FUEL CELL PERFORMANCE AND DURABILITY

FC136 – FC-PAD: Components and Characterization

Presenter: Karren L. More

Tuesday, June 6th 2017

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FC-PAD: Consortium to Advance Fuel Cell Performance and Durability

Approach

Couple national lab capabilities with funding opportunity announcements (FOAs) for an influx of innovative ideas and research

FCPAD
FUEL CELL PERFORMANCE AND DURABILITY

Objectives

- Improve component stability and durability
- Improve cell performance with optimized transport
- Develop new diagnostics, characterization tools, and models

Consortium fosters sustained capabilities and collaborations

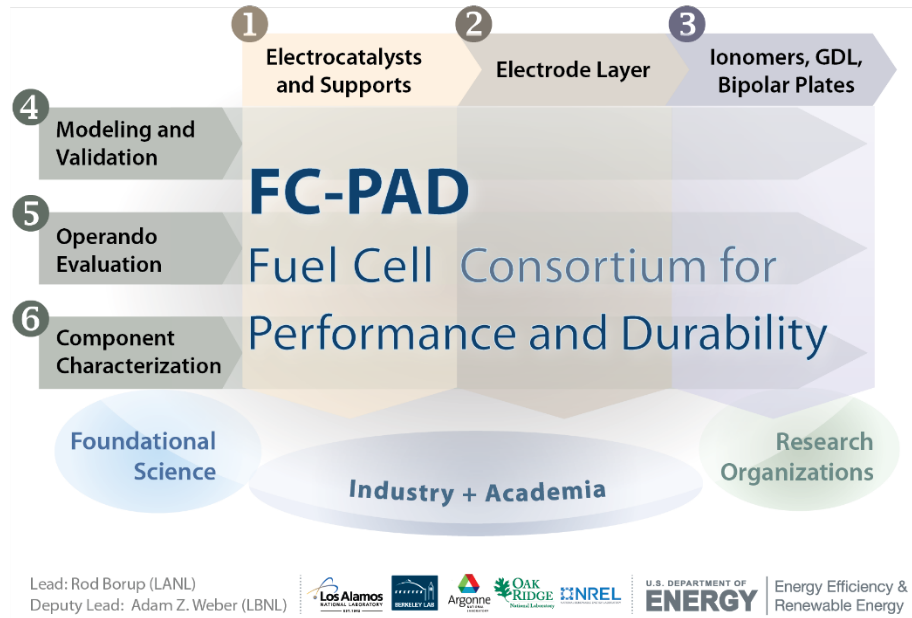
Core Consortium Team

Argonne National Laboratory, NREL National Renewable Energy Laboratory, Los Alamos National Laboratory, Berkeley Lab, Oak Ridge National Laboratory

Prime partners added in 2016 by DOE solicitation (DE-FOA-0001412)

3M, GM, United Technologies Research Center, Vanderbilt

Structured across six component and cross-cutting thrusts



FC-PAD Consortium - Overview

Fuel Cell Technologies Office (FCTO)

- FC-PAD coordinates activities related to fuel cell performance and durability
  - The FC-PAD team consists of five national labs and leverages a multi-disciplinary team and capabilities to accelerate improvements in PEMFC performance and durability
  - The core-lab team consortium was awarded beginning in FY2016; builds upon previous national lab (NL) projects
- Provide technical expertise and harmonize activities with industrial developers
- FC-PAD serves as a resource that amplifies FCTO's impact by leveraging the core capabilities of constituent members

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FC-PAD Consortium: Relevance and Objectives

Overall Objectives:

- **Advance *performance* and *durability* of polymer electrolyte membrane fuel cells (PEMFCs) at a pre-competitive level**
- **Develop the knowledge base and optimize structures for more durable and high-performance PEMFC components**
- **Improve high current density performance at low Pt loadings**
  - Loading: 0.125 mg_{Pt} / cm^2 total
  - Performance @ 0.8 V: 300 mA / cm^2
  - Performance @ rated power: 1,000 mW / cm^2
- **Improve component durability (e.g., membrane stabilization, self-healing, electrode-layer optimization)**
- ***Provide support to industrial and academic developers from FOA-1412***
- ***Each thrust area has a sub-set of objectives, which support the overall performance and durability objectives***

FC-PAD Overview and Relevance

Timeline

Project start date: 10/01/2015
Project end date: 09/30/2020

Budget

- FY17 project funding: $5,150,000
- As proposed: 5-year consortium with quarterly, yearly milestones & Go/No-Go
- Total Expected Funding: $25M (NLs only)

Partners/Collaborations

(To Date Collaborations Only)

- IRD Fuel Cells, Umicore, NECC, GM, TKK, USC, 3M, JMFC, W.L. Gore, Ion Power, Tufts, KIER, PSI, UDelaware, CSM, SGL, NPL, NIST, CEA,ULorraine
- Partners added by DOE DE-FOA-0001412

Barriers

- Cost: $40/kW system;
  $\$14/kW_{net}$ MEA
- Performance @ 0.8 V: 300 mA / cm^2
- Performance @ rated power: 1,000 mW / cm^2 (150 kPa abs)
- Durability with cycling: 5,000 (2020) – 8,000 (ultimate) hours, plus 5,000 SU/SD Cycles

- **Mitigation** of Transport Losses
- **Durability** targets have not been met

- The **catalyst layer** is not fully under-stood and **is key in lowering costs** by meeting rated power
- Rated power@ low Pt loadings reveals unexpected losses

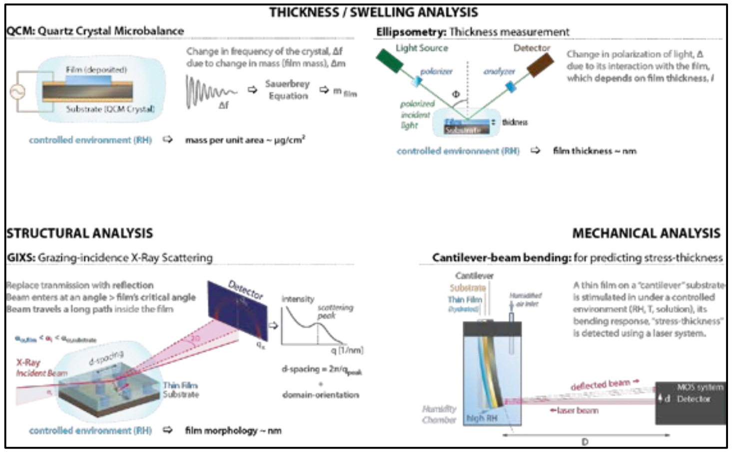
FC-PAD Objectives: How We Get There

- Develop the knowledge base and optimize structures for more durable and high-performance PEMFC components
- Understanding Electrode Layer Structure
  - Characterization
- New Electrode Layer Design and Fabrication
  - Stratified (Spray, Embossed, Array), Pt - Deposition, Jet Dispersion
- Defining/Measuring Degradation Mechanisms
  - Membrane, Catalyst Pt-alloy dissolution

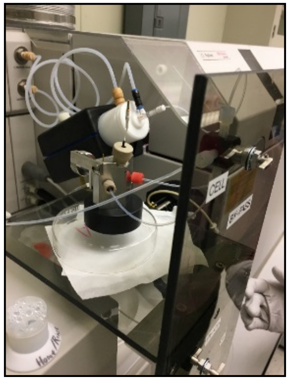
FC-PAD Presentations

- **FC135: FC-PAD: Fuel Cell Performance and Durability Consortium (Rod Borup, LANL)**
  - Overview, Framing, Approach, and Highlights/**Durability**
- **FC136: FC-PAD: Components and Characterization (Karren L. More, ORNL)**
  - Concentration on **Catalysts** and **Characterization**
- **FC137: FC-PAD: Electrode Layers and Optimization (Adam Weber, LBNL)**
  - Concentration on **Performance** - MEA construction and modeling
- **FC155 (3M), FC156 (GM), FC157 (UTRC), FC158 (Vanderbilt) FOA-1412 Projects**

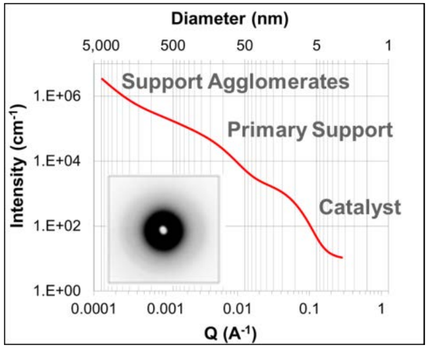
FC-PAD: Component Characterization - Capabilities

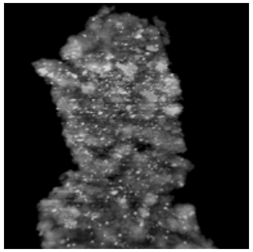


Thin film characterization

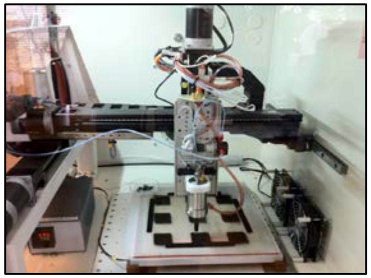


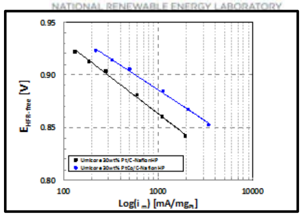
Time-resolved on-line ICP-MS

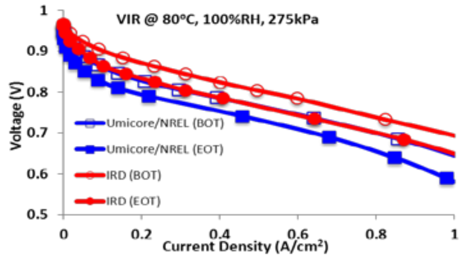


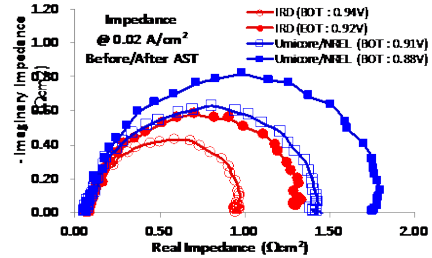


Synchrotron X-ray techniques



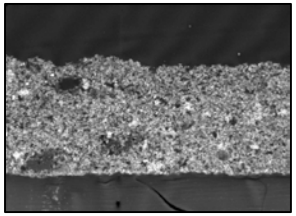


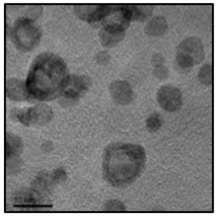


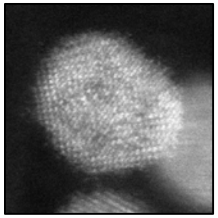


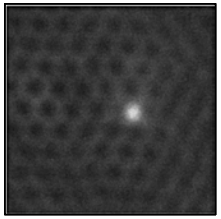
AST Development/Refinement

Advanced microscopy & spectroscopy



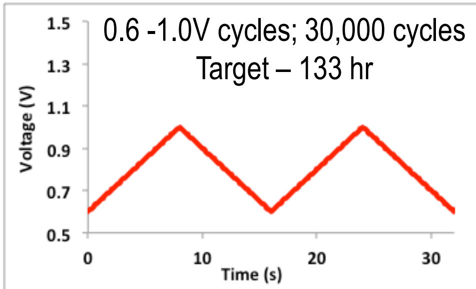


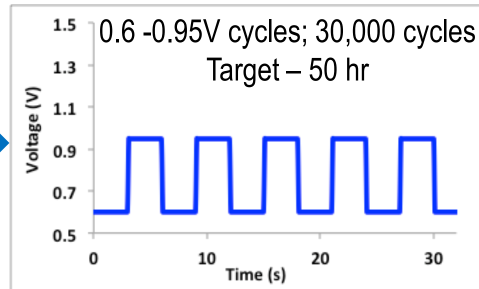




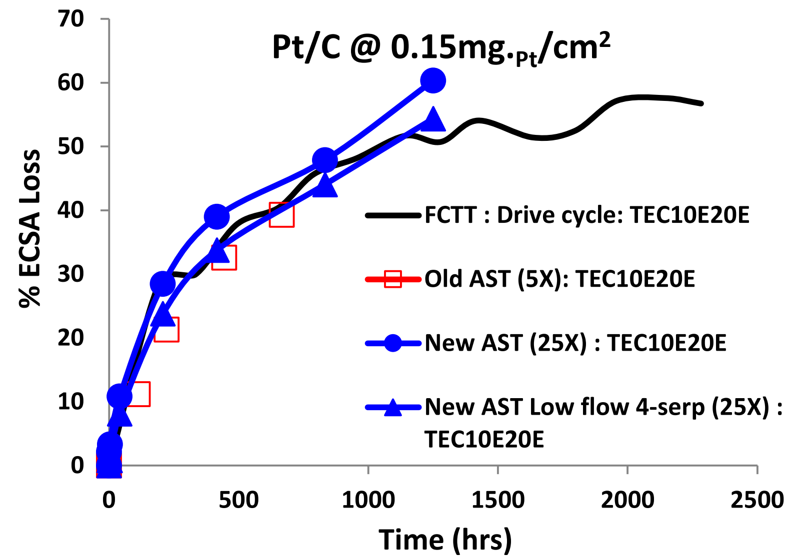
Technical Progress: AST Development & Refinement

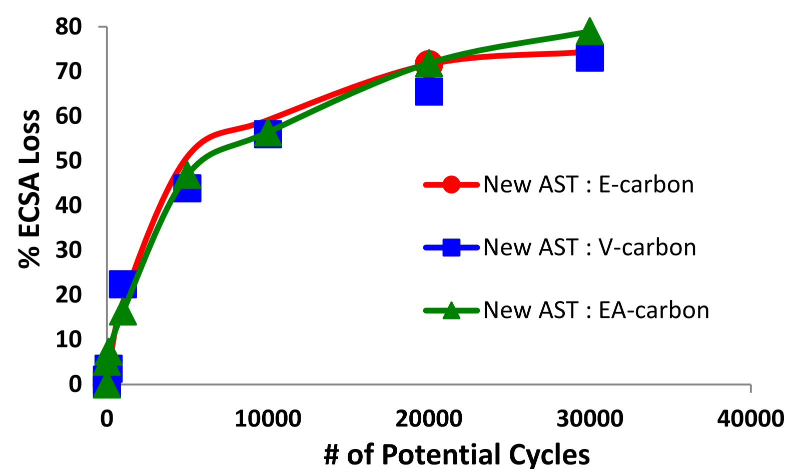
New catalyst durability AST is 5X faster than *old* AST and 20X faster than *FCTT* durability protocol





- Square wave lowers test duration from 133 to 50 hours (does not include characterization time)
- Square wave still representative of drive cycle degradation
- AST reflective of Pt dissolution and independent of carbon type





Other durability protocols under development and refinement:

- Membrane durability
- Carbon durability
- SU/SD protocols
- Freeze protocols
- Drive cycle protocols

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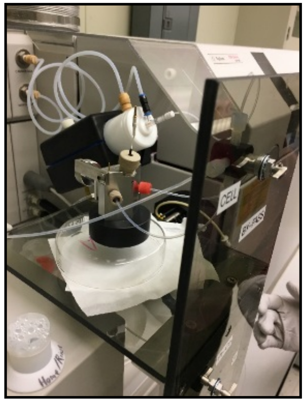
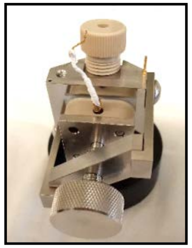
Technical Progress: Aqueous Stability of PtCo Alloys Time-Resolved On-Line ICP-MS Measurements

Objectives:
- Real time measurements of Pt and Co dissolution under cyclic potentials
- Resolve anodic vs. cathodic dissolution of Pt and Co

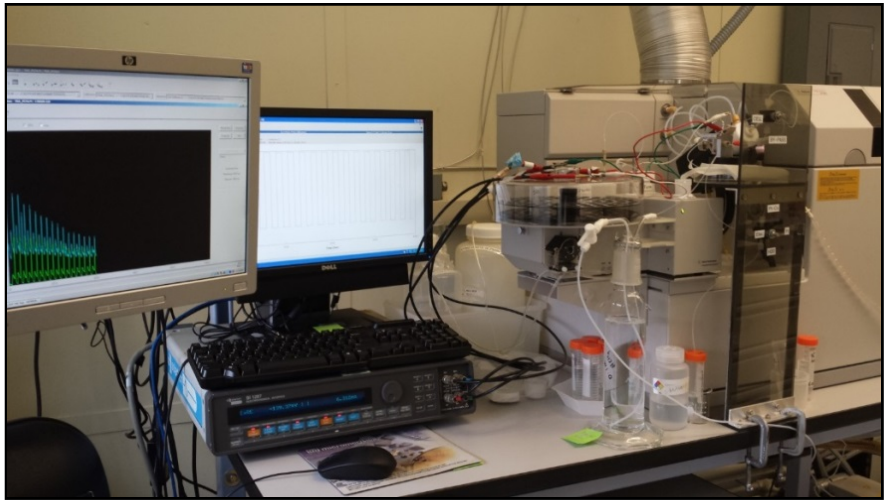
Catalysts:
- TEC36E52, Pt_3Co/HSC, 46.5 wt% Pt, 4.7 wt% Co, 5.7 nm TEM
- Umicore Elyst P30 0670, 27.5 wt% Pt, 3 wt% Co, 4.4 nm TEM
- Catalyst-ionomer ink deposited on GC at 2 µg-Pt/cm²

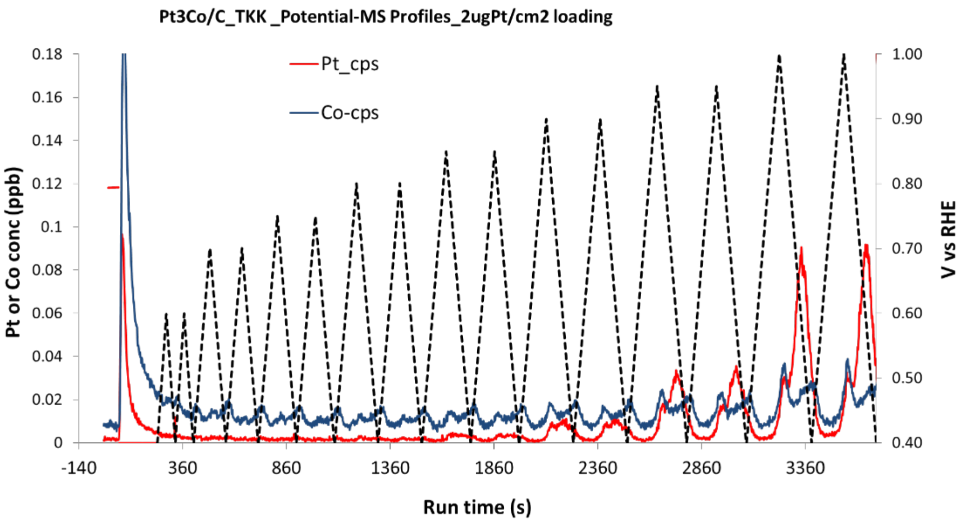




ICP-MS: Agilent 7500ce Octopole; Cell: BASi

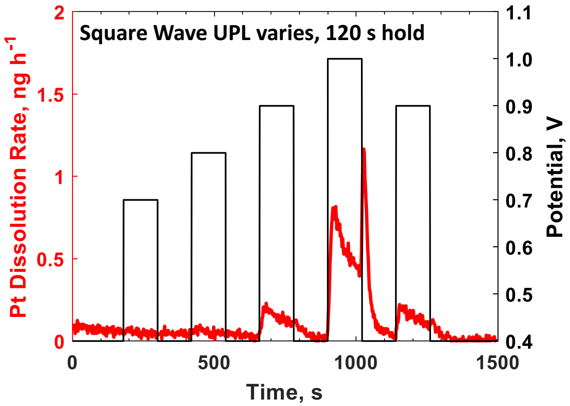
- Co dissolution observed at all potentials
- Distinct peaks in anodic and cathodic dissolution of Pt above 0.9 V
- Potential dependent dissolution rates of Pt and Co



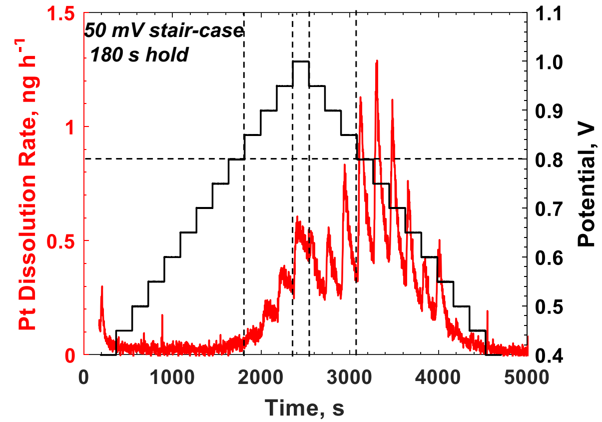


Technical Progress: Dissolution of Pt from Umicore Pt_7Co_3/C Cathode Catalyst on Stair-Case Potentials

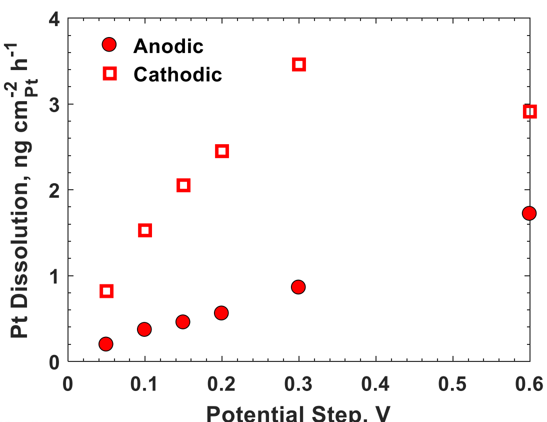
Cathodic dissolution not significant for UPL ≤0.9 V in square wave potentials



- Distinct anodic and cathodic peaks
- Anodic peaks higher at higher potentials
- Highest cathodic peak on potential step from 0.8 to 0.75 V

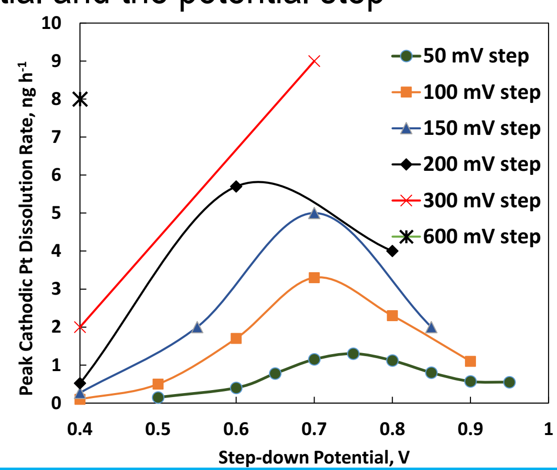


- **~3-time higher Pt dissolution during cathodic than anodic steps, stair-case potential, 1 V UPL**
- Both anodic and cathodic Pt dissolution rates (amount dissolved divided by cycle time) increase at higher potential steps



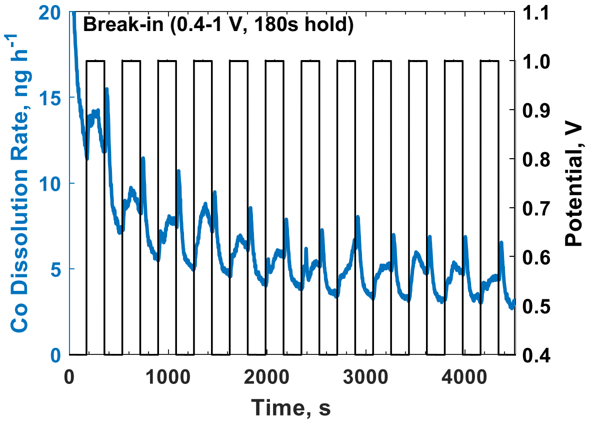
Peak cathodic dissolution rate depends on the initial potential and the potential step

Peak cathodic rate reaches a maximum at 0.65-0.75 V step down potential

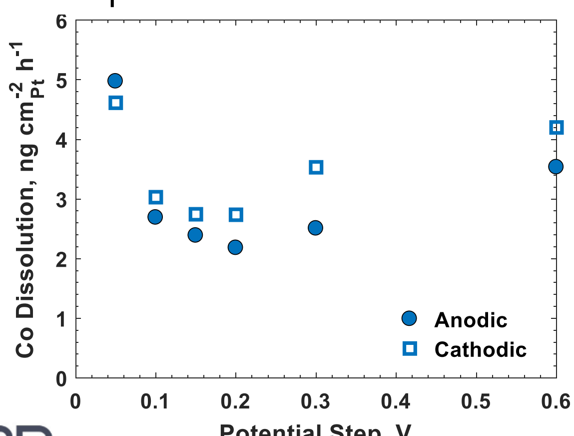


Technical Progress: Dissolution of Co from Umicore Pt_7Co_3/C Cathode Catalyst on Stair-Case Potentials

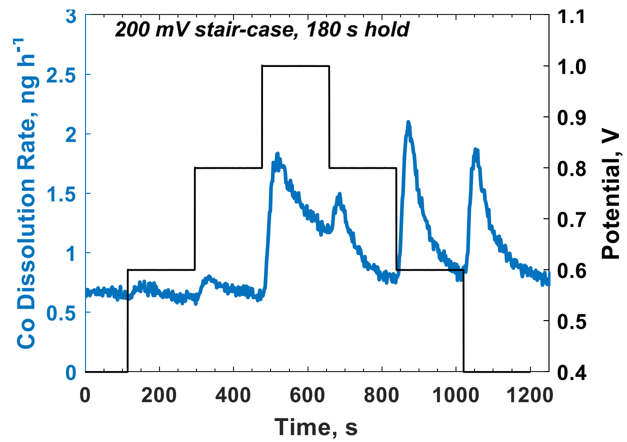
Break-in protocol requires >1-h conditioning on 0.4-1.0 V square wave potentials



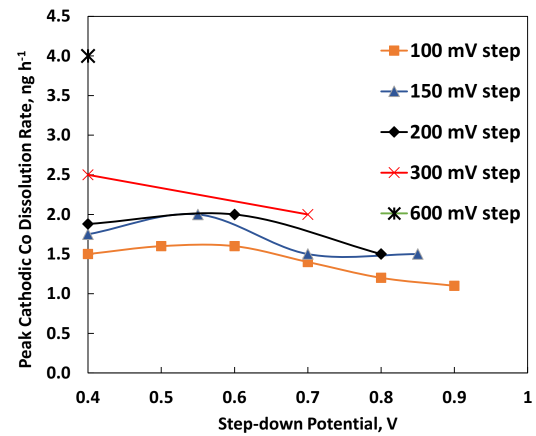
- **Comparable Co dissolution during anodic and cathodic steps**
- Anodic and cathodic Co dissolution rates (amount dissolved divided by cycle time) lowest for 200 mV potential step



- **Anodic Co dissolution rate nearly constant for potentials up to 0.8 V**
- Anodic peaks observed at potentials >0.8 V
- Highest cathodic peak on potential step from 0.8 to 0.6 V



Peak cathodic dissolution rate depends on the initial potential and the potential step

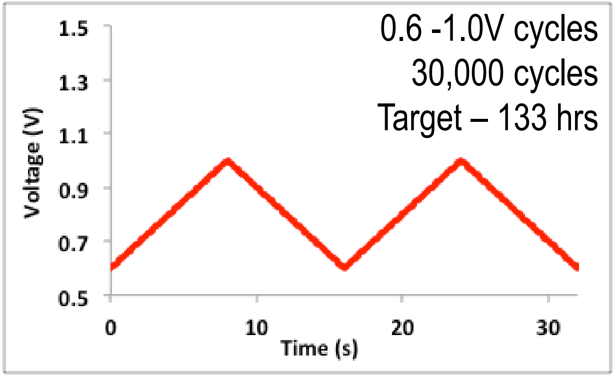


Technical Progress: Extensive Study of PtCo Catalysts

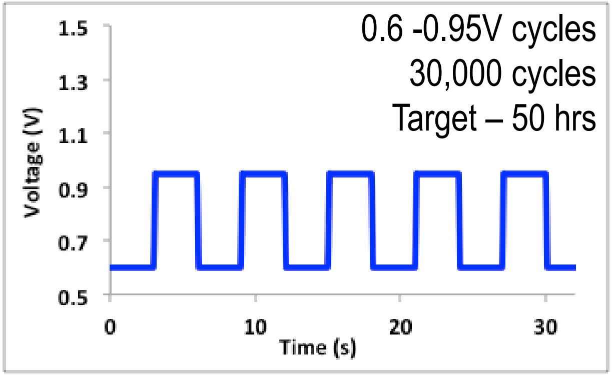
Catalyst Supplier	Catalyst/HSAC	Catalyst Loading (mg_{Pt}/cm^2) & ECSA (m^2_{Pt}/g_{Pt})	Membrane
Umicore	PtCo (Elyst Pt30 0670) spray-coated CCL @ NREL	0.1 & 37	Nafion 211
IRD (*EWII*)	Pt_3Co (IRD SOA catalyst) IRD-prepared MEA	0.2 & 41	Reinforced
GM - SOA	GM SOA PtCo catalyst GM-prepared MEA	0.1 & 43	DuPont XL-100

MEAs characterized:

- *Conditioned / BOL*
- *NEW Catalyst AST*
- *OLD Catalyst AST*
- *1200 hr Wet Drive Cycle*



Old triangle-wave catalyst AST



New square-wave catalyst AST

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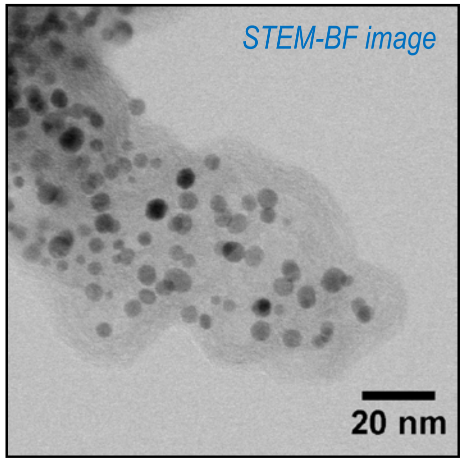
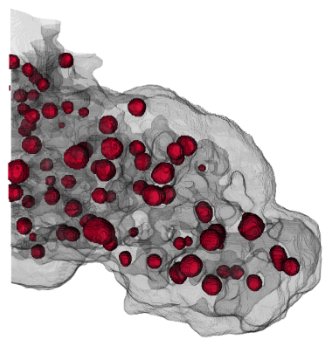
Technical Progress: Extensive Study of PtCo Catalysts

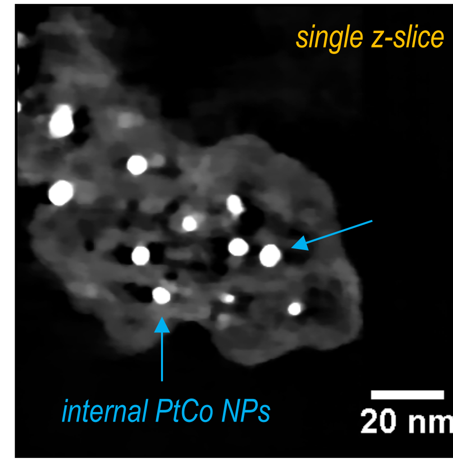
SOA **Pt-Co/HSAC Fresh MEA:**

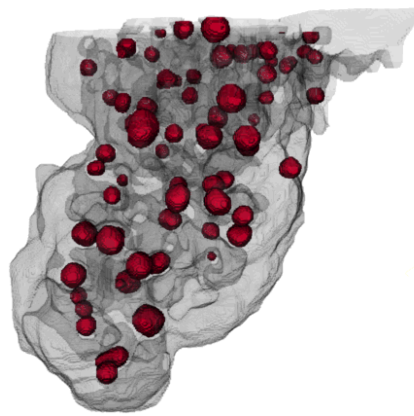
- Avg. PtCo particle size
  - 4.4nm diameter
- Avg. PtCo composition
  - 85% Pt – 15% Co
- majority of PtCo particles are *inside* HSAC support:
  - 77% within core
  - 23 % on surface



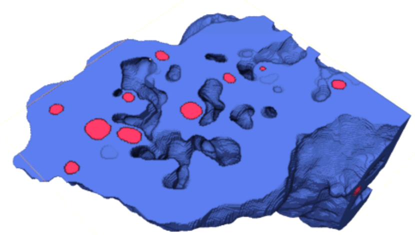
segmented Pt/C 3D surfaces



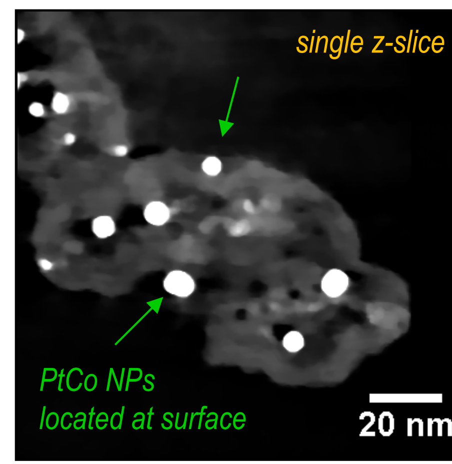




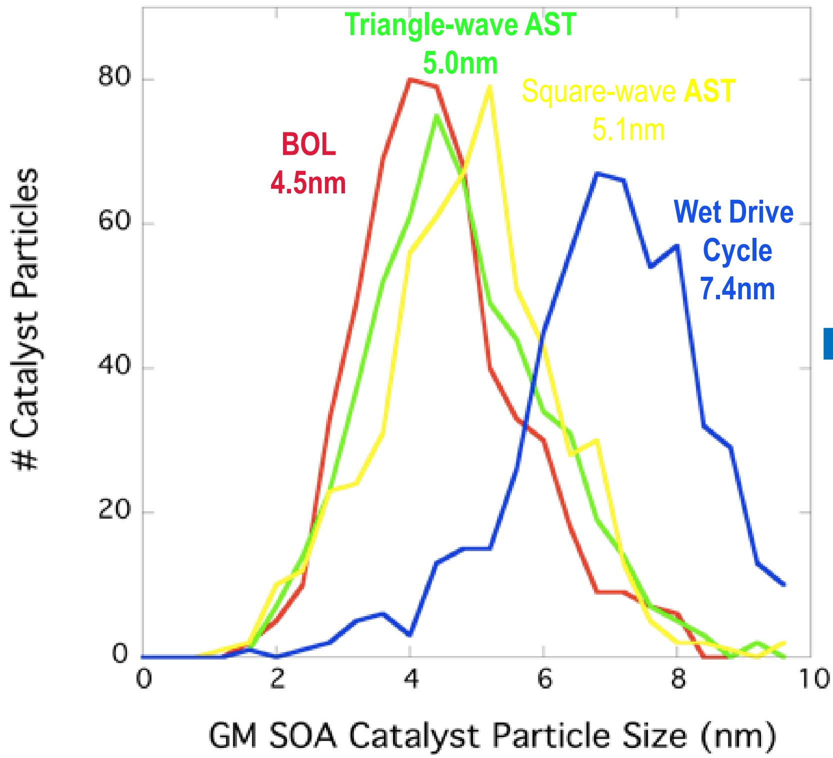
rotation animation

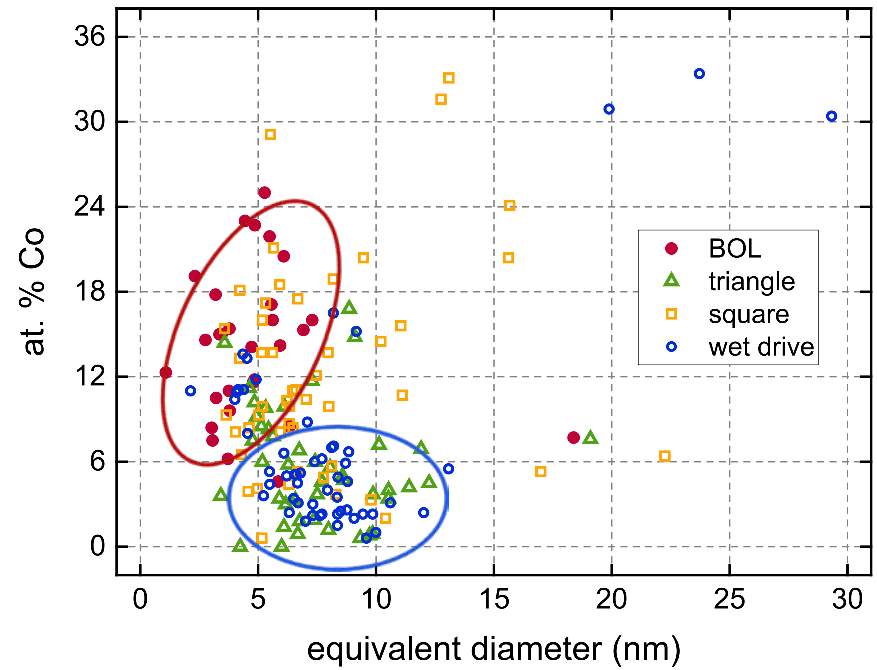


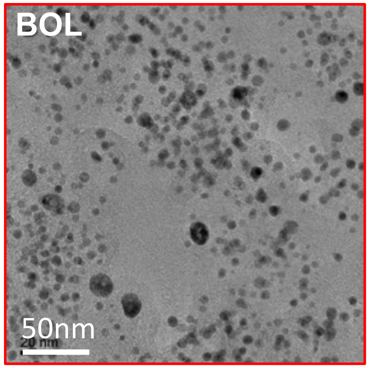
volume clipping animation

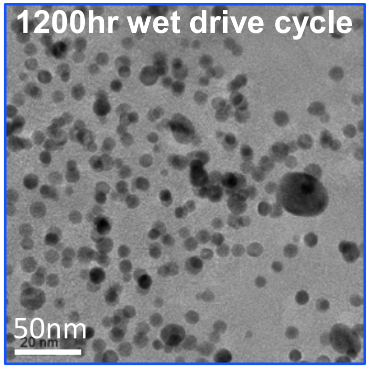


Technical Progress: Extensive Study of PtCo Catalysts









- Significant increase in PtCo particle size from **4.5nm to ~7.4nm** during 1200 hr wet drive cycle
  Significant drop in Co content within CCL - average particle composition changes from **85Pt:15Co to ~95Pt:5Co**
- Significant Pt-enrichment of most particles (except for very large particles)

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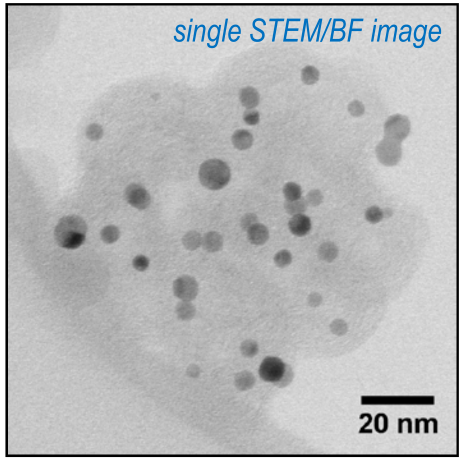
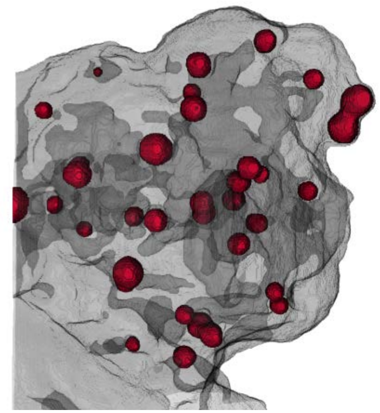
Technical Progress: Extensive Study of PtCo Catalysts

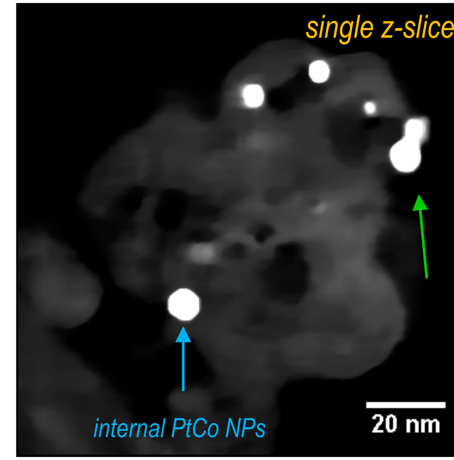
SOA **Pt-Co/HSAC**
Wet Drive cycle 1200 hrs:

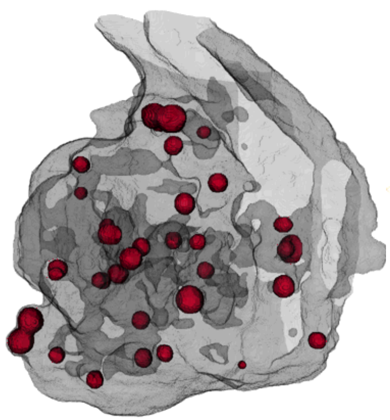
- Avg. PtCo particle size
  - 7.5nm diameter
- Avg. PtCo composition
  - 95% Pt – 5% Co
- Some change of PtCo particles from *inside* to *surface* of HSAC support:
  - 65% remain in core
  - 35% on surface



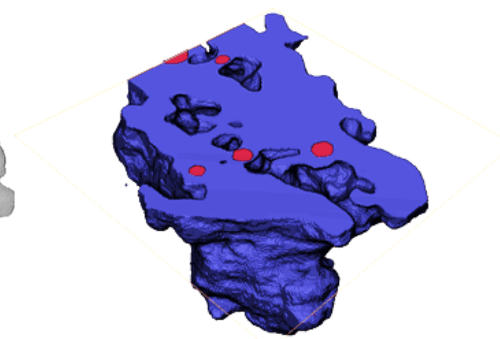
segmented Pt/C 3D surfaces



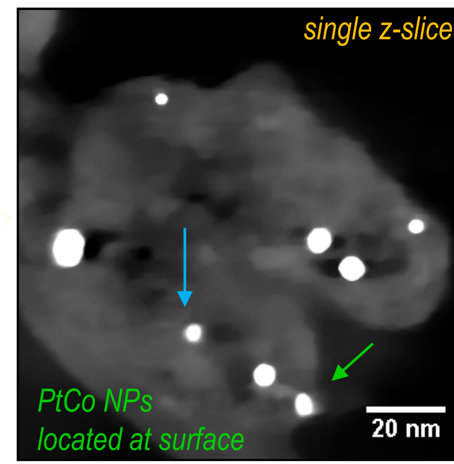




rotation animation

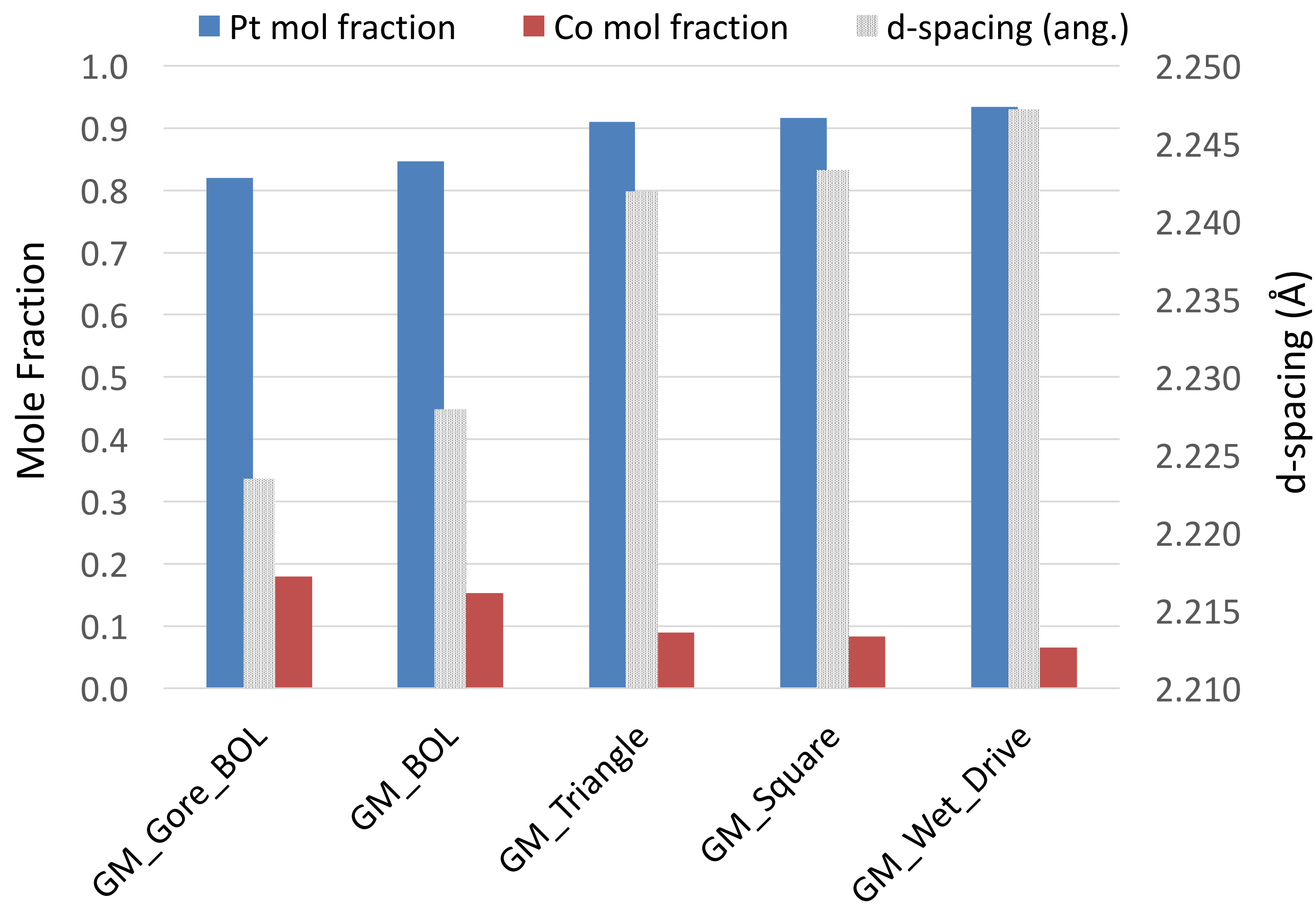


volume clipping animation



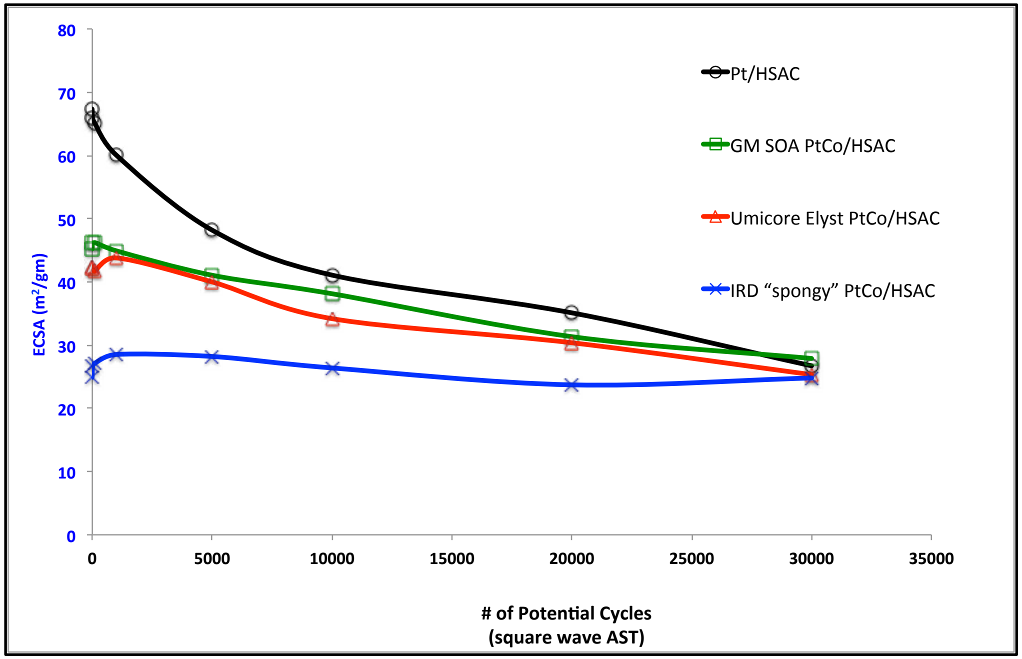
Increased PtCo particles on surface of HSAC after testing due to Pt and Co dissolution

Technical Progress: Extensive Study of PtCo Catalysts



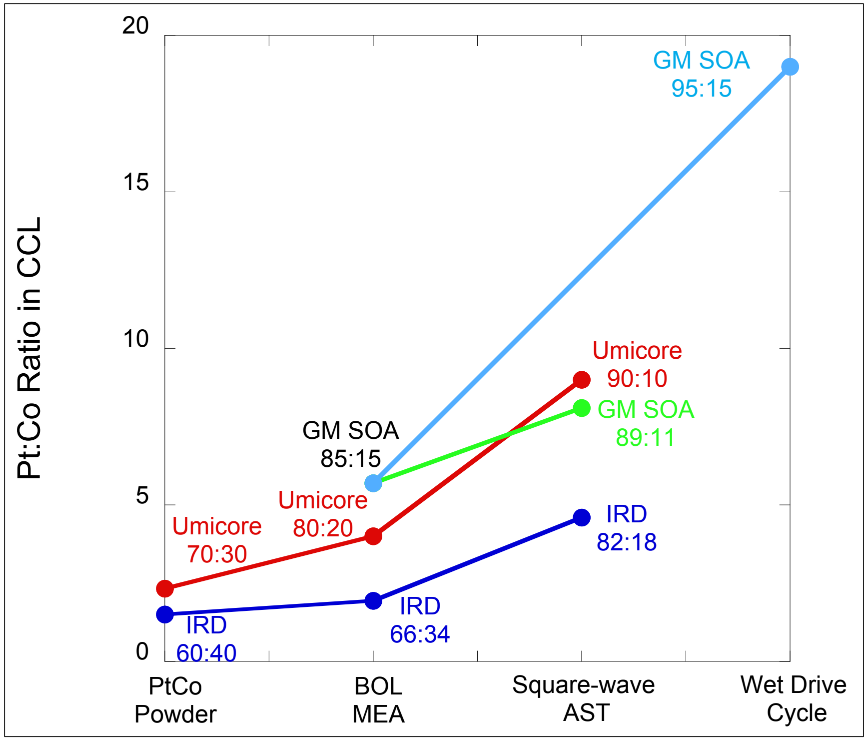
Pt and Co mol fractions in particles and d-spacing calculated from fit to position of WAXS (111) peak – *PtCo catalysts become more "Pt-like" during ASTs*

Technical Progress: Co Loss During ASTs



SOA PtCo exhibits improved initial performance (ECSA) compared to other PtCo/HSAC catalysts, but after 30,000 cycles, ECSA values are the same

Performance (ECSA) loss can be directly attributed to extensive Co loss from catalyst/CCL into membrane during AST



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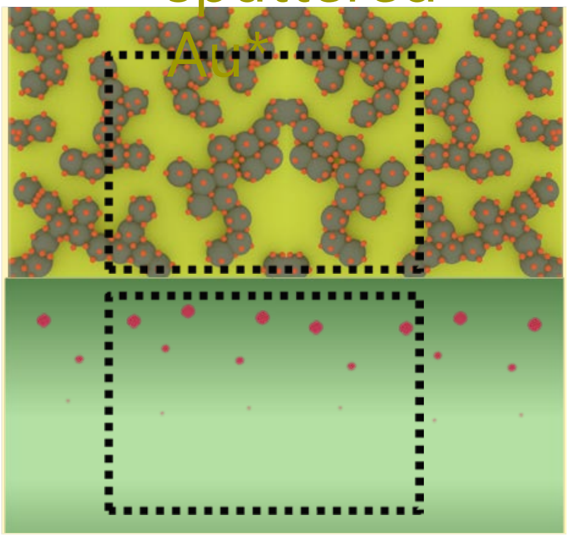
Technical Progress: Quantifying Co Loss to Membrane

Method:

- Au-coat MEAs for internal standard (should not use Cu, Pt, C)
- Acquire EDS maps of cathode catalyst layer (CCL) and membrane
- Assume most Pt lost redeposits in "Pt-band" in membrane near the CCL, calculate Pt migration from cathode into membrane using Au reference/standard
- Use average Pt:Co ratio in untested CCL and amount of Co in tested CCL to calculate ~Co in membrane

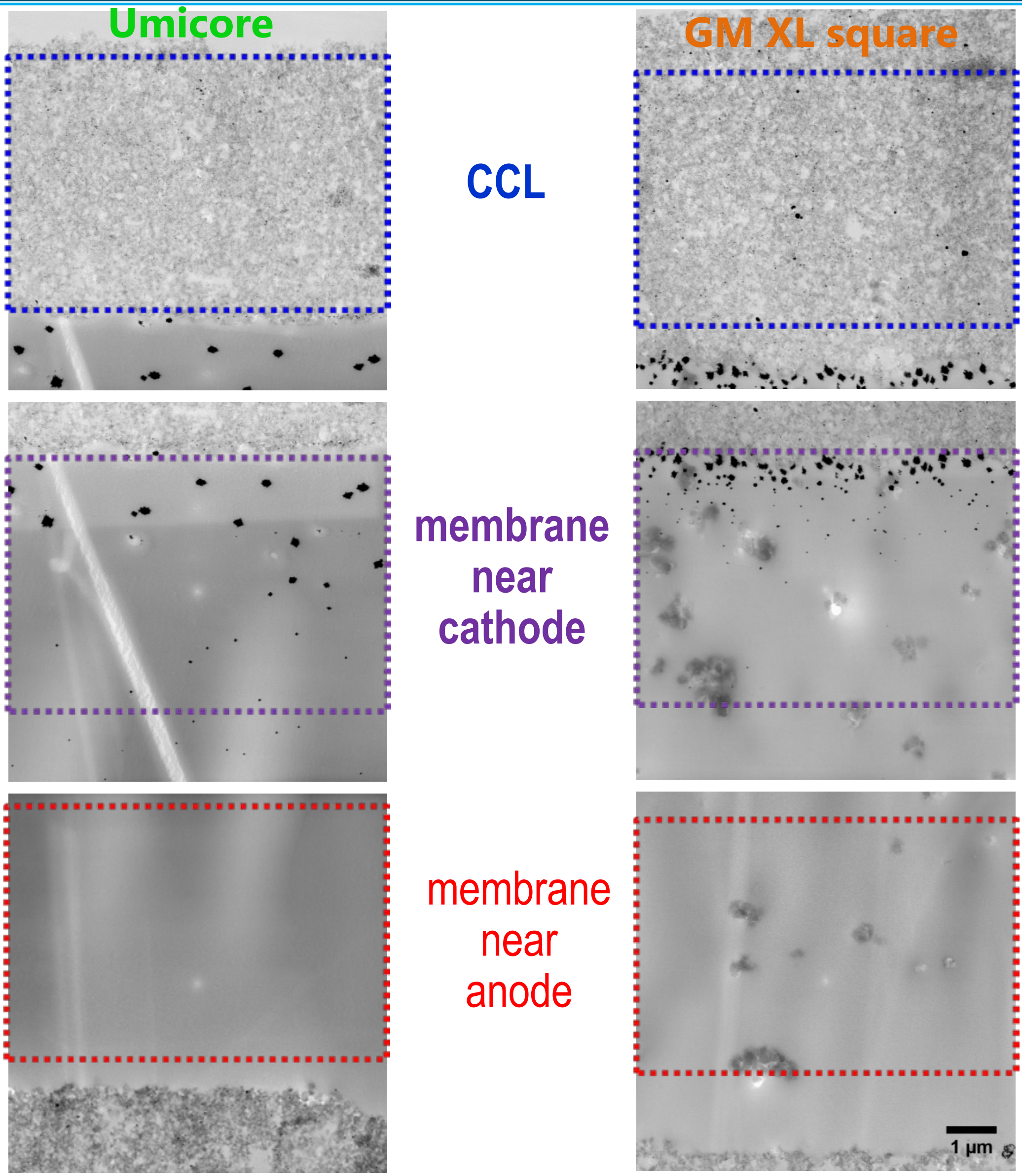


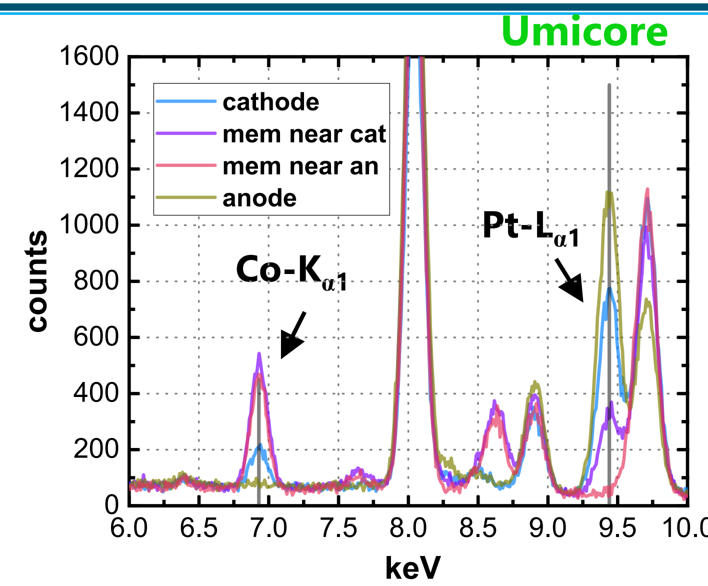
$$\frac{Pt_{mem}/Au_{mem}}{Pt_{cat}/Au_{cat} + Pt_{mem}/Au_{mem}} = Pt_{loss}$$

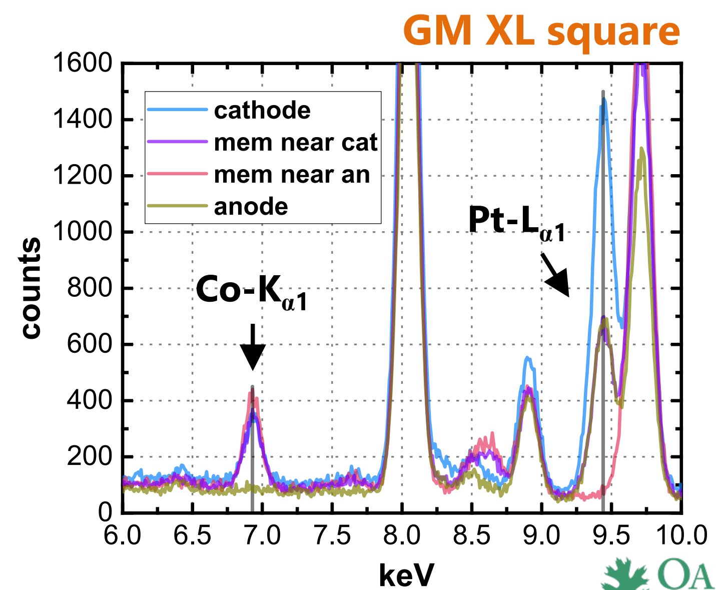
W. Bi, G.E. Gray, and T.F. Fuller, *Electrochemical and Solid-State Letters* 10 (5) B101 (2007).

D.A. Cullen, R. Koestner, R.S. Kukreja, Z.Y. Liu, S. Minko, O. Trotsenko, A. Tokarev, L. Guetaz, H.M. Meyer III, C.M. Parish, and K.L. More, *Journal of the Electrochemical Society* 161 (10) F1111 (2014).

Technical Progress: Quantifying Co Loss to Membrane







Technical Progress: Quantifying Co Loss

Co migration from cathode to membrane:

	nominal loading -BOL conditioned- (mg/cm^2)	AST STEM/EDS quantification	Loss to membrane (mg/cm^2)	remaining cathode content(mg/cm^2)
GM XL (square wave)	0.1	32% Pt loss	0.032	0.068 Pt
	0.018	50% Co loss	0.009	0.009 Co
Umicore (triangle wave)	0.1	28% Pt loss	0.028	0.072 Pt
	0.025	52% Co loss	0.013	0.012 Co

Next step - how much Co remains within the ionomer in CCL?

Technical Progress: RDE Testing - Film Deposition, Impurities

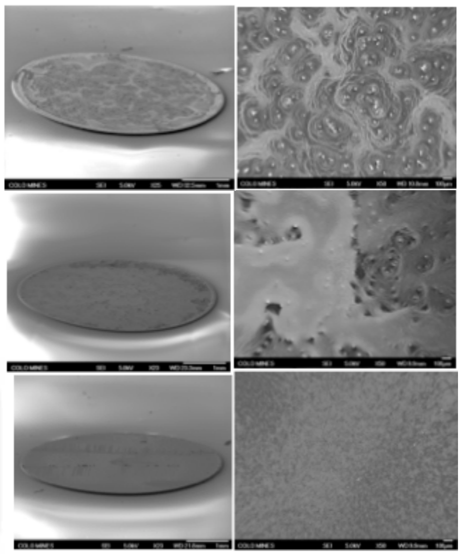
- RDE technique used by basic/applied science community for PEMFC electrocatalyst screening
- Standard test protocol and best practices can enable procedural consistency and less variability
- Test protocol and best practices validated at NREL and ANL using poly-Pt, Pt/C-TKK, JM, Umicore

3 film deposition/drying methods evaluated @ NREL

SAD (stationary air-dry)

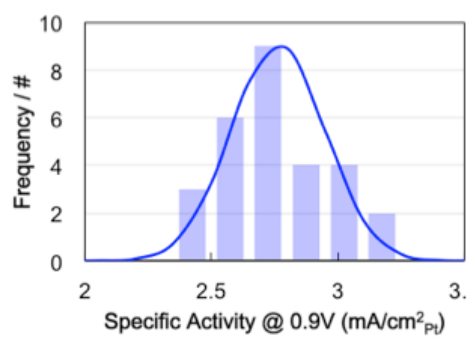
RAD (rotational air-dry)

SIPAD (stationary IPA dry)

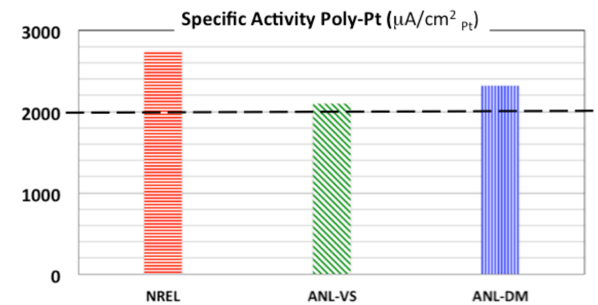


Nafion-based Rotational Air Drying (N-RAD) most reliable method for routine screening

Cell and Electrolyte Impurity Levels—poly-Pt specific activity as a diagnostic



Statistical reproducibility
Poly-Pt specific activity @ NREL



Poly-Pt specific activity
inter-lab comparison

RDE cell configurations used at NREL and ANL

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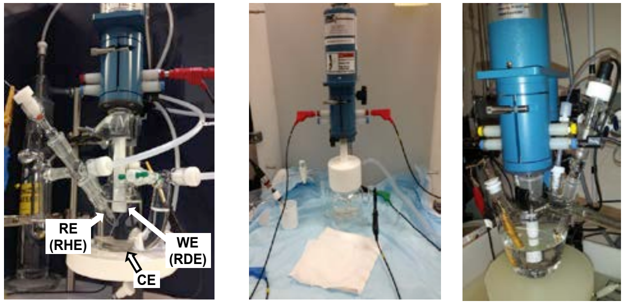
Argonne NATIONAL LABORATORY



RHE, No Salt Bridge **ECCL, NREL**

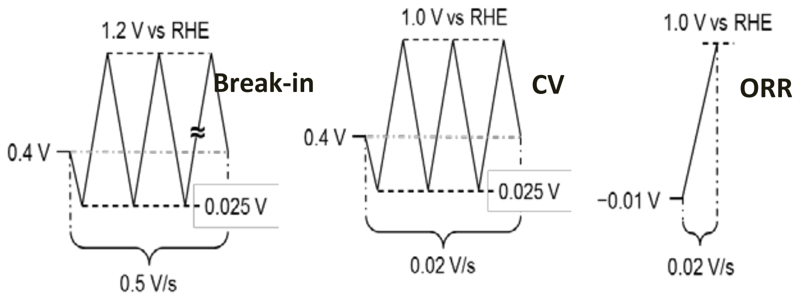
SCE, Salt Bridge **ESC, ANL**

Hg/Hg_2SO_4, Salt Bridge **HFCM, ANL**

S.S. Kocha, K. Shinozaki, J.W. Zack, D. Myers, N. Kariuki, T. Nowicki, V. Stamenkovic, Y. Kang, D. Li, and D. Papageorgopoulos, "Best Practices and Testing Protocols for Benchmarking ORR Activities of Fuel Cell Electrocatalysts using RDE," *Electrocatalysis* (2017) DOI:

Technical Progress: TF-RDE Protocols and Baselines

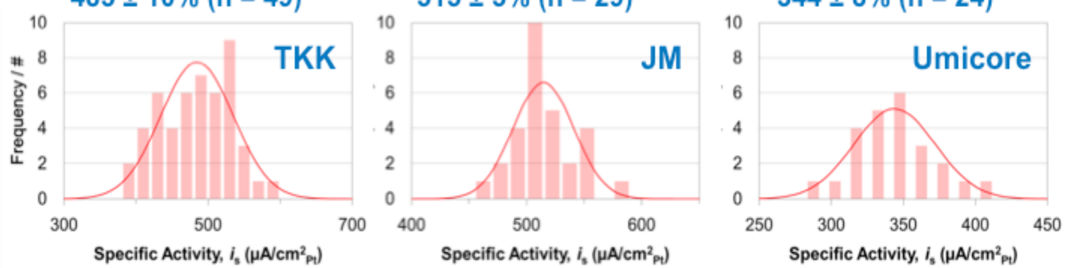
RDE Protocols



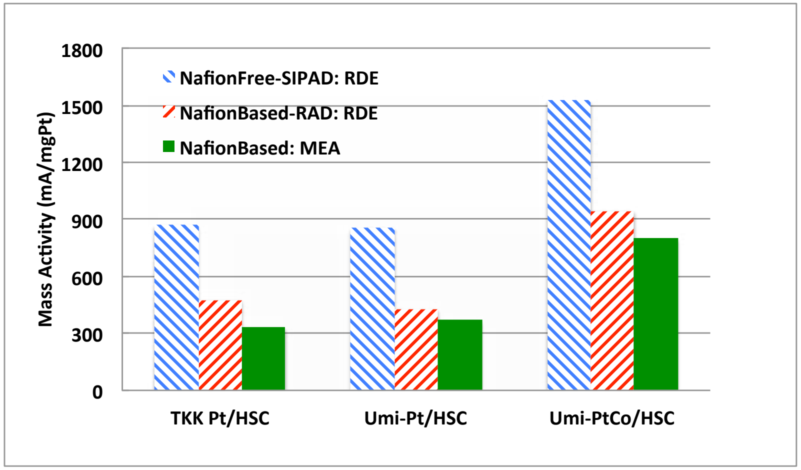
ORR Protocol Details

Gas	N_2 or O_2
Temperature	r.t.
Rotation Rate [rpm]	1600
Potential Range [V vs. RHE]	−0.01 to 1.0 (anodic)
Scan Rate [V/s]	0.02
R_{sol} measurement method	i-interrupter or EIS (HFR)
iR compensation	applied during measurement
Background Subtraction	LSV (O_2)−LSV (N_2)

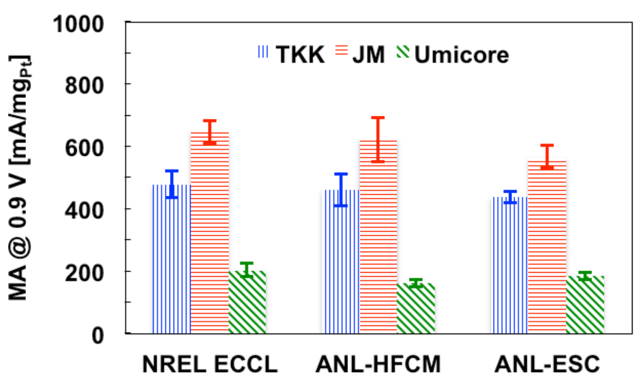
Statistical Reproducibility Pt/C Specific Activity ($\mu A/cm^2_{Pt}$) at NREL (Rotational Air Dry or N-RAD technique)



46.4 wt% Pt; d~2.5nm | 37.6 wt% Pt; d<2nm | 47.2 wt.% Pt; d~4.9nm



Pt/C mass activity (mA/mg_{Pt})
Inter-lab comparison
(N-RAD technique)



Test protocol and best practices validated at NREL and ANL

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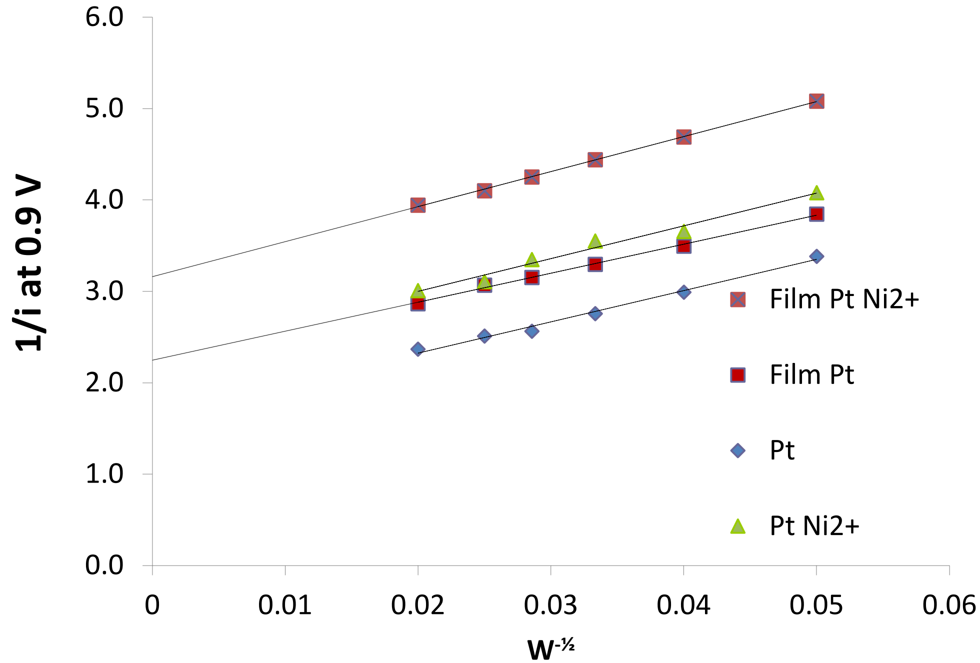
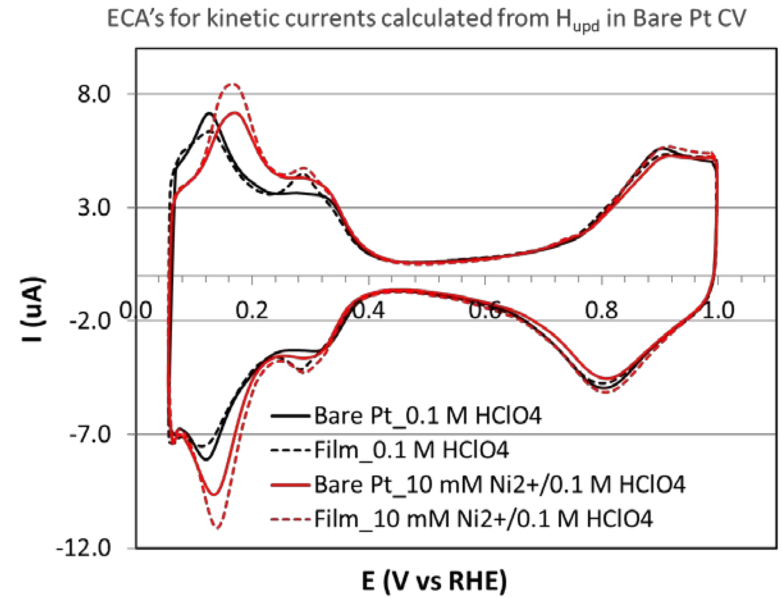
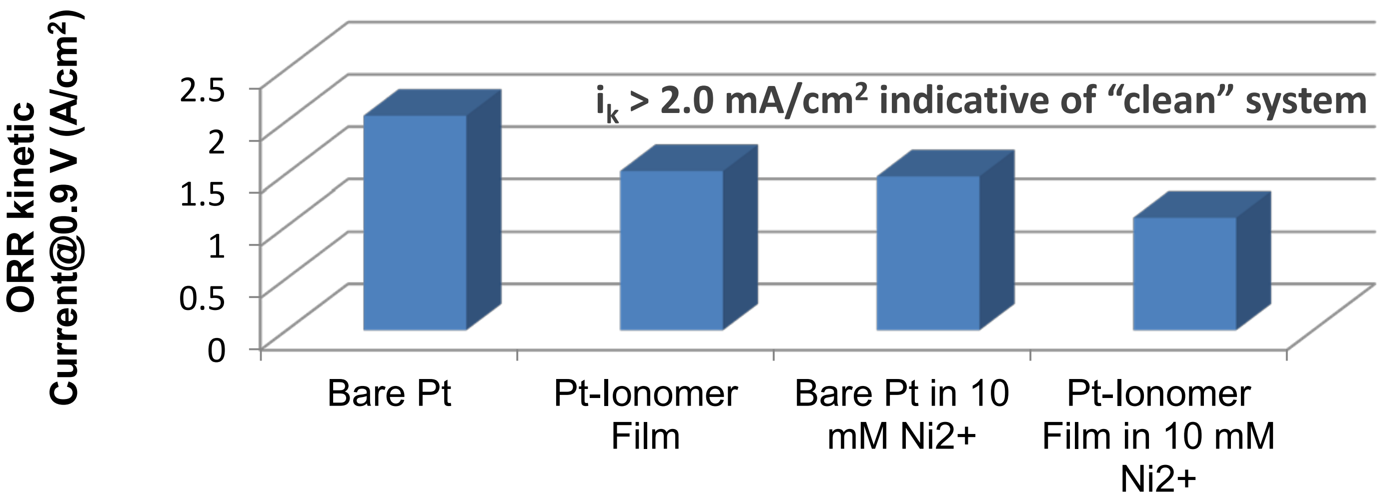
FCPAD FUEL CELL PERFORMANCE AND DURABILITY

Technical Progress: Ionomer-TM Effect on ORR Kinetics RDE







ORR Kinetics on bare and PFSA thin film-coated Poly-Pt with 10 mM Ni^{2+} in electrolyte

Studies on Co^{2+} underway

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FCPAD FUEL CELL PERFORMANCE AND DURABILITY

Proposed Future Work

- **Catalysts and Catalyst Layers**
  - Characterize new catalysts incorporated into MEAs and new CCL architectures before and after ASTs (ANL, BNL, Umicore, etc.)
  - Work with FOA partners and implement FC-PAD capabilities to characterize novel catalysts/MEAs
  - Coordinate characterization results with refined models
- **Testing and AST Refinement**
  - Quantify the effect of Co and Ce in the ionomer and how it affects performance (both sheet resistance and local oxygen resistance)
  - Complete 5000 hr benchmarking test
  - Initiate durability testing using a differential cell (currently using GMs 5cm^2 cell) and validate using new 10cm^2 differential cell hardware
  - Understand the effect of Co alloying on carbon corrosion at 30C
- **Dissolution Studies**
  - Correlate Pt and Co dissolution with extent of oxidation and oxide structure for PtCo alloy catalysts
  - Measure Pt re-deposition rates as a function of potential using on-line ICP-MS for input to catalyst degradation models
  - On-line ICP-MS measurements of Pt and TM dissolution as a function of catalyst particle size and support
  - EXAFS analysis of changes in Pt and Co coordination and bonding after AST

Summary

- **Relevance/Objective:**
  - Optimize performance and durability of fuel-cell components and assemblies
- **Approach:**
  - Use synergistic combination of modeling and experiments to explore and optimize component properties, behavior, and phenomena
- **Technical Accomplishments:**
  - Understanding of the aqueous stability of PtCo alloys using time-resolved on-line ICP-MS measurements
  - Refinement of catalyst durability AST to better simulate FCTT drive cycle protocol
  - Extensive characterization of multiple PtCo catalysts showed performance loss correlation with accelerated Co leaching/dissolution
  - Quantification of Co loss from CCL to membrane during AST
  - Initiated work with FOA partners
- **Future Work:**
  - Further our understanding of Pt-alloy durability by incorporating new catalyst/MEAs in FC-PAD
  - Elucidate critical bottlenecks for performance and durability from ink to CCL formation to conditioning to testing
  - Use critical characterization data as input for multiscale modeling of cell and components
  - Expand dissolution studies to better understand the behavior of Pt-based TM catalysts

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  - Dimitrios Papageorgopoulos
  - Greg Kleen

- Organizations we have collaborated with to date

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  - DOE Office of Science: SLAC, ALS-LBNL, APS-ANL, LBNL-Molecular Foundry, CNMS-ORNL, CNM-ANL
  - NIST: BT-2