FC144

Highly-Accessible Catalysts for Durable High-Power Performance

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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: 75%

Budget

- Total Funding Spent as of 12/31/18: $2.4M
- Total DOE Project Value: $4.0M

  (additional direct funding to NREL $0.6M)
- Cost Share: 21.7%

Barriers

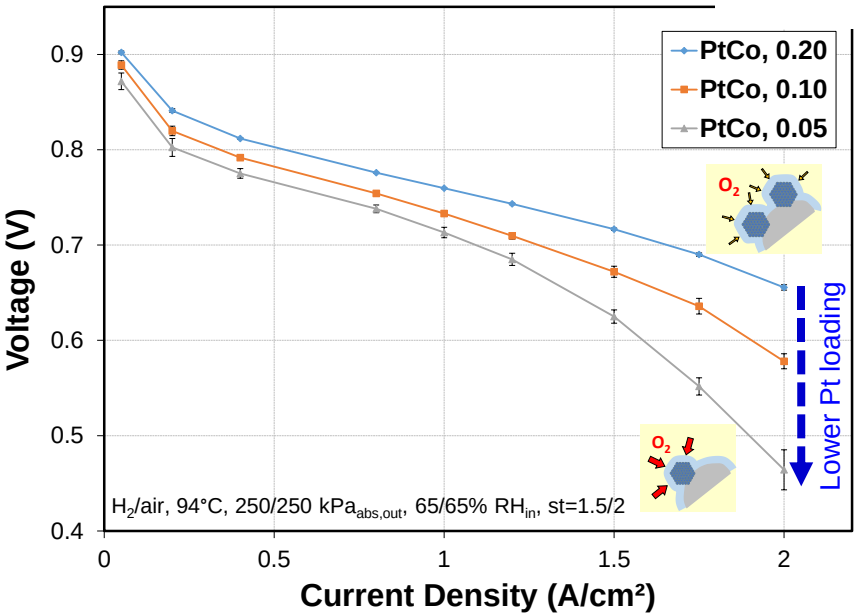
- B. Cost
  - Decrease amount of precious metals.
- A. Durability
  - Improve kinetic activity and high current density performance
- C. Performance
  - Achieve and maintain high current densities at acceptably-high voltages

Partners

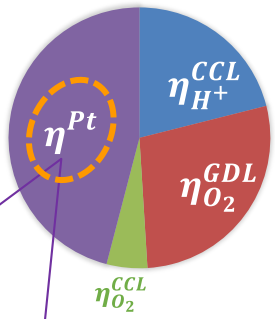
- Subcontractors:
  - 3M Company
  - Carnegie Mellon University
  - Cornell University
  - Drexel University
  - NREL
- Project lead: GM

Relevance:

Challenge: Local Transport Losses

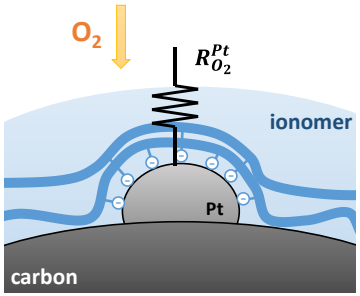


Mass-transport Voltage Losses

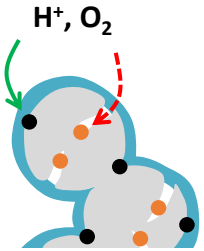


1.75 A/cm² on a 0.10 mg_{Pt}/cm^2 cathode

O_2 through Ionomer/Pt Interface



H+ and O_2 through Carbon Micropores



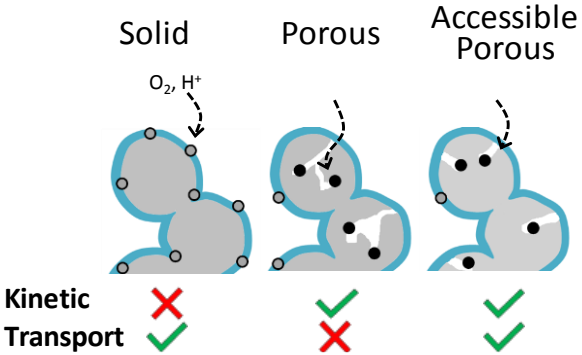
- FC087 Dealloyed PtCo and PtNi *met Catalyst Targets* (activity and durability) ***but not MEA Targets*** (high current density, HCD).
- At HCD, high flux of O_2 and proton per a given Pt area causes large voltage loss on low-Pt cathode.
- The 'local transport resistance' dominates the mass transport 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.

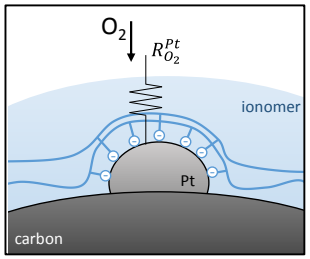
Approach:

Work Focuses in the Past Year

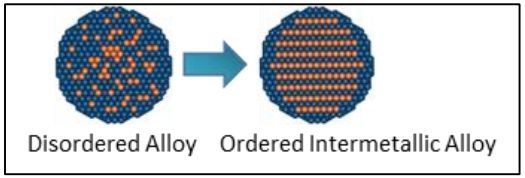
- New Carbon Supports
  - Study local transport using MEA electrochemical diagnostics, microscopy, and simulation.
  - Understand support effects on durability.
  - Optimize PtCo on accessible carbon with emphasis on stability



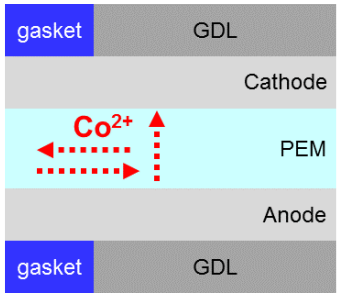
- Electrolyte-Pt Interfaces: Ionomer and Ionic Liquid
  - Develop process to add ionic liquid in MEA and study its effect.
  - Identify new electrolyte-Pt interface affects fuel cell performance.



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



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



Relevance:

Targets and Status

Metric	Units	PtCo/KB 2016	PtCo/HSC-f	Ordered-PtCo/HSC-f	Ordered-PtCo/KB	PtCo/HSC-f	DOE 2020 Target	Project Target
PGM total loading (both electrodes)	mg/cm^2	0.125 (0.025+0.10)	←	←	←	0.075 (0.015+0.06)	<0.125	←
Mass activity @ 900 $mV_{iR\text{-}free}$	A/mg_{PGM}	0.62†	0.7†	0.7†	0.53†	0.7†	>0.44	←
Loss in catalytic (mass) activity	% loss	30%	59%*	45%*	16%	tbd	<40%	←
Performance at 0.8V (150kPa, 80°C)	A/cm^2	0.304	tbd	tbd	0.301	tbd	>0.3	←
Power at rated power (150kPa, 94°C)	W/cm^2	0.8	0.95	0.94	tbd	0.91	>1.0	-
Power at rated power (250kPa, 94°C)	W/cm^2	1.01	**1.31**	1.29	1.15	1.23	-	>1.1
PGM utilization (150kPa, 94°C)	kW/g_{PGM}	6.4	7.6	7.5	tbd	**12.1**	>8	←
PGM utilization (250kPa, 94°C)	kW/g_{PGM}	8.1	10.5	10.3	9.2	**16.4**	-	>9.1
Catalyst cycling (0.6-0.95V, 30k cycles)	mV loss at $0.8A/cm^2$	24	39*	25	8	tbd	<30	←
Support cycling (1.0-1.5V, 5k cycles)	mV loss at $1.5A/cm^2$	>500	>500	tbd	tbd	tbd	<30	-

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

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

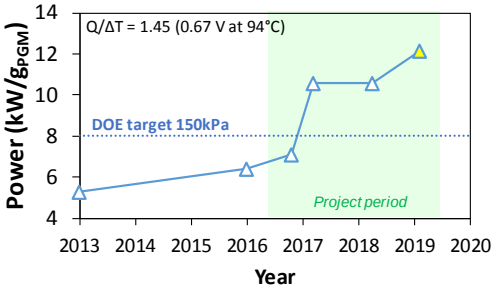
** Meet target in absolute term (e.g. >0.26 A/mg_{PGM})*
† MA at $0.9V_{RHE}$ in cathodic direction

Objectives

- Reduce overall stack cost by improving high-current-density (HCD) performance adequate to meet DOE heat rejection and Pt-loading targets.
- Maintain high kinetic mass activities.
- Minimize catalyst HCD degradation.

This Year Target Highlights

- Improved durability of accessible-PtCo with minimal performance penalty using intermetallic ordering.
- Narrowed gap to 1 W/cm^2 (150kPa) target (now 0.95 W/cm^2).
- Boosted PGM Utilization (to 12.1 vs target of 8 kW/g_{PGM} at 150kPa) by reducing Pt in both anode and cathode.



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 ✓

	2018 AMR	2019 AMR
❑ Downselect carbon support, ionomer, ionic liquid	100%	100%
❑ Measure the effect of leached Co^{2+} and Pt surface area	100%	100%
❑ Develop dealloyed catalyst from ordered intermetallic alloy	100%	100%
❑ Visualize carbon structure and Pt location on selected catalysts	100%	100%
❑ Model baseline material	100%	100%

TASK 2 - Development of Dealloyed Catalyst with Preferred Catalyst Design

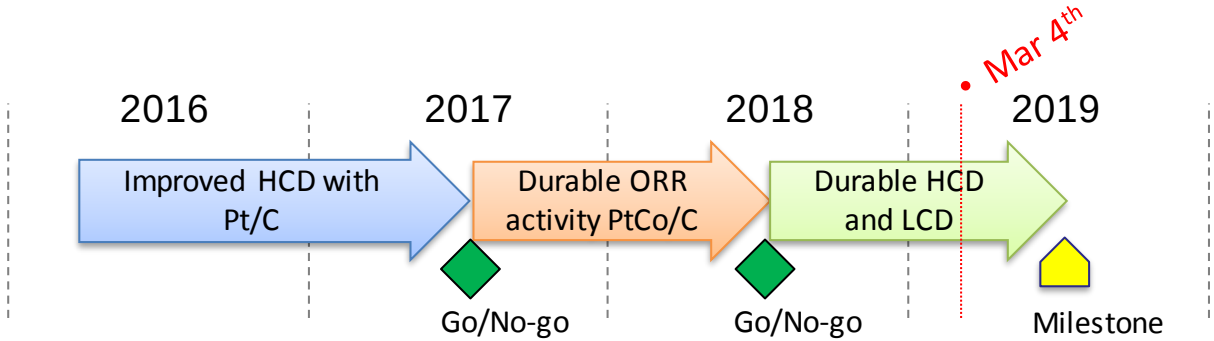
Go/No-go criteria : >0.44 A/mg$_{PGM}$, <40% mass activity loss with preferred design ✓

❑ Develop dealloyed catalyst on preferred support	80%	100%
❑ Implement selected ionomer and ionic liquid with selected catalysts	60%	100%
❑ Visualize fresh PtCo/C and post-AST Pt/C	90%	100%
❑ Model PtCo/C before and after AST	70%	100%

TASK 3 - Optimization for Durable HCD and LCD Performance

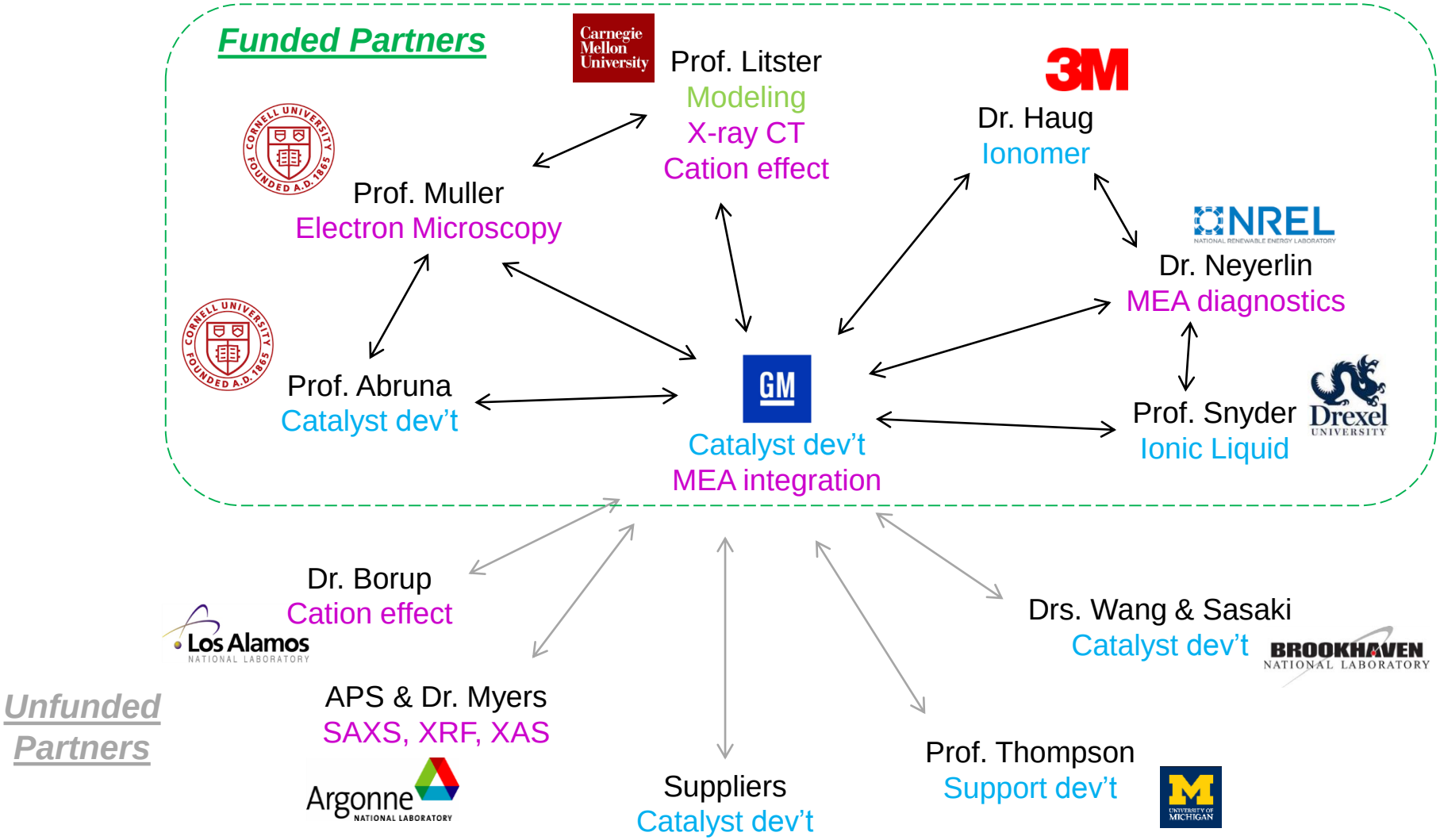
Milestone: >1.1 W/cm^2, >9.1 kW$_{rated}$/g$_{Pt}$, and Q/ΔT <1.45 ✓ ***Jun 2019***

❑ Identify root cause and improve durability and performance of PtCo/C	20%	70%
❑ Evaluate effect of selected ionomer/IL on HCD and durability of improved PtCo catalyst	10%	80%
❑ Integrate new catalyst design with other state-of-the-art FC components	20%	80%
❑ Make available to DOE the improved catalyst in 50 cm^2 MEAs	10%	10%
❑ Visualize and model improved catalyst	10%	50%



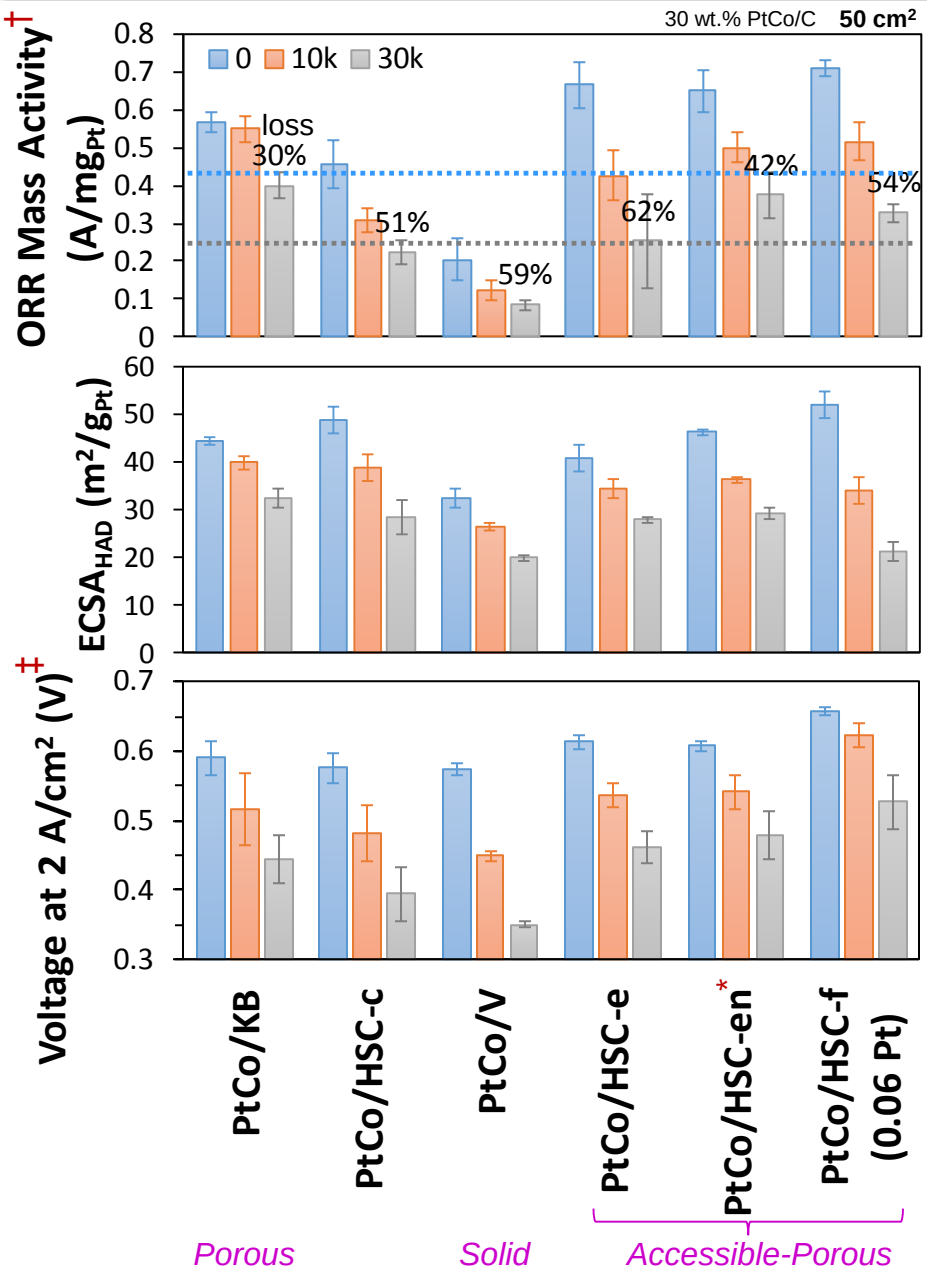
Collaborations

Materials dev't
Characterization
Modeling



From 2018 AMR

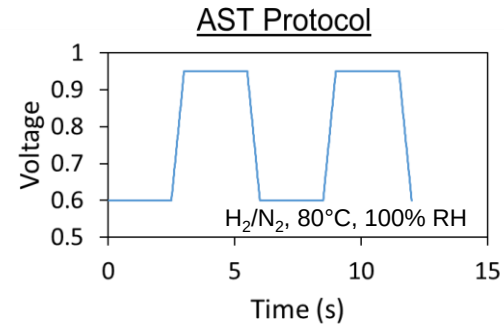
Accessible-PtCo Stability



ORR Targets

.44 A/mg$_{Pt}$ BOL

.26 A/mg$_{Pt}$ EOT

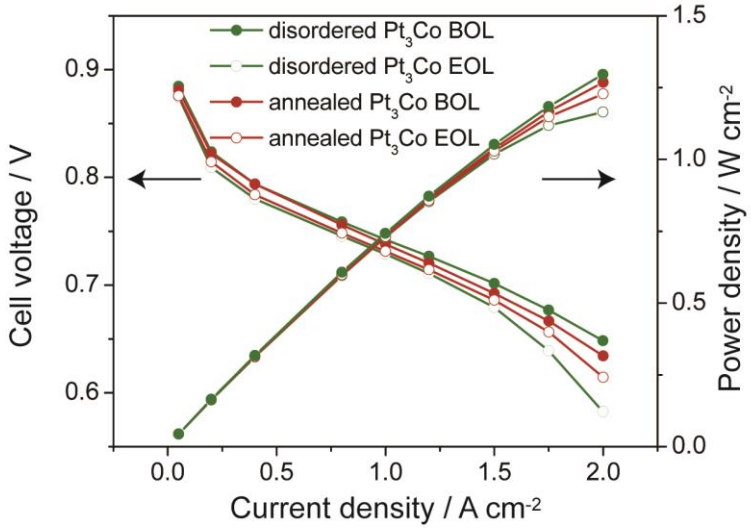


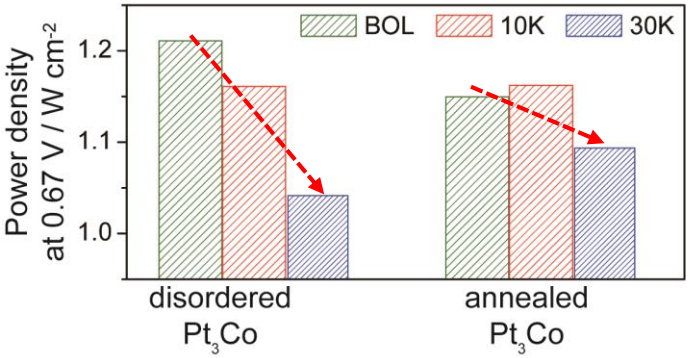
- Although catalysts with Accessible-porous carbons outperform other catalysts at HCD (2 A/cm²) throughout the test, they show larger % losses of ORR MA and ECSA compared to KB.

* 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:

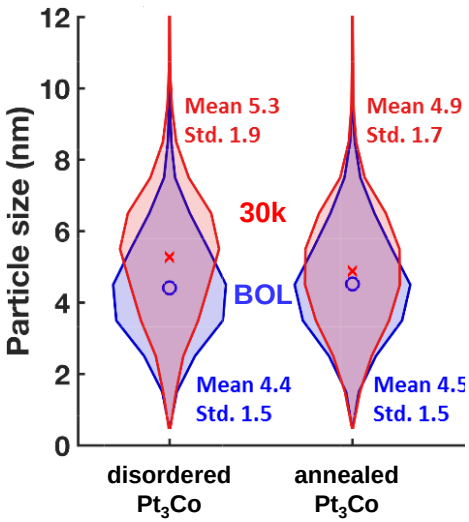
Improving Stability with Intermetallic Pt_3Co

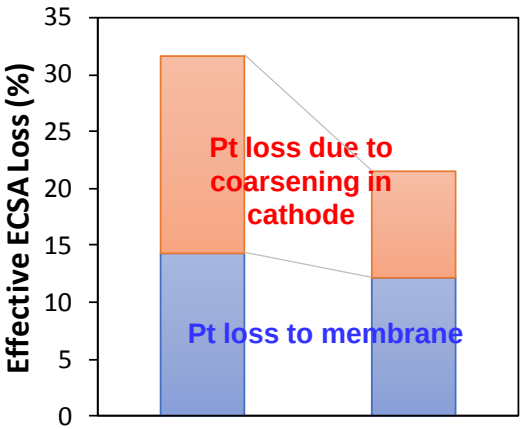




PNAS (2019) 116, 1974

Pt Loss Determined by TEM



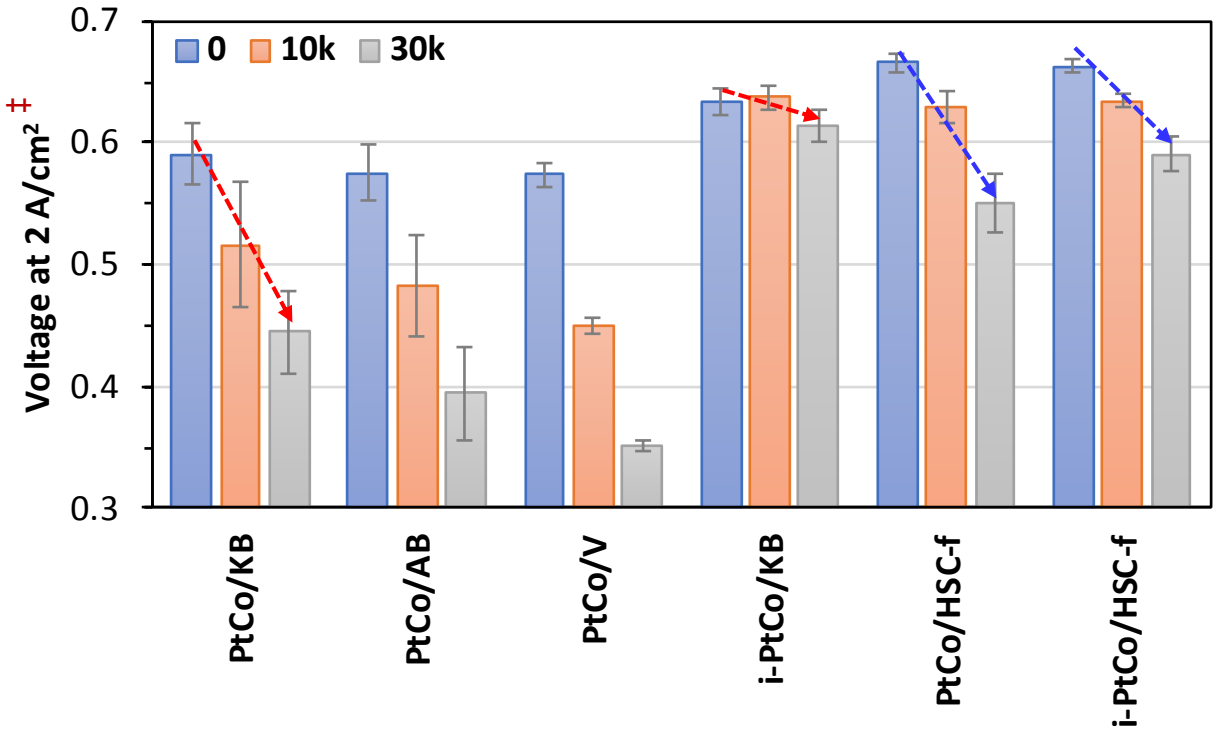


- Thermal annealing to encourage intermetallic ordering decreases ORR activity, ECSA, and HCD losses by about one half.
- TEM confirms MEA results: less particle growth, less Pt loss to membrane.
- Changes in Co/Pt ratio in cathode catalyst were comparable (~45%).

Technical Accomplishment:

Also Effective on Accessible-PtCo

Carbon Supports and Annealing Effects on HCD Stability



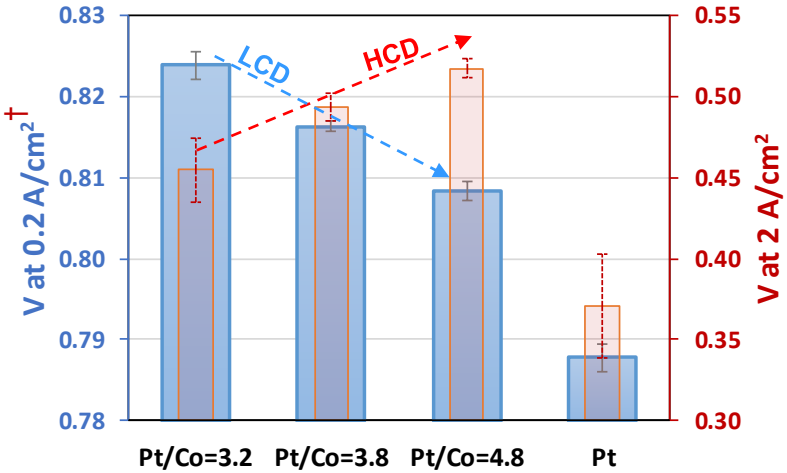
- Thermal annealing optimization study (time & temperature) was done on PtCo/KB and PtCo/HSC-f.
- Results from the best treatment condition are shown, although it was found that similar results were achievable among a wide range of condition, reflecting its robustness.
- Appears to be effective on accessible-porous carbon as well.

‡ H_2/air, 94°C, 250 kPa_{abs}, 65% RH, stoich 1.5/2
Error bars: two σ

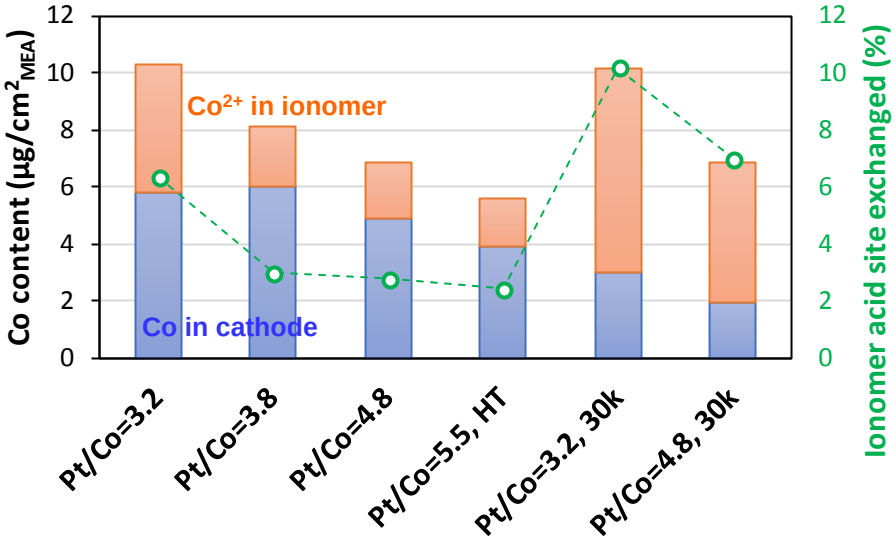
Technical Accomplishment:

Pt/Co Composition Trade-off

Voltages at LCD and HCD vs Pt/Co ratio



Co loss to ionomer phase‡



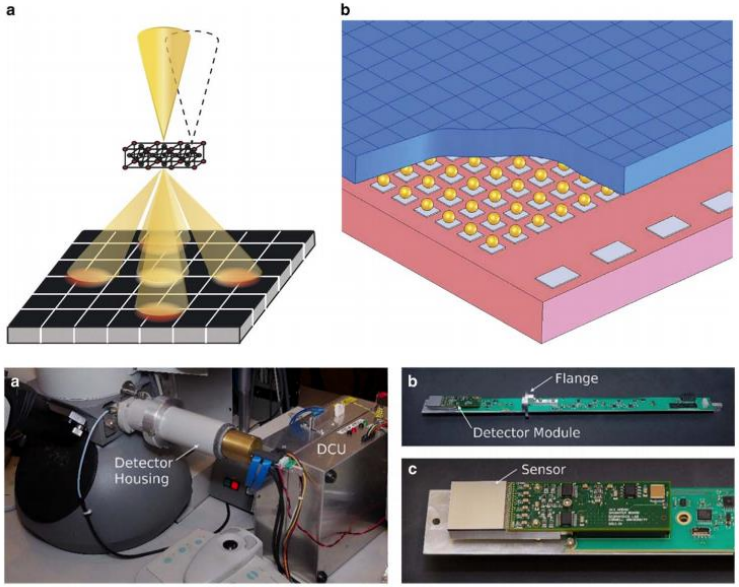
- Catalysts with higher Co content give higher LCD but lower HCD.
- Noticeable amount of Co is lost from the catalyst even at beginning-of-life, further loss after AST.
- Trade-off is not simple, depending on users' operating condition, drive cycle, and MEA design.
- Need to better quantify/monitor Co amount during life, and ultimately, make the catalyst less prone to Co dissolution.

† H_2/air, 80°C, 150 kPa_{abs}, 40% RH_{in}, stoich 1.5/1.8
Error bars: two σ
‡ Co content measured by EPMA and ICP

Technical Accomplishment:

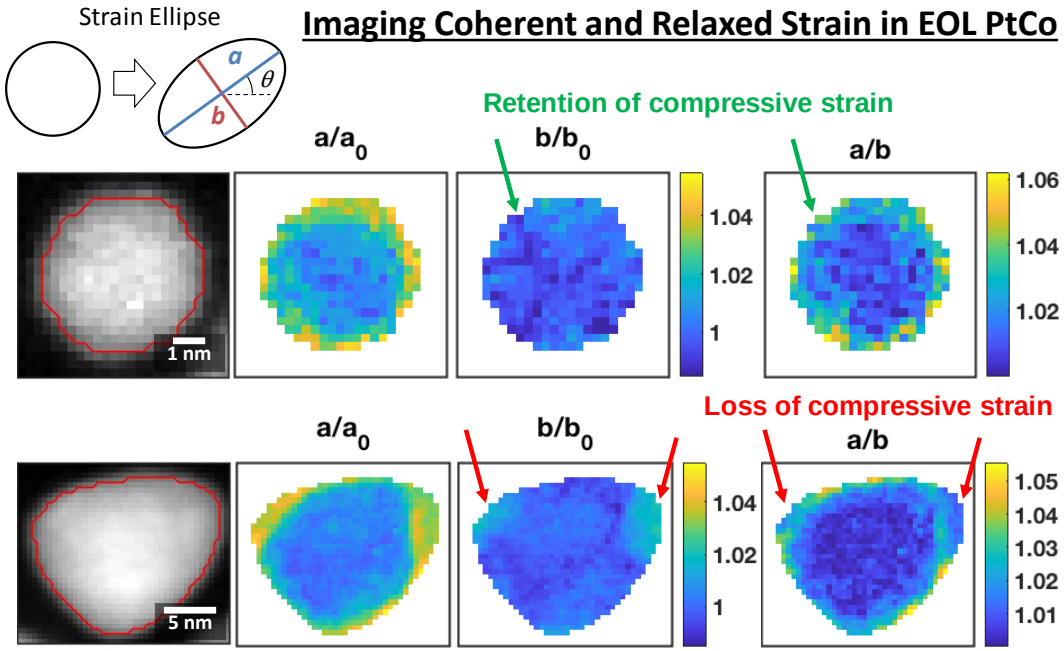
Sub-nm Resolution Lattice Strain Mapping

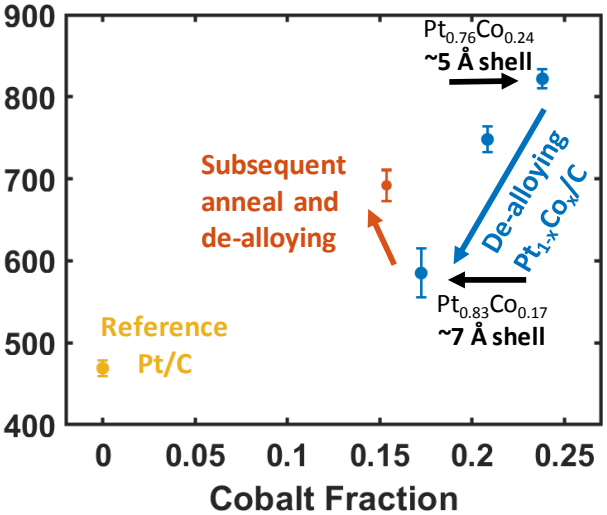
Cornell's Electron Microscope Pixel Array Detector



Microscopy and Microanalysis, *22*(1), 237–249, 2016.

Imaging Coherent and Relaxed Strain in EOL PtCo

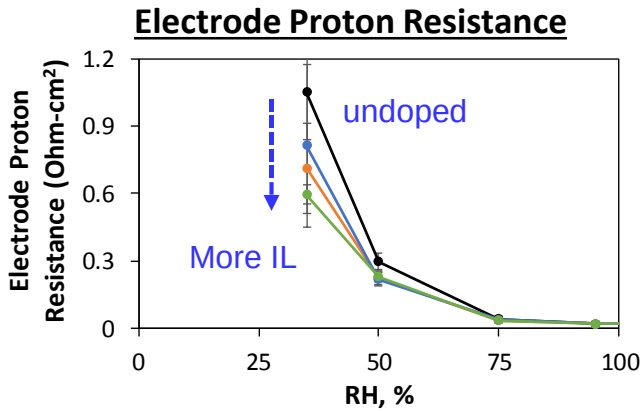


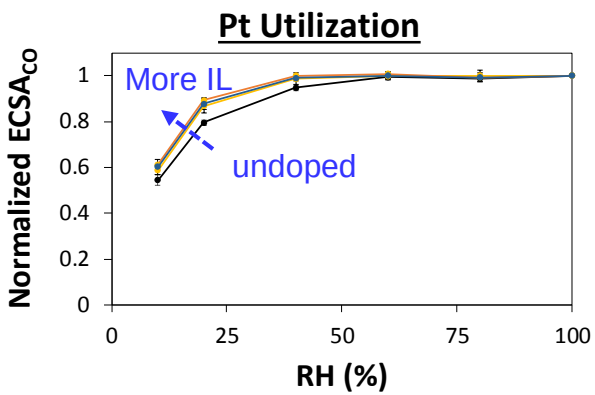


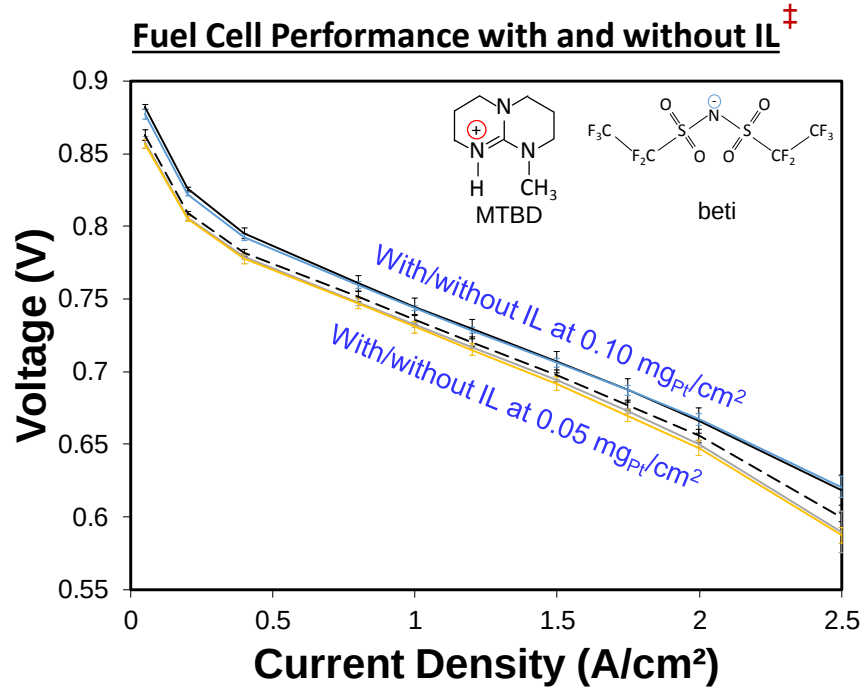
- Fast *direct* characterization of lattice strain with <1nm resolution
- When acid leached PtCo, activity loss is more than expected from geometric strain relaxation alone.
- Subsequent annealing can recover activity, possibly by removing lattice dislocations
- Observed some dislocations (defects) in cycled and aggressively leached particles.

Technical Accomplishment:

Ionic Liquid with Accessible-PtCo







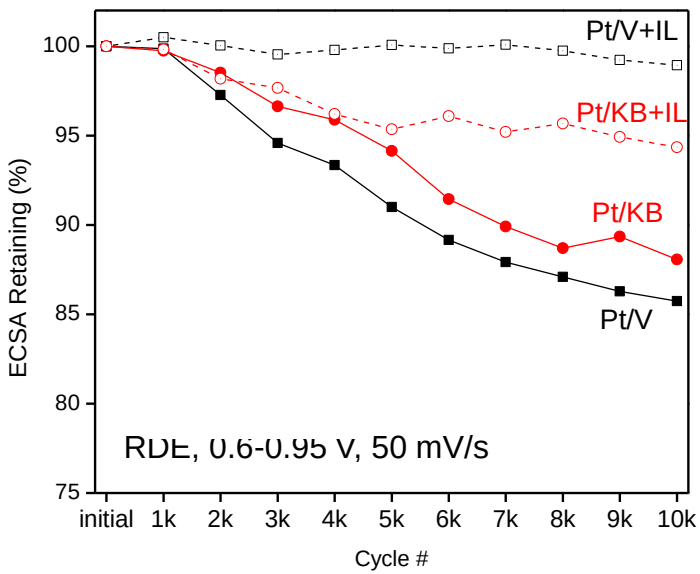
‡ H_2/air, 94°C, 250 kPa$_{abs}$, 65% RH, stoich 1.5/2
Error bars: two σ

- Improved electrode proton conduction and Pt utilization under dry conditions were confirmed.
- Unfortunately, IL benefits on fuel cell HCD performance hasn't been observed on PtCo/HSC-f.
  - Because of the fact that we had observed several times its benefit on PtCo/KB, makes us believe that the benefit is muted on PtCo/HSC-f due to its already-high Pt utilization at a relatively wet condition under normal operation.
- Ongoing effort to optimize IL application, and to evaluate IL potential durability benefit (next slide).

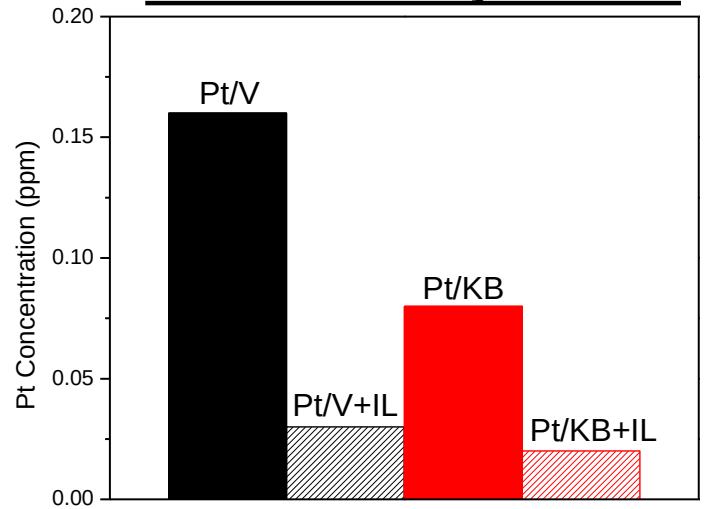
Technical Accomplishment:

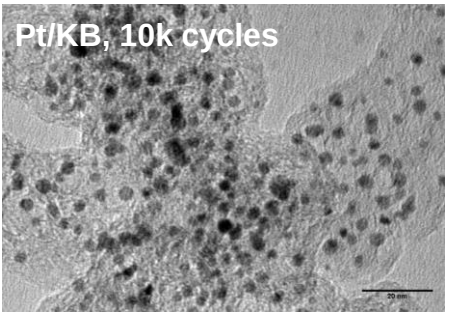
Ionic Liquid Reduces Pt Dissolution

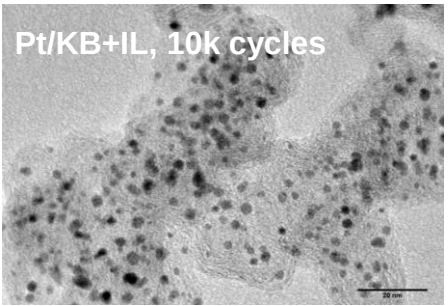
ECSA Retained during RDE-AST



Pt Dissolution by ICP-OES





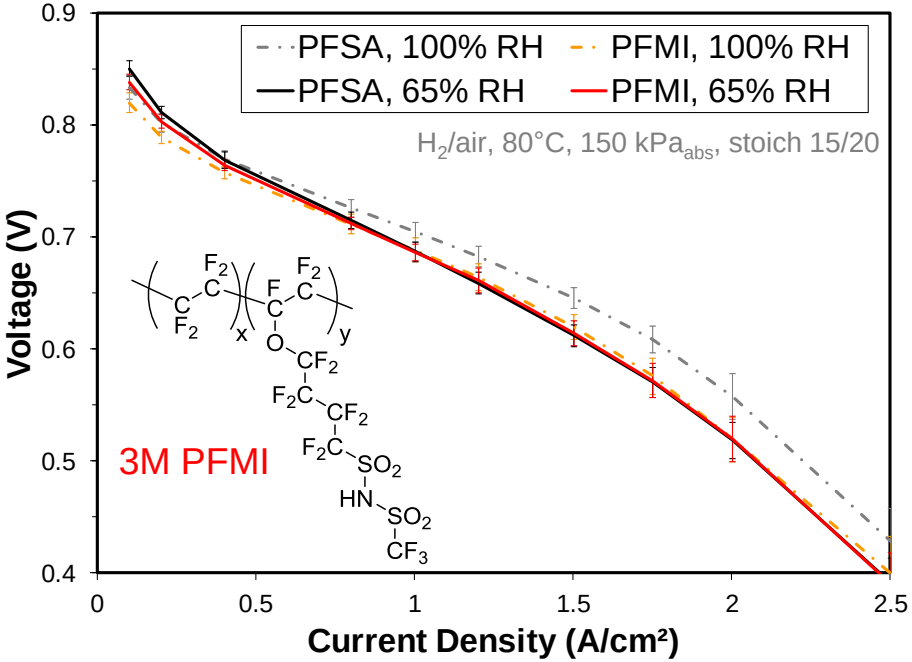


- Presence of IL thin film on Pt/V and Pt/HSC leads to significant improvements in ECSA and ORR activity retention during RDE AST test (0.6-0.95 and 0.6-1.1 V). Lower Pt dissolution was confirmed by ICP.
- Ex-situ XPS and UPS analysis of IL thin film on Pt electrodes pre- and post-AST (0.6 – 1.2 V vs. RHE, 10,000 cycles) indicates little changes in IL chemistry.
- CO displacement charge at 0.4 V is lower in the presence of IL, indicating decreased anionic species. Intermediary IL thin film both limits ionic species specific adsorption, screening of SO^{3-} groups, and lower site blocking from hydrophobic domains of PFSA polymer.

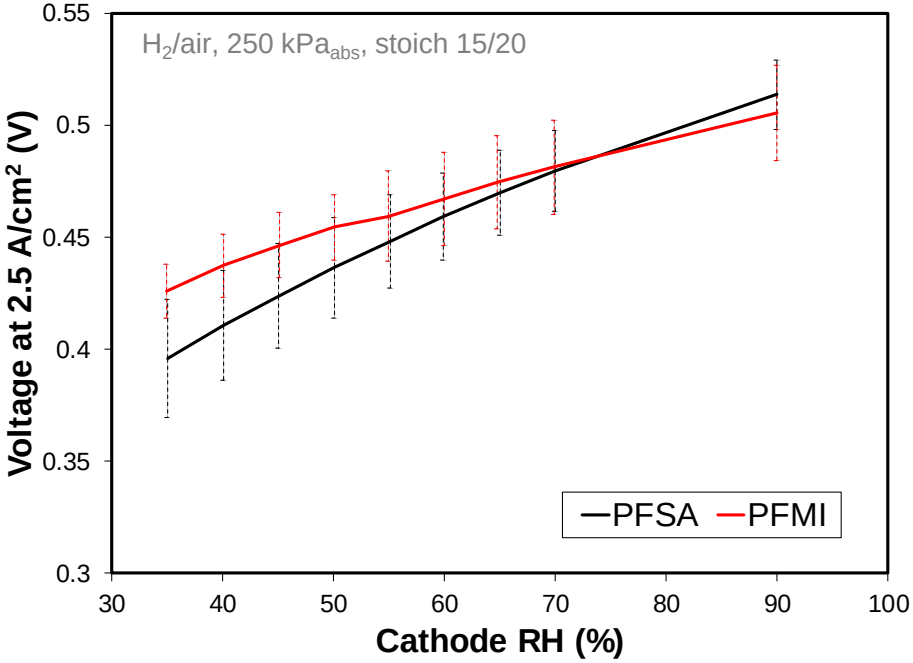
Technical Accomplishment:

PFMI Ionomer

Fuel Cell Performance under Wet and Dry



RH Sensitivity. V at 2.5 A/cm²



- While 3M observed improved performance when PFMI [Perfluoromethyl bis(sulfonyl)imide] ionomer was used with Pt/C, first test at GM with PtCo/KB gave lower mass activity compared to PFSA ionomer.
- PFMI appeared to have less performance sensitivity to humidity.
- Were not yet able to confirm whether PFMI ionomer can improve HCD through less adsorbing acid group.

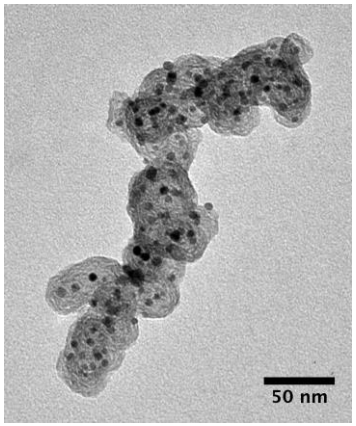
PtCo/KB, 0.1 mg_{Pt}/cm^2
Error bars: two σ

Technical Accomplishment:

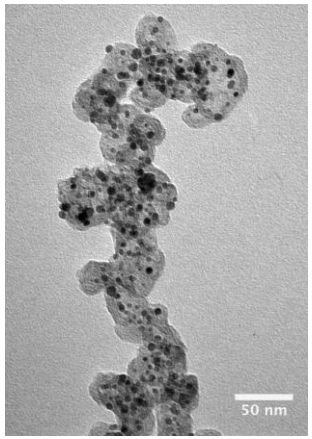
Accessible Carbons Appears More Open

STEM Tomography

PtCo/KB

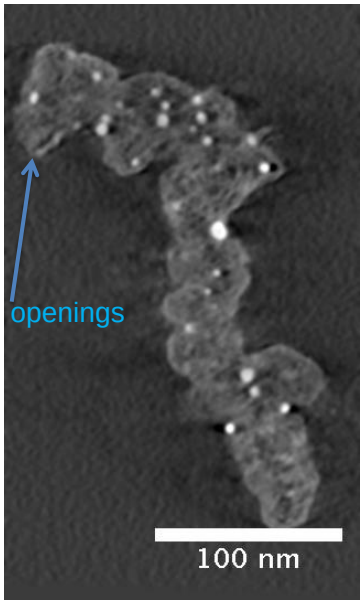


Accessible-PtCo/HSC

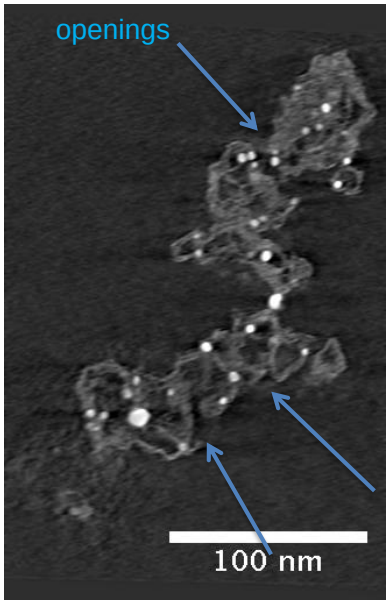


Sliced Images showing Pore Openings

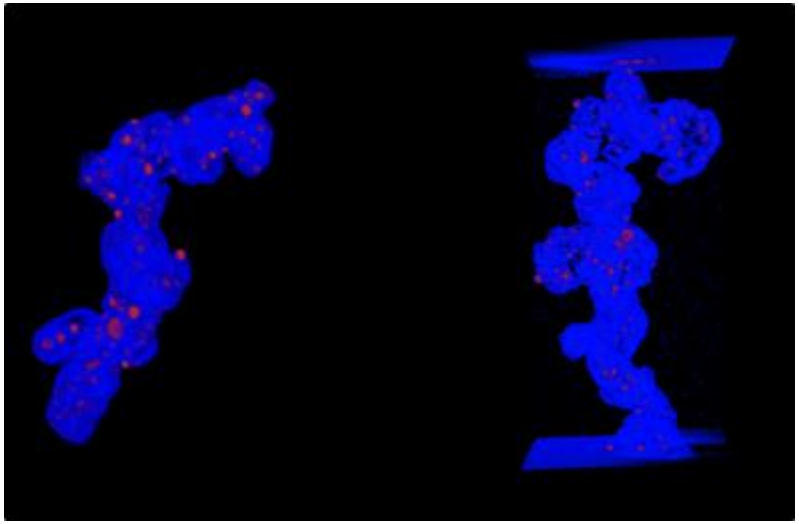
PtCo/KB



Accessible-PtCo/HSC



Reconstructing Carbon, Pore, and Pt

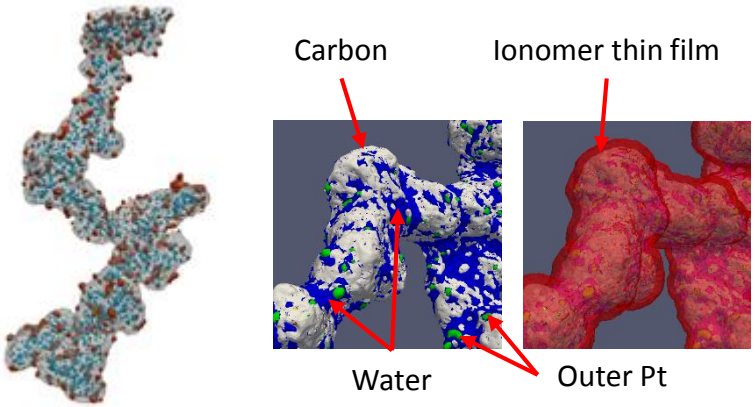


- Comparatively, KB has smaller pore size (2-5 vs 5-10 nm) and smaller pore opening (1-2 vs 3-7 nm), and likely a more tortuous path.
- Neither looks optimized

STEM-CT based Catalyst Aggregate Model

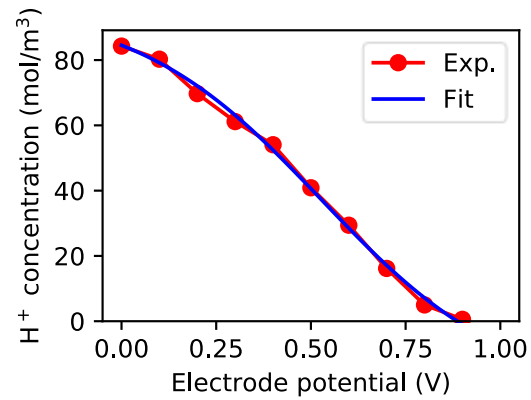
Microscopy data input

50 wt. % Pt/HSC STEM CT images

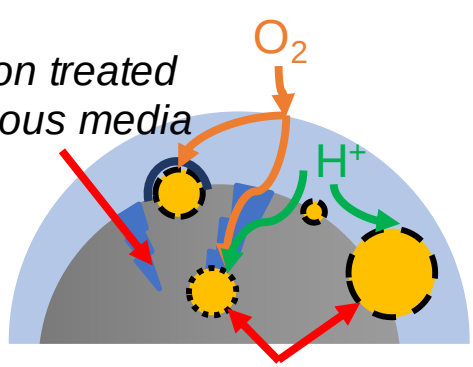


Synthetic addition of ionomer and water volumes to STEM images

Potential dependent H^+ conc. from EIS conductivity measurements on ionomer-free carbon black



Carbon treated as porous media



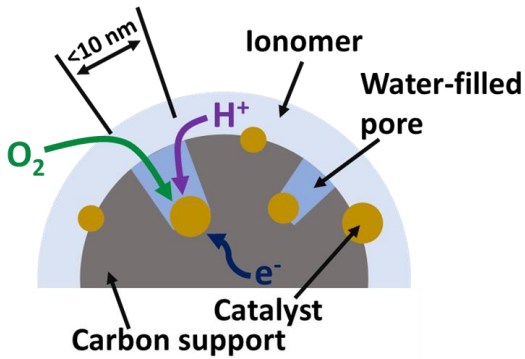
Partially oxidized Pt with negative surface charge

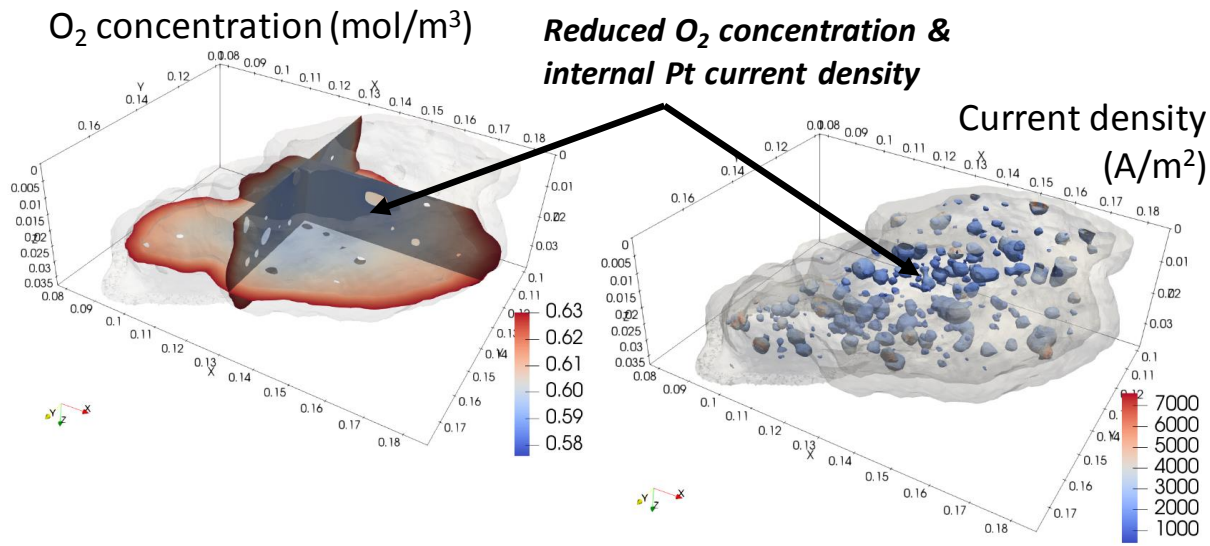
Transport and reaction models

- Poisson-Nernst-Planck equation to resolve various charge effects for H^+ concentration and electric potential in the electrolytes
- Fixed space charges in ionomer and porous carbon
- Constant negative surface charge on Pt surfaces
- Diffusion equation for O_2 concentration
- Pt/ionomer interface O_2 transport limited Butler-Volmer type reaction model with Pt oxide coverage model

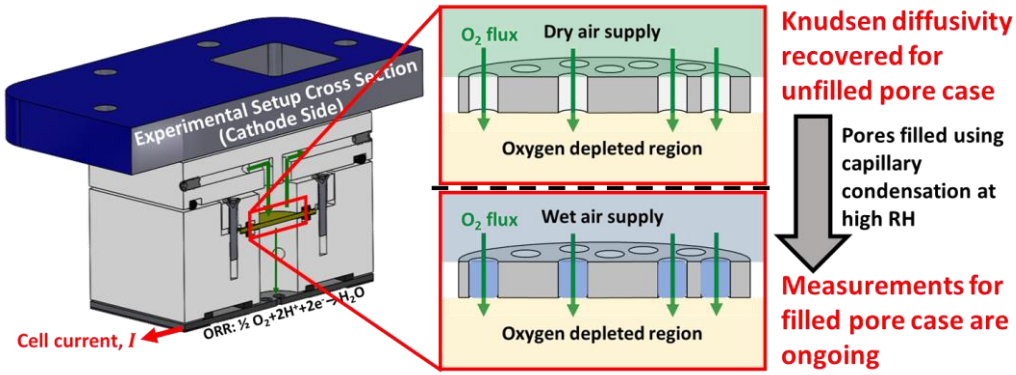
Technical Accomplishment:

O_2 Diffusivity Through Water-Filled Pores





Measurement of O_2 diffusivity in 10 nm water-filled micropores



- Cannot explain performance difference between PtCo/KB and Accessible-porous catalysts, with their relatively small difference in pore sizes, using known values for O_2 transport.
- Literature has indicated quickly reduced gas diffusivity in <10 nm liquid-filled micropores (*J. Phys. Chem. C*, 2017, 26539 & *J. Phys. Chem. C*, 2017, 15675)
- Ex-situ O_2 diffusivity measurement in water-filled <10 nm pore is underway.

Technical Accomplishment:

SOA Integration & DOE Validation

SOA Components

Cathode: 30 wt.% Intermetallic ordered Pt_3Co/HSC-f at 0.06 and 0.10 mg_{Pt}/cm^2, PFSA ionomer, 900 EW, I/C ratio of 0.8,

Anode: Pt/HSC, 0.015 mg_{Pt}/cm^2

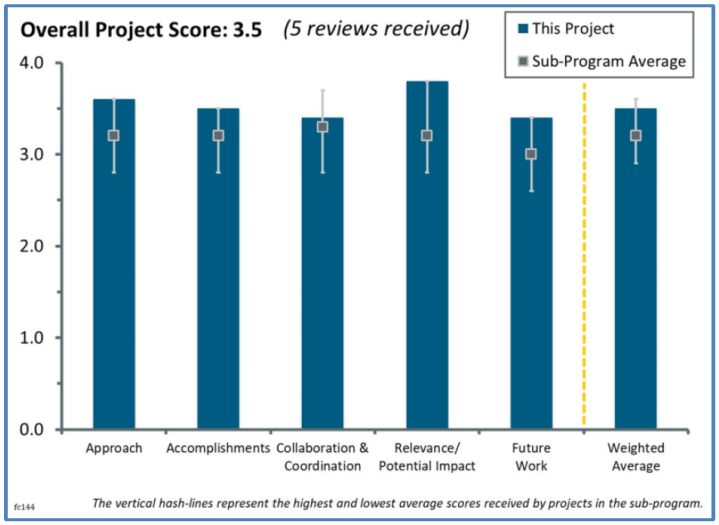
PEM: PFSA with reinforcement layer, ~10 µm thick

GDL: ~100 µm thick carbon fiber layer with 30 µm MPL. Water proof.

Metric	Units	PtCo/KB 2016	PtCo/HSC-f	Ordered-PtCo/HSC-f	Ordered-PtCo/KB	PtCo/HSC-f	DOE 2020 Target	Project Target
PGM total loading (both electrodes)	mg/cm^2	0.125 (0.025+0.10)	←	←	←	0.075 (0.015+0.06)	<0.125	←
Mass activity @ 900 $mV_{iR\text{-}free}$	A/mg_{PGM}	0.62†	0.7†	0.7†	0.53†	0.7†	>0.44	←
Loss in catalytic (mass) activity	% loss	30%	59%*	45%*	16%	tbd	<40%	←
Performance at 0.8V (150kPa, 80°C)	A/cm^2	0.304	tbd	tbd	0.301	tbd	>0.3	←
Power at rated power (150kPa, 94°C)	W/cm^2	0.8	0.95	0.94	tbd	0.91	>1.0	-
Power at rated power (250kPa, 94°C)	W/cm^2	1.01	**1.31**	1.29	1.15	1.23	-	>1.1
PGM utilization (150kPa, 94°C)	kW/g_{PGM}	6.4	7.6	7.5	tbd	**12.1**	>8	←
PGM utilization (250kPa, 94°C)	kW/g_{PGM}	8.1	10.5	10.3	9.2	**16.4**	-	>9.1
Catalyst cycling (0.6-0.95V, 30k cycles)	mV loss at $0.8A/cm^2$	24	39*	25	8	tbd	<30	←
Support cycling (1.0-1.5V, 5k cycles)	mV loss at $1.5A/cm^2$	>500	>500	tbd	tbd	tbd	<30	-

- Reduce anode Pt loading by shifting to high ECSA Pt/HSC catalyst.
- Will prepare MEAs ($38cm^2$) for DOE validation at NREL.

Responses to Last Year AMR Reviewers' Comments



- "should benchmark against new commercial catalysts, which are showing very high mass activity in MEAs"
  - We routinely benchmark against suppliers' catalysts. Our PtCo/KB and PtCo/V baseline catalysts reported here are competitive. Note that some high mass activity reported by some groups are due to difference in measurement protocols.
- "Investigate whether increased ORR activities after more conditioning has any effect on HCDs"
  - It does. We're aware of it and ensure that it does not affect our conclusion.
- Modeling "serves only as a confirmation of what is already understood", "not apparent that it is critical to the project", "benefit for the greater community are difficult to derive"
  - Fuel cell is a complicated device and until we apply numbers with reasonable assumption to try to explain the phenomenon, it is impossible to prove the hypothesis. The model allows us to do so.
  - Notable findings from modeling: (a) how internal vs external Pt dissolve/redeposit, (b) importance of high negative Pt surface charge in carbon pores on kinetic and proton transport, (c) existence of high O_2 diffusion resistance in carbon pores. These will be published in detail.
- "should increase the understanding of ionic liquid stability"
  - Although we agree that durability testing should be done, we do not have resource to do so. Another issue is that we do not have a method to characterize the IL once it is made into an MEA, other than watching the voltage which is an indirect measurement. This complicates the effort.
  - That being said, we value IL as a tool to understand the Pt-ionomer interface. It's also shown that IL could mitigate Pt dissolution.

Future Work

Validation

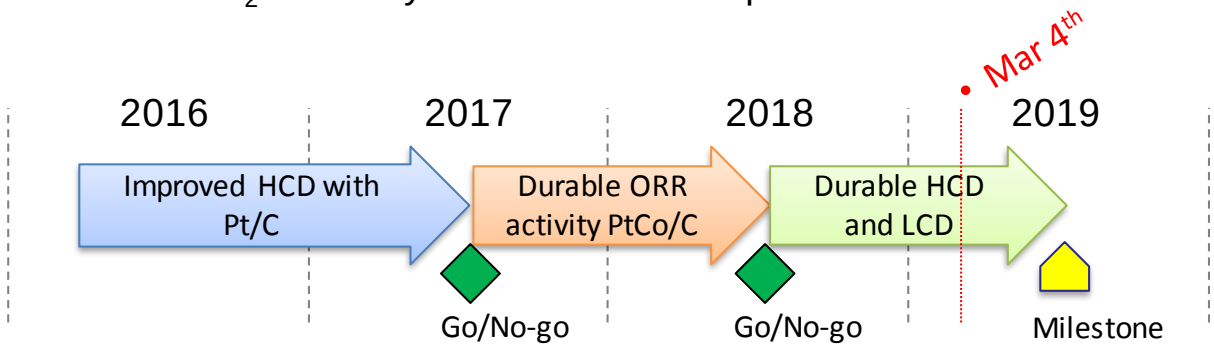
- Evaluate durability of low-loaded (0.075 mg_{Pt}/cm^2, cathode+anode) MEA. Employ MEA diagnostics and modeling to understand performance loss.
- Prepare MEAs for DOE validation at NREL.

Materials Development

- Implement new ionomer on accessible-porous carbons.
- Optimize IL application and evaluate potential durability benefit of IL.
- Catalyst synthesis path for intermetallic ordered PtCo with well controlled size.

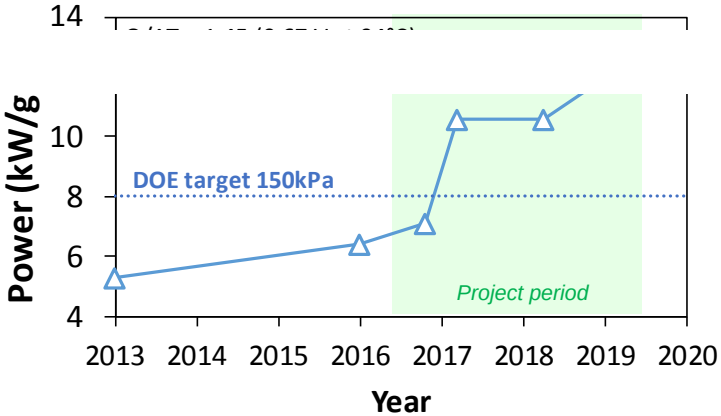
Fundamentals

- Finalize catalyst particle-pore performance model and cation fundamental performance model.
- Study effects of local lattice strain on ORR activity using STEM with pixel array detector.
- Ex-situ measurement of O_2 diffusivity in water-filled nanopores



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

Summary



- Progress to DOE target status
  - Advanced PGM Utilization status by 15% by reducing Pt in both anode and cathode.
  - Narrowed gap to 1 W/cm^2 (150kPa) target (now 0.95 W/cm^2).
- Promising materials
  - Intermetallic ordering was effective for improving durability of accessible-PtCo with minimal performance penalty.
  - While ionic liquid were beneficial for some PtCo/HSC, benefits on our best accessible-catalyst was not yet realized. Potential merit on stability awaits confirmation in MEA.
- Improved understanding of low-PGM electrode
  - 3D-TEM and modeling confirmed that internal pore size (opening) is the key factor for good ORR activity and transport properties in porous carbon catalysts.
  - Ex-situ tests and modeling highlighted (a) importance of high negative Pt surface charge in carbon pores on kinetic and proton transport and (b) unusually strong dependent of O_2 diffusivity on carbon pore size.
  - STEM Nanobeam Diffraction allows study of how lattice strain and defect in Pt shell affect ORR activity in MEAs.

This Year: 3 Articles, 12 Talks (3 invited)

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- Mark F. Mathias

3M

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

Carnegie Mellon University

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

Cornell University

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

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- Yawei Li

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- Dr. Nancy N. Kariuki
- Dr. Ross N. Andrews
- Dr. Jan Ilavsky

LANL

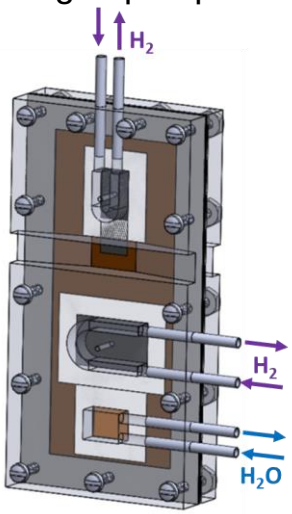
- Dr. Andrew M. Baker
- Dr. Rangachary Mukundan
- Dr. Rod L. Borup

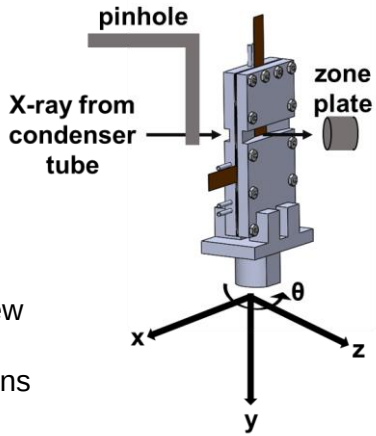
Technical Back-Up Slides

Technical Accomplishment:

In-Operando Co^{2+} Migration with Nano-CT

Migration Cell
(Hydrogen pump config.)

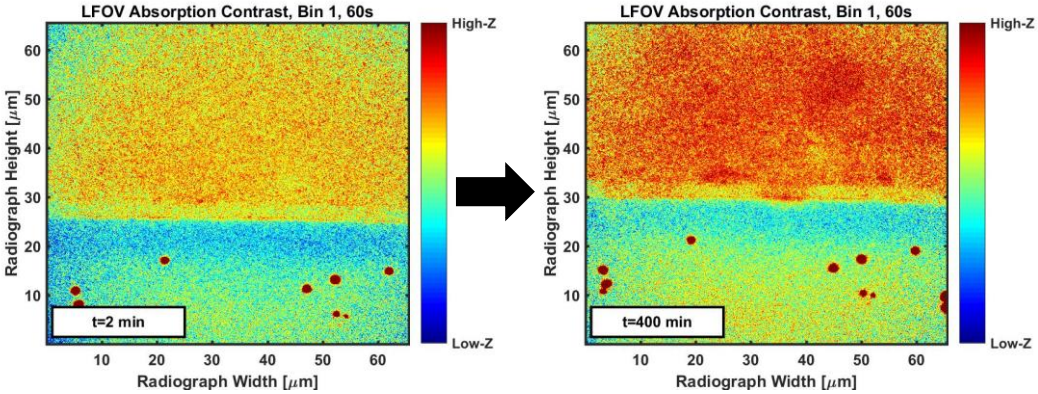




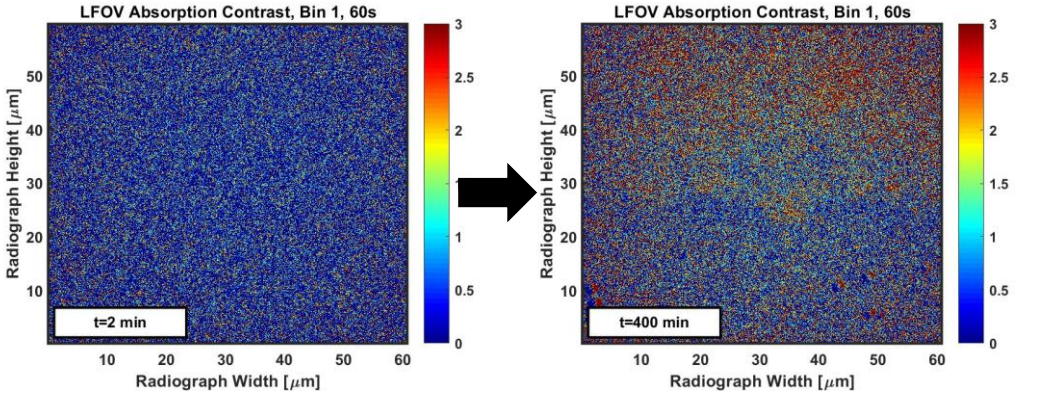
Experimental details:

- 20 wt% Pt/V CL in X-ray view
- Nafion 211 membrane
- Migration under 1V conditions
- Nano-CT imaging
  - LFOV (65x65 μm)
  - Absorption contrast mode
  - 60s per image, bin1 (64 nm pixel)
- >10 hour duration, data shown at 2 & 400 min

Raw high-Z color mapping
(histogram adjusted)

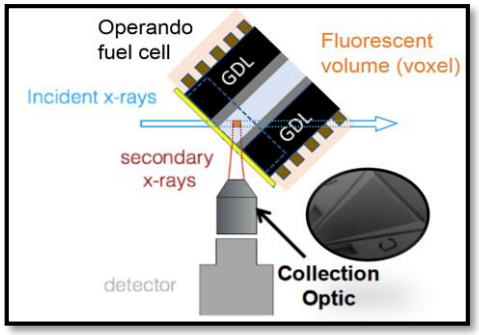


Co^{2+} attenuation mapping

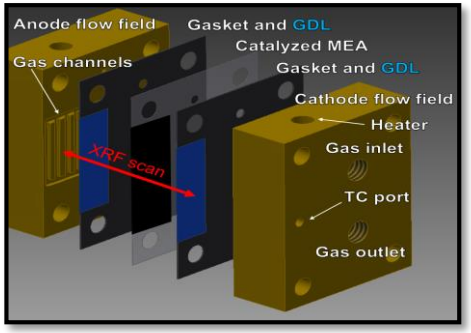


In-Operando Cation Transport with Confocal µ-XRF

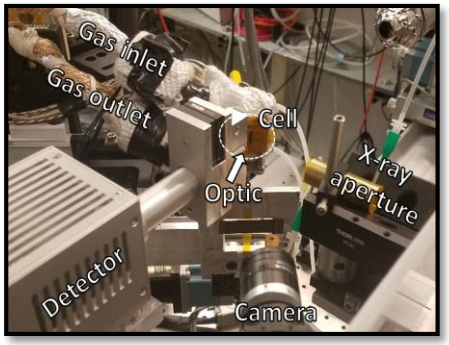
- ***Experimental Setup***



Confocal micro-XRF



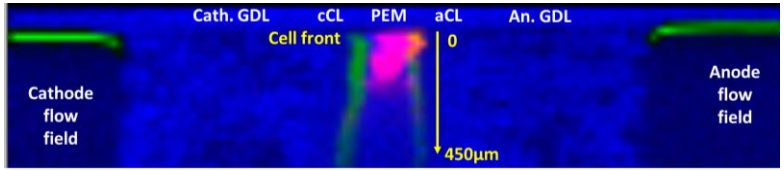
Operando Cell



Setup at CHESS beamline G3

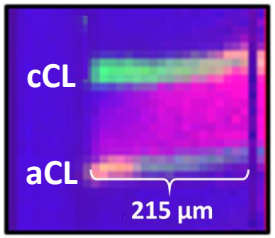
- ***3D-Cation Transport:*** Ce profile in a MEA (13% Ce-NR212) under a load of 50mA/cm^2

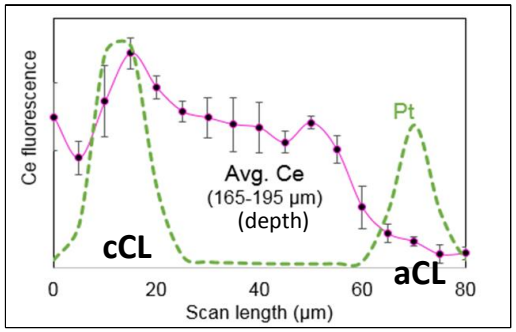
80°C, 50% RH, H_2/air at 100/200 sccm



● Ce L ● Pt (Au) L3

* :at depth > 200um, Ce signal is greatly attenuated by the PFSA/water matrix.



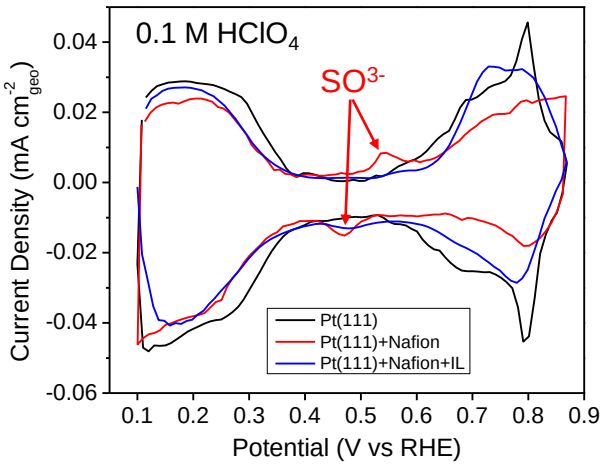


- At cell front (~30µm of depth) , Ce cations at cCL move toward the inner cell due to the in-plane potential gradient in addition to the through-plane potential from the load.
- At >150µm of depth, Ce cations accumulate toward cCL side driven by through-plane potential only.

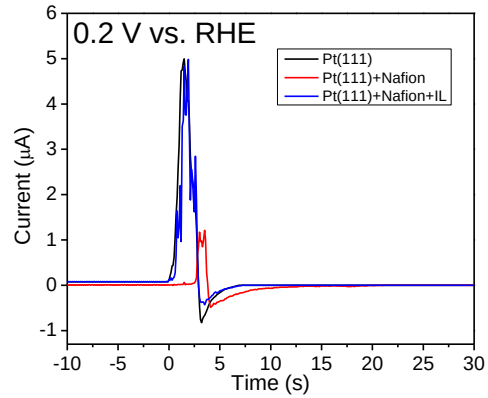
Technical Accomplishment:

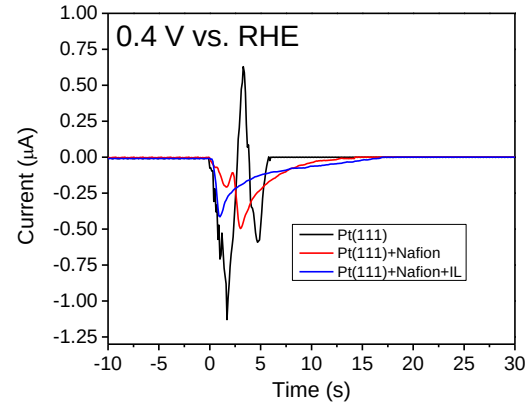
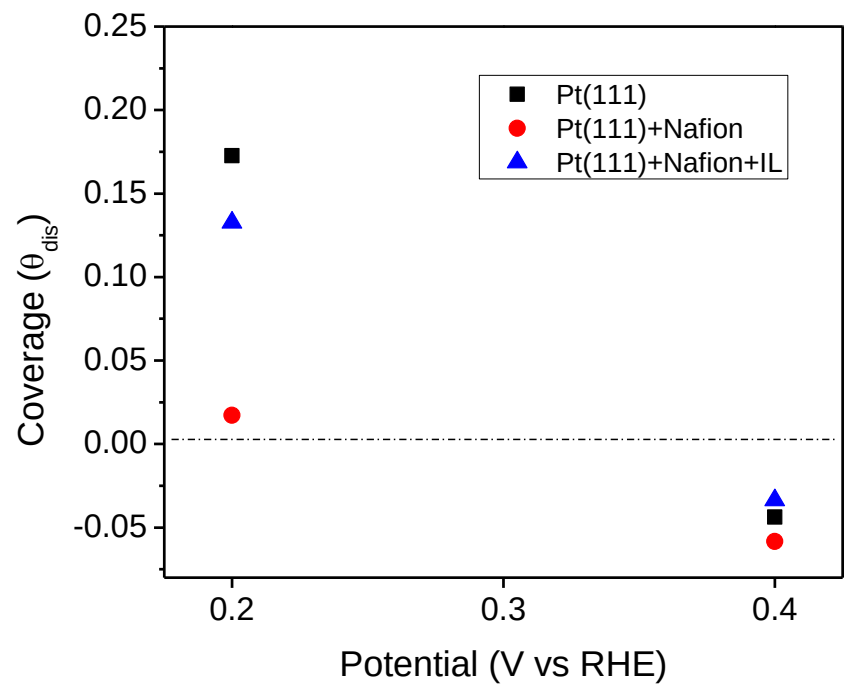
IL Mediation of Nafion Specific Adsorption

Nafion/IL Thin Films on Pt(111)



CO displacement





- CO displacement charge at 0.4 V vs. RHE is lower in the presence of IL, indicating decreased anionic species
- CO displacement below the Pt PZC, < 0.3 V vs. RHE at pH 1, indicates increased H adsorption, approaching that of bare Pt(111), in the presence of IL
- Intermediary IL thin film both limits ionic species specific adsorption, screening of SO^{3-} groups, and lower site blocking from hydrophobic domains of Nafion polymer