FC144

Highly-Accessible Catalysts for Durable High-Power Performance

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General Motors, Fuel Cell Activities

June 14, 2018

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

Overview

Timeline

- Project start date: 1 Apr 2016
- Project end date: 30 Jun 2019
- Percent complete: 47%

Budget

- Total Funding Spent as of 3/31/18: $1.8M
- Total DOE Project Value: $4.59M
- Cost Share: 21.7%

Barriers

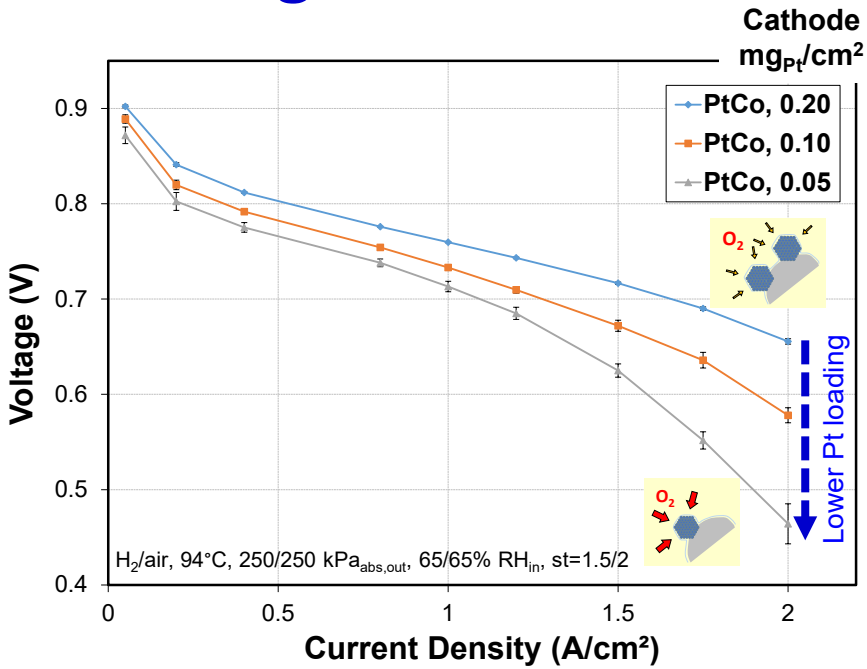
- B. Cost
  - Decrease amount of precious metals.
- A. Durability
  - Improve kinetic activity and high current density performance
- C. Performance
  - Achieve and maintain high current densities at acceptably-high voltages

Partners

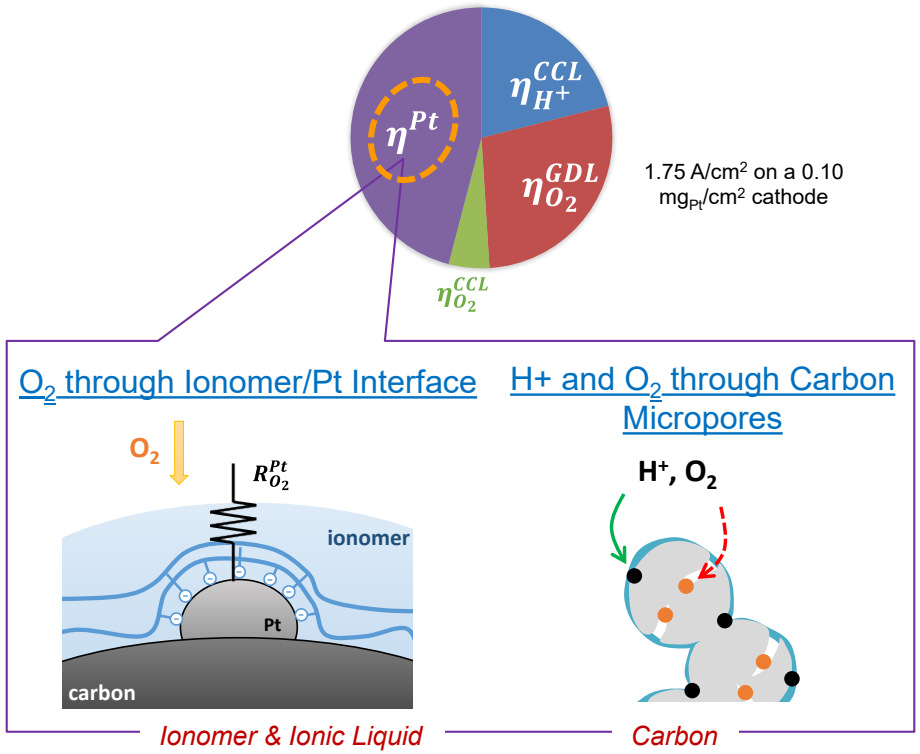
- Subcontractors:
  - 3M Company
  - Carnegie Mellon University
  - Cornell University
  - Drexel University
  - NREL
- Project lead: GM

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 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.

Relevance:

Targets and Status

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

Metric	Units	PtCo/KB 2016	PtCo/HSC-en‡ 2018-1	PtCo/HSC-f 2018-2	Ordered-PtCo/KB 2018-3	DOE 2020 Target	Project Target
PGM total loading (both electrodes)	mg/cm^2	0.125	0.125	0.088	0.125	<0.125	←
Mass activity @ 900 $mV_{iR\text{-}free}$	A/mg_{PGM}	0.62†	0.6†	0.7†	0.53†	>0.44	←
Loss in catalytic (mass) activity	% loss	30%	42%*	54%*	16%	<40%	←
Performance at 0.8V (150kPa, 80°C)	A/cm^2	0.304	0.363	0.382	0.301	>0.3	←
Power at rated power (150kPa, 94°C)	W/cm^2	0.80	tbd	0.93	tbd	>1.0	-
Power at rated power (250kPa, 94°C)	W/cm^2	1.01	1.31	1.26	1.15	-	>1.1
PGM utilization (150kPa, 94°C)	kW/g_{PGM}	6.4	tbd	10.6	tbd	>8	←
PGM utilization (250kPa, 94°C)	kW/g_{PGM}	8.1	10.5	14.3	9.2	-	>9.1
Catalyst cycling (0.6-0.95V, 30k cycles)	mV loss at $0.8A/cm^2$	(24, 15)	(34, 23)*	(47, 32)*	(8, 5)	<30	←
Support cycling (1.0-1.5V, 5k cycles)	mV loss at $1.5A/cm^2$	>500	>500	>500	tbd	<30	-

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

(measured at 40, 100% RH)

** Meet target in absolute term (e.g. >0.26 A/mg_{PGM}) (slide 10)*
† MA at $0.9V_{RHE}$ in cathodic direction
‡ HSC-en is an optimized and up-scale (20 g) of HSC-e

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.

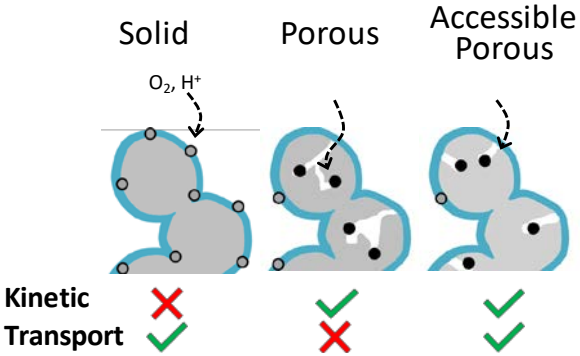
Target Highlights

- 10-20% improvement in overall FC performance with HSC-en over previous generation (HSC-e).
- Meet durability target in *absolute* terms, but some narrowly miss in *percentage* loss.
- Excellent stability with ordered intermetallic PtCo.

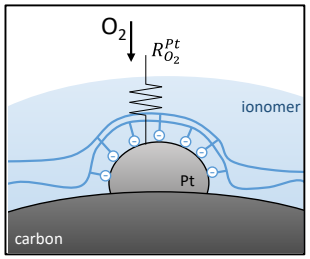
Approach:

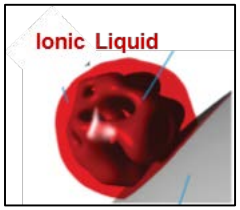
Work Focuses in the Past Year

- 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

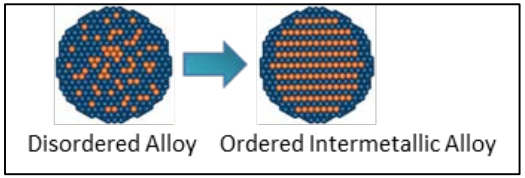


- Electrolyte-Pt Interfaces: Ionomer and Ionic Liquid
  - Develop process to add ionic liquid in MEA and study its effect.
  - Identify new electrolyte-Pt interface affects fuel cell performance.

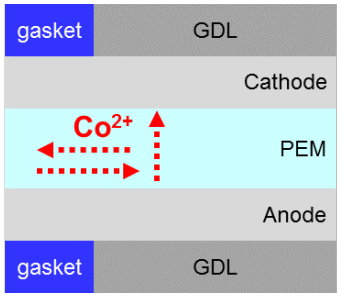




- Ordered Intermetallic Alloys
  - Use advanced in-situ techniques to optimize activity/stability vs Pt-particle-size growth



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



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 ✓

	2017 AMR	2018 AMR
❑ Downselect carbon support, ionomer, ionic liquid	70%	100%
❑ Measure the effect of leached Co^{2+} and Pt surface area	80%	100%
❑ Develop dealloyed catalyst from ordered intermetallic alloy	50%	100%
❑ Visualize carbon structure and Pt location on selected catalysts	70%	100%
❑ Model baseline material	80%	100%

TASK 2 - Development of Dealloyed Catalyst with Preferred Catalyst Design

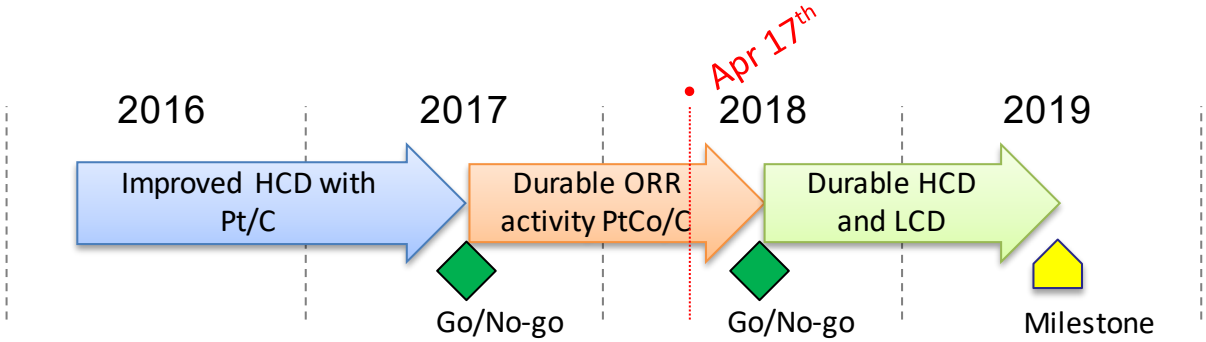
Go/No-go criteria : >0.44 A/mg$_{PGM}$, <40% mass activity loss with preferred design ✓ ***June 2018***

❑ Develop dealloyed catalyst on preferred support	30%	80%
❑ Implement selected ionomer and ionic liquid with selected catalysts	0%	60%
❑ Visualize fresh PtCo/C and post-AST Pt/C	50%	90%
❑ Model PtCo/C before and after AST	0%	70%

TASK 3 - Optimization for Durable HCD and LCD Performance

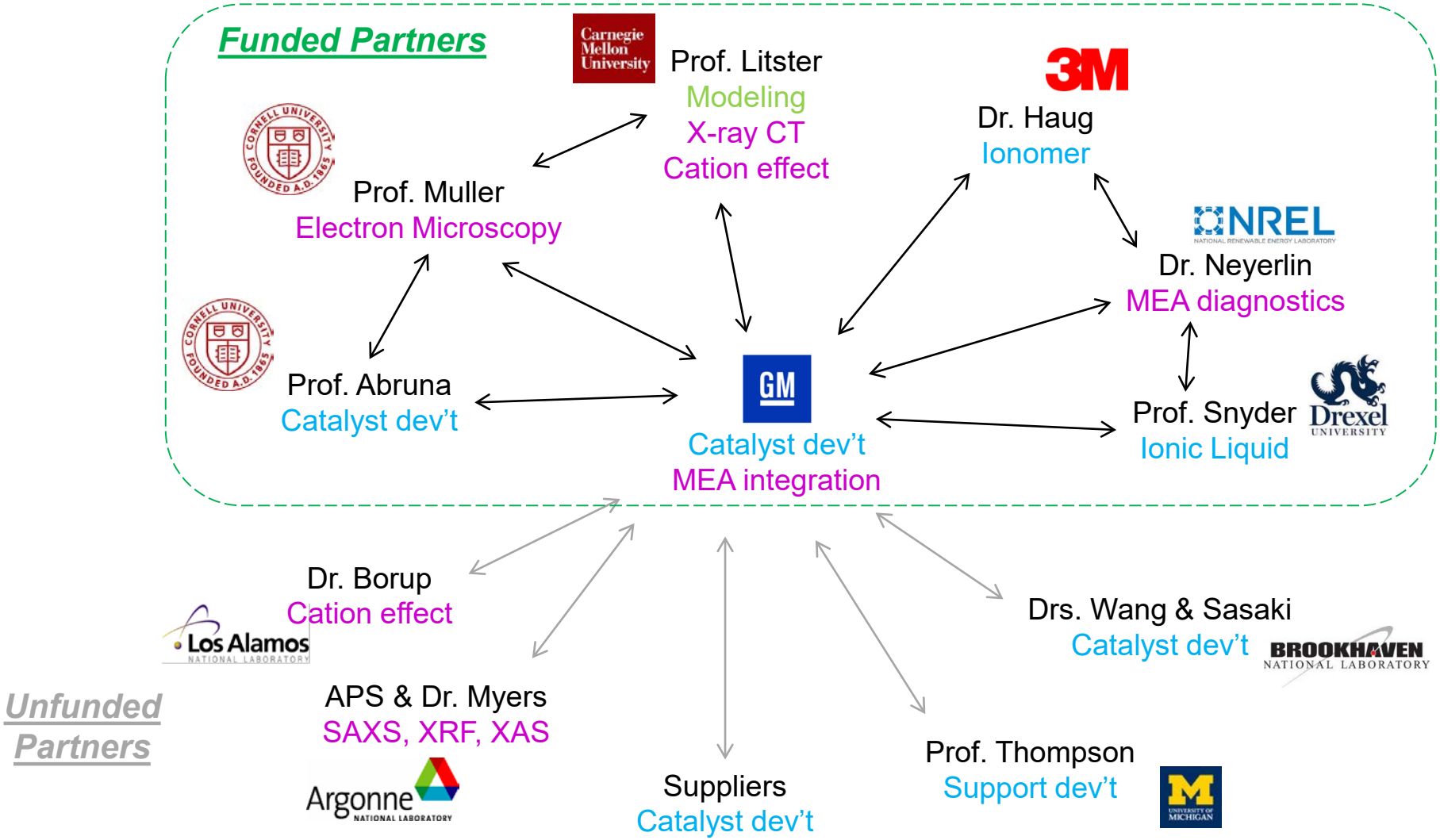
Milestone: >1.1 W/cm^2, >9.1 kW$_{rated}$/g$_{Pt}$, and Q/ΔT <1.45 ✓

❑ Identify root cause and improve durability and performance of PtCo/C	0%	20%
❑ Evaluate effect of selected ionomer/IL on HCD and durability of improved PtCo catalyst	0%	10%
❑ Integrate new catalyst design with other state-of-the-art FC components	20%	20%
❑ Make available to DOE the improved catalyst in 50 cm^2 MEAs	10%	10%
❑ Visualize and model improved catalyst	0%	10%



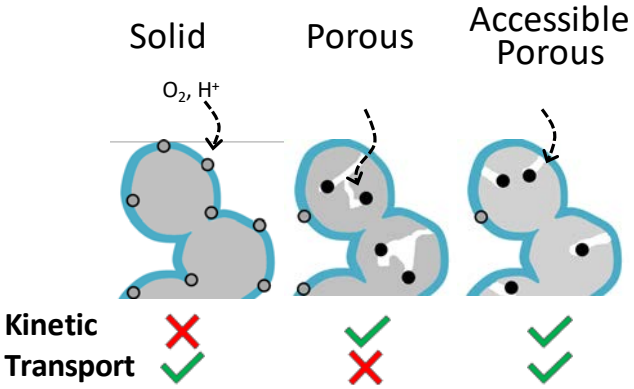
Collaborations

Materials dev't
Characterization
Modeling

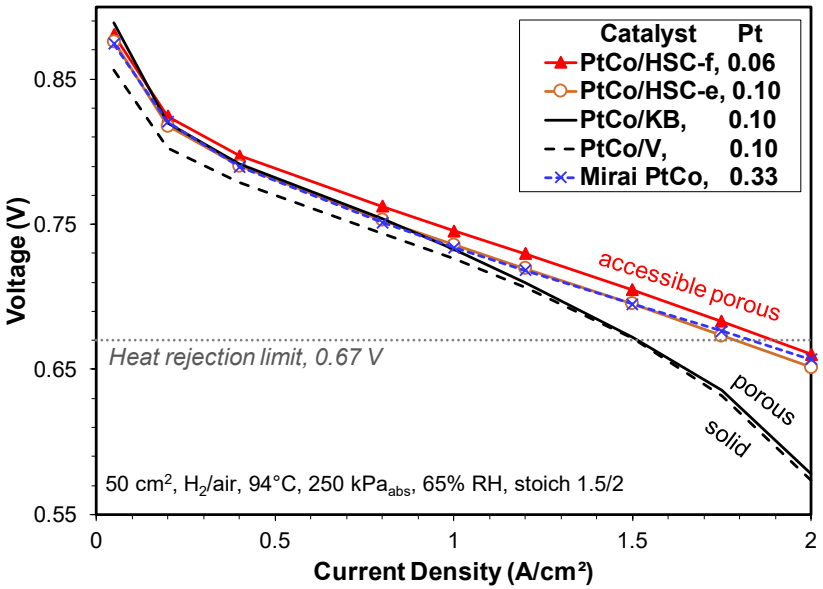


Technical Accomplishment:

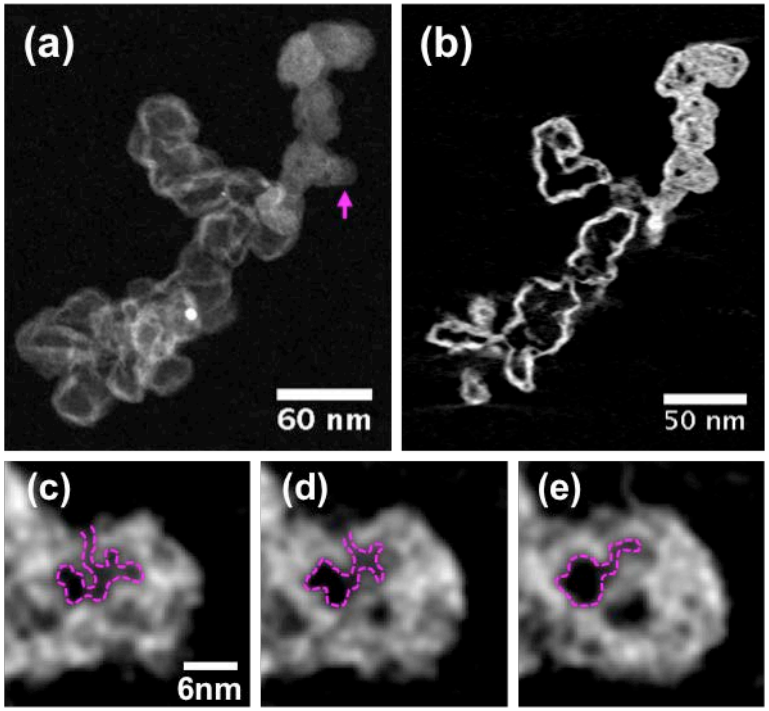
Internal Carbon Pore Accessibility



Fuel Cell Performance



3D LAADF STEM image of KetjenBlack



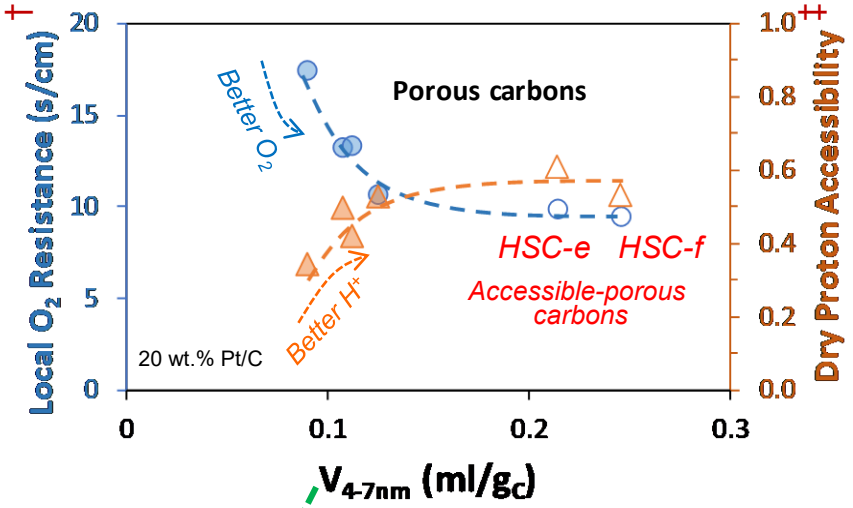
- The type of carbon support affects not only the *transport* properties of the catalyst layer but also the *kinetic activity* of the catalysts.
- Can achieve both good activity and transport with optimized carbon mesopores.
- Carbon morphology is very important but not easy to evaluate (due to its size, low-contrast, complex/non-uniform morphology)

ACS Energy Lett. (2018) 3, 618
J. Electrochem. Soc (2018), 165, F173

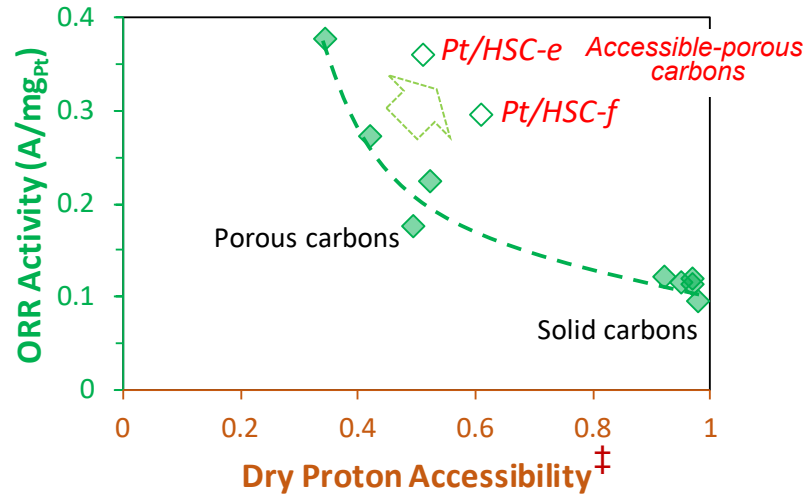
Technical Accomplishment:

Internal Mesopores Size

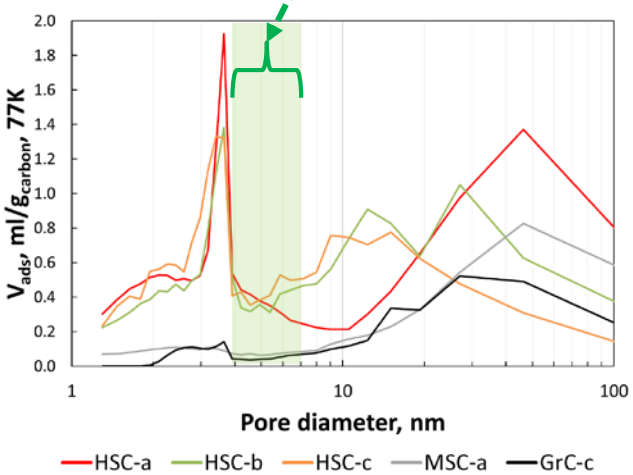
Transport vs Mesopore (4-7nm) Volume



Activity vs Proton Accessibility



BET-BJH of Carbons



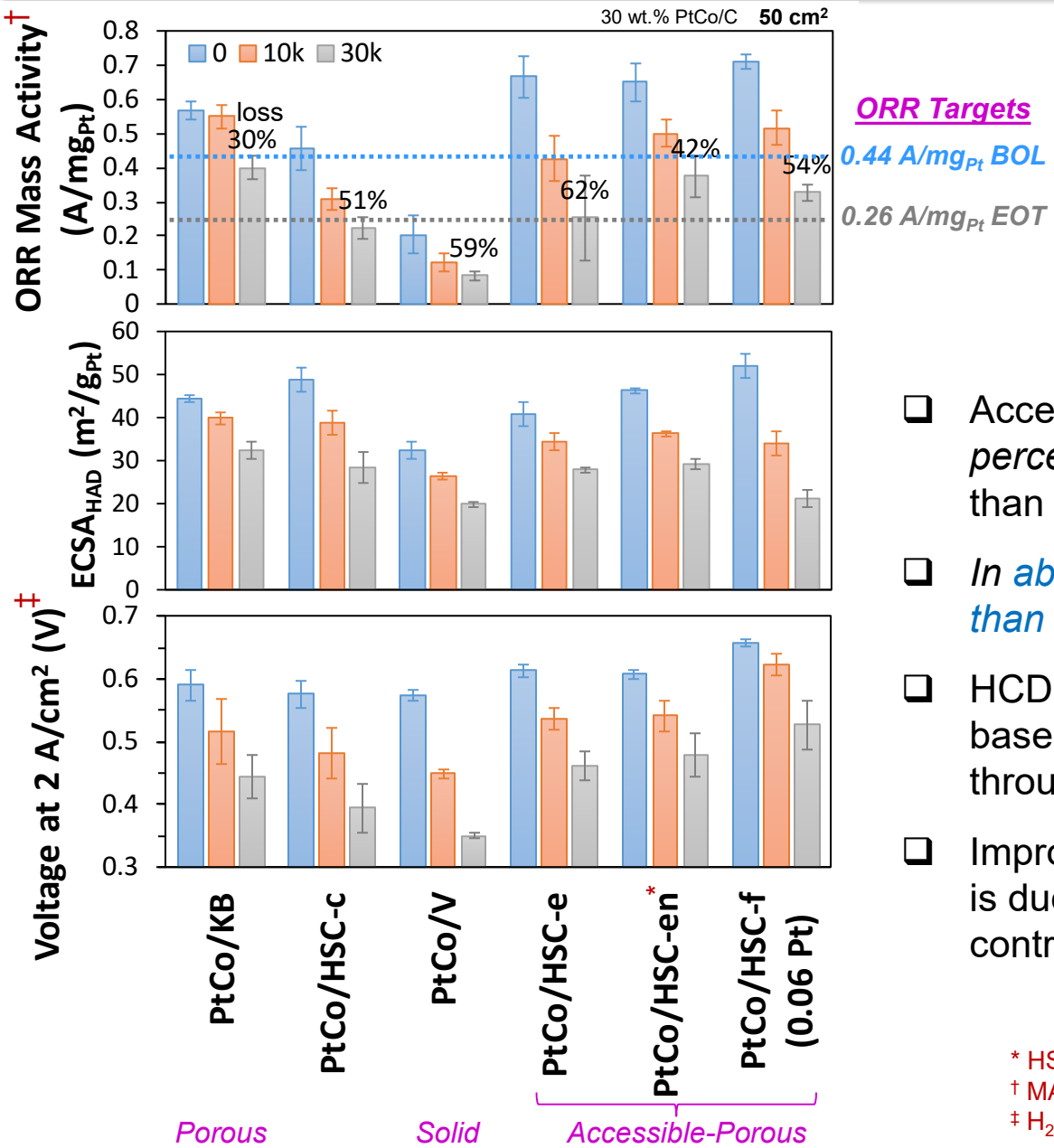
- Local transport properties (O_2 and proton) correlate well with mesopores of 4-7 nm in size.
  - Too large → ionomer intrudes into pores and poisons Pt activity
  - Too small → O_2/proton transport is restricted
- Appropriate pore geometry (opening size and pore depth) yields both good transport and activity.

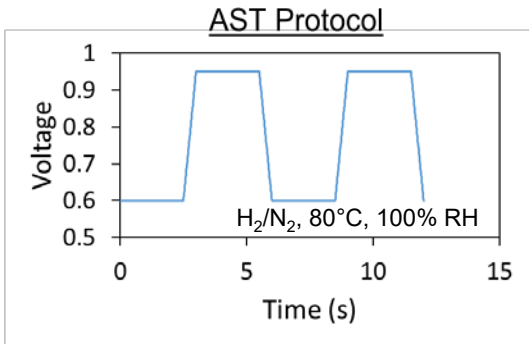
† by limiting current, see JES (2012) 159, F831
‡ by CO stripping, see 2017 AMR or JES (2018), 165, F173

ACS Energy Lett. (2018) 3, 618

Technical Accomplishment:

Accessible-PtCo Stability





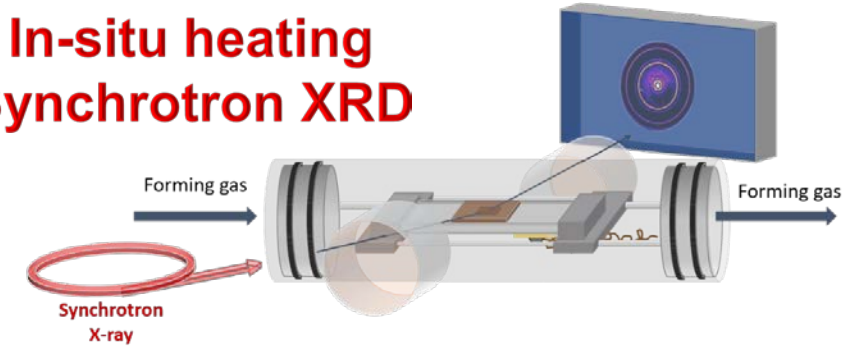
- Accessible-porous carbons show larger *percentage* losses of ORR MA and ECSA than KB.
- *In absolute term*, end-of-test MA is *better than 0.26 A/mg$_{Pt}$* (or 40% loss from 0.44 A/mg$_{Pt}$).
- HCD performance (2 A/cm²) is better than baseline porous and solid carbons throughout the test.
- Improved stability of *HSC-en* over *HSC-e* is due to pore optimization and quality control.

* HSC-en is an optimized and up-scale (20 g) of HSC-e
† MA at 0.9 V_{RHE} measured in cathodic direction
‡ H_2/air, 94°C, 250 kPa$_{abs}$, 65% RH, stoich 1.5/2

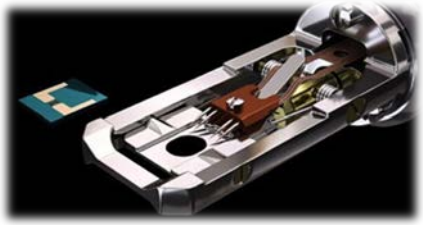
Technical Accomplishment:

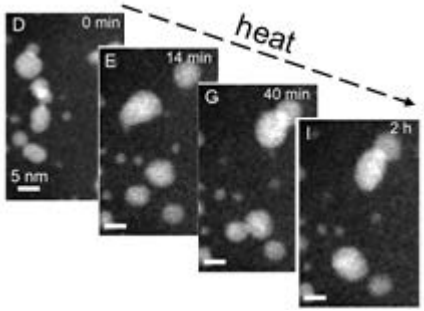
Optimize Pt_3Co Ordering with in-situ Techniques

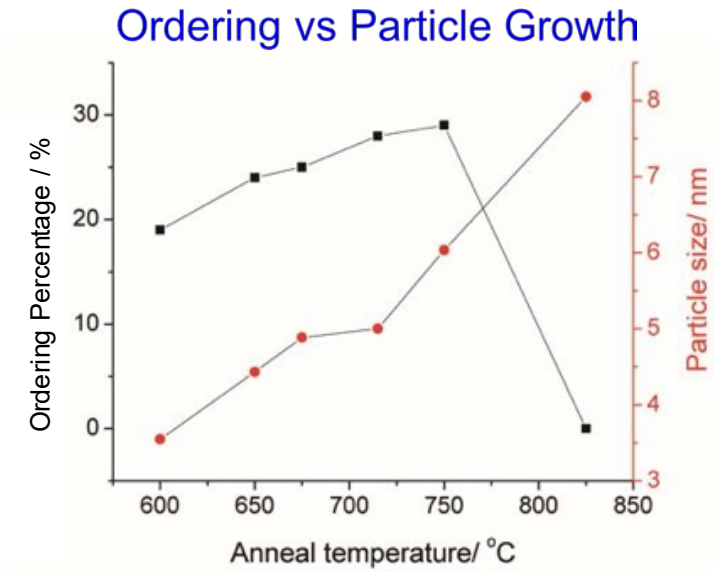
In-situ heating Synchrotron XRD

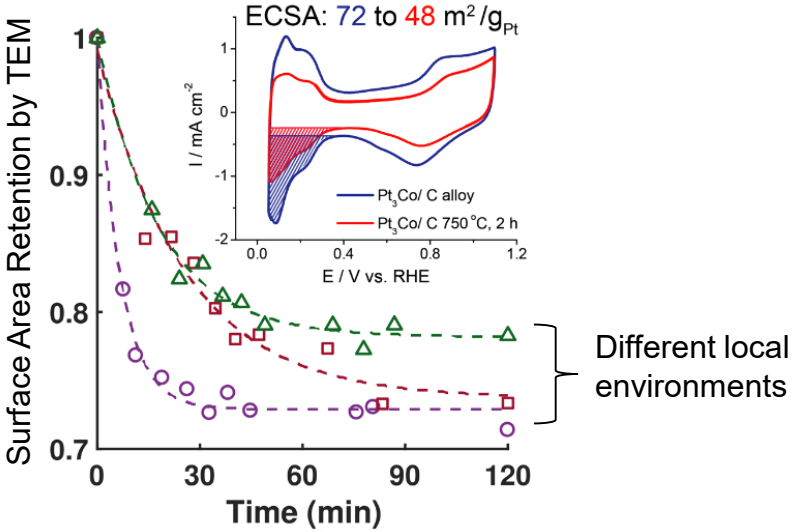


In-situ heating STEM





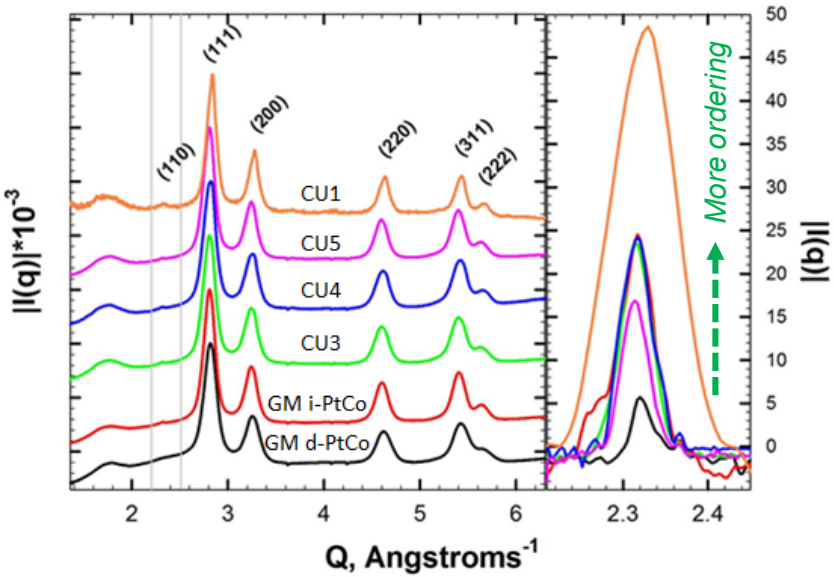




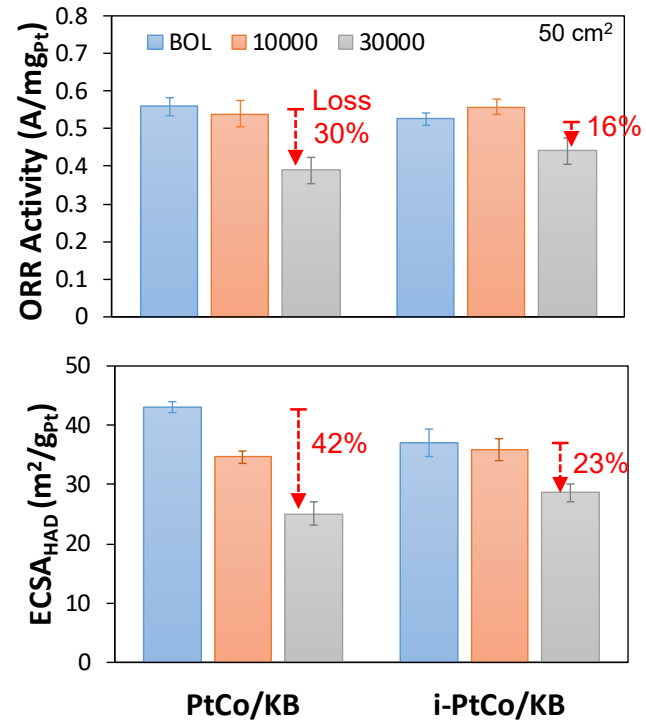
- Determine annealing parameters (temperature, time, cooling procedure) for best ordering & lattice contraction without excessive particle size growth.
- Cornell prepared 5 catalysts which were tested/being tested at GM. In parallel, GM also applies learnings to its own synthesis for faster scale up for MEA test.

Stabilization with Ordered Pt_3Co

Degree of Ordering Measured by WAXS for multiple Cornell- and GM-made ordered Pt_3Co



MEA AST of GM-made ordered Pt_3Co



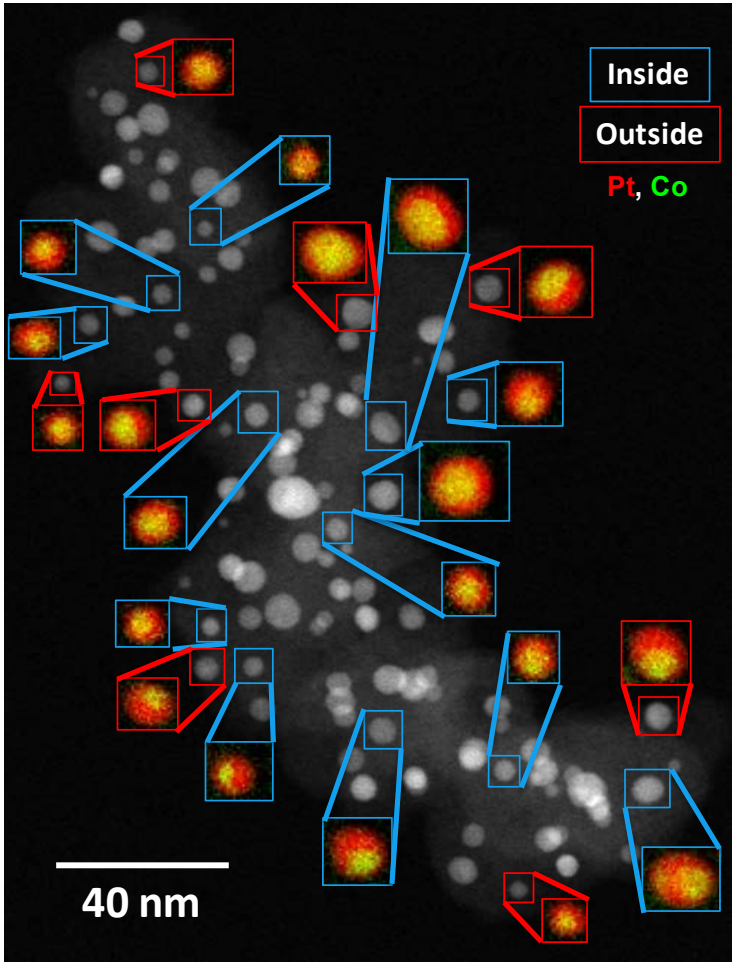
- WAXS confirmed formation of ordered structure in the particle cores.
- Degree of ordering is very sensitive to particle size and annealing condition.

- MEA tests showed improved stability for Cornell-made and GM-made ordered Pt_3Co/KB catalysts prepared by the same annealing procedure.
- Losses in ORR activity and ECSA, of an already-very-stable Pt_3Co/KB, were ***reduced in half.***
- Very promising. Will apply on new carbons.

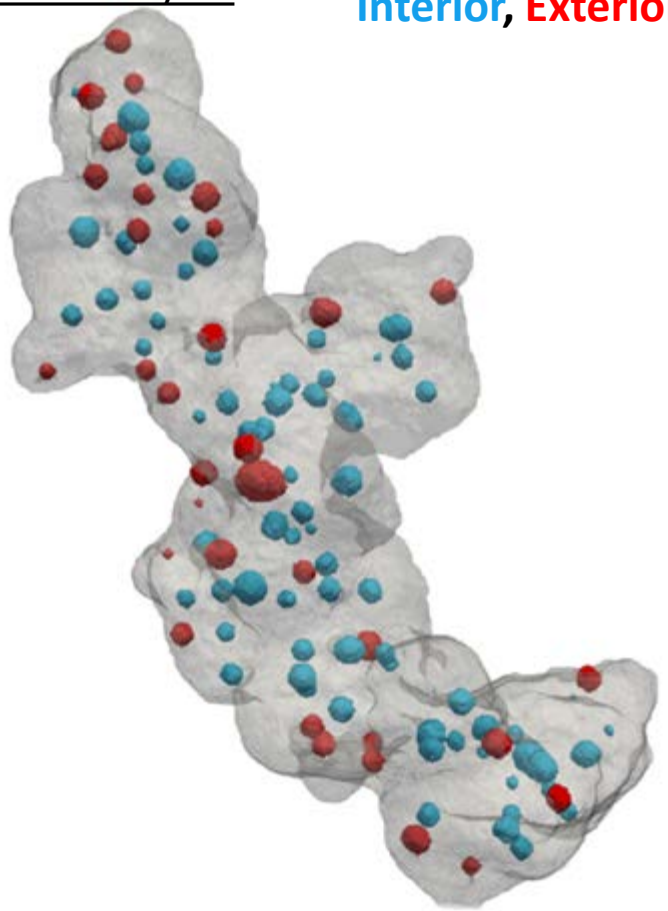
20-30 wt.% PtCo/C

Technical Accomplishment:

Tomography and EELS Show Similar PtCo Degradation Inside and Outside Carbon



30k AST PtCo/KB

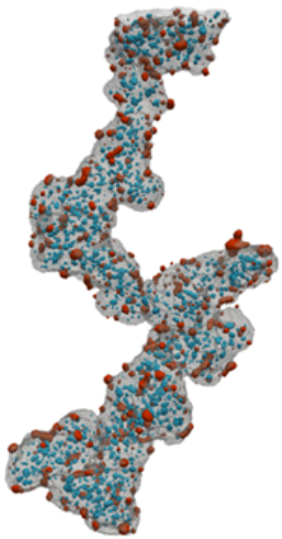


- No significant differences in the changes during AST of Pt/Co composition and Pt-shell thickness between inside and outside particles.
- Somewhat surprising that Co dissolution is similar, considering difference in electrolyte environment.

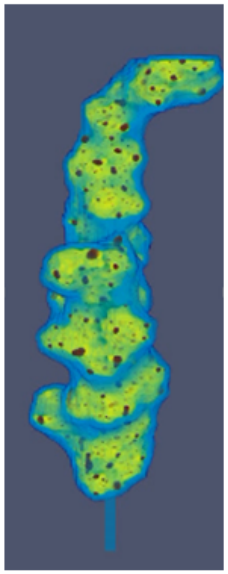
Technical Accomplishment:

STEM-CT based Catalyst Aggregate Model

50 wt% on high surface area carbon black



With Nafion (blue) added by modeling

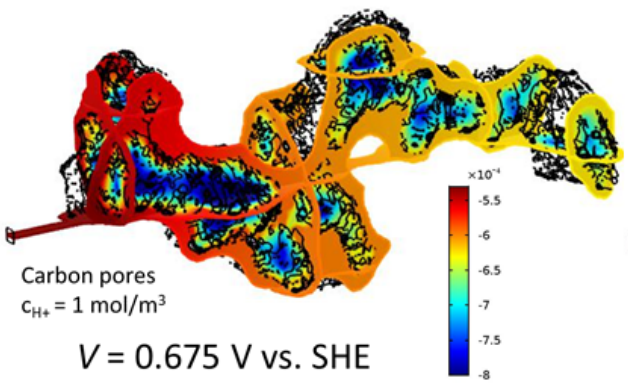


External platinum

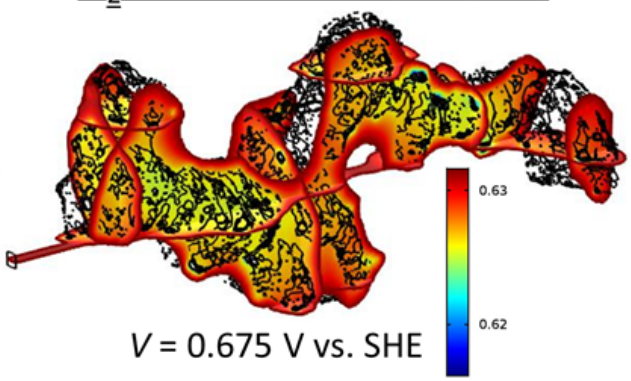
Internal platinum

Modeling of oxygen and proton transport plus ORR at the catalyst scale to evaluate the effects of carbon support aggregate surface area, morphology, surface chemistry, and ionomer properties.

Potential (V)



O_2 concentration (mol/m³)



1.3 A/cm² and R.F. of 70

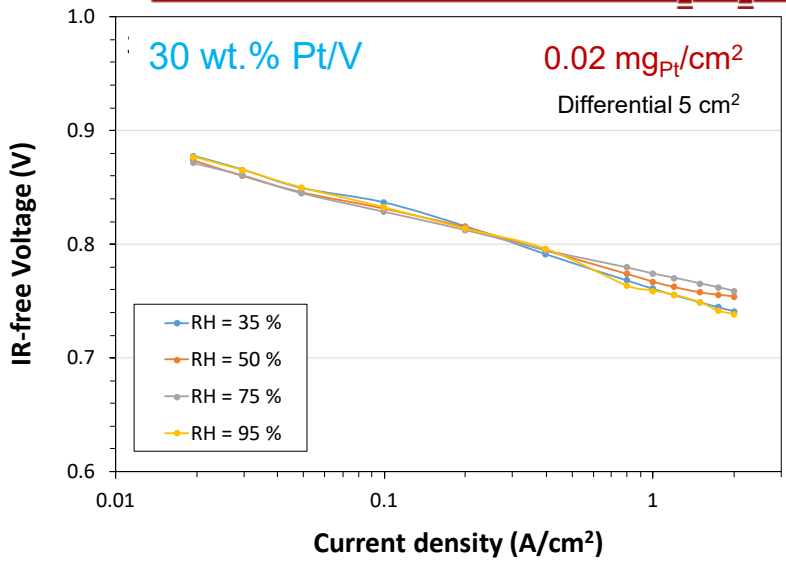
→Small gradient of potential and O_2 concentration in carbon particle

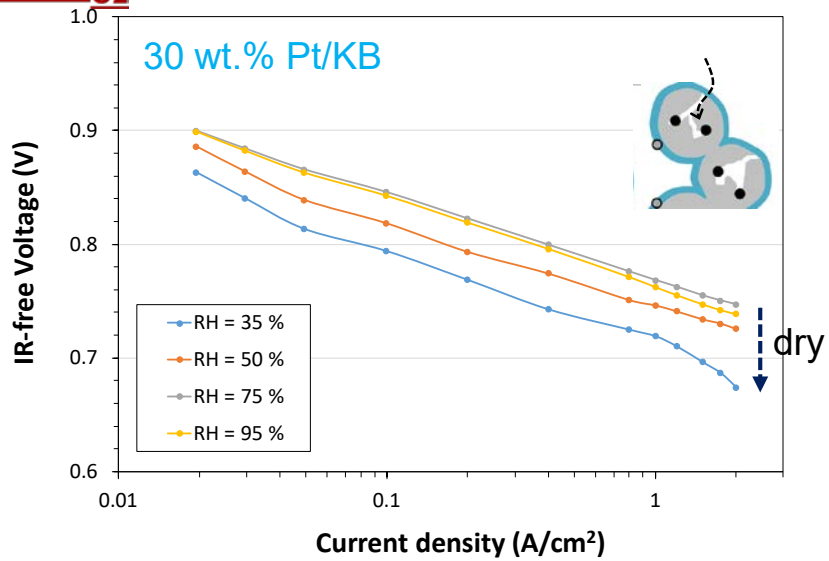
- Losses due to proton and O_2 transport in the internal pores are small with known physics and morphology. → agree with those observed in *accessible porous* carbons
- Sensitivity study shows significant voltage loss with lower O_2 diffusivity. → can occur in KetjenBlack. Need O_2 measurement (and method development) with appropriate materials to support assumption
- See Back-up slides for *Achievements* on *ex-situ* transport measurements.

Technical Accomplishment:

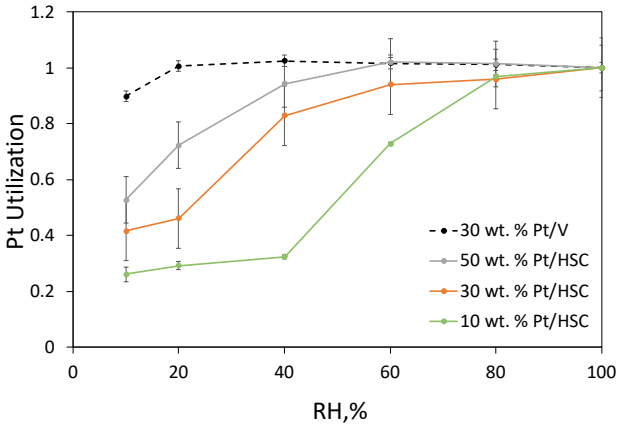
Sufficient H^+ Transport in Internal Pores

I-V Characteristic under H_2/O_2, 252 kPa_{O2}





Pt wt.% and Proton Accessibility

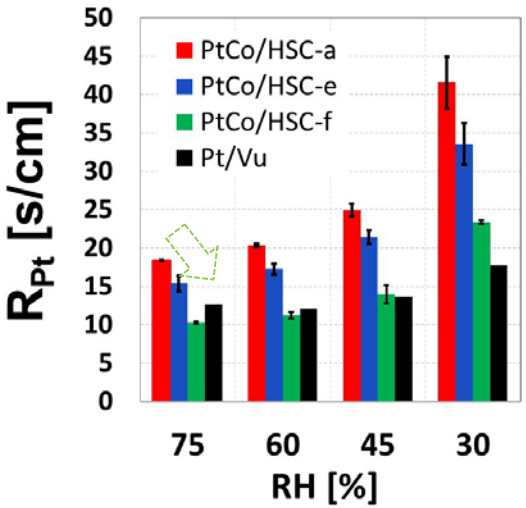


- Beneficial for future development to know how much of the *local resistance* is caused by proton and O_2.
- Under relatively high humidity (>75% RH), where water can condense in carbon primary pores, *proton transport loss* in internal pores is *negligible*.
  - Can support >0.13 A/cm^2_{Pt} (>6 A/cm^2_{MEA} for 0.1 mg_{Pt}/cm^2)
- Transport mechanism under dry condition still unknown.
- Proton accessibility increases with Pt wt.% at lower RH.
  - Likely because of increased condensed water due to changes in pore size and hydrophilicity from increased Pt particle concentration.

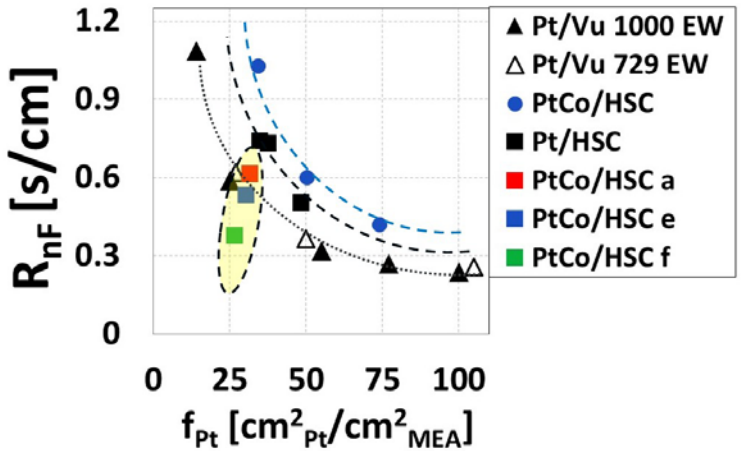
Technical Accomplishment:

Improved O_2 Transport in New Carbons

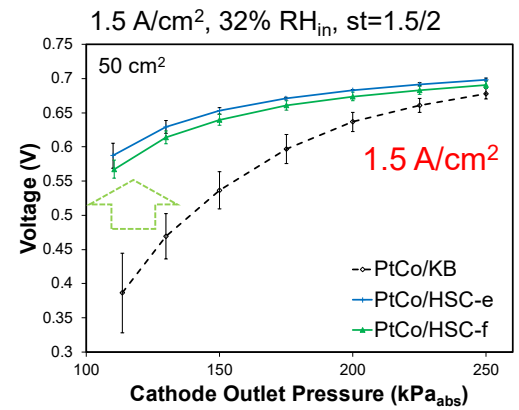
Local Pt Resistance



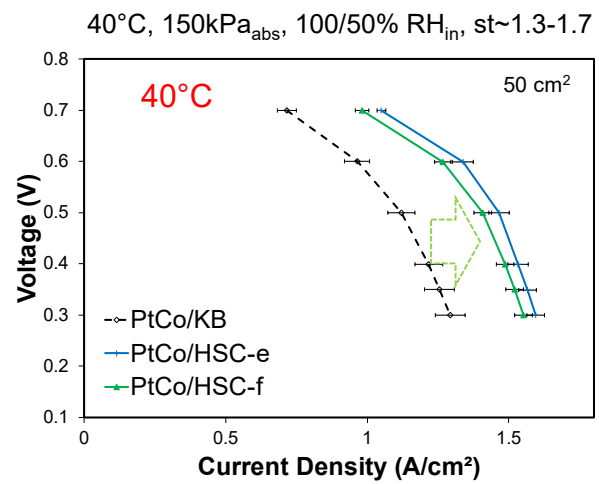
$R_{O2,NF}$ vs Roughness Factor



Pressure Dependence



Low Temperature

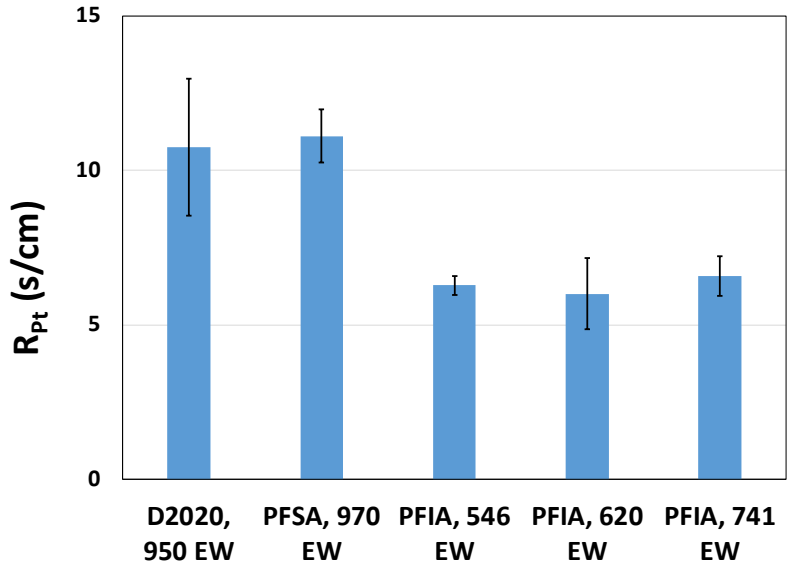


- NREL confirms greatly improved local-O_2 transport with new porous carbons (18→10 s/cm at 75% RH).
- New carbons show less gas-pressure dependency and better low-temperature performance.
  → *characteristics of improved O_2 transport*

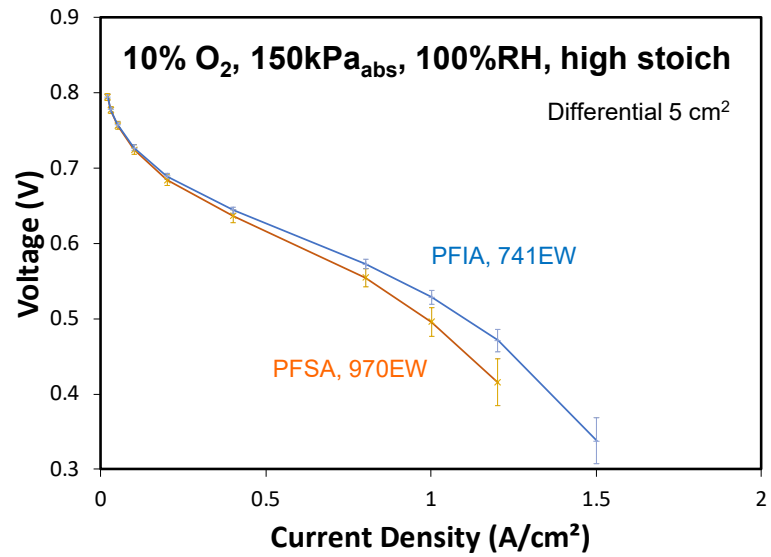
Technical Accomplishment:

PFIA Ionomers

Local Pt Resistance



Low O_2 partial pressure

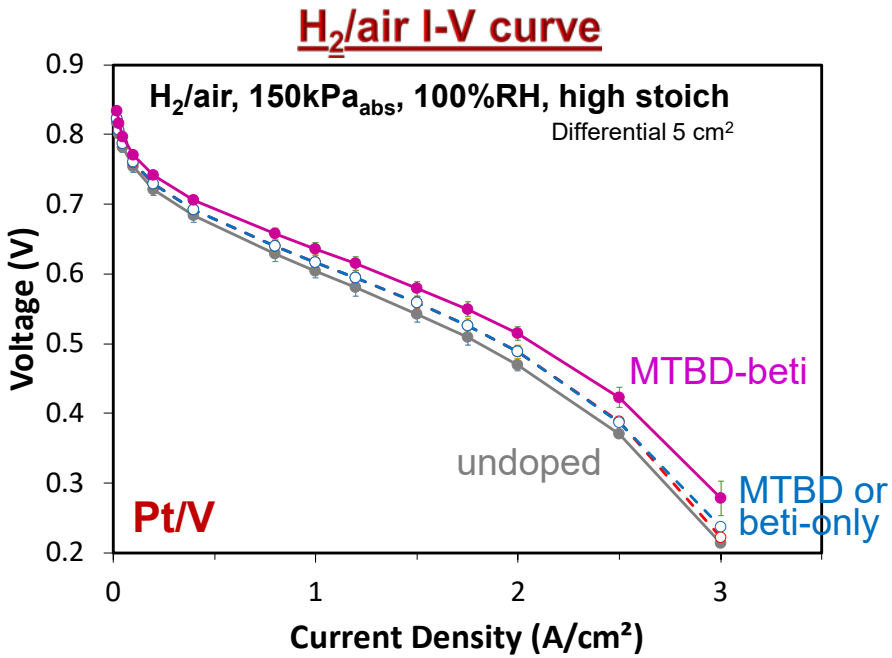


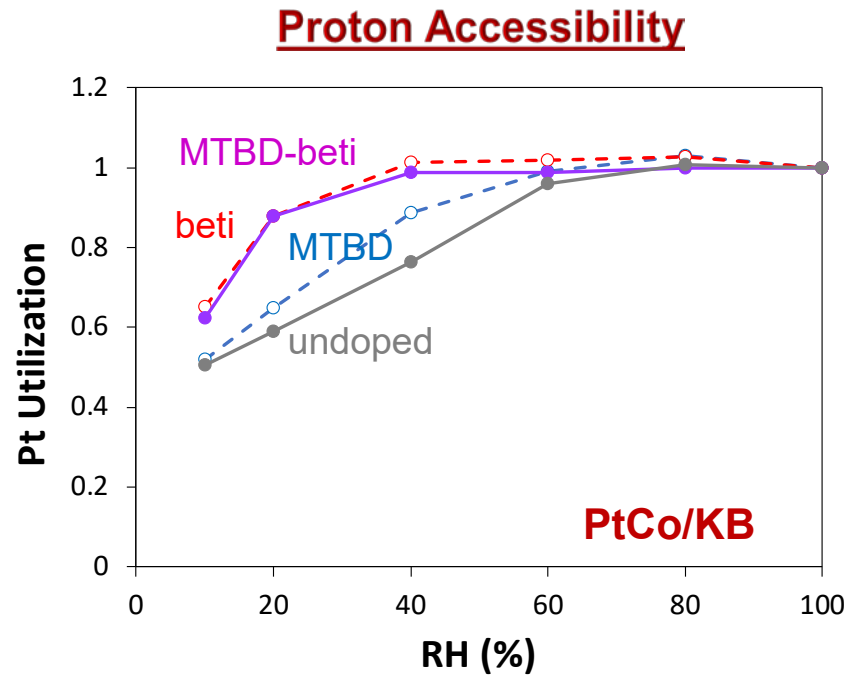
- *Preliminary* 5 cm^2 differential cell testing with 20 wt% Pt/Vu cathodes, 0.06 mgPt/cm^2 loading. I/C ratios were adjusted to give constant ionomer sulfonic acid concentrations
- Limiting current measurement shows lower local-Pt resistance. Preliminary fuel cell testing showed benefit at low O_2 partial pressure.
- Learnings of traditional PFSAs (effects of EW, I/C) shared through FC-PAD projects.

- New advanced 3M ionomers will be evaluated with PtCo candidates in the future.

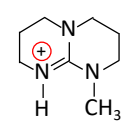
Technical Accomplishment:

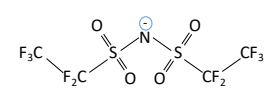
Ionic Liquid Boosts Activity and Proton Access





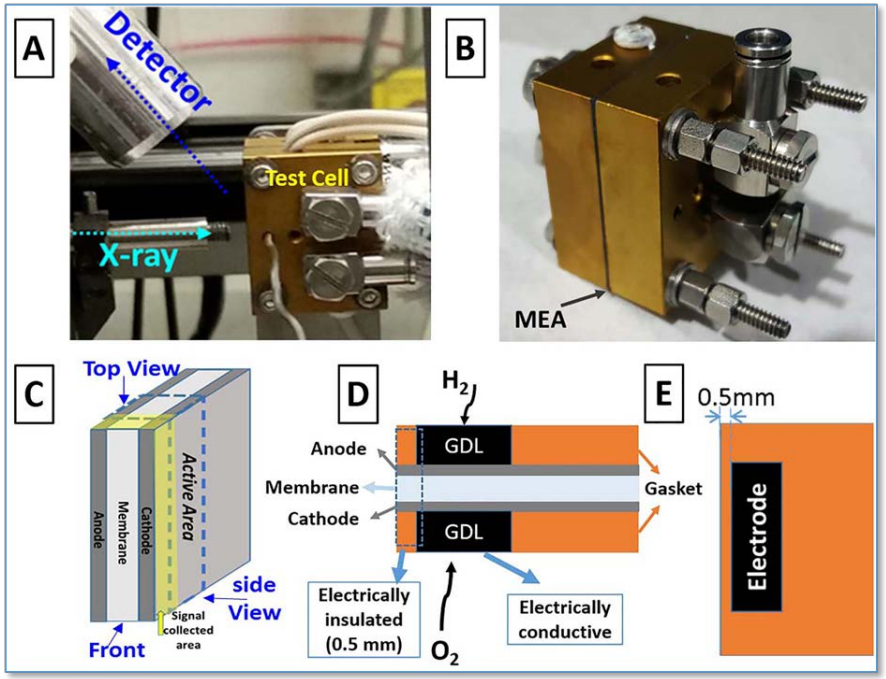
- By adding ionic liquid (IL) to the cathode after electrode coating, successfully confirmed performance benefit in MEA.
- Improvement was confirmed for Pt/V and PtCo/HSC. (up to 20-40 mV at 2.5 A/cm^2)
- Have investigated 10 other combinations of IL, but MTBD-beti is still the best.
- NREL diagnostics confirmed that the improvement is primarily due to *higher ORR activity*.
- On porous carbon, IL also *improves proton accessibility* to internal Pt particles, thanks to its free anions.
- Have not observed loss of benefit after >1 weeks.

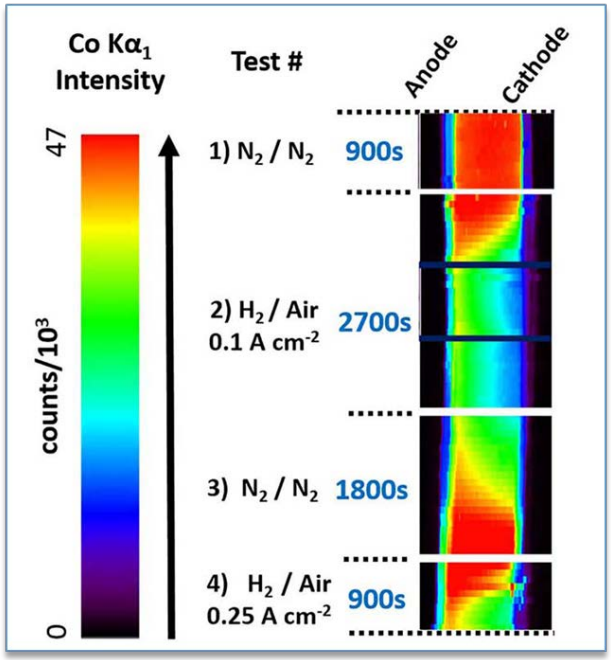

MTBD


beti

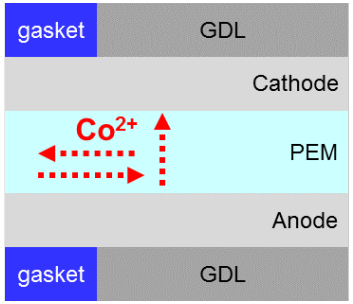
Technical Accomplishment:

Validating Cation Transport Model with *in-situ* μ-XRF





- Understanding loss due to cations in the MEA is required for efficient fuel cell design and operation. Real-time cation transport data are needed to validate model.
- μ-XRF showed sufficient spatial and time resolution to monitor Co^{2+} and Ce^{3+} across the MEA.
- Due to device constraint, only MEA under the inactive area was observable. Transport in the active area will be studied next.



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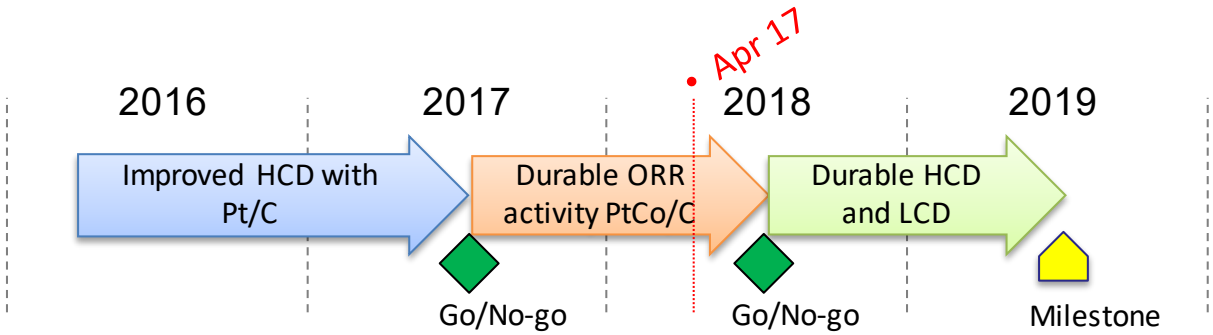
Responses to Last Year AMR Reviewers' Comments

- "Unclear why the project has such a large portion of electrode development"
  - The present **FOA Subtopic 1b.1** (see back-up) clearly states the important of improving high current density MEA performance. Additionally, its **key metrics table** include targets that only obtainable at MEA level. Thus, MEA evaluation is a big role in our catalyst development.
  - Note that, with the exception of ionic liquid addition, ***no MEA integration or electrode development is done***. MEA is only used as a tool to evaluate new materials.
- "Has shown considerable success for HCD without evaluating durability.", "should also be tested for low-temperature performance"
  - Durability is a focus of Year2. Now provided this year.
- "Not clear how the team will get ionic liquid to work in an MEA", "Should quantify IL in electrode", "study its stability in MEA"
  - We now successfully developed a method to add IL and realize its benefit in MEA.
  - Still have no practical method to quantify IL in MEA. Welcome suggestions.
  - Has not observed stability issue after >1 week. Long-term evaluation of IL is not within the SOPO scope.
- "should show that the knowledge/results from parallel approaches can be combined"
  - As noted earlier, it is not required that benefits must be combined in order to achieve the targets. Yet, we've found that some benefits can be combined (e.g., ionic liquid + porous carbon, ordered PtCo + porous carbon).

Future Work

- Implement intermetallic alloy (stability), ionomer, and ionic liquid (activity) with new carbons.
- Evaluate performance and durability of new catalysts using MEA diagnostics, tomography, and modeling.
- Optimize catalyst for both activity & HCD durability.
- Develop and validate cation fundamental performance model.
- End of June 2018 Go/No-go: >0.44 A/mg$_{PGM}$, <40% mass activity loss with preferred design
- Prepare MEAs for DOE validation.



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

Summary

- Clear paths to better activity and durability with promising new materials
  - Ordered intermetallic PtCo showed exceptional stability.
  - Improved ORR activity can be obtained with ionic liquid in MEA
  - Continual improvement in durability of accessible carbons

- Improved understanding of low-PGM electrode
  - Internal pore size (opening) is the key factor for good ORR activity and transport properties.
  - Proton transport in internal pore is sufficient. Local-O_2 transport is a neck.
  - Accessible catalysts degrade more quickly than KetjenBlack, but their absolute performance is still very good.
  - Made progress toward validating understanding of cation performance effect.

This Year: 7 Articles, 24 Talks (6 invited), 2 Patent Applications

Acknowledgements

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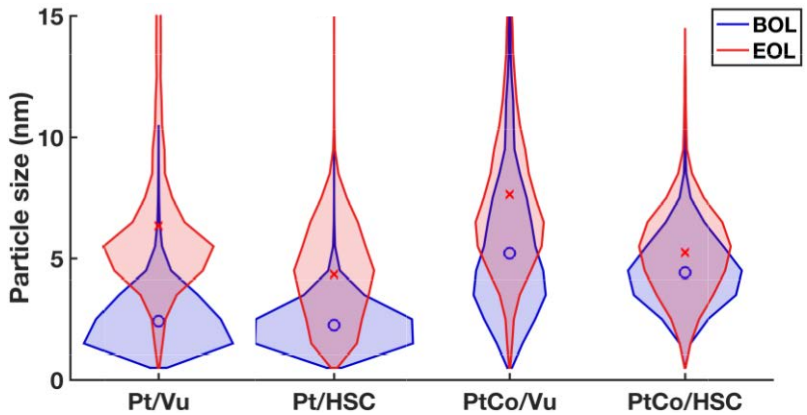
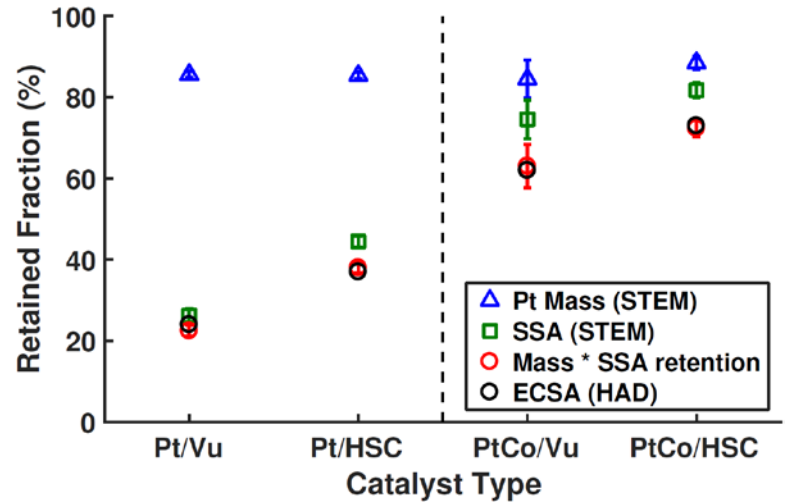
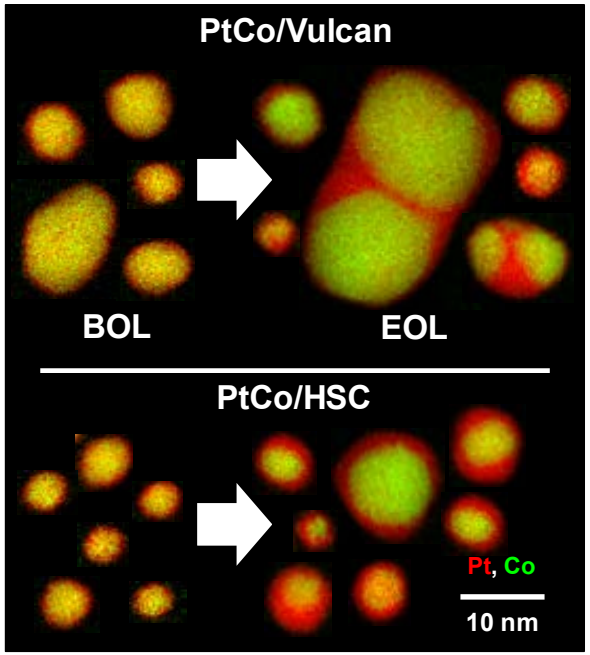
Technical Back-Up Slides

Technical Accomplishment:

Imaging Statistics and EELS Composition Mapping Explain Mechanisms of Catalyst Surface Area Loss



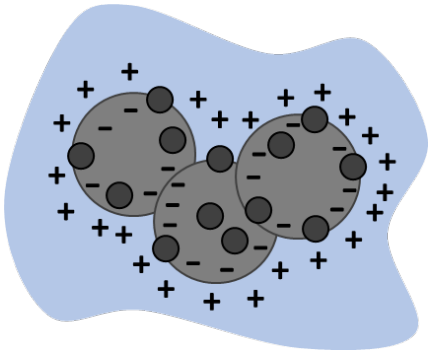




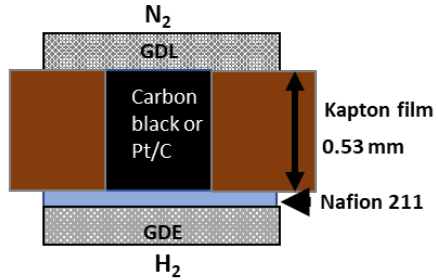
- Vulcan-supported catalysts have more severe coarsening and form large irregular particles by coalescence.
- Coarsening is less severe for HSC-supported catalysts, which maintain smaller particles with roughly spherical morphology, suggesting most coarsening by Ostwald ripening only.
- Pt loss to the membrane combined with catalyst coarsening together explain all ECSA loss.

Ex-Situ Transport Measurements

Evaluating potential dependent surface charge and proton conductivity

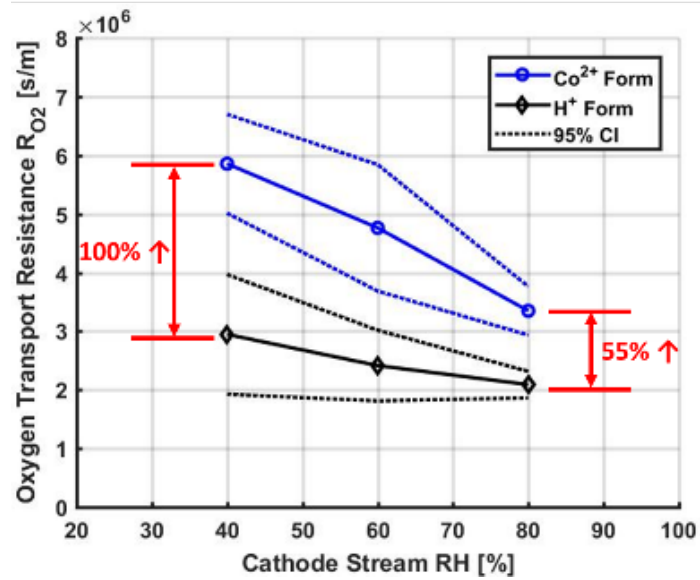


Conductivity measurement cell with cavity electrode

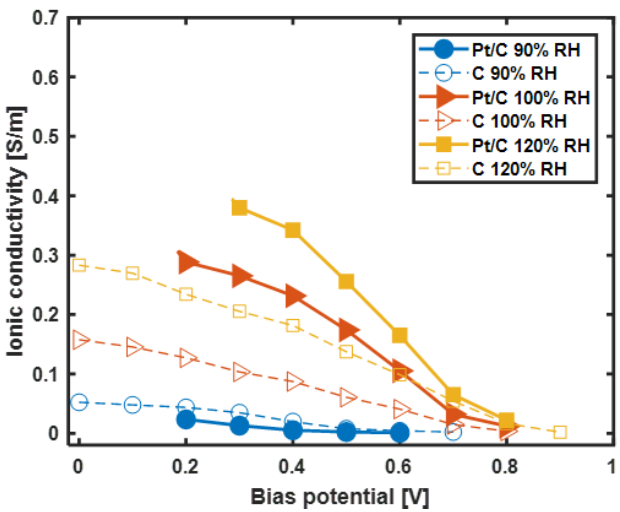


Cell temperature: 65 °C
RH range: 90%~120%

Oxygen transport resistance of cobalt contaminated ionomer membrane



H^+ conductivity of Vulcan carbon black (VCB) and 10 wt% Pt/VCB



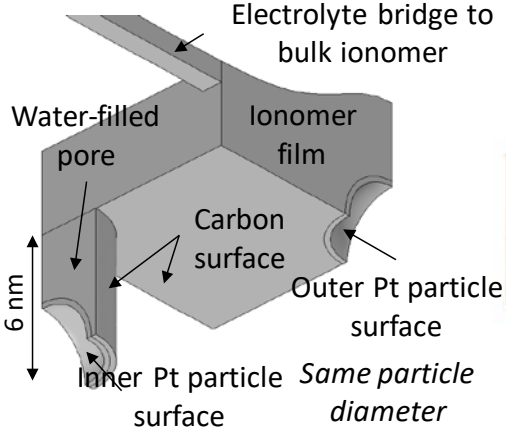
- Carbon support H^+ conductivity strongly potential dependent with low value at ORR potentials
- Strong RH dependence due to proton transport in adsorbed liquid water
- The presence of Co^{2+} cations causes a significant increase in the oxygen transport resistance of PFSA membranes, especially at high cation loading and low membrane water content.
- Consistent with increase in local-Pt resistance measured in Co^{2+}-doped MEAs at GM.

Technical Accomplishment:

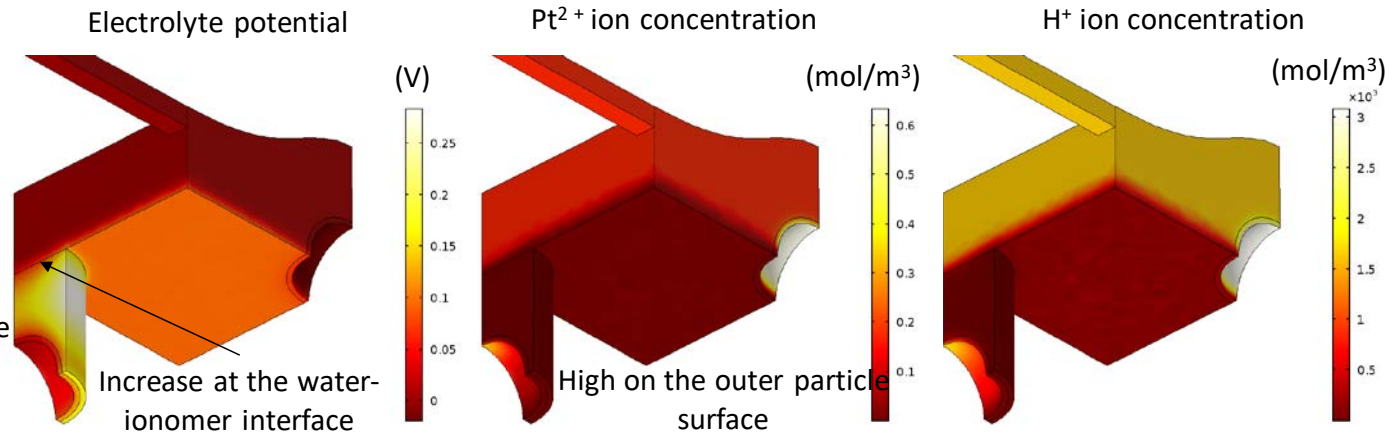
Dissolution of Interior & Exterior Pt

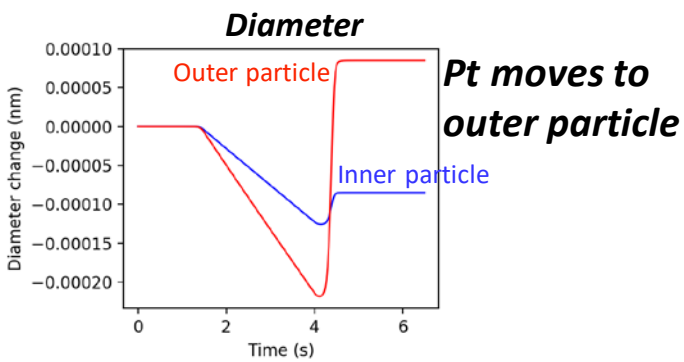
Carnegie Mellon University

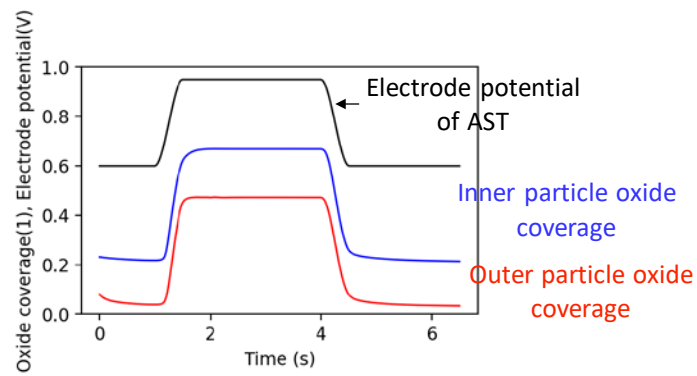
Model geometry



Results at the electrode potential: 0.95 V







- ❑ The outer particle in contact with the ionomer film grows.
- ❑ Because interior particles are generally smaller, this trend is further accelerated on real catalysts.

Subtopic 1b: Catalysts and Supports

Catalysts are key cost components for both transportation and stationary PEM fuel cells and catalyst/support/electrode degradation is often the factor determining fuel cell durability. The focus of this subtopic is novel catalyst and support research that will improve mass activity at high potentials, improve performance at high current density, and improve durability while decreasing cost. Studies of interest will decrease loading of platinum group metals (PGM) in the fuel cell and increase performance and durability. These catalyst studies include research on low PGM loading cathode catalysts for membrane electrode assemblies (MEAs) with total PGM loadings less than the 2020 target of 0.125 mg PGM/cm2 and 0.125 mg PGM/kW. Support studies include novel carbon-based support materials and structures and non-carbon concepts. Applications should show the potential to meet all of the 2020 targets in Table 1 simultaneously.

a. Durability testing consists of 30,000 voltage cycles performed according to Appendix E Table E1.
b. Durability testing consists of 5,000 voltage cycles performed according to Appendix E Table E2.
c. Test at 80°C H_2/O_2 in MEA; fully humidified with total outlet pressure of 150 kPa (abs); anode stoichiometry 2; cathode stoichiometry 9.5

Applications must clearly indicate the status of their proposed technology in terms identified in the metrics table. The metrics table must identify key metrics and targets associated with catalyst performance and durability. The key barriers to meeting these targets must be clearly identified, as well as proposed technology innovations for addressing them.

The application must encompass work up to and including single cell MEA testing at a size of ≥50 cm^2. The work plan should include a discussion of durability testing of sufficient duration to show viability. At a minimum, durability testing should include Accelerated Stress Tests (AST) according to the protocols in Appendix E, Tables E1 and E2.

The deliverable in this subtopic is a set of MEAs (6 or more, each with active area ≥50 cm^2) that is made available for independent testing and evaluation at a DOE-approved location.

Table 1: Technical Targets for Catalysts

	Units	2020 Target
Platinum group metal (PGM) total content (both electrodes)	g/kW	<0.125
PGM total loading (both electrodes)	mg/cm^2	<0.125
Loss in catalytic (mass) activity[a,b]	% loss	<40
Loss in performance at 0.8 A/cm^2 [a]	mV	30
Loss in performance at 1.5 A/cm^2 [b]	mV	30
Mass activity @ 900 $mV_{iR\text{-}free}$[c]	A/mg_{PGM}	0.44

Subtopic 1b.1: Low PGM Cathode Catalysts

FCTO seeks approaches that show the potential to decrease PGM loadings below the 2020 target, while increasing durability, especially in the high power density region. Applicants should clearly state the status of their current catalyst technology and provide sufficient justification that the approach can reduce total PGM content below 0.125 g/kW. Rare or precious metals other than platinum group metals can be part of the strategy, but prices of these materials can increase dramatically with demand; therefore, minimizing loading of rare or precious metals is desired. If other rare or precious metals are included, expected loadings of these materials should also be provided.

Catalyst performance under high power conditions in real operating environments is critical to meeting fuel cell cost targets. Applicants should discuss performance issues at current densities of 1.5 A/cm^2 and above and strategies for overcoming transport and durability issues for performance at high current density. Performance degradation at high current density has been correlated to a loss in electrochemical surface area. Applicants should outline strategies to decrease ECSA losses with potential cycling as well as strategies to deal with other degradation losses their approach may incur, such as decreased ionomer conductivity due to ion exchange of proton conducting sites with leached metal ions.