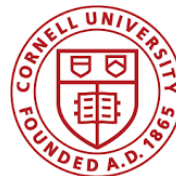


FC144

# Highly-Accessible Catalysts for Durable High-Power Performance

Anusorn Kongkanand (PI)  
General Motors LLC, Fuel Cell Business

May 30, 2020



This presentation does not contain any proprietary, confidential, or otherwise restricted information

# 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%

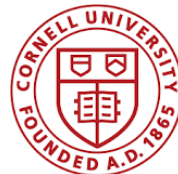
\*Amounts shown are based on invoices to DOE and do not reflect final invoice amounts with remaining subcontractor expenditures.

## 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

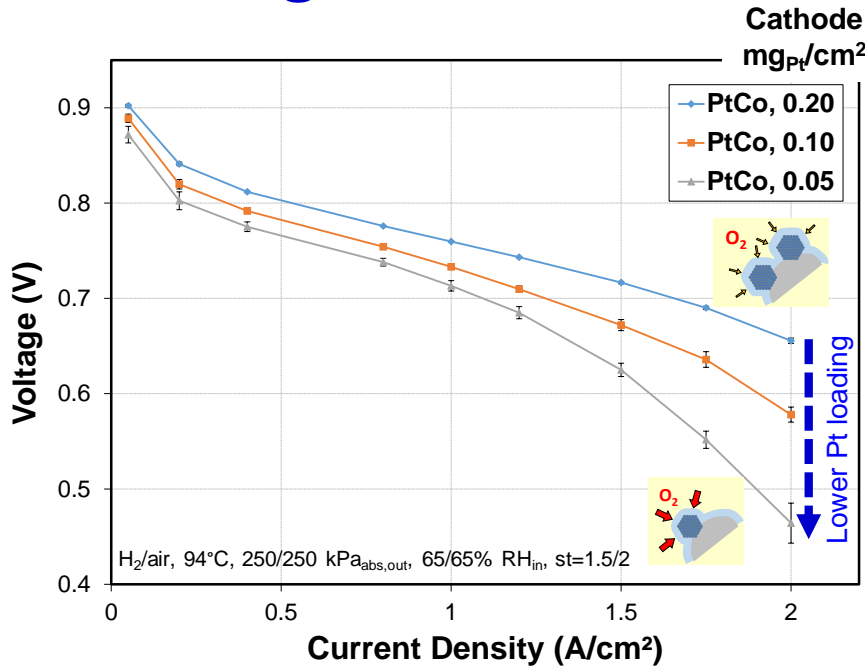
## Partners

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

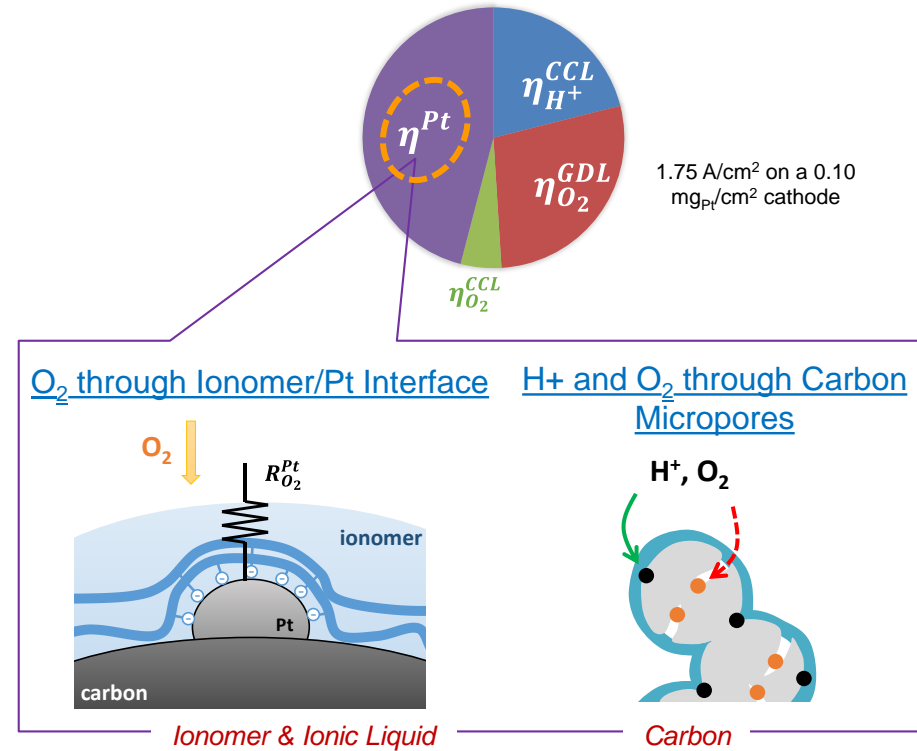


# Relevance:

## Challenge: Local Transport Losses



## Mass-transport Voltage Losses



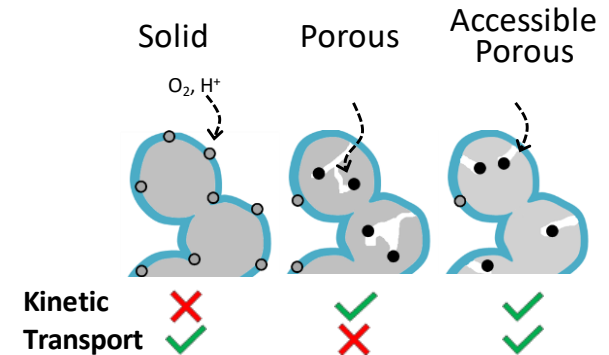
- ❑ FC087 Dealloyed PtCo and PtNi *met Catalyst Targets* (activity and durability) **but not MEA Targets** (high current density, HCD).
- ❑ At HCD, high flux of  $\text{O}_2$  and proton per a given Pt area causes large voltage loss on low-Pt cathode.
- ❑ The 'local transport resistance' dominates the mass transport related loss (purple).
- ❑ Likely a sum of  $\text{H}^+$  and  $\text{O}_2$  resistance at ionomer/Pt interface and in carbon micropores.
- ❑ Want to reduce *apparent*  $R^{\text{Pt}}$  from  $\sim 25 \text{ s}/\text{cm}$  to  $< 10 \text{ s}/\text{cm}$ , or double the Pt ECSA.

## Approach:

# Work Focuses in the Past Year

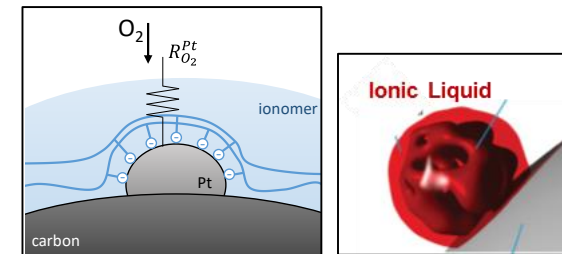
### □ New Carbon Supports

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



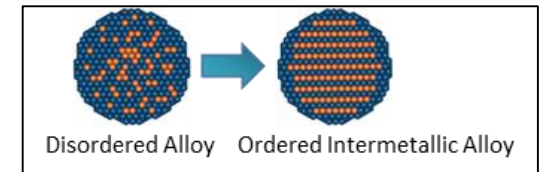
### □ Electrolyte-Pt Interfaces: Ionomer and Ionic Liquid

- Develop process to add ionic liquid in MEA and study its effect.
- Identify new electrolyte-Pt interface affects fuel cell performance.



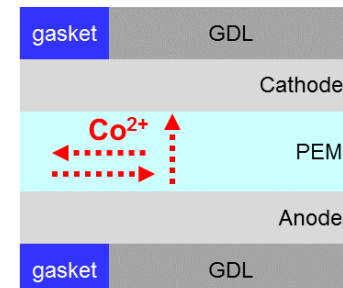
### □ Ordered Intermetallic Alloys

- 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

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

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

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

\* Meet target in absolute term (e.g. >0.26 A/mg<sub>PGM</sub>)  
† MA at 0.9V<sub>RHE</sub> 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.

# Milestones and Go/No Go

## TASK 1 - Development of Highly-Accessible Pt Catalysts

Go/No-go criteria:  $>1.0 \text{ W/cm}^2$ ,  $>8 \text{ kW}_{\text{rated}}/\text{g}_{\text{Pt}}$ , and  $Q/\Delta T < 1.7$  with Pt/C ✓ **2019 AMR** **Today**

	2019 AMR	Today
<input type="checkbox"/> Downselect carbon support, ionomer, ionic liquid	100%	100%
<input type="checkbox"/> Measure the effect of leached $\text{Co}^{2+}$ and Pt surface area	100%	100%
<input type="checkbox"/> Develop dealloyed catalyst from ordered intermetallic alloy	100%	100%
<input type="checkbox"/> Visualize carbon structure and Pt location on selected catalysts	100%	100%
<input type="checkbox"/> Model baseline material	100%	100%

## TASK 2 - Development of Dealloyed Catalyst with Preferred Catalyst Design

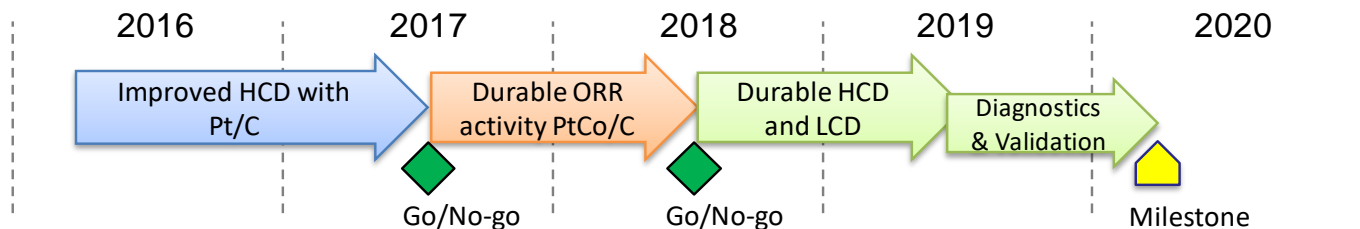
Go/No-go criteria :  $>0.44 \text{ A/mg}_{\text{PGM}}$ ,  $<40\%$  mass activity loss with preferred design ✓

	2019 AMR	Today
<input type="checkbox"/> Develop dealloyed catalyst on preferred support	100%	100%
<input type="checkbox"/> Implement selected ionomer and ionic liquid with selected catalysts	100%	100%
<input type="checkbox"/> Visualize fresh PtCo/C and post-AST Pt/C	100%	100%
<input type="checkbox"/> Model PtCo/C before and after AST	100%	100%

## TASK 3 - Optimization for Durable HCD and LCD Performance

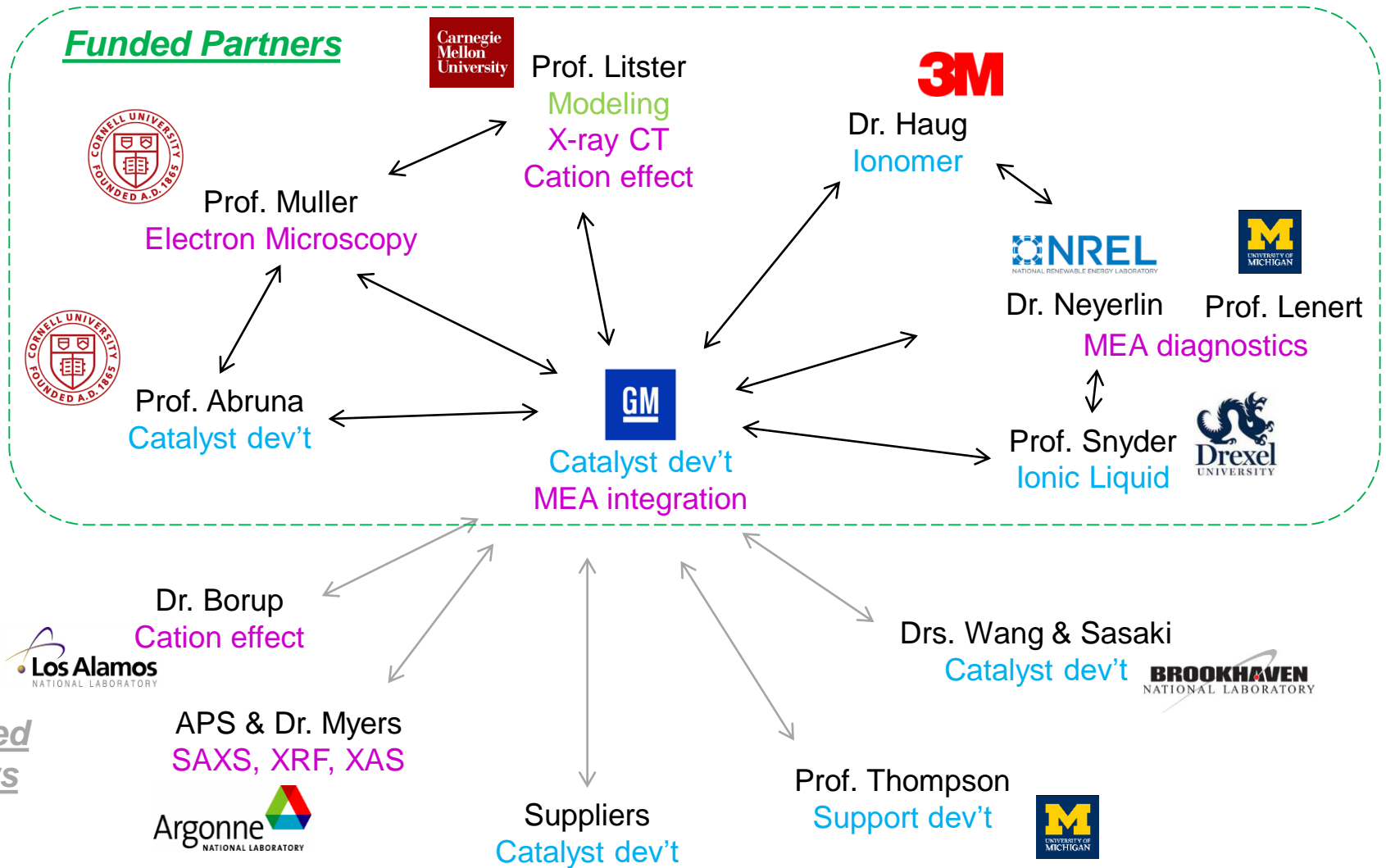
Milestone:  $>1.1 \text{ W/cm}^2$ ,  $>9.1 \text{ kW}_{\text{rated}}/\text{g}_{\text{Pt}}$ , and  $Q/\Delta T < 1.45$  ✓

	2019 AMR	Today
<input type="checkbox"/> Identify root cause and improve durability and performance of PtCo/C	70%	100%
<input type="checkbox"/> Evaluate effect of selected ionomer/IL on HCD and durability of improved PtCo catalyst	80%	100%
<input type="checkbox"/> Integrate new catalyst design with other state-of-the-art FC components	80%	100%
<input type="checkbox"/> Make available to DOE the improved catalyst in $50 \text{ cm}^2$ MEAs	10%	100%
<input type="checkbox"/> Visualize and model improved catalyst	50%	100%



# Collaborations

Materials dev't  
Characterization  
Modeling



# SOA Integration & DOE Validation

## SOA Components

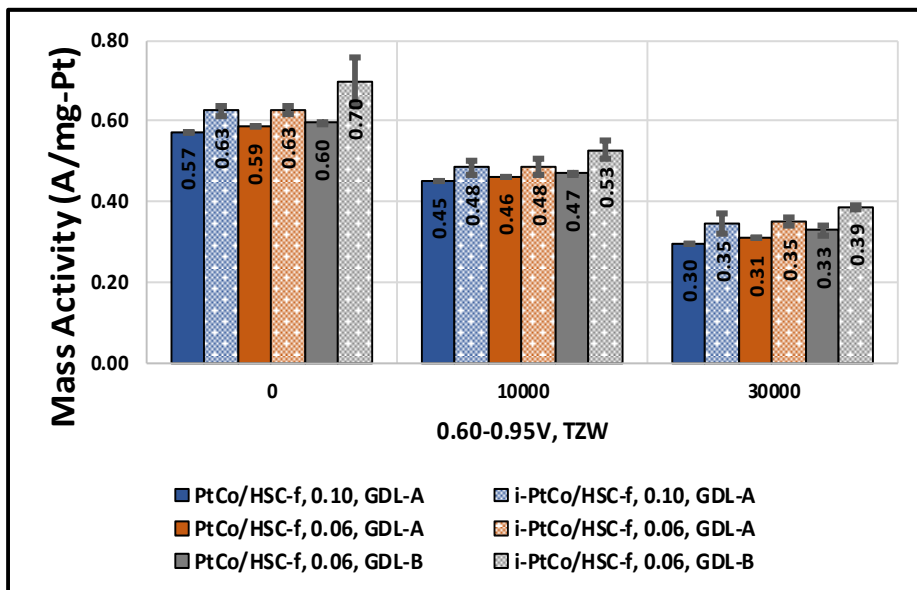
<b>Cathode:</b>	30 wt.% Intermetallic ordered Pt <sub>3</sub> Co/HSC-f at 0.06 and 0.10 mg <sub>Pt</sub> /cm <sup>2</sup> , PFSA ionomer (D2020), 900 EW, I/C ratio of 0.8,
<b>Anode:</b>	Pt/HSC, 0.015 mg <sub>Pt</sub> /cm <sup>2</sup>
<b>PEM:</b>	PFSA with reinforcement layer, 18 μm thick
<b>GDL:</b>	~210 and ~120 μm thick carbon fiber layer with 30 μm MPL. Water proof.

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

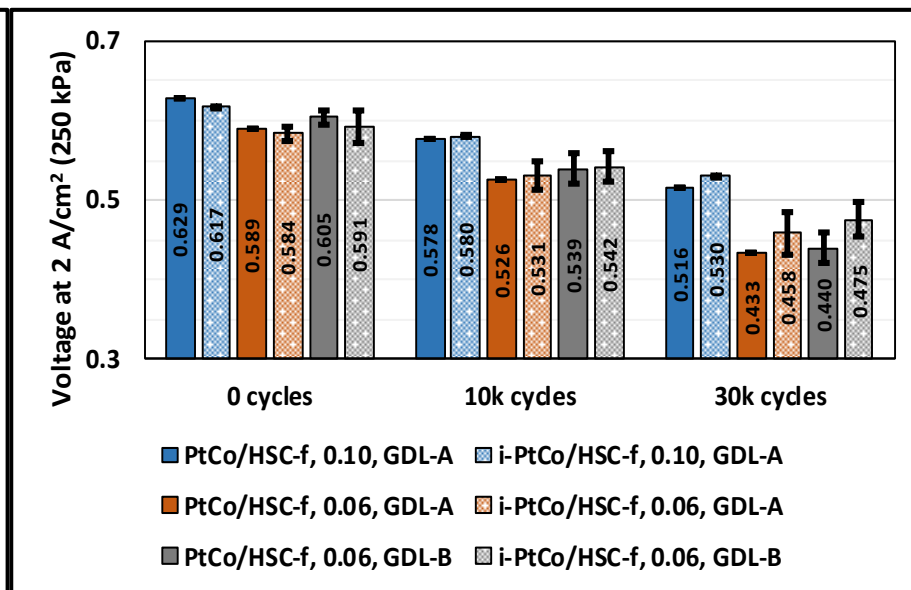
- ❑ As a deliverable, project catalysts were integrated into an MEA with other SOA subcomponents (within confidentiality constraint), and evaluated at both GM and NREL.
- ❑ Anode Pt loading was further reduced by using high-ECSA Pt/HSC catalyst.



## ORR Mass Activity



## Voltage at 2 A/cm<sup>2</sup>



H<sub>2</sub>/air, 94°C, 250/250 kPa<sub>abs,out</sub>, 65/65% RH<sub>in</sub>, 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<sub>Pt</sub>/cm<sup>2</sup>).
- ❑ 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.

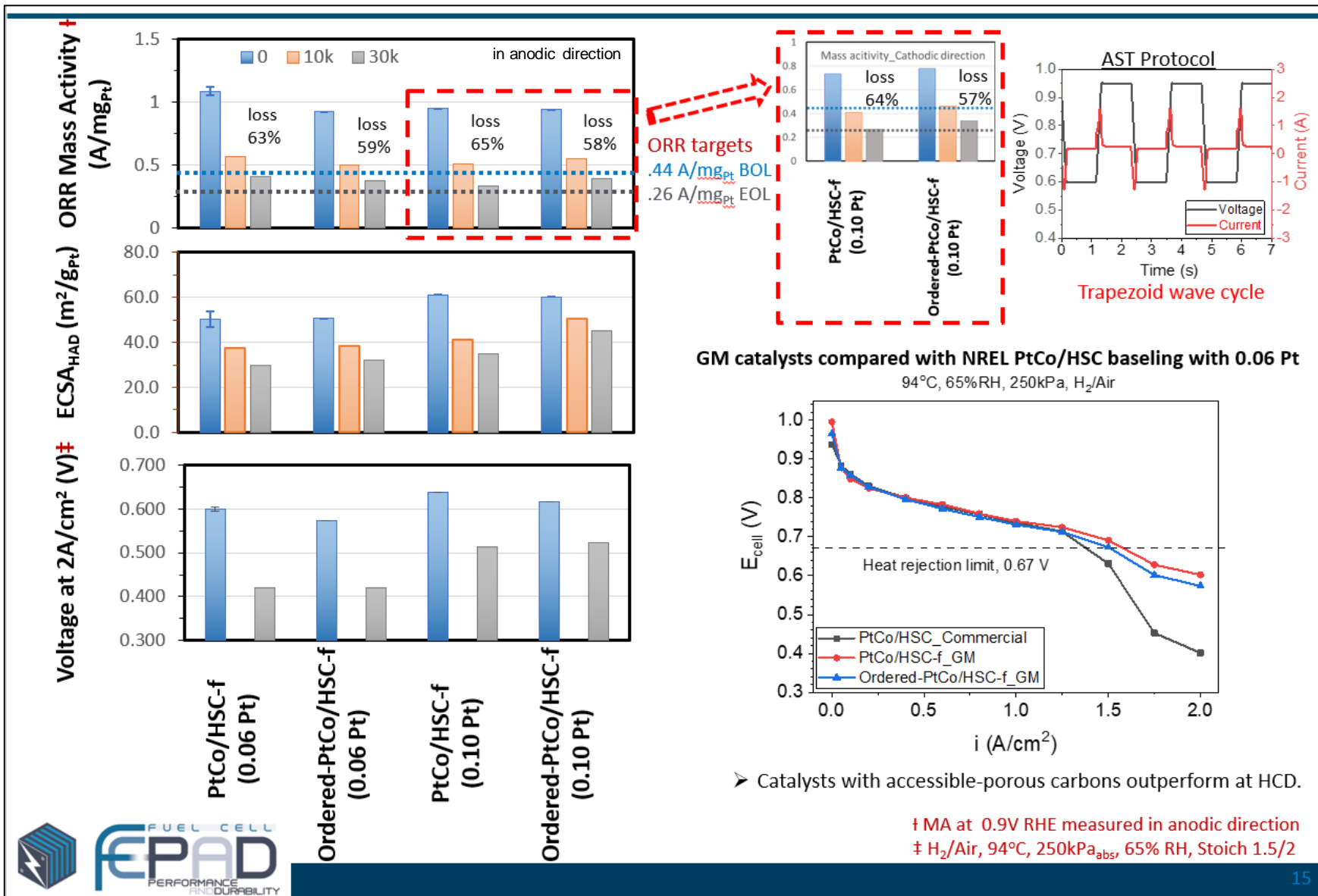
# DOE Validation at NREL

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 <sup>2</sup>	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 <sub>IR-free</sub>	A/mg <sub>PGM</sub>	1.108 (Anodic)	0.924 (Anodic)	0.95(Anodic) 0.734(Cathodic)	0.943(Anodic) 0.777(Cathodic)	>0.44	←
Loss in catalytic (mass) activity (10k cyc	% loss	49	46	45	40	-	-
Loss in catalytic (mass) activity (30k cyc	% loss	63	59	64	57	<40%	←
Performance at 0.8V (150kPa, 80°C)	A/cm <sup>2</sup>	~ 0.3	~ 0.3	0.36	0.34	>0.3	
Power at rated power (250kPa, 94°C)	W/cm <sup>2</sup>	1.1	1.05	1.2	1.1	-	>1.1
PGM utilization (250kPa, 94°C)	kW/g <sub>PGM</sub>	14.6	14	10.4	9.6	-	>9.1
Catalyst cycling (0.6-0.95V, 10k cycles)	mV loss at 0.8A/cm <sup>2</sup>	75	59	36	37	-	-
Catalyst cycling (0.6-0.95V, 30k cycles)	mV loss at 0.8A/cm <sup>2</sup>	179	179	86	86	<30	←
Catalyst cycling (0.6-0.90V, 30k cycles)	mV loss at 0.8A/cm <sup>2</sup>	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



# DOE Validation at NREL



➤ Catalysts with accessible-porous carbons outperform at HCD.

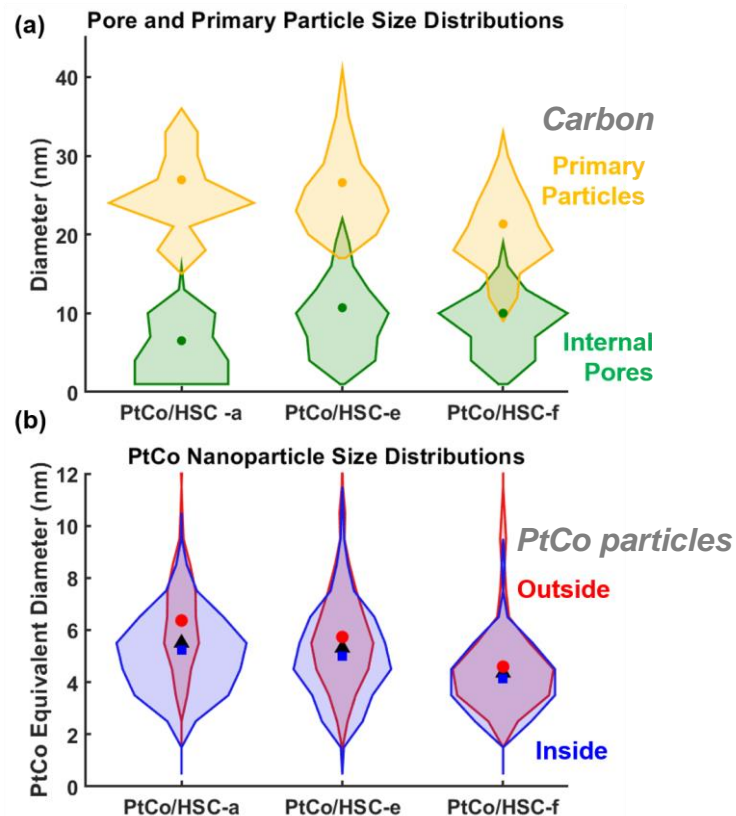
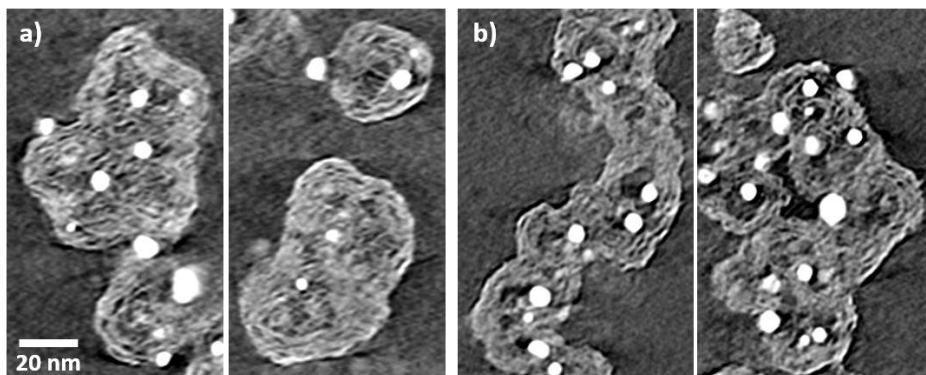
† MA at 0.9V RHE measured in anodic direction  
 ‡ H<sub>2</sub>/Air, 94°C, 250kPa<sub>abs</sub>, 65% RH, Stoich 1.5/2

➤ Agree with GM results

## Close-up STEM Tomography

PtCo/KB

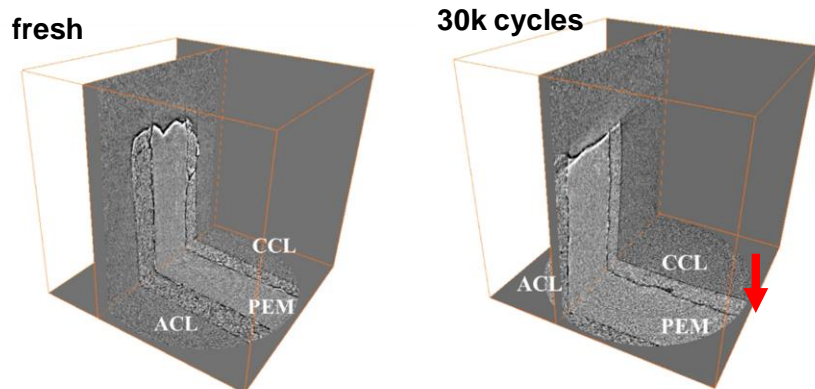
Accessible-PtCo/HSC



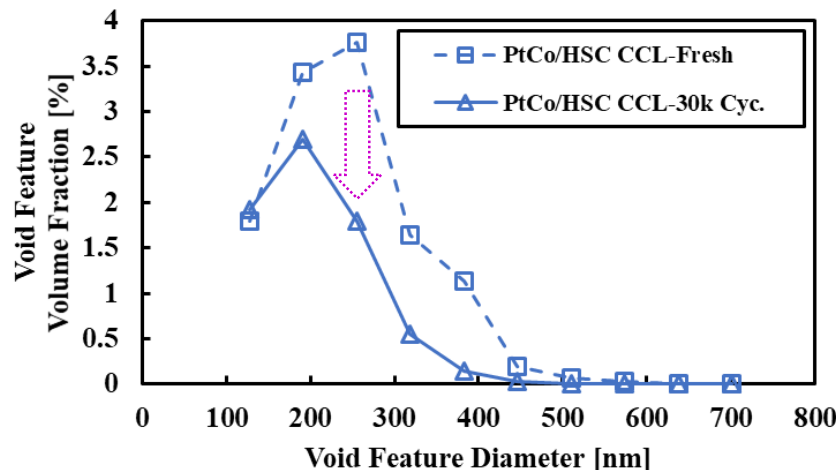
- ❑ Closer examination with TEM tomography led us to conclude that while some larger carbon pore openings are observable, they are not abundant enough to be the primary factor.
  - ❑ Even though the accessible carbons have larger pores and thinner shells, they do not show significant increase in the 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<sub>2</sub> 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

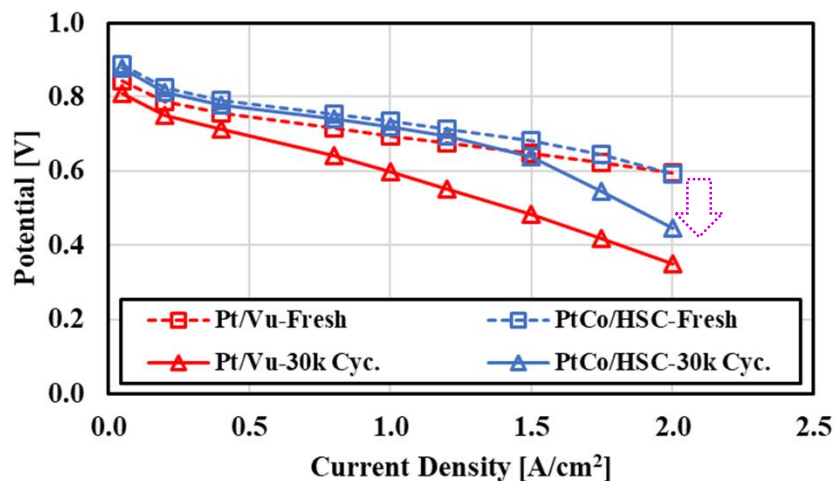
X-ray CT Zernike phase contrast slice renderings of PtCo/KB MEAs



Large-scale void feature distributions of PtCo/KB CCLs



FC polarization curve before and after AST

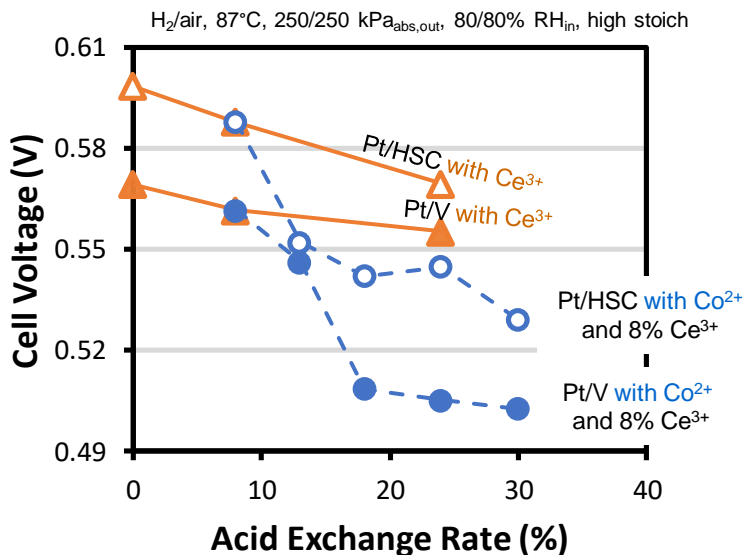


- ❑ Noticeable drop in cathode pore volume was observed after AST test.
  - ❑ Similar observation has been reported earlier using electron and optical microscopes but with less confidence level.
- ❑ This could explain the sharp drop in voltage at HCD of PtCo/KB after AST, previously not understandable 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.

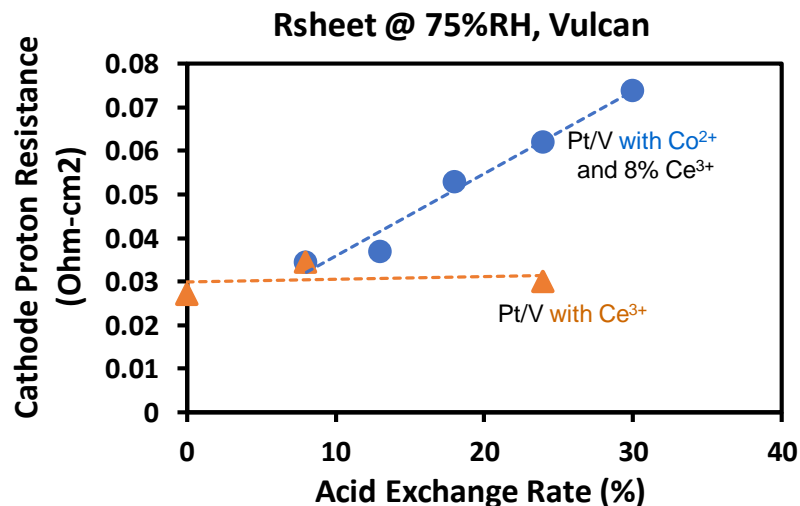
# Co-doping of $\text{Co}^{2+}$ & $\text{Ce}^{3+}$



## Voltage at 2.5 A/cm<sup>2</sup>



## Cathode Proton Resistance

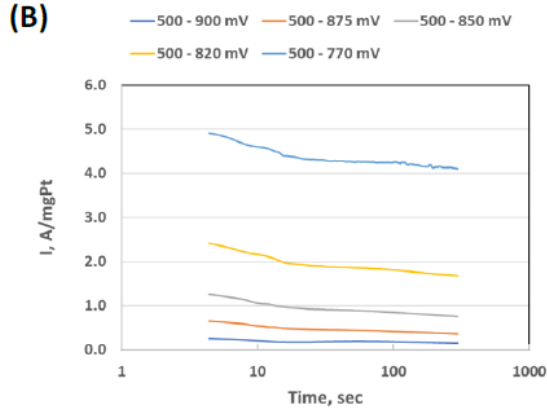
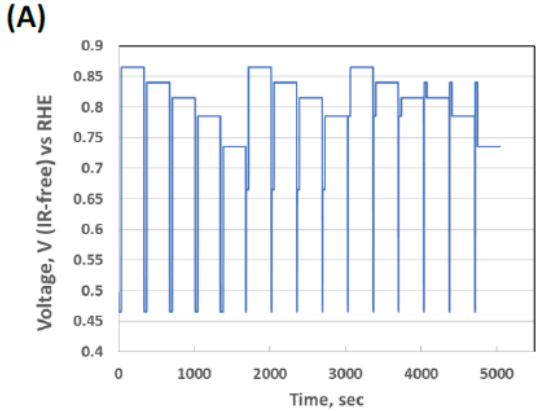


- ❑ While the effects of  $\text{Co}^{2+}$  and  $\text{Ce}^{3+}$  were studied earlier, the effect when both cations are present was not systematically studied.
- ❑ We found that the effect was about the same as the combined effect of individual cation, i.e., the interaction was small.
- ❑ The study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

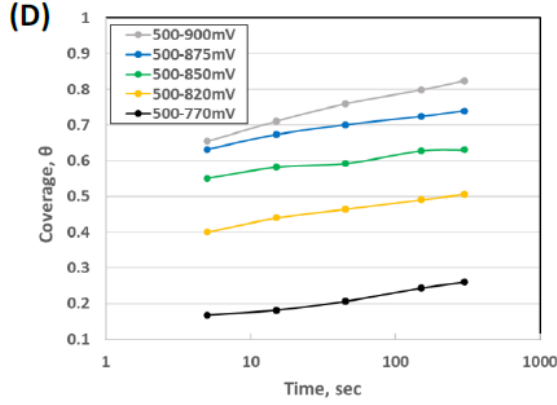
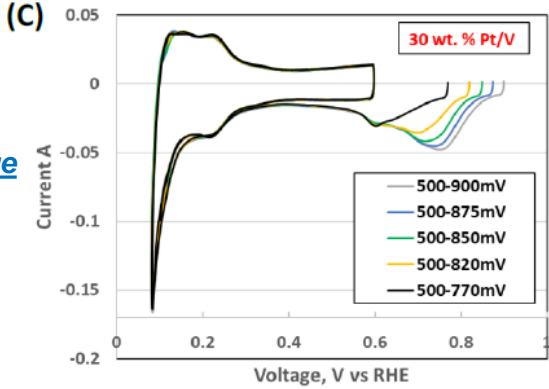


# Dynamic ORR Model Development

ORR kinetic



Oxide coverage



**Oxide-coverage kinetic equation**

$$i = i_0 \left( \frac{p_{O_2}}{p_{O_2,ref}} \right)^{\gamma} (1 - \theta) \exp \left( \frac{-\alpha F \eta}{RT} \right) \exp \left( -\frac{\omega \theta}{RT} \right)$$

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

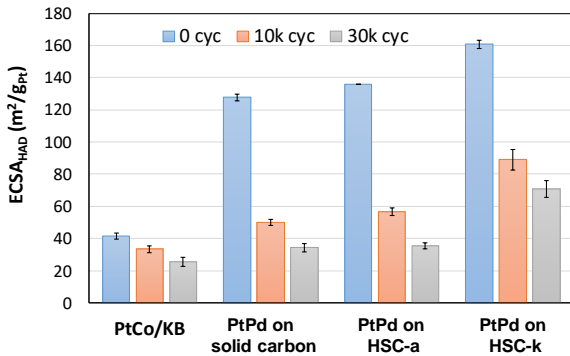
Actual measurement (green arrow)  
new (red arrow)  
Actual E on PtCo (blue arrow)

0.15 mg<sub>Pt</sub>/cm<sup>2</sup> Pt/V with NR212 membrane  
75°C, 100% RH<sub>in</sub>, high stoich of O<sub>2</sub> or N<sub>2</sub>

- ❑ 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.

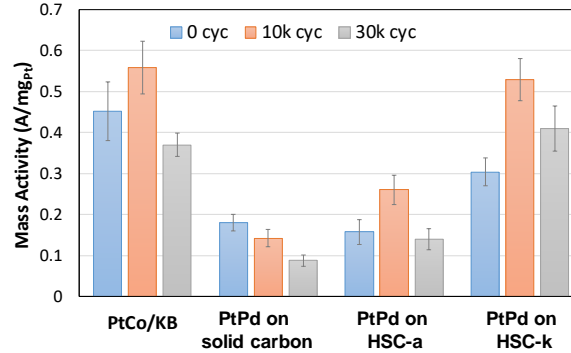
# PtPd ML catalysts on Mesoporous Carbons

## ECSA

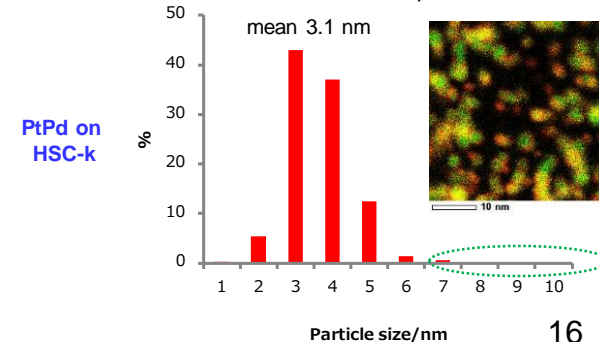
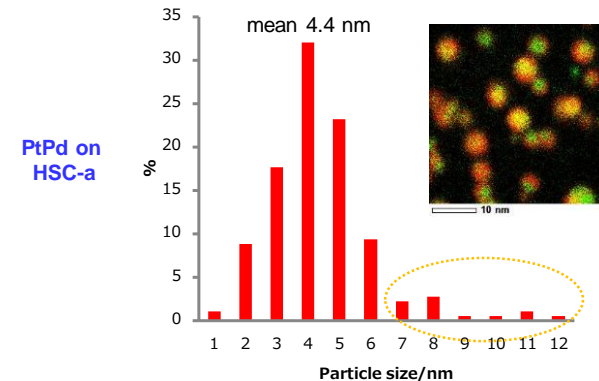
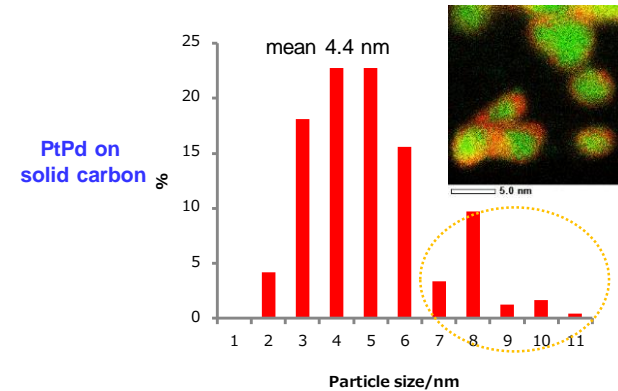


## ORR Activity

GM 38 cm<sup>2</sup> platform. 0.07 mg<sub>Pt</sub>/cm<sup>2</sup> with Gen1 membrane&GDL



## TEM after 30k cycles



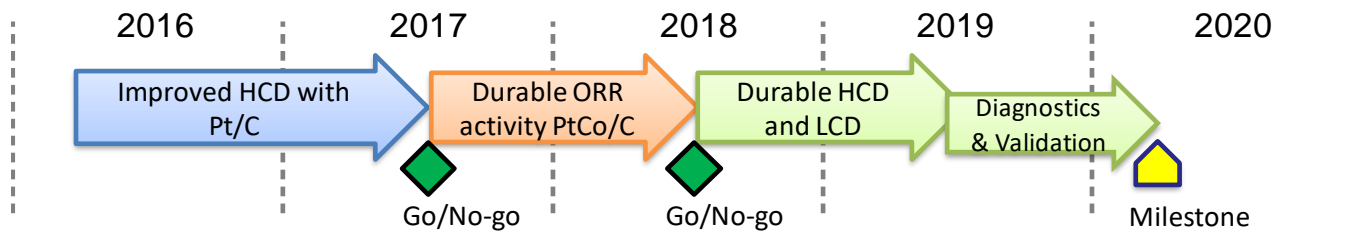
- ❑ With some discussion with GM, NECC independently developed PtPd monolayer catalyst on mesoporous carbons.
- ❑ Thanks to high ECSA of ML catalysts, HCD issue associated with local O<sub>2</sub> transport is absent.
- ❑ On the other hand, significant improved stability was observed with mesoporous 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



# Future Work

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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”

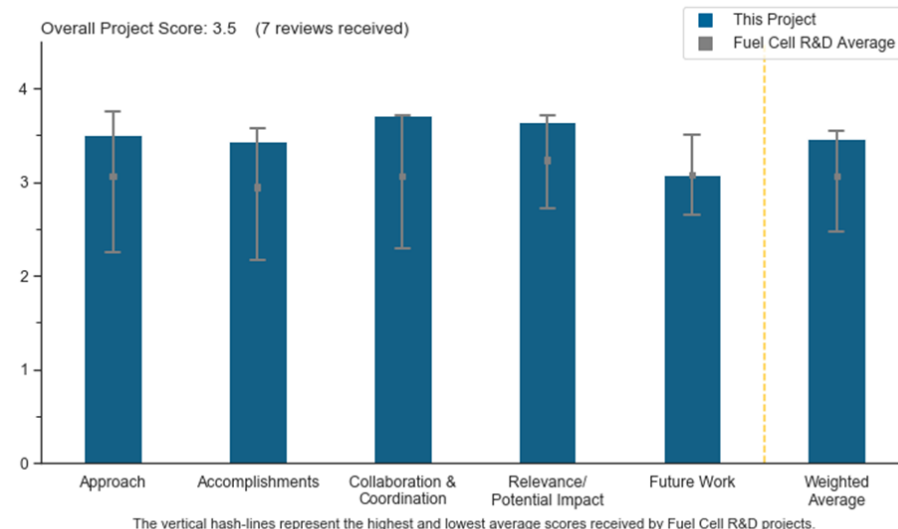
- This is also a question we are interested in. While we do not have resources to take this on at the moment, we see opportunity to leverage a model that was developed within the project to study this, i.e., CMU's Pt dissolution in absent of ionomer model.

- “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 an important point. However, it cannot be done under the scope of this project. Pt loading sensitivity must be done under realistic operating conditions (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

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- ❑ 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<sub>2</sub> 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<sup>2+</sup> and C<sup>e3+</sup> 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***

# Acknowledgements

## DOE

- Greg Kleen (Program Manager)
- Donna Ho (Technology Manager)
- Shaun Onorato

## General Motors LLC

- Aida Rodrigues, Yevita Brown, Carissa Miller, Sheryl Forbes, Charles Gough (Contract Administration Group)
- Venkata Yarlagadda
- Michael K. Carpenter
- Yun Cai
- Thomas E. Moylan
- Joseph M. Ziegelbauer
- Ratandeeep Singh Kukreja
- Wenbin Gu
- Srikanth Arisetty
- Roland Koestner
- Cristin L. Keary
- Qiang Li and team
- Peter Harvey and team
- Kathryn Stevick and team
- Tim Fuller
- Shruti Gondikar
- Mohammed Atwan
- Nagappan Ramaswamy
- Dave Masten
- Swami Kumaraguru
- Craig Gittleman
- Mark F. Mathias

## 3M Company

- Dr. Andrew Haug (sub-PI)
- Matthew Lindell
- Tyler Matthews

## Carnegie Mellon University

- Prof. Shawn Litster (sub-PI)
- Shohei Ogawa
- Jonathan Braaten
- Leiming Hu
- Yuqi Guo

## Cornell University

- Prof. David A. Muller (sub-PI)
- Prof. Héctor Abruña
- Elliot Padgett
- Matthew Ko
- Barnaby Levin
- Yin Xiong
- Yao Yang

## Drexel University

- Prof. Joshua Snyder (sub-PI)
- Yawei Li

## NREL

- Dr. K.C. Neyerlin (sub-PI)
- Guanxiong Wang
- Luigi Osmieri
- Jason Christ
- Shaun Alia
- Jason Zack

## ANL / APS

- Dr. Deborah J. Myers
- Dr. Nancy N. Kariuki
- Dr. Ross N. Andrews
- Dr. Jan Ilavsky

## LANL

- Dr. Andrew M. Baker
- Dr. Rangachary Mukundan
- Dr. Rod L. Borup

