

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

Debbie Myers, Xiaoping Wang, Nancy Kariuki,
Stacy DeCrane, Tammy Nowicki, Ram Subbaraman,
Srikanth Arisetty, and Rajesh Ahluwalia
Argonne National Laboratory

2012 U.S. DOE Hydrogen Program and Vehicle Technologies Program
Annual Merit Review and Peer Evaluation Meeting
Washington D.C.

May 14-18, 2012

Project ID# FC012

Overview

Timeline

- Project start data: October, 2009
- Project end data: September, 2012
- Percentage complete: 83%

Budget

- Total project funding:
 - DOE: \$3,754 K
 - Contractor share: \$544 K
- Funding received in FY11
 - \$626 K
- Funding expected for FY12
 - \$ 1265 K

Barriers

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

Partners

- Johnson Matthey Fuel Cells
 - Sarah Ball, Jonathan Sharman, Brian Theobald, Stephen Thorpe, Alex Martinez, Elvis Christian, and Graham Hards
- United Technologies Research Center
 - Mallika Gummalla, Zhiwei Yang, and Steve Zhitnik
- Massachusetts Institute of Technology
 - Yang Shao-Horn and B.H. Han
- University of Texas at Austin
 - Paulo Ferreira, Shreyas Rajasekhara, Daniel Groom, Stephanie Matyas, Somaye Rasouli, and Kang Yu
 - Jeremy Meyers, Preethi Mathew, and Seok Koo Kim
- University of Wisconsin – Madison
 - Dane Morgan, James Gilbert, and Brian Puchala

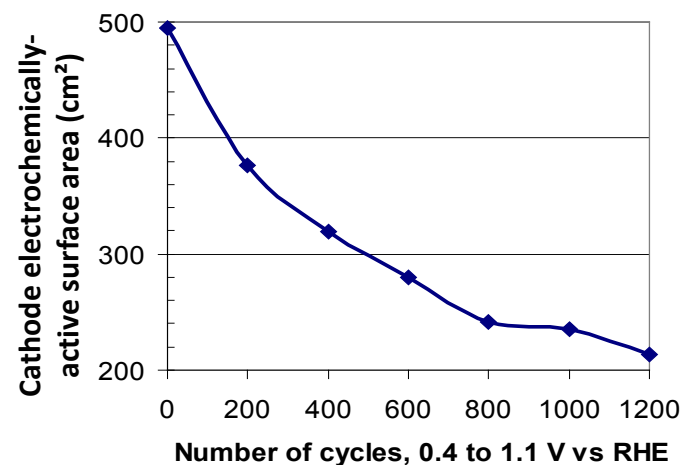
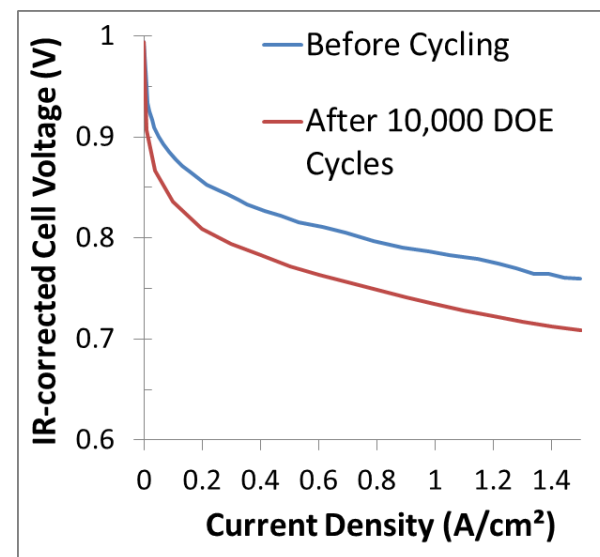
Relevance

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.

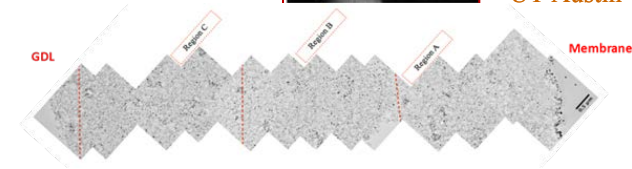
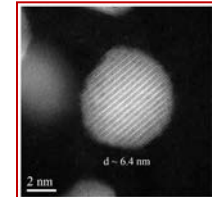
Impact

- To enable catalysts to achieve DOE Technical Targets
 - Durability with cycling 5,000 hours ($\leq 80^{\circ}\text{C}$) and 2,000 hours ($> 80^{\circ}\text{C}$)
 - $\leq 40\%$ loss of initial catalytic mass activity;
 < 30 mV loss at 0.8 A/cm^2



Approach: Methods and Variables

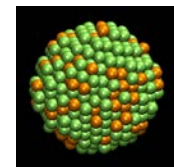
- Identify the degradation modes and factors contributing to degradation, using
 - Systematic cell degradation tests (JMFC and UTRC)
 - *In situ* and *ex situ* structural characterization of the catalyst (ANL and UT)
 - Small angle X-ray scattering, X-ray absorption spectroscopy, TEM, HAADF-STEM, etc.
 - 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 degradation effects (ANL and UT)



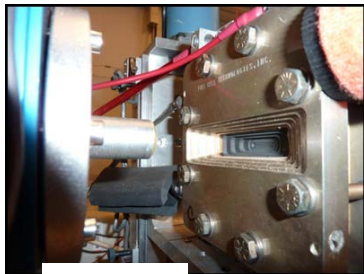
ANL

Variables

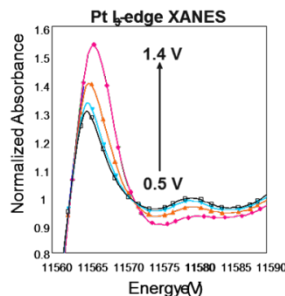
- Catalyst type and oxophilicity
 - Pt, Pt alloys, acid-leached Pt alloys, core-shell, 3M’s NSTF
- Catalyst particle size (Pt and one Pt alloy)
- Catalyst impurities (e.g., chloride)
- Type of carbon support
 - Surface area and pore size
- Cell operating parameters
 - Potential cycling profile, upper potential limit, cell temperature, RH on cathode



UW



ANL



Approach

Project timeline

May, 2012



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 2011 AMR has been on compositional studies of Pt-Co alloys, Pt₃Sc, effects of acid-leaching, effects of potential profile, dissolution studies of Pt-Co alloys and NSTF, and Kinetic Monte Carlo-based modeling of Pt-Co alloys

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

- FY'11 and FY'12 Milestones
 - Determine the effect of Pt alloy composition on the rates and mechanisms of cathode catalyst performance degradation - 09/11
 - Completed: results discussed here
 - Develop a macroscopic model of Pt dissolution and place exchange, and complete CV and ORR catalyst performance models - 09/11
 - Cyclic voltammetry, oxide coverage, and dissolution models have been completed; place-exchange is implicit in dependence of Pt activity on oxide coverage
 - Develop a Kinetic Monte Carlo model to predict alloy nanoparticle evolution in the fuel cell cathode environment - 09/11
 - KMC model has been developed and demonstrated for Pt-Co de-alloying: results discussed here
 - Prepare and evaluate 2 Pt-Co alloy compositions and 1 Pt-M alloy to correlate performance degradation with composition and alloying element, catalyst component dissolution, and extent of oxidation - 05/12
 - Completed 2 Pt-Co's and Pt₃Sc performance degradation and component dissolution
 - Prepare and evaluate 2 or more catalyst samples of Pt on different carbon supports and Pt samples with 2 different levels of chloride impurity to quantify the effects of support and precursor impurity on the rates and mechanisms of cathode catalyst performance degradation - 09/12
 - On-track: Samples have been prepared and characterized; cells are being fabricating
 - Complete cathode catalyst layer performance model that integrates ORR degradation and cathode transport property evolution - 09/12
 - Work in progress
- 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
 - Aqueous dissolution and oxide coverage measurements are being used as input to degradation model. Degradation model accurately predicts evolution of particle size distribution

Proposed Future Work for FY12

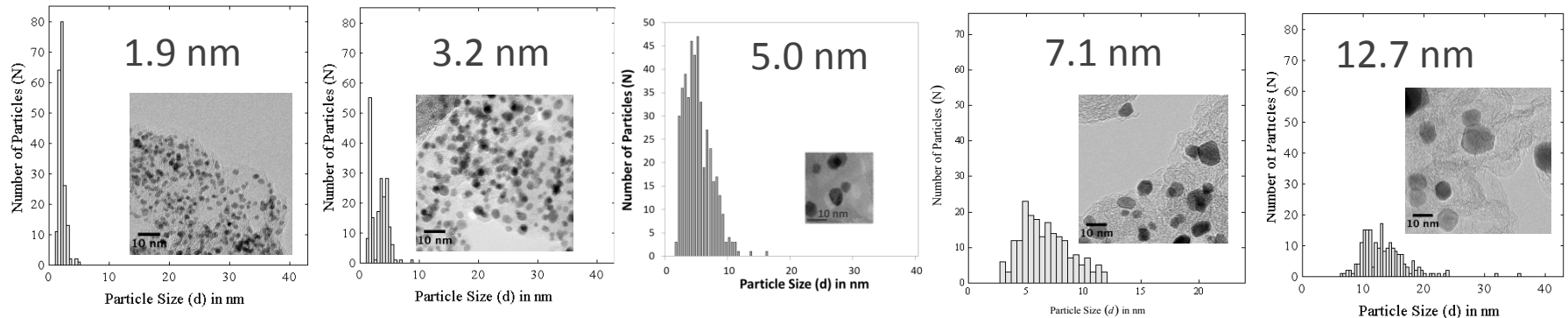
- Task 1 (JMFC)
 - Supply membrane-electrode assemblies to project partners using prepared Pt-Ni/C materials
 - Provide Pt on alternative carbons and clean and doped versions of Pt/Ketjen to explore effect of impurities
 - Provide additional $\text{Pt}_x\text{Co}_{1-x}/\text{C}$ materials for dissolution studies to validate KMC modeling parting limits
- Task 2 (UTRC)
 - Evaluate the impact of carbon types and advanced alloy formulation on performance decay
 - Post-test analysis of the membrane-electrode assemblies
- Task 3 (ANL and MIT)
 - Cycling dissolution rates for $\text{Pt}_3\text{Co}/\text{C}$ catalysts of varying particle size, NSTF, and advanced alloy catalysts
 - Effect of temperature on Pt dissolution for “benchmark” Pt/C catalyst (3.2 nm dia.)
 - Oxygen reduction reaction activity of advanced alloy catalysts and evolution of activity with potential cycling
- Task 4 (UT-Austin and ANL)
 - Analysis of *in situ* ASAXS/X-ray absorption characterization of Pt/C and $\text{Pt}_3\text{Co}/\text{C}$ membrane-electrode assemblies
 - TEM and ASAXS characterization of the membrane-electrode assembly cathodes from the Pt/C potential profile studies, Pt_3Sc , PtCo, and advanced catalyst studies
- 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 cathode performance and performance degradation model



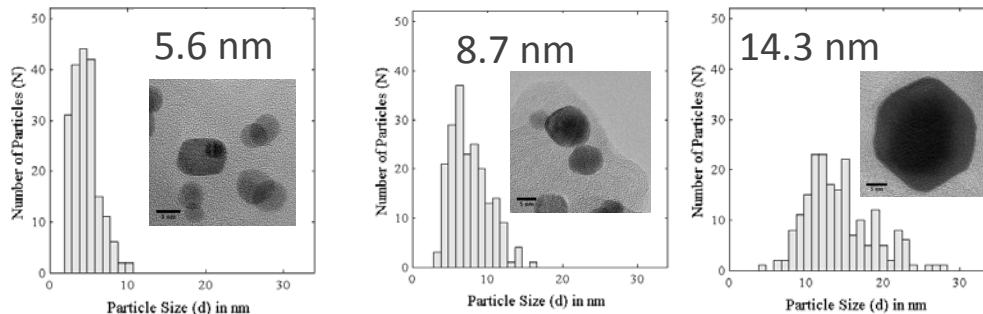
Technical Progress (Tasks 1 and 4)

Catalyst synthesis and characterization

40 wt% Pt/Ketjen: five particle sizes (1.9, 3.2, 5.0, 7.1, 12.7 nm)



40 wt% Pt₃Co/Ketjen: three particle sizes (5.6, 8.7, 14.3 nm)



Acid treatment (pre-leaching):
80°C, 0.5 M H₂SO₄,
2 days

40 wt% Pt₃Co/Ketjen: one particle size (5.6 nm), acid treated (80 Pt:20 Co)

35 wt% PtCo/Ketjen: one particle size (4.1 nm), acid treated (71 Pt:29 Co)

40 wt% Pt₃Y (11 m²/g) and 40 wt% Pt₃Sc (7.5 nm)

Technical Progress (Tasks 2.1 and 2.2)

Particle size and parametric studies

Cathode Cat.	TEM Mean Particle size (nm)	Cathode loading (mg-Pt/cm ²)	Anode loading (mg-Pt/cm ²)
Pt	1.9	0.20	0.2
Pt	3.2	0.21	0.18
Pt	5.0	0.23	0.25
Pt	7.1	0.21	0.2
Pt	12.7	0.21	0.2
Pt ₃ Co	5.6	0.23	0.20
Pt ₃ Co	8.7	0.22	0.20
Pt ₃ Co	14.3	0.22	0.20

Particle size studies:

- Triangle wave potential cycle: 0.6 V to 1.0 V, 50 mV/s (DOE-U.S. Drive Protocol)
- Cell Temperature: 80°C
- Fuel/Oxidant : 100% RH H₂ at 100 sccm and 100% RH N₂ at 50 sccm
- Pressure: Atmospheric

Parametric studies: effect of upper potential limit, RH, temp., and potential profile.

Pt: 3.2 nm mean particle size; Pt₃Co: 5.6 nm mean particle size; Pt₃Co and PtCo: Pre-leached

Cell ID	Potential cycle
BL	<ul style="list-style-type: none"> • 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%H₂ / 0.5SPLM N₂ • Pressure: Atmospheric pressure
1.05V	<ul style="list-style-type: none"> • Square wave potential cycle: 10s at 0.4V, 10s at 1.05V (20s / cycle) • All other parameters were same as BL
30%RH	<ul style="list-style-type: none"> • Humidity: Anode = Cathode = 30%RH • All other parameters were same as BL
90 °C	<ul style="list-style-type: none"> • Cell Temperature: 90°C • All other parameters were same as BL

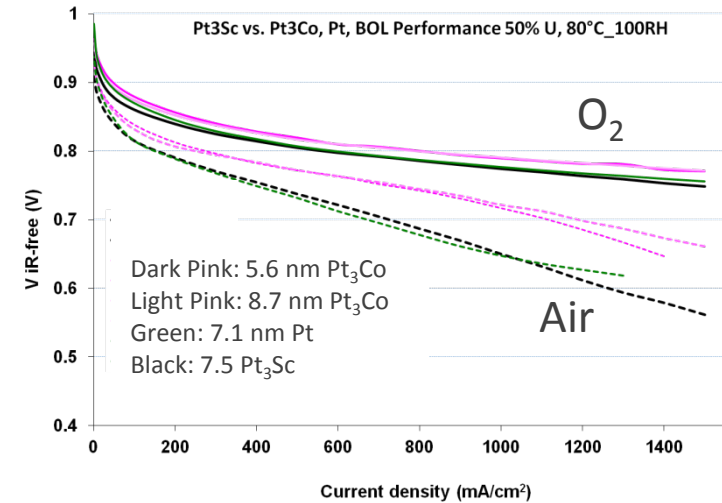
Diagnostics:

- Electrochemically-active surface area (ECA)
- Oxygen reduction activity per g Pt@0.9 V (MA)
- Polarization curves on oxygen and air
- Hydrogen pump - ionic resistance of electrode
- Post-test SEM, TEM, EMPA, and ASAXS

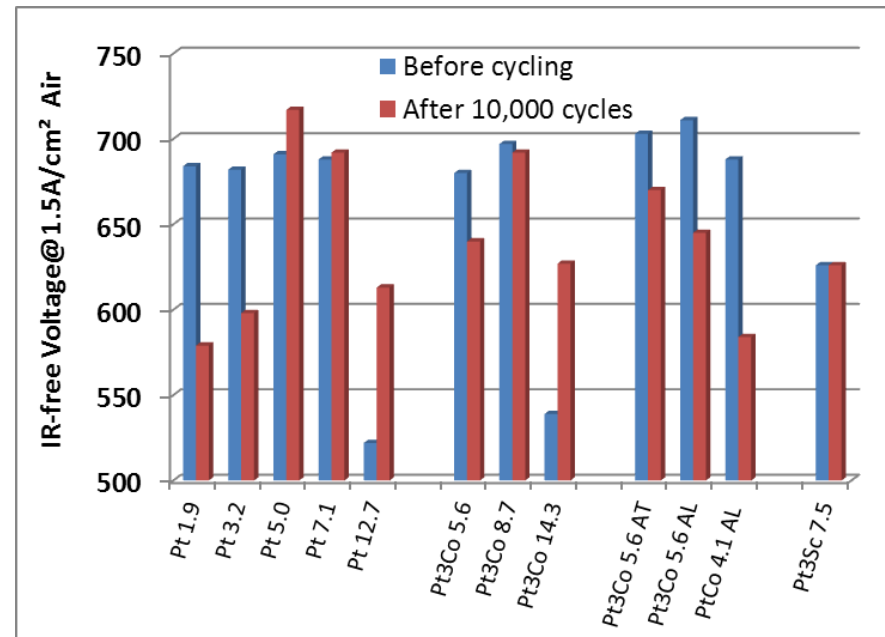
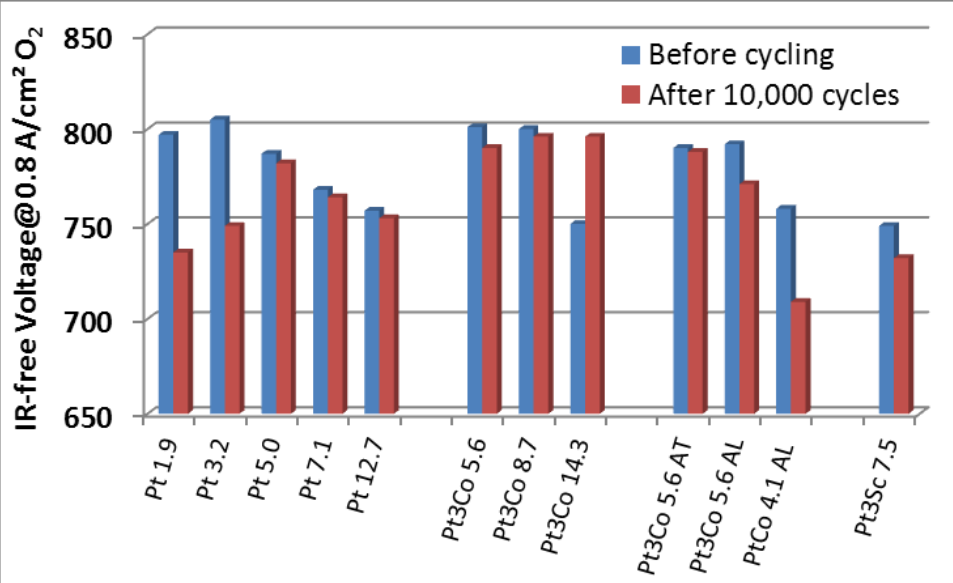
Technical Progress (Task 2.2)

Summary of cell performances with different cathode catalysts

- General trends in initial cell performance
 - Higher kinetic performance with smaller particles and upon alloying with Co
 - Kinetic benefits offset by mass transport effects at higher current densities
- General trend in cycling durability
 - Higher stability with larger cathode catalyst particle sizes
 - Degradation increased by increasing upper potential limit and temperature, decreased by decreasing RH



DOE Cycling Protocol: 0.6 to 1.0 V Triangle, 50 mV/s



Technical Progress (Tasks 2.1, 2.2, and 4)

Characterization results DOE cycling - ECA, TEM, and ASAXS

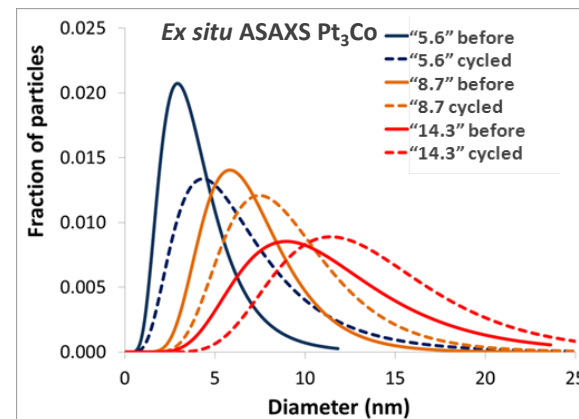
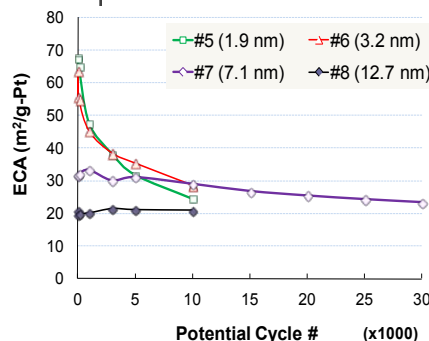
Pt in MEA before and after 10,000 DOE cycles

Initial mean particle dia. (nm)	TEM Final particle dia. three regions (nm)	ECA GSA from TEM PSD Cycled/Initial (m ² /g-Pt)
"1.9" 2.4 0.1	A: 10.3±0.9 B: 10.0 ±0.6 C: 7.7 ±0.4	24.5/67.9=0.36 19.4/105.4=0.18
"3.2" 3.4 0.2	A: 9.8±0.5 B: 9.1 ±0.5 C: 9.4 ±0.5	28.7/60.8=0.47 22.8/63.0=0.36
"7.1" 6.9 0.3	A: 6.5±0.3 B: 6.6±0.3 C: 6.5±0.3	29.1/33.3=0.87 35.6/35.1=1.01
"7.1" 6.9 0.3 (30,000 cyc.)	A: 10.0 ±0.6 B: 9.5±0.5 C: 9.3 ±0.5	24.0/33.3=0.72 21.3/35.1=0.61
"12.7" 13.8 ± 0.6	A: 16.6 ±2.2 B: 13.4 ± 0.6 C: 14.5 ± 0.7	21.0/21.1=1.00 16.3/21.2=0.77

Pt₃Co in MEA before and after 30,000 DOE cycles

Initial TEM mean particle dia. (ASAXS) (nm)	TEM Final particle dia. three regions (ASAXS) (nm)	ECA GSA from TEM PSD GSA from ASAXS PSD Cycled/Initial (m ² /g-Pt)
"5.6" 4.9 0.2 (3.7)	A: 6.2±0.3 B: 6.1±0.3 C: 6.2±0.4 (5.8)	22.6/37.0=0.61 43.2/57.6=0.75 42.9/59.2=0.71
"8.7" 8.1 0.4 (6.7)	A: 8.4±0.4 B: 8.5±0.4 C: 7.9±0.4 (8.6)	23.8/27.4=0.87 34.9/36.8=0.95 29.4/38.6=0.76
"14.3" 14.8 0.6 (10.6)	A: 12.5±0.6 B: 13.0±0.9 C: 13.0±0.7 (13.0)	17.6/22.8=0.77 21.6/20.2=1.07 19.9/23.1=0.85

- Particle size and ECA loss relatively stable at >6 nm initial size
- Pt and Pt₃Co show similar particle size dependence of particle growth and ECA loss
- Predominantly spherical particles, except "1.9", "3.2", and 30,000 "7.1" Pt

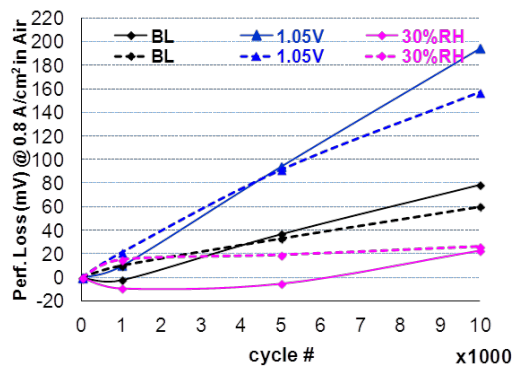
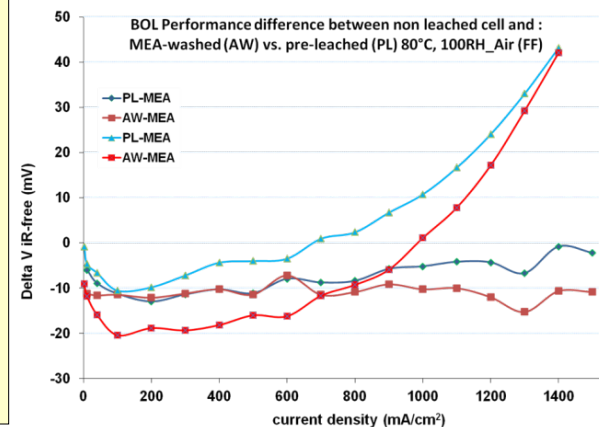


Technical Progress (Tasks 2.2)

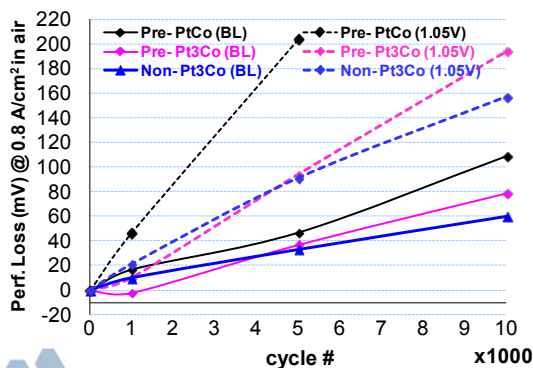
Impact of acid-leaching and Co content on Pt-Co MEA decay

DOE Cycling Protocol

- Pt₃Co catalyst – effect of acid-leach (AL) and MEA acid wash
 - AL and MEA acid wash: ~ 10 mV lower O₂ perf. (dec. in ORR activity); higher perf. in H₂/Air at high current (< H₂ pump resist.)
 - ECA, MA, SA, and O₂ performance decay trends with cycling are not effected by AL or MEA acid wash;
 - AL Pt₃Co vs. AL PtCo – effect of cobalt composition
 - Comparable initial performance at high currents
 - Comparable ECA, MA, SA, and perf. decay trends with cycling



Solid line – AL Pt₃Co
Dashed line – Pt₃Co



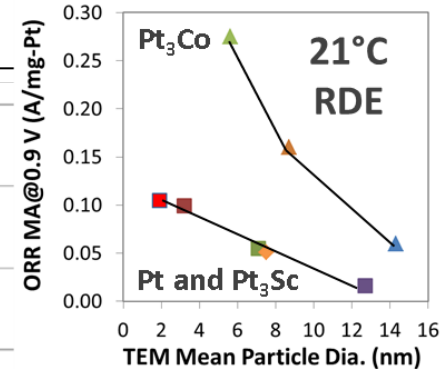
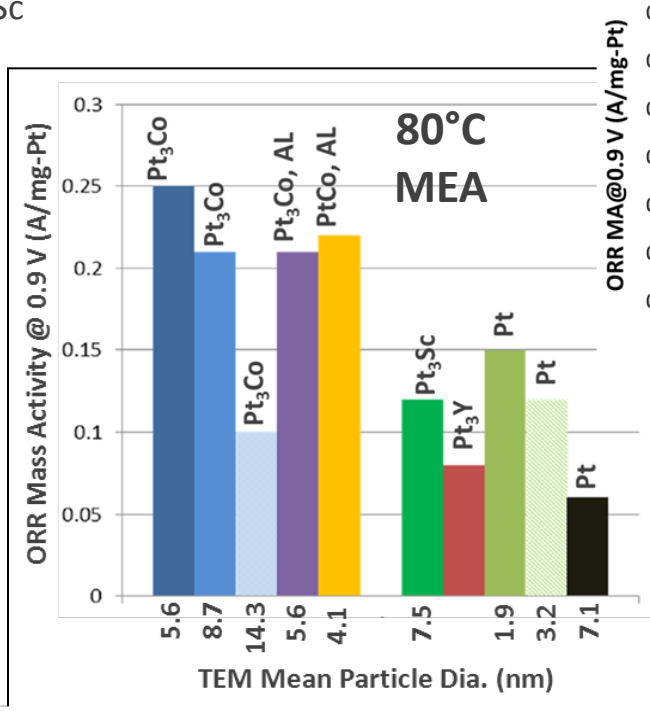
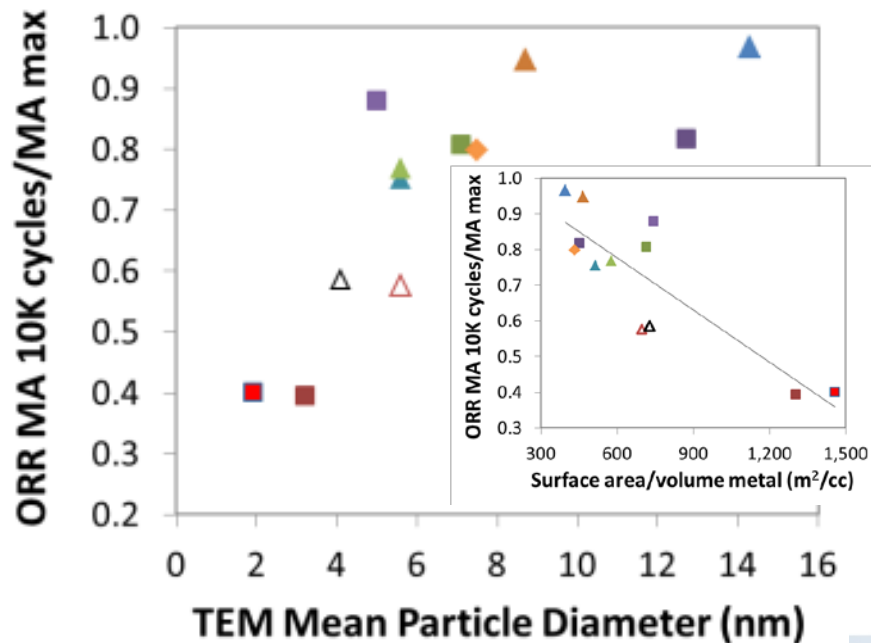
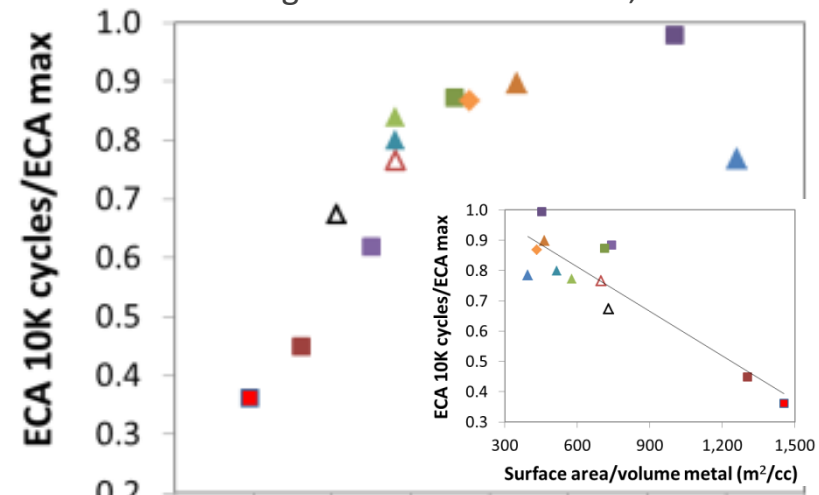
Parametric studies: Square wave – 0.95 (BL), 1.05 V, 30% RH

- Initial performances of MEAs with AL Pt₃Co and AL PtCo were lower than with Pt₃Co (>15 mV, low cd and >25 mV, high cd)
- No acid-leaching of Pt₃Co: higher decay in high cd air performance with BL cycling (>inc. in H₂ pump resist.)
- Acid-leaching of Pt₃Co does not effect the decay trends of ECA, MA, SA, and performance with cycling (1.05 V > BL > 30% RH)
- MA durability: 0.95 V - AL Pt₃Co > Pt₃Co > AL PtCo; 1.05 V – AL Pt₃Co > Pt₃Co >> AL PtCo
- ECA durability: 0.95 V – Pt₃Co > AL Pt₃Co > AL PtCo; 1.05 V – Pt₃Co > AL Pt₃Co > AL PtCo
- Perf. Durability, air, 0.8 A/cm²: 0.95 V – Pt₃Co ≥ AL Pt₃Co > AL PtCo; 1.05 V – Pt₃Co > AL Pt₃Co >> AL PtCo

Technical Progress (Task 2)

ORR activity and DOE cycling-induced ECA and MA loss in MEAs

Triangle wave potential cycle, 0.6 V to 1.0 V, 50 mV/s; Squares: Pt, Triangles: Pt₃Co, Hollow Triangles: Acid-leached Pt₃Co, Hollow black triangle: Acid-leached PtCo, Diamond: Pt₃Sc



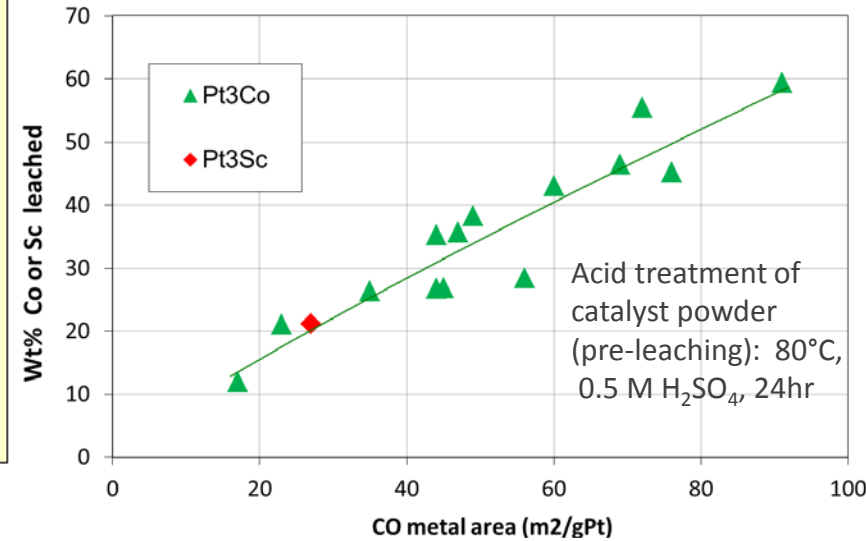
- Alloying with Co increases ORR activity of Pt
- Acid-leaching of Pt-Co lowers ORR activity
- No ORR activity benefit of alloying with Sc or Y
- ECA and ORR MA loss are dependent on initial mean diameter (surface area) of catalyst nanoparticles
- No clear effect of alloying or leaching on ECA and MA loss

Technical Progress (Task 3)

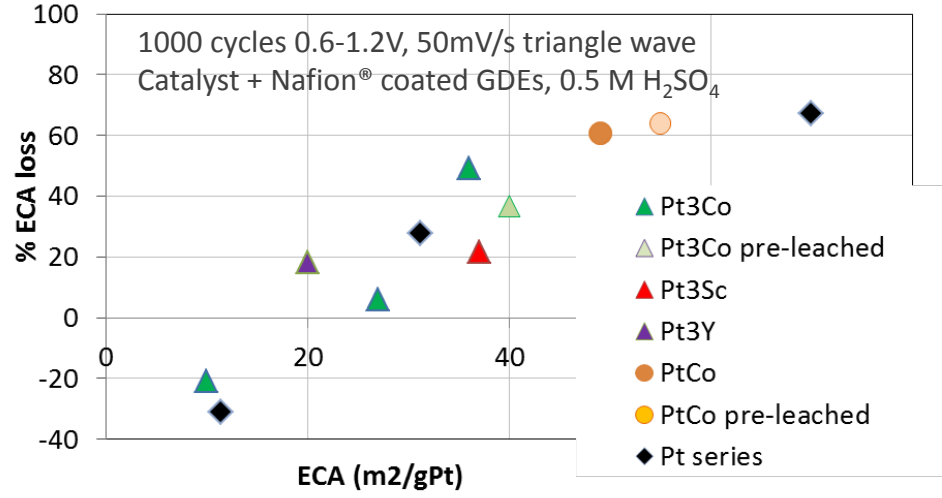
Aqueous electrolyte leaching and ECA loss - Pt and Pt alloys

- Leaching of base metal from alloys is dependent on catalyst surface area (particle size), but independent of identity of base metal
 - no additional stabilization with Sc and Y versus Co
- Pre-leaching of catalyst decreases subsequent loss of base metal in acidic electrolyte
- ECA loss is dependent on initial catalyst surface area and not affected by alloying

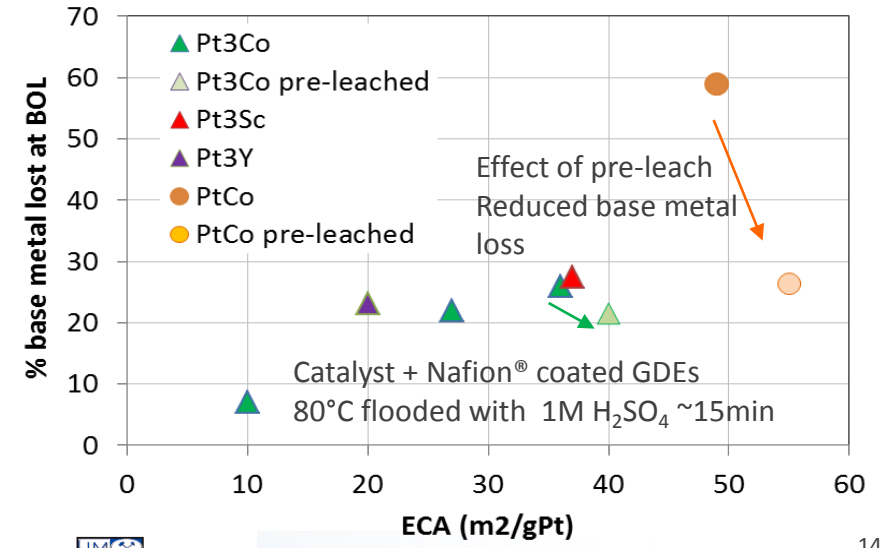
Powder leaching



ECA loss with electrochemical cycling

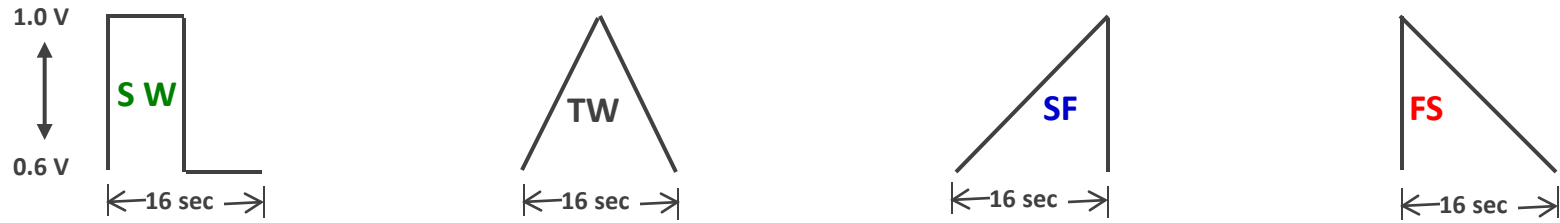


BOL electrochemical cycling

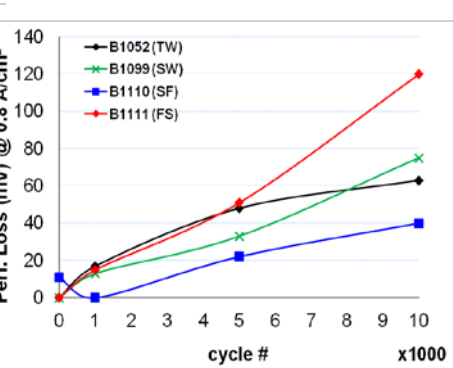
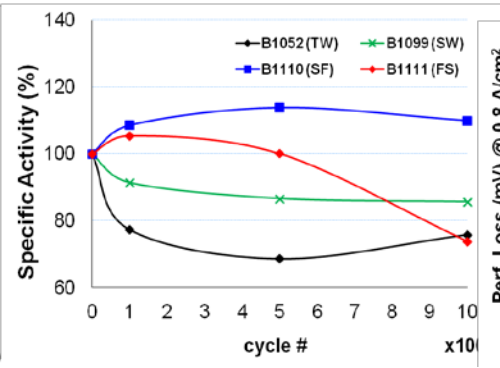
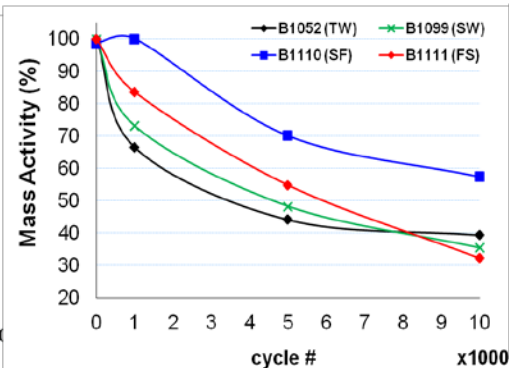
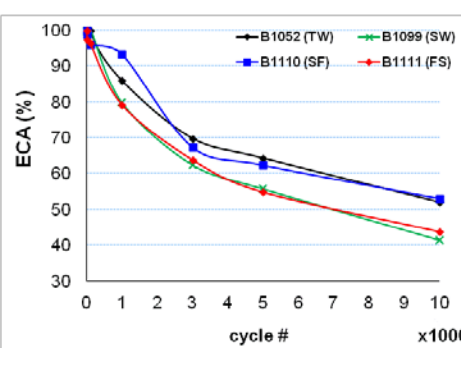
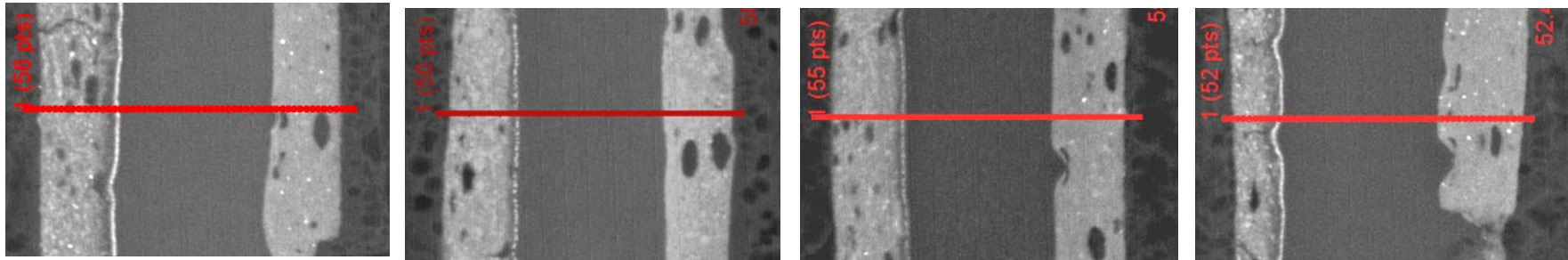


Technical Progress (Task 2.1)

Impact of cycle profile on 3.2 nm Pt catalyst decay



Middle



- Perf. loss : SW \cong FS > TW > SF
- SA loss with cycling: TW \cong FS > SW >> SF
- ECA loss with cycling: SW \cong FS >> TW \cong SF
- Degree of Pt in membrane: SW \cong FS >> TW \cong SF
- MA decay with cycling: SW \cong FS \cong TW >> SF

Technical Progress (Tasks 2.1, 2.2, and 4)

Characterization results parametric studies - ECA, TEM, ASAXS

Parametric study of 3.2 nm Pt; 10,000 square wave cycles

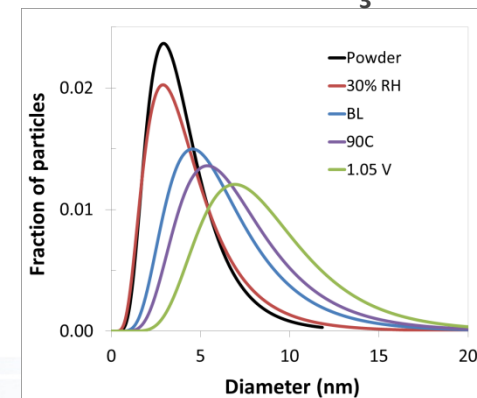
Cycling conditions	ECA GSA from TEM PSD Cycled/Initial (m ² /g-Pt)	Final particle dia. three regions (nm) A=near membrane C=near GDL
BL	26.0/45.0=0.58 47.5/63.0=0.75	A: 4.9±0.2 B: 5.2±0.2 C: 4.9±0.2
1.05V	16.0/43.0=0.37 25.3/63.0=0.40	A: 8.1±0.4 B: 8.3±0.4 C: 7.9±0.5
30%RH	39.0/46.0=0.85 55.7/63.0=0.88	A: 4.0±0.2 B: 4.3±0.2 C: 4.3±0.2
90 C	27.0/52.0=0.52 33.4/63.0=0.53	A: 6.6±0.6 B: 5.3±0.3 C: 5.4±0.2

Parametric study of 5.6 nm Pt₃Co; 10,000 square wave cycles

Cycling conditions	ECA GSA from TEM PSD GSA from ASAXS PSD Cycled/Initial (m ² /g-Pt)	Final particle dia. three regions TEM (ASAXS) (nm)
BL	27.4/35.0=0.78 50.5/57.6=0.88 36.4/59.2=0.61	A: 5.7±0.3 B: 5.8±0.3 C: 4.9±0.4 (5.7)
1.05V	18.0/33.0 =0.54 32.0/57.6=0.56 29.7/59.2=0.54	A: 9.2±0.4 B: 8.8±0.4 C: 8.5±0.4 (8.1)
30%RH	29.3/30.0=0.98 40.0/57.6=0.69 46.1/59.2=0.77	A: 6.6±0.5 B: 5.8±0.3 C: 5.2±0.2 (3.8)
90 C	19.8/31.6=0.63 36.1/57.6=0.63 33.5/59.2=0.56	A: 9.1±0.6 B: 7.3±0.3 C: 6.7±0.3 (6.6)

- Particle growth, surface area loss: 1.05 V > 90 C > Baseline >> low RH
- Mass activity loss: 1.05 V > 90 C > low RH > Baseline
- Specific activity loss: 1.05 V > Baseline = low RH > 90 C (Pt₃Co);
low RH > 90 C ≥ 1.05 V > Baseline (Pt)
- Significant “coalesced” particles evident only in 1.05 V Pt cell

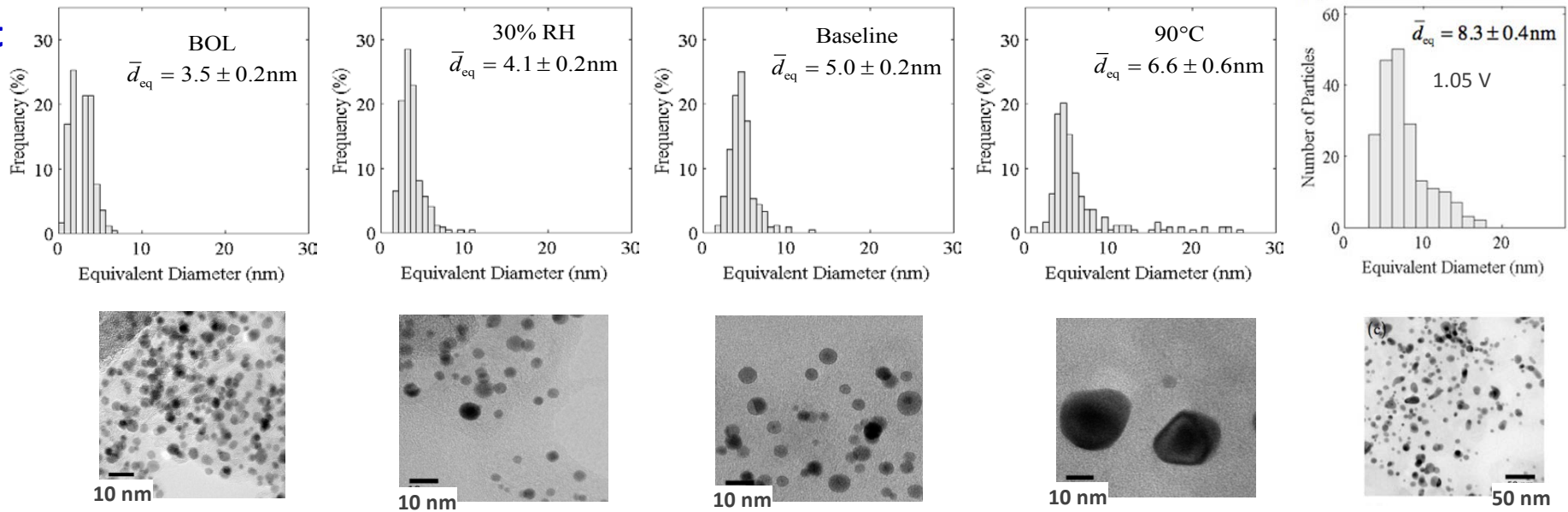
Ex situ ASAXS Pt₃Co



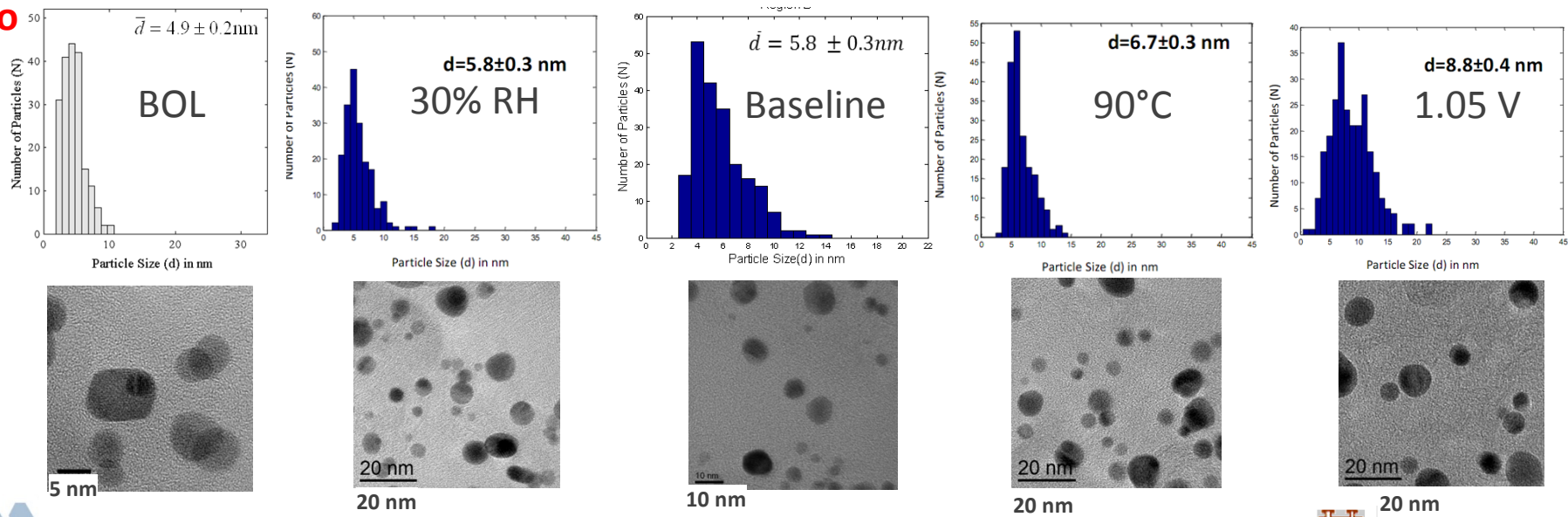
Technical Progress (Tasks 2.1 and 4.1)

Parametric study - post-cycling TEM

Pt



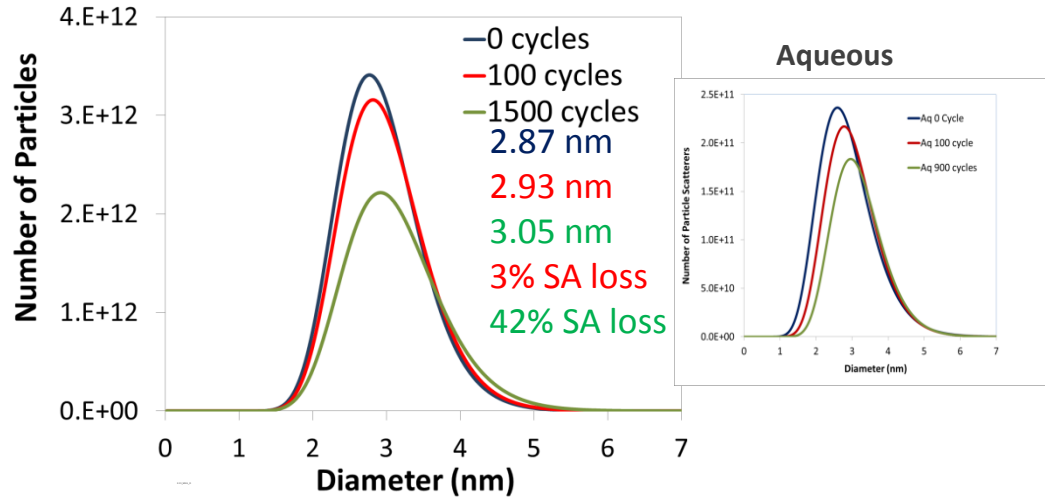
Pt₃Co



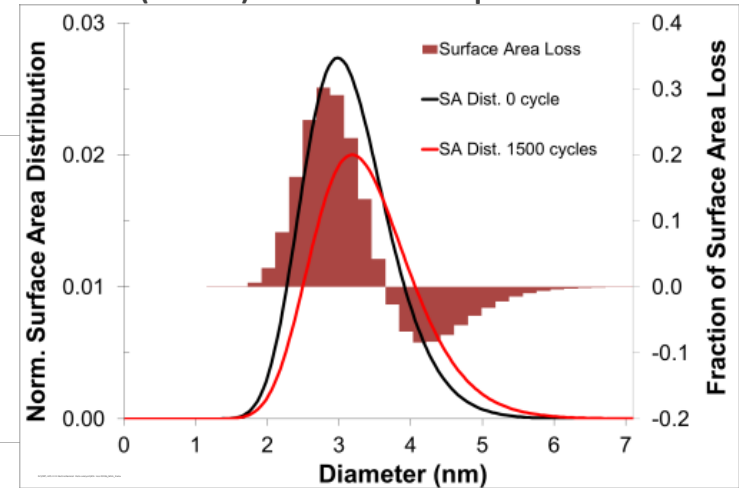
Technical Progress (Task 3)

In situ and in operando PSD evolution - small angle X-ray scattering

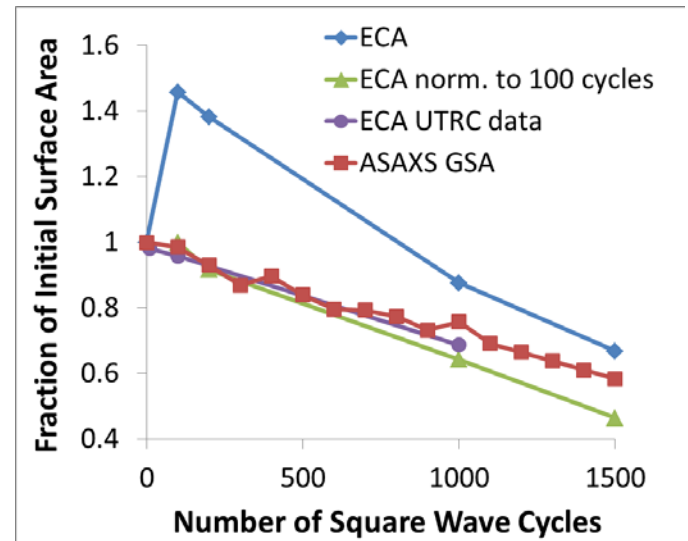
Pt (3.2 nm): 0.4 to 1.05 V Square Wave MEA



Pt (3.2 nm): 0.4 to 1.05 V Square Wave MEA



MEA Square wave cycles 0.4 to 1.05 V

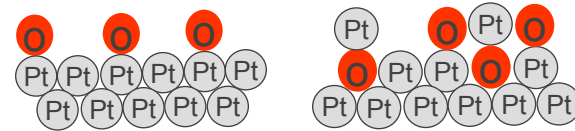
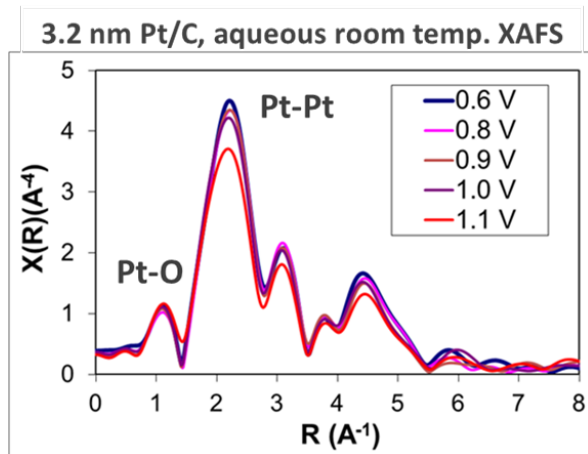
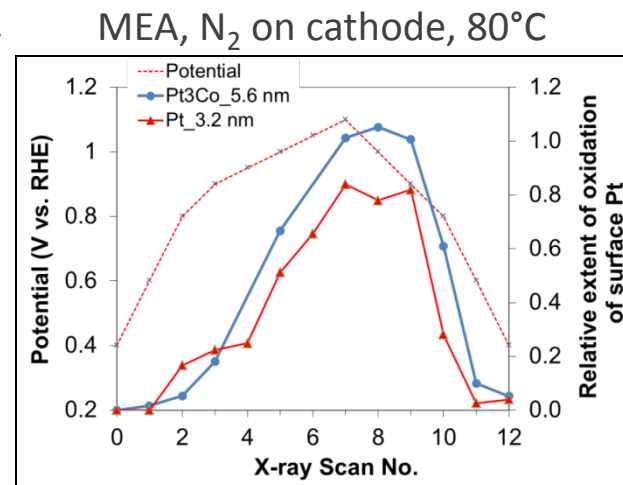
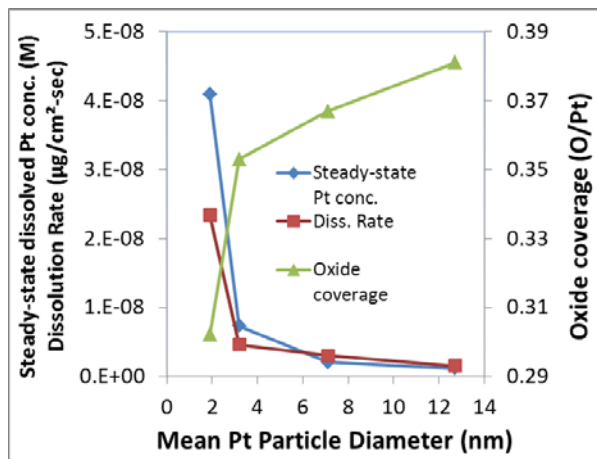
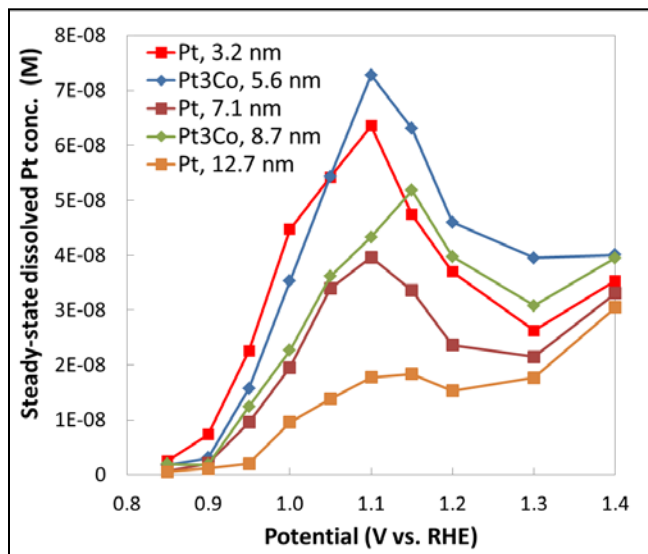


- Evolution of PSD in MEA differs from that in aqueous environment – effect of crossover hydrogen*
- Decrease in Pt surface area in aqueous and MEA environments is primarily due to loss of particles with diameters $< \sim 3.5$ nm diameter
- In operando* X-ray scattering shows that geometric surface area decreases during initial ECA increase (conditioning)

Technical Progress (Task 3)

Aqueous electrolyte and X-ray studies of Pt dissolution and oxide coverage

Potentiostatic – 72h, room-temperature, 0.57 M HClO₄



<1.1 V

1.1 V

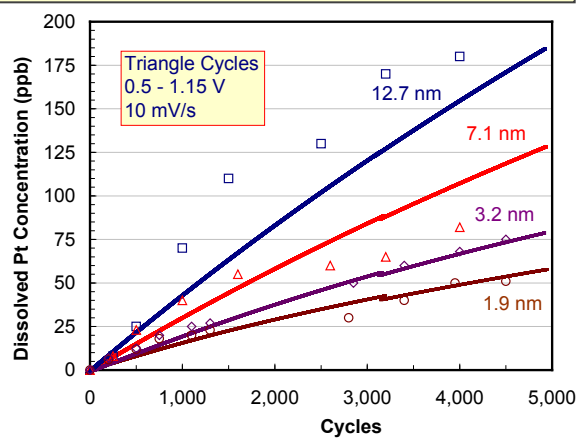
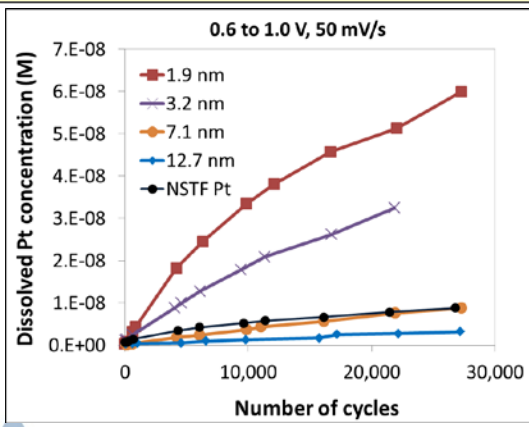
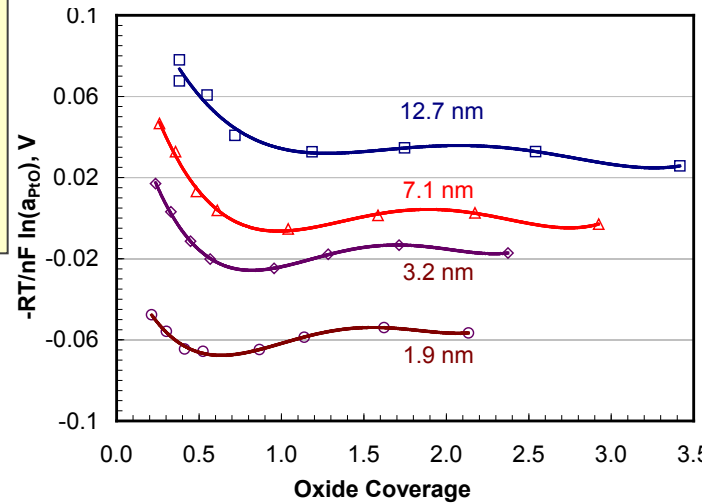
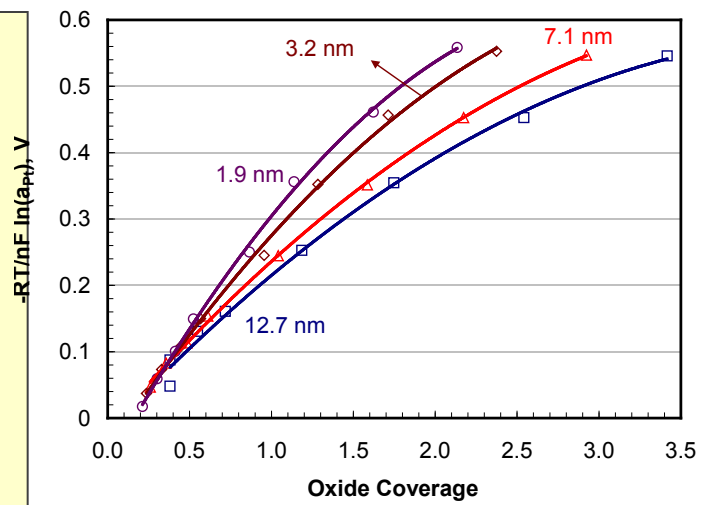
19

- Steady-state dissolved Pt concentrations and potentiostatic dissolution rates increase with decreasing mean particle size of Pt and Pt₃Co
- Steady-state oxide coverage of Pt decreases with decreasing mean particle size
- Dissolved Pt concentration peaks at an oxide coverage of ~1 O/Pt; XAFS evidence for change of oxide structure
- Oxide protects Pt against dissolution under steady-state conditions

Technical Progress (Task 5.2)

Catalyst degradation modeling

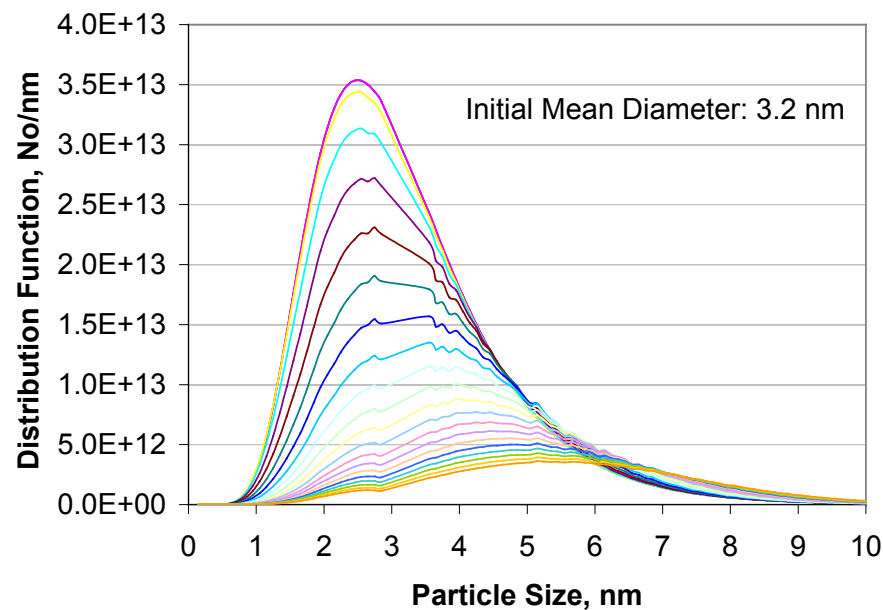
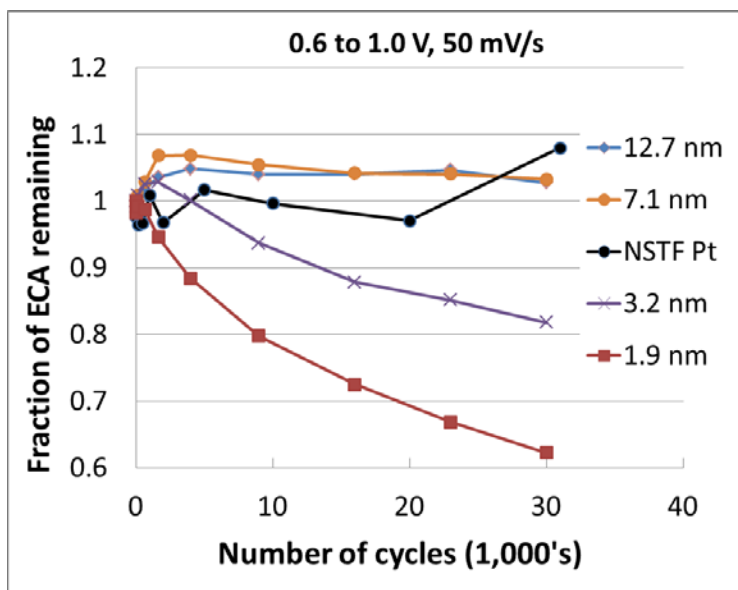
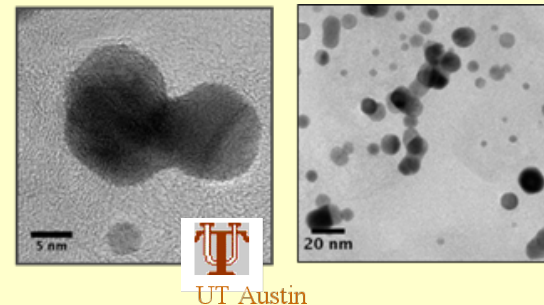
- Thermodynamics of Pt Dissolution and Oxide Growth:
 - Non-ideal solid solution formulation for Pt dissolution
 - Activity of Pt and PtO_x in solid solution related to equilibrium oxide coverage and particle size
 - Decrease in Pt activity with oxide coverage consistent with the changing slope in the measured Pt^{2+} concentration with potential and its peak at approx. 1.1 V
 - Changes in PtO_x activity beyond unity oxide coverage reflects multiple oxidation states ($PtOH$, PtO_2 , etc.) with different E^0 and n
- Platinum dissolution – Cycling conditions:
 - Pt Dissolution kinetics modeled using transient data at 1.1 V
 - Oxide growth/reduction kinetics modeled using CV oxidation scans
 - Dissolution model validated with cyclic data: 40-cm² ECA GDE in 130 mL perchloric acid electrolyte
 - Dissolution rates are strong functions of upper potential limit, lower potential limit, scan rates, times, and oxide coverage



Technical Progress (Task 5.2)

Catalyst degradation modeling - ECA loss and particle growth

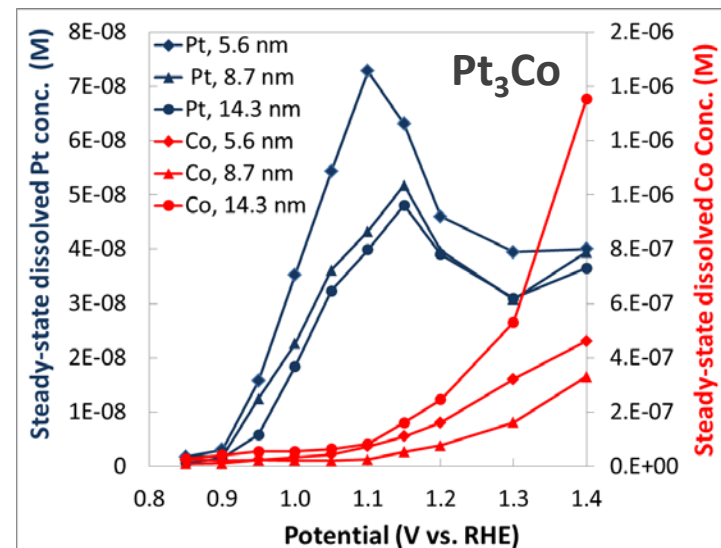
- Measured ECA loss cannot be explained solely on the basis of Pt dissolution or change in size distribution due to preferential dissolution of smaller particles and re-deposition on larger particles
- Model expanded to include coalescence due to re-deposition
 - Smoluchowski equation with Pt dissolution, Pt re-deposition, and particle coalescence
 - Coagulation kernel function of re-deposition rate
 - Implicit finite-difference scheme in time and size coordinate*



Technical Progress (Task 3)

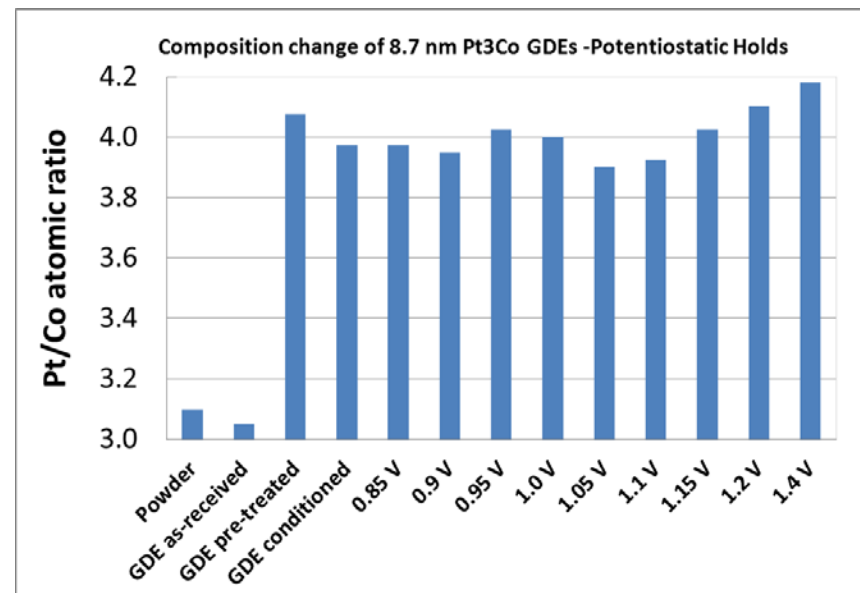
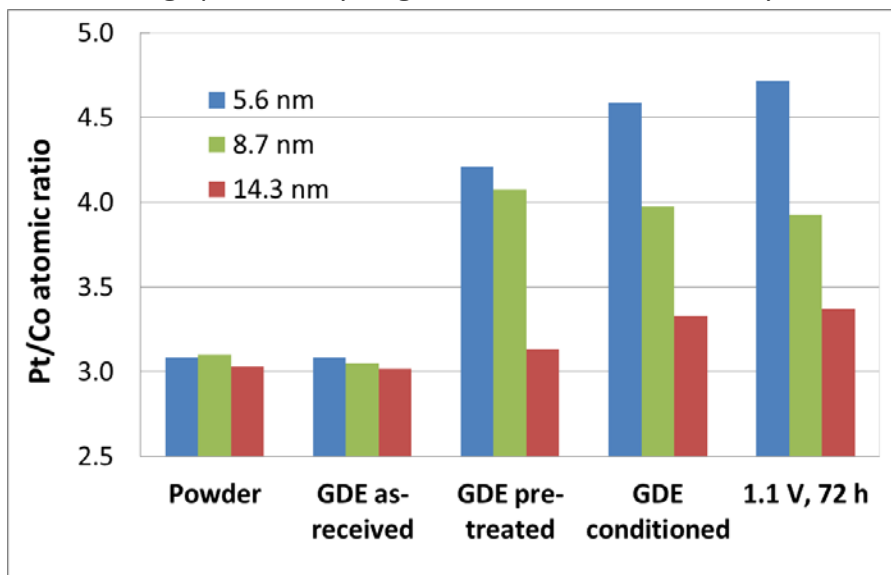
Aqueous electrolyte studies of Pt₃Co dissolution

- Largest loss of cobalt is observed during electrode preparation/wet-up
- Fraction of total cobalt leached from catalyst decreases with increasing particle size
- Loss of cobalt from catalyst is potential independent at potentials >0.85V and <~1.0 V
- Potential region for increased extent of cobalt dissolution coincides with decreased platinum dissolution



Pre-treatment: Soaking in room temp. H₂O;

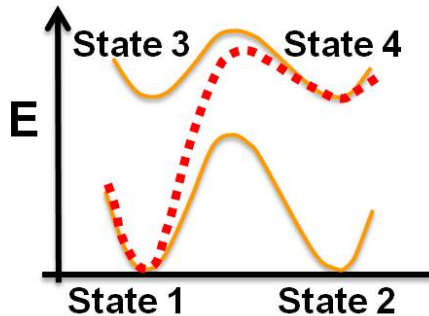
Conditioning: potential cycling from 0.05 to 1.1 V, 15-20 cycles



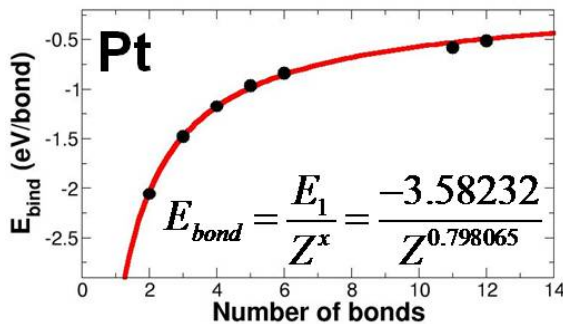
Technical Progress (Task 5.1)

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

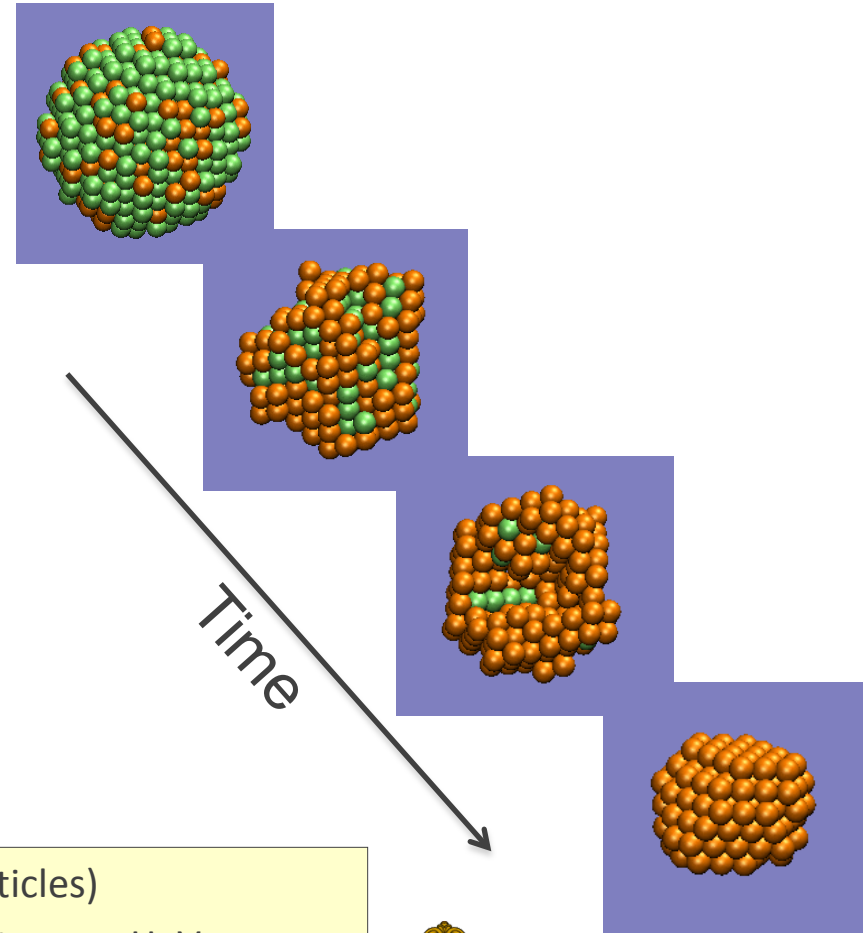
- KMC Model of Pt-Co **Diffusion** and **Dissolution**.



- Bond-Energy Hamiltonian from DFT Fits



- Can simulate composition and structure of Pt-Co dealloying

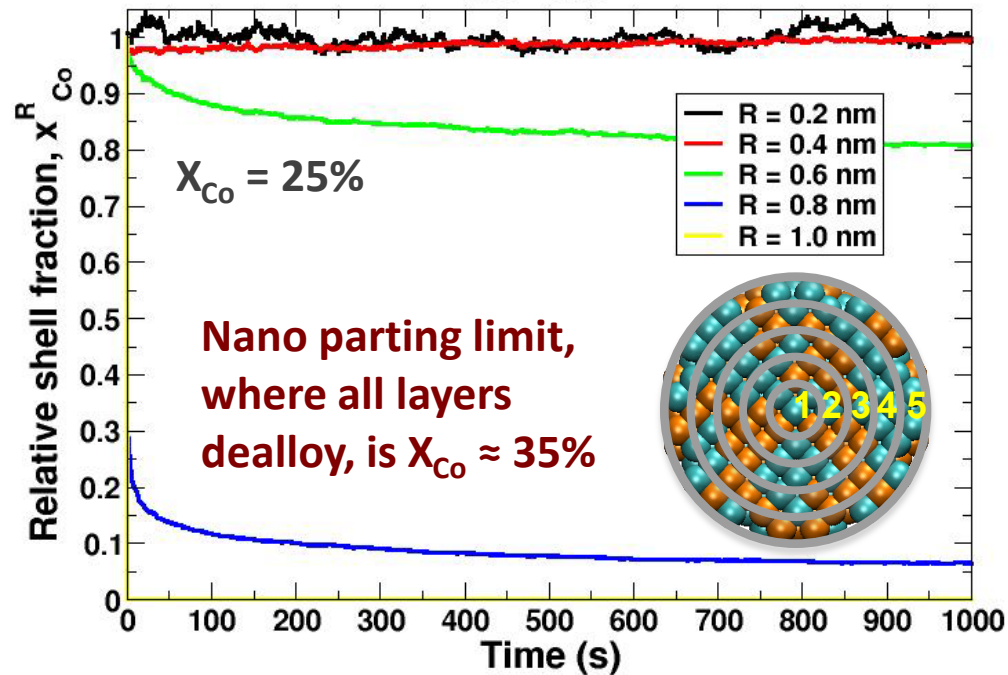


- Basic KMC model completed (~20min, 1000 particles)
- Can simulate Pt-Co evolution vs. time, X_{Co} , size, temp, pH, V, ...

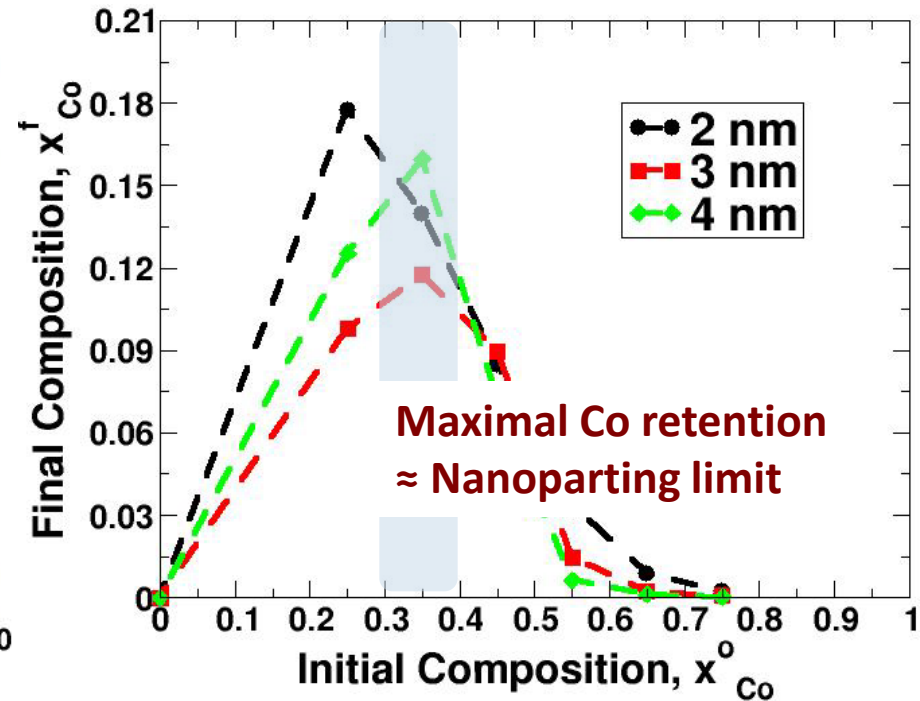
Technical Progress (Task 5.1)

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

Understanding Dealloying



Maintaining Co Concentration



- Identified how particles dealloy and nanoparticle dealloying limit at $X_{Co} \approx 35\%$
- Retained Co peaks near nanoparting limit

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:

- Prepared Pt/alternative carbons, Pt/C different levels of Cl impurities. Fabricated and tested MEAs of $Pt_xCo_{(1-x)}$, acid-leached, Pt_3Sc , and various Pt/C
- Established relationship between loss of ECA, mass activity, and particle size: dominating factor in ECA and MA loss is initial particle size
- Determined that the operating parameters of upper potential limit and anodic sweep rate have the most significant impact on cell degradation
- Established most significant factors governing cycling-induced change in PSD and ECA loss: competition between Pt dissolution and oxide formation and coalescence of particles via re-deposition

Collaboration:

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

Future Work:

- Preparation, characterization and MEA testing of Pt-Ni; characterization and MEA testing of Pt/alternative carbons, Pt/C with Cl impurities
- Complete analysis of ASAXS and XAFS data for Pt and Pt_3Co MEAs
- Study effect of temperature on oxide structure and dissolution
- Complete cathode performance degradation model



Collaborations and acknowledgments

- Project team (subs) within DOE H₂ 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”

Thanks!

- Yifen Tsai, Analytical Chemistry Laboratory, Chemical Sciences and Engineering Division, Argonne National Laboratory, ICP-MS
- Nadia Leyarovska, Sönke Seifert, Sungsik Lee, Sector 12, Advanced Photon Source, Argonne National Laboratory
- DOE, Office of Energy Efficiency and Renewable Energy, Fuel Cell Technologies Program – Nancy Garland (Technology Development Manager)
- DOE, Office of Science, Basic Energy Sciences
 - Argonne National Laboratory Advanced Photon Source
 - Argonne National Laboratory’s Electron Microscopy Center



Technical Back-Up Slides



Technical Progress: Catalyst and MEA fabrication (Task 1)

Pt/C - Ketjen EC300J and corrosion resistant carbons (A and B)

Catalyst identifier	Carbon surface area (m ² /gC)	Calculated Wt% carbon loss 24hr 1.2V hold 80C*	Annealing conditions	Pt (%)	CO area (m ² g ⁻¹ -Pt)	XRD C.S. (nm)	TEM Mean particle size (nm)	ECA CO stripping (1M H ₂ SO ₄ , 80°C)
Pt/Ketjen (1.9 nm)	831	32	none	35.6	96	<2 nm	1.9	94
Pt/Ketjen (3.2 nm)	831	32	T ₁	40.7	63	Non-gaussian peaks – crystallite size not determined	3.2	60
Pt/Ketjen (4.9 nm)	831	32	T _{1.5}	40.7	35	~4.9 (non gaussian peaks)	tbd	tbd
Pt/Ketjen (7.1 nm)	831	32	T ₂	40.2	26	5.8	7.1	22
Pt/Carbon A	136	1	T ₁	29.6	32	4.6	tbd	32
Pt/Carbon B	232	12	tbd	35 (nom)	tbd	tbd	tbd	tbd

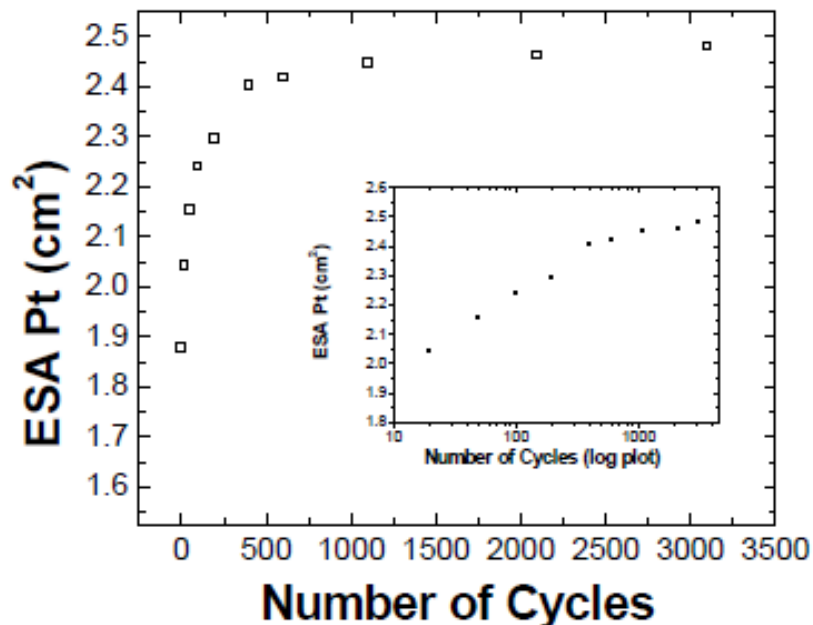
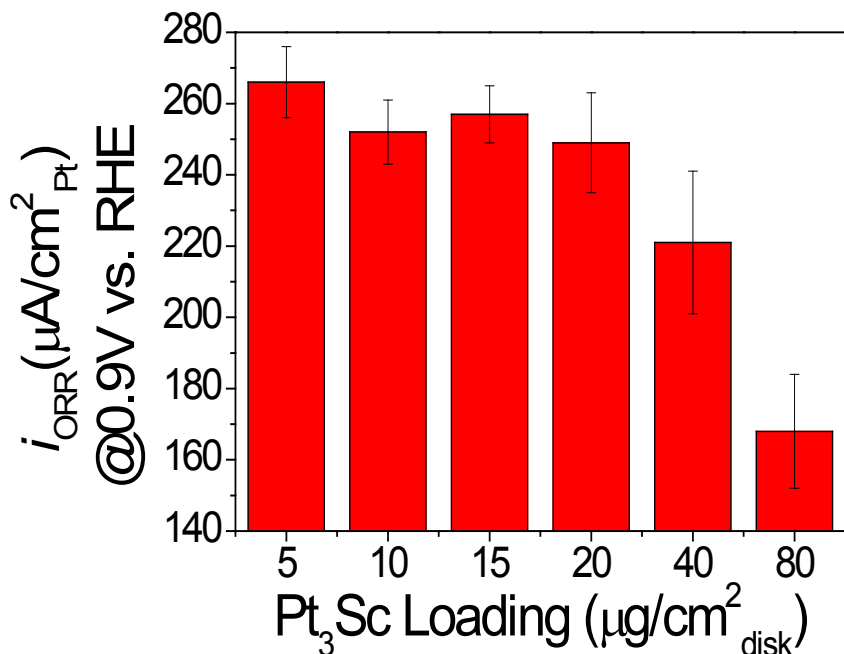
Pt/Carbon A (low corrosion rate carbon) and similar particle size and gas phase metal area to Pt/Ketjen 4.9 nm Pt/Carbon B (intermediate corrosion rate carbon) to be annealed to target similar particle size

* wt % carbon calculated for carbon only electrode by integration of charge as described in JPS 171, 2007, 18.

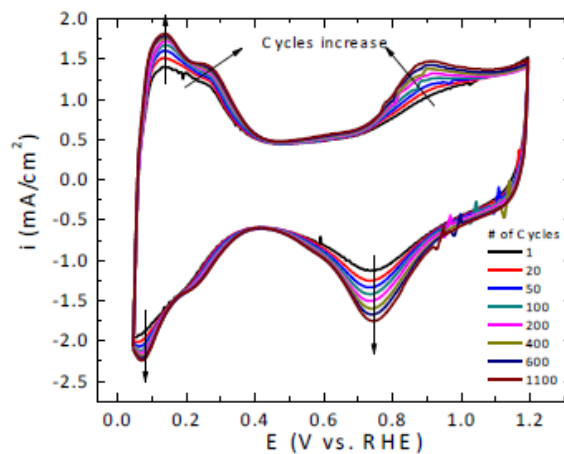


Technical Progress (Task 3)

Rotating-disk electrode measurements of Pt_3Sc/C ORR activity and stability



1600 rpm, 0.1 M $HClO_4$,
room temp., 10 mV/s

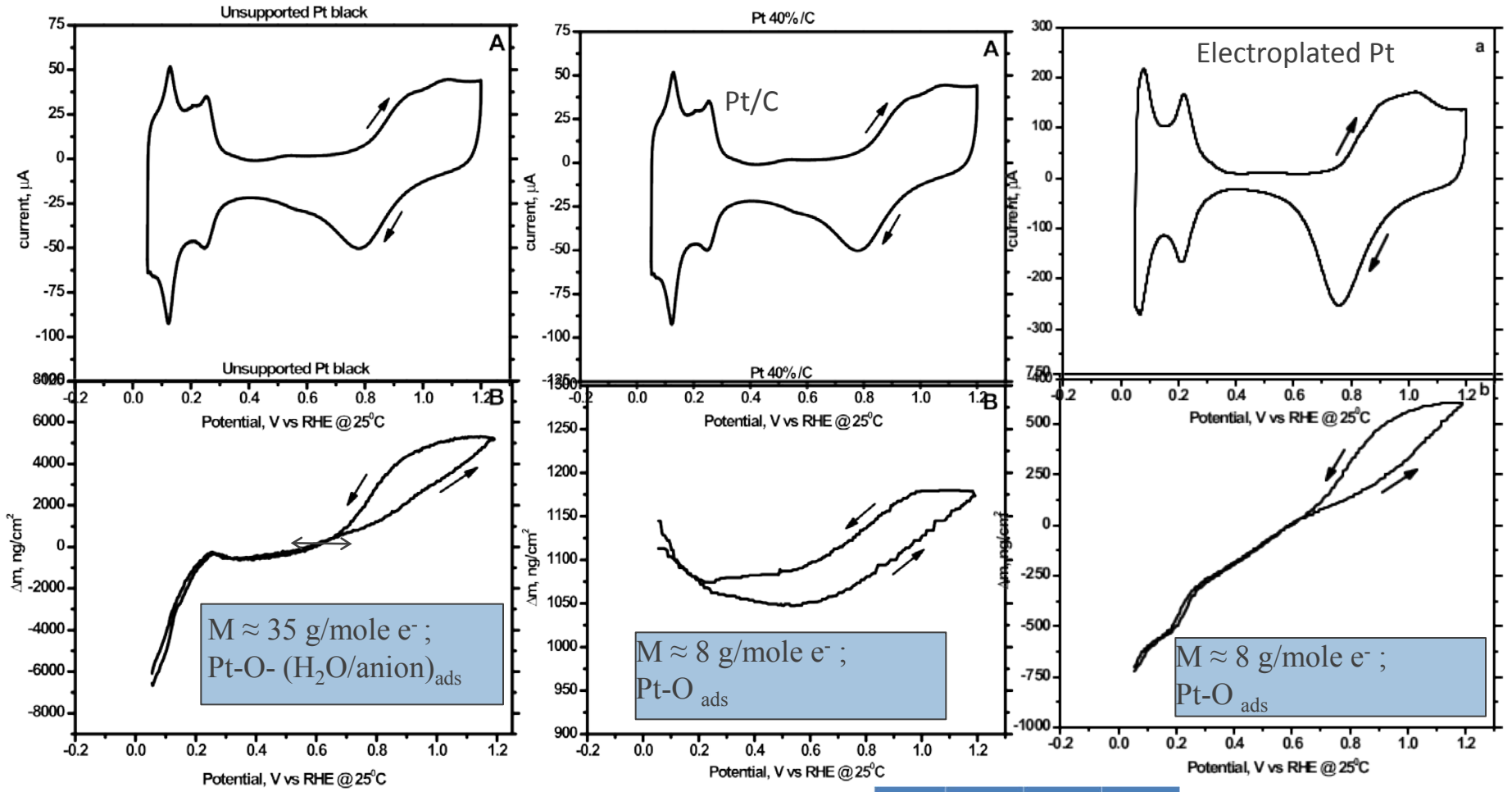


Cycling protocol:
0.06 to 1.19 V,
0.1 M $HClO_4$,
room temp.,
40 $\mu g Pt_3Sc/cm^2$



Technical Progress (Task 3)

Electrochemical quartz crystal microbalance studies of Pt oxidation/dissolution



0.5 M H₂SO₄; 50 mV/s

species	g/mole	e-	g/e- mol
O	16	2	8
O ₂	32	1	32
OH	17	1 or 2	17 or 8.5
(OH) ₂	34	2	17 or 8.5
(O ₂ H)	33	1	33
OH ₂	18	1 or 2	18/9



Technical Progress (Task 5)

Components of mathematical model at UT-Austin

Model	Model components
i Anodic film formation-direct deposition	Charge transfer, chemical reaction
ii Anodic film formation-direct deposition	Charge transfer, chemical reaction
iii Anodic film formation-dissolution precipitation	Charge transfer, chemical reaction (precipitation), film resistivity, diffusion
iv Film growth – solid state diffusion	Charge transfer, chemical reaction, solid state diffusion
v Film growth – place exchange	Charge transfer, place exchange
vi Film growth – surface roughening	Charge transfer, irreversible place exchange
vii Film growth – ionic migration	High field growth