FC144

Highly-Accessible Catalysts for Durable High-Power Performance

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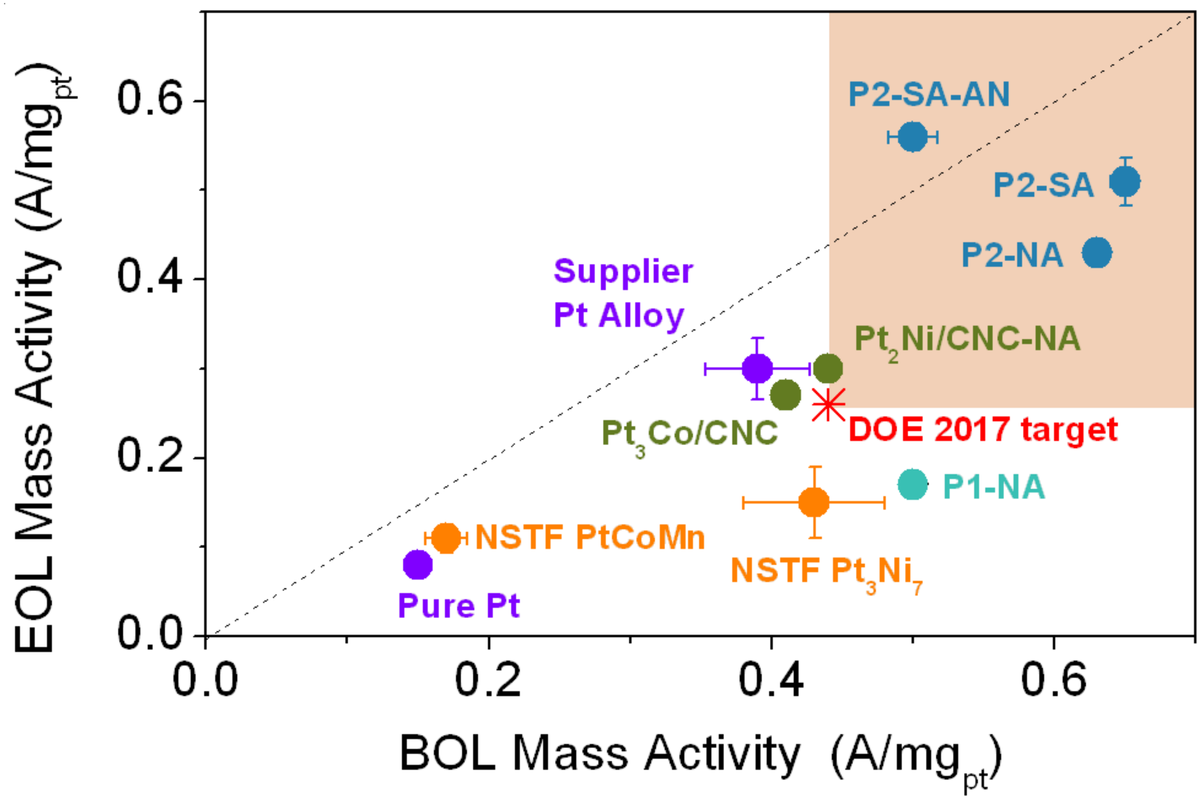
General Motors, Fuel Cell Activities

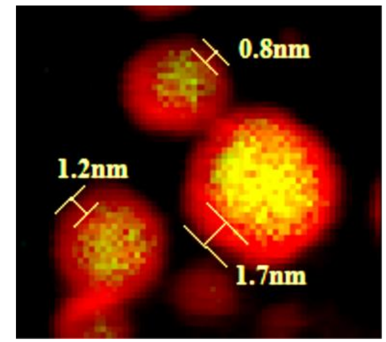
DOE Catalyst Working Group

at Argonne National Lab

July 27, 2016

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





Energy Environ. Sci., 2014.

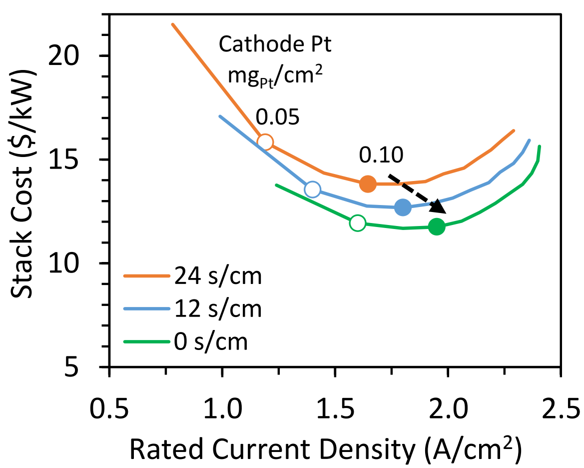
- Meeting DOE ORR durability in MEA. Validated at multiple sites.
- Need thicker Pt shell for MEA stability (>4ML). *Optimization point is very different from RDE*.

Relevance/Impact

Metric	Units	GM PtCo/HSC 2013	GM PtCo/HSC 2016	End of Project Target	DOE 2020 Target
Power per PGM content (150kPa)	kW_{rated}/g_{PGM}	5.3	6.9	***[7.5]***	>8
Power per PGM content (250kPa)	kW_{rated}/g_{PGM}	6.4	7.7	***8.8***	-
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 $0.8 A/cm^2$	30	30	<30	<30
Support cycling (1.0-1.5V, 5k cycles)	mV loss at $1.5 A/cm^2$	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***	-

Values in [..] are unofficial project targets

<u>Stack cost at high volume</u>

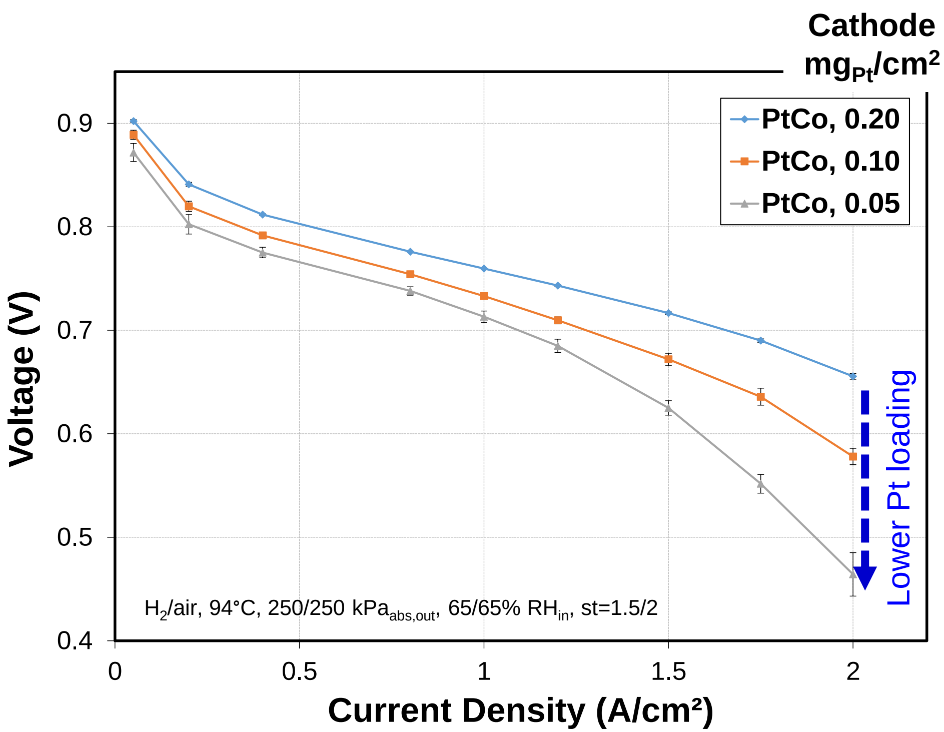


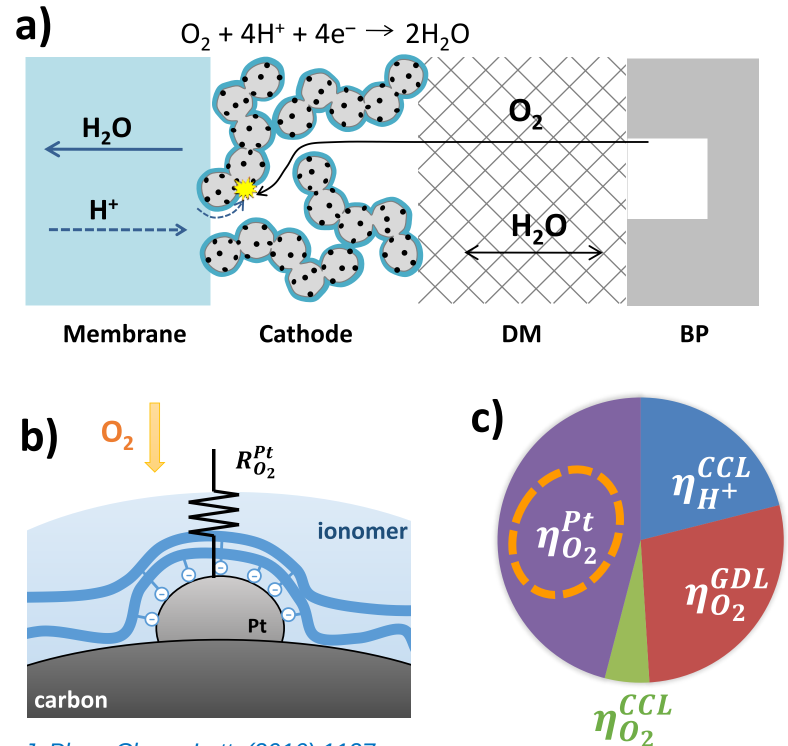
J. Phys. Chem. Lett. (2016) 1127.

- 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





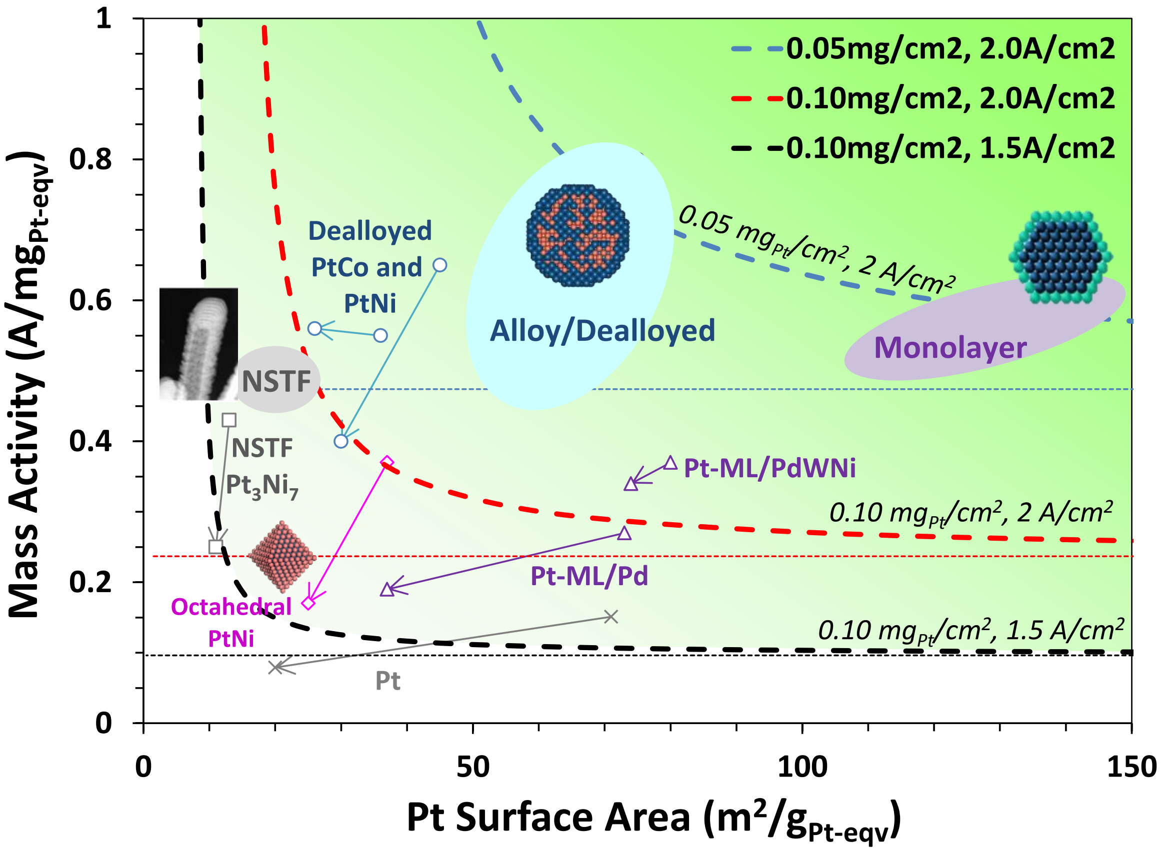
J. Phys. Chem. Lett. (2016) 1127.

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.

Relevance:

Catalyst Roadmap for High-Power Performance

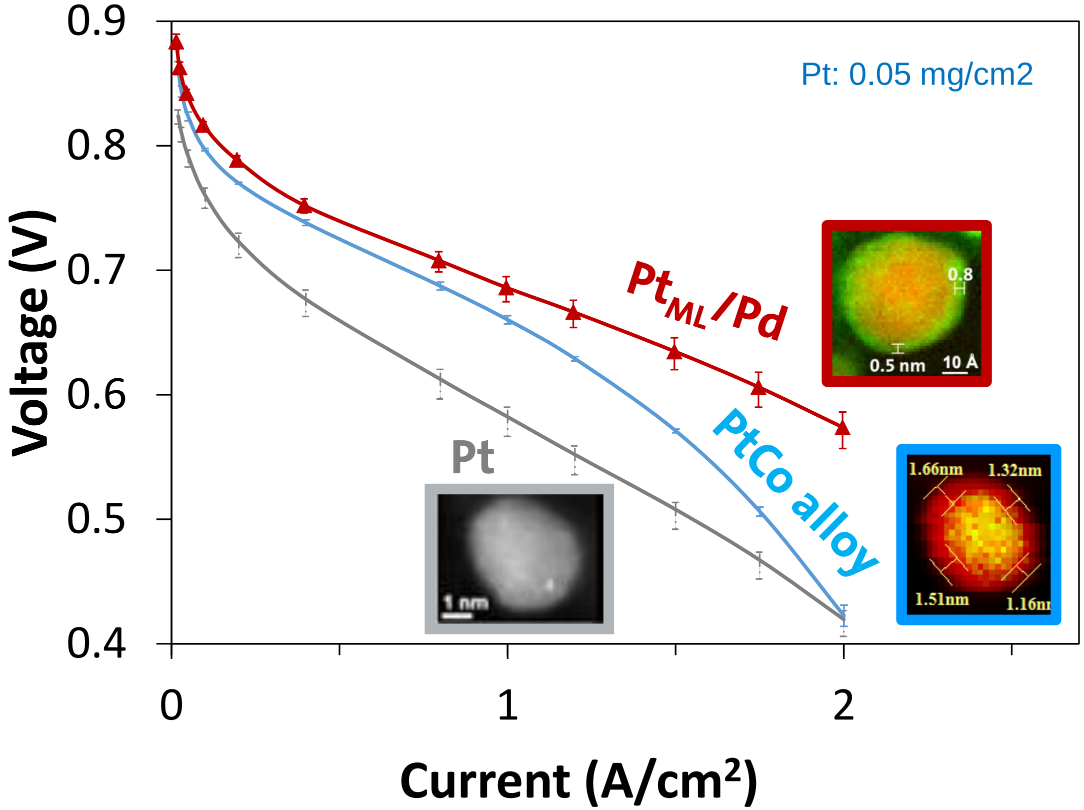


- A catalyst must have a combination of oxygen reduction mass activity and Pt surface area that is higher than these dashed lines.
- Catalysts with *low surface area will have a very hard time* meeting the requirement.
- It is *important to use fuel cell testing (not RDE)* in developing a new catalyst.

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

Relevance:

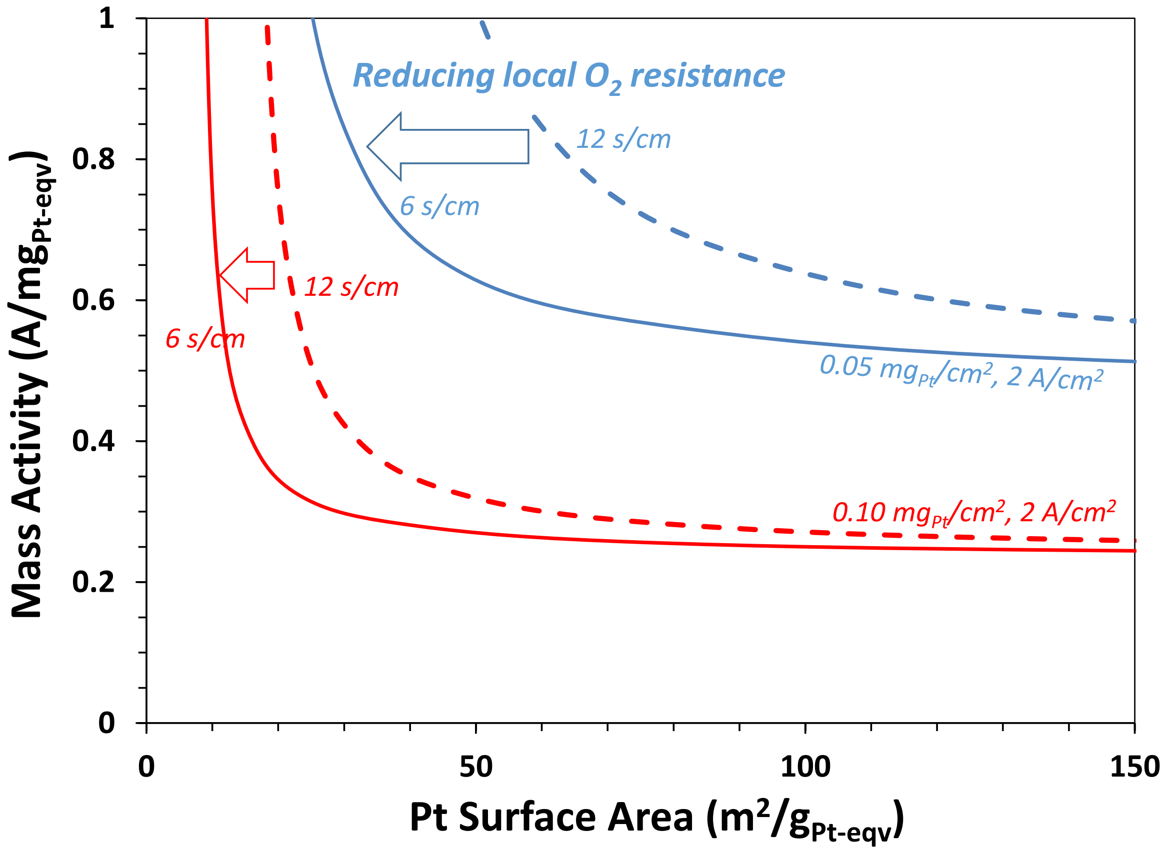
High Surface Area Catalyst *Can* Meet High-Power Performance



- ❑ Still too much PGM in the core (Pd cost about one-third of Pt cost per atom). Not currently economically competitive.
- ❑ Not sufficiently stable. Need improvement in core stability.

ACS Catalysis. (2016) 1578.

Implication of Lower Local O_2 Resistance

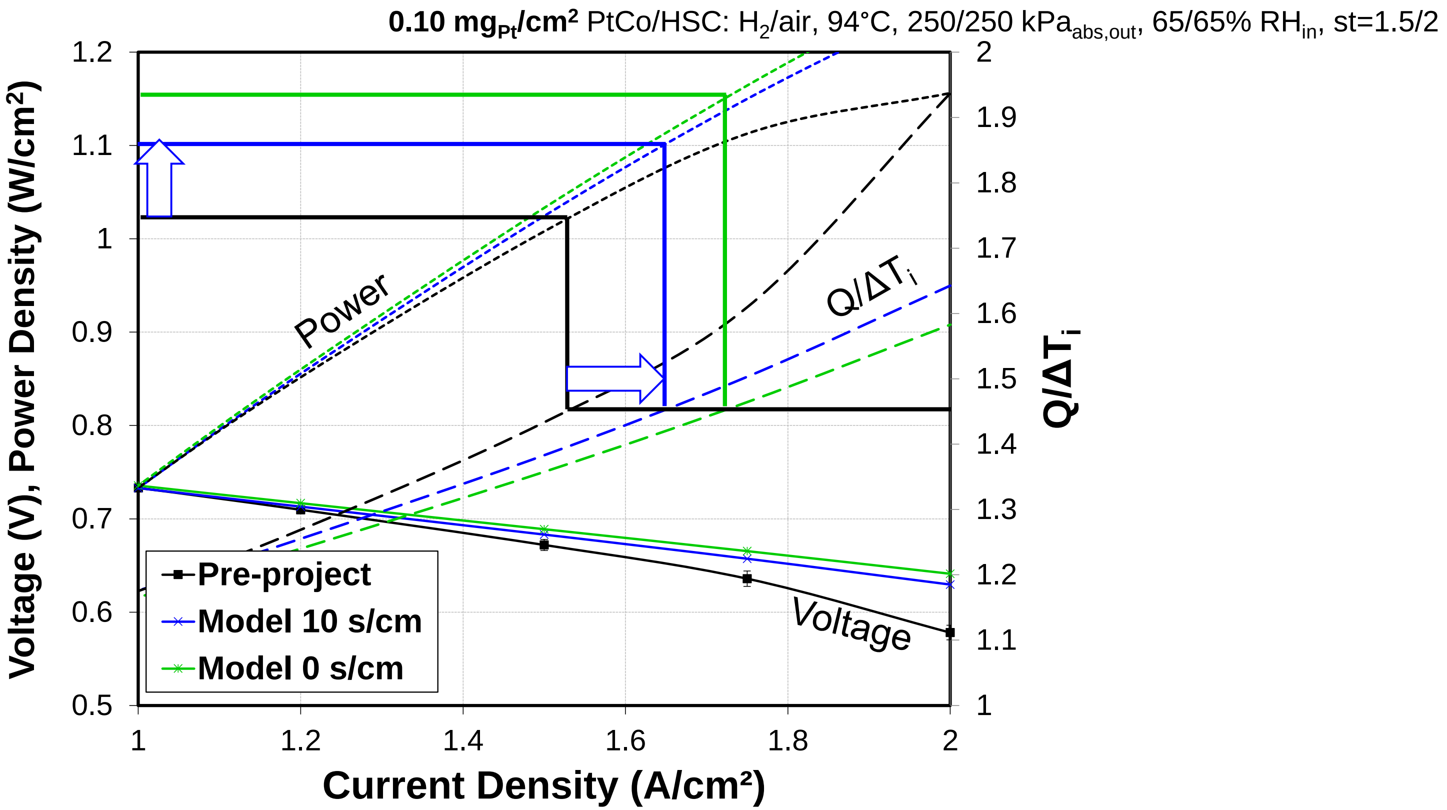


- ❑ If we reduce the resistance by half, the requirement line will basically move left halfway to the Y-axis, enabling many catalysts.

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

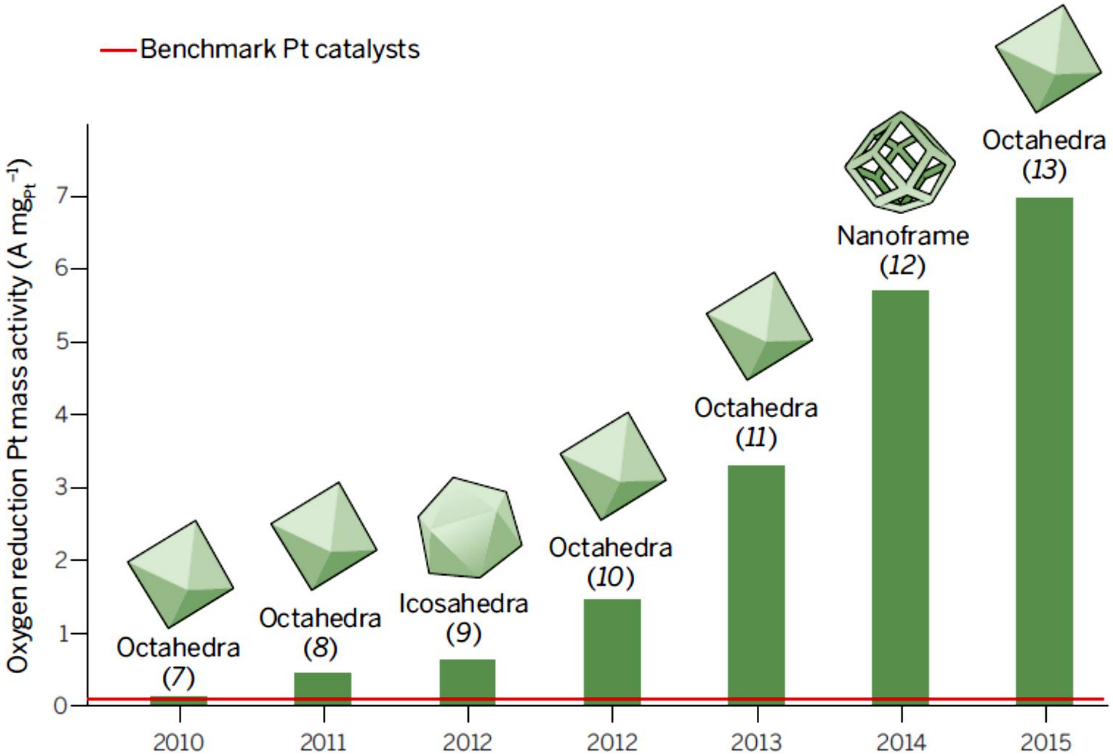
Approach:

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$_{Pt}$**).

Faceted Catalysts

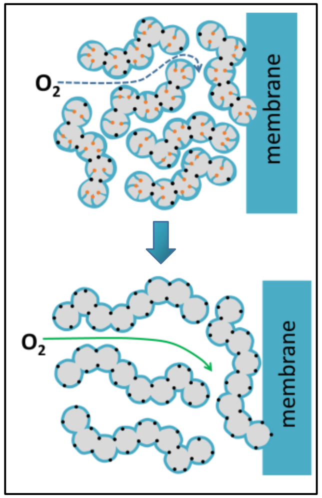


Strasser, *Science* 2015

- Extraordinary progress has been made over the last 6 years. Up to 70x Pt activity enhancement has been demonstrated ex-situ in RDE measurements.
- This translates to **16% improvement in fuel efficiency** or **70x lower Pt usage**, compared to current best (dealloyed PtCo/PtNi).
- Can we make it work in the real world?

Approach:

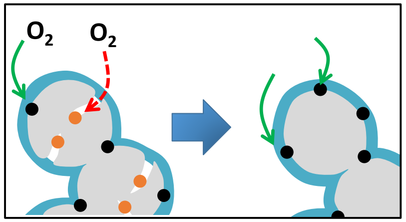
Basic Concept: *Will Succeed if At Least One Works*



❑ Improve O_2 Transport with New Carbon Support

GM/CMU/ Cornell/NREL

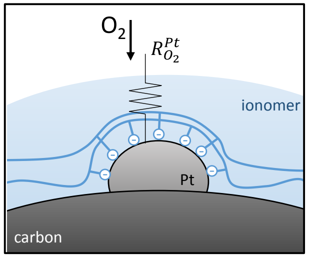
- ➢ Which support is best for performance?
- ➢ Which is best for durability?
- ➢ Do we need HSC to get high ORR kinetic?



❑ Reduce Electrolyte-Pt Interaction

3M/Drexel/GM

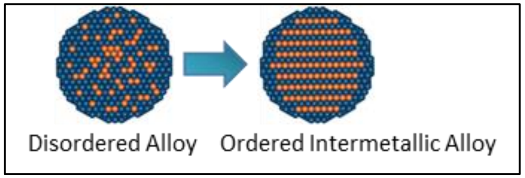
- ➢ From current selection of ionomer/ionic liquid which is the best?
- ➢ Does Pt-ionomer interface change overtime?



❑ Enhance Dispersion and Stability of PtCo Particles

Cornell/GM/NREL

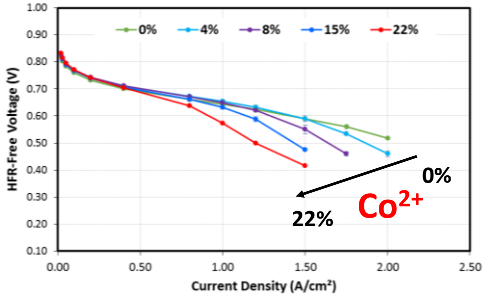
- ➢ Can activity or durability be improved?
- ➢ Can ECSA be improved?



❑ 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?

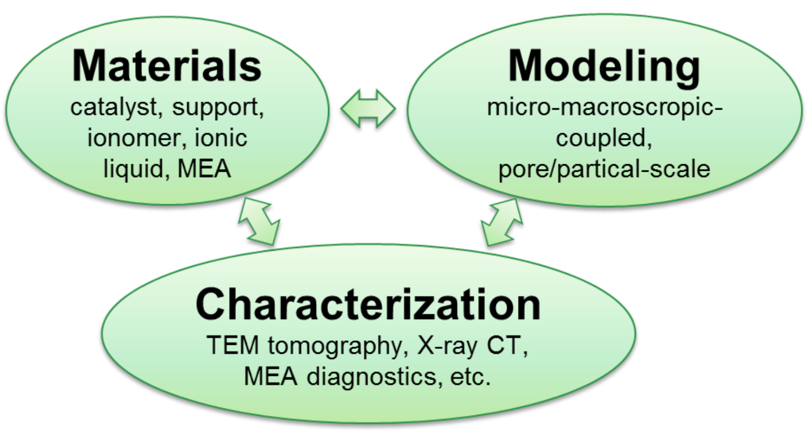


Collaborations:

Project Team

Not signed

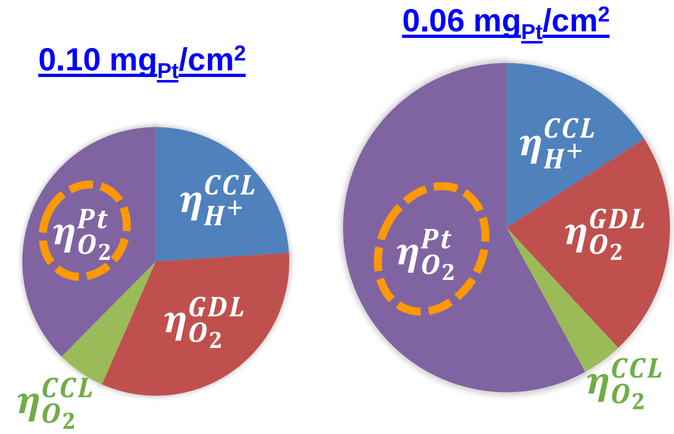
- General Motors (industry)
  - Overall project guidance, synthesis and testing of catalysts.
- 3M Company (industry) – **Dr. Andrew Haug**
  - Selection and pre-fuel-cell evaluation of ionomer candidates.
- Drexel University (university) – **Prof. Joshua Snyder**
  - Selection and pre-fuel-cell evaluation 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

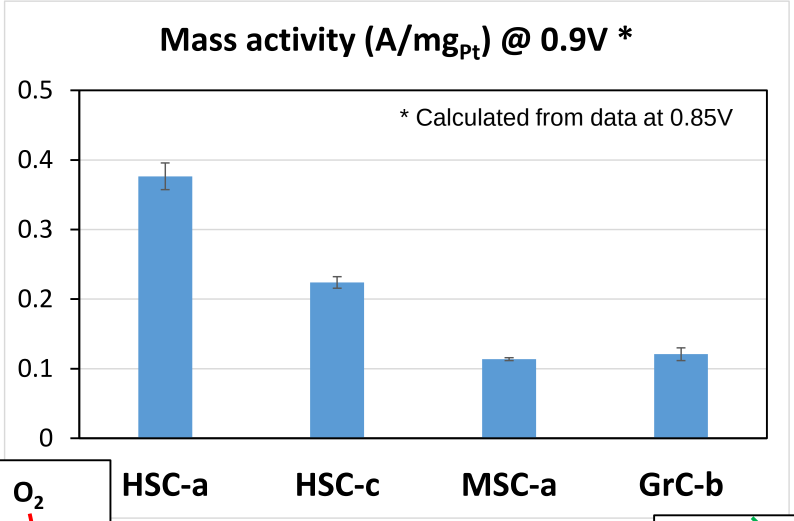


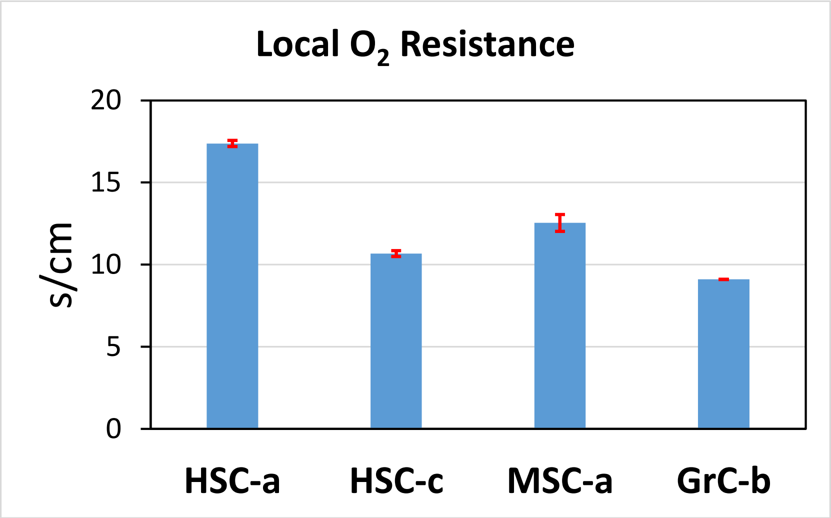
All Pt/C, 20 wt% Pt, D2020, 18µm membrane

Catalyst Support Type	BET (m^2/g_C)	Pt loading (mg/cm^2)	ECSA (m^2/g_{Pt})	Thickness (µm)	Packing thickness (µm/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

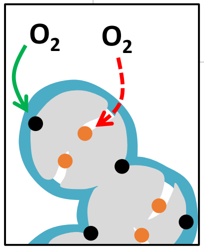
HSC: High-surface-area carbon black
MSC: Medium-surface-area carbon black
GrC: Graphitized carbon black
CNT: Carbon nanotube

Carbon Support Selection: MEA Diagnostics





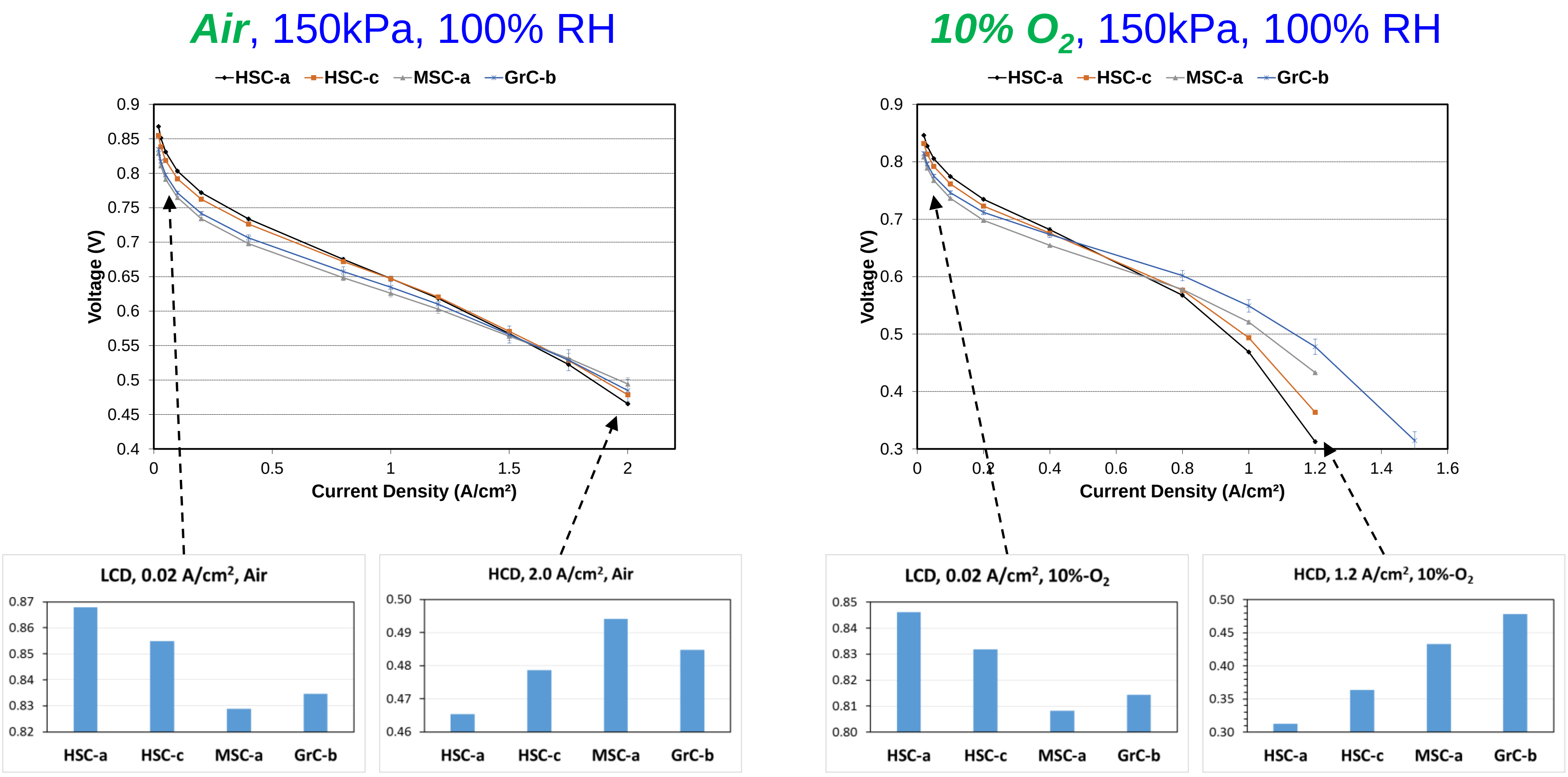
By Limiting current measurement *J. Electrochem. Soc. (2012) F831.*



- 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).

Technical Accomplishment:

Carbon Support Selection: Fuel Cell Performance

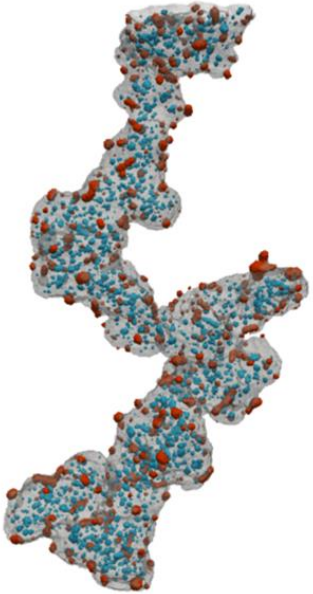


- Fuel cell performance agrees well with diagnostic results. HSC with large amount of internal porosity gives better voltage at LCD but worse voltage at HCD.
- Test at low O_2 partial pressure helps differentiate good vs bad supports, in terms of O_2 transport.

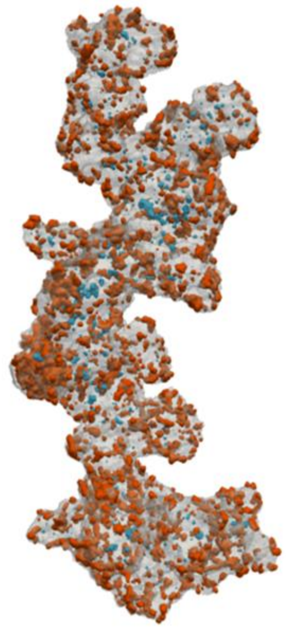
Technical Accomplishment:

Visualization

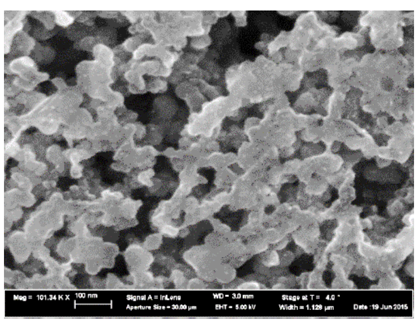
Pt/HSC-a



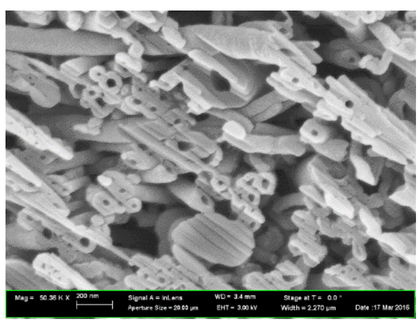
Pt/MSC-a



Pt/HSC-a



Pt/CNT-a

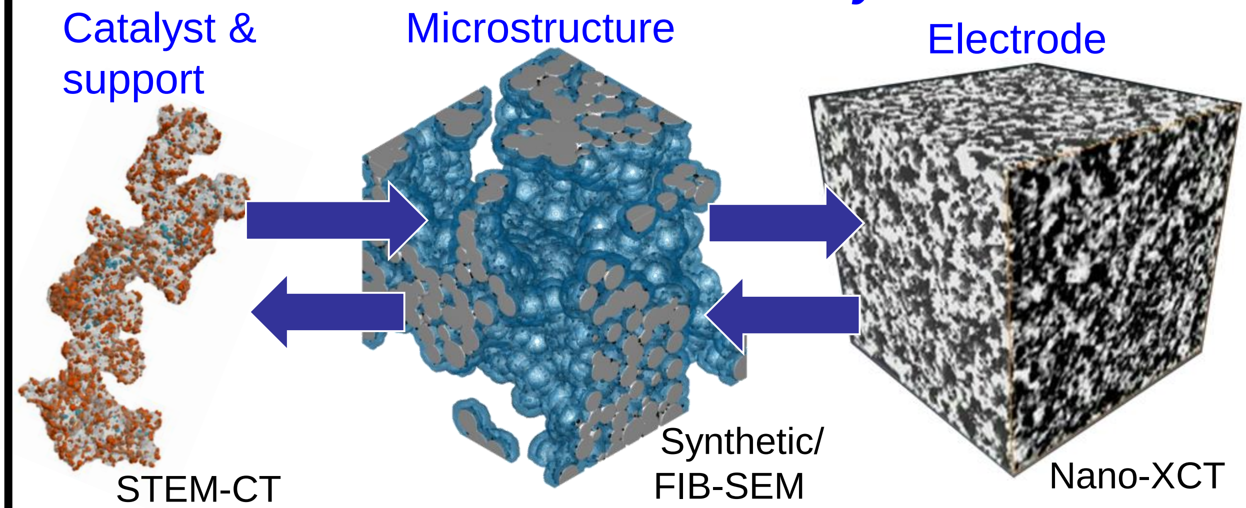


- STEM tomography will be used to locate Pt particles in relation to carbon.
- As shown on the left, the majority of Pt on HSC-a is embedded (blue) in the carbon, in contrast to MSC-a where its majority is on the carbon surface (brown).
- Similar quantitative analyses will be done on selected catalysts.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

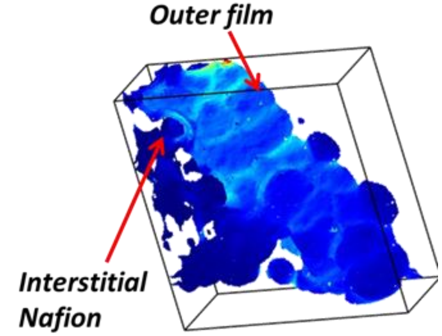
Technical Accomplishment:

Modeling: Refining at Pore/Particle Scale

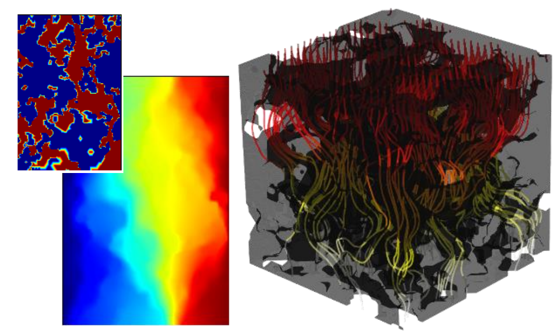
Domains and Geometry



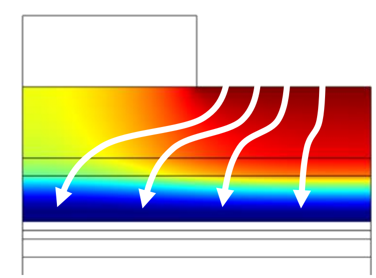
Local Transport & Reaction



Electrode Performance



MEA Performance

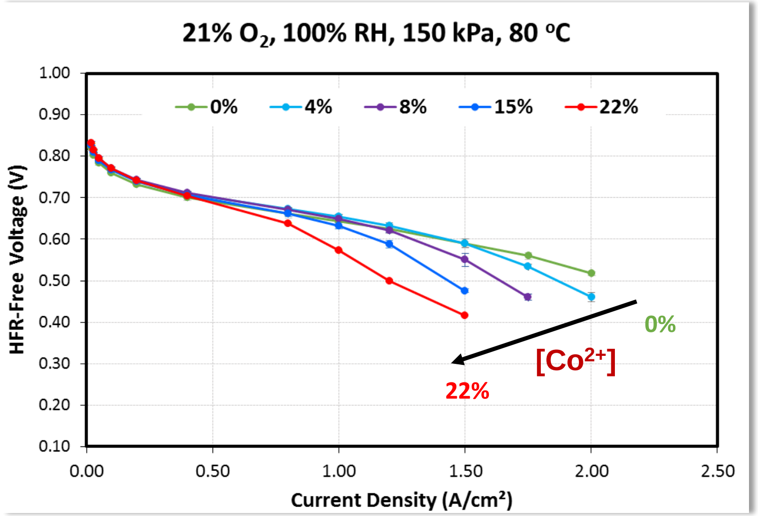


- Understand and develop solutions to transport limitations and performance bottlenecks at the catalyst & support, in the electrode microstructure, and across electrode thickness.
- 3D geometry extracted from visualizations at multiple length scales and synthetic structures for scale bridging.
- Understand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

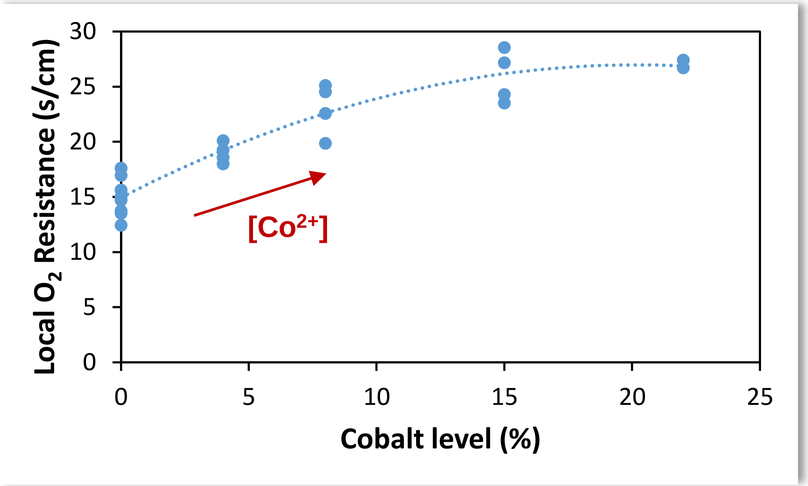
Technical Accomplishment:

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

Co^{2+}-doped Pt/C



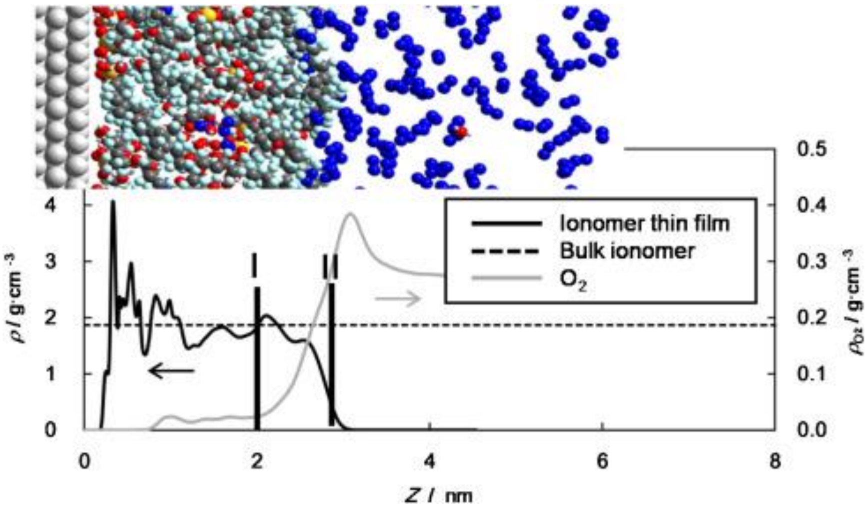
Local O_2 Transport Resistance



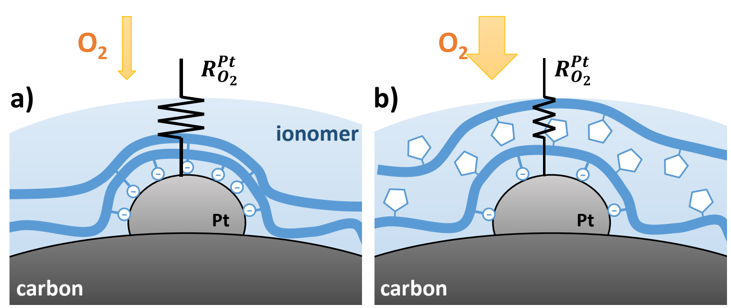
- Because the maximum amount of Co available in a 0.10 mg_{Pt}/cm^2 PtCo cathode is equivalent to 8% exchange rate, **8% is the worst case scenario** with regard to MEA performance.
- However, at HCD, local $[Co^{2+}]$ can be much higher in the cathode, therefore, it is important to study electrode properties 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.

Dense Ionomer at the Interface *May* Lead to Loss

MD/DFT of ionomer-Pt interface

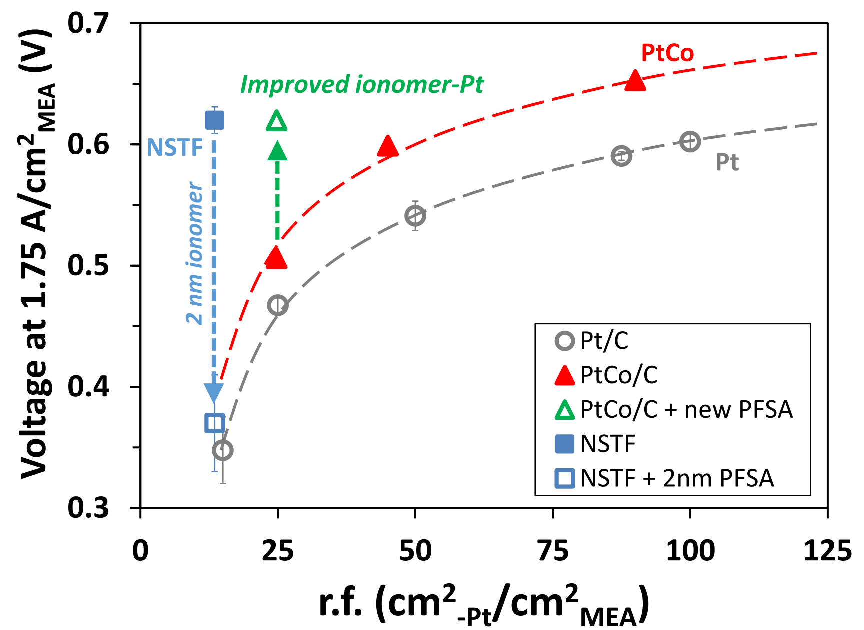


Jinnouchi et al. *EC Acta,* 2016, 188, 767



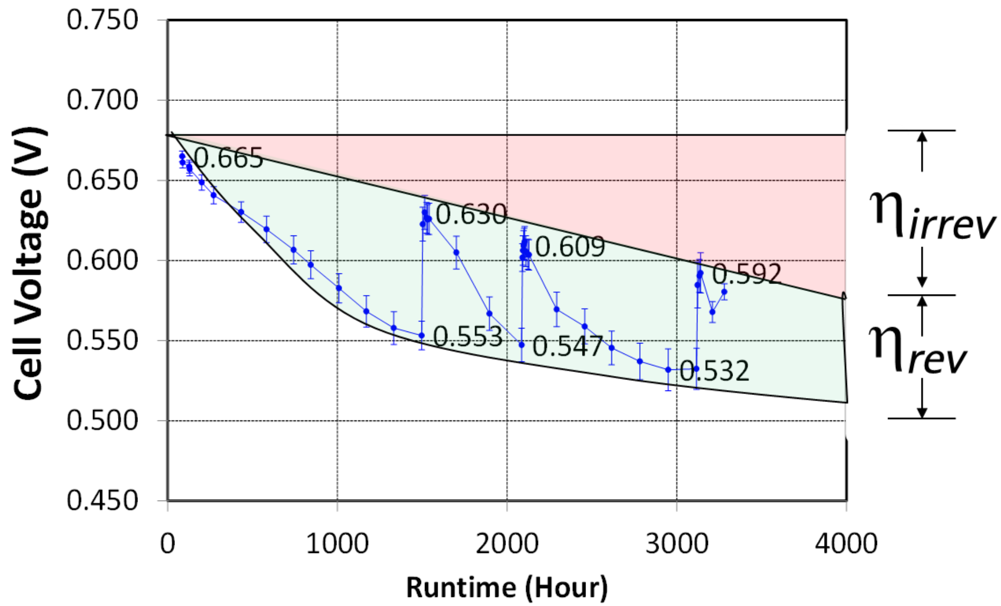
JPC Lett. 2016, 7, 1127

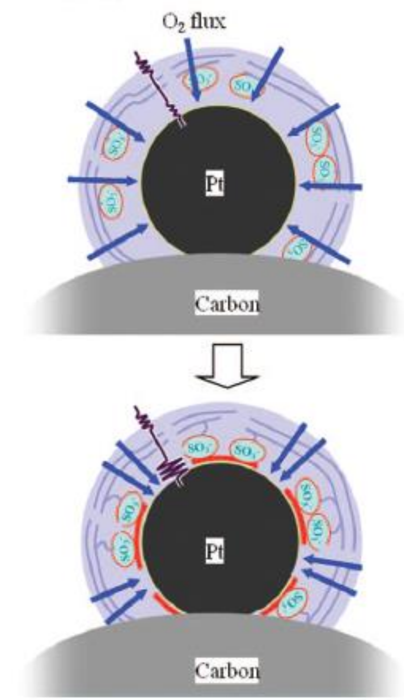
- MD-DFT simulation showed formation of a dense layer of ionomer adjacent to the Pt surface reducing O_2 concentration leading to large O_2 resistance.
- It is shown that performance can be substantially improved with ***alternative ionomer*** that has open structure. However, the ionomer did not have prolonged effect.
- ***Need better fundamental understanding*** to provide materials development guideline.



Interface Appears to Change Over Time in Fuel Cell

Long-term operation in a fuel cell

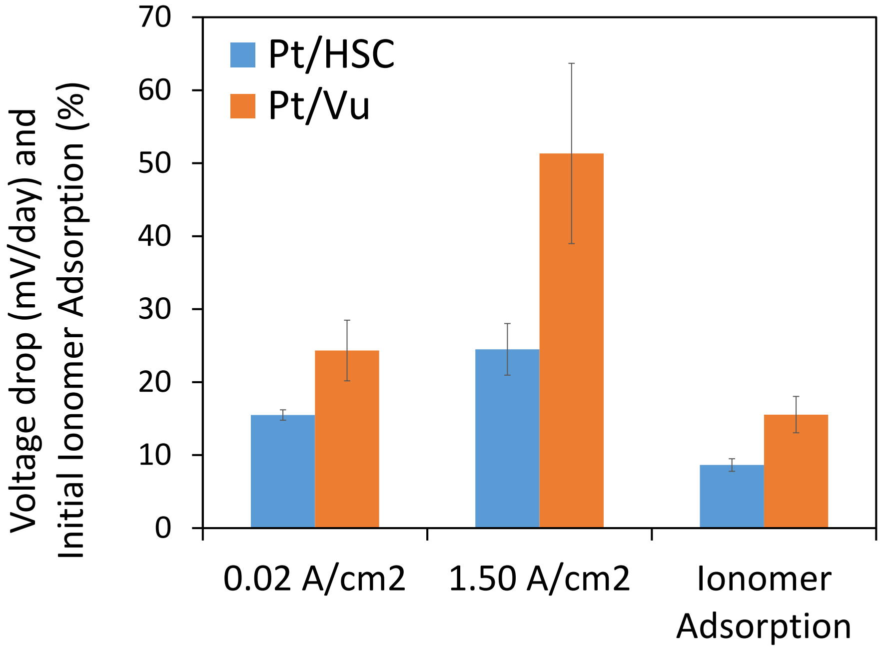




Jomori et al., *JES* (2013) 160, F1067.

- On low-Pt electrode, ‘recoverable’ performance loss is substantial. Will limit real-life efficiency. Need to ***understand the source*** better.
- How can we characterize this interface and ***correlate it to fuel cell performance*** ?

Catalyst with Larger Ionomer Adsorption Shows Larger Reversible Degradation



- Reversible decay during dry operation is larger for catalyst with larger initial ionomer adsorption.

Comparison of Some Properties

GM

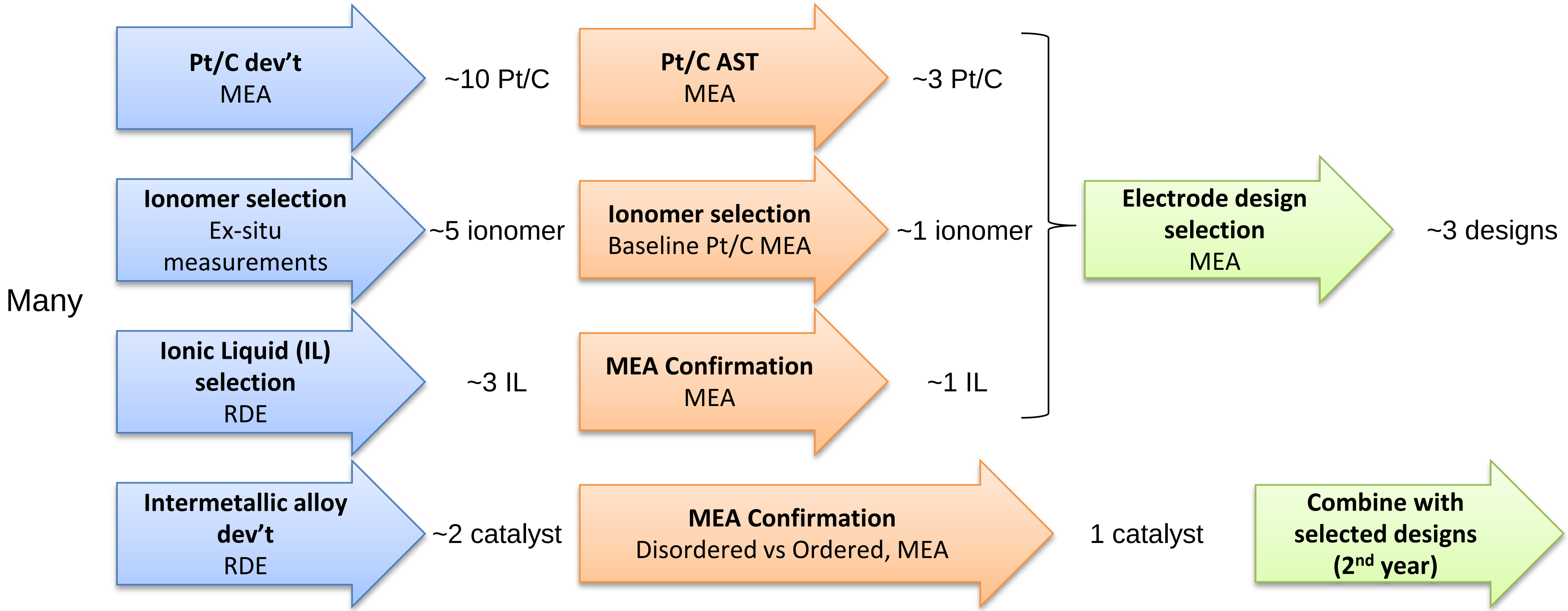
Check marks (✓) indicate superior properties

	Porous Carbon	Solid Carbon
ORR activity	✓✓	
Proton transport		✓
O_2 transport		✓
Water transport		✓
Pt dispersion	✓	
Carbon corrosion		✓
Particle coalescence	✓	
Reversible degradation	✓	

- ❑ Decision between porous and solid carbons is not simple.

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.

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.
- CO displacement method to evaluate ionomer-Pt adsorption and correlate the adsorption to fuel cell performance was developed.

Acknowledgements

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- Wenbin Gu
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- Nagappan Ramaswamy
- Shruti Gondikar
- Mohammed Atwan
- Craig Gittleman
- Mark F. Mathias
- Peter Harvey and team
- Sonam Patel, Kathryn Stevick and team

3M

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- Prof. Shawn Litster (sub-PI)

Cornell University

- Prof. David A. Muller (sub-PI)
- Prof. Héctor Abruña
- Elliot Padgett

Drexel University

- Prof. Joshua Snyder (sub-PI)

NREL

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- Jason Christ
- Jason Zack
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