FC144

Highly-Accessible Catalysts for Durable High-Power Performance

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General Motors LLC, Fuel Cell Business

May 30, 2020

Overview

Timeline

- Project start date: 1 Apr 2016
- Project end date: 31 Mar 2020
- Percent complete: 100%

Budget

- Total Funding Spent as of 3/31/20: $3.23M*
- Total DOE Project Value: $3.99M
- Cost Share: 21.7%

*Amounts shown are based on invoices to DOE and do not reflect final invoice amounts with remaining subcontractor expenditures.

Barriers

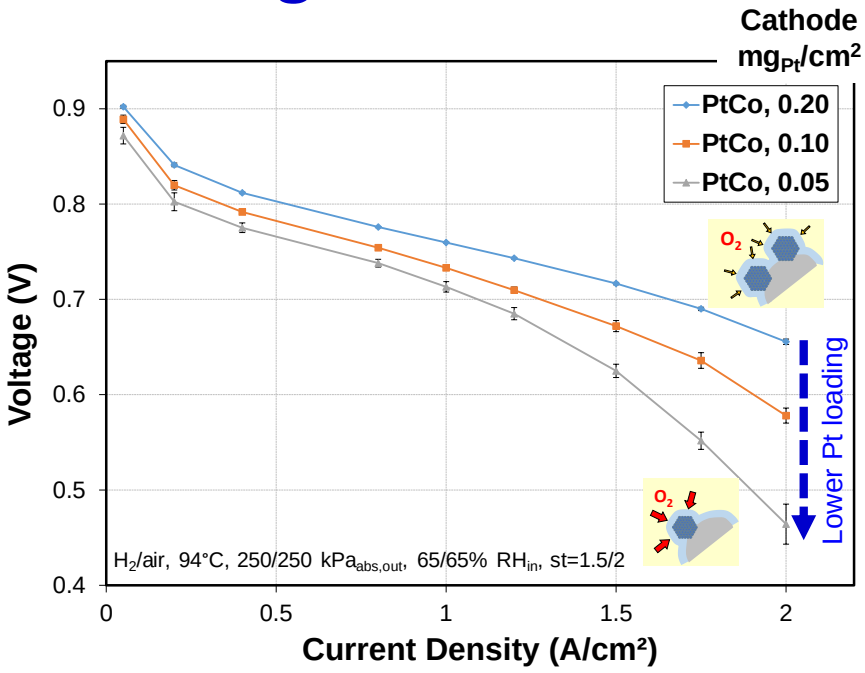
- B. Cost
  - Decrease amount of precious metals.
- A. Durability
  - Improve kinetic activity and high current density performance
- C. Performance
  - Achieve and maintain high current densities at acceptably-high voltages

Partners

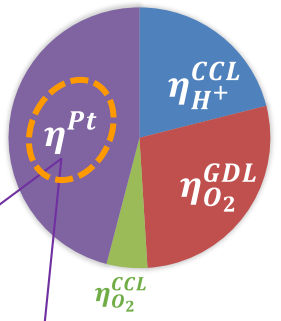
- Subcontractors:
  - 3M Company
  - Carnegie Mellon University
  - Cornell University
  - Drexel University
  - NREL
- Project lead: General Motors LLC

Relevance:

Challenge: Local Transport Losses

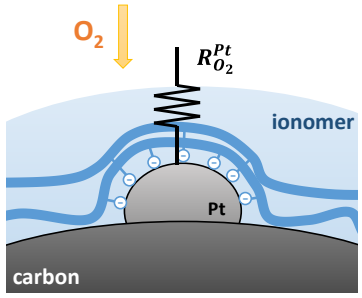


Mass-transport Voltage Losses

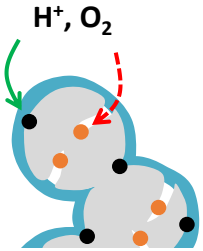


1.75 A/cm^2 on a 0.10 mg$_{Pt}$/cm^2 cathode

O_2 through Ionomer/Pt Interface



H+ and O_2 through Carbon Micropores



Ionomer & Ionic Liquid *Carbon*

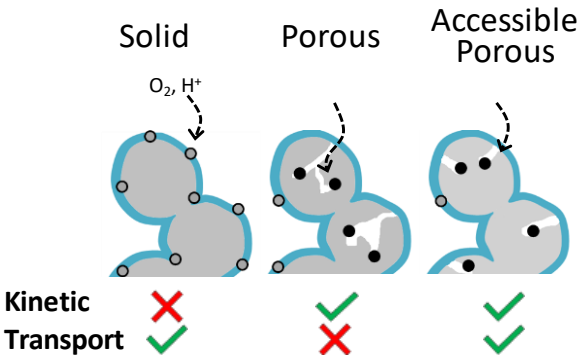
- FC087 Dealloyed PtCo and PtNi *met Catalyst Targets* (activity and durability) ***but not MEA Targets*** (high current density, HCD).
- At HCD, high flux of O_2 and proton per a given Pt area causes large voltage loss on low-Pt cathode.
- The 'local transport resistance' dominates the mass transport related loss (purple).
- Likely a sum of H^+ and O_2 resistance at ionomer/Pt interface and in carbon micropores.
- Want to reduce *apparent* R^{Pt} from ~25 s/cm to <10 s/cm, or double the Pt ECSA.

J. Phys. Chem. Lett. (2016) 1127.

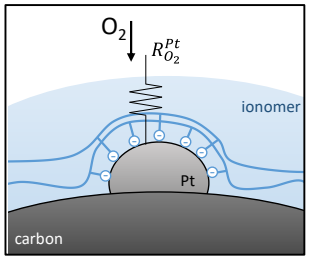
Approach:

Work Focuses in the Past Year

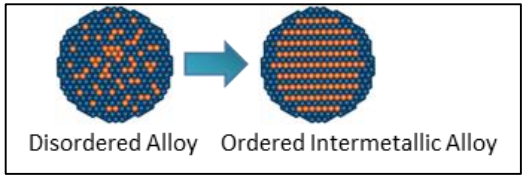
- ❑ New Carbon Supports
  - ➢ Study local transport using MEA electrochemical diagnostics, microscopy, and simulation.
  - ➢ Understand support effects on durability.
  - ➢ Optimize PtCo on accessible carbon with emphasis on stability



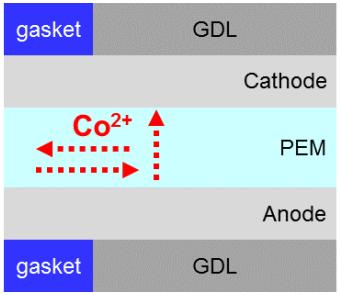
- ❑ Electrolyte-Pt Interfaces: Ionomer and Ionic Liquid
  - ➢ Develop process to add ionic liquid in MEA and study its effect.
  - ➢ Identify new electrolyte-Pt interface affects fuel cell performance.



- ❑ Ordered Intermetallic Alloys
  - ➢ Use advanced in-situ techniques to optimize activity/stability vs Pt-particle-size growth



- ❑ Effects of Co^{2+} and Ce^{3+}
  - ➢ Validate cation performance model with in-situ visualization.



Relevance:

Targets and Status

Metric	Units	PtCo/KB 2016	PtCo/HSC-f	Ordered-PtCo/HSC-f	Ordered-PtCo/KB	PtCo/HSC-f	DOE 2020 Target	Project Target
PGM total loading (both electrodes)	mg/cm^2	0.125 (0.025+0.10)	←	←	←	0.075 (0.015+0.06)	<0.125	←
Mass activity @ 900 $mV_{iR\text{-}free}$	A/mg_{PGM}	0.62†	0.7†	0.7†	0.53†	0.7†	>0.44	←
Loss in catalytic (mass) activity	% loss	30%	59%*	45%*	16%	tbd	<40%	←
Performance at 0.8V (150kPa, 80°C)	A/cm^2	0.304	tbd	tbd	0.301	tbd	>0.3	←
Power at rated power (150kPa, 94°C)	W/cm^2	0.8	0.95	0.94	tbd	0.91	>1.0	-
Power at rated power (250kPa, 94°C)	W/cm^2	1.01	**1.31**	1.29	1.15	1.23	-	>1.1
PGM utilization (150kPa, 94°C)	kW/g_{PGM}	6.4	7.6	7.5	tbd	**12.1**	>8	←
PGM utilization (250kPa, 94°C)	kW/g_{PGM}	8.1	10.5	10.3	9.2	**16.4**	-	>9.1
Catalyst cycling (0.6-0.95V, 30k cycles)	mV loss at $0.8A/cm^2$	24	39*	25	8	tbd	<30	←
Support cycling (1.0-1.5V, 5k cycles)	mV loss at $1.5A/cm^2$	>500	>500	tbd	tbd	tbd	<30	-

Must meet Q/ΔT <1.45 or >0.67 V at 94°C

Green: meet target
Red: not yet meet target
Black: NA

** Meet target in absolute term (e.g. >0.26 A/mg_{PGM})*
† MA at 0.9V_{RHE} in cathodic direction

Objectives

- Reduce overall stack cost by improving high-current-density (HCD) performance adequate to meet DOE heat rejection and Pt-loading targets.
- Maintain high kinetic mass activities.
- Minimize catalyst HCD degradation.

This Year Target Highlights

- No change in status regarding targets.
- However, validation test result by NREL supports key improvement reported earlier by the project.

Approach:

Milestones and Go/No Go

TASK 1 - Development of Highly-Accessible Pt Catalysts

Go/No-go criteria: >1.0 W/cm^2, >8 kW$_{rated}$/g$_{Pt}$, and Q/ΔT <1.7 with Pt/C ✓

	2019 AMR	Today
❑ Downselect carbon support, ionomer, ionic liquid	100%	100%
❑ Measure the effect of leached Co^{2+} and Pt surface area	100%	100%
❑ Develop dealloyed catalyst from ordered intermetallic alloy	100%	100%
❑ Visualize carbon structure and Pt location on selected catalysts	100%	100%
❑ Model baseline material	100%	100%

TASK 2 - Development of Dealloyed Catalyst with Preferred Catalyst Design

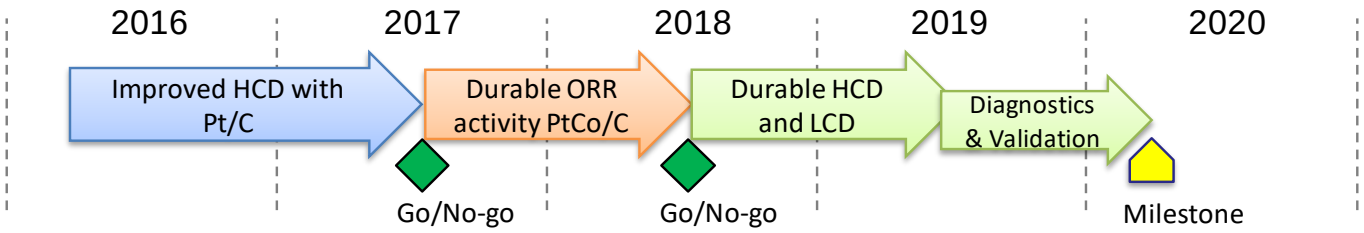
Go/No-go criteria : >0.44 A/mg$_{PGM}$, <40% mass activity loss with preferred design ✓

❑ Develop dealloyed catalyst on preferred support	100%	100%
❑ Implement selected ionomer and ionic liquid with selected catalysts	100%	100%
❑ Visualize fresh PtCo/C and post-AST Pt/C	100%	100%
❑ Model PtCo/C before and after AST	100%	100%

TASK 3 - Optimization for Durable HCD and LCD Performance

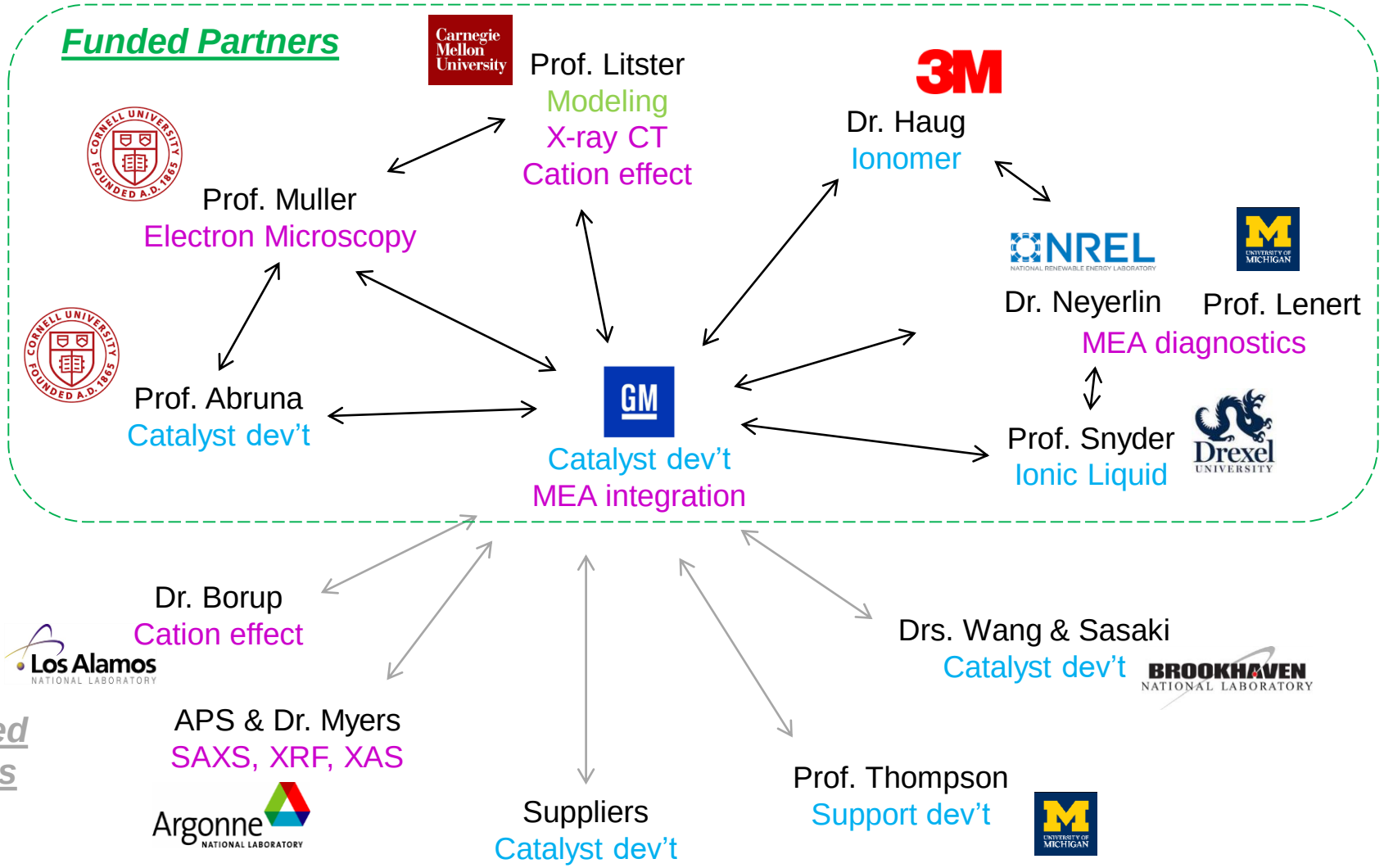
Milestone: >1.1 W/cm^2, >9.1 kW$_{rated}$/g$_{Pt}$, and Q/ΔT <1.45 ✓

❑ Identify root cause and improve durability and performance of PtCo/C	70%	100%
❑ Evaluate effect of selected ionomer/IL on HCD and durability of improved PtCo catalyst	80%	100%
❑ Integrate new catalyst design with other state-of-the-art FC components	80%	100%
❑ Make available to DOE the improved catalyst in 50 cm^2 MEAs	10%	100%
❑ Visualize and model improved catalyst	50%	100%



Collaborations

Materials dev't
Characterization
Modeling



SOA Integration & DOE Validation

SOA Components

Cathode:	30 wt.% Intermetallic ordered Pt_3Co/HSC-f at 0.06 and 0.10 mg_{Pt}/cm^2, PFSA ionomer (D2020), 900 EW, I/C ratio of 0.8,
Anode:	Pt/HSC, 0.015 mg_{Pt}/cm^2
PEM:	PFSA with reinforcement layer, 18 μm thick
GDL:	~210 and ~120 μm thick carbon fiber layer with 30 μm MPL. Water proof.

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Mass activity @ 900 $mV_{iR\text{-}free}$	A/mg_{PGM}	0.62†	0.7†	0.7†	0.53†	0.7†	>0.44	←
Loss in catalytic (mass) activity	% loss	30%	59%*	45%*	16%	tbd	<40%	←
Performance at 0.8V (150kPa, 80°C)	A/cm^2	0.304	tbd	tbd	0.301	tbd	>0.3	←
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Power at rated power (250kPa, 94°C)	W/cm^2	1.01	**1.31**	1.29	1.15	1.23	-	>1.1
PGM utilization (150kPa, 94°C)	kW/g_{PGM}	6.4	7.6	7.5	tbd	**12.1**	>8	←
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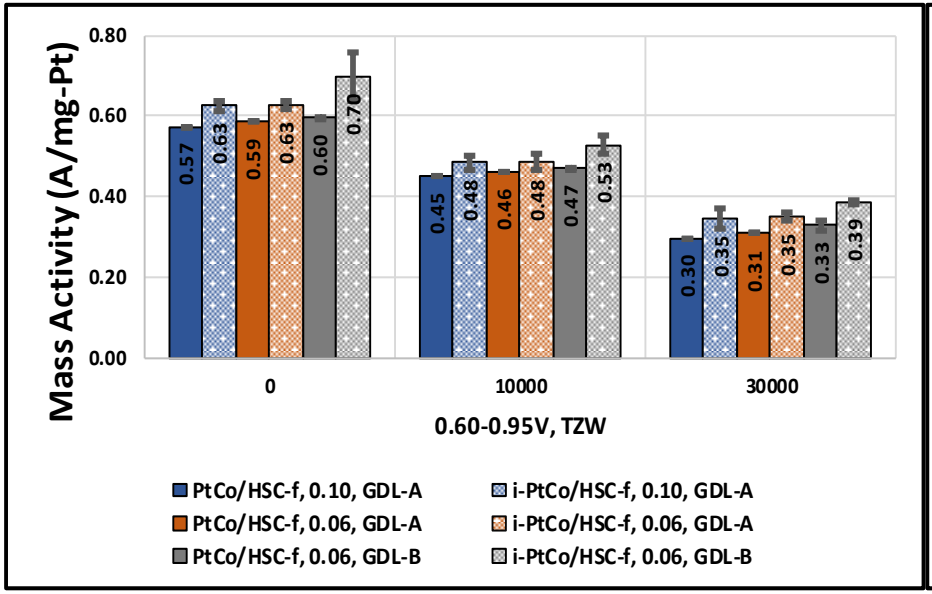
Catalyst cycling (0.6-0.95V, 30k cycles)	mV loss at $0.8A/cm^2$	24	39*	25	8	tbd	<30	←
Support cycling (1.0-1.5V, 5k cycles)	mV loss at $1.5A/cm^2$	>500	>500	tbd	tbd	tbd	<30	-

- As a deliverable, project catalysts were integrated into an MEA with other SOA subcomponents (within confidentiality constraint), and evaluated at both GM and NREL.
- Anode Pt loading was further reduced by using high-ECSA Pt/HSC catalyst.

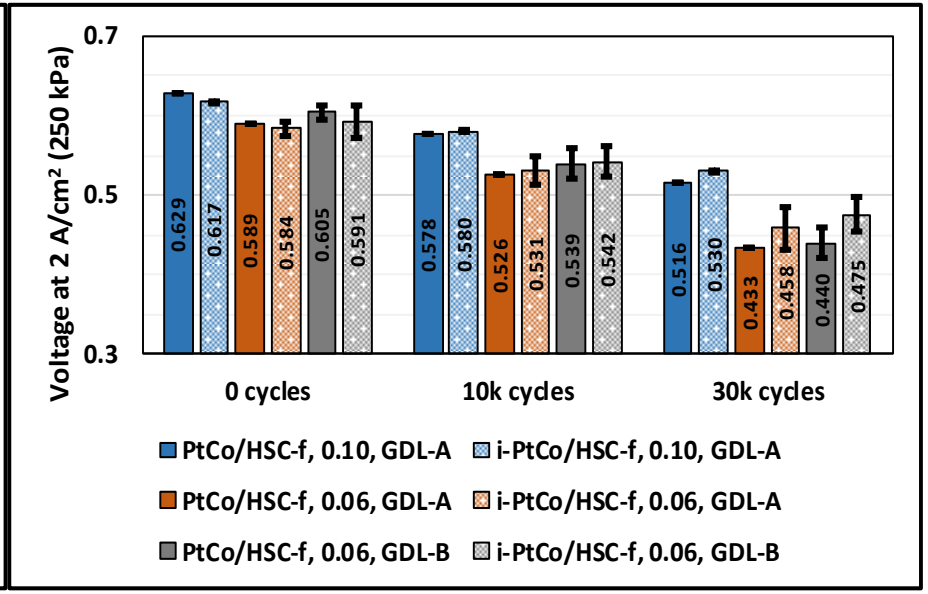
Technical Accomplishment:

DOE Validation at GM Lab

ORR Mass Activity



Voltage at 2 A/cm^2



H_2/air, 94°C, 250/250 $kPa_{abs,out}$, 65/65% RH_{in}, st=1.5/2

- The prepared MEAs were first tested at GM, with two GDLs (240&150 μm thick) and two Pt loadings (0.10&0.06 mg_{Pt}/cm^2).
- Although for this validation study, we were not able to use some of our best MEA subcomponents (electrode ionomer, membrane, and GDL) due to confidentiality, the GM tests results largely agree with prior conclusion.
  - Annealed PtCo to encourage ordered intermetallic structure show slightly higher BOL and EOT mass activity.
  - Annealed PtCo lost less ECSA after voltage cycling leading to higher HCD at EOT.

DOE Validation at NREL

Metric	Units	PtCo/HSC-f	Ordered PtCo/HSC-f	PtCo/HSC-f	Ordered PtCo/HSC-f	DOE 2020 Target	Project Target
PGM total loading (both electrodes)	mg/cm^2	0.075 (0.015+0.06)	0.075 (0.015+0.06)	0.115 (0.015+0.1)	0.115 (0.015+0.1)	<0.125	←
Mass activity @ 900 $mV_{iR\text{-}free}$	A/mg_{PGM}	1.108 (Anodic)	0.924 (Anodic)	0.95(Anodic) 0.734(Cathodic)	0.943(Anodic) 0.777(Cathodic)	>0.44	←
Loss in catalystic (mass) activity (10k cyc	% loss	49	46	45	40	-	-
Loss in catalystic (mass) activity (30k cyc	% loss	63	59	64	57	<40%	←
Performance at 0.8V (150kPa, 80°C)	A/cm^2	~ 0.3	~ 0.3	0.36	0.34	>0.3	
Power at rated power (250kPa, 94°C)	W/cm^2	1.1	1.05	1.2	1.1	-	>1.1
PGM utilization (250kPa, 94°C)	kW/g_{PGM}	14.6	14	10.4	9.6	-	>9.1
Catalyst cycling (0.6-0.95V, 10k cycles)	mV loss at $0.8A/cm^2$	75	59	36	37	-	-
Catalyst cycling (0.6-0.95V, 30k cycles)	mV loss at $0.8A/cm^2$	179	179	86	86	<30	←
Catalyst cycling (0.6-0.90V, 30k cycles)	mV loss at $0.8A/cm^2$	44	-	-	-	<30	←

- Mass activity was measured in both anodic and cathodic directions
- Cathodic mass activities match well with GM
- ECSA, PGM utilization and power density matched previous GM results
- Low Pt loading (0.06 Pt) electrodes degraded fast;
- Not much difference of catalyst durability was observed between PtCo/HSC-f and Ordered-PtCo/HSC-f

FUEL CELL PERFORMANCE AND DURABILITY

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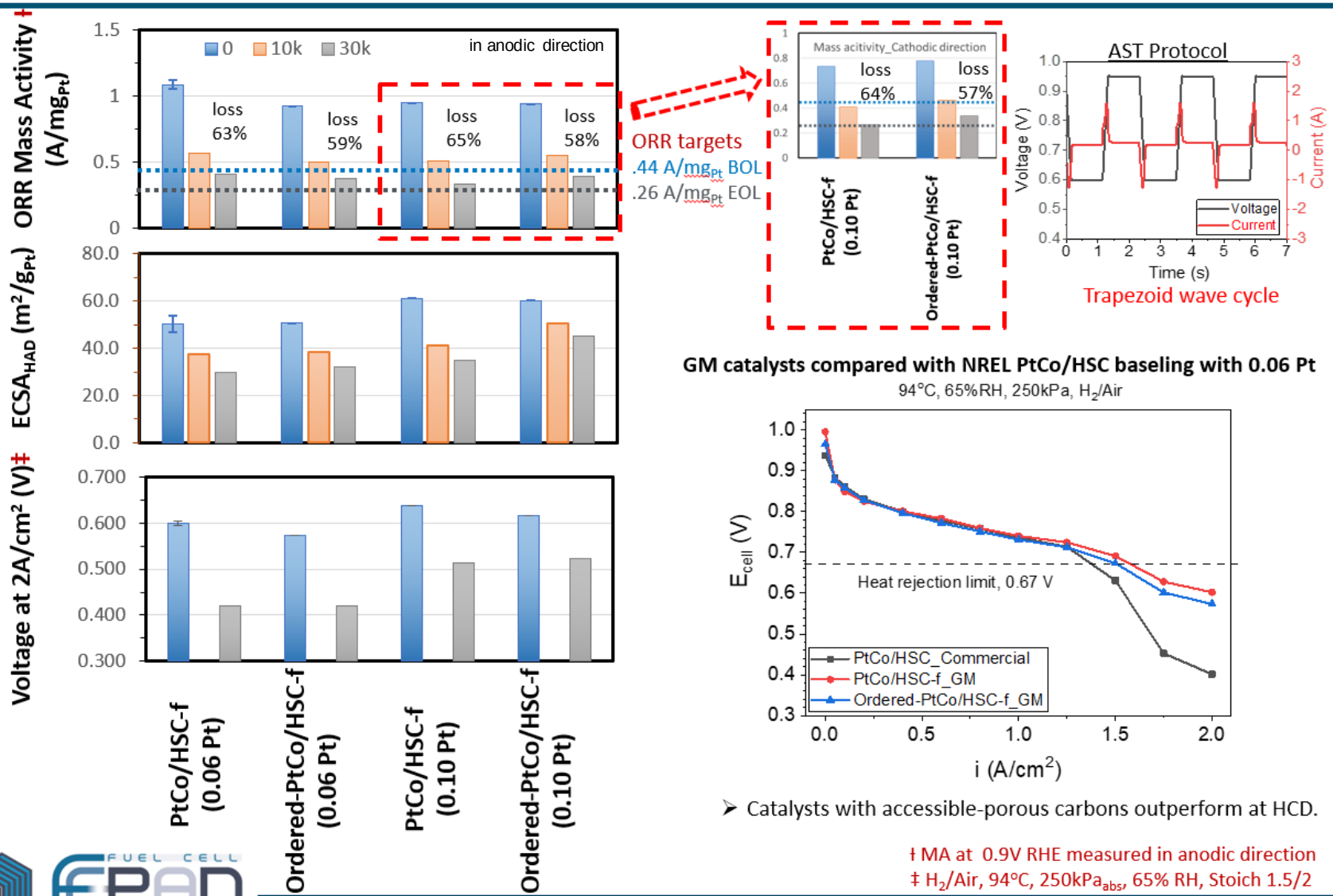
➢ Agree with GM results

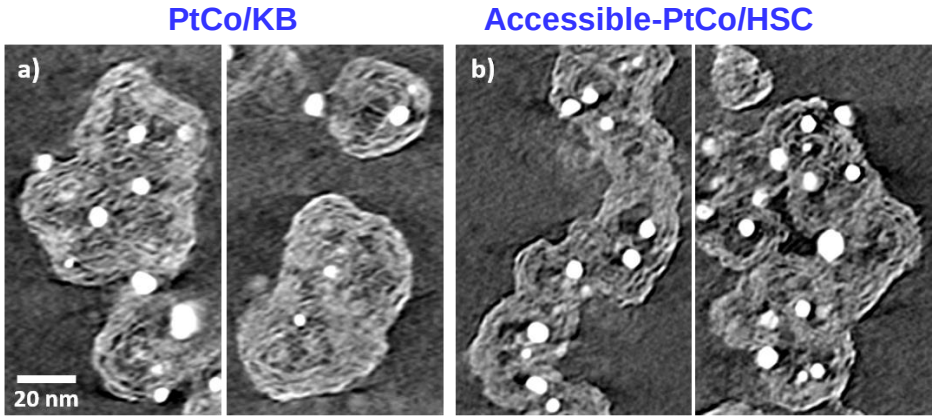
DOE Validation at NREL

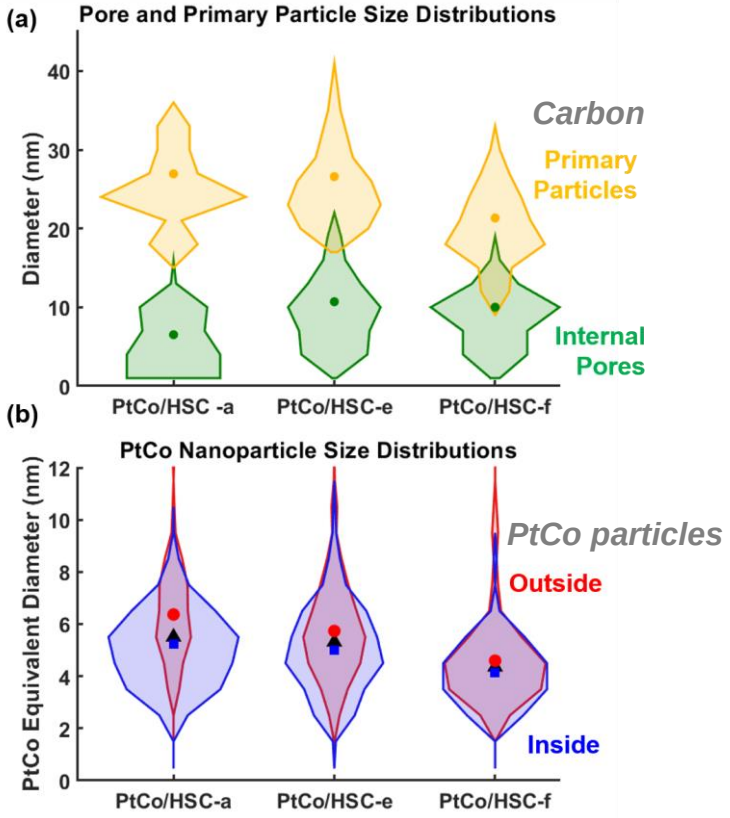


➢ Agree with GM results

Accessible Carbons Structure

Close-up STEM Tomography

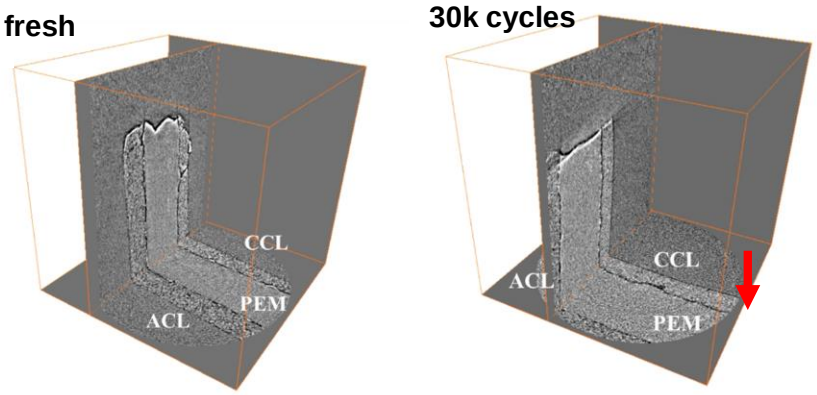




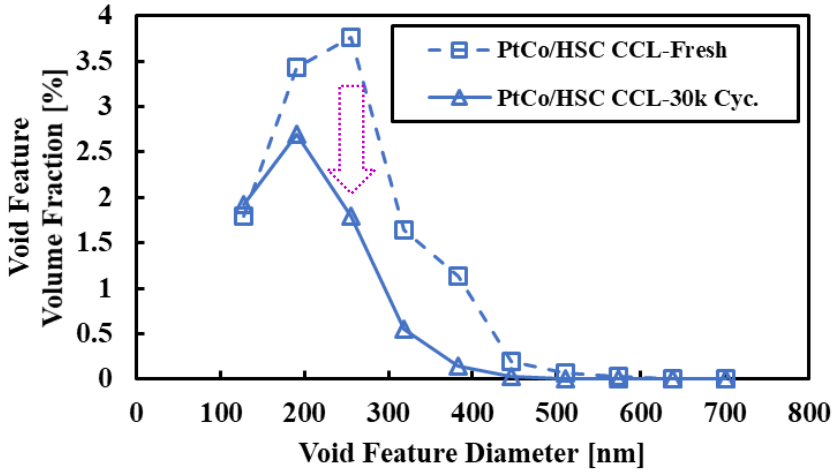
- Closer examination with TEM tomography led us to conclude that while some larger carbon pore openings are observable, they are not abundant enough to be the primary factor.
  - Even though the accessible carbons have larger pores and thinner shells, they do not show significant increase in the number and size of pore openings
- Instead, it is the larger interior pore volume, thinner carbon shell, and less tortuous diffusion path together that help lower the O_2 transport resistance.
- At the same time, small pore openings effectively exclude ionomer from entering carbon pores and poisoning Pt surfaces. This enables high ORR activities

X-CT indicates potential CCL compaction

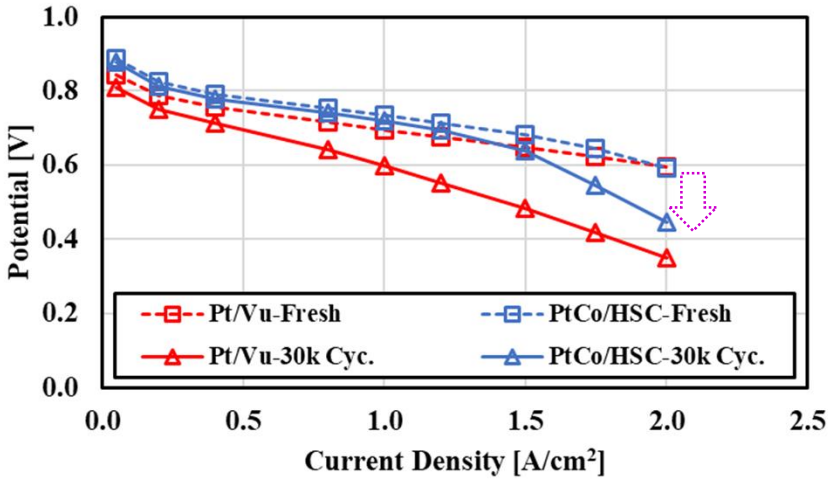
X-ray CT Zernike phase contrast slice renderings of PtCo/KB MEAs



Large-scale void feature distributions of PtCo/KB CCLs



FC polarization curve before and after AST

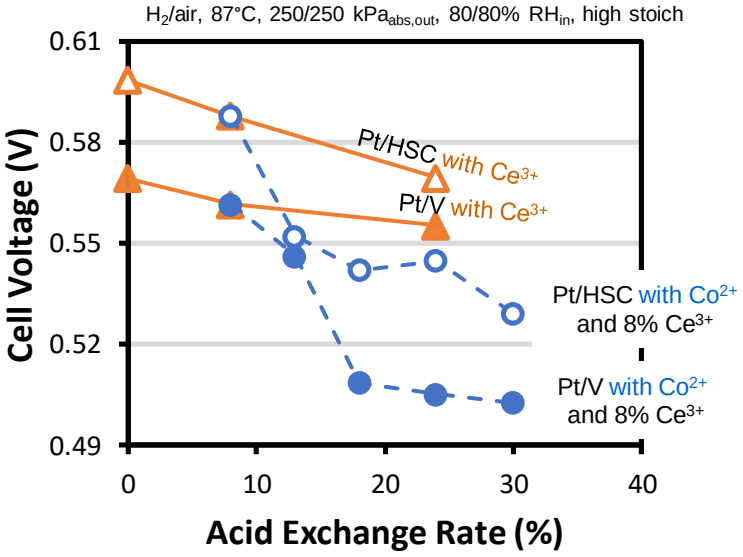


- Noticeable drop in cathode pore volume was observed after AST test.
  - Similar observation has been reported earlier using electron and optical microscopes but with less confidence level.
- This could explain the sharp drop in voltage at HCD of PtCo/KB after AST, previously not understandable with known parameters.
- When consider the operating window, the decrease in pore volume is unlikely due to carbon corrosion. It could be due to electrode compaction from cell compression. Need further study.

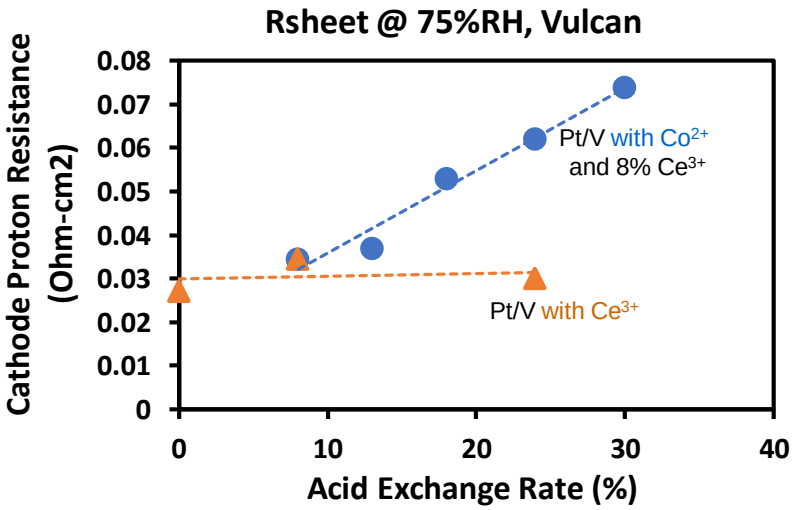
Technical Accomplishment:

Co-doping of Co^{2+} & Ce^{3+}

Voltage at 2.5 A/cm2



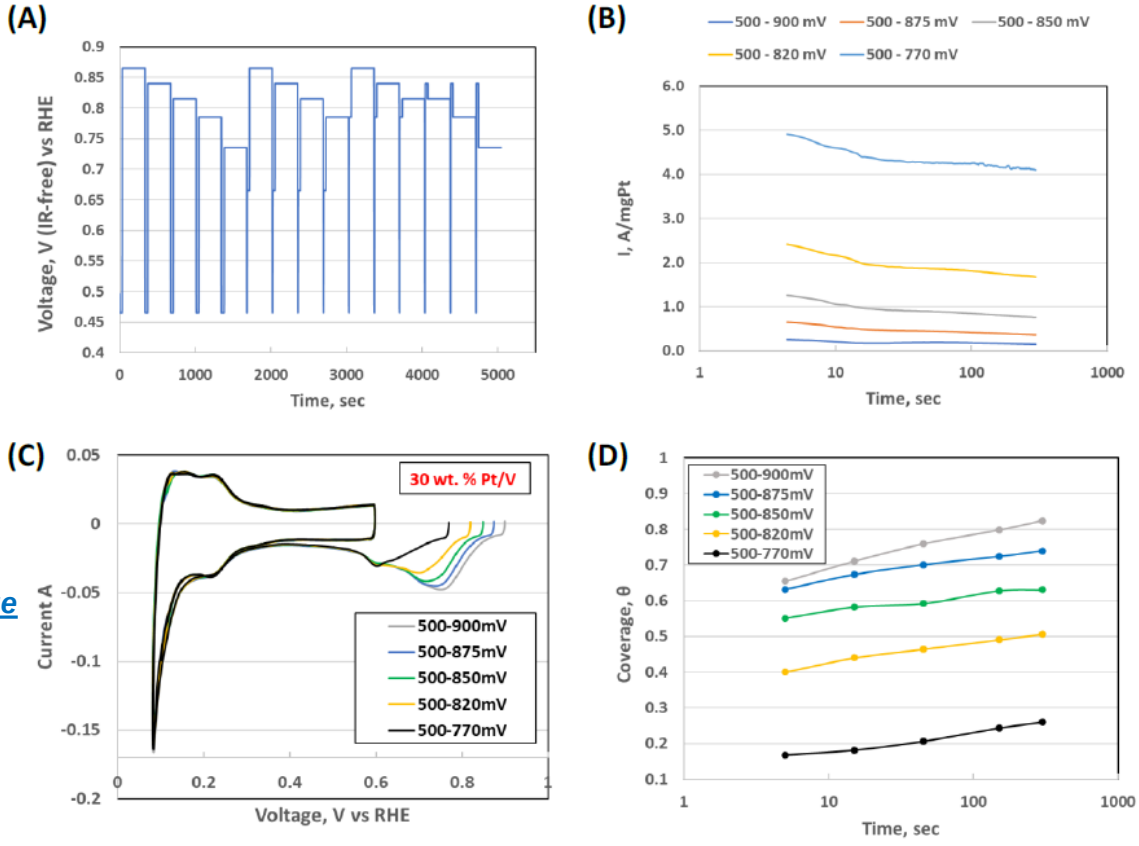
Cathode Proton Resistance



- While the effects of Co^{2+} and Ce^{3+} were studied earlier, the effect when both cations are present was not systematically studied.
- We found that the effect was about the same as the combined effect of individual cation, i.e., the interaction was small.
- The study also confirmed previous findings.
  - At LCD, both Co^{2+} and Ce^{3+} have negligible effect.
  - At HCD, Co^{2+} causes larger voltage loss and larger increase in electrode and membrane proton resistance.

Dynamic ORR Model Development

ORR kinetic



Oxide coverage

Oxide-coverage kinetic equation

$$i = i_0 \left(\frac{p_{o2}}{p_{o2,ref}}\right)^{\gamma} (1-\theta) \exp\left(\frac{-\alpha F \eta}{RT}\right) \exp\left(-\frac{\omega\theta}{RT}\right)$$

$$\theta_{PtO} = f(E, t, T, RH)$$

Actual measurement

new

Actual E on PtCo

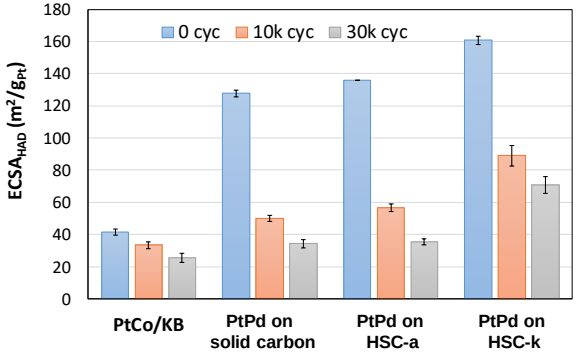
0.15 mg_{Pt}/cm^2 Pt/V with NR212 membrane
75°C, 100% RH_{in}, high stoich of O_2 or N_2

- Because fuel cell is operated in a transient mode most of the time, understanding ORR kinetic as a function time is important, not only to predict its performance, but also understanding its durability.
- Preliminary results showed that Pt oxide follows logarithm growth behavior, while ORR kinetic current follows logarithm decay behavior. This indicates that oxide-coverage kinetic can be applied for transient ORR as well.
- Measurement and model development underway for Pt and PtCo catalysts.

Technical Accomplishment:

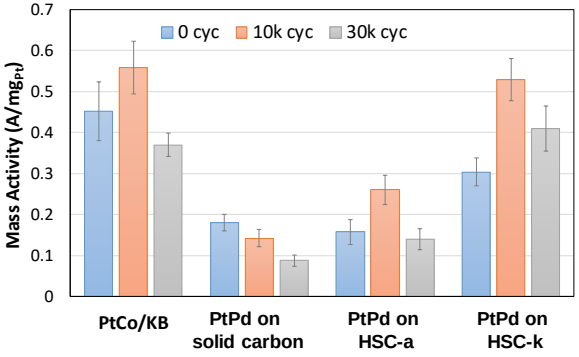
PtPd ML catalysts on Mesoporous Carbons

ECSA



ORR Activity

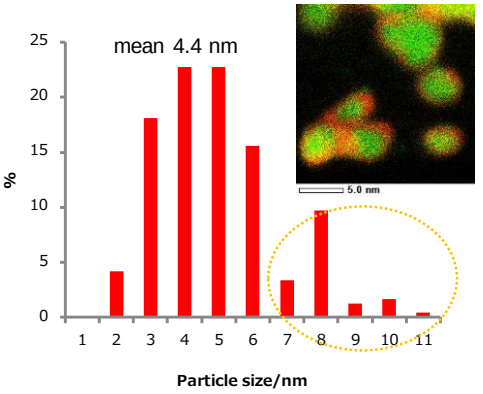
GM 38 cm^2 platform. 0.07 mg_{Pt}/cm^2 with Gen1 membrane&GDL



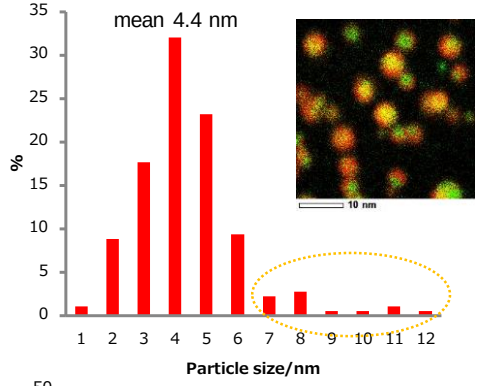
- With some discussion with GM, NECC independently developed PtPd monolayer catalyst on mesoporous carbons.
- Thanks to high ECSA of ML catalysts, HCD issue associated with local O_2 transport is absent.
- On the other hand, significant improved stability was observed with mesoporous carbons. The following are confirmed:
  - Better retention of HCD performance, ECSA, and ORR activity
  - Less number of aggregated particles
  - Less Pt and Pd losses from the catalyst

TEM after 30k cycles

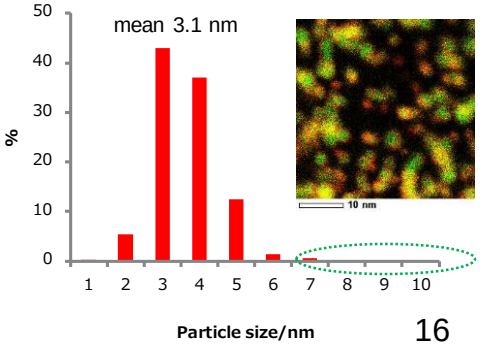
PtPd on solid carbon



PtPd on HSC-a

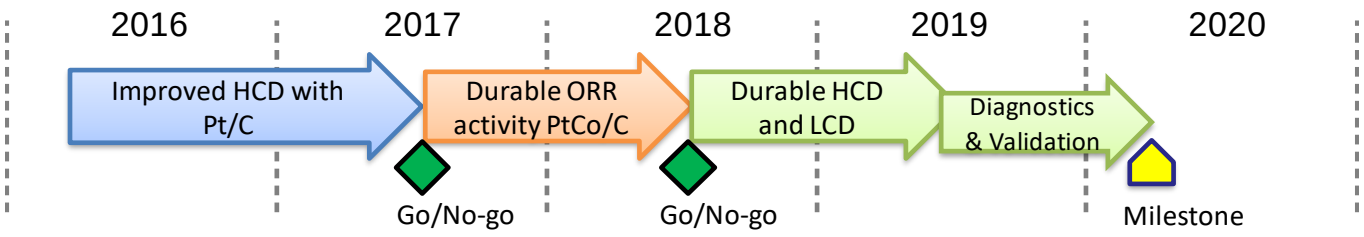


PtPd on HSC-k



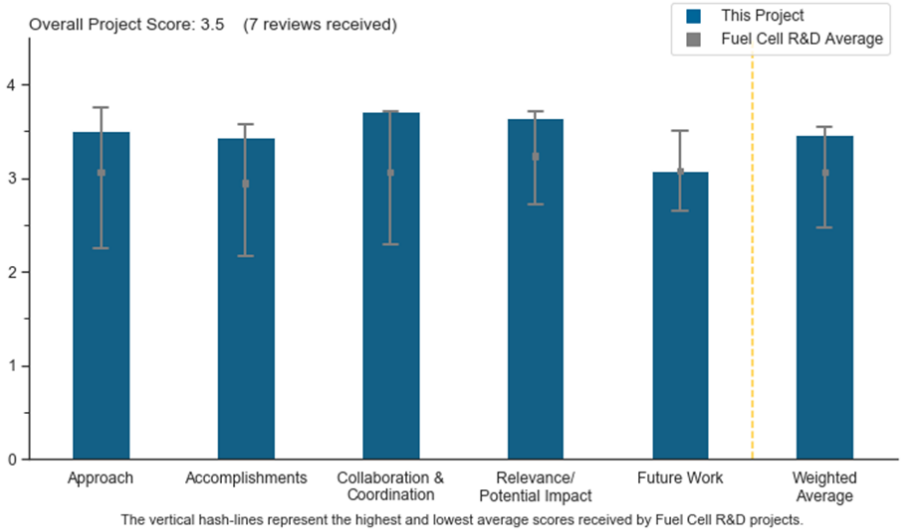
Future Work

The project has concluded.



Responses to Last Year AMR Reviewers' Comments

- "ionomer-related progress lags behind"
  - This complication arises because, a 3M-led project (FC155) solely focusing on this ionomer topic was awarded by DOE after our project has started. While this accelerates our learning, it isn't done within this project. As a result, the ionomer scope was reduced and a portion of this DOE funding was returned.
- "how the ILs are limiting catalyst dissolution"
  - This is also a question we are interested in. While we do not have resources to take this on at the moment, we see opportunity to leverage a model that was developed within the project to study this, i.e., CMU's Pt dissolution in absent of ionomer model.



- "keep durability in focus and conduct sensitivity studies at higher (Pt) loading. The impact on MEA cost is understood, but durability is critical"
  - This is a important point. However, it cannot be done under the scope of this project. Pt loading sensitivity must be done under realistic operating condition (i.e., not AST), and this is strongly dependent on applications. FCPAD consortium will be more suited to study this.
  - That being said, as shown in this work, the improved local transport property of the developed materials does enable a more durable MEA despite slightly faster ECSA degradation. This benefit will be transferrable to a wide range of applications, as long as the FCS design limiting factor is the power, and not efficiency.
- "understanding the impact of the IL system on durability" "Evaluating the leaching of IL from the electrode matrix "
  - Unfortunately, in this very last phase of the project, we could not address this technically challenging task. We hope the new project led by Drexel on block copolymer-IL composites (FC309) will shed some light.

Summary

- Validation test at NREL confirmed improved HCD performance with catalyst with accessible carbon.
- Stability improvement from the ordered intermetallic PtCo on accessible carbon was less than on baseline porous carbon (consistent with earlier result)
  - The cause still unknown. Could be due to more open structure, shallower pores, less carbon corrosion tolerance, etc.
- Improved understanding of low-PGM electrode
  - TEM tomography revealed the nanostructure of accessible carbons and how it can affect O_2 transport.
  - Experiment and simulation study highlight the role of internal pore structure on adsorbing/condensing water and conducting proton.
  - Quantified the effects of cation when both Co^{2+} and Ce^{3+} coexist in the membrane. Performance model development ongoing.
  - Dynamic ORR kinetic model development underway.
- PtPd ML catalysts development demonstrated that different catalysts may have different requirement for their supports. (e.g. catalyst with high ECSA prefers a support that promote stability over a support with good local transport)

Product: 21 published articles, 6 planned articles, 52 talks, 2 patent applications

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