Polymer Electrolyte Fuel Cell Lifetime Limitations: The Role of Electrocatalyst Degradation

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2011 U.S. DOE Hydrogen and Fuel Cells Program and
Vehicle Technologies Program
Annual Merit Review and Peer Evaluation Meeting
Washington D.C.

May 9-13, 2011

Project ID# FC012

This presentation does not contain any proprietary or confidential information

Overview

Timeline

- Project start data: October, 2009
- Project end data: September, 2012
- Percentage complete: 40%

Budget

- Total project funding:
  - DOE: $3,754 K
  - Contractor share: $544 K
- Funding received in FY10
  - $ 1,003 K
- Funding expected for FY11
  - $ 566 K

Barriers

- Barriers addressed
  - A. Durability
  - B. Cost
  - C. Electrode performance

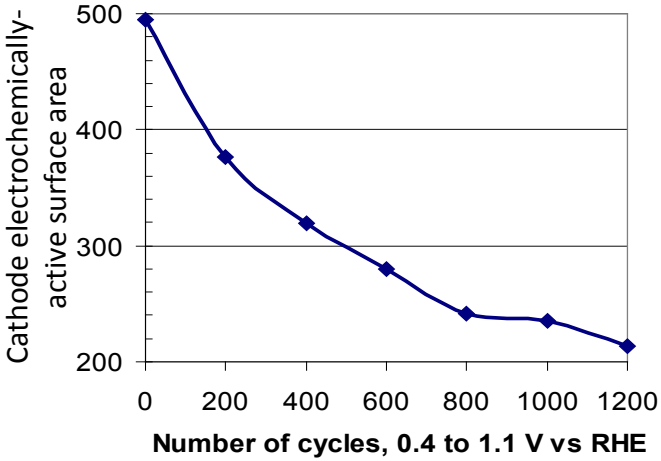
Partners

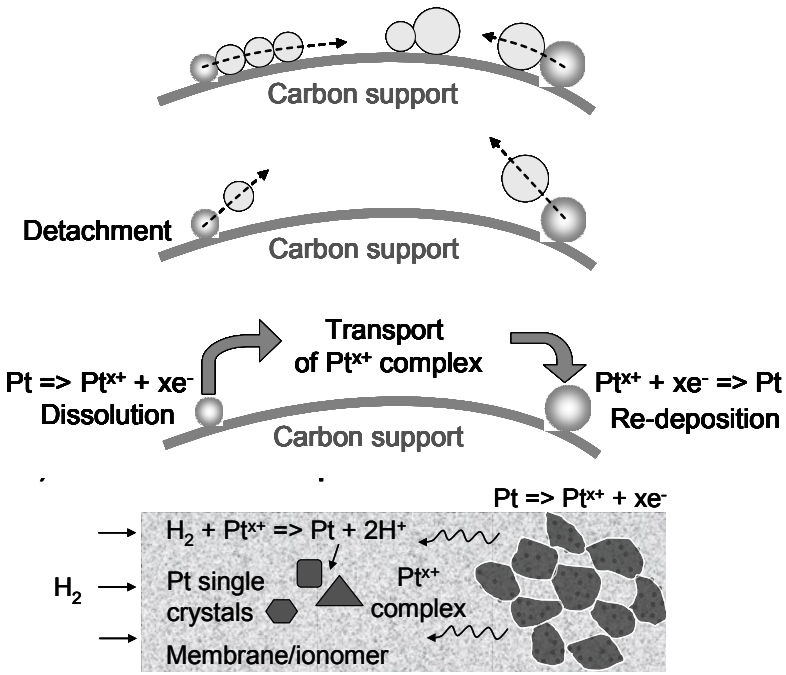
- Johnson Matthey Fuel Cells
  - Sarah Ball, Jonathan Sharman, Brian Theobald, and Graham Hards
- United Technologies Research Center
  - Mallika Gummalla and Zhiwei Yang
- Massachusetts Institute of Technology
  - Yang Shao-Horn and Wenchao Sheng
- University of Texas at Austin
  - Paulo Ferreira, Shreyas Rajasekhara, Daniel Groom, and Stephanie Matyas
  - Jeremy Meyers, Preethi Mathew, and Seok Koo Kim
- University of Wisconsin – Madison
  - Dane Morgan, Shih-kang Lin, Ted Holby, and James Gilbert

Relevance

- Objectives
  - Understand the role of cathode electrocatalyst degradation in the long-term loss of PEMFC performance,
  - Establish dominant catalyst and electrode degradation mechanisms,
  - Identify key properties of catalysts and catalyst supports that influence and determine their degradation rates,
  - Quantify the effect of cell operating conditions, load profiles, and type of electrocatalyst on the performance degradation, and
  - Determine operating conditions and catalyst types/structures that will mitigate performance loss and allow PEMFC systems to achieve the DOE lifetime targets.

- Impact
  - To enable catalysts to achieve DOE Technical Targets
    - Durability with cycling 5,000 hours (≤80°C) and 2,000 hours (>80°C)
    - ≤40% loss of initial catalytic mass activity; <30 mV loss at 0.8 A/cm²



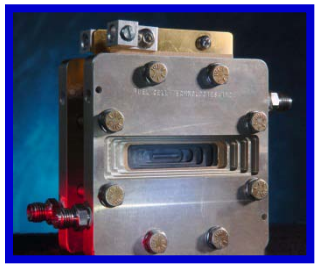


Y. Shao-Horn et al., *Topics in Catalysis*, **46** (2007) 285–305.

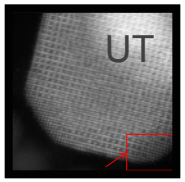
Approach

Methods and Variables

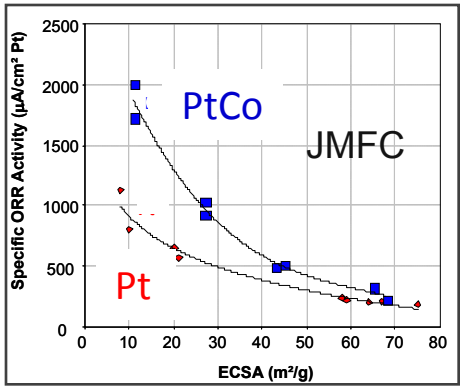
- **Identify the degradation modes and factors contributing to degradation, using**
  - **Systematic cell degradation tests (JMFC and UTRC)**
  - ***In situ* and *ex situ* structural characterization of the catalyst (ANL and UT)**
    - **Small angle X-ray scattering, X-ray absorption spectroscopy, TEM, HAADF-STEM, etc.**
  - **Fundamental out-of-cell studies**
    - **Aqueous cell dissolution/corrosion measurements (ANL, MIT, and JMFC)**
    - ***"In situ"* TEM (UT)**
  - **Theoretical modeling**
    - ***Ab initio*-based modeling of Pt, Pt alloy, and core-shell dissolution (UW)**
    - **Cell kinetic and transport modeling, incorporating kinetics and degradation effects (ANL and UT)**

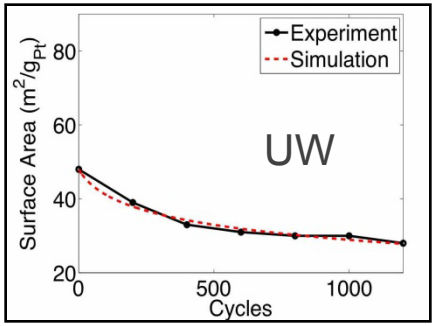


ANL



- **Variables**
  - **Catalyst type and oxophilicity**
    - **Pt, Pt alloys, acid-leached Pt alloys, core-shell, NSTF**
  - **Catalyst particle size (Pt and one Pt alloy)**
  - **Catalyst impurities (e.g., chloride)**
  - **Type of carbon support**
    - **varied surface area, pore size, and relative proportions of micro- and mesopores**
  - **Cell operating parameters**
    - **Potential cycling profile, upper potential limit, cell temperature, RH on cathode**





Approach

Project timeline

May, 2011

Project Schedule	Year 1				Year 2				Year 3			
	Q1	Q2	Q3	Q4	Q1	Q2	Q3	Q4	Q1	Q2	Q3	Q4
Task 1. Catalyst and Membrane-Electrode Assembly Fabrication												
1.1 Benchmark Pt and one Pt alloy with varying particle sizes												
1.2 Pt alloys, acid-leached alloy, core-shell on standard support												
1.3 Pt alloy catalysts with varying degrees of oxophilicity												
1.4 Pt on supports with varying surface area, pore size, and pore size distribution												
1.5 Catalysts with post-doping of catalyst precursor impurities												
Task 2. Cell degradation studies/single cell cycling/parametric aging studies												
2.1 Accelerated stress testing of baseline MEAs and impact of operating conditions												
2.2 Advanced catalyst degradation mode identification												
2.3 Effect of carbon support on MEA electrode performance loss												
2.4 Effect of catalyst impurities on MEA electrode performance loss												
Task 3. Mechanisms of catalyst degradation and underlying physicochemical catalyst properties responsible for degradation												
3.1 Roles of catalyst oxophilicity, extent of oxide formation, and structure of oxide in catalyst degradation												
3.2 Influence of potential, temperature, and physical properties of catalyst on the rates and mechanisms of catalyst component dissolution												
3.3 Role of catalyst-support interactions and support degradation												
3.4 Effect of particle size and catalyst type on ORR activity												
Task 4. Ex situ microscopic and X-ray scattering characterization of catalysts and MEAs												
4.1 Optical microscopy, aberration-corrected STEM and high-resolution TEM w/ EDAX, EELS, XPS												
4.2 Small angle X-ray scattering												
Task 5. Modeling												
5.1 Ab initio based modeling of Pt, Pt alloy, and core-shell dissolution												
5.2 Catalyst degradation models including nature and role of oxide formation in catalyst degradation												
5.3 Cell kinetic, transport model incorporating degradation effects/kinetics												

- **Focus since 2010 AMR has been on parametric and particle size studies of Pt_3Co MEAs, comparison with Pt MEA results, degradation mechanism experiments and modeling of Pt cathode catalysts, and ab initio-based modeling of Pt-Co alloys**

Approach: *Milestones and Go/No-Go Decision Point*

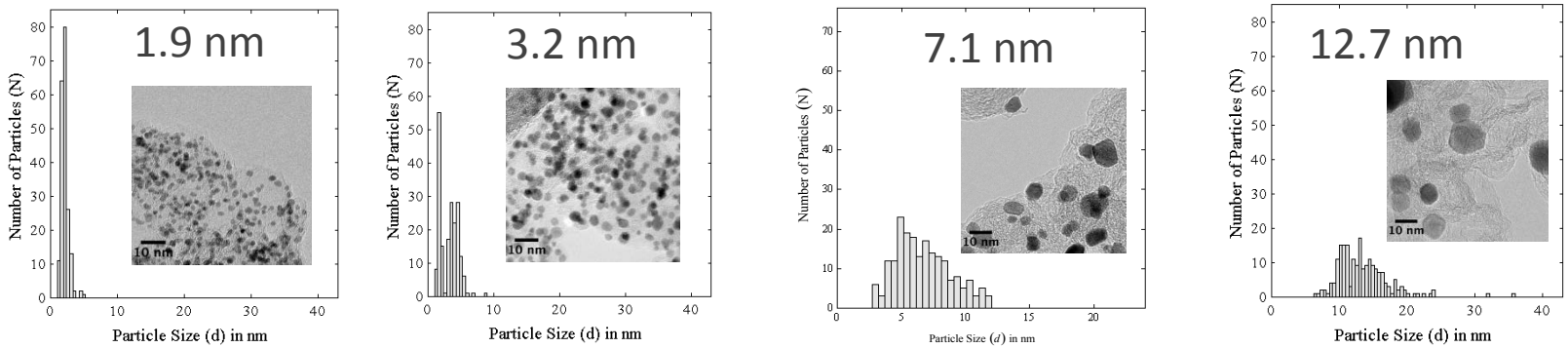
- FY'10 and FY'11 Milestones
  - Determine the effect of initial Pt particle size on the degradation rate of cathode catalyst performance and on Pt dissolution rates - 05/10
    - Completed effect of Pt particle size on performance degradation rate
    - Potentiostatic dissolution rate and steady-state dissolved Pt concentrations are completed
  - Determine the effect of Pt alloy composition on the rates and mechanisms of cathode catalyst performance degradation - 09/11
    - Pt_3Co studies are nearing completion
  - Develop a macroscopic model of Pt dissolution and place exchange, and complete CV and ORR catalyst performance models - 09/11
    - Initial CV, oxide coverage, and dissolution models have been completed and are being refined
  - *In situ* and *ex situ* characterization of two classes of catalysts - 09/10
    - Completed ASAXS measurements of Pt particle growth during DOE protocol potential cycling in 0.1 M $HClO_4$ electrolyte and analyzed all data
    - Completed TEM analysis of Pt powders with different initial particle sizes; Completed post-test TEM, SEM, and ASAXS analyses of cycled MEAs
    - Completed TEM analysis of Pt_3Co powders with different initial particle size; performed aberration-corrected STEM analysis on Pt_3Sc nanoparticles
  - Develop a Kinetic Monte Carlo model to predict alloy nanoparticle evolution in the fuel cell cathode environment - 09/11
    - KMC model has been developed on track for completion; dominant contribution is dissolution, driven by potential and acidity
- Go/No-Go Decision Point
  - Demonstrate link between aqueous electrolyte studies of degradation mechanisms of three classes of catalysts and degradation observed in MEA tests – 09/11
    - On-track

Technical Progress (Tasks 1 and 4)

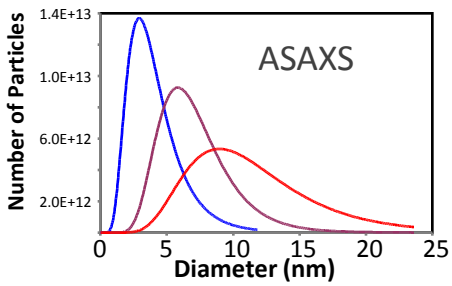
Particle size studies of Pt and Pt_3Co

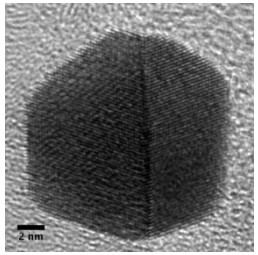
UT Austin

40 wt% Pt/Ketjen: four particle sizes (1.9, 3.2, 7.1, 12.7 nm)

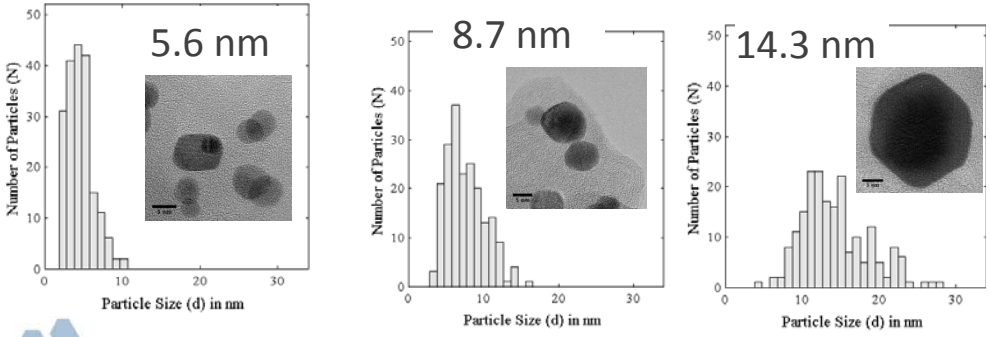


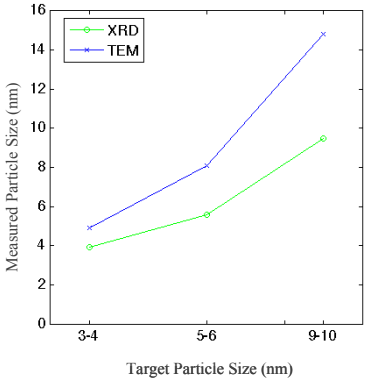
40 wt% Pt_3Co/Ketjen: three particle sizes (5.6, 8.7, 14.3 nm)

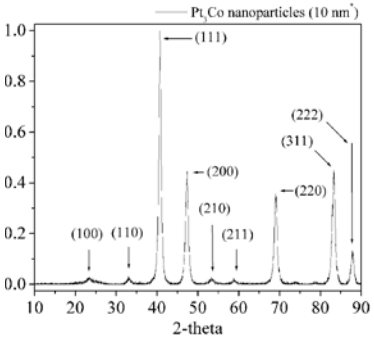




- Particle size distribution broadens with increasing mean particle size
- Increased ordering observed with increasing particle size
- Twinning observed for Pt_3Co – prevalence increasing with increasing particle size







Technical Progress (Tasks 2.1 and 2.2)

Particle size and parametric studies of Pt and Pt_3Co catalysts

Cathode Cat.	TEM Mean Particle size (nm)	Cathode loading (mg-Pt/cm²)	Anode loading (mg-Pt/cm²)
Pt	1.9	0.20	0.2
Pt	3.2	0.21	0.18
Pt	7.1	0.21	0.2
Pt	12.7	0.21	0.2
Pt_3Co	5.6	0.23	0.20
Pt_3Co	8.7	0.22	0.20
Pt_3Co	14.3	0.22	0.20

Cycling Protocol for particle size studies:

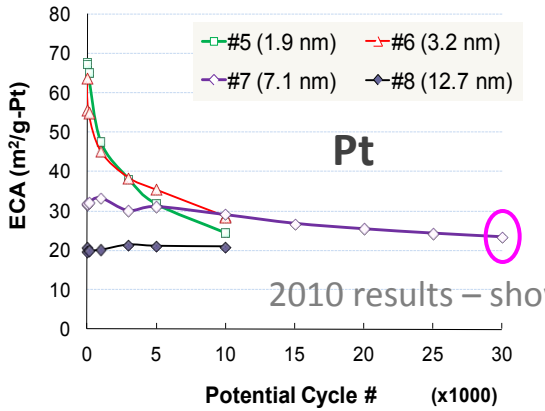
- Triangle wave potential cycle: 0.6 V to 1.0 V (50 mV/s ramp rate)
- Cell Temperature: 80 °C
- Fuel/Oxidant : 100% RH H_2 at 100 sccm and 100% RH N_2 at 50 sccm
- Pressure: Atmospheric

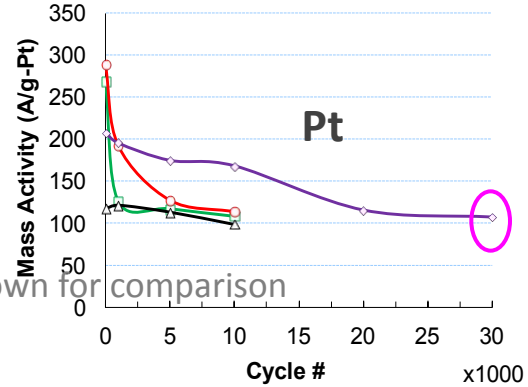
- **Parametric studies**: effect of upper potential limit, relative humidity, temperature
- Pt: 3.2 nm mean particle size; Pt_3Co: 5.6 nm mean particle size

Cell ID	Potential cycle
BL	• Square wave potential cycle: 10s at 0.4V, 10s at 0.95V (20s / cycle) • Cell Temperature: 80°C • Humidity: Anode = Cathode = 100% RH • Fuel/Oxidant : 0.5SPLM 4%H_2 / 0.5SPLM N_2 • Pressure: Atmospheric pressure
1.05V	• Square wave potential cycle: 10s at 0.4V, 10s at 1.05V (20s / cycle) • All other parameters were same as BL
30%RH	• Humidity: Anode = Cathode = 30%RH • All other parameters were same as BL
90 °C	• Cell Temperature: 90°C • All other parameters were same as BL

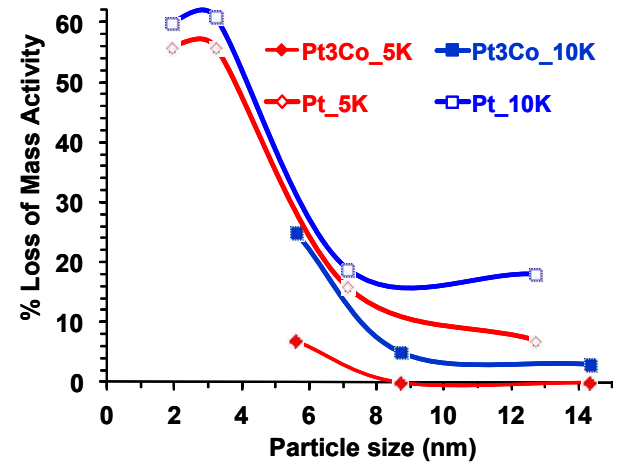
Technical Progress (Tasks 2.1 and 2.2)

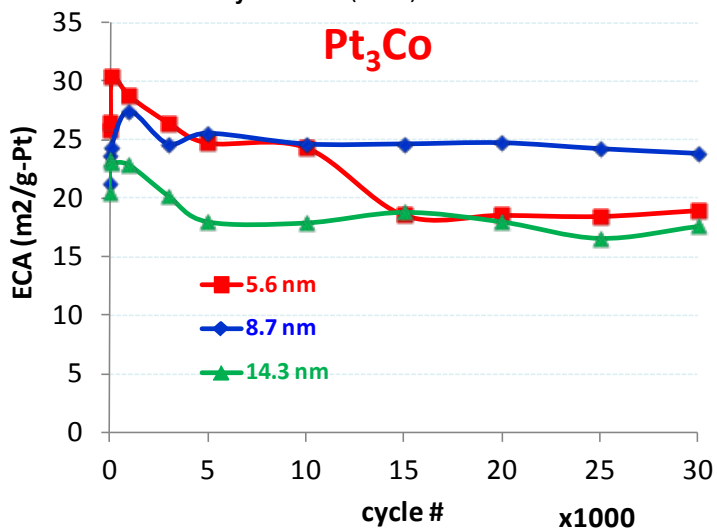
Particle size studies of Pt_3Co

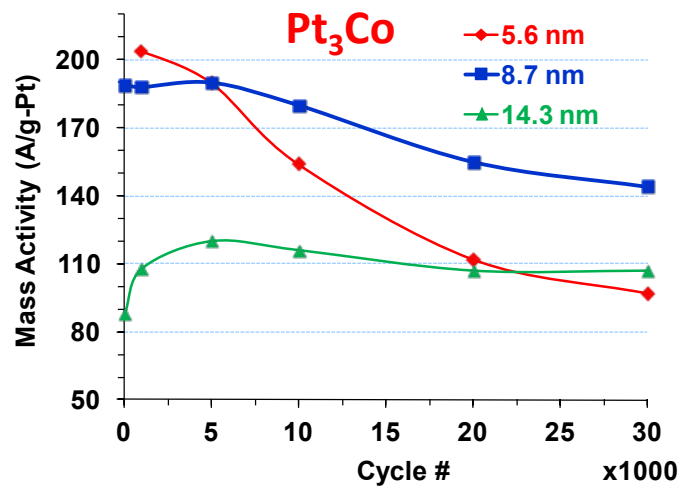




2010 results – shown for comparison



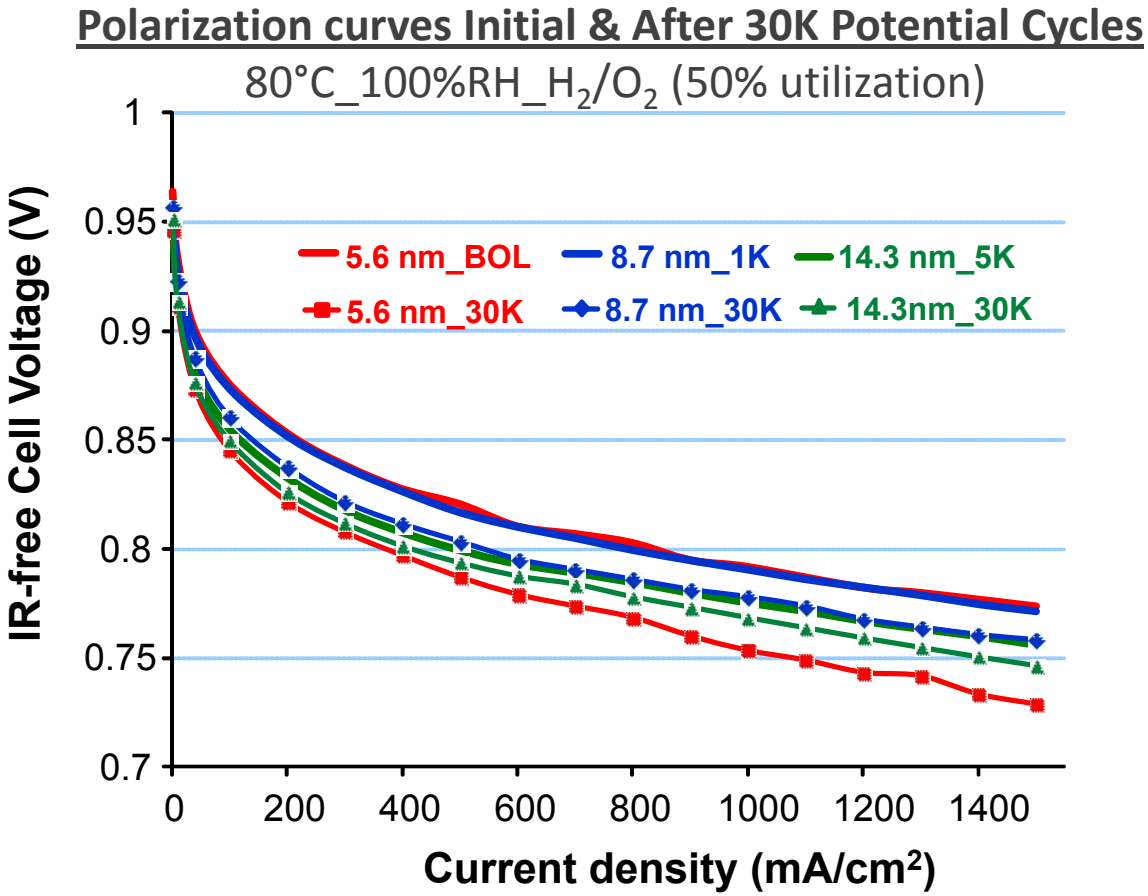




- Cycling to 1.0 V has minimal impact on catalysts with large initial particle size
- Cycling degrades performance of catalysts with smaller initial particle size toward that of larger particles
- Similar decay trends observed for Pt 7.1 nm and Pt_3Co 5.6 nm; Pt 12.7 nm and Pt_3Co 8.7 nm
- Mass activity decay of the Pt_3Co cells is lower than Pt cells over the range of particle sizes

Technical Progress (Task 2.2)

Particle size studies of Pt_3Co catalyst

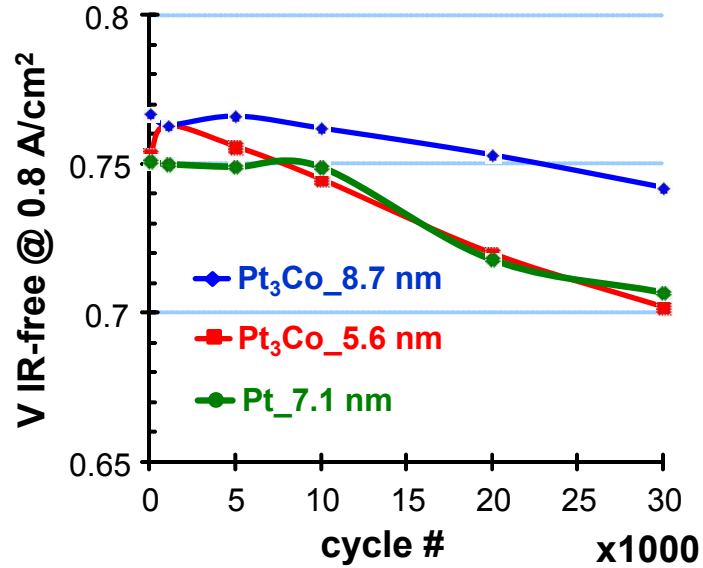


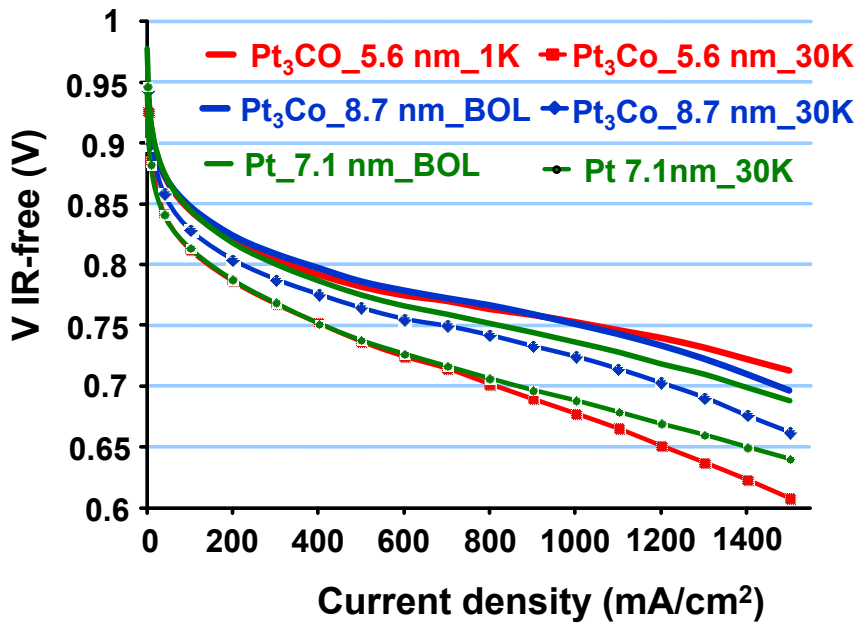
- Beginning of life performance of MEAs with smaller cathode catalyst particle size (5.6 nm) is highest, but voltage cycling degrades performance to below that of MEAs with larger initial particle size
- MEAs with large cathode catalyst particles (14.3 nm) show minimal O_2 performance degradation over 30,000 cycles

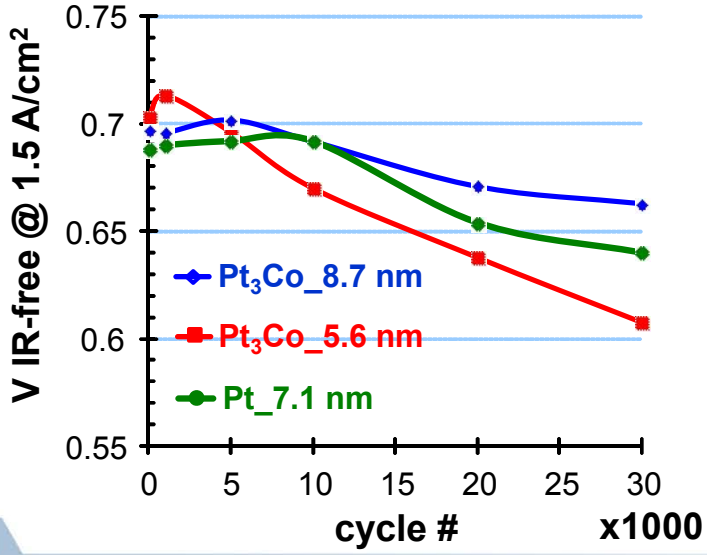
Technical Progress (Task 2.2)

Particle size studies of Pt_3Co - comparison with Pt

IR-free performance, air, fixed flow, Pt and Pt_3Co cathode catalysts



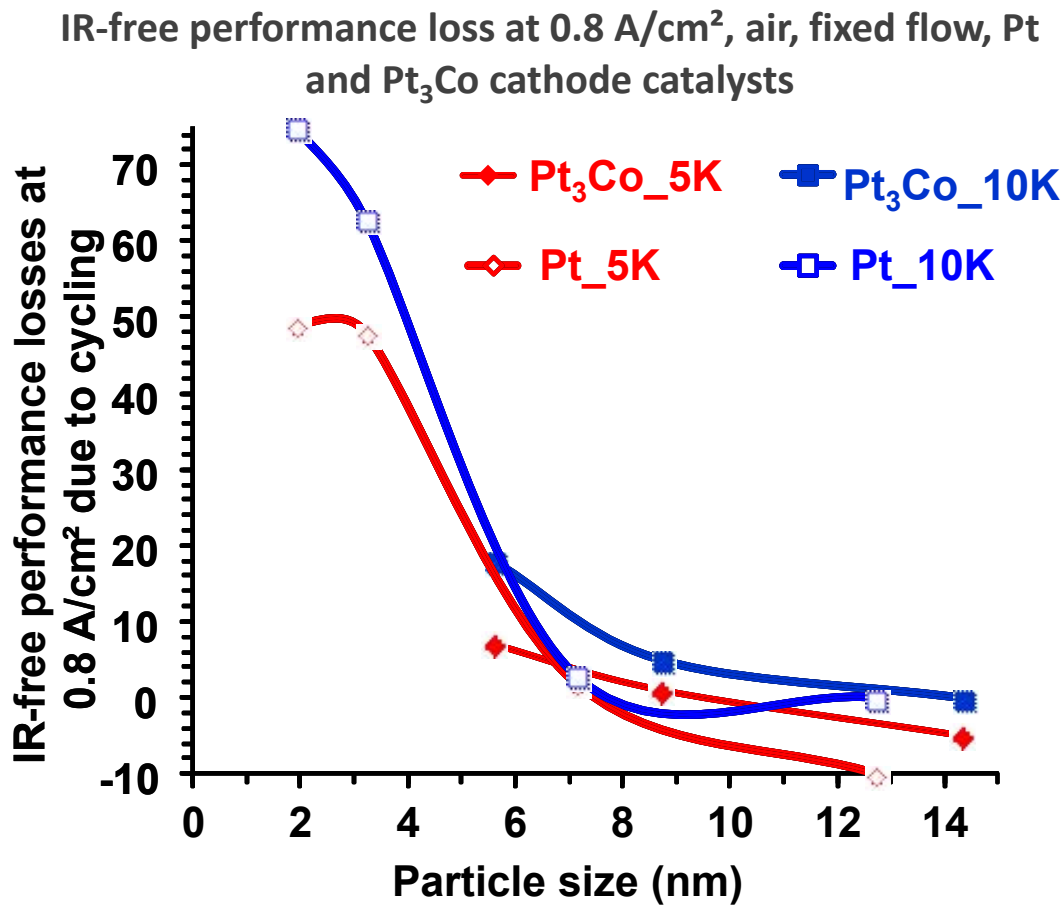




- Initial IR-free performance of 8.7 nm Pt_3Co cell is the best and exceeds Pt performance
- IR-free decay rate of 8.7 nm Pt_3Co cell is lower than 7.1 nm Pt cell
- Difference between IR-free performance after 30,000 cycles of 8.7 nm Pt_3Co and 7.1 nm Pt decreases with increasing current density

Technical Progress (Tasks 2.1 and 2.2)

Particle size studies of Pt_3Co - comparison with Pt

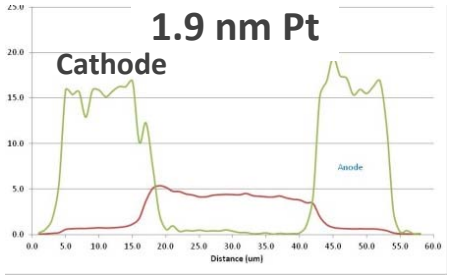


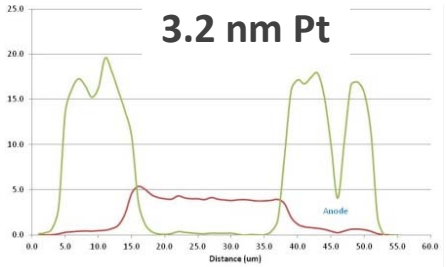
H_2 Pump mOhm•cm²	BOL	EOL (number of cycles)
Pt_3Co 5.6 nm	111	170 (30K)
Pt_3Co 8.7 nm	122	127 (30K)
Pt_3Co 14.3 nm	156	283 (30K)
Pt 1.9 nm	126	145 (10K)
Pt 3.2nm	134	144 (10K)
Pt 7.1 nm	93	108 (30K)
Pt 12.7 nm	138	171 (10K)

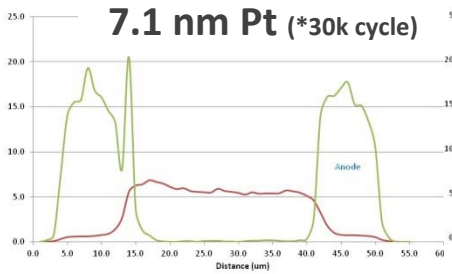
- The absolute performance losses of the Pt and Pt_3Co cells are similar for larger particle sizes
- The ionic resistance in the electrode is higher for Pt_3Co cells, which offsets the improved mass activity stability of the alloy

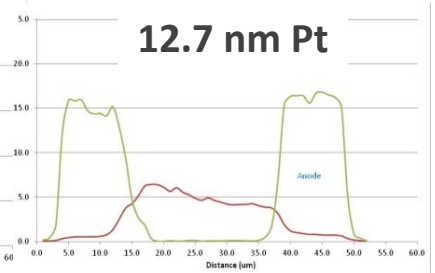
Technical Progress (Tasks 2.1 and 2.2)

Particle size studies of Pt and Pt_3Co catalysts

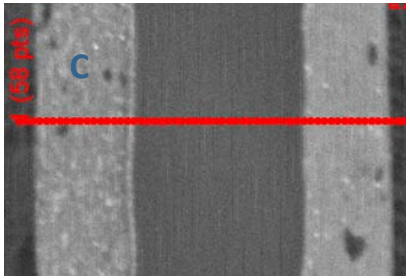


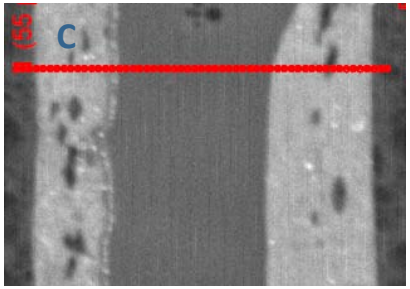


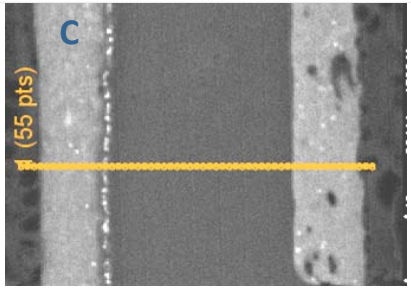


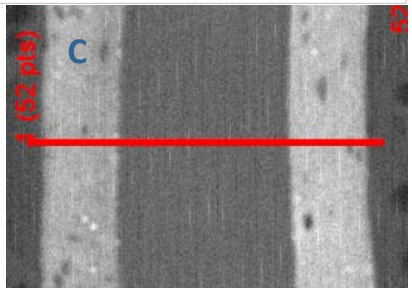


Middle

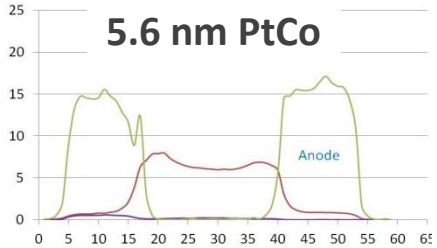


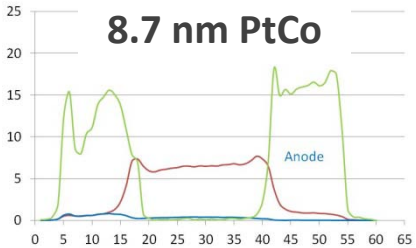


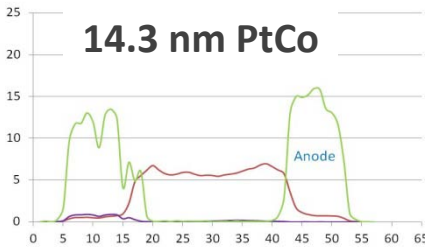


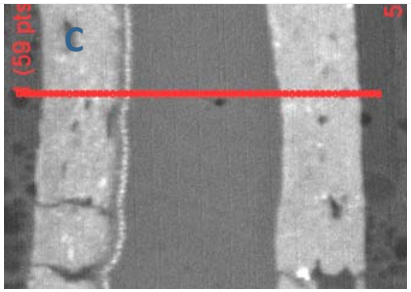


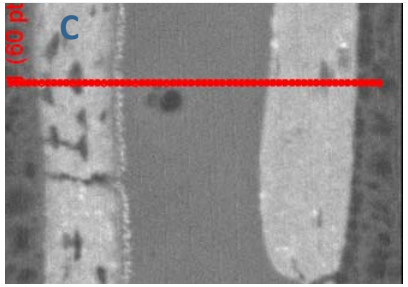
- Triangle wave, 0.6 to 1.0 V, 80°C, 100%RH
- Lower Pt content observed in membrane with larger initial Pt particle sizes
- In general, change in electrode thickness with cycling increases with decreasing particle size

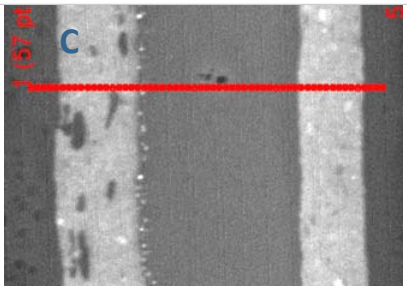








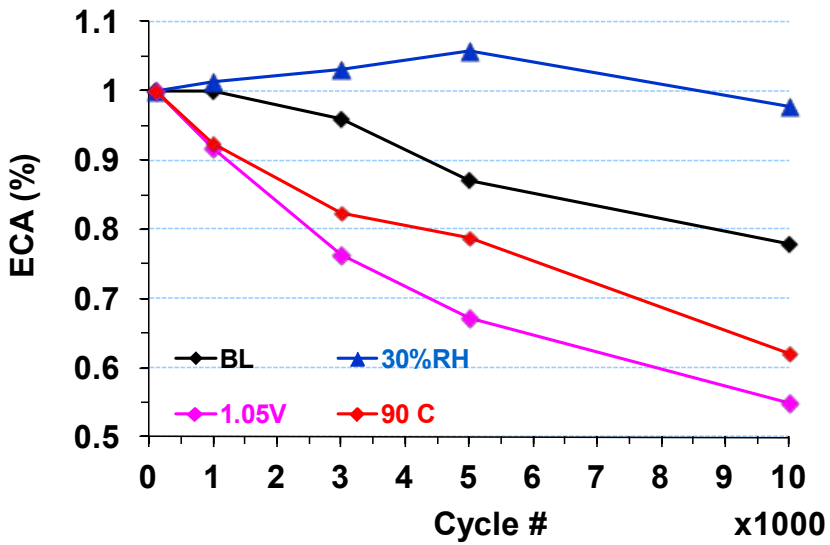


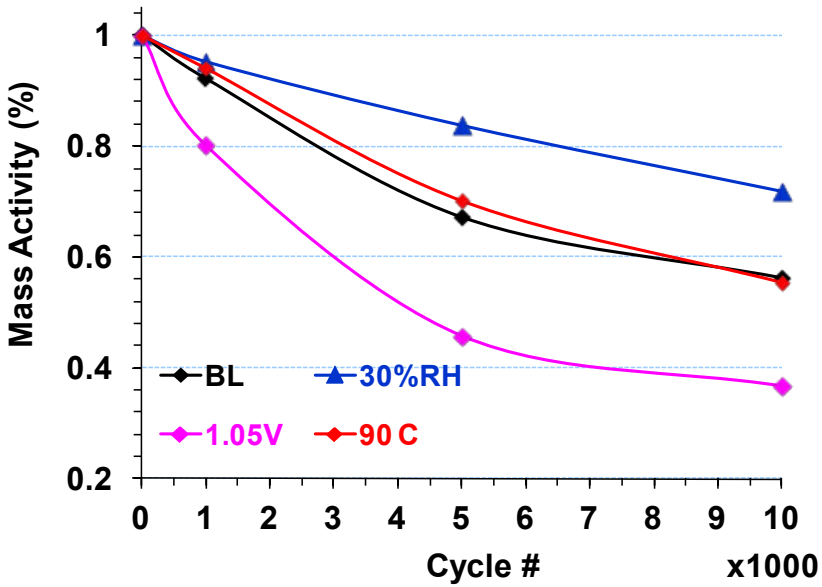


Technical Progress (Task 2.2)

Parametric studies of Pt_3Co catalyst (5.6 nm)

Cell #	Potential cycle
#11 (BL)	• Square wave potential cycle: 10s at 0.4V, 10s at 0.95V (20s / cycle) • Cell Temperature: 80°C • Humidity: Anode = Cathode = 100% RH • Fuel/Oxidant : 0.5SPLM 4%H_2 / 0.5SPLM N_2 • Pressure: Atmospheric pressure
#12 (1.05V)	• Square wave potential cycle: 10s at 0.4V, 10s at 1.05V (20s / cycle) • All other parameters were same as #11
#13 (30%RH)	• Humidity: Anode = Cathode = 30%RH • All other parameters were same as #11
#14 (90 °C)	• Cell Temperature: 90°C • All other parameters were same as #11

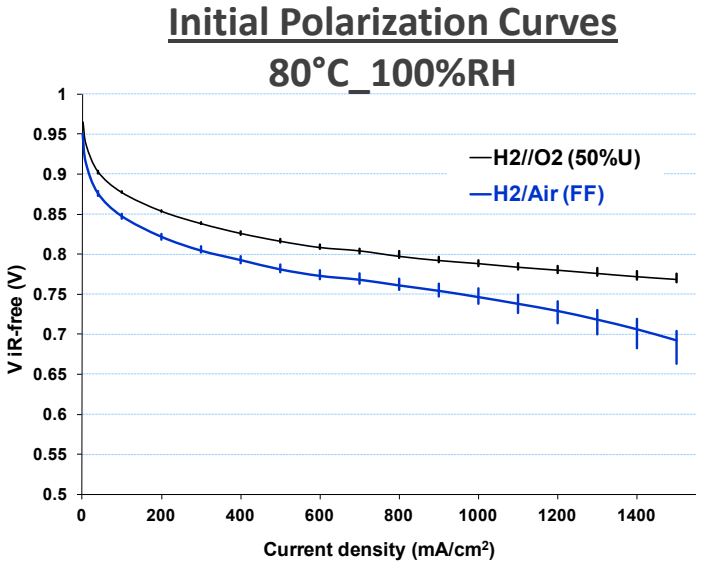


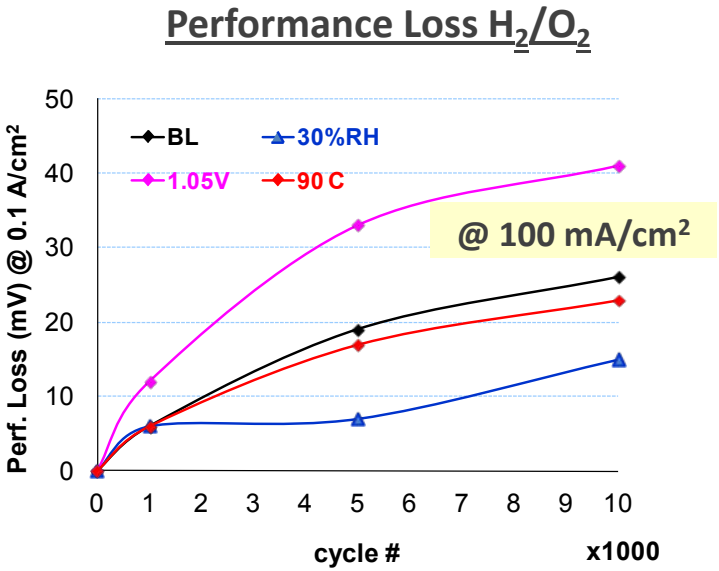


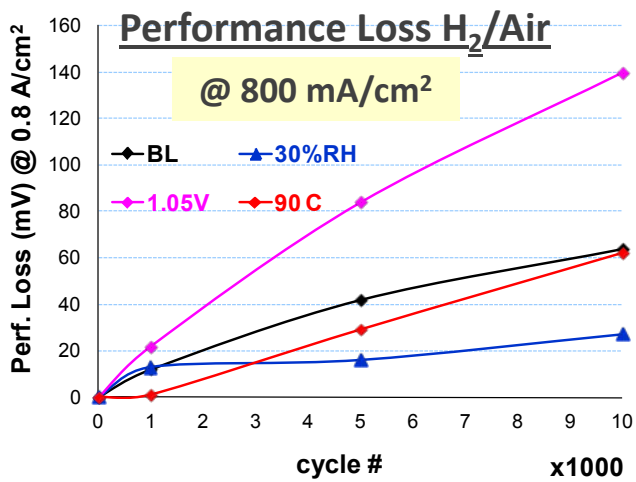
- **Increasing upper limit of voltage cycling increases cathode catalyst surface area and mass activity loss**
- **Low inlet RH decreases cathode catalyst degradation**

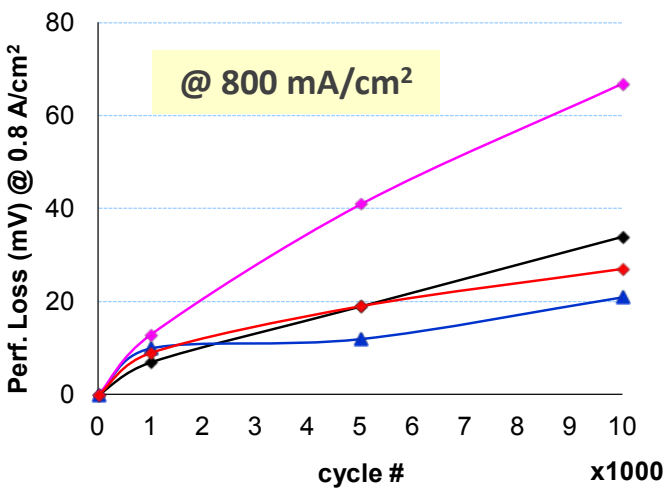
Technical Progress (Task 2.2)

Parametric studies of Pt_3Co catalyst (5.6 nm)





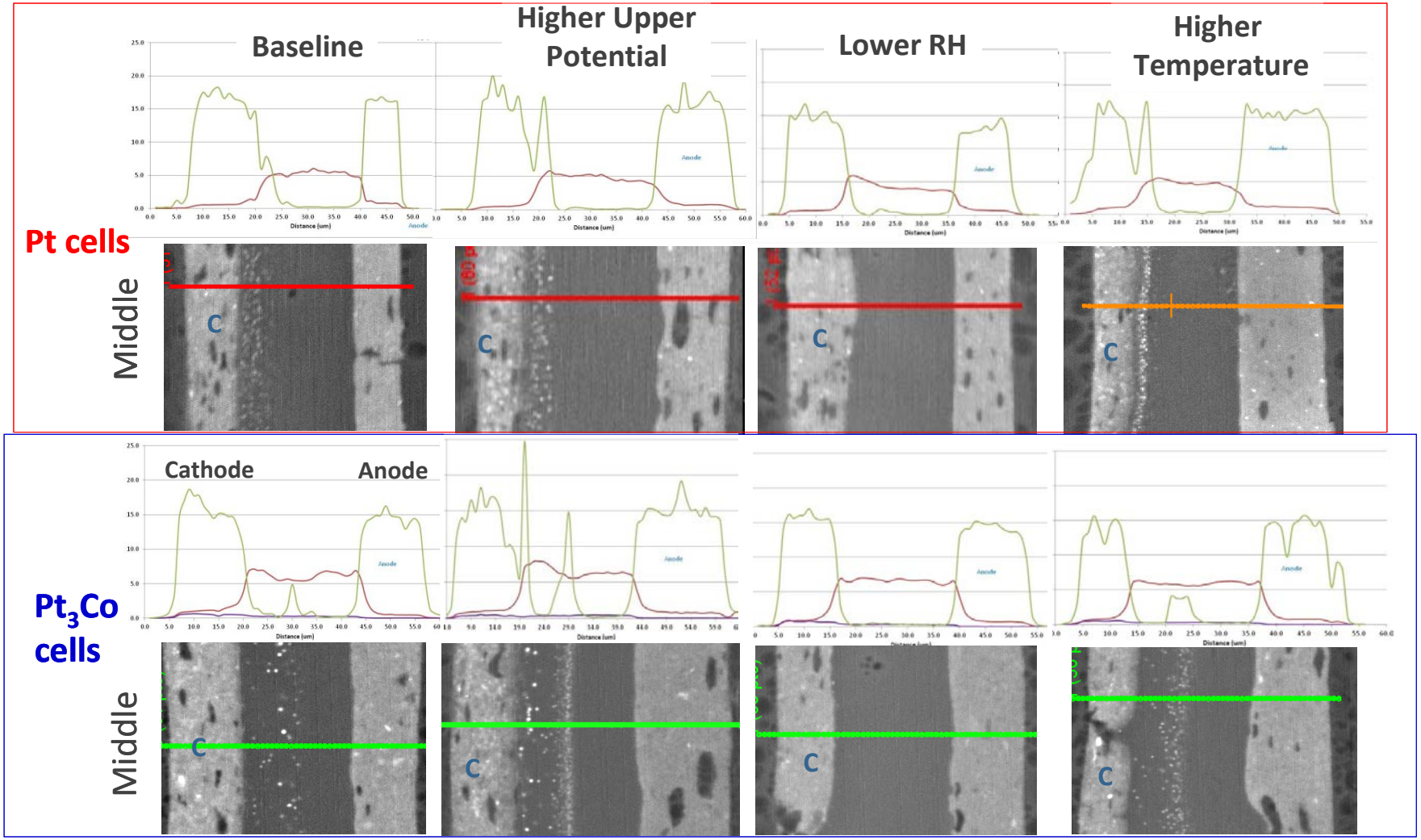




- Cycling to high potentials significantly affects cathode transport losses

Technical Progress *(Tasks 2.1 and 2.2)*

Parametric studies of Pt_3Co and Pt cells



- Higher Pt content in the membrane for cells cycled to higher voltages and at higher temp.
- Lowest Pt content in the membrane for low RH cycled cells
- Pt band is more diffuse compared to triangle wave cycled cells

Technical Progress (Tasks 2.1 and 2.2)

Comparison of particle size and parametric study results for Pt and Pt_3Co catalysts

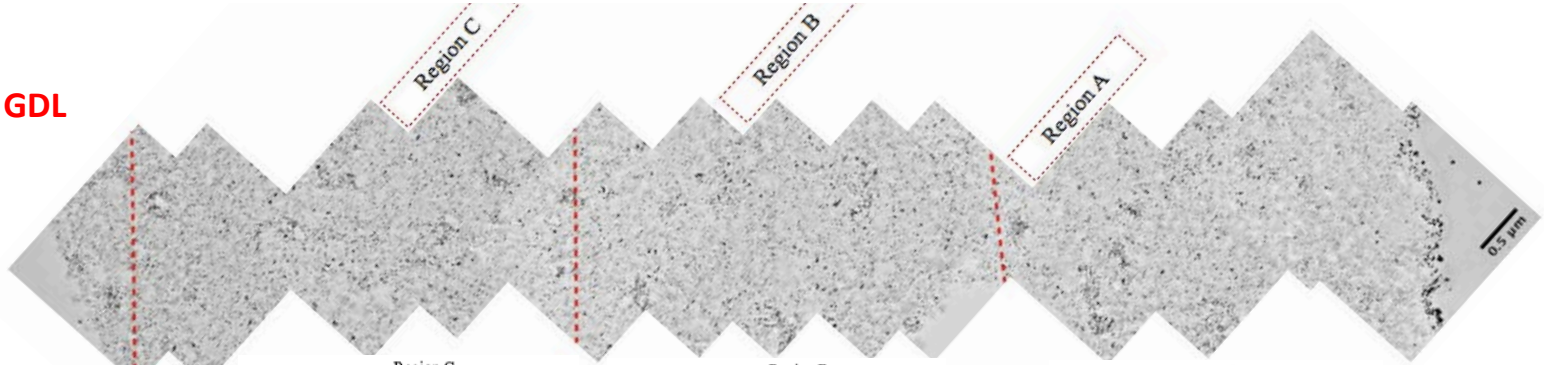
- Increasing upper limit of voltage cycling increases cathode catalyst surface area and mass activity loss
- Low inlet RH decreases cathode catalyst degradation
- Initial performance: Pt_3Co-based MEAs showed better BOL performance than Pt-based MEAs (~ 20mV in H_2/O_2 or ~ 15mV in H_2/Air @ 1A/cm^2)
- Performance degradation: At high currents, the performance loss depends on catalyst particle size, no statistically meaningful difference was observed between Pt MEAs and Pt_3Co MEAs
- ECA loss: Depends on catalyst particle size. No statistically meaningful difference was observed between Pt MEAs and Pt_3Co MEAs
- Mass activity loss: Depends on catalyst particle size. The mass activity of Pt-based MEAs is less stable than Pt_3Co-based MEAs
- Electron microprobe results: The trends of migration of Pt into the membrane are the same for Pt and Pt_3Co MEAs, including:
  - Lower Pt content in the membranes with larger catalyst particle sizes
  - Lower Pt content in the membrane for low RH cycled cell
  - Greater Pt content in the membrane for high voltage and high temp cycled cell
  - Pt MEA (7.1 nm) has a higher Pt content in the membrane than Pt_3Co MEAs (5.6 nm & 8.7 nm) after 30K triangle cycles. More tests are needed to quantify Pt loss

Technical Progress (Tasks 2.1 and 4.1)

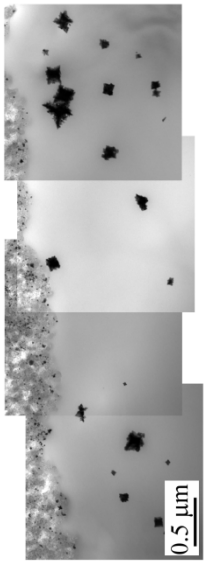
Pt catalyst degradation mechanisms - particle size study

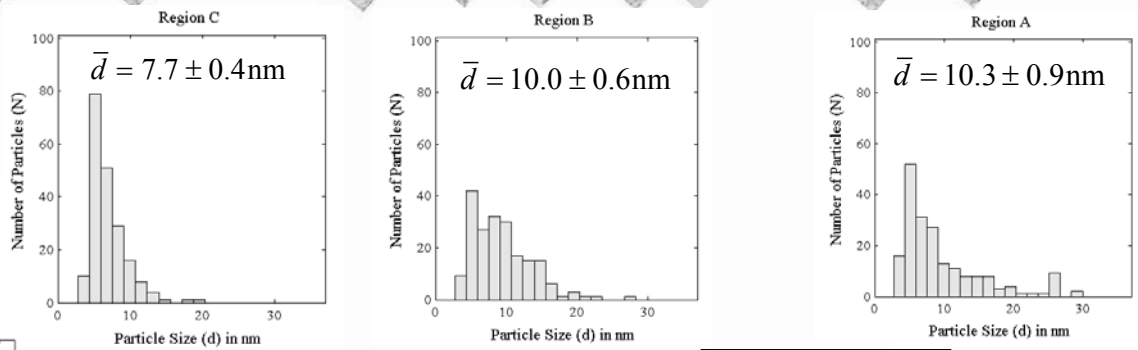
Cathode layer of MEA with initial 1.9 nm Pt, 10,000 cycles 0.6 to 1.0 V, 50 mV/s

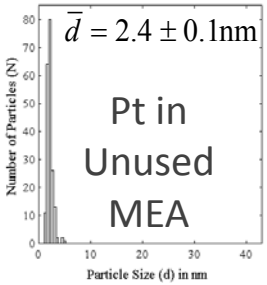
GDL

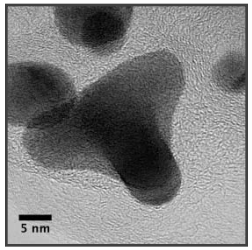


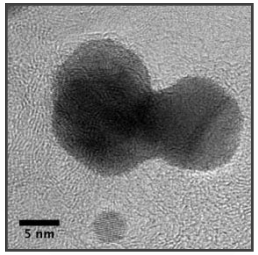
Membrane

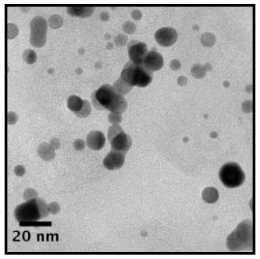












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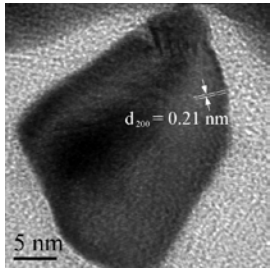


- Extent of growth in mean particle size and size distribution dependent on position in electrode
- Evidence of dendrite formation and particle coalescence within electrode (quantification underway)
- Pt particles in membrane are single crystals

Technical Progress (Tasks 2.1 and 4.1)

Pt catalyst degradation mechanisms - particle size study

Comparison of Pt particle sizes before and after 10,000 cycles in MEA (0.6 to 1.0 V, 50 mV/s)

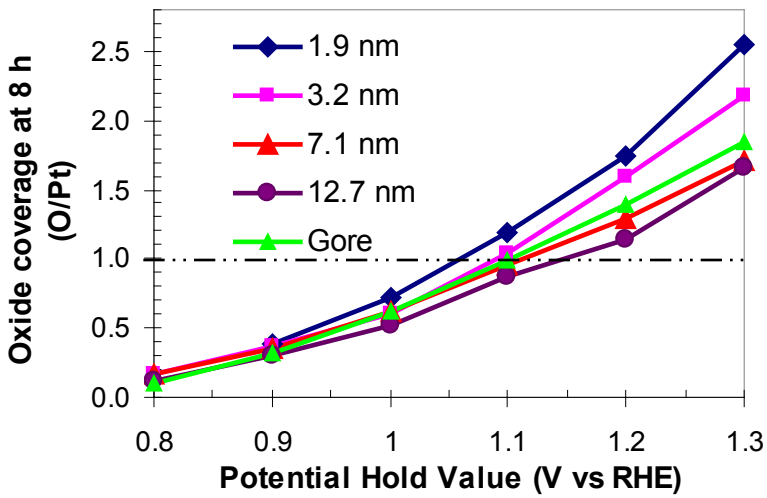
Initial mean particle dia. (nm)	Initial ECA (m^2/g)	Final ECA (m^2/g)	Final particle dia. in three regions (nm)	ECA estimated from average dia. (m^2/g)	Estimate of post-cycling utilization (%)
2.4 ± 0.1	67.9	24.5	A: 10.3±0.9 B: 10.0 ±0.6 C: 7.7 ±0.4	30	82
3.4 ±0.2	55.7	28.7	A: 9.8±0.5 B: 9.1 ±0.5 C: 9.4 ±0.5	30	96
6.9 ± 0.3 (30,000 cycles)	31.5	24.0	A: 10.0 ±0.6 B: 9.5±0.5 C: 9.3 ±0.5	29	83
13.8 ± 0.6	20.8	21.0	A: 16.6 ±2.2 B: 13.4 ± 0.6 C: 14.5 ± 0.7	20	95

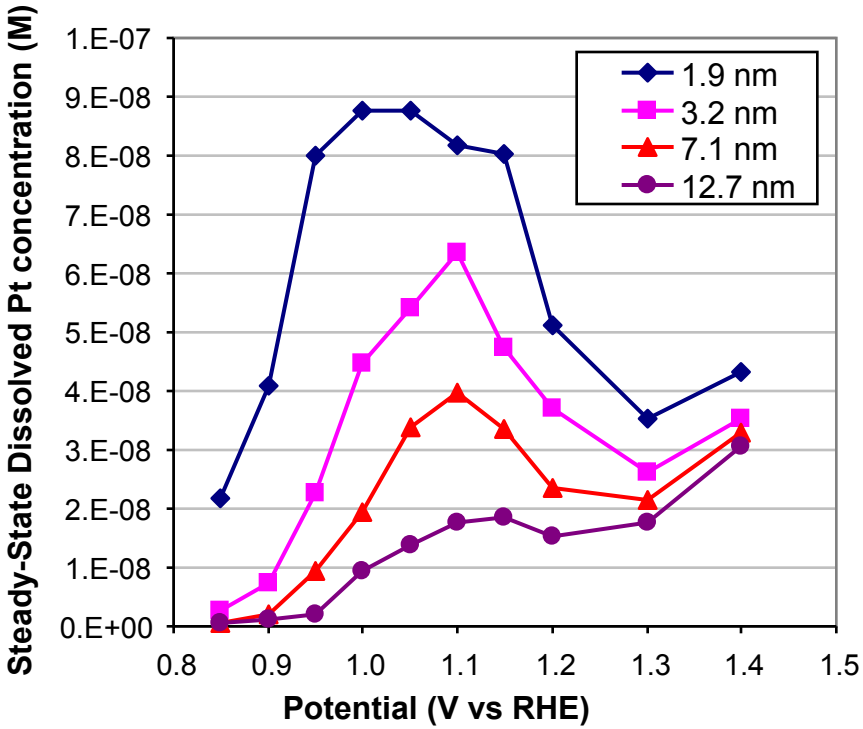
- Three smallest particle sizes evolve to approximately the same average particle size (9.5 nm) after extended potential cycling
- Decreased utilization of two intermediate particle sizes is being verified
- Largest particle size shows no loss of ECA, but particle growth (a few very large particles observed)
- Coalesced and dendritic particles observed in all used electrodes – evidence of particle migration and dissolution/re-deposition (extent of each is currently being calculated)

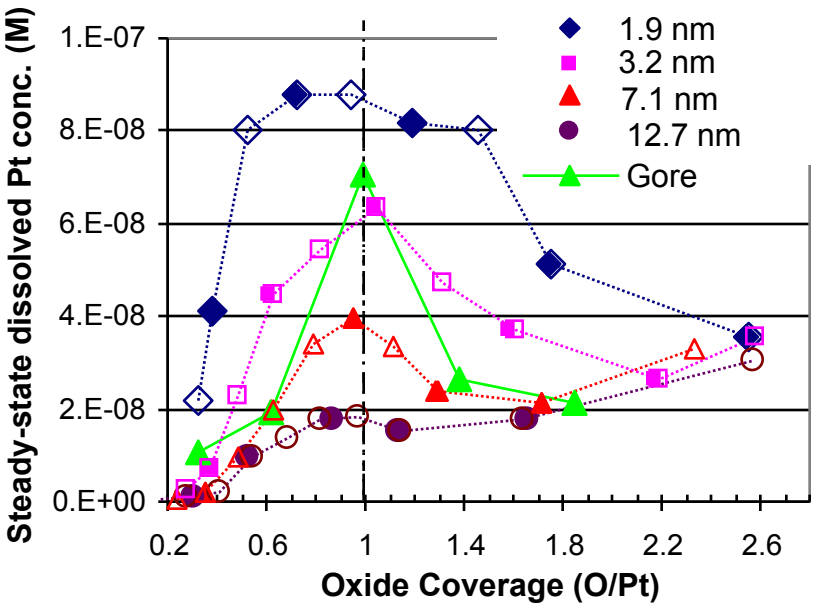
Technical Progress (Tasks 3.1 and 3.2)

Pt particle size dependence of oxide coverage and Pt dissolution

- Steady-state dissolved Pt concentration increases with decreasing mean particle size
- Oxide coverage at constant potentials >0.9 V increases with decreasing particle size
- Dissolved Pt concentration peaks at an oxide coverage of ~1 O/Pt







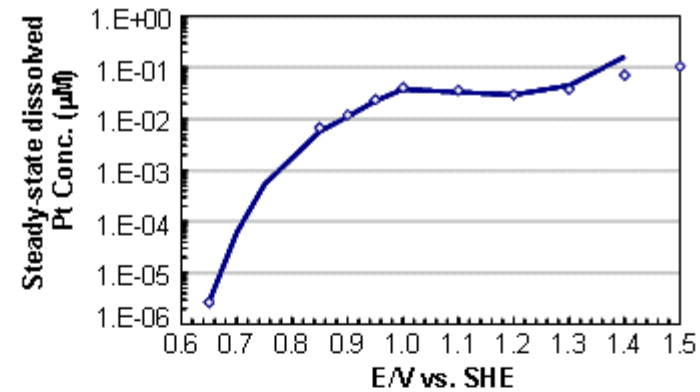
Technical Progress (Task 5.2)

Catalyst degradation modeling

1) $Pt = Pt^{2+} + 2e^-$ $E = E^o - RT/2F (\ln a_{Pt}) + RT/2F (\ln C_{Pt2+})$; $E^o = 1.1095$ V

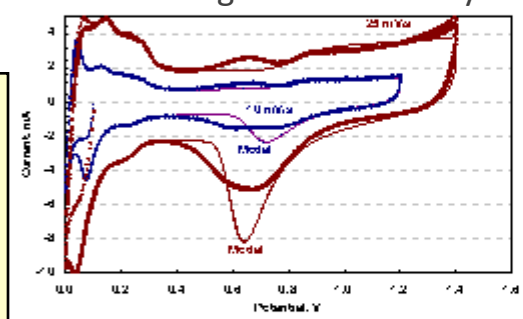
2) $Pt + H_2O = PtO + 2H^+ + 2e^-$ $E = E^o - RT/2F (\ln (a_{Pt}/a_{PtO})) + RT/F (\ln C_{H+})$; $E^o = 0.9494$ V

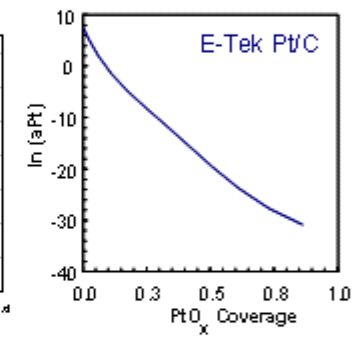
3) $PtO + H_2O = PtO_2 + 2H^+ + 2e^-$ $E = E^o - RT/2F (\ln (a_{PtO}/a_{PtO2})) + RT/F (\ln C_{H+})$; $E^o = 1.45$ V



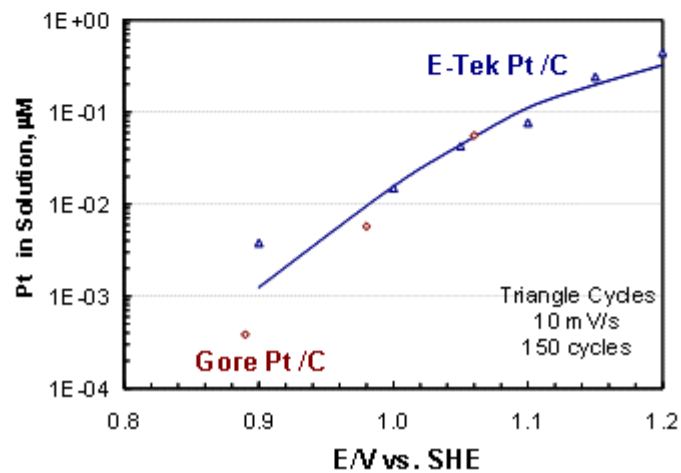
- Steady-state:
  - Assumption of non-ideal solid solution between PtO_x and Pt, activities of Pt calculated using experimentally determined Pt conc., PtO_x surface coverage from voltammetry
  - Balance between dissolution and protective oxide formation at >0.8 V
  - Activity of Pt strongly dependent on oxide coverage, which is strongly dependent on potential at >0.8 V
  - Slope of $\ln(C_{Pt2+})/E$ is lower than 2F/RT due to non-unit activity of Pt caused by formation of oxide

Modeling of voltammetry





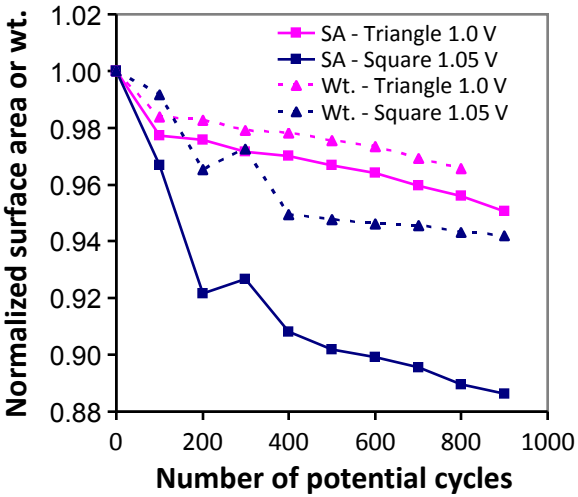
- Cycling (triangle 10 mV/s aqueous):
  - Kinetic constants for dissolution rate determined from potentiostatic data at 0.9 V and 72-h equilibrium data for other potentials, kinetic constants for re-deposition rate determined from potential cycling data
  - Below 0.9 V, cycling dissolved Pt conc. < steady-state, deposition competitive with dissolution
  - Above 1 V, cycling accelerated Pt dissolution, incomplete oxide protection

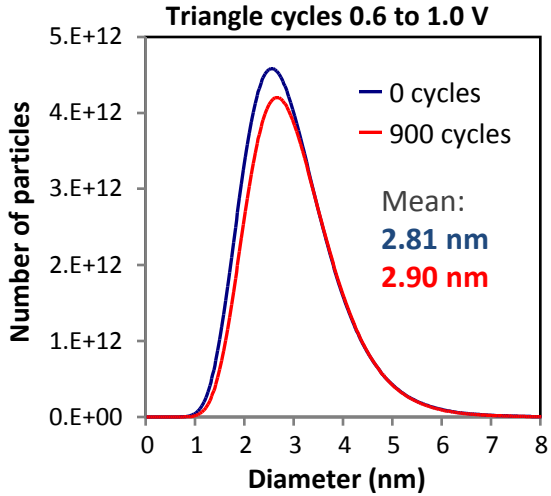


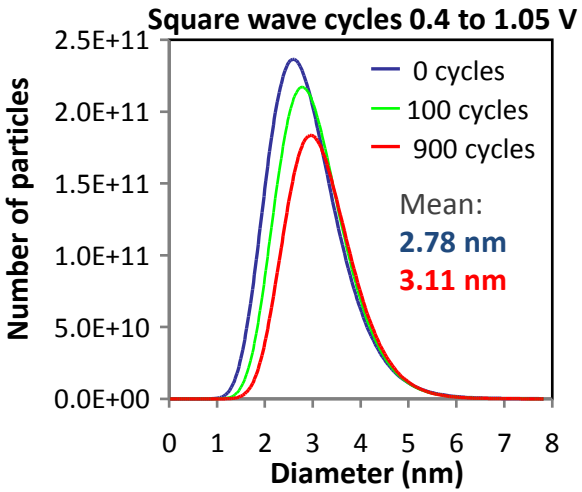
Collaboration with LANL (R. Borup) and Nuvera durability projects

Technical Progress (Tasks 3 and 4)

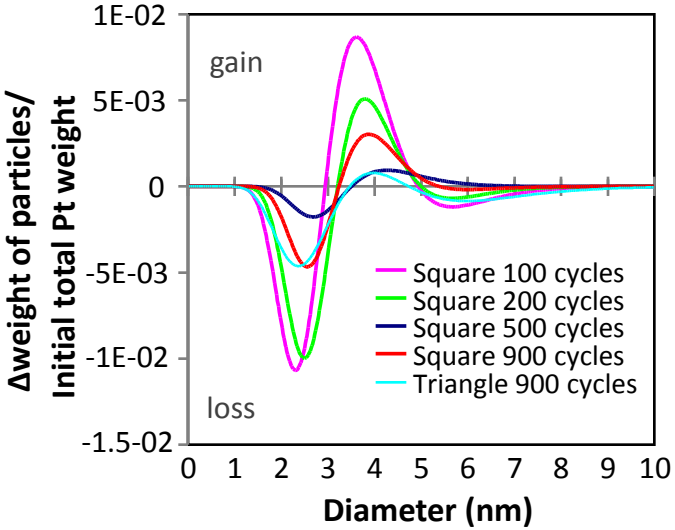
- **Anomalous small-angle X-ray scattering (ASAXS) of Pt/C catalysts to determine mean particle size and particle size distribution changes with potential cycling in 0.1 M perchloric acid electrolyte**





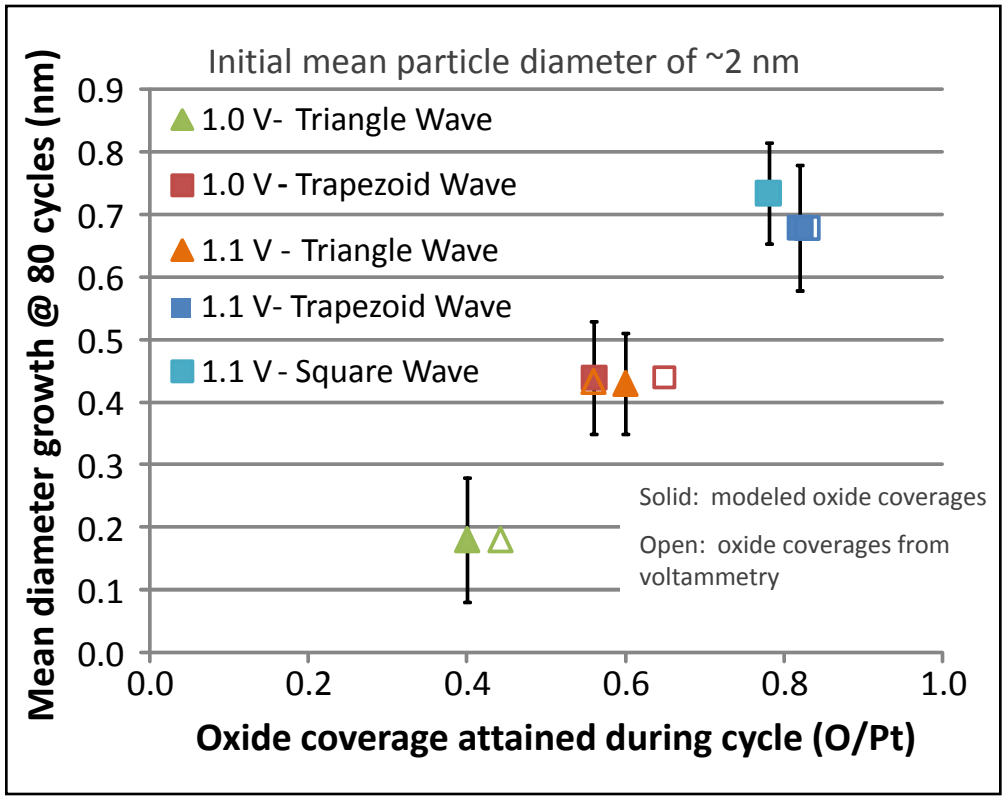


- ECA loss is more severe in MEA than in aqueous
  - MEA triangle – 81% remaining after 1,000 cycles
  - MEA square – 67% remaining after 1,000 cycles
- Pt is lost from electrode during potential cycling in both aqueous and MEA environments
  - Overall Pt loss is greater for square wave cycling to 1.05 V
    - Electron microprobe analysis of MEAs
    - ASAXS results in aqueous cell
      Triangle: 5.1 x 10^{-11} g/cm^2-cyc, Square: 7.6 x 10^{-11} g/cm^2-cyc
- Particles <3 nm and >5 nm are lost during first 100 cycles, accompanied by a gain in 3 to 5 nm particles



Technical Progress (Tasks 3, 4, and 5)

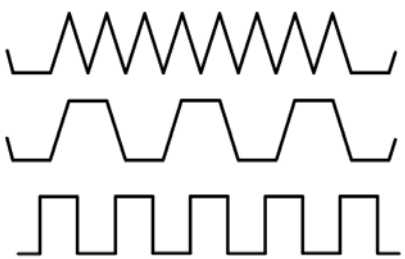
Pt Cathode Particle Coarsening: ASAXS measurement of particle growth and modeling of oxide coverage



Triangle Wave -

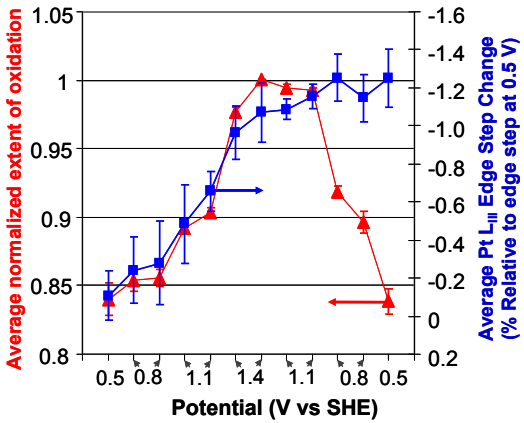
Trapezoid Wave -

Square Wave -



- **Results**
  - Pt particle growth proportional to maximum oxide coverage
  - Factors affecting maximum oxide coverage
    - *Potential Profile*
    - *Upper or Lower Turning Potential*
    - *Sweep Rate*
- **Impact**
  - Oxide plays a key role in Pt dissolution under cycling conditions
    - Enhanced dissolution due to oxidation induced roughening?
  - Studies should be aimed at differences in maximum oxide coverage
- **Future Goals**
  - Identify oxidation mechanisms that facilitate Pt dissolution
  - Identify maximum oxide coverage where no Pt growth is observed (reversibility)

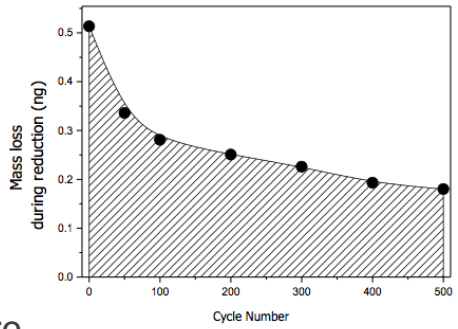
Correlations between Pt dissolution and Pt oxidation



- Pt dissolution and extent of particle growth are correlated with extent of oxide formation, which is correlated with potential
- Pt dissolution rates: <~1.1 V potentiostatic≈ potential cycling >~1.1V potential cycling>potentiostatic
- Rotating ring-disk experiments (RRDE): no detectable mobile reducible species generated on potential cycling; oxidizable species generated only during stripping of the oxide layer
- Oxidizable species detected in RRDE account for only ~1-2% of mass loss observed in quartz crystal nano-balance studies
- X-ray absorption spectroscopy: Pt lost during oxide formation

- Oxide layer protects the surface from dissolution at oxide coverages >1 O/Pt
- Amount of Pt lost is dependent on competitive Pt metal dissolution and oxide formation reactions
- At <~1.1 V oxide formation kinetics are fast compared to dissolution kinetics
  - Cycling oxide coverages ≈ potentiostatic oxide coverages: potentiostatic≈cycling Pt loss rates
- At >~1.1 V oxide formation kinetics are slow compared to dissolution kinetics
  - Initial dissolution rates when cycling or stepping from lower potentials are those of higher Pt activities (i.e., lower oxide coverages)
  - Cycling oxide coverages << potentiostatic oxide coverages: potential cycling > potentiostatic Pt loss rates

EQCN

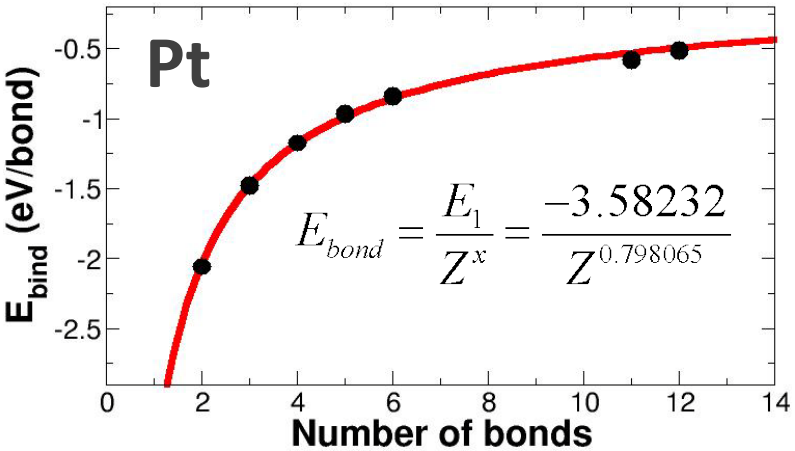


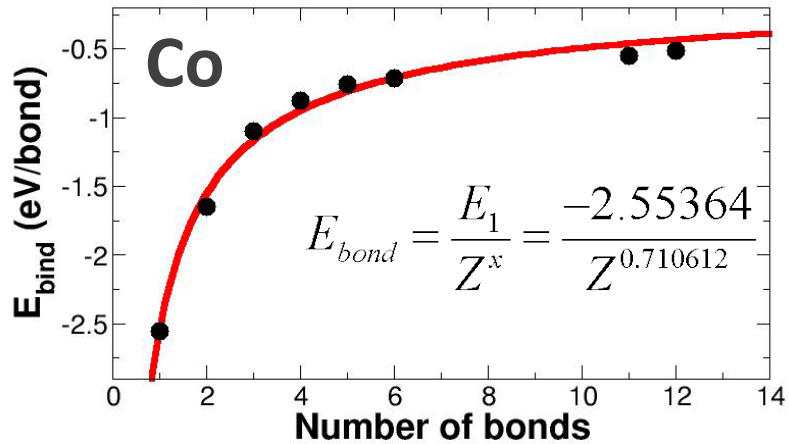
- Oxide reduction may result in physical detachment of electro-inactive Pt (e.g., Pt atoms, oxide)
- Oxidation-reduction cycling may induce formation of unstable low coordinated sites

Technical Progress (Task 5.1)

Kinetic Monte Carlo (KMC) Model of Pt Alloy Nanoparticles: Structural Evolution and Dissolution

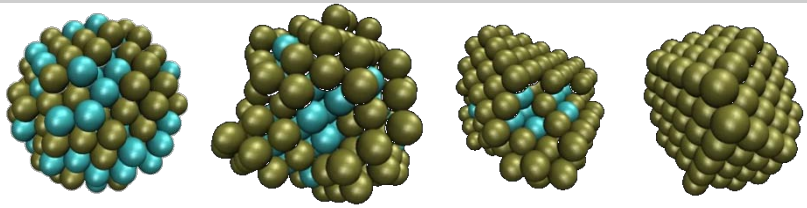
Developed Effective Bond-Energy Hamiltonian from DFT Fits





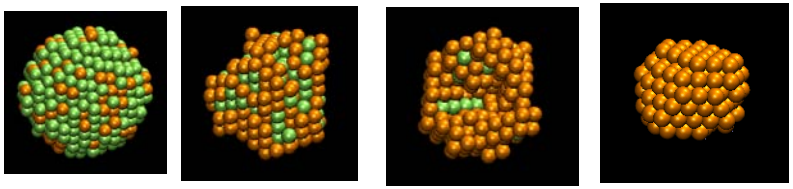
Developed KMC Model for Alloy Nanoparticle Dissolution

2 nm
$Pt_{50}Co_{50}$

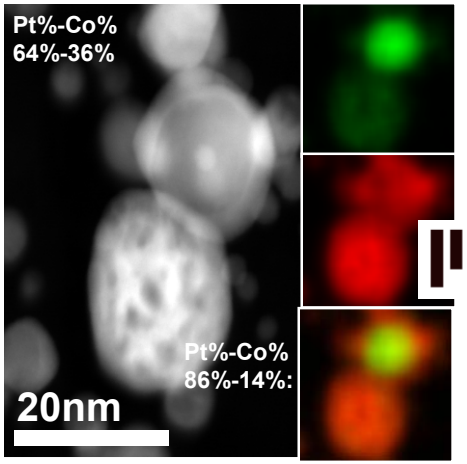


300K,pH=0
~5 sec

2 nm
$Pt_{25}Co_{75}$

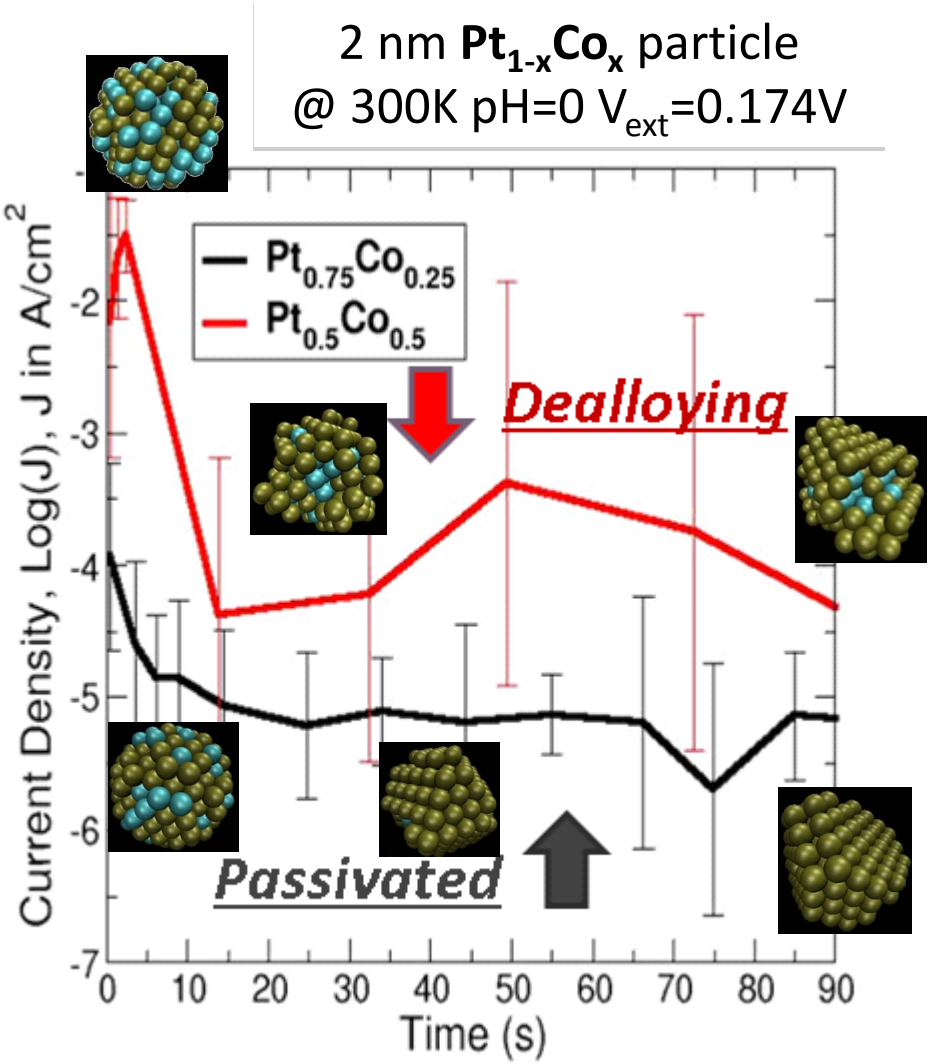


Uniform → *Core-shell*



Technical Progress (Task 5.1)

Kinetic Monte Carlo (KMC) Model of Pt Alloy Nanoparticles: Structural Evolution and Dissolution



- **Results**
  - KMC code predicts rapid $Pt_{1-x}Co_x$ nanoparticle dealloying starts for 0.25 < x < 0.5. Suggests nanoparticle 'parting limit' < 0.55 bulk value.
- **Impact**
  - Nanoparticle parting limit sets key concentration dependence for short-time dealloying.
- **Future Goals**
  - Understand nanoparticle corrosion and identify optimal concentration and sizes for stability for alloy nanoparticles.

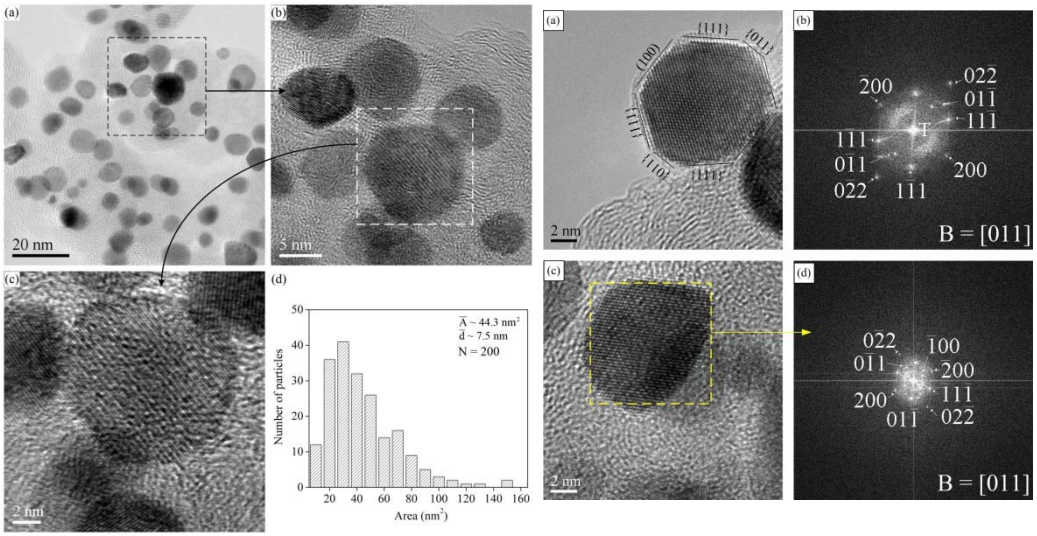
Technical Progress (Tasks 1 and 4)

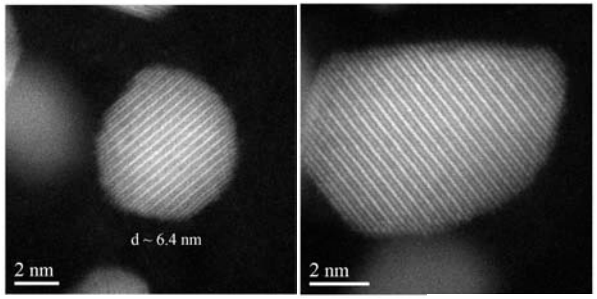
Preparation and characterization of advanced alloy catalysts

- Pt_3Sc and Pt_3Y explored as potential candidates for project tasks on "advanced catalysts" based on literature claims of high ORR activity and proposed "kinetic" stability*
- Pt_3Sc prepared at a larger scale, characterized, and acid-leached
- Attempted to prepare single phase Pt_3Y, but all samples thus far are multi-phase due to complex phase behavior of this system

High-resolution TEM

- Transmission electron microscopy shows JMFC Ketjen-supported Pt_3Sc nanoparticles have:
  - Mean particle diameter of 7.5 nm
  - $Pm\bar{3}m$ space group – same as Pt_3Co
  - Atomic ordering even at small particle size, unlike Pt_3Co
  - Pt-rich outer three layers, as determined by aberration-corrected scanning transmission electron microscopy (STEM)





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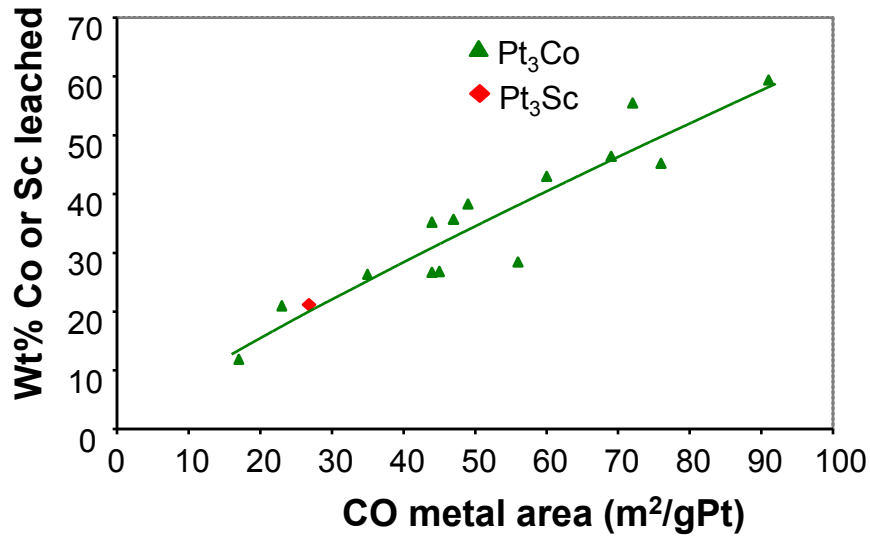
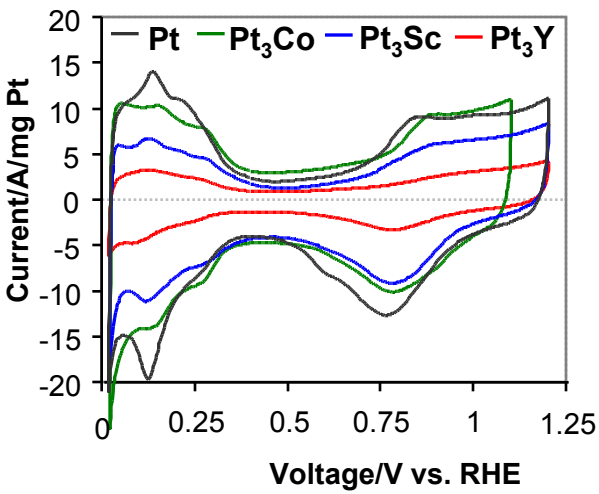
*J. Greeley, I. E. L. Stephens, A. S. Bondarenko, T. P. Johansson, H. A. Hansen, T. F. Jaramillo, J. Rossmeisl, I. Chorkendorff, and J. K. Nørskov, Nature Chemistry 1, 552 - 556 (2009).

Technical Progress (Tasks 1 and 4)

Preparation and characterization of advanced alloy catalysts

- Pt_3Sc prepared at larger scale and acid leached (24 hr 80°C, 0.5M H_2SO_4)
- On leaching the lattice expansion of Pt_3Sc is preserved
- Leaching of Sc from Pt_3Sc fits trend established for Pt_3Co (i.e., leaching α catalyst surface area)
- Initial RDE data show ORR mass and specific activity are highest for Pt_3Co
  - SA: $Pt < Pt_3Y \approx Pt_3Sc < Pt_3Co$
  - MA: $Pt_3Y << Pt_3Sc \approx Pt < Pt_3Co$
- Pt_3Y is multi-phase, low surface area
- MEA testing in progress using leached and un-leached versions of Pt_3Sc





(L)= leached	Pt (%)	%Co or %Sc	Pt:M ratio	% Co/Sc loss w/ leach	CO area ($m^2\ g^{-1}$-Pt)	XRD C.S. (nm)	XRD L.P (Å)
Pt_3Co	38.5	3.94	2.9:1	n/a	23	5.6	3.850
Pt_3Co L	36.9	3.13	3.57:1	21	25	5.4	3.850
Pt_3Sc	40.8	2.65	3.54:1	n/a	27	5.9	3.951
Pt_3Sc L	39.5	2.09	4.4:1	21	29	5.9	3.949

Collaborations

- Project team (subs) within DOE H_2 Program
  - Johnson Matthey Fuel Cells
  - United Technologies Research Center
  - Massachusetts Institute of Technology
  - University of Texas at Austin (Ferreira and Meyers)
  - University of Wisconsin – Madison
- Los Alamos National Laboratory, Nuvera, and 3M
- Co-chairing "Durability Working Group"
- Collaborators outside of DOE H_2 Program
  - Dane Morgan (UW-Madison) is collaborating with Peter Strasser (Technical University of Berlin) and Michael Toney (Stanford)
    - Modeling Pt coarsening of SAXS data by Strasser and Toney helps enhance the accuracy of the models being developed for this program
    - Strasser/Toney research is funded by DOE-BES

Proposed Future Work for FY11-12

- Task 1 (JMFC)
  - Supply MEAs to project partners using prepared Pt_3Sc/C, PtCo/C and $PtCo_3/C$ materials
  - Provide additional annealed Pt reference samples with 40-45m^2/g Pt surface area
  - Provide Pt_3Y/C catalyst for RDE and other characterization
  - Provide 2x Pt on alternative carbons and clean and doped versions of Pt/Ketjen to explore effect of impurities
- Task 2 (UTRC)
  - Evaluate the impact of catalyst leaching, carbon types under the same protocols
  - Post-test analysis of the MEAs
- Task 3 (ANL and MIT)
  - Pt dissolution rates for Pt/C and Pt_3Co/C catalysts of varying particle size
  - Effect of temperature on Pt dissolution rates for "benchmark" Pt/C catalyst (3.2 nm dia.)
  - Oxygen reduction reaction activity of Pt/C and Pt_3Co/C catalysts of varying particle size and evolution of activity with potential cycling
- Task 4 (UT-Austin and ANL)
  - *In situ* ASAXS/X-ray absorption characterization of Pt/C MEAs and Pt_3Co/C MEAs
  - TEM characterization of the Pt/C MEA cathodes from parametric studies, the Pt3Co/C MEA cathodes from particle size studies and from parametric studies
  - STEM simulations of Pt_3Sc nanoparticles to determine the amount of surface segregation.
  - Modeling the shape of nanoparticles present in the used MEAs
- Task 5 (UW and UT-Austin)
  - Further development of Kinetic Monte Carlo (KMC) model of Pt alloy nanoparticles under fuel cell conditions,
  - Use KMC simulation to predict how de-alloying occurs in nanoparticles (de-alloying rate, the formation of pores, and the stability of core-shell and acid-leached structures),
  - Complete cyclic voltammetry and dissolution model including effect of oxide structure

Summary

Relevance:

- Mitigate catalyst-related PEMFC performance loss and enable PEMFC systems to achieve lifetime targets by defining catalyst properties and operating conditions that will enhance catalyst lifetimes.

Approach:

- Identify catalyst degradation modes and factors contributing to degradation using a variety of in-cell and out-of-cell techniques and systematic variation of catalyst physicochemical properties.

Accomplishments:

- Completed parametric and particle size studies comparing MEA performance degradation for Pt_3Co and Pt cathodes
- Determined that voltage cycling from 0.6 to 1.0 V causes Pt particles of <~7 nm to grow to ~9.5 nm, with evidence for both dissolution and coalescence growth mechanisms
- Determined that Pt dissolution increases with decreasing Pt particle size and is correlated with oxide formation
- Developed Pt cyclic voltammetry and dissolution models and Kinetic Monte Carlo model of alloy nanoparticle dissolution and parting limit

Collaboration:

- Project team of JMFC, UTRC, MIT, UT-Austin, and UW-Madison
- LANL, Nuvera, and 3M; co-chairing "Durability Working Group"

Future Work:

- Evaluate the impact of Pt:Co ratio, catalyst leaching, alloying with Sc, alternative carbon support, and impurity doping on degradation
- Quantify ECA loss due to particle coalescence/dissolution, re-deposition/Pt loss by modeling TEM images
- Complete cyclic voltammetry and dissolution models

Technical Back-Up Slides

Technical Progress

Advanced catalyst synthesis and characterization

1. Methods and materials

Materials:

AuPt/C with different surface composition: 10%Au, 32%Au, 50%Au, 85%Au (same bulk composition: $Au_{0.5}Pt_{0.5}/C$)

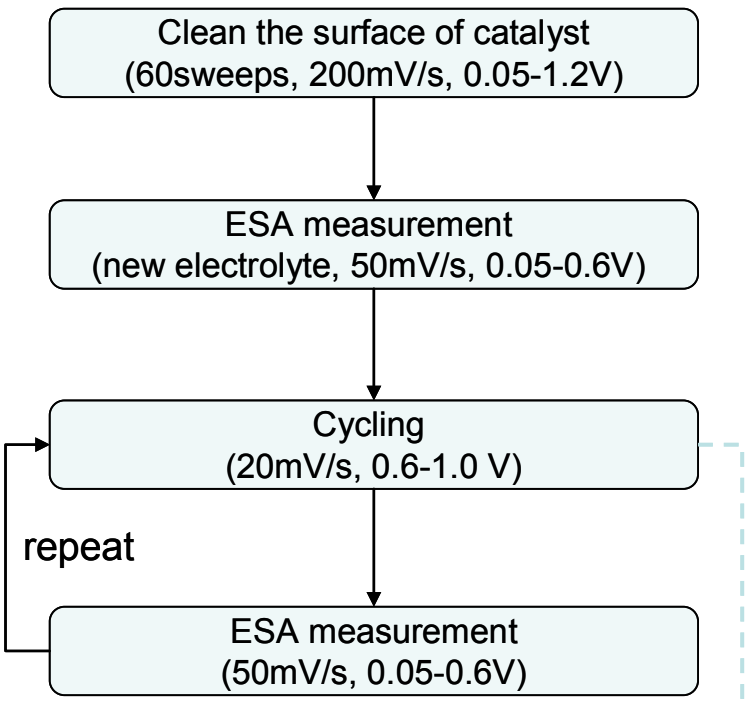
ESA Measurements:

- ❑ 0.05-6.0 V (vs RHE)
- ❑ 50 mV/s
- ❑ Room temperature
- ❑ Ar-saturated 0.5 M H_2SO_4

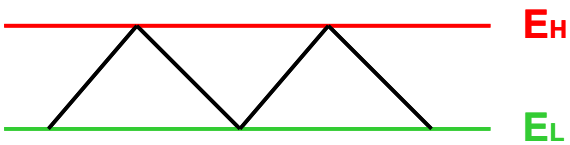
Cycling:

- ❑ 0.6-1.0 V (vs RHE)
- ❑ 20 mV/s
- ❑ Room temperature
- ❑ Ar-saturated 0.5 M H_2SO_4
- ❑ 1,800 potential cycles (3,600 sweeps)

Procedure:



Symmetric Triangular wave

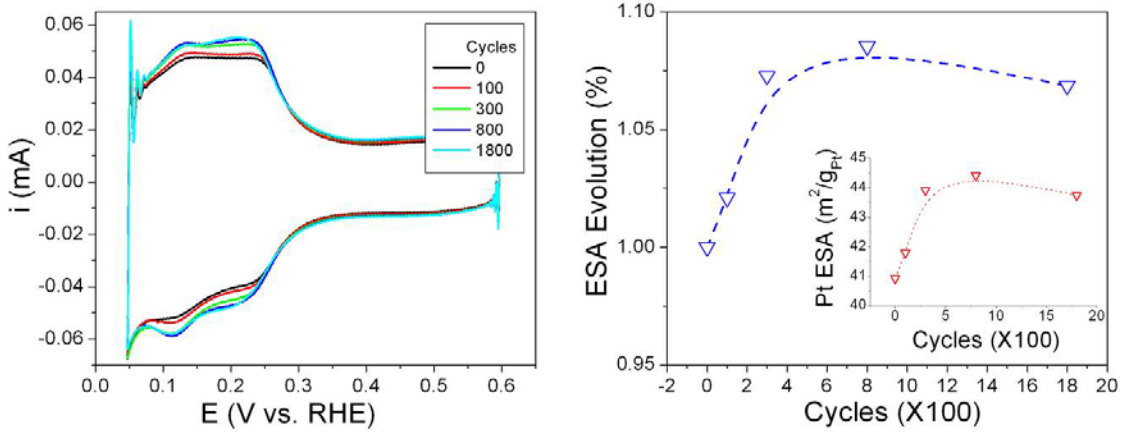


Technical Progress

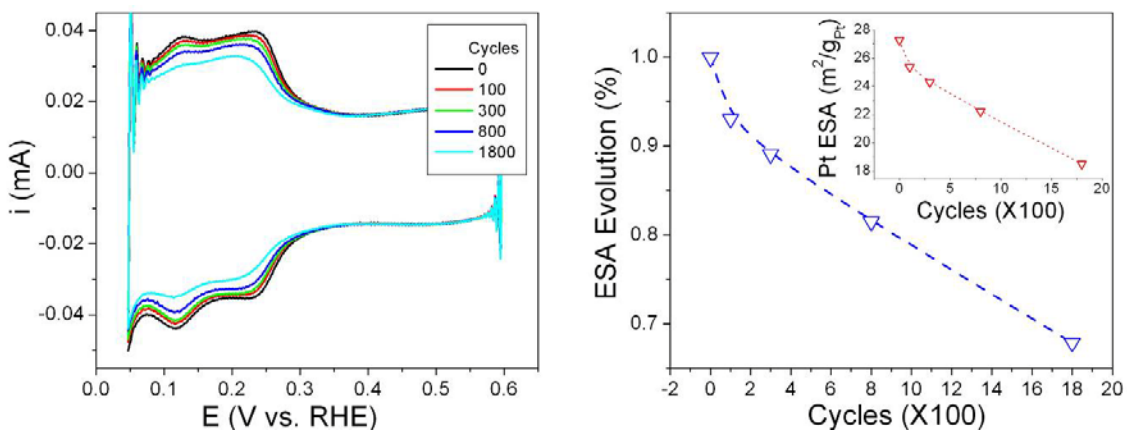
Advanced catalyst synthesis and characterization

Primary Results of Cycling Experiments on $Au_{0.5}Pt_{0.5}/C$

1) AuPt/C 10%Au (carbon supported colloid)



2) AuPt/C 32%Au (250ºC Air)

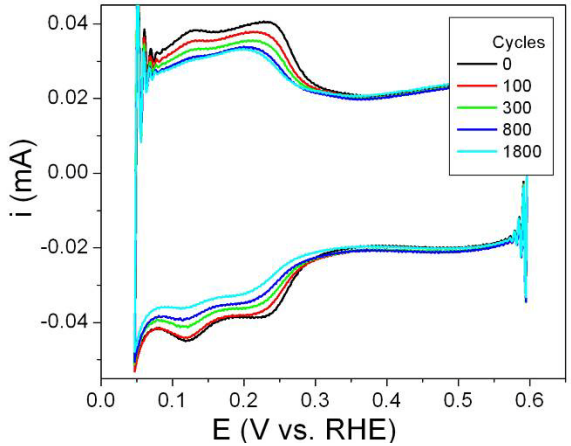


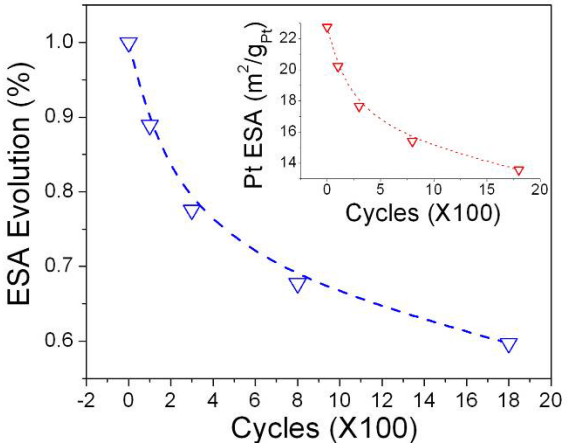
Technical Progress

Advanced catalyst synthesis and characterization

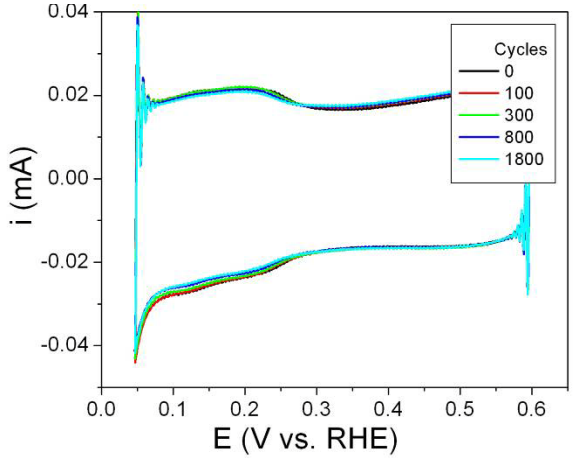
Primary Results of Cycling Experiments on $Au_{0.5}Pt_{0.5}/C$

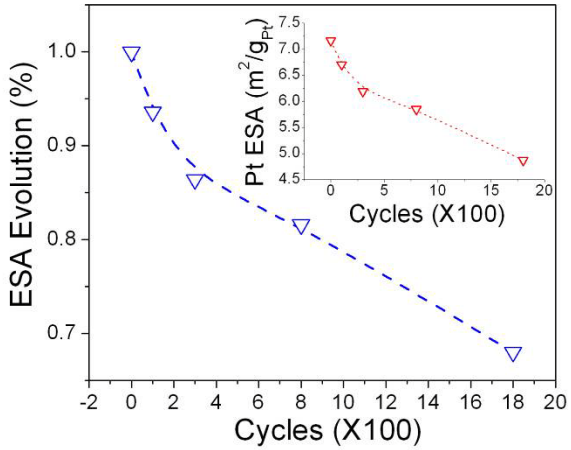
3) AuPt/C 50%Au (250ºC Air / 350ºC CO)





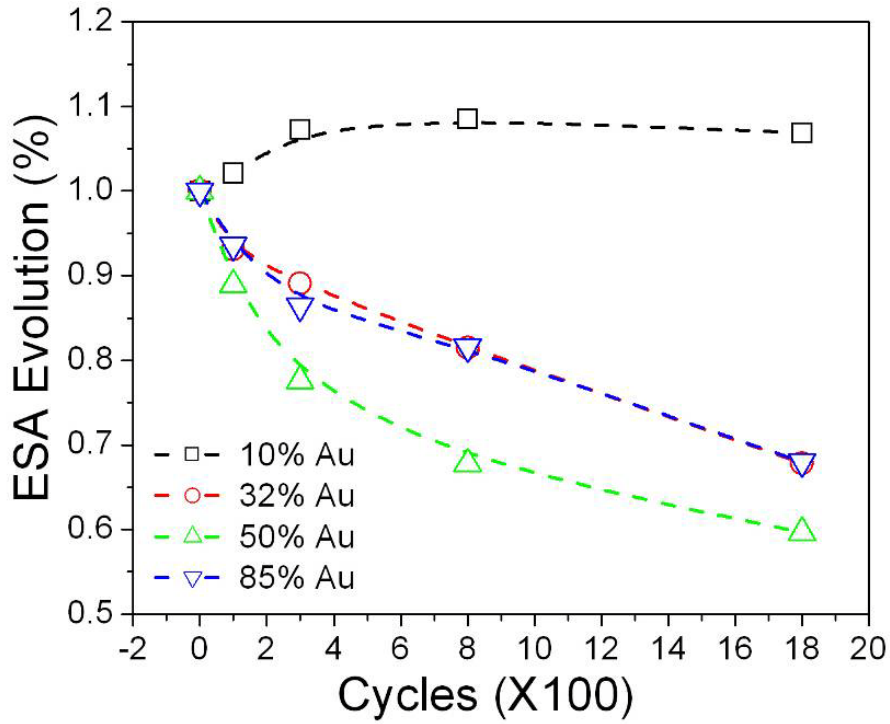
4) AuPt/C 85%Au (250ºC Air / 500ºC Ar)





Technical Progress

Advanced catalyst synthesis and characterization

Summary

1) $Au_{0.5}Pt_{0.5}/C$ catalyst with 10% Au on surface is most stable out of all $Au_{0.5}Pt_{0.5}/C$ studied
2) All the other AuPt NPs show Pt surface area loss during cycling between 0.6-1.0 V (vs RHE)