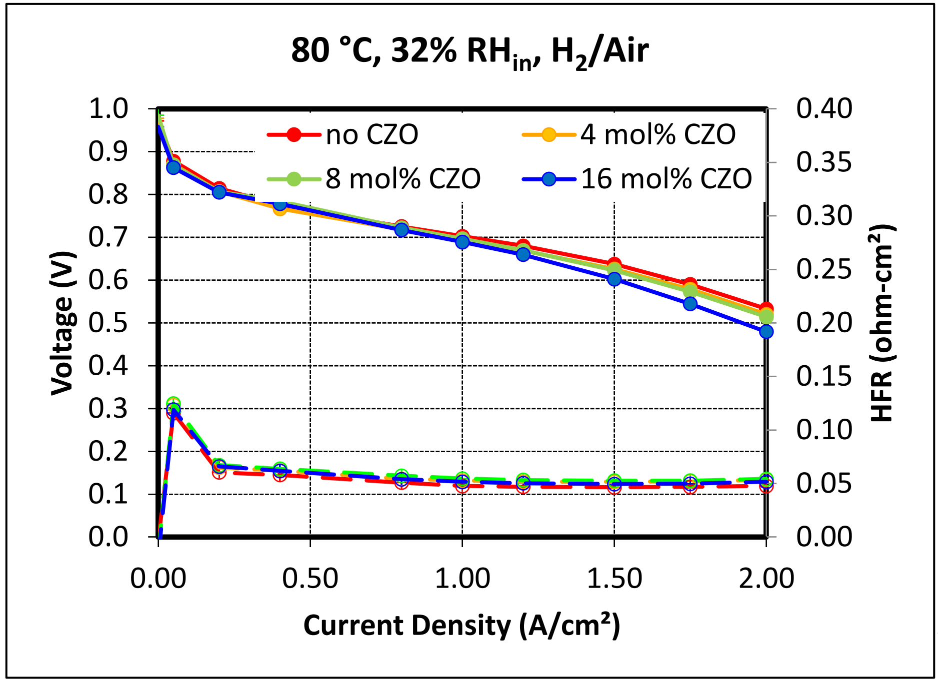
CZO electrode additives – OCV durability and H_2/air performance

- CZO nanofiber additives have been successfully incorporated into cathode at various loadings (4 to 16 mole % CZO)
- OCV durability shows improved chemical durability (reduced FRR)
- H_2/air iV curves show comparable MEA performance at low CZO levels (≤ 8 mol %). Minor Performance penalty observed at higher CZO loadings.
- XRF: EOT XRF shows Ce redistribution after performance and OCV durability tests. CZO additives still observed in electrode layers after tests.









- Next steps: Evaluate CZO additives incorporated directly into the membrane

Reviewer-Only Slides

Assumptions and Risks

Technical assumptions:

- The project has 5 main approaches to address the technical barriers – 2 approaches to immobilize chemical stabilizer in the membrane and 3 approaches to mitigate catalyst dissolution and surface area loss. All of these have shown promising results at TRL 3-4.
  - Pt migration/coalescence is the dominant mechanism of surface area loss.
  - M/MO$_x$ additives anchor catalyst nanoparticles on the support and that they do not have any negative impacts by itself
  - HD truck operating conditions and drive cycle profiles are not overly restrictive than LD vehicles
  - CZO is stable and active for peroxide radical decomposition
  - While HPAs have been tethered to fluoroelastomer in the past, we assume that it can be tethered to the PFSA backbone. HPA remains stable and active when anchored to the PFSA backbone.

Execution risks:

- M^{2}FCT resources (support & timing) are critical to accomplishing project objectives as laid out.
- Delays in receiving the DOE award contract, internal approvals, etc. were experienced but are complete now
  - Conditional award received on Oct. 1, 2019 which was lifted on Feb. 27. 2020.
  - The Subrecipient Agreements have been finalized and approved.
  - Approvals for NDA to work with M^{2}FCT consortium are complete.
- Due to the ongoing pandemic situation caused by the outbreak of Covid-19 virus, we are experiencing significant delays in experimental work with minimal or no access to the lab since mid-March 2020. Major delays were experience, particularly in 2020 Q2. Since the end of June 2020, better on-demand access to the laboratory facilities were available that helped significantly ramp up activities to accomplish the Tasks and Milestones.

Proposed Future Work

M^2FCT engagement and timeline

- ❑ M^2FCT consortium laboratories will be engaged for achieving the overall goals of the project (electrochemical diagnostics, x-ray characterizations, analytical measurements, post-mortem experiments, fuel cell system modeling studies)

M2FCT Engagement Timeline

				Year 1				Year 2				Year 3			
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.

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)	Progress
1.2.1	Catalyst characterizations	Milestone	M1.1	Establish baseline catalysts and ex situ surface area measurement protocols	GM/Pajarito/Cornell/FC-PAD	Q1	80%
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	80%
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	80%
1.1.3	Polymer Synthesis	Milestone	M1.4	Copolymers with 3 different levels of tetherable monomer delivered for functionalizing with HPA	3M	Q4	80%
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**	**Completed, GO**
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	50%
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	60%
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	40%
2.2.3 2.2.4	1) Quantify anchored GMC support corrosion in MEA using in situ NDIR 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	10%
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.** **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**	**Completed, GO**
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 3.2.1	Catalyst, support and membrane AST on SOA MEA MEA post-mortem analysis	Milestone	M3.3	1) MEA that achieves 1750h of 90 °C HAST testing 2) Report on the Pt nanoparticle location before and after AST	All/FC-PAD	Q11	
3.3.1 3.3.2	1) MEA durability modeling and life-projections 2) Deliver Final MEA with High Efficiency and Durability to DOE	Milestone	M3.4	1) Report on the MEA life projections using durability models 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**	