FC144

Highly-Accessible Catalysts for Durable High-Power Performance

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General Motors Global Product Development,
Fuel Cell Activities

June 7, 2016

Overview

Timeline

- Project start date: 1 Apr 2016
- Project end date: 31 Mar 2019
- Percent complete: 1.2%

Budget

- Total Funding Spent as of 3/31/16: $0.05M
- 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

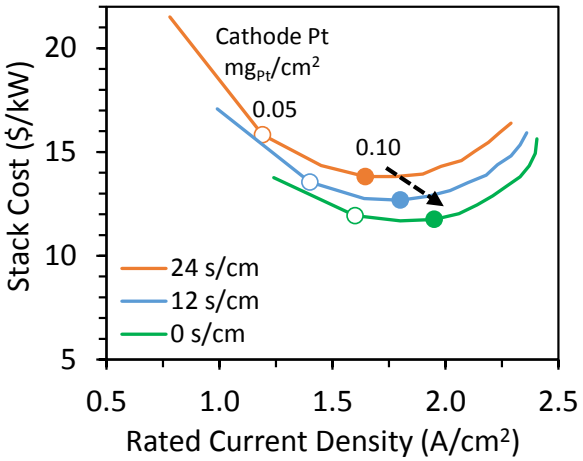
- Subcontractors: *Not yet signed*
  - 3M Company
  - Carnegie Mellon University
  - Cornell University
  - Drexel University
  - NREL
- Project lead: GM

Relevance:

Relevance/Impact

Metric	Units	GM PtCo/HSC 2013	GM PtCo/HSC 2016	End of Project Target	DOE 2020 Target
Platinum group metal (PGM) total content	g/kW_{rated}	0.16	0.125	***<0.11***	<0.125
PGM total loading (both electrodes)	mg/cm^2	0.15	0.125	0.125	<0.125
Loss in catalytic (mass) activity	% loss	0-40%	0-40%	<40%	<40%
Catalyst cycling (0.6-1.0V, 30k cycles)	mV loss at $0.8A/cm^2$	30	30	<30	<30
Support cycling (1.0-1.5V, 5k cycles)	mV loss at $1.5A/cm^2$	Not tested	Not tested	<30	<30
Mass activity @ 900 $mV_{iR\text{-}free}$	A/mg_{PGM}	0.6-0.75	0.6-0.7	>0.6	>0.44
Performance at rated power (150kPa)	W/cm^2	0.80	0.86	(0.94)	>1.0
Performance at rated power (250kPa)	W/cm^2	**0.96**	**1.01**	***>1.1***	-

Stack cost at high volume

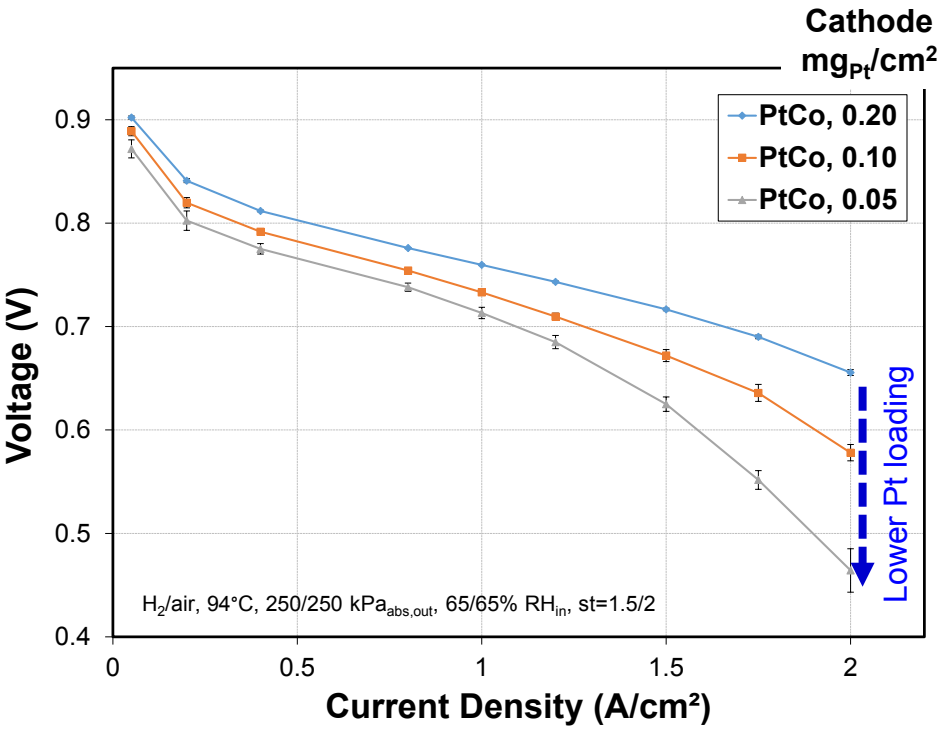


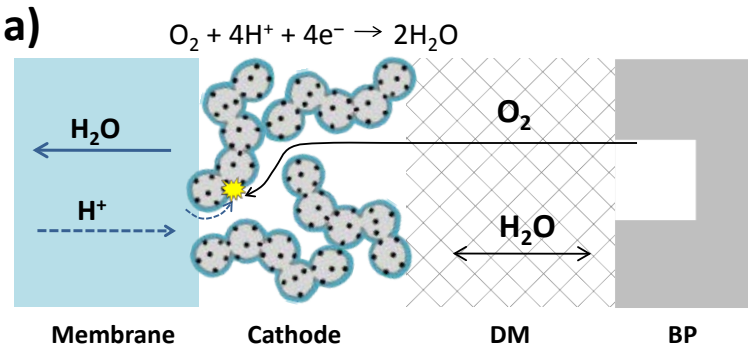
J. Phys. Chem. Lett. (2016) 1127.

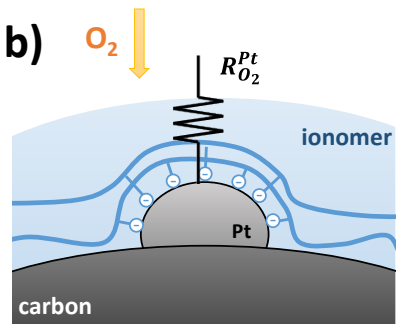
- Reduce overall stack cost by improving high-current-density (HCD) performance in H_2/air fuel cells adequate to meet DOE heat rejection and Pt-loading targets.
- Maintain high kinetic mass activities.
- Mitigate catalyst degradation by using supports with more corrosion resistance than the current high-surface-area carbon (HSC).

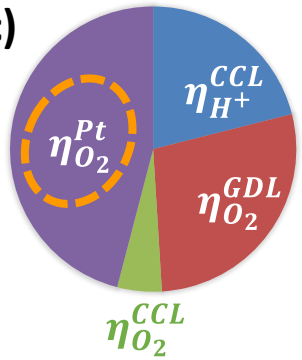
Relevance:

Challenge: Local O_2 Transport Resistance









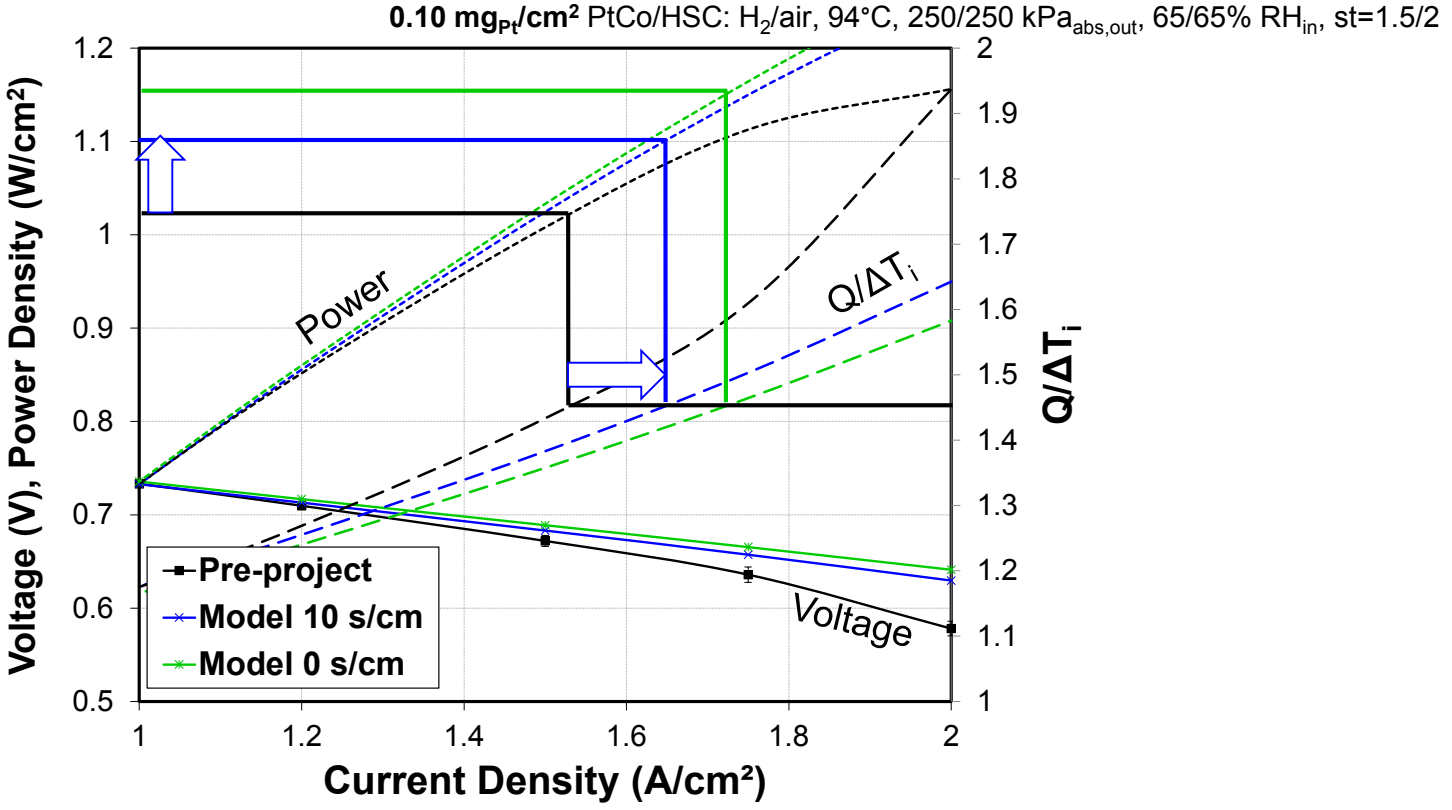
J. Phys. Chem. Lett. (2016) 1127.

Mass-transport voltage losses at 1.75 A/cm^2 on a **0.10 mg$_{Pt}$/cm^2** cathode

- Large performance loss at high-current density is observed on low-Pt cathodes due to higher flux of O_2 per a given Pt area.
- The 'local O_2 transport resistance' dominates the mass transport related loss (purple) at HCD on low-Pt electrode. Must be addressed.

Approach:

PtCo/HSC Status and Subtarget Setting

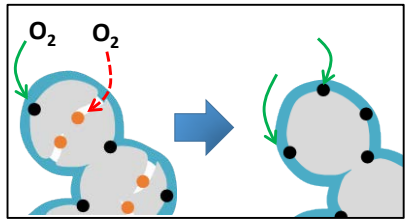


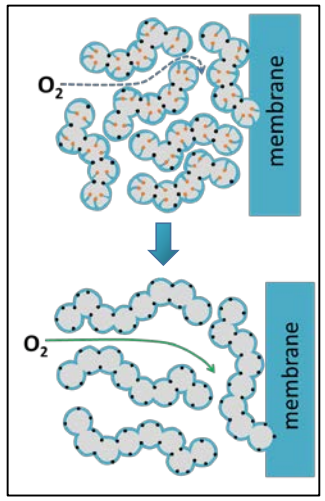
- Current PtCo/HSC catalyst shows relatively high 'local O_2 transport resistance' of ***20-25 s/cm***, resulting in a peak power density of ~1 W/cm^2. (0.67 V at 1.5 A/cm^2)
- We aim to ***halve*** the loss due to local resistance, with ***one or more*** of the project approaches (next slide).
  - Reduce local resistance (**20→10 s/cm**): restricted pores, Pt-ionomer interaction.
  - Reduce local current density: increase Pt surface area (**ECSA, 40→80 m^2/g$_{Pt}$**).

Approach:

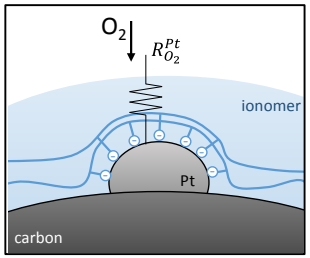
Basic Concept: *Will Succeed if At Least One Works*

- Improve O_2 Transport with New Carbon Support — **GM/CMU/ Cornell/NREL**
  - Which support is best for performance?
  - Which is best for durability?
  - Do we need HSC to get high ORR kinetic?

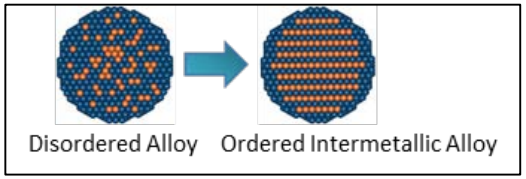




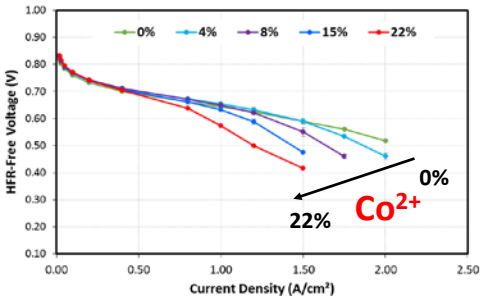
- Reduce Electrolyte-Pt Interaction — **3M/Drexel/GM**
  - From current selection of ionomer/ionic liquid which is the best?
  - Does Pt-ionomer interface change overtime?



- Enhance Dispersion and Stability of PtCo Particles — **Cornell/GM/NREL**
  - Can activity or durability be improved?
  - Can ECSA be improved?



- Understand and Better Control Leached Co^{2+} — **GM/CMU**
  - How is performance affected?
  - How much is too much?
  - What can we do to mitigate the effect?



Milestones and Go/No Go

TASK 1 - Development of Highly-Accessible Pt Catalysts

Go/No-go criteria: >1.0 W/cm^2, <0.125 g_{Pt}/kW_{rated}, and Q/ΔT <1.7 with Pt/C

- ❑ Downselect carbon support, ionomer, ionic liquid 5%
- ❑ Understand the effect of leached Co^{2+} and Pt surface area 10%
- ❑ Develop dealloyed catalyst from ordered intermetallic alloy 0%
- ❑ Visualization of carbon structure and Pt location on selected catalysts 0%
- ❑ Modeling baseline material 5%

TASK 2 - Development of Dealloyed Catalyst with Preferred Catalyst Design

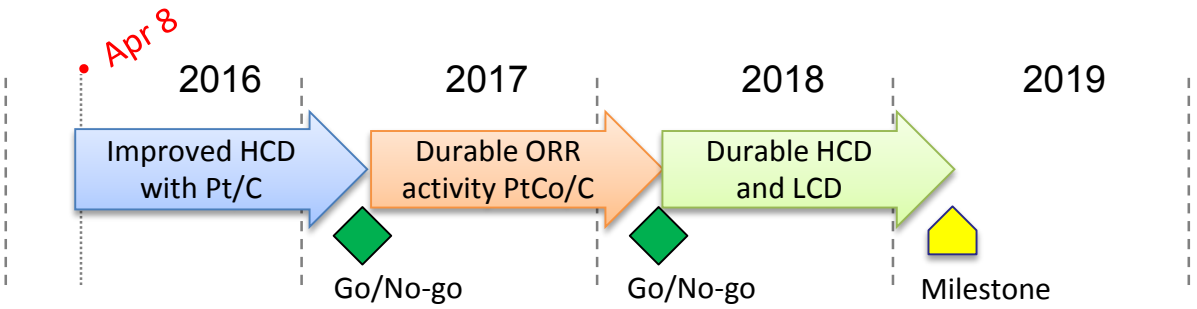
Go/No-go criteria : >0.44 A/mg_{PGM}, <40% mass activity loss with preferred design

- ❑ Develop dealloyed catalyst on preferred support 0%
- ❑ Implement selected ionomer and ionic liquid with selected catalysts 0%
- ❑ Visualization of fresh PtCo/C and post-AST Pt/C 0%
- ❑ Modeling of PtCo/C before and after AST 0%

TASK 3 - Optimization for Durable HCD and LCD Performance

Milestone: >1.1 W/cm^2, <0.11 g_{Pt}/kW_{rated}, and Q/ΔT <1.45

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

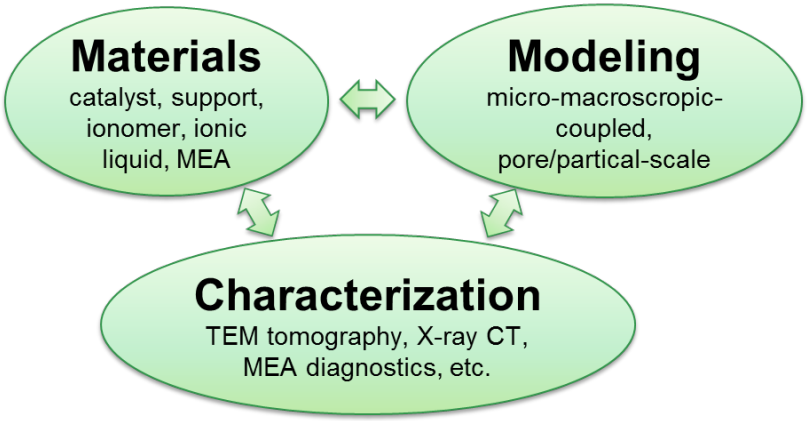


Collaborations:

Project Team

Not signed

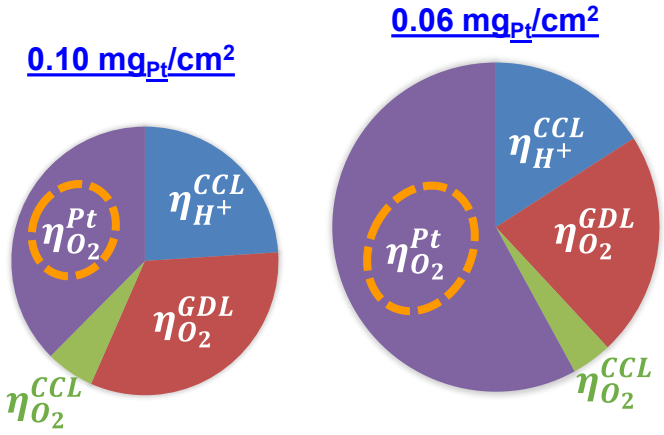
- General Motors (industry)
  - Overall project guidance, synthesis and testing of catalysts.
- 3M Company (industry) – **Dr. Andrew Haug**
  - Selection and pre-fuel-cell evaluation of ionomer candidates.
- Drexel University (university) – **Prof. Joshua Snyder**
  - Selection and pre-fuel-cell evaluation of ionic liquid candidates. Incorporation strategy of IL into MEA.
- Cornell University (university) – **Prof. David Muller** and **Prof. Héctor Abruña**
  - TEM and tomography.
  - Synthesis of intermetallic alloys.
- Carnegie Mellon University (university) – **Prof. Shawn Litster**
  - Modeling and X-ray tomography.
- National Renewable Energy Lab (federal) – **Dr. K.C. Neyerlin**
  - Support N-doping, MEA fabrication and diagnostics.



Carbon Support Selection: MEA Test Methodology

- Will first focus on this 'local O_2 transport resistance' by using low-loaded 0.06 mg_{Pt}/cm^2 cathodes with similar thicknesses.
- Use 5 cm^2 differential cell platform (high gas flows) in order to mitigate non-uniformity in water and reactant concentration.
- Table below are the catalysts studied to date. Will study several more in the Year 1.

Mass-transport voltage loss terms at 1.75 A/cm^2

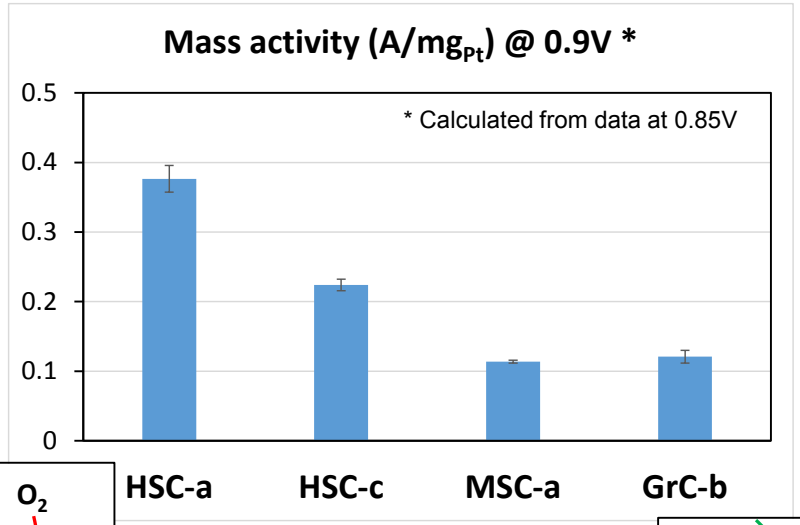


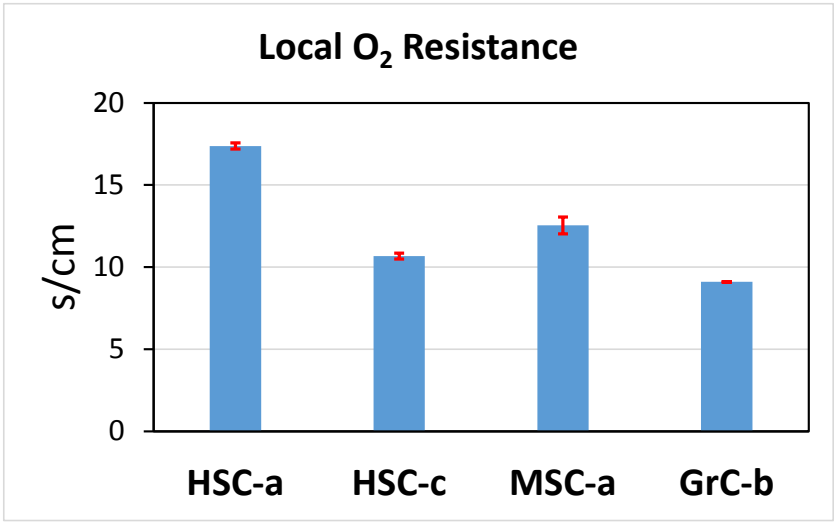
All Pt/C, 20 wt% Pt, D2020, 18µm membrane

Catalyst Support Type	BET (m^2/g_C)	Pt loading (mg/cm^2)	ECSA (m^2/g_{Pt})	Thickness (µm)	Packing thickness ($\mu m/mg_C$)
HSC-a	800	0.056	81	7.6	27
HSC-c	800	0.063	52	9.0	29
MSC-a	250	0.062	68	5.6	18
GrC-a	100	0.062	52	6.6	21
GrC-b	100	0.065	67	7.4	23
CNT-a	60	0.060	55	7.3	25

HSC: High-surface-area carbon black
MSC: Medium-surface-area carbon black
GrC: Graphitized carbon black
CNT: Carbon nanotube

Carbon Support Selection: MEA Diagnostics



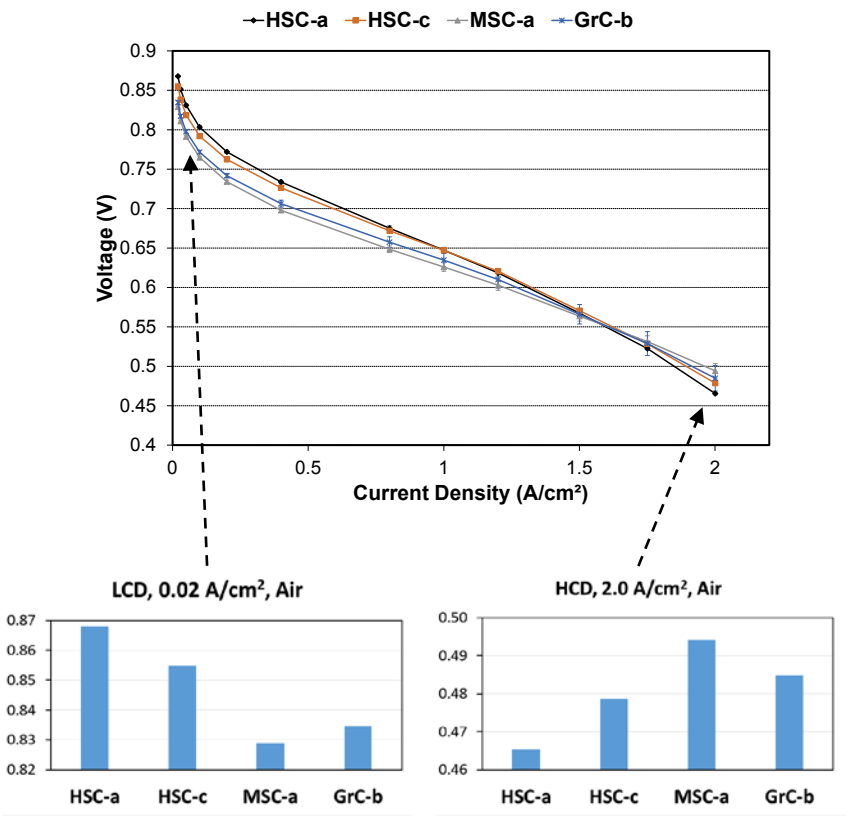


By Limiting current measurement *J. Electrochem. Soc. (2012) F831.*

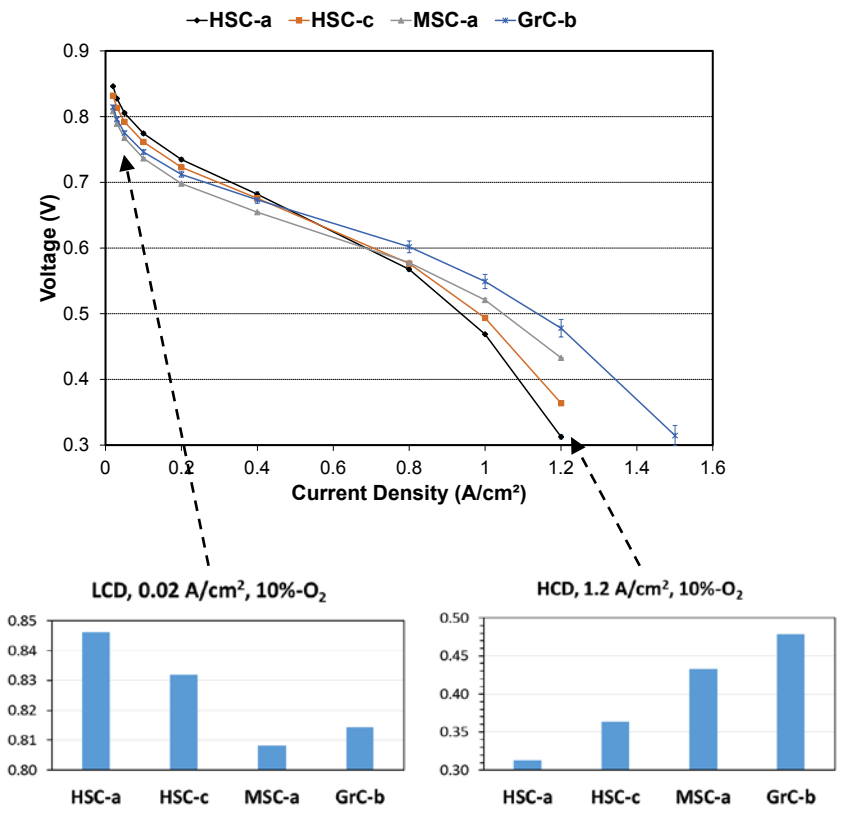
- Higher ORR activity on Pt/HSC is due to less direct contact area between Pt and ionomer, also shown by others.
- HSC with large amount of internal porosity shows higher apparent local O_2 resistance than other supports.
- Solid carbons show promising low local O_2 resistance (<10 s/cm).

Carbon Support Selection: Fuel Cell Performance

Air, 150kPa, 100% RH



10% O_2, 150kPa, 100% RH

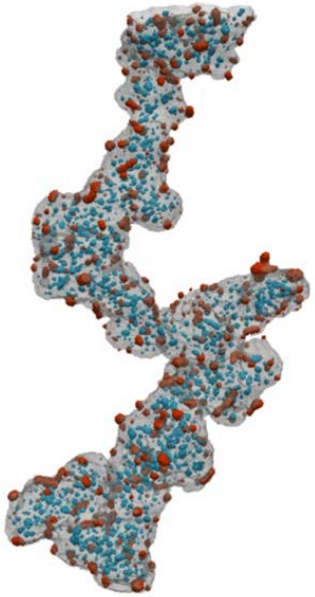


- Fuel cell performance agrees well with diagnostic results. HSC with large amount of internal porosity gives better voltage at LCD but worse voltage at HCD.
- Test at low O_2 partial pressure helps differentiate good vs bad supports, in terms of O_2 transport.

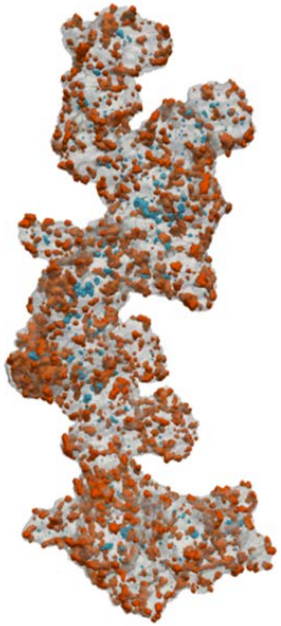
Technical Accomplishment:

Visualization

Pt/HSC-a

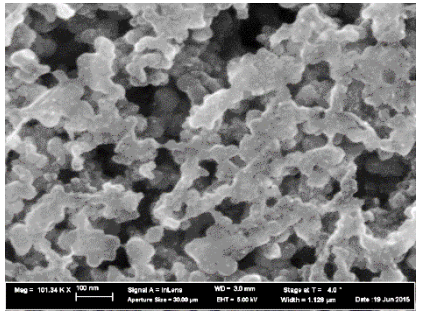


Pt/MSC-a

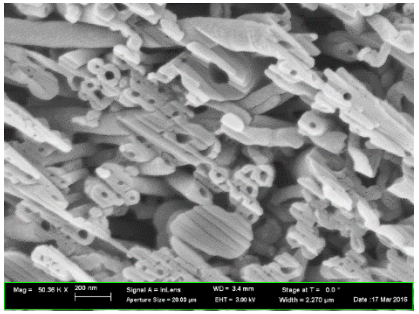


- STEM tomography will be used to locate Pt particles in relation to carbon.
- As shown on the left, the majority of Pt on HSC-a is embedded (blue) in the carbon, in contrast to MSC-a where its majority is on the carbon surface (brown).
- Similar quantitative analyses will be done on selected catalysts.

Pt/HSC-a



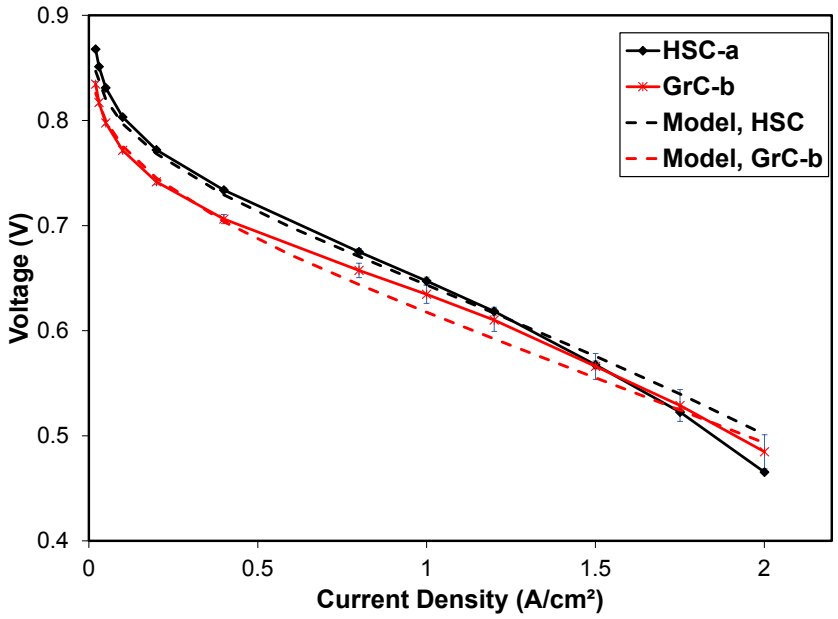
Pt/CNT-a



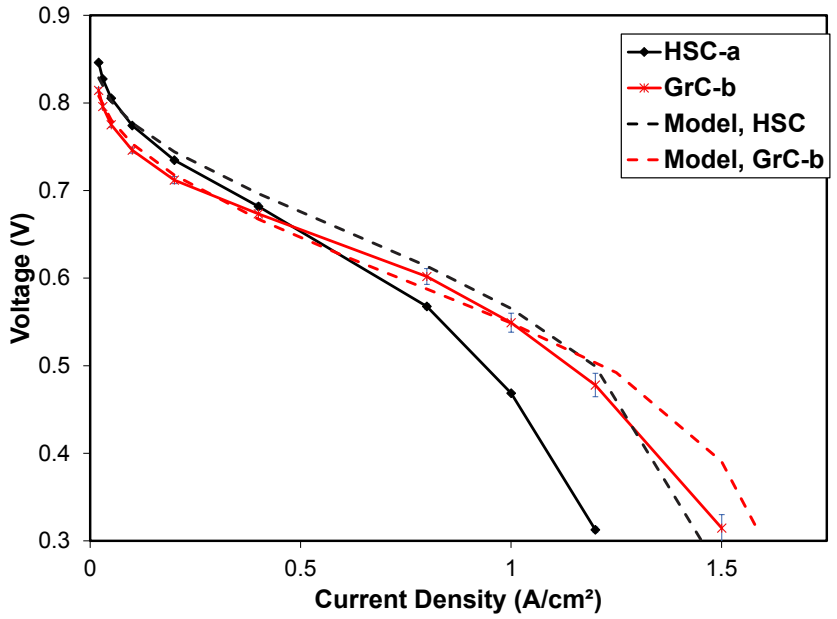
- In combination with other ex-situ gas measurements, ion-milled cross-sectional SEM is used to evaluate the pore size and porosity in the coated electrodes.

Modeling: Understanding Performance

Air, 150kPa, 100% RH

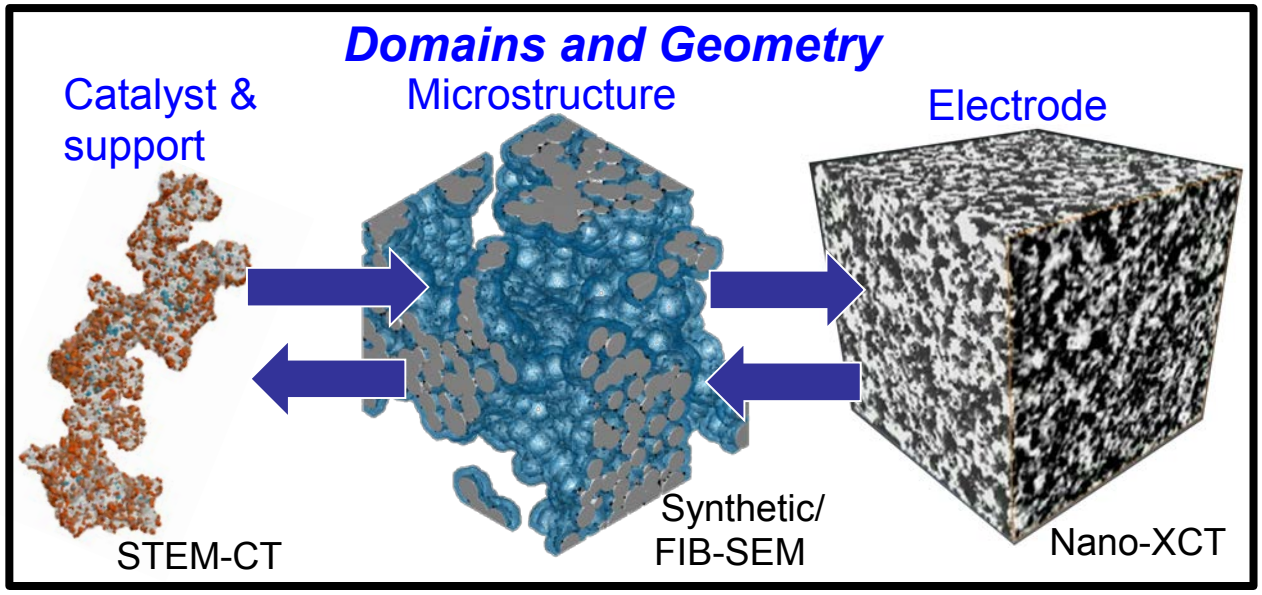


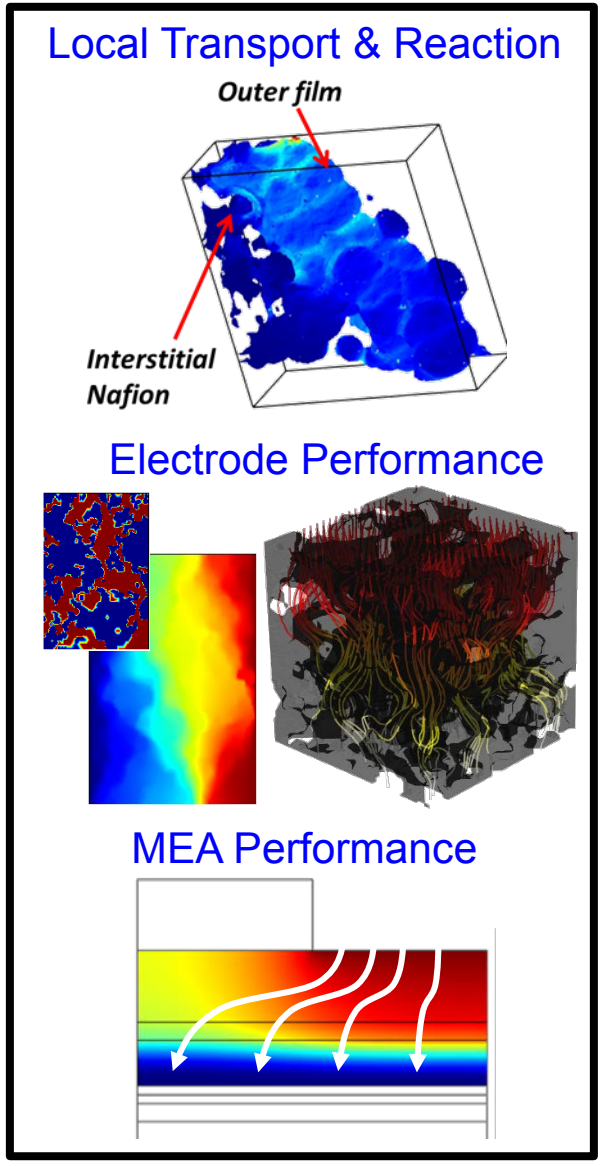
10% O_2, 150kPa, 100% RH



- Using MEA diagnostics (EIS, limiting current, ORR, ECSA), fuel cell performance can be simulated reasonably well on solid carbon (red) using previously developed 1D micro-macroscopic-coupled model (Gu, FC092).
  - We can focus on properties that matter most to performance.
- Additional loss at HCD for the porous HSC is noticeable, likely due to inaccessibility of internal Pt particles. (This project SOW aims to move away from this type of carbon. Therefore, narrowing this gap for HSC is not the scope of this project.)

Modeling: Refining at Pore/Particle Scale

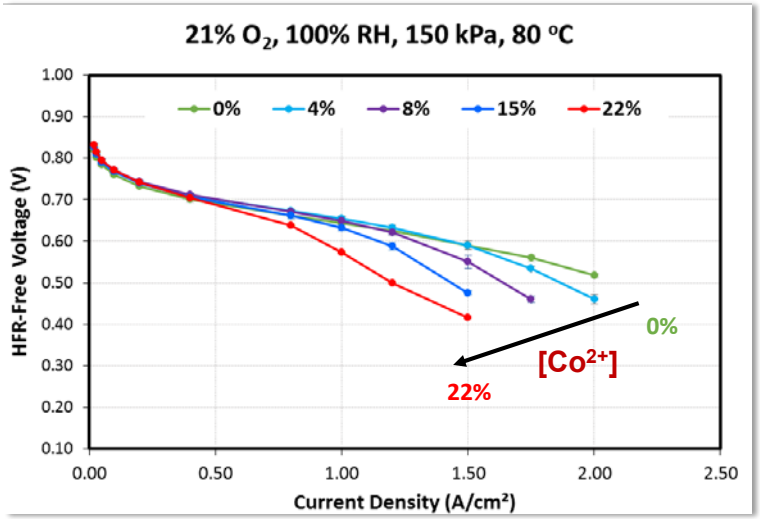




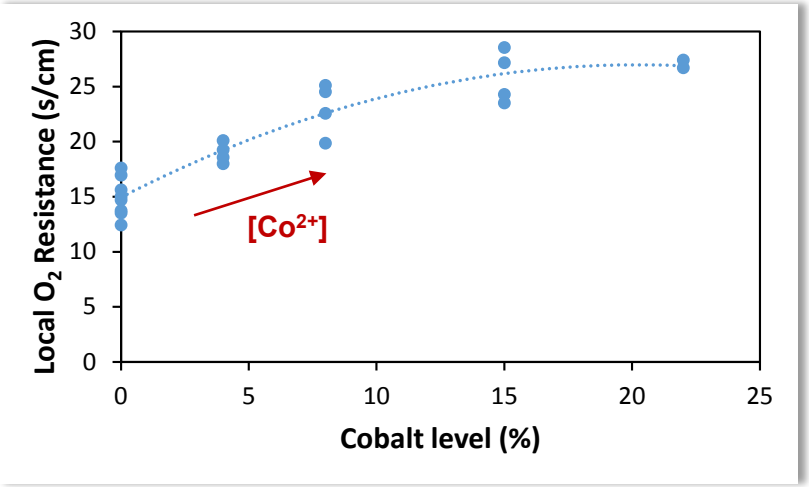
- Understand and develop solutions to transport limitations and performance bottlenecks at the catalyst & support, in the electrode microstructure, and across electrode thickness.
- 3D geometry extracted from visualizations at multiple length scales and synthetic structures for scale bridging.
- Understand local resistance and leached cobalt effects.

Leached Metal Effects: Co^{2+} doped Pt/C MEA

Co^{2+}-doped Pt/C

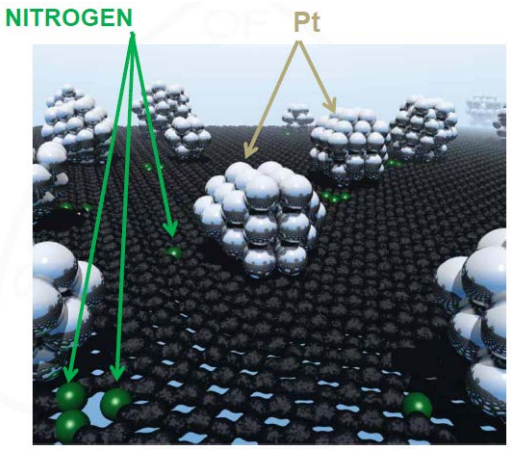


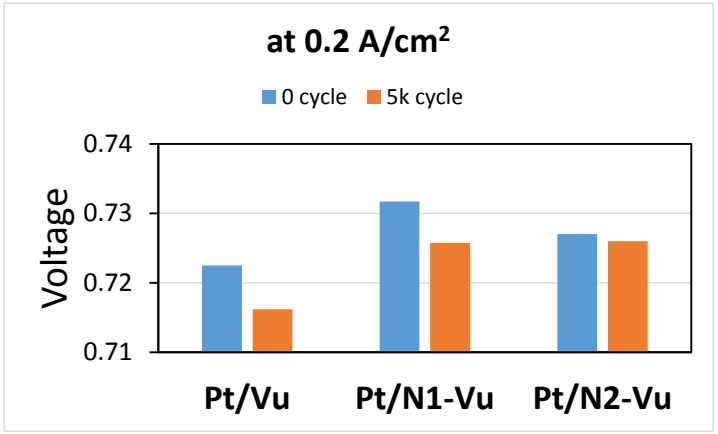
Local O_2 Transport Resistance

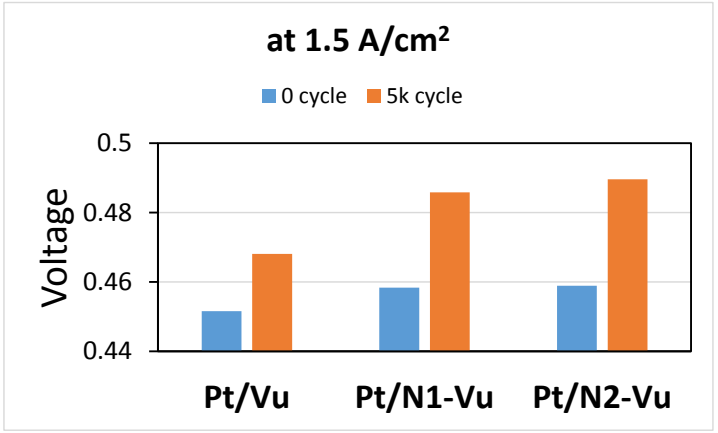


- Because the maximum amount of Co available in a 0.10 mg_{Pt}/cm^2 PtCo cathode is equivalent to 8% exchange rate, **8% is the worst case scenario** with regard to MEA performance.
- However, at HCD, local $[Co^{2+}]$ can be much higher in the cathode, therefore, it is important to study electrode properties at higher $[Co^{2+}]$.
- **Local O_2 resistance increases with $[Co^{2+}]$!!**
  - Similar results were observed on thick membranes – attributed to affinity to ionomer acid groups.
  - This will cause large adverse impact at HCD. Will need to design the electrode to avoid such situation.

Metal-Support Interaction: Anchoring Pt with N-sites







- To investigate if doping carbon surface with N would decrease coalescence of Pt particles, Vulcan carbon was doped with N at 2 levels using NREL's rotating ion beam implantation, then platinized and tested at GM.
- After a mild MEA cycling test (5k cycles, 0-0.925 V), N-doped samples showed somewhat superior voltage than the control, despite all having similar ECSA loss (62→40 m^2/g_{Pt}).
- Will investigate its effectiveness on graphitized carbon.

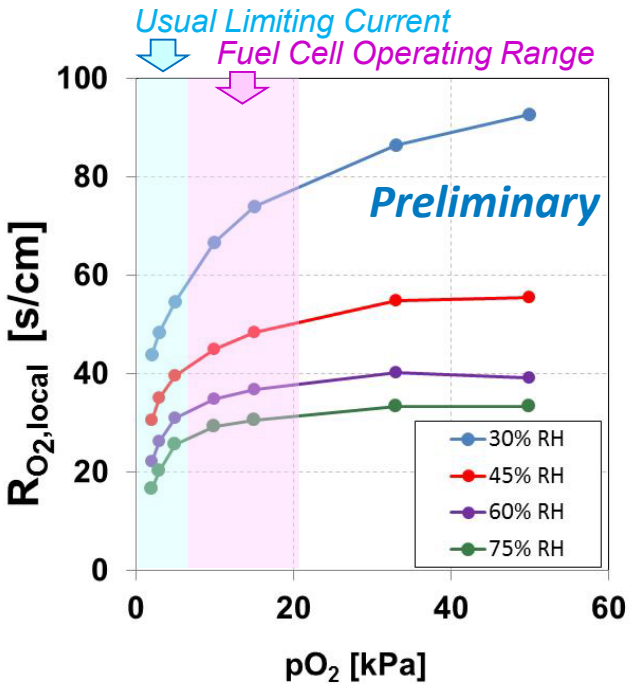
Advanced MEA Diagnostics

More at FC137

O_2 Transport under Relevant Condition

$$R_{\text{Total}} = \frac{4F c_{O_2}}{i_{\text{lim}}} = R_{\text{CH}} + R_{\text{DM}} + R_{\text{MPL}} + \frac{R_{O_2}^{\text{Pt}}}{f_{\text{Pt}}}$$

Greszler, et al. *J. Electrochem. Soc.* (2012) F831.

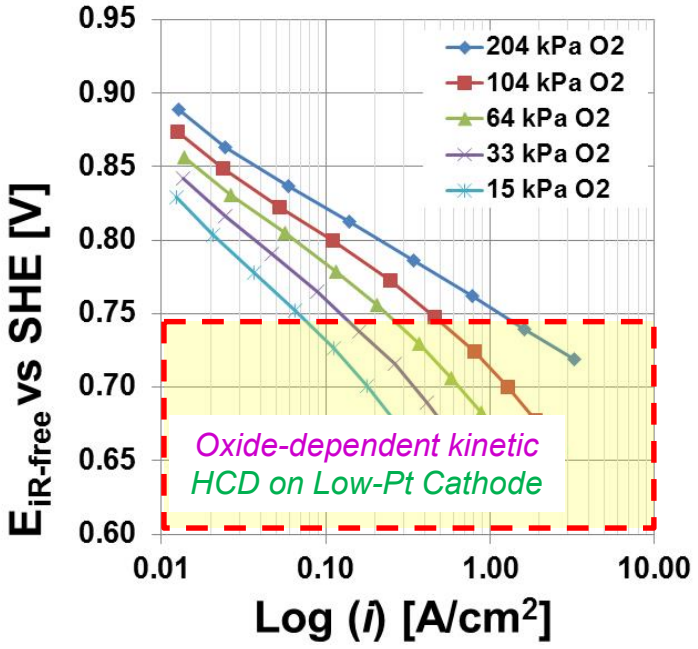


- Local resistance appears to be larger under condition relevant to fuel cell – more study needed to understand

O_2 Reduction Kinetic at HCD

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

Subramanian, et al. *J. Electrochem. Soc.* (2012) B531.



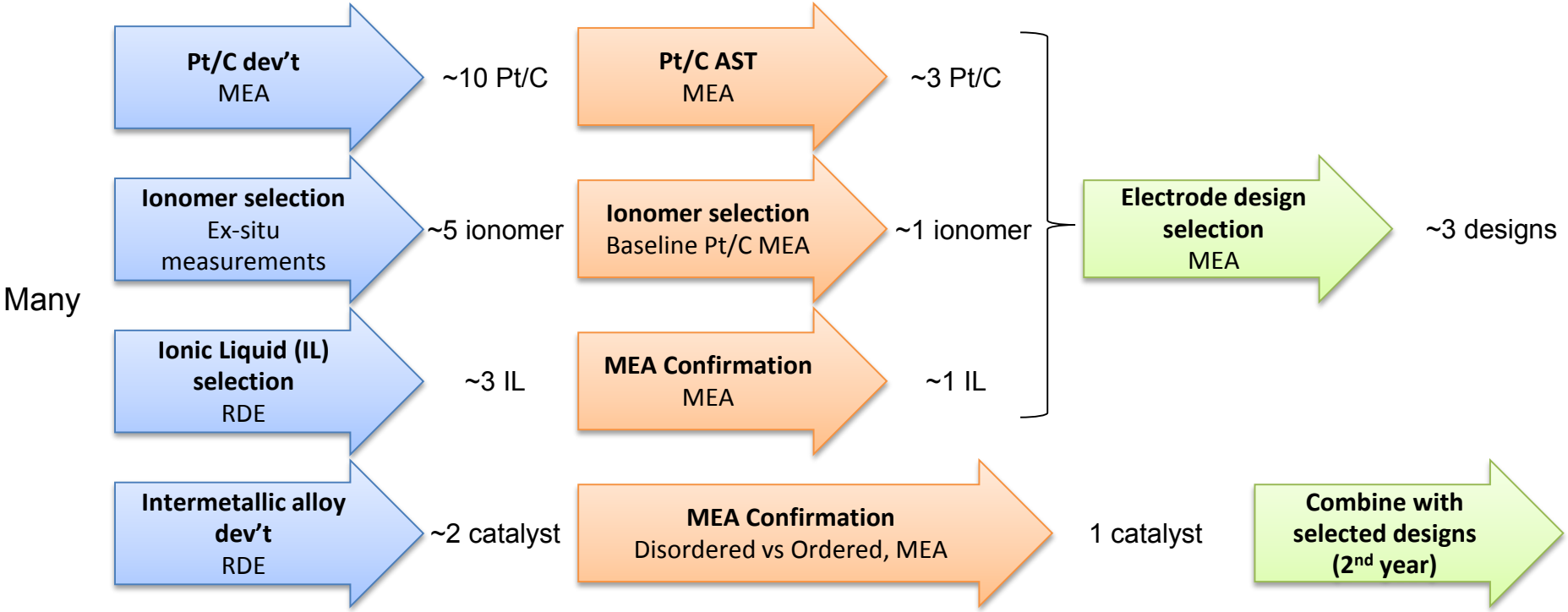
- At HCD on low-Pt cathode, Pt oxide gets reduced changing the kinetic – need to resolve to understand loss contribution from different mechanisms.
- Technically very challenging – need to test under partial vacuum to bring O_2 pressure down.

Responses to Last Year AMR Reviewers' Comments

- New Project. This project was not reviewed last year.

Future Work (1/2):

Materials Selection: 1st Year Workflow



- From the overall performance, ~3 support candidates will be selected 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.
- Visualization and Modeling will support Materials Development throughout the project.

Future Work (2/2):

Selection Methods

Component	Property	Method
MEA	O_2 transport	Limiting current, I-V curves, ex-situ gas measurements, X-ray CT, SEM
	Proton transport	EIS
	ORR activity	I-V curves, O_2 vacuum
	Catalyst anchor-ability	DOE AST catalyst-cycling test
	Support corrosion resistivity	DOE AST support-cycling test
	Pt-electrolyte	CO displacement
	Co^{2+} distribution	μ-XRF
Support	Catalyst anchor-ability O_2 transport	Ex-situ thermal test TEM tomography
Ionomer	O_2 and proton transport	Ex-situ thin film measurements, EC-QCM
Ionic liquid	ORR activity and adsorption strength	Single crystal RDE, CO displacement

- Many techniques were identified to use for selection although not all will be applied.
- Some techniques are solely for understanding performance (modeling).
- MEA performance will ultimately be the overriding selection criteria.

Summary

- Six types of carbon supports were evaluated (shown here 4 representative types) with particular focus on their high-current-density performance.
- HSC with porous structure showed high ORR activity but low high-power performance when compared to carbon with solid structure.
  - If we can obtain the same ORR activity with Pt alloy on solid carbon, targets at both LCD and HCD can be achieved.
- Fuel cell performance of Pt/C with different carbon structures can be largely predicted using a set of electrochemical diagnostics and separately determined morphology.
- An attempt to improve the Pt-carbon adhesion using N-doping showed promising MEA result. May provide a path to utilize a more corrosion resistant support.
- Analysis on cobalt-doped MEA showed increased 'local O_2 resistance', suggesting a larger than previously predicted performance loss at HCD.

Technical Back-Up Slides

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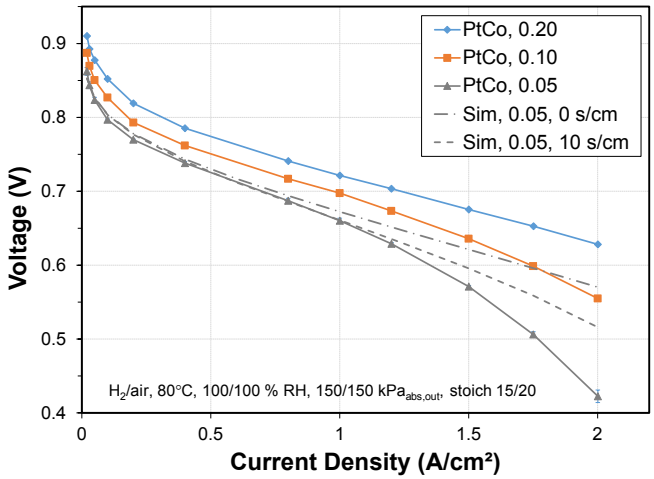
Differential Cell for Benchmarking

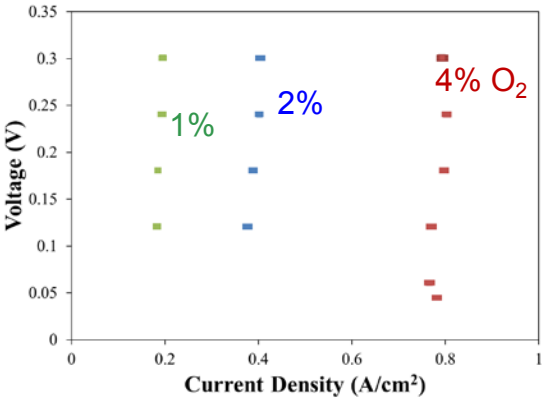
Fuel Cell Performance Benchmarking

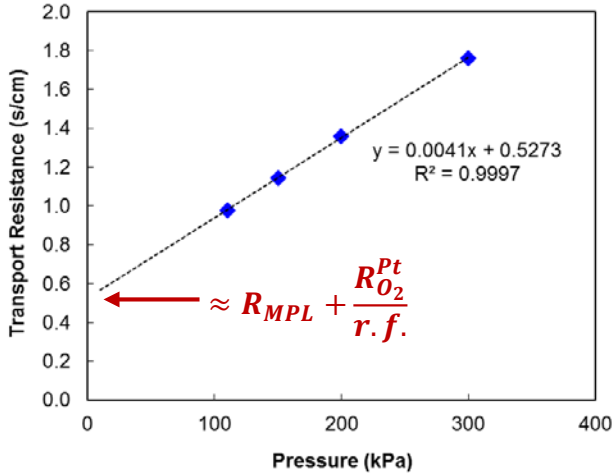


- Use small active area cell (5 cm^2) with high gas flows to mitigate variability between test equipment and flow fields, focusing on the MEA performance.
- Amplify loss from local O_2 transport resistance by testing cathode Pt even below DOE target (0.06 mg/cm^2 and below)

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

O_2 Transport Measurement





$$R_{\text{Total}} = \frac{4Fc_{O_2}}{i_{\text{lim}}} = R_{\text{CH}} + R_{\text{DM}} + R_{\text{MPL}} + \frac{R_{O_2}^{\text{Pt}}}{f_{\text{Pt}}}$$

- Local O_2 transport resistance can be measured in the same cell as above by varying gas pressure and O_2 concentration.

Greszler, et al. *J. Electrochem. Soc.* (2012) F831.