FC144

Highly-Accessible Catalysts for Durable High-Power Performance

Anusorn Kongkanand (PI)
General Motors, Fuel Cell Activities

June 7, 2017

Overview

Timeline

- Project start date: 1 Apr 2016
- Project end date: 30 Jun 2019
- Percent complete: 12.2%

Budget

- Total Funding Spent as of 2/28/17:
  $0.5M
- Total DOE Project Value:
  $4.59M
- Cost Share: 21.7%

Barriers

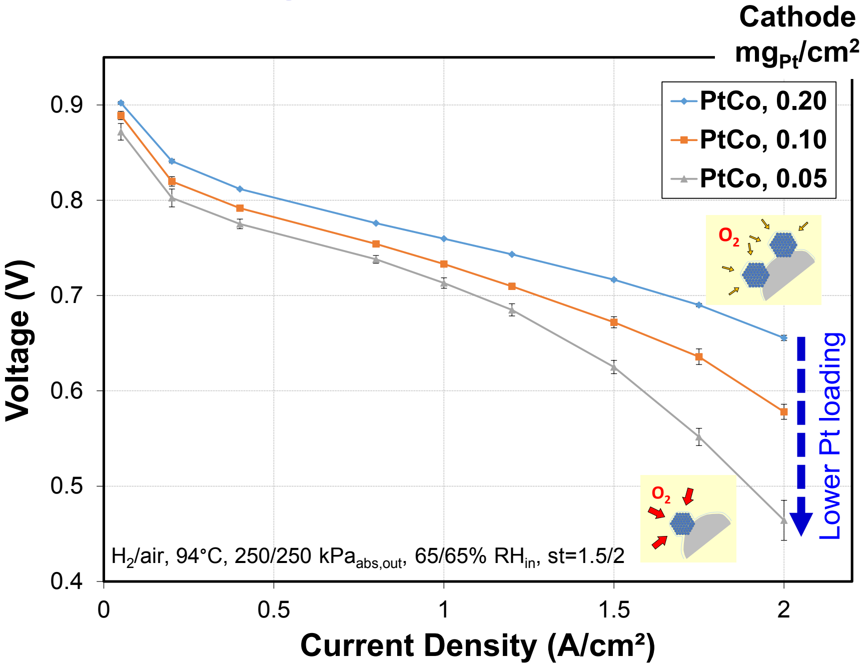
- B. Cost
  - Decrease amount of precious metals.
- A. Durability
  - Improve kinetic activity and high current density performance
- C. Performance
  - Achieve and maintain high current densities at acceptably-high voltages

Partners

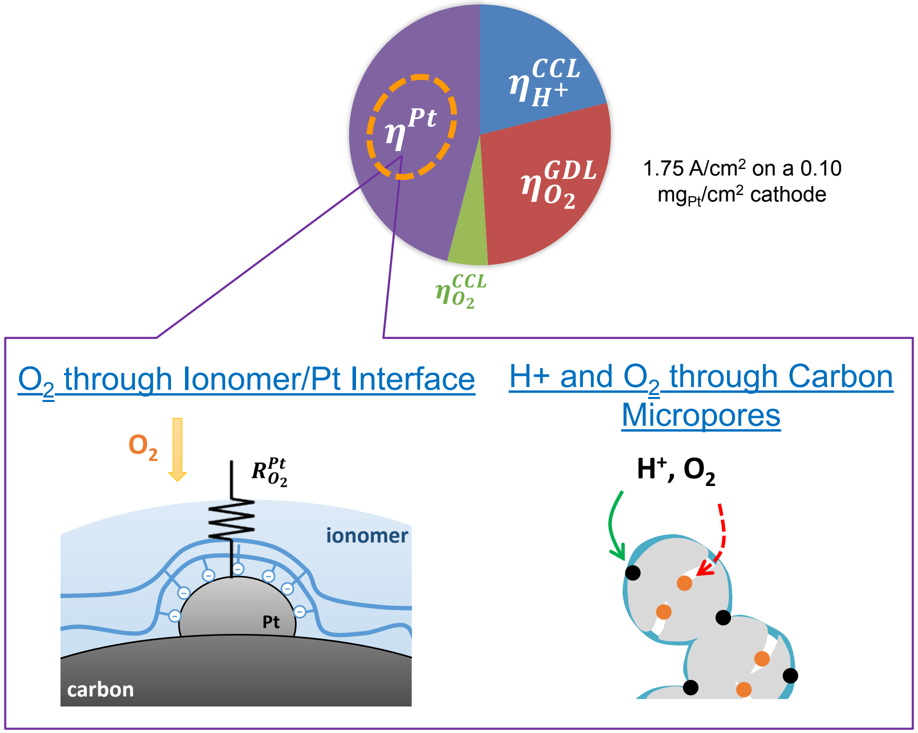
- Subcontractors:
  - 3M Company *Not signed*
  - Carnegie Mellon University *Signed 3/2017*
  - Cornell University *Signed 4/2017*
  - Drexel University *Not signed*
  - NREL *Signed 8/2016*
- Project lead: GM

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

- ❑ FC087 Dealloyed PtCo and PtNi *met Catalyst Targets* ***but not MEA Targets***.
- ❑ Large performance loss at high-current density is observed on low-Pt cathodes due to higher flux of O_2 and proton per a given Pt area.
- ❑ The ‘local transport resistance’ dominates the mass transport related loss (purple) at HCD on low-Pt electrode.
- ❑ 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. (see back-up slide)

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

Relevance:

Targets and Status

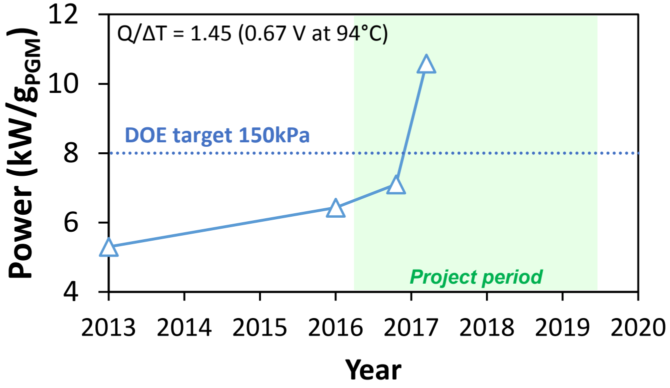
Metric	Units	PtCo/HSC-a 2016	PtCo/HSC-e 2017-1	PtCo/HSC-f 2017-2	DOE 2020 Target	Project Target
PGM total loading (both electrodes)	mg/cm^2	0.125	0.125	0.088	<0.125	←
Mass activity @ 900 mV$_{iR\text{-}free}$	A/mg$_{PGM}$	0.6-0.7	0.6	0.7	>0.44	←
Loss in catalytic (mass) activity	% loss	0-40%	40%	TBD	<40%	←
Performance at 0.8V (150kPa, 80°C)	A/cm^2	0.304	0.306	**0.382**	>0.3	←
Power at rated power (150kPa, 94°C)	W/cm^2	0.80	0.89	0.93	>1.0	-
Power at rated power (250kPa, 94°C)	W/cm^2	1.01	**1.19**	**1.26**	-	>1.1
PGM utilization (150kPa, 94°C)	kW/g$_{PGM}$	6.4	7.1	**10.6**	>8	←
PGM utilization (250kPa, 94°C)	kW/g$_{PGM}$	8.1	**9.5**	**14.3**	-	>9.1
Catalyst cycling (0.6-1.0V, 30k cycles)	mV loss at 0.8A/cm^2	30	20	TBD	<30	←
Support cycling (1.0-1.5V, 5k cycles)	mV loss at 1.5A/cm^2	>500	>500	TBD	<30	-

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

Objectives

- ❑ Reduce overall stack cost (not only catalyst cost) by improving high-current-density (HCD) performance adequate to meet DOE heat rejection (>0.67 V at 94°C) and Pt-loading targets.
- ❑ Maintain high kinetic mass activities.
- ❑ Mitigate catalyst HCD degradation.

This Year Highlights



- ❑ ***2.2x kW/g$_{PGM}$*** *vs pre*project by reducing resistance in micropores.

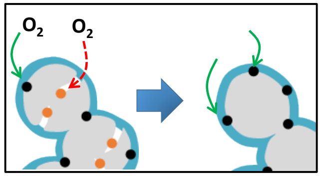
Approach:

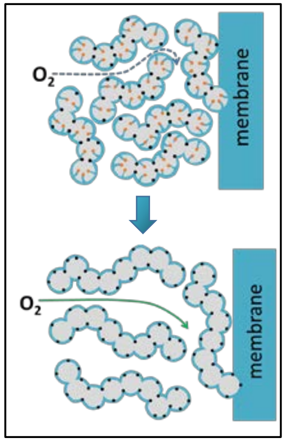
Basic Approaches: *Will Succeed if At Least One Works*

☐ Improve O_2 Transport with New Carbon Support

- Use low-loaded-electrode (<0.06 mg_{Pt}/cm^2) differential cells to study local properties. Validate performance in 50 cm^2.
- Study support effects on kinetic, transport, durability.
- Explore new carbon supports, develop platinization strategy for each carbon, modify support to provide better PSD or transport.

GM/CMU/ Cornell/NREL

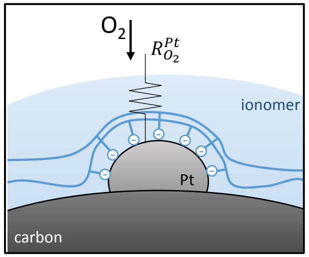




☐ Reduce Electrolyte-Pt Interaction

- Screen from current selection of ionomer/ionic liquid.
- Use electrochemical diagnostics to study Pt-ionomer interface change over time in MEA.

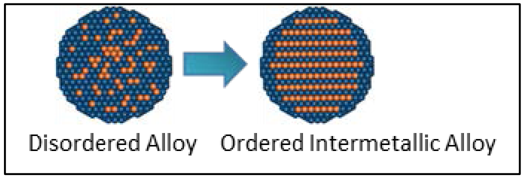
3M/Drexel/GM



☐ Enhance Dispersion and Stability of PtCo Particles

- Enhance activity and stability with more ordered structure.
- Improve Pt surface area with better PSD.

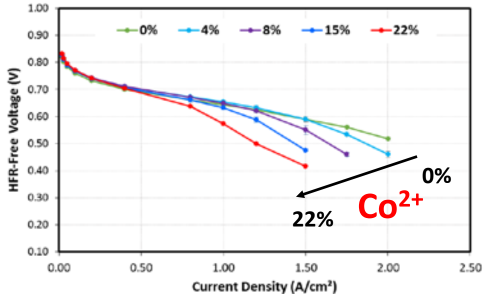
Cornell/GM/NREL



☐ Understand and Better Control Leached Co^{2+}

- Study MEA with known amount of Co^{2+}. Develop semi-empirical model
- Provide guideline for tolerable amount of Co and for operating conditions.
- Use nano-mesostructured model to eliminate gap in understanding.

GM/CMU



PSD: particle size distribution

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 $Q/\Delta T$ <1.7 with Pt/C ✓

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

TASK 2 - Development of Dealloyed Catalyst with Preferred Catalyst Design

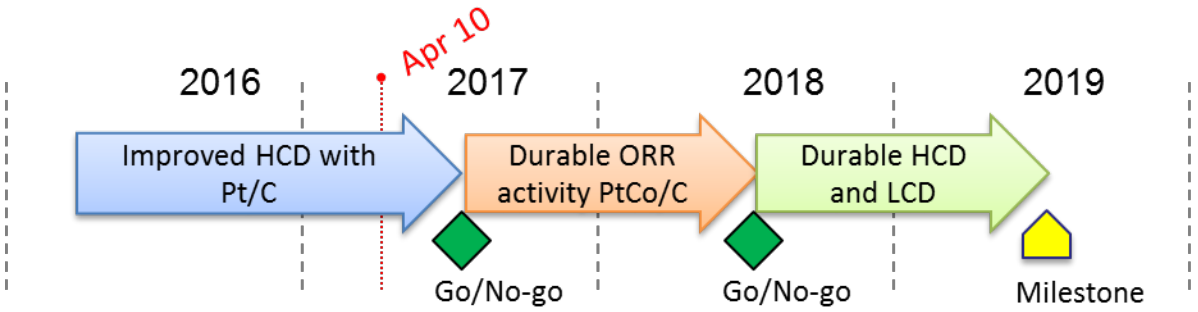
Go/No-go criteria : >0.44 A/mg_{PGM}, <40% mass activity loss with preferred design ✓

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

TASK 3 - Optimization for Durable HCD and LCD Performance

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

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



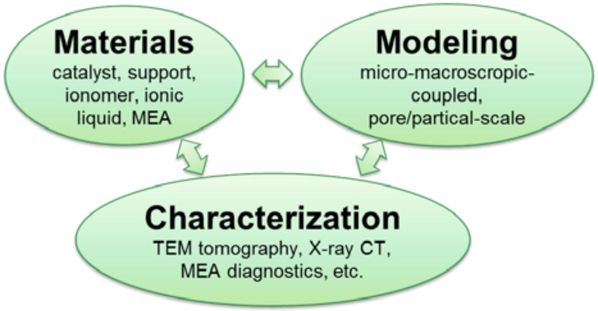
Collaborations:

Project Team

- ☐ General Motors (industry)
  - Overall project guidance, synthesis and testing of catalysts.
- ☐ 3M Company (industry) – **Dr. Andrew Haug** *Not signed*
  - Selection and pre-fuel-cell evaluation of ionomer candidates.
- ☐ Drexel University (university) – **Prof. Joshua Snyder** *Not signed*
  - Selection and pre-fuel-cell evaluation of ionic liquid candidates. Incorporation strategy of IL into MEA.
- ☐ Cornell University (university) – **Prof. David Muller** and **Prof. Héctor Abruña**
  - TEM and tomography. *Signed 4/2017*
  - Synthesis of intermetallic alloys.
- ☐ Carnegie Mellon University (university) – **Prof. Shawn Litster** *Signed 3/2017*
  - Modeling and X-ray tomography.
- ☐ National Renewable Energy Lab (federal) – **Dr. K.C. Neyerlin** *Signed 8/2016*
  - Support N-doping, MEA fabrication and diagnostics.

Non-funded Partners

- ☐ 6 catalyst suppliers (industry)
  - Provide benchmark and experimental samples. Idea exchange.
- ☐ Argonne National Lab (federal) – **Drs. Ross Andrews, Nancy Kariuki, Debbie Myers**
  - SAXS measurement at APS (beamline 9ID), Contract No. DE-AC02-06CH11357.



Materials
catalyst, support, ionomer, ionic liquid, MEA

Modeling
micro-macroscropic-coupled, pore/partical-scale

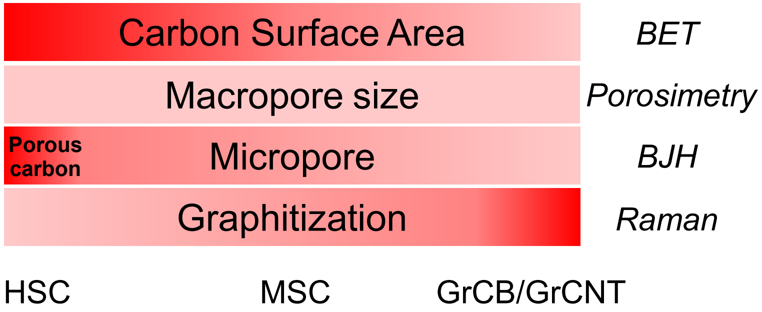
Characterization
TEM tomography, X-ray CT, MEA diagnostics, etc.

Responses to Last Year AMR Reviewers' Comments

- "catalyst development should be stressed, not just its integration and electrode layer performance", "does not seem appropriate for a catalysis development project"
  - First, note that the project is under "Catalysts and Electrodes" section. Therefore, it should be no surprise that there is a significant level of electrode evaluation. DOE and the community realize it is the electrode performance that matters after all. Additionally, ***Catalyst Targets* had been met but *Electrode Targets* had not**. That being said it can be seen in this update that there is a significant catalyst-level work, as every new carbon support requires a different approach in making a good catalyst.
- "hard to see what the new development is" "new materials and diagnostics"
  - Please see Summary for key achievements.
- "needs to … resolve the issues of stability of Co" "how to optimize the physicochemical properties of nanoparticles for activity and stability"
  - Although we cannot entirely prevent cobalt from dissolving, this year we studied the Pt and Co dissolution and deposition rate, and the impact of cobalt on performance. They will help us more intelligently design and operate the fuel cell.
- "stability of ionic liquid is unclear"
  - This remains an issue of interest and we will address this in near future. We should also note that the project achievement does not rely on a successful implementation of ionic liquid alone.
- "a catalyst manufacturer should be included in the initial stage of the project"
  - Indeed, OEM privilege allows us to involve several catalyst suppliers (non-funded) while protecting their confidentiality.

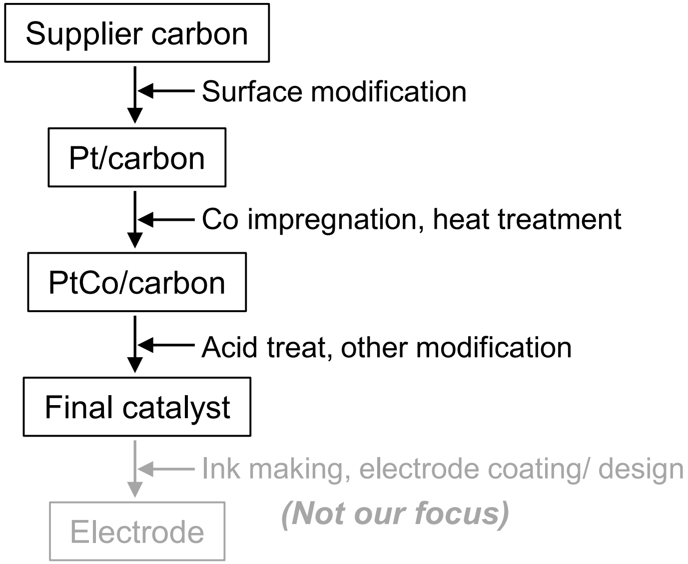
Technical Accomplishment:

Carbon Support Development: Methodology



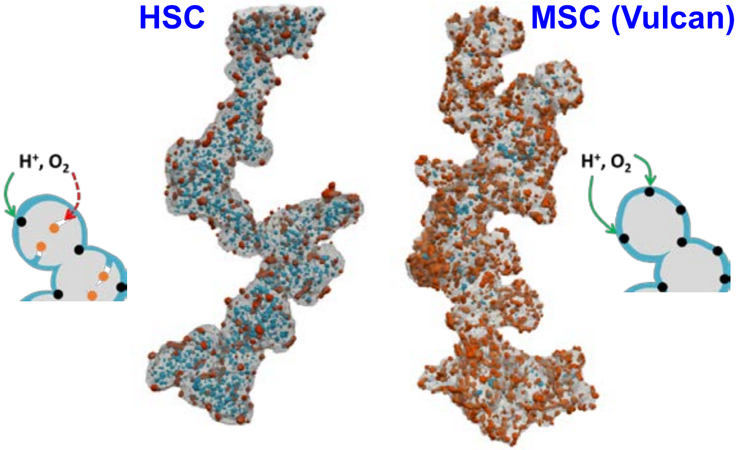
Ketjen, Acetylene, Vulcan, Graphitized CB, CNT, Graphene, Engineered carbon, Mesoporous carbon, etc.

Development Flow



Porous carbon
HSC

Solid carbon
MSC (Vulcan)



✓ High Pt dispersion
✓ High ORR activity
✓ Easy to make good alloy

✓ Good O_2/proton transport
✓ Better stability

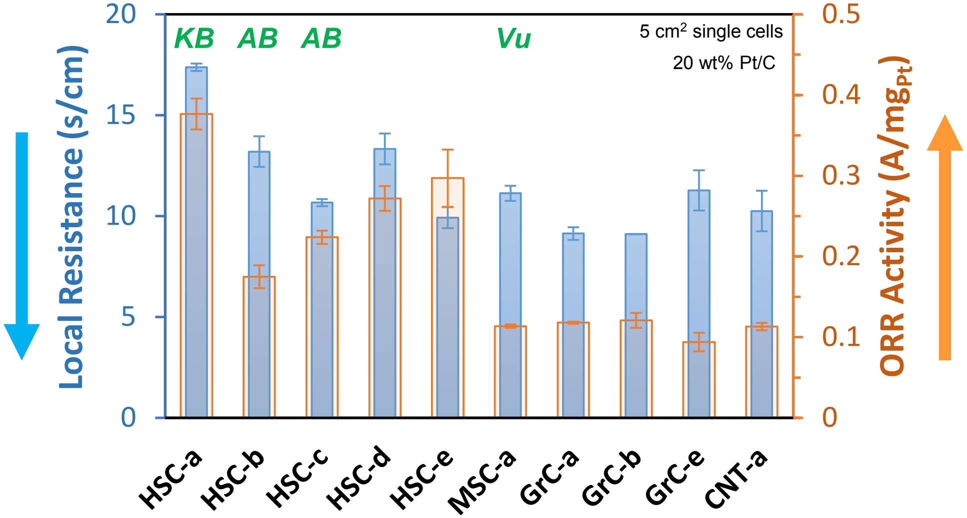
- ❑ Attempt to find carbon with good balance of high surface area, porosity, and graphitization.
- ❑ Porous vs solid carbon is one focus.
- ❑ For every carbon type, adjustments of procedure must be made. No one fits all.
- ❑ Collaborate with support and catalyst suppliers at several stages.

Technical Accomplishment:

Carbon Support Development: Pt/C

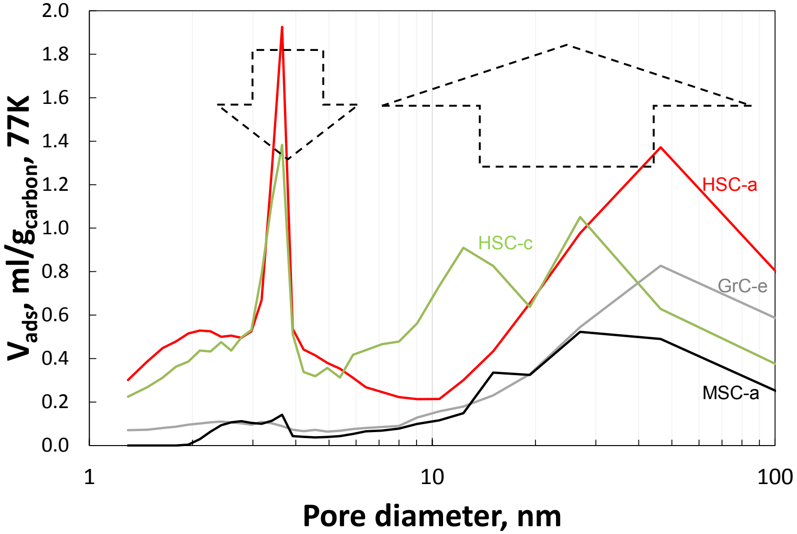
Local O_2 resistance and ORR Activity

MEA differential cell tests of Pt supported on different carbons



Pore Size Distribution of Carbon Powder

BET-BJH



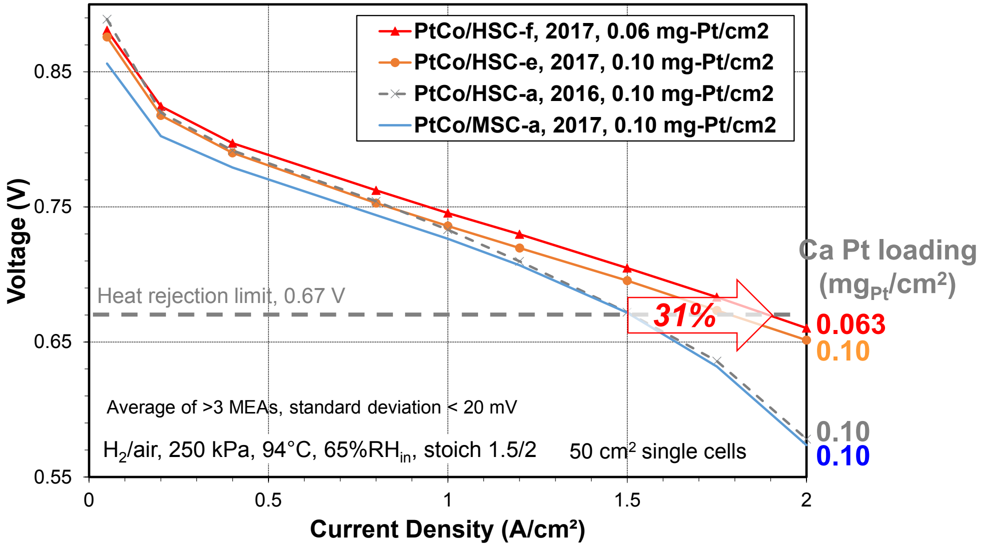
- ❑ Differential cell tests for 'local O_2 resistance' and 'ORR mass activity' have shown to be reliable predictors for MEA performance.
- ❑ Porosity measurement on 'final electrode' does not give good correlation with MEA performance.
- ❑ Rather, the pore size distribution on carbon or catalyst powder gives better correlation. Want less micropores (<4 nm) and more mesopores (>5-50 nm), confirming resistance *local to Pt* particles.
- ❑ ORR activity drops 3-fold if all small pores are removed. Likely because of ionomer poisoning effect. *Unless Ionomer-Pt interaction is solved, may not want an all solid carbon. Want small pores but with good accessibility*.

See back-up slides for more details on carbon characterization

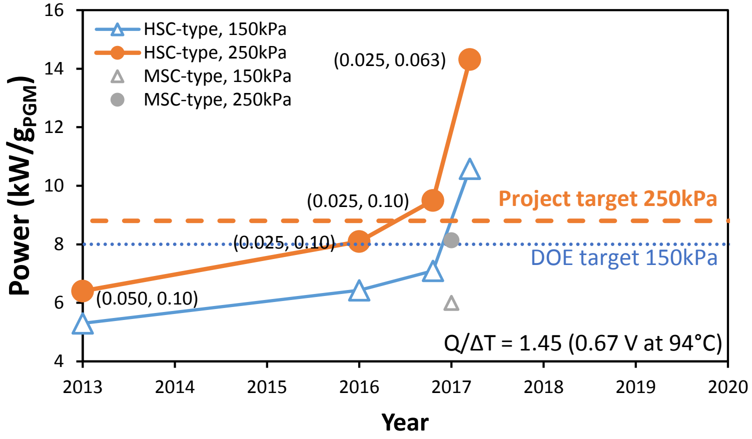
Technical Accomplishment:

New PtCo/HSC Surpassed High-Power Targets

31% Increase in Power over Baseline PtCo

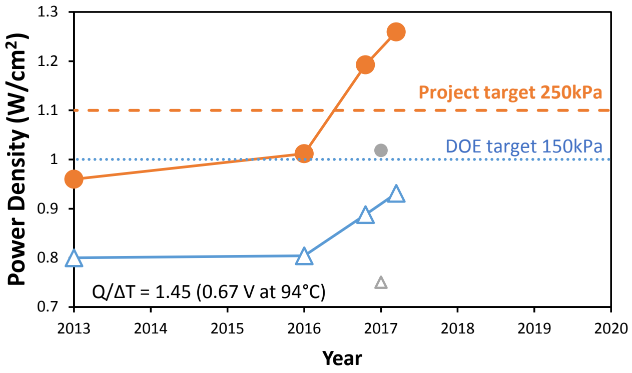


124% Increase in PGM Utilization over pre-project



- Large improvement at high current density (HCD) with new HSC, thanks to more accessible pores, hence lower local transport resistance.
- **Surpassed DOE kW/g_{PGM} target by a large margin (10.6 vs 8).**
- Sent to NREL for validation.
- Approaching Power Density 150kPa target, but to achieve this, need advancement in other areas: *ORR activity, GDL/plate O_2 transport, and membrane resistance*. Electrode transport alone not enough.
- Solid carbon performance (gray symbols on right plots) suffers from lower ORR activity and alloy quality, consistent with Pt/C results.

31% Increase in Power Density



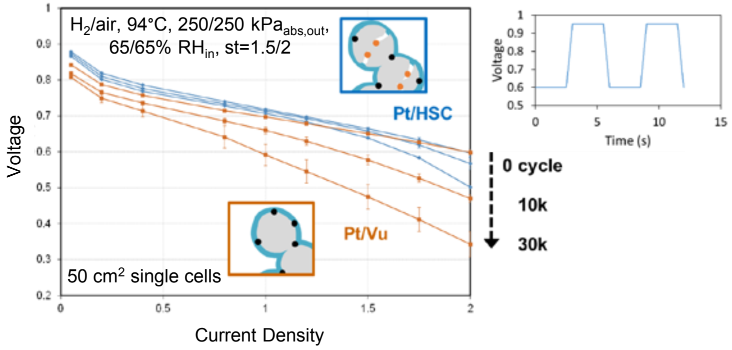
Gray symbols: best PtCo/Solid carbon

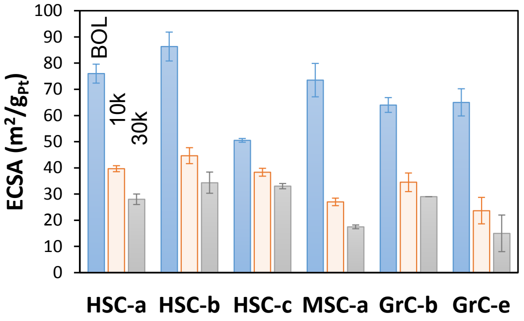
Technical Accomplishment:

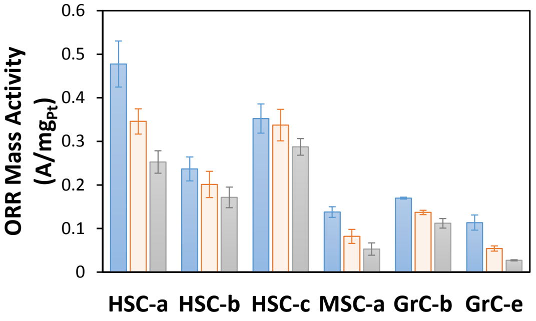
Accelerated Stability Tests on Pt

Catalyst AST

Representing *normal* operation (0.60-0.95 V, 6 s/cycle, 30,000 cycles)

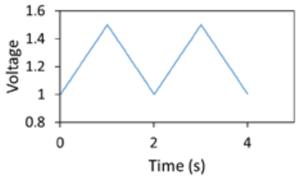


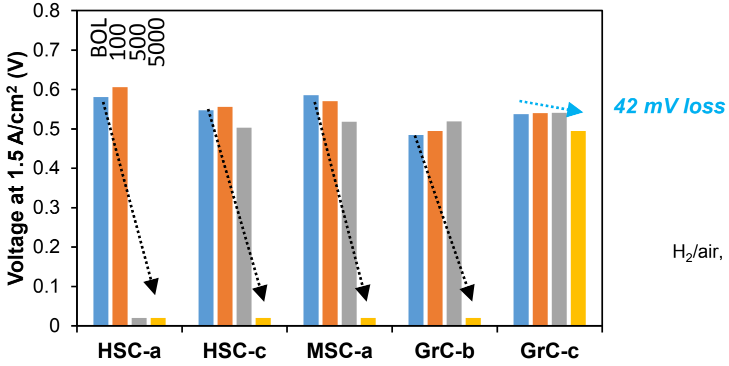




Support AST

Representing *lots of very unusual* operation (1.0-1.5 V, 0.5 V/s, 5,000 cycles)





50 cm^2 single cells

H$_2$/air, 80°C, 150 kPa$_{abs,out}$, 40% RH$_{in}$, st=1.5/1.8

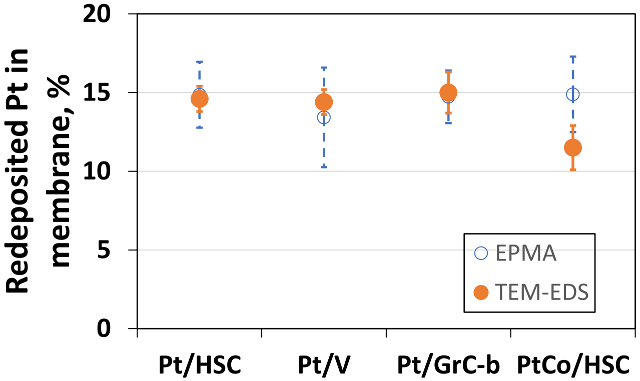
- HSC shows better initial ECSA, ORR activity, and fuel cell performance.
- In Catalyst-AST, retention of ORR activity and fuel cell performance were better for HSC. Similar trend with PtCo.
- In Support-AST, most carbons failed miserably. HSC degraded the fastest. GrC-e surprisingly held up close to target (42 vs <30 mV loss target), however, it performed poorly under Catalyst-AST.

Technical Accomplishment:

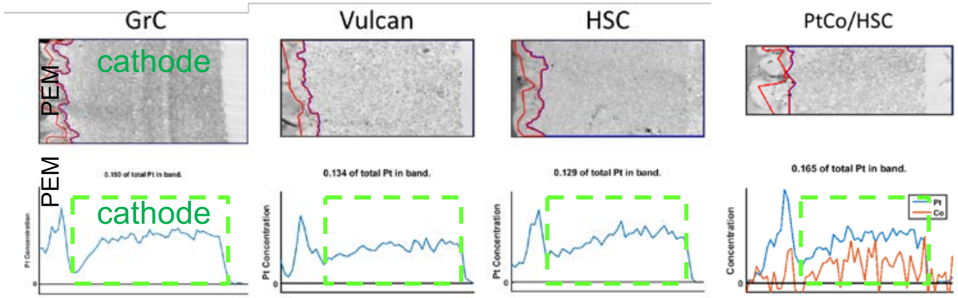
Postmortem Analyses

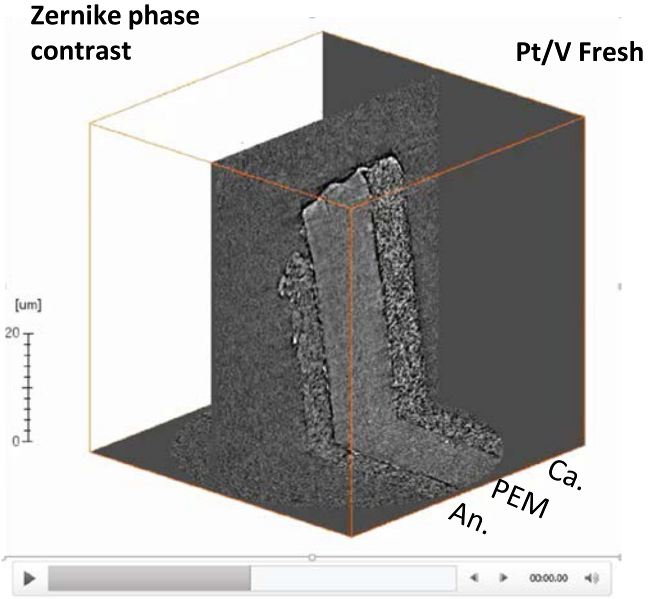
TEM *X-CT* *SAXS* *EPMA ICP*

Pt Band by TEM and EPMA

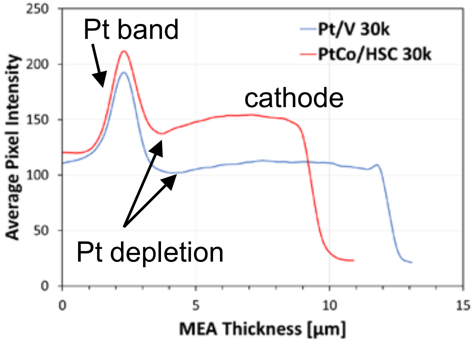


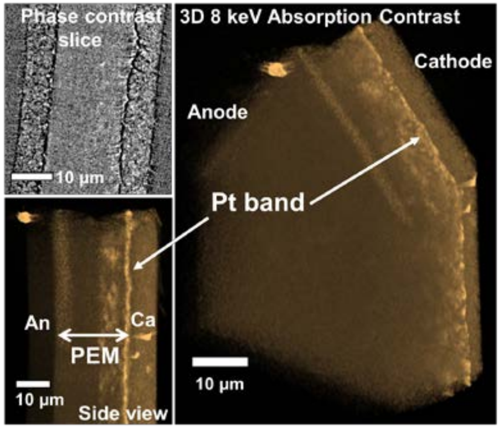
Pt and Co Depletion in Cathode by TEM





Pt Depletion in Cathode by X-CT



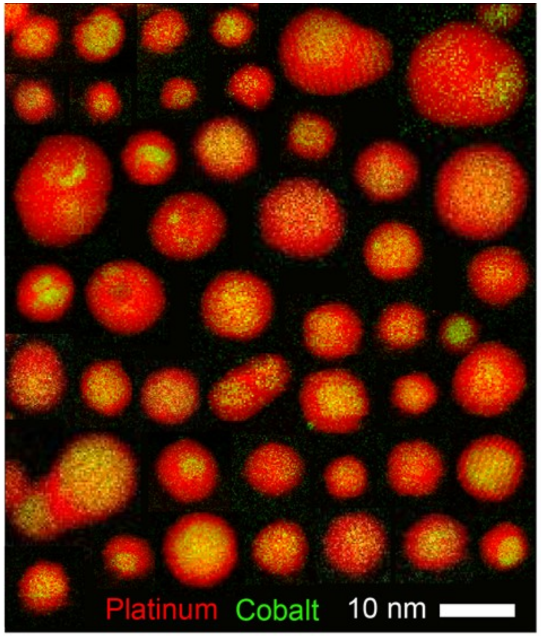


- ❑ Carbon type has *negligible* effect on how Pt degrades at a *macroscopic scale*. Expected as Pt dissolution and migration dominate, not coalescence.
- ❑ Will be using these data to refine degradation model.

Technical Accomplishment:

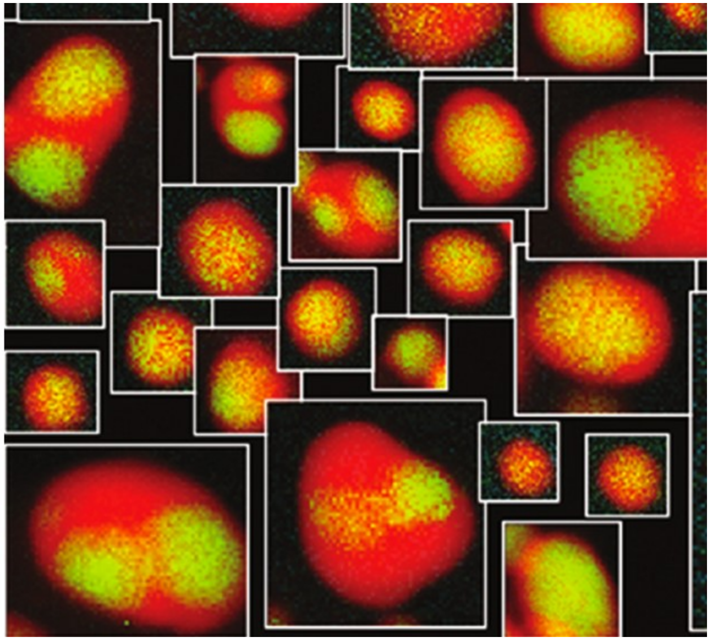
PtCo Particles Coalesced Less on HSC Support

PtCo/HSC after AST



This work

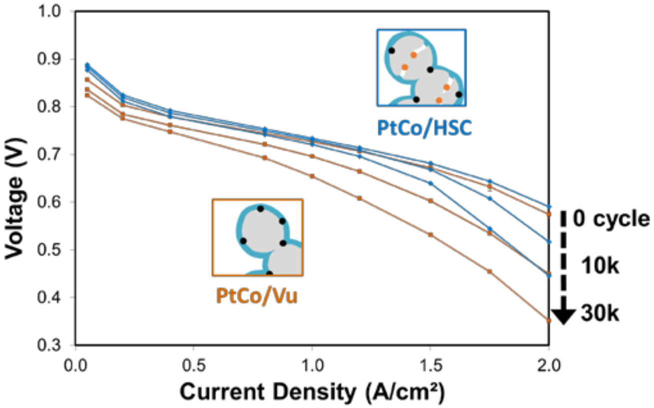
PtCo/Vu after AST



Xin et al. Nano Lett. (2012), 490.

27% vs 39% drop in ECSA

45→33 vs 33→20 m^2/g_{Pt}

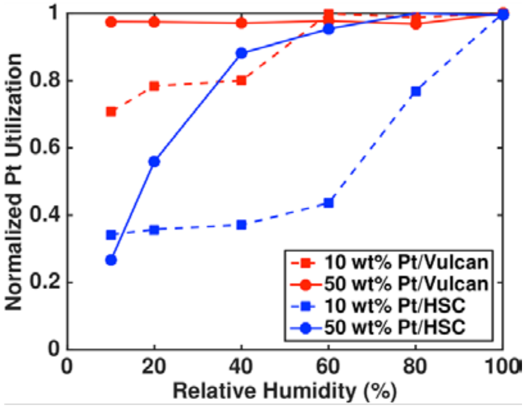


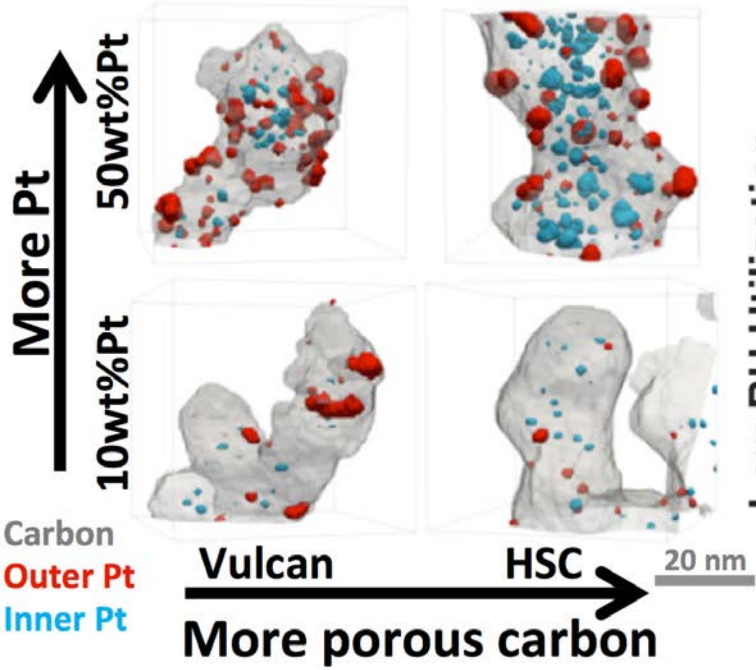
- ❑ Pt losses at the macroscopic level (formation of Pt band, changes in Pt amount across the electrode thickness) are similar among different carbon supports.
- ❑ However, at microscopic level, EELS composition maps show that coalesced (multi-core) PtCo particles appear rarely on HSC carbon support compared to Vulcan carbon support.
- ❑ The high surface area and confining pores of HSC appear to suppress particle coalescence.
- ❑ Agrees with electrochemical results.
  - ➢ *May not want an all solid carbon. Want small pores but with good accessibility*.

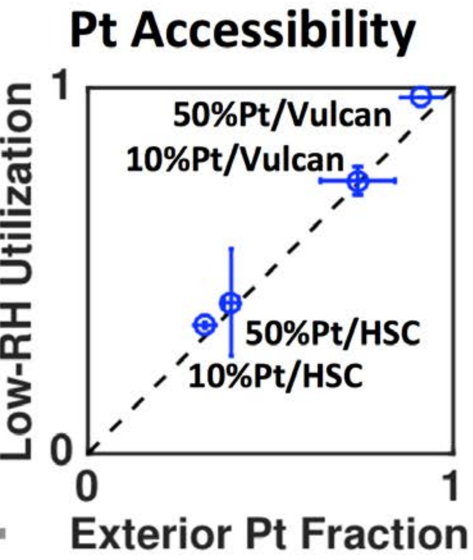
Technical Accomplishment:

New Capability: Quantify Inside & Outside Pt Particles

CO Stripping in MEA







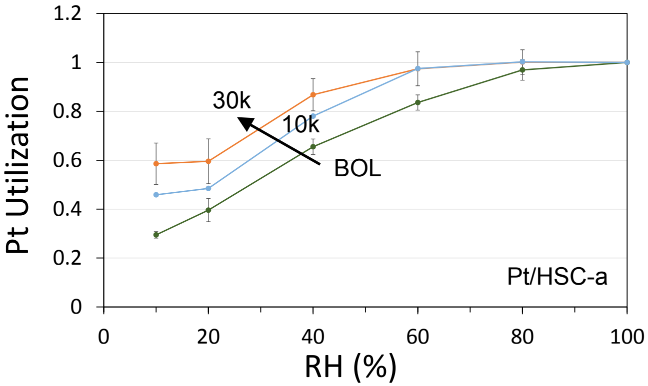
- ❑ CO stripping in MEA was found to give a good correlation with cryo-STEM results for determining the location of Pt (inside and outside of carbon particles)
- ❑ This can become a simple routine measurement for every MEA sample.

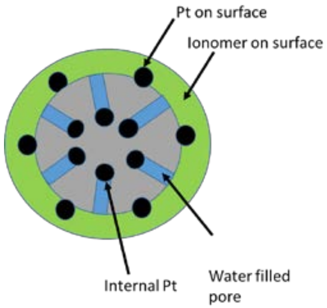
Padgett et al. (2017) submitted.

Technical Accomplishment:

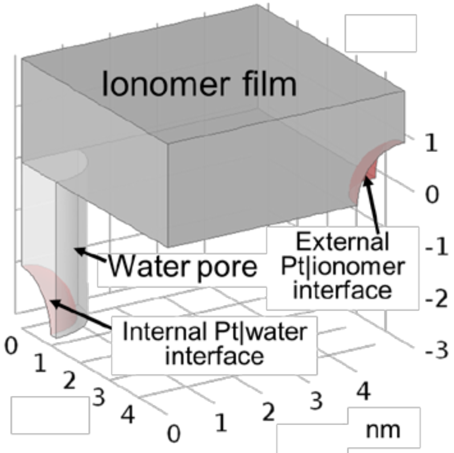
Pt Location as HSC Catalyst Ages

Electrochemical Pt Utilization

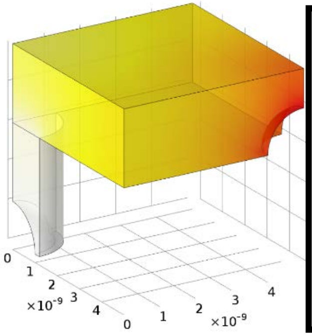




Local Catalyst Site



Pt^{2+} concentration



Transport and surface reactions

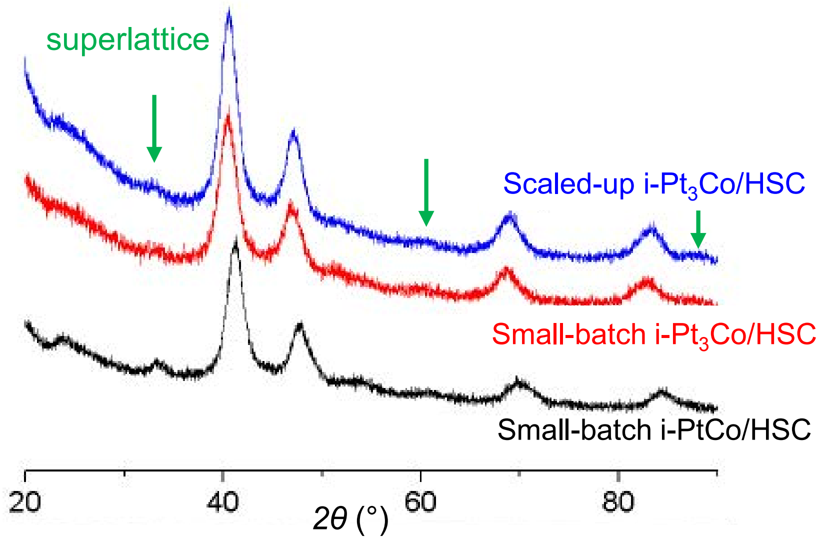
- *Oxide coverage & oxygen reduction*
- *H^+ & O_2 transport*
- *Pt & Co dissolution and transport*
- *Pt redeposition*

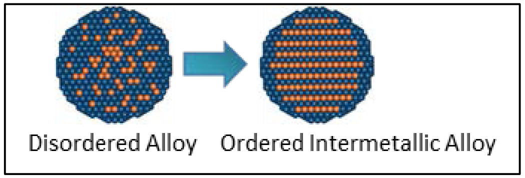
- Pt utilization appears to improve after AST for Pt and PtCo on HSCs, suggesting increase in the fraction of outer Pt particles.
- Being studied by TEM tomography (Cornell) and modeling (CMU).
- Preliminary simulation at CMU suggests the confined morphology of pore filled water and ionomer may play a role as well as the difference in particle size distribution of outer vs inner particles.

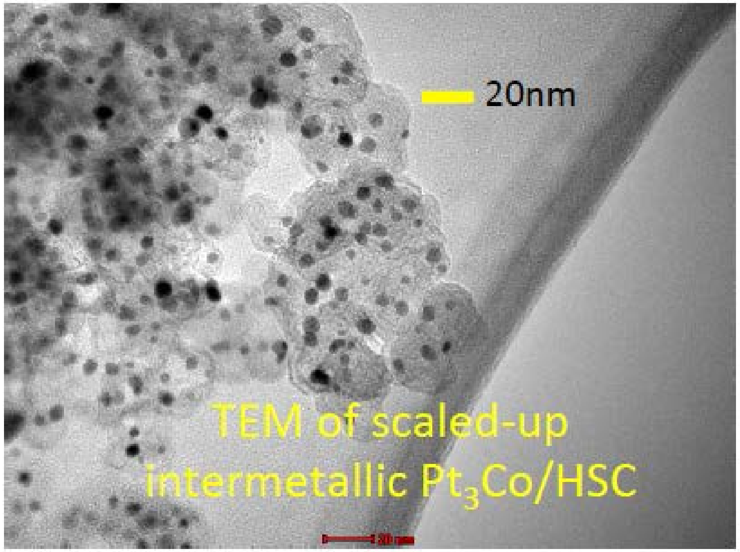
Technical Accomplishment:

Improving ECSA and Stability with Intermetallic PtCo

XRD of intermetallic Pt_3Co and PtCo





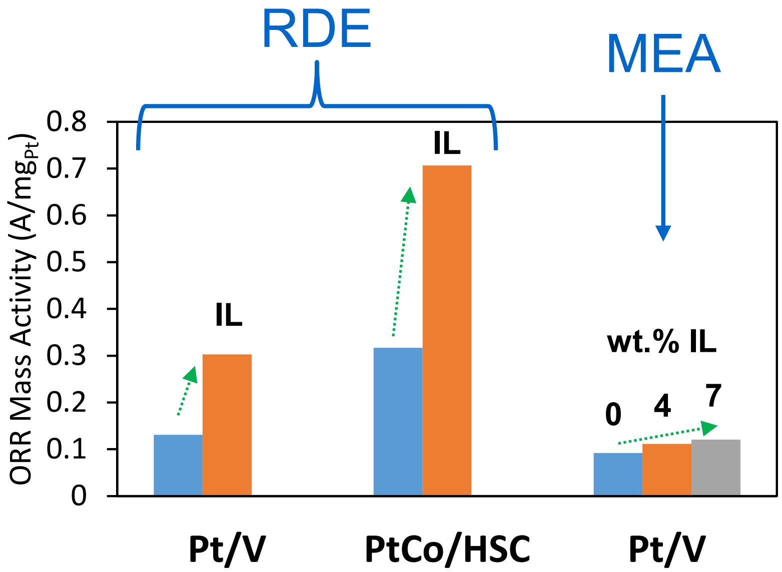


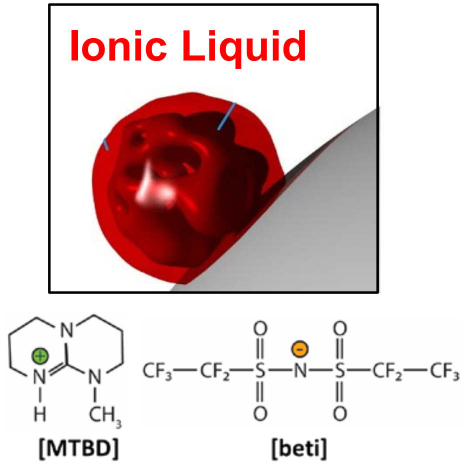
TEM of scaled-up intermetallic Pt_3Co/HSC

- ❑ RDE mass activity of 0.65 A/mg_{Pt} for intermetallic-Pt_3Co/HSC.
- ❑ Developed procedure for scale up. Achieved equivalent ordered crystalline quality and RDE activity in scaled up samples.
- ❑ Developed chloride-free catalyst and scaled up to 3 grams. To be tested in MEA at GM as soon as contract is signed.

Technical Accomplishment:

Ionic Liquid Boosts ORR Activity



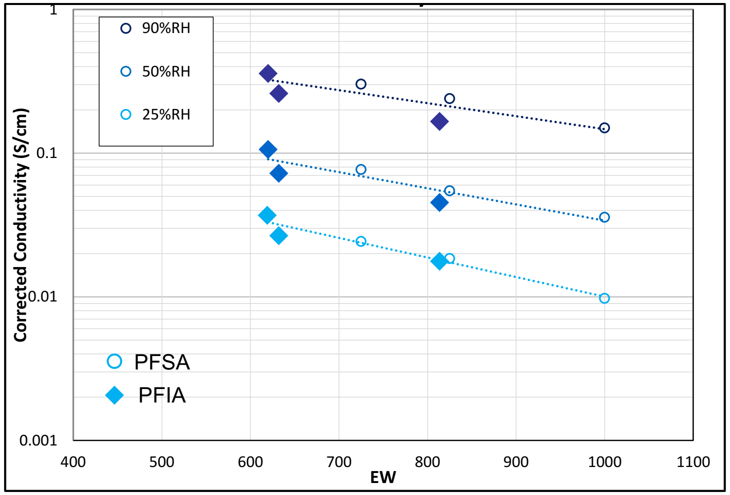


- ❑ Confirmed ORR activity boost with preferred PtCo/HSC catalyst in RDE.
- ❑ Scaled up IL-composite catalyst synthesis to >1 gram batch size.
- ❑ So far, in MEA observed 1.3x improvement in ORR activity with 7 wt% IL, smaller than RDE (2-3x). MEA may require much higher IL loading than RDE.
- ❑ Next
  - ➢ Develop method to quantify IL in electrode.
  - ➢ Optimize IL loading, implement on PtCo, investigate the operating condition sensitivity and electrode stability.
  - ➢ Qualification of different IL chemistries including aprotic formulations and assessment of their half-cell ORR activity.

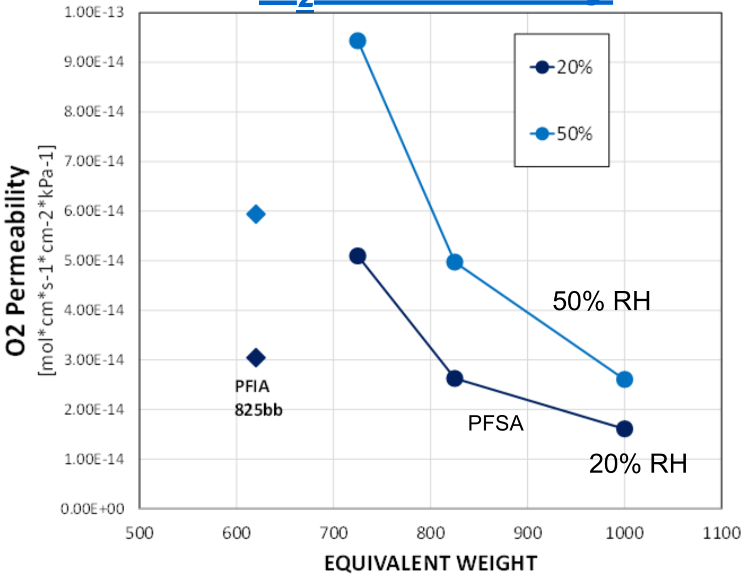
Technical Accomplishment:

Ionomer Screening

Proton Conductivity



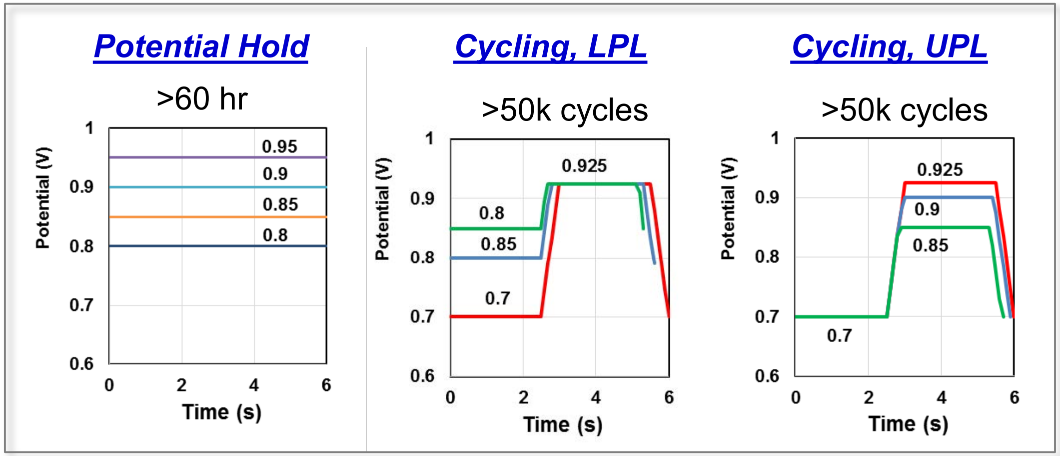
O$_2$ Permeability

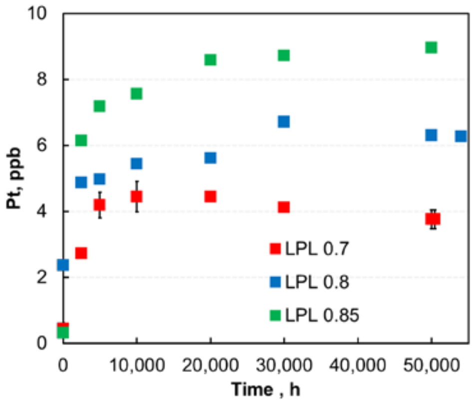


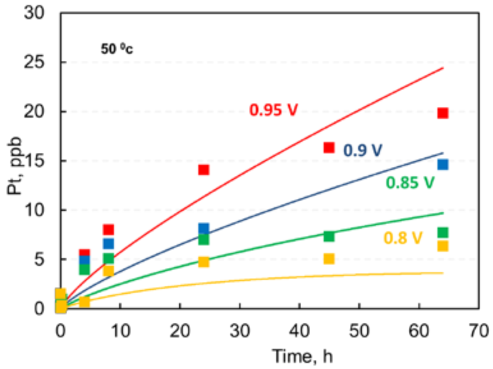
- 3M PFSA and PFIA ionomers with EW of ~700, 800, 1000 were studied for their O_2 permeability and proton conductivity.
- O_2 permeability reduces as EW increases.
- PFIA doesn't seem to follow this trend. Raises the question of the backbone vs. sidechain contributions to O_2 permeability.
- Ionomer coated Pt RDE is being studied for ionomer-Pt interaction.
- MEAs with different ionomers and Pt loadings were prepared and shipped to NREL and GM.
- MEA diagnostics focusing on local O_2 transport are being done at NREL in collaboration with FCPAD. GM will then integrate with other MEA components.

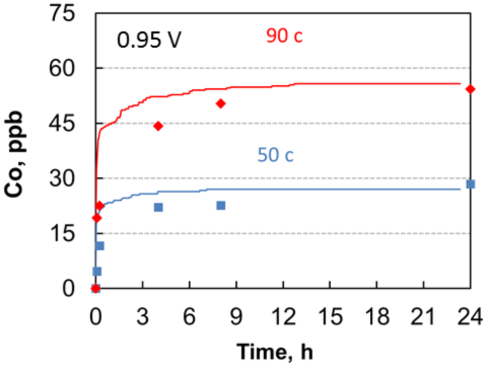
Technical Accomplishment:

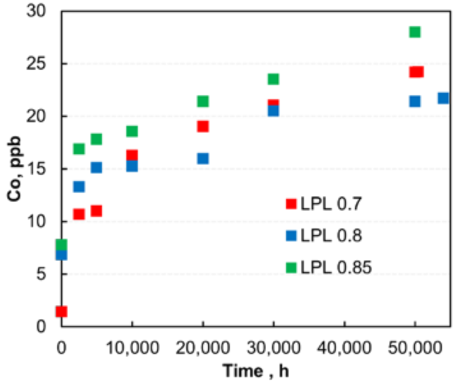
Quantifying Pt and Co Losses









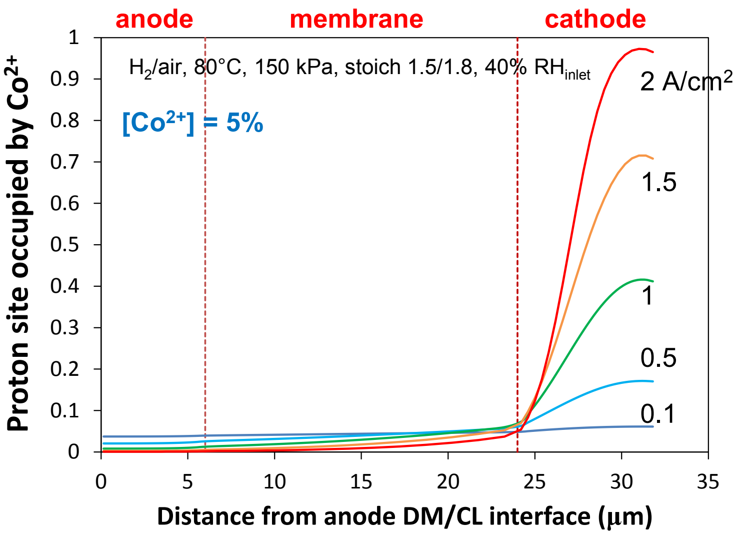


- ❑ PtCo GDE immersed in 0.5 H_2SO_4.
- ❑ Dissolved Pt and Co were monitored under a number of potentiodynamic and potentiostatic conditions.
- ❑ Rate parameters and model are being developed to estimate degradation rates.

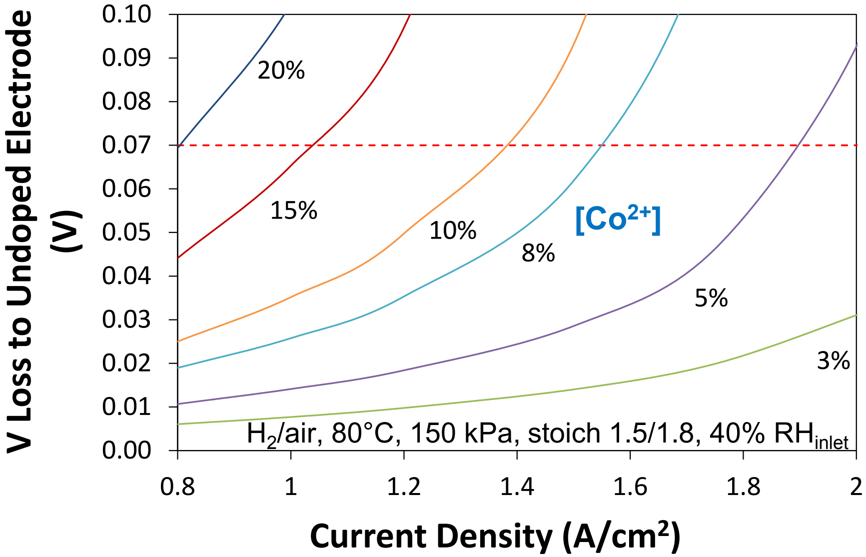
Technical Accomplishment:

Effects of Dissolved Cobalt: Design Guideline

Cobalt distribution across MEA



Simulated V Loss



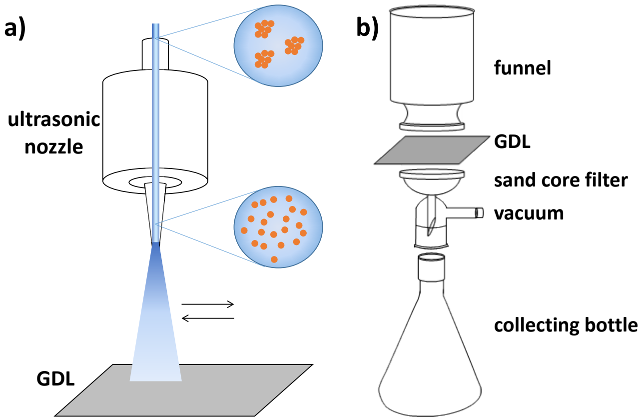
- ☐ Addition of analytical equation to simulate cobalt behavior in the electrodes to further resolve the voltage losses.
- ☐ Simulated various conditions to determine allowable cobalt amount for a given criteria to provide guideline for MEA design. (e.g. 0.1 mg_{Pt}/cm2 Pt_3Co will be 3-8% $[Co^{2+}]$)
- ☐ Still several *fundamental questions* left unanswered regarding observed higher-than-expected proton resistivity and unaccounted-for water transport.

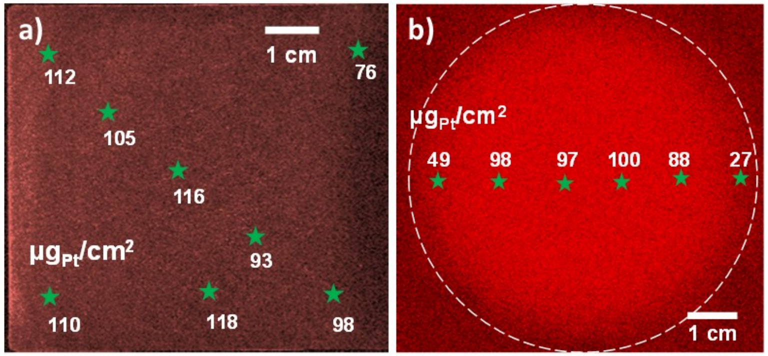
Provide guidelines for determining:

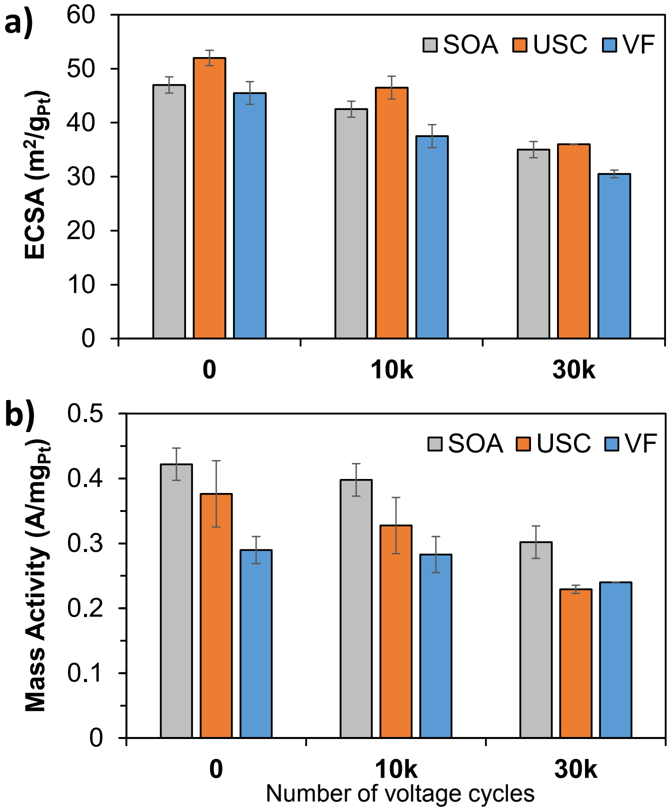
- ➢ Operating condition: T, RH, P, current density.
- ➢ Co/Pt ratio
- ➢ Pt loading
- ➢ Transient and dynamic operation strategy

Technical Accomplishment:

New Capability: MEA Preparation from mg of Catalyst





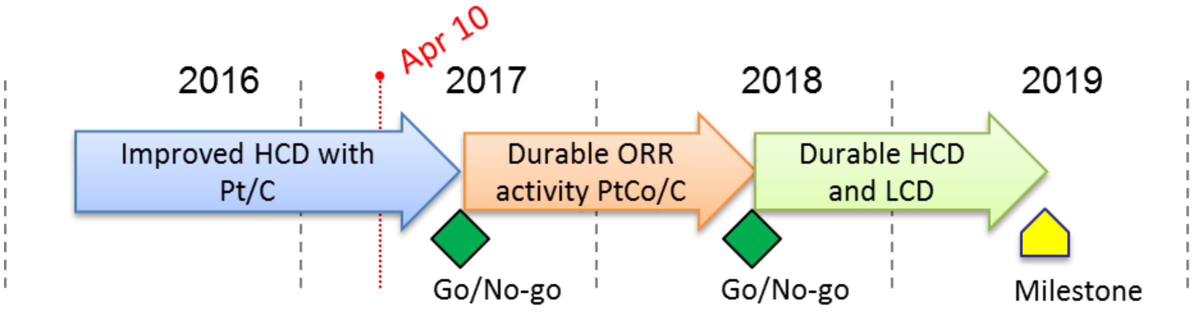


- ☐ Developed two procedures to coat fuel cell electrodes from 30 mg of catalyst powder *(same amount as an RDE ink)*.
- ☐ Observed reasonable coating quality and fuel cell performance.
- ☐ Expedite learning cycles. No scale-up required.

Yarlagadda et al. (2017) submitted.

Future Work:

Future Work



Apr 10

2016 2017 2018 2019

Improved HCD with Pt/C

Durable ORR activity PtCo/C

Durable HCD and LCD

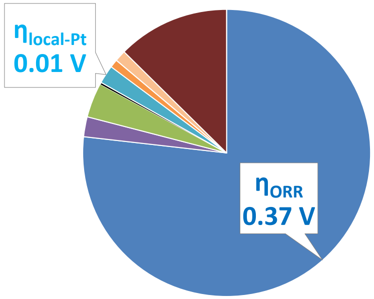
Go/No-go

Go/No-go

Milestone

until 6/2017

- ☐ Select ~3 support candidates for PtCo integration in the 2nd year. Most likely one with the best performance, one with the best durability, and one with a balanced performance.
- ☐ Evaluate activity/stability of intermetallic PtCo in MEA.
- ☐ Study the loading/stability of ionic liquid in MEA.
- ☐ Develop nano-mesostructure performance model for baseline PtCo/HSC. Identify understanding gaps for cobalt model.



Voltage Loss at 2 A/cm²

Further HCD advance relies on ORR activity
See back-up slide

7/2017 ~ 6/2018

- ☐ Optimize PtCo deposition on selected carbons. Better PSD, alloy quality and smaller particle size. Evaluate durability.
- ☐ Implement intermetallic alloy if proven beneficial.
- ☐ Integrate/Evaluate ionomer/ionic liquid. Focus on stability.
- ☐ Study local transport losses, using MEA diagnostics, tomography, and modeling.
- ☐ Develop cobalt fundamental model and PtCo dissolution model. Explore methods to visualize Co^{2+} distribution during operation.
- ☐ Update model with advanced ionomer/ionic liquid properties.

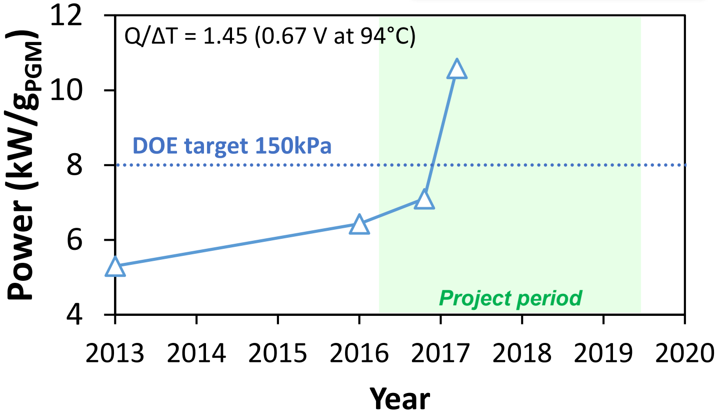
Any proposed future work is subject to change based on funding levels.

Summary

- ☐ Differential cell tests for ‘local resistance’ and ‘ORR mass activity’ have shown to be reliable predictors for MEA performance.
- ☐ Catalysts with high carbon surface area and large amount of micropore (e.g. HSC) tend to have higher ORR activity, higher stability under normal operation, but also higher local transport loss.
- ☐ Made significant progress in reducing resistance in carbon micropores (R_{O2}^{micro}, R_{H+}^{micro}) while maintaining high ORR activity.
  - ☐ Will/can these be as *durable* as baseline PtCo/HSC?
- ☐ Promising early results with *intermetallic PtCo* and *ionic liquid*. Expect faster progress once subcontracts are signed.
- ☐ Improved understanding of the performance tolerance to dissolved cobalt.

- ☐ New Key Capabilities
  - ➢ MEA preparation from small amount of catalyst powder
  - ➢ New in-situ MEA diagnostics
    - ➢ Pt-ionomer interaction by CO displacement
    - ➢ Pt location by CO stripping
  - ➢ Co^{2+} model and MEA design guideline
  - ➢ Model with nano/meso morphology consideration

2.2x kW/g_{PGM}
30% less Pt



6 articles, 18 talks (5 invited), 1 patent application

Acknowledgements

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- Shaun Onorato

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- Dave Masten
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3M

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

Carnegie Mellon University

- Prof. Shawn Litster (sub-PI)
- Shohei Ogawa
- Jonathan Braaten

Cornell University

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

Drexel University

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- Yawei Li

NREL

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- Jason Christ
- Shaun Alia
- Jason Zack
- Shyam Kocha
- Bryan Pivovar

ANL / APS

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- Dr. Nancy N. Kariuki
- Dr. Ross N. Andrews (beamline 9ID)

Technical Back-Up Slides

Carbon Support Development: Pt/C

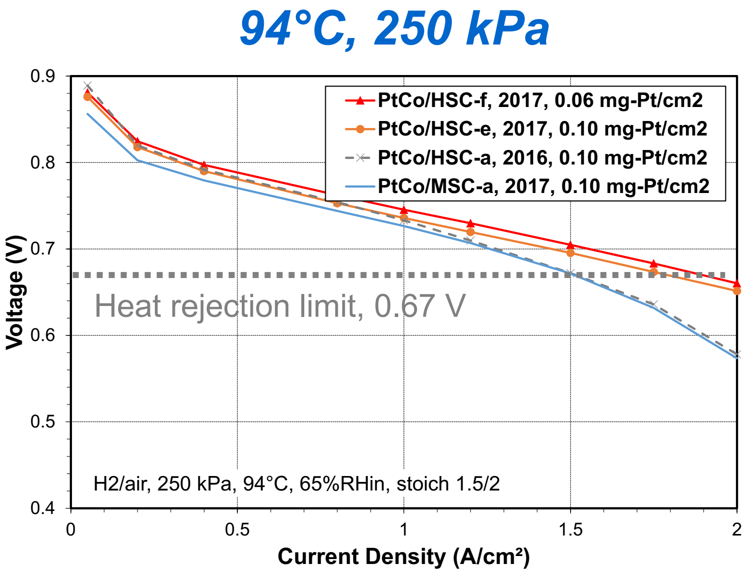
Catalyst Powder and Electrode Properties

	Powder		Electrode				
Carbon type	**Surface area (m^2/g_C)**	**Avg pore size (nm)**	**Pt Loading (mg/cm2)**	**Electrode thickness (µm)**	**Pore volume, ml/g_C**	**ECSA (m^2/g_{Pt})**	**Pt accessibility under dry condition**
HSC-a, Ketjen EC300J	780	7.9	0.056	7.6 ± 0.5	2.9	81 ± 1.4	35%
HSC-b, Acetylene Black	770	6.7	0.061	8.8 ± 0.9	3.1	80 ± 5.0	49%
HSC-c, Acetylene Black	750	7.0	0.063	9.0 ± 0.4	3.1	58.5 ± 0.7	52%
HSC-d	800		0.048	6.1 ± 0.7	2.7	73.3 ± 4.1	42%
HSC-e	800		0.060	7.0 ± 0.7	2.4	48.7 ± 1.5	61%
MSC-a, Vulcan XC72	230	13.6	0.062	5.6 ± 0.5	1.8	67.5 ± 4.9	95%
GrC-a	170	25.4	0.062	6.6 ± 0.5	2.2	52 ± 0	97%
GrC-b	150		0.065	7.4 ± 0.3	2.3	66.5 ± 2.1	92%
GrC-e	80	14.6	0.064	4.9 ± 0.2	1.4	61 ± 1.0	98%
CNT-a	1000		0.060	7.3 ± 1.1	2.5	54.5 ± 0.7	

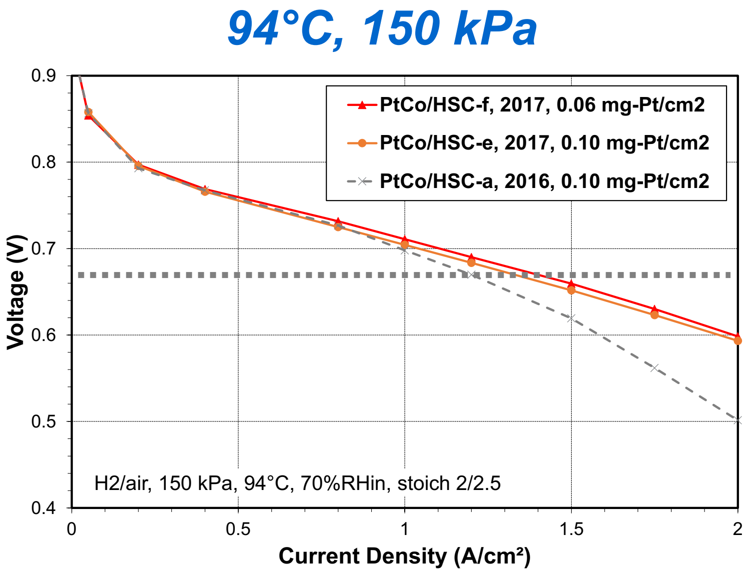
- Porosity measurement on ‘final electrode’ does not give good correlation with MEA performance.
- Rather, the pore size distribution on carbon or catalyst powder gives better correlation. Want less micropores (<4 nm) and more mesopores (>5-50 nm), confirming resistance ***local to Pt*** particles.

Technical Accomplishment:

Fuel Cell Performance at Different Conditions



94°C, 250 kPa

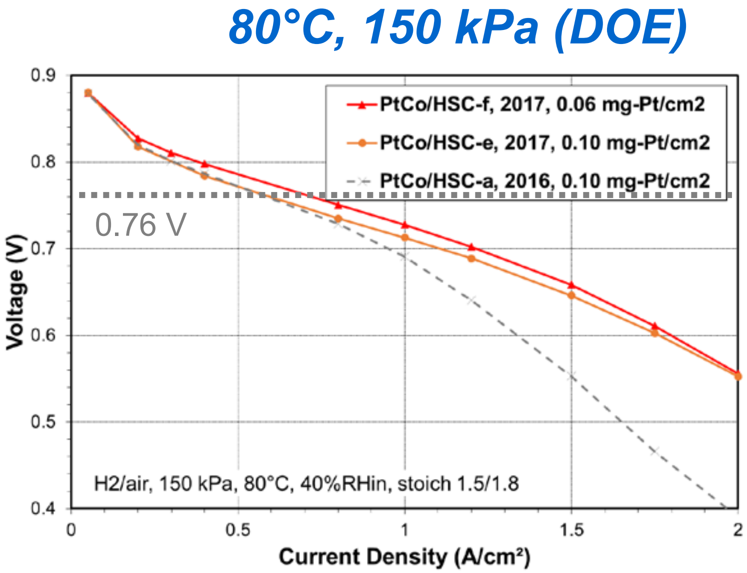


94°C, 150 kPa

DOE heat rejection requirement (Q/ΔT)

$$Q/\Delta T = \frac{Stack\ Power \times (1.25 - V_{rated})/V_{rated}}{Stack\ Temp - Ambient\ Temp}$$

$$\frac{Q}{\Delta T} = \frac{90kW \times \frac{1.25 - V_{rated}}{V_{rated}}}{Stack\ Temp - 40°C} < \mathbf{1.45}\ \text{kW/°C}$$



80°C, 150 kPa (DOE)

Average of >3 MEAs, standard deviation < 20 mV

Technical Accomplishment:

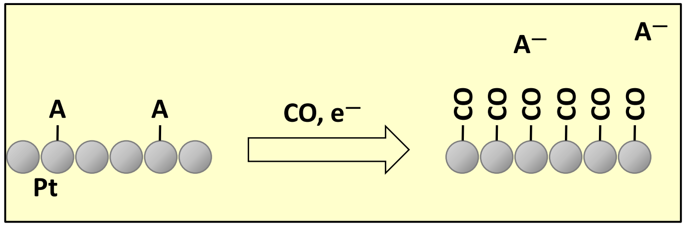
Pt-Electrolyte Interaction: Measuring Ionomer Coverage in-situ

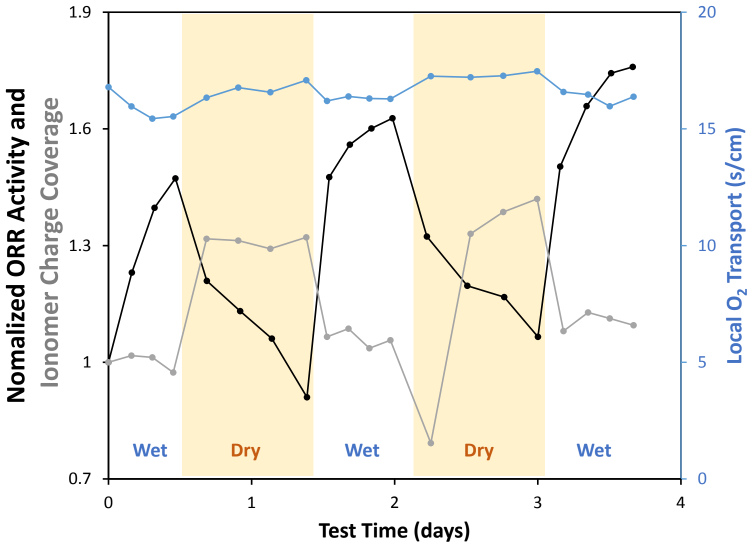
CO displacement

$$\text{Pt–C} + \text{CO} \rightarrow \text{Pt–CO} + \text{C}^+ + e^-$$

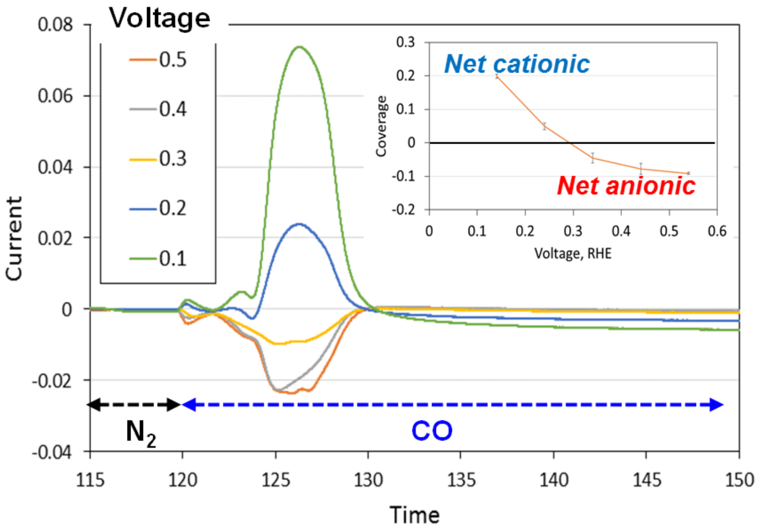
$$\text{Pt–A} + \text{CO} + e^- \rightarrow \text{Pt–CO} + \text{A}^-$$

$$q_{displacement} = q_{free\ charge} - q_{initial}$$





MEA Current-Time Response as CO is Introduced

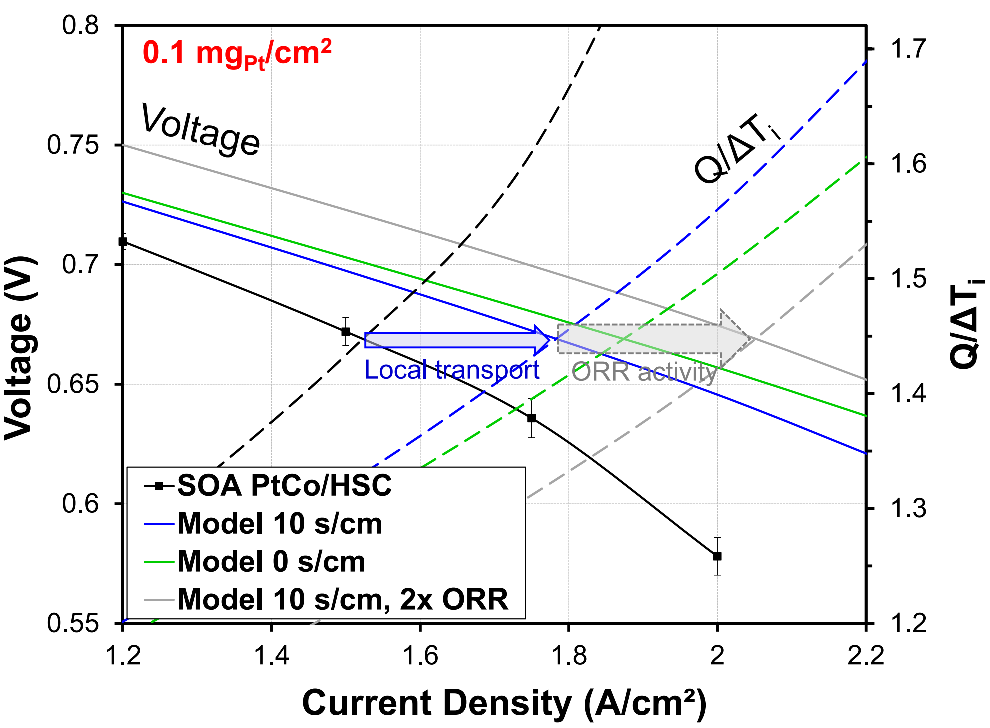


- ☐ Followed original concept used by *Clavilier and Feliu* on single crystals [*J. Electroanal. Chem.* (1992) 489].
- ☐ Validated on poly-Pt and Pt/C, then developed into in-situ MEA diagnostic.
- ☐ Enable quantification of adsorbed species in MEA in the potential range of 0.1-0.55 V.
- ☐ Demonstrated that CO displacement charge (ionomer adsorption) correlates with fuel cell performance.
- ☐ Will be used to quantify adsorption behavior of different type of ionomers, and any changes as they are aged.

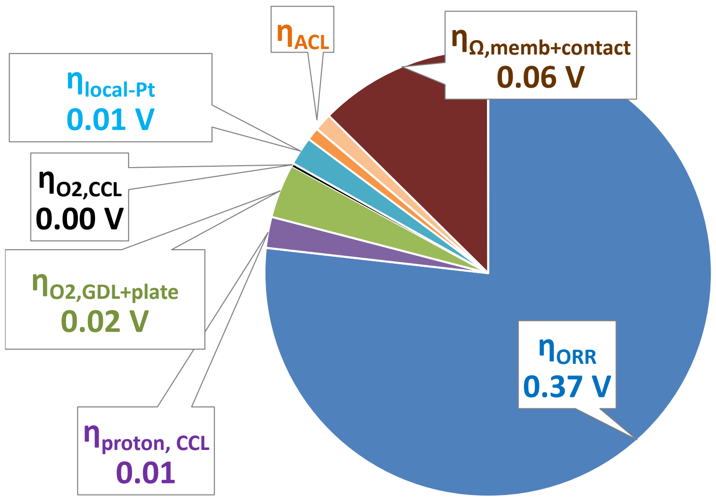
Kongkanand et al. ECS Trans. (2016) 75, 25.
Garrick et al. J. Electrochem. Soc. (2016) 164, F60.

Future work:

Further Improvement at High Power



Voltage Loss Contributors at 2 A/cm² (0.1 mg_{Pt}/cm^2)

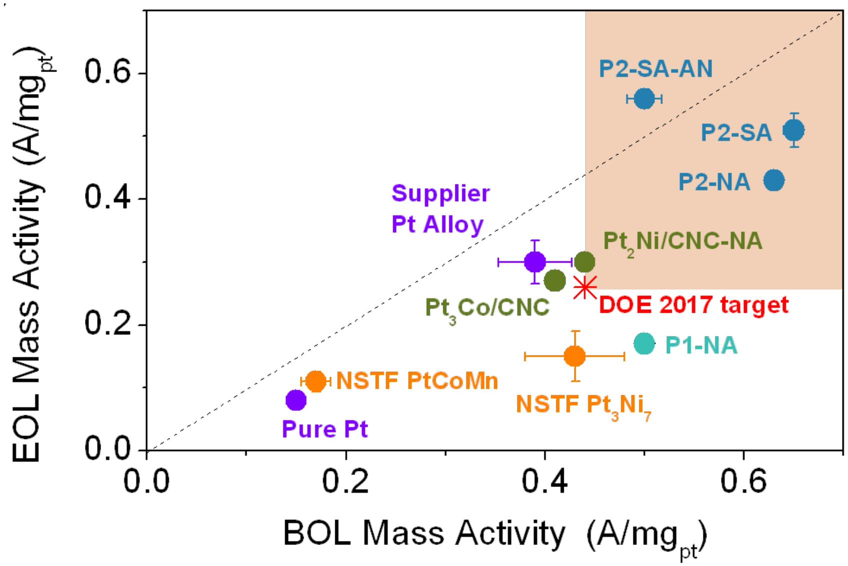


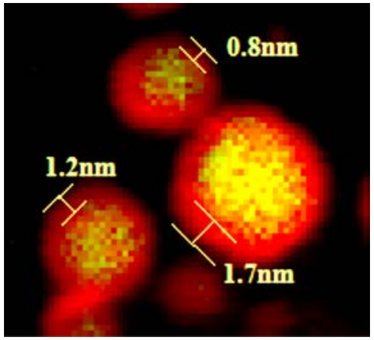
0.10 mg_{Pt}/cm^2 PtCo/HSC: H_2/air, 94°C, 250/250 $kPa_{abs,out}$, 65/65% RH_{in}, st=1.5/2

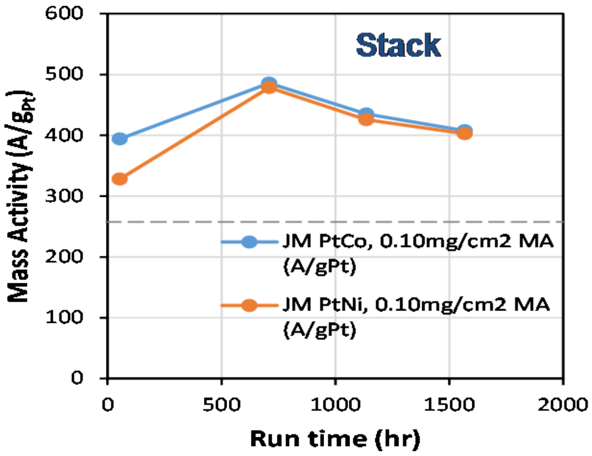
- For a 0.1 mg_{Pt}/cm^2 cathode, most gain is obtained with local-Pt resistance of 10 s/cm. For lower Pt loading, more gain from local transport can be obtained.
- Must also work on other issues. Within ‘catalyst & electrode’, ORR activity is the largest.
- In this project, ordered intermetallic alloy and ionic liquid are promising approaches.

FC087 2011-2014

Exceptional Durability of ORR Activity with Dealloyed PtNi/HSC and PtCo/HSC







Energy Environ. Sci., 2014.

DOE Final Report, 2014. https://www.osti.gov/scitech/biblio/1262711

- Meeting DOE ORR durability in MEA. Validated at multiple sites.
- Durable ORR kinetic in stack testing.
- Need thicker Pt shell for MEA stability (>4ML). *Optimization point is very different from RDE*.

GM

TU berlin

JM Johnson Matthey Fuel Cells the power within

Massachusetts Institute of Technology

Northeastern UNIVERSITY

THE GEORGE WASHINGTON UNIVERSITY WASHINGTON DC