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

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Argonne National Laboratory

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Washington D.C.

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Project ID# FC012

Overview

Timeline

- Project start data: October, 2009
- Project end data: September, 2012
- Percentage complete: 10%

Budget

- Total project funding:
  - DOE: $3,754 K
  - Contractor share: $544 K
- Funding received in FY09
  - $ 590 K
- Funding expected for FY10
  - $ 1,003 K

Barriers

- Barriers addressed

A. Durability

B. Cost

C. Electrode performance

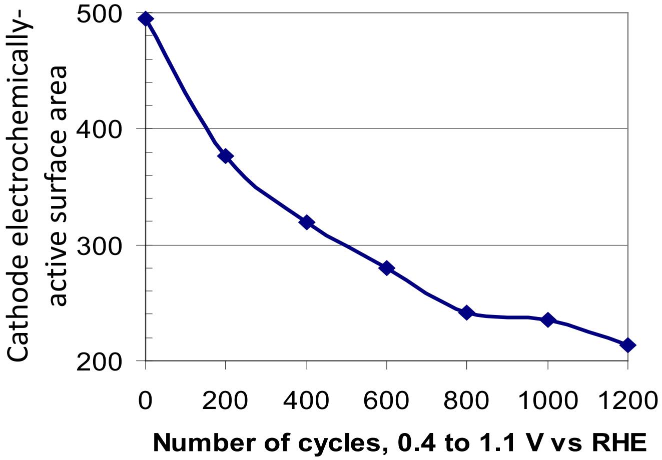
Partners

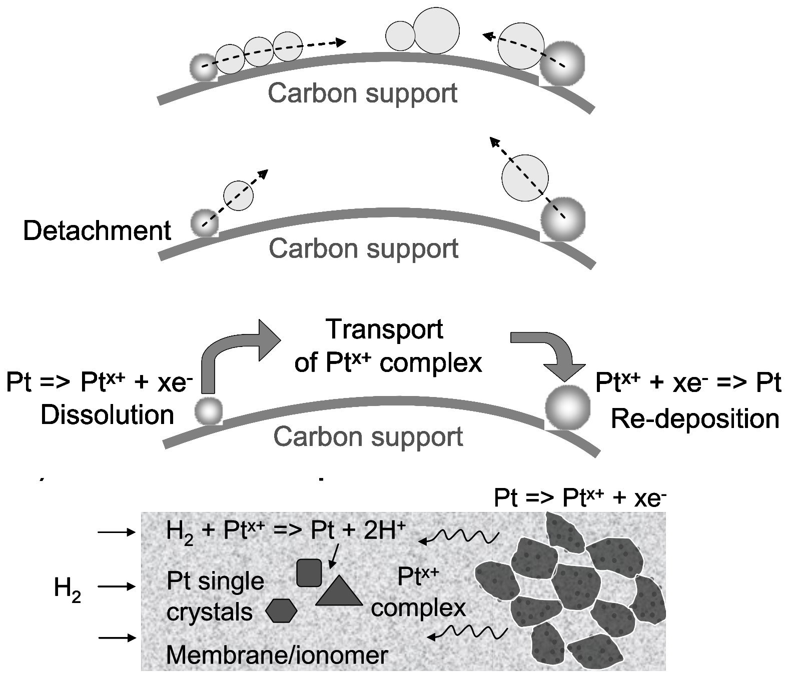
- Johnson Matthey Fuel Cells
  - Sarah Ball, Jonathan Sharman, Brian Theobald, and Graham Hards
- United Technologies Research Center
  - Mallika Gummalla and Zhiwei Yang
- Massachusetts Institute of Technology
  - Yang Shao-Horn and Wenchao Sheng
- University of Texas at Austin
  - Paulo Ferreira
  - Jeremy Meyers, Preethi Mathew, and Seok Koo Kim
- University of Wisconsin – Madison
  - Dane Morgan, Ligen Wang, 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

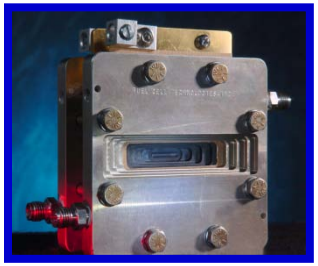




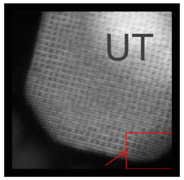
Y. Shao-Horn et al., *Topics in Catalysis*, **46** (2007) 285–305.

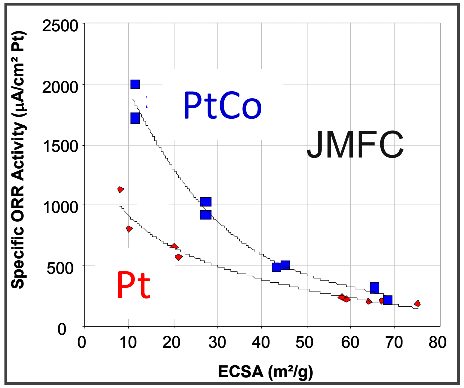
Approach

- **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 (UT)

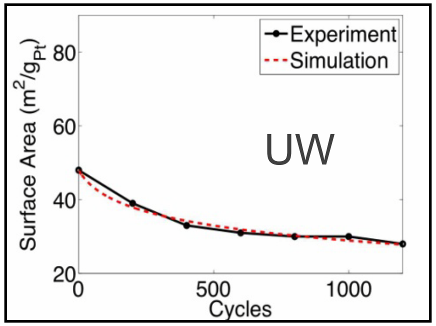


ANL





- **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

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	■	■	■	■	■	■	■	■	■	■	■	■

- **First year's focus is baseline performance degradation mode identification for Pt and one Pt alloy**

Approach

Milestones and Go/No-Go Decision Point

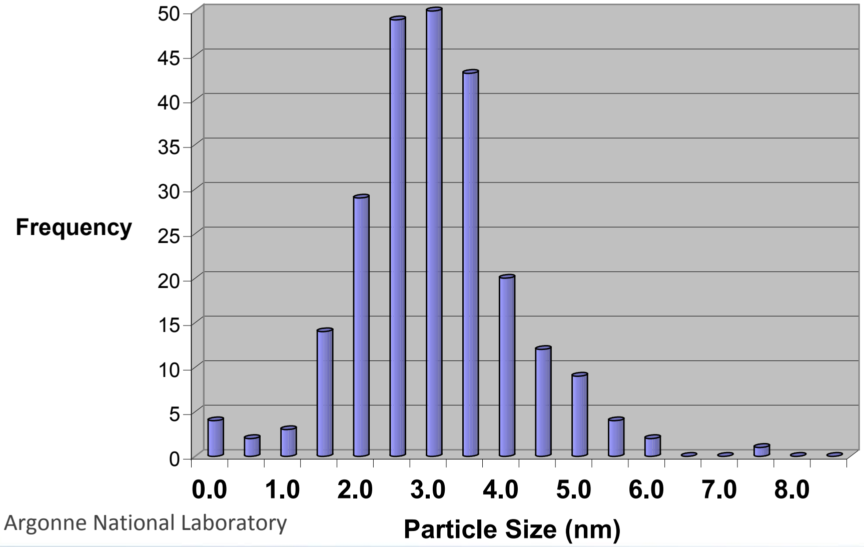
- Year 1 Milestones
  - Determine the effect of initial Pt particle size on the degradation rate of cathode catalyst performance and on Pt dissolution rates - 05/10
    - Completed effect of Pt particle size on performance degradation rate
    - Pt dissolution rate studies are underway
  - Development of initial macroscopic-based CV model plus ORR catalyst layer performance model, identification of parameters still needed - 09/10
    - Modeling efforts are on-going
  - *In situ* and *ex situ* characterization of two classes of catalysts - 09/10
    - Completed *ex situ* anomalous small angle X-ray scattering (ASAXS) and TEM characterization of as-prepared Pt/C catalysts with different initial particle sizes (four sizes)
    - Completed ASAXS measurements of Pt particle growth during DOE protocol potential cycling in 0.1 M $HClO_4$ electrolyte – data analysis is on-going
    - Post-test analyses of cycled MEAs is underway

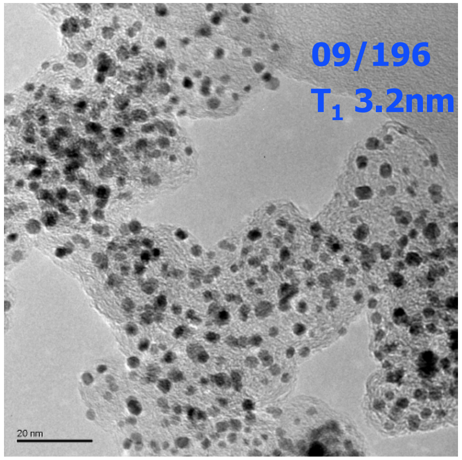
- Go/No-Go Decision Point
  - Demonstrated link between aqueous electrolyte studies of degradation mechanisms of three classes of catalysts and degradation observed in MEA tests – 09/11

Technical Progress (Task 1.1)

- Prepared Pt/Ketjen catalysts of varying particle size,
- Prepared MEAs with 0.2 mg/cm² 09/152 in anode and 0.2 mg Pt/cm² of 09/152-204 in cathode,
- Multiple MEAs with 09/196 catalyst in cathode supplied to UTRC for parametric studies.

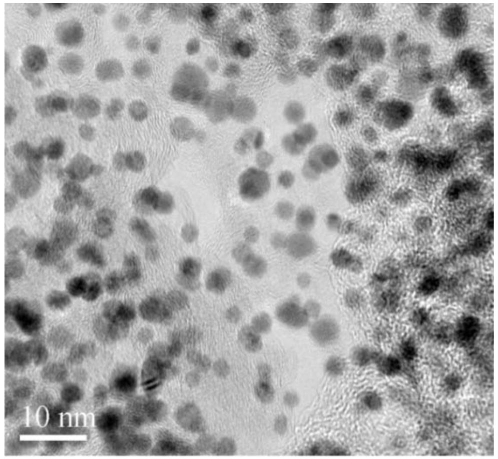
Code	Annealing conditions	Pt (%)	CO area ($m^2\ g^{-1}$-Pt)	TEM Mean particle size (nm)	
09/152	As-prepared	35.6	96	1.9	
09/196	T_1	40.7	63	3.2	Benchmark
09/203	T_2	40.2	26	7.1	
09/204	T_3	40.9	11	12.7	

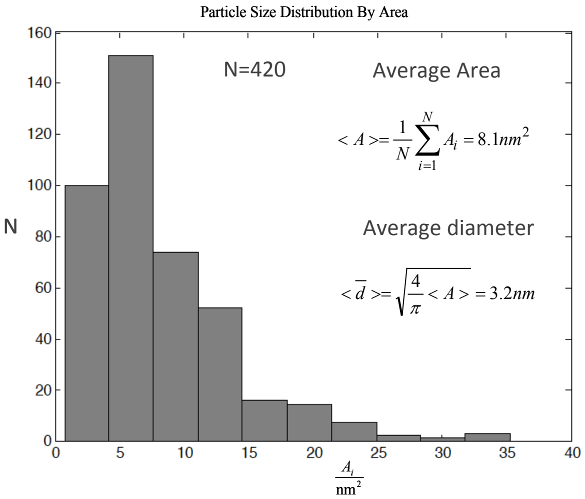




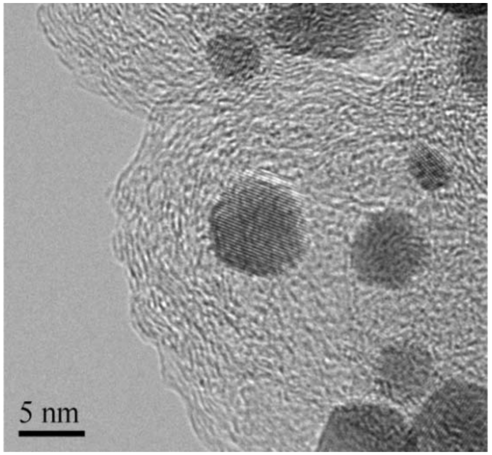
Technical Progress (Task 4)
TEM characterization: Pt nanoparticles

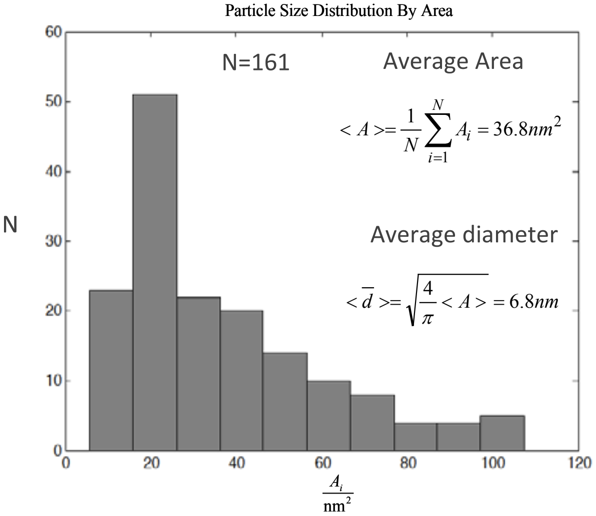
09/196



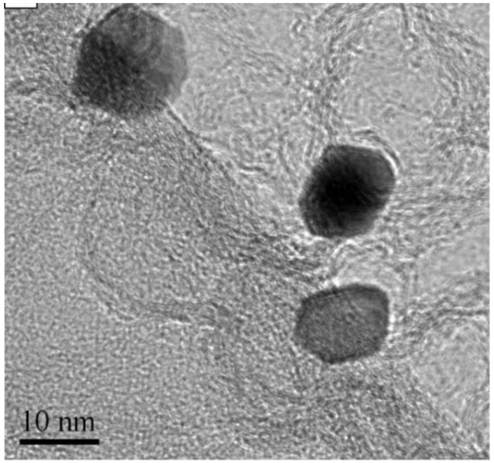

Particle Size Distribution By Area

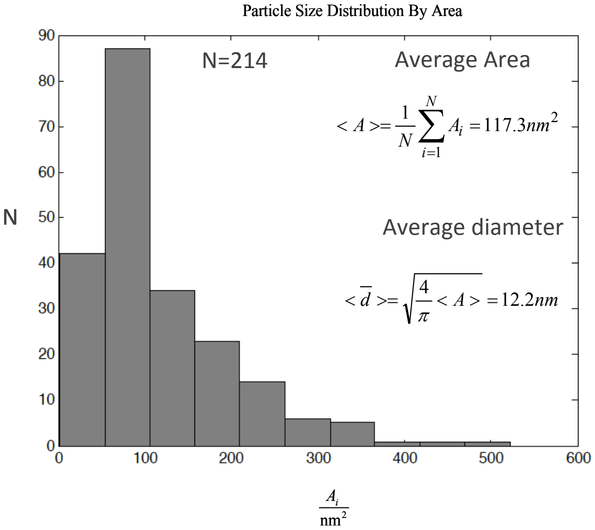
09/203




Particle Size Distribution By Area

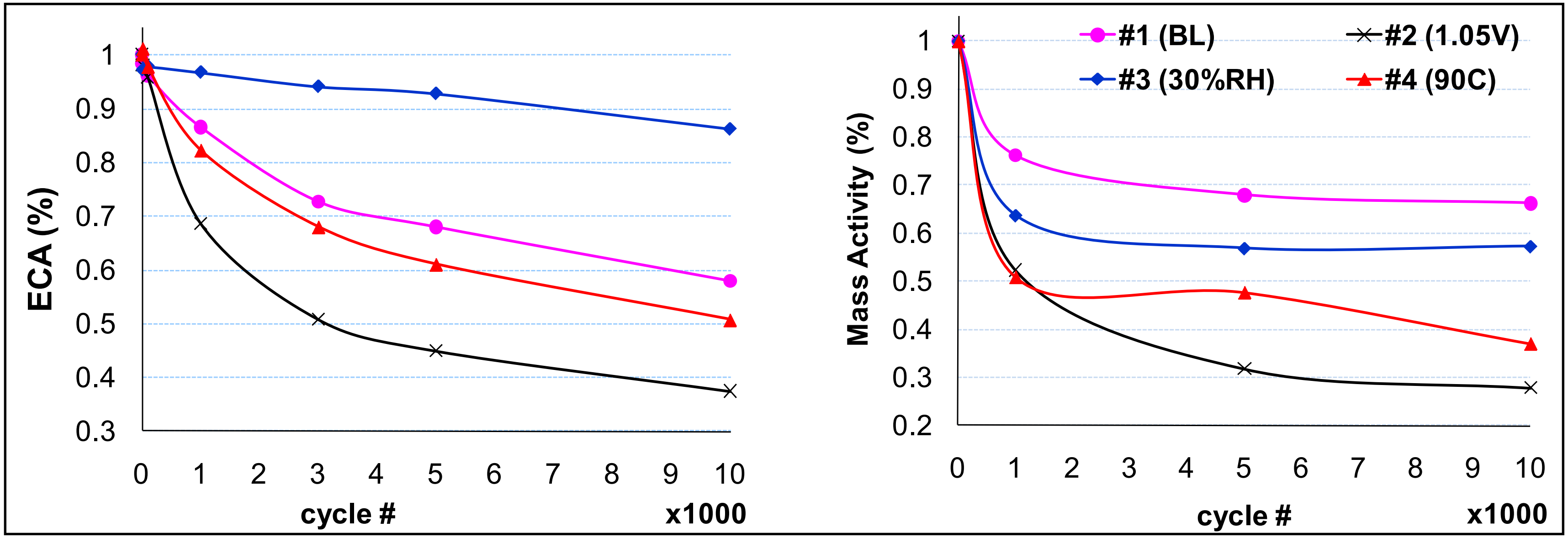
09/204




Particle Size Distribution By Area

Technical Progress (Task 2.1)
Parametric studies of benchmark Pt catalyst

Cell #	Potential cycle
#1 (BL)	• Square wave potential cycle: 10s at 0.4V, 10s at 0.95V (20s / cycle) • Cell Temperature: 80ºC • Relative Humidity: Anode / Cathode = 100% / 100% • Fuel/Oxidant : 4%N_2 at 500 sccm and N_2 at 500 sccm • Pressure: Atmospheric pressure
#2 (1.05V)	• Square wave potential cycle: 10s at 0.4V, 10s at 1.05V (20s / cycle) • All other parameters were same as cell #1
#3 (30%RH)	• Relative Humidity: Anode / Cathode = 30%RH / 30%RH • All other parameters were same as cell #1
#4 (90C)	• Cell Temperature: 90ºC • All other parameters were same as cell #1

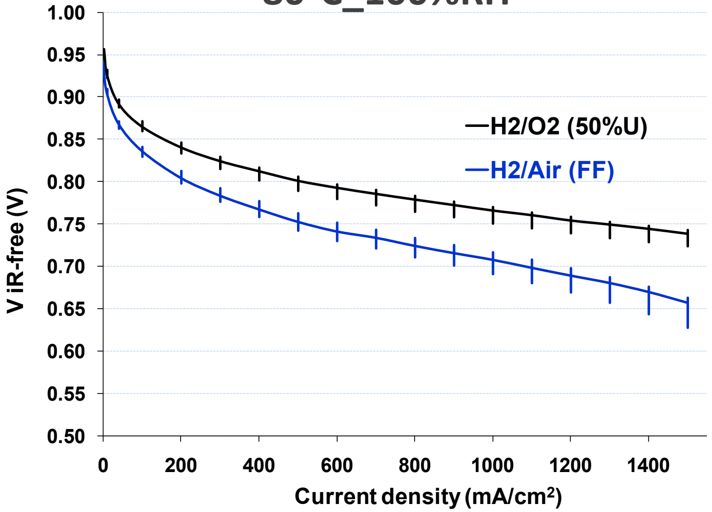


- Increasing upper limit of voltage cycling increases cathode catalyst surface area and mass activity loss
- Low inlet RH decreases cathode catalyst degradation
- Increased cell temperature increases cathode catalyst degradation

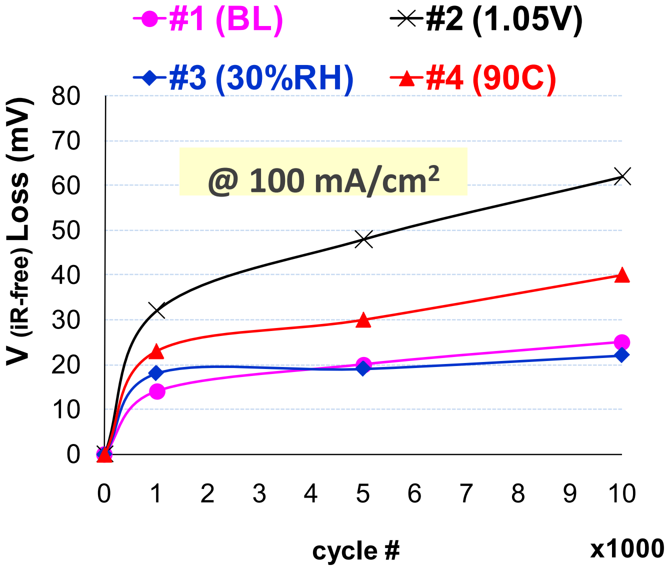
Technical Progress (Task 2.1)
Parametric studies of benchmark Pt catalyst

Initial Polarization Curves

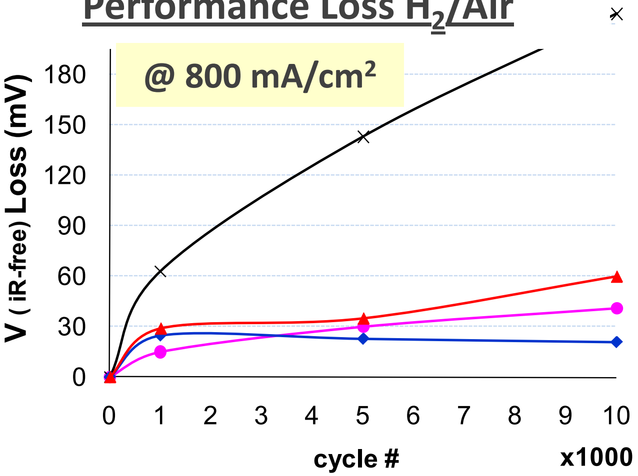
80°C_100%RH

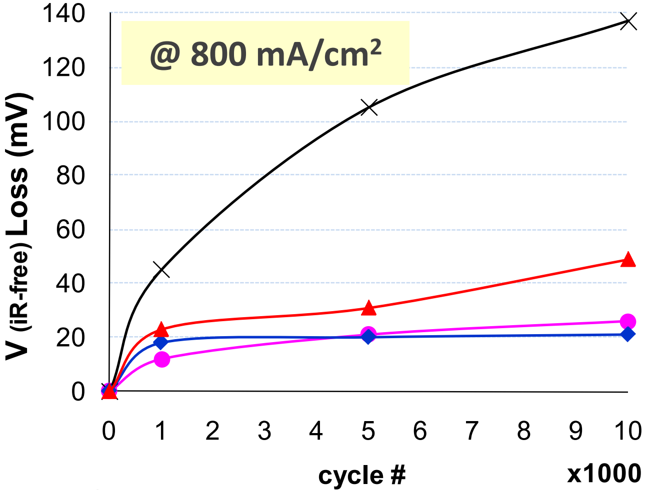


Performance Loss H_2/O_2



Performance Loss H_2/Air





- Cycling to high potentials effects cathode transport losses

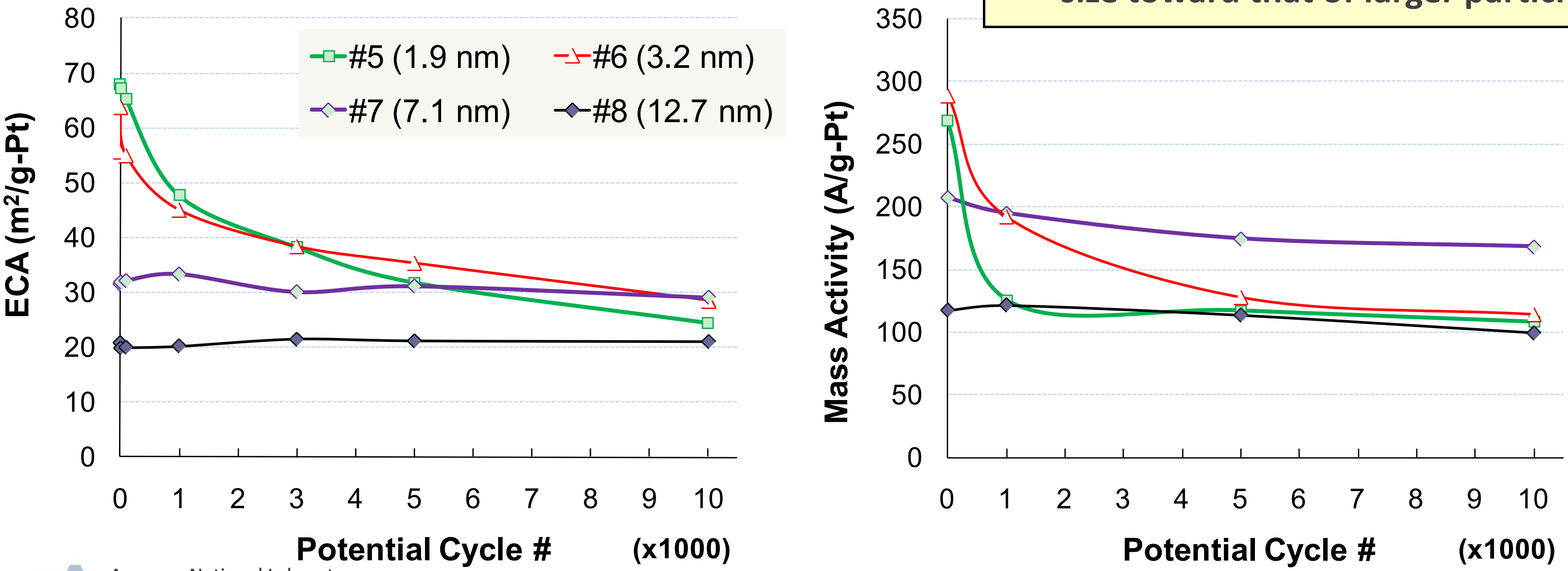
Technical Progress (Task 2.1)
Particle size studies

Cell #	Particle size	Cathode CCM code	Cathode loading (mg-Pt/cm^2)	Anode loading (mg-Pt/cm^2)
#5	1.9	09-152	0.20	0.2
#6	3.2	09-196	0.21	0.18
#7	7.1	09-203	0.21	0.2
#8	12.7	09-204	0.21	0.2

Cycling Protocol :

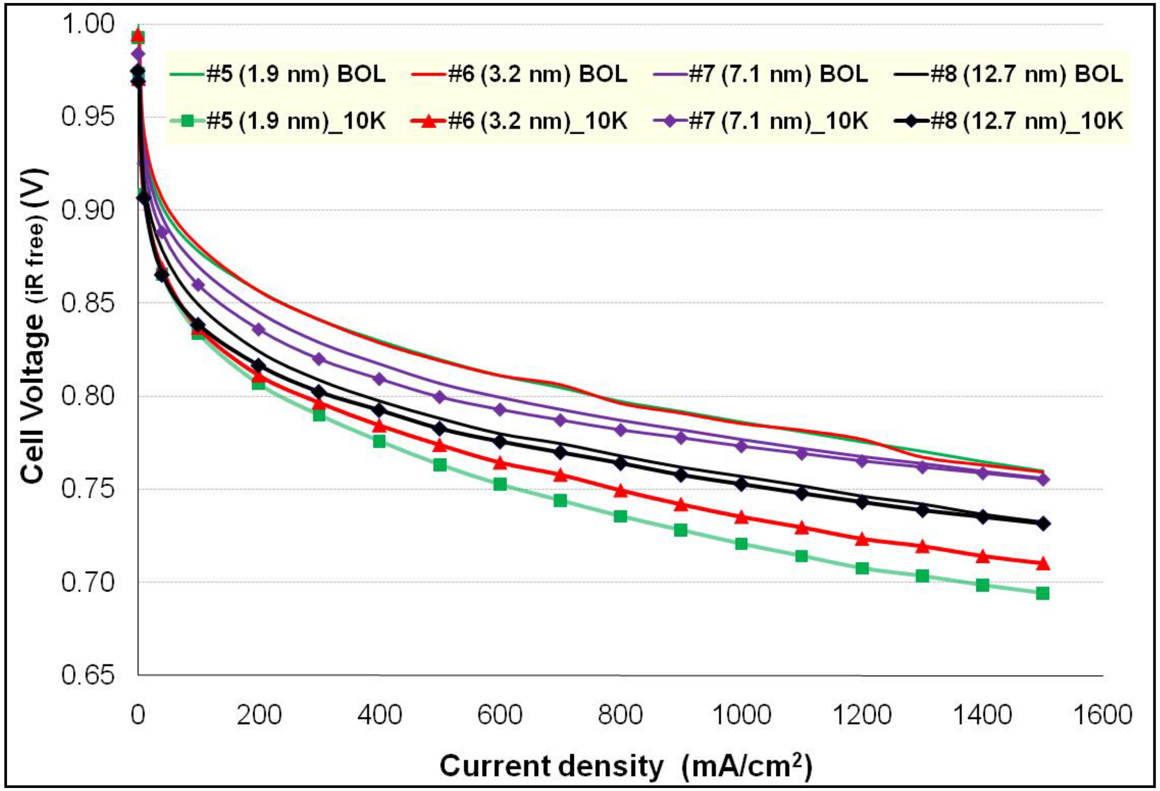
- Triangle wave potential cycle: 0.6 V to 1.0 V (50 mV/s ramp rate)
- Cell Temperature: 80 ^oC
- Fuel/Oxidant : 100% RH H_2 at 100 sccm and 100% RH N_2 at 50 sccm
- Pressure: Atmospheric

- **Cycling to 1.0 V has minimal impact on catalysts with large initial particle size (7.1 and 12.7 nm)**
- **Cycling degrades performance of catalysts with small initial particle size toward that of larger particles**



Technical Progress (Task 2.1) Particle size studies

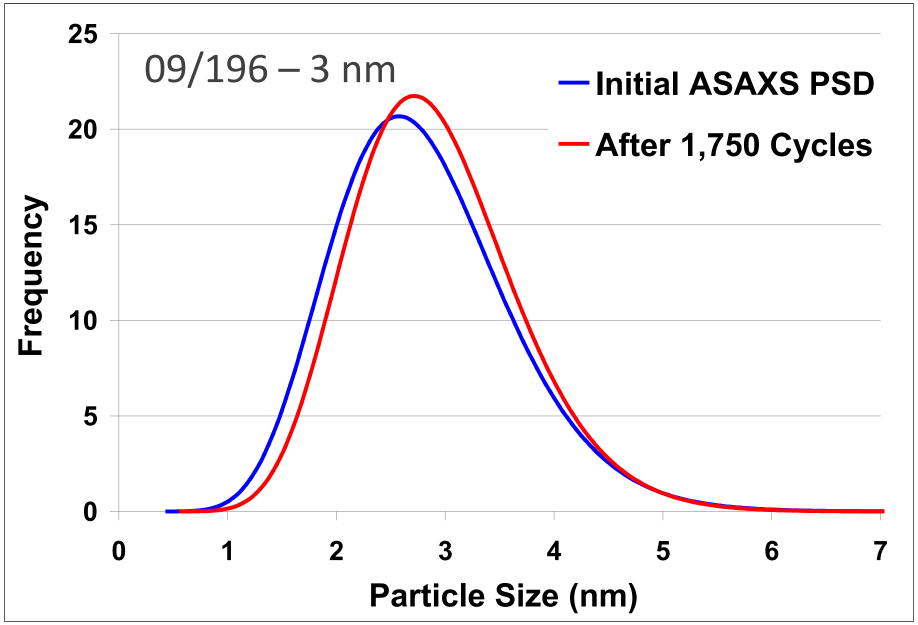
Polarization curves Initial & After 10K Potential Cycles, 80°C_100%RH_H_2/O_2 (50% utilization)

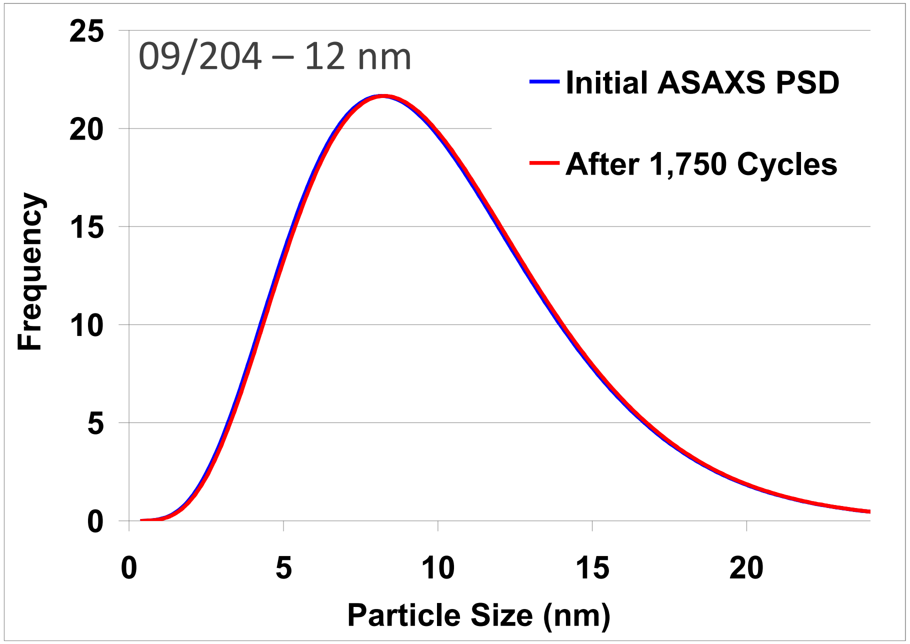


- Beginning of life performance of MEAs with smaller cathode catalyst particle size is highest, but voltage cycling degrades performance to below that of MEAs with larger initial particle size
- MEAs with large cathode catalyst particles (7.1 and 12.7 nm) show minimal O_2 performance degradation over 10,000 cycles

Technical Progress (Tasks 3 and 4)

- Anomalous Small-angle X-ray scattering (ASAXS) of JMFC Pt/C catalysts to determine mean particle size and particle size distribution
- *Ex situ* analysis of as-prepared catalyst and i*n situ* analysis of catalyst/Nafion® composite electrodes in 0.1 M $HClO_4$
  - DOE cycling protocol: 0.6 to 1.0 V, 50 mV/s triangle wave



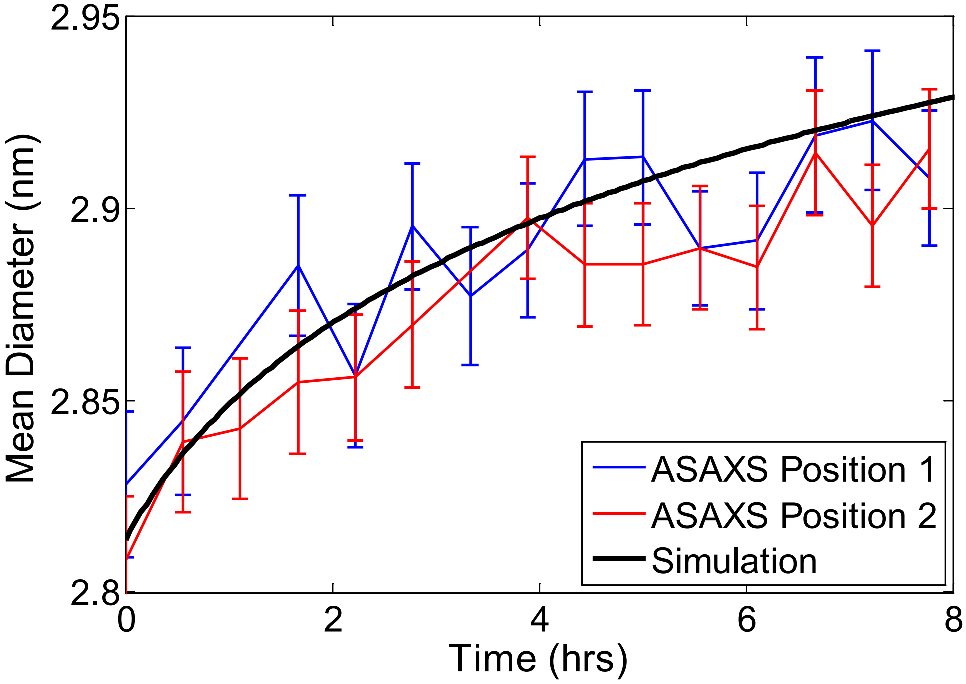


- Particles of ~ 3 nm show growth and narrowing of distribution over 1,750 cycles
- Particles of ~12 nm show no growth or change in distribution over 1,750 cycles

Technical Progress (Tasks 3, 4, and 5)

Pt Cathode Particle Coarsening: ASAXS Experiments and Simulation

1,750 total cycles between 0.6 and 1.0 V, 50 mV/s, 0.1 M $HClO_4$, room temperature

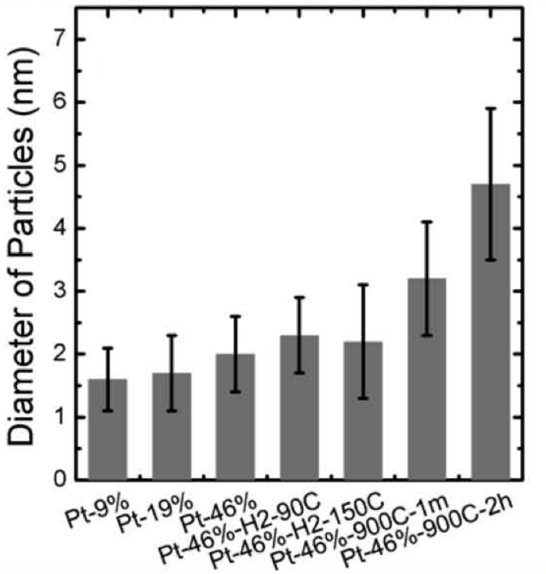


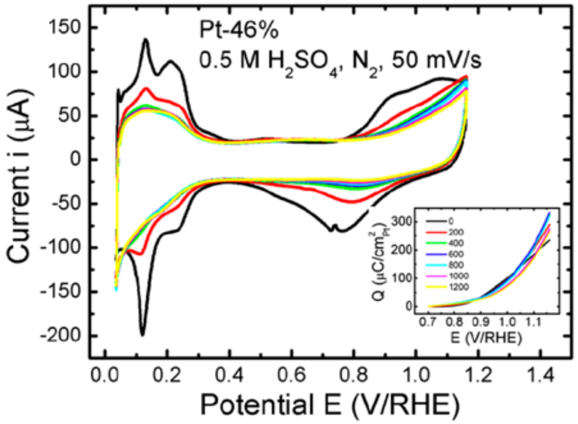
Reference: E. F. Holby et al., Energy Environ. Sci., 2009.

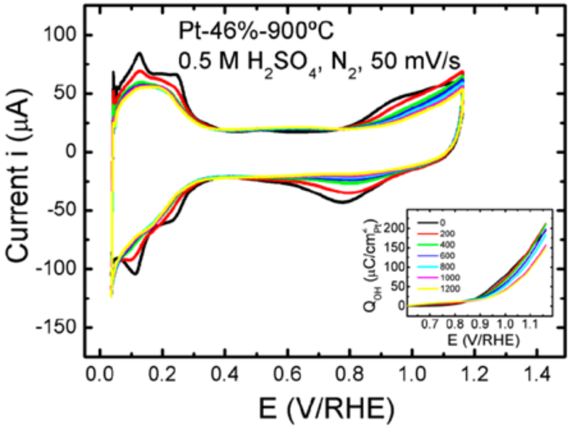
- **Results**
  - **ASAXS shows that mean particle diameter of ~3 nm catalyst grows by ~0.1 nm over 1,750 cycles**
  - **Majority of particle growth occurs during first 900 cycles**
  - **Reproduced mean diameter evolution with simulation**
- **Impact**
  - **Identifies loss mechanisms (dissolution vs. coarsening)**
  - **Determines thermodynamic parameters that govern coarsening**
- **Future Goals**
  - **Identify further properties and mechanisms that control coarsening**
  - **Develop models to predict long-term degradation**

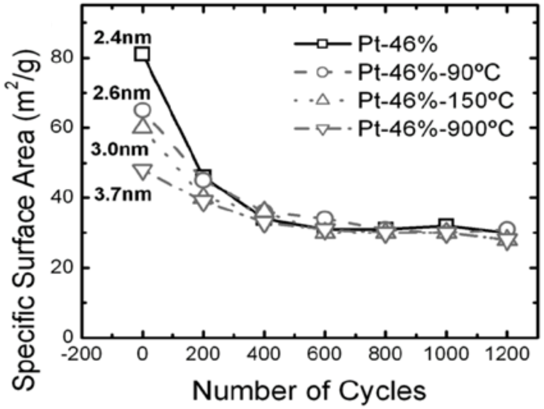
Technical Progress (Task 3)

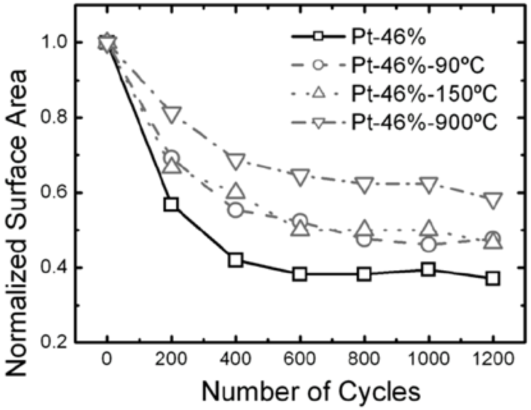
Pt Nanoparticles of Different Sizes

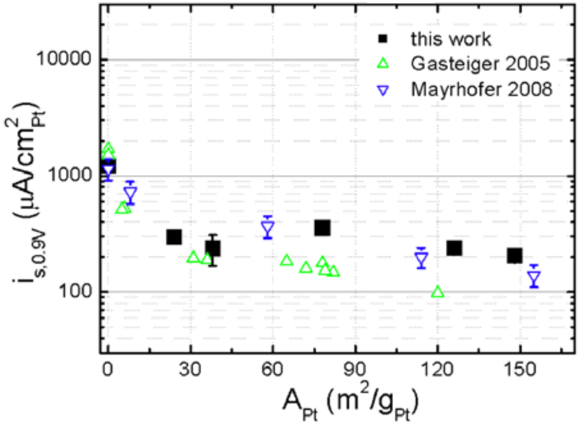










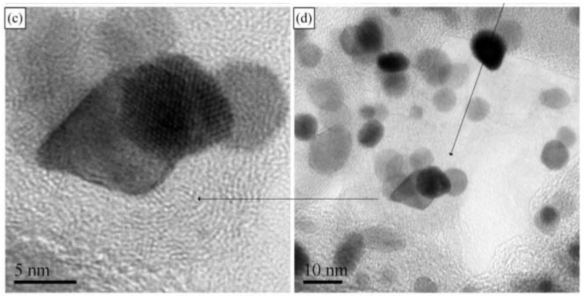


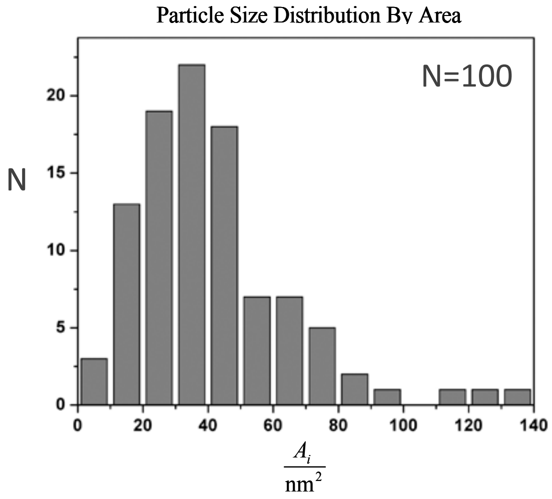
- **Cycling causes Pt catalysts to evolve to identical specific surface areas, independent of initial particle size**
- **Data shown on this slide are for TKK catalysts**
- **Measurements on JMFC catalysts are in progress**

W.C. Sheng et al., JPCC to be submitted 2010

Technical Progress (Task 4)
Preliminary/initial exploration of Pt-Sc

UT Austin



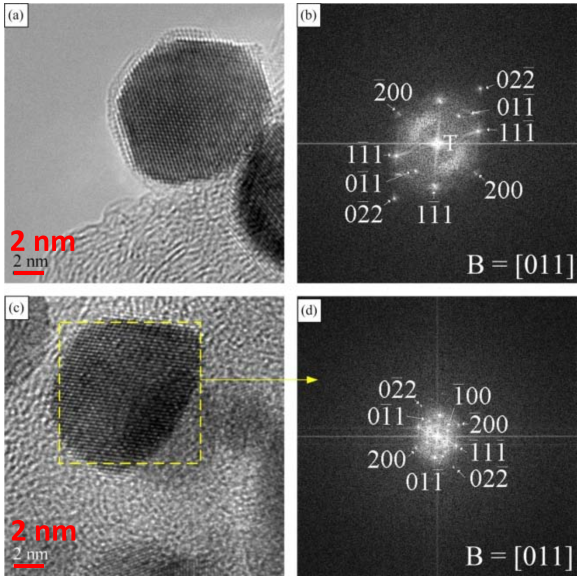


Average Area

$$< A >= \frac{1}{N}\sum_{i=1}^{N} A_i = 41.2nm^2$$

Average diameter

$$< \overline{d} >= \sqrt{\frac{4}{\pi} < A >} = 7.2nm$$



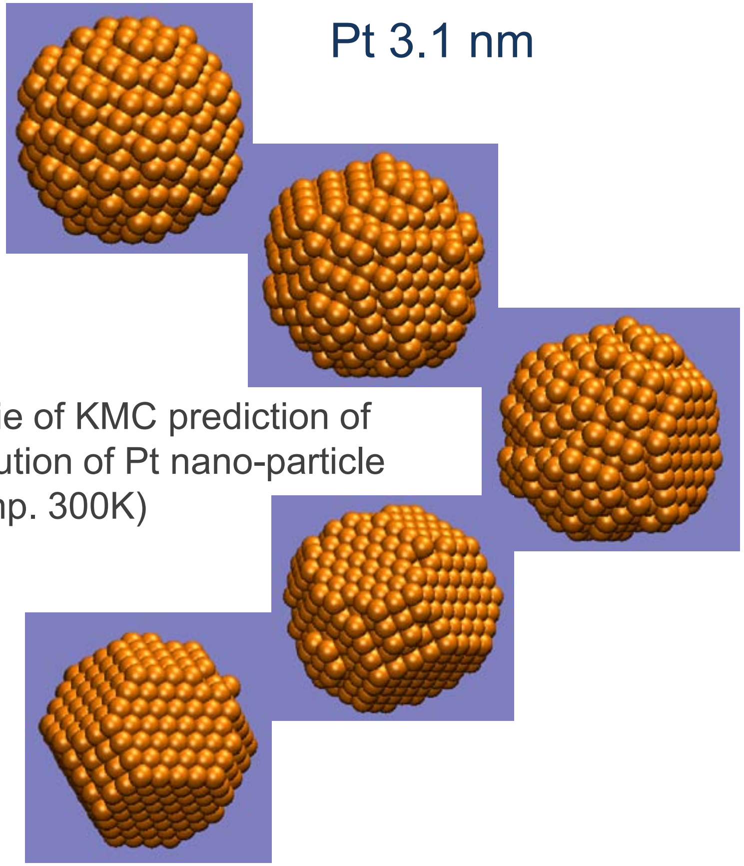
FFTs show that the nano-particles exhibit a $L1_2$ ordered structure with space group $Pm\bar{3}m$

- **We are exploring Pt_3Sc and Pt_3Y as potential candidates for project tasks on "advanced catalysts" based on recent claims of high ORR activity and proposed "kinetic" stability***
- **This catalyst represents the initial attempts by JMFC to make these materials**

*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 (Task 5)

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



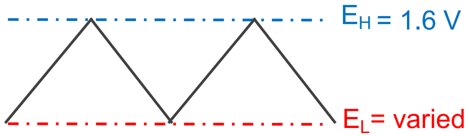
Movie of KMC prediction of evolution of Pt nano-particle (Temp. 300K)

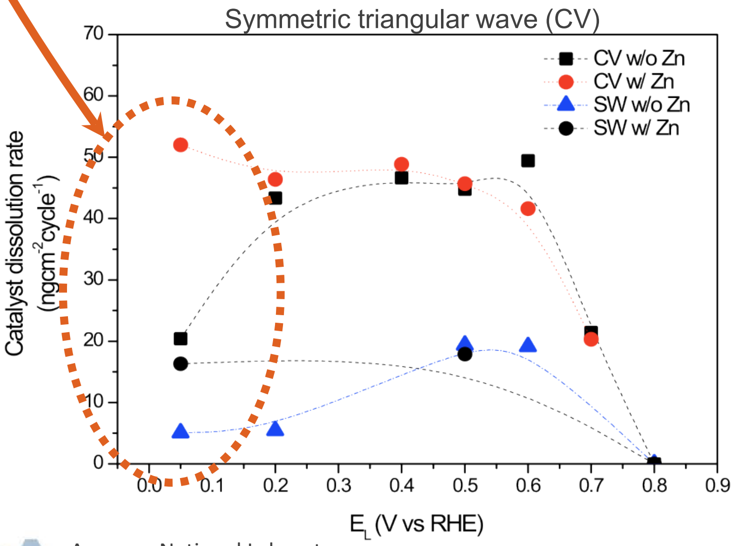
- **Results**
  - **Developed a KMC code which can predict Pt nano-particle evolution under fuel cell conditions**
- **Impact**
  - **KMC tool will identify causes of stability/instability in nano-particle alloys**
- **Future Goals**
  - **Extend KMC code to predict *alloy* nano-particle evolution under fuel cell conditions**
  - **Use model to identify properties and mechanisms that control degradation**
  - **Integrate nano-particle evolution model into full degradation model**

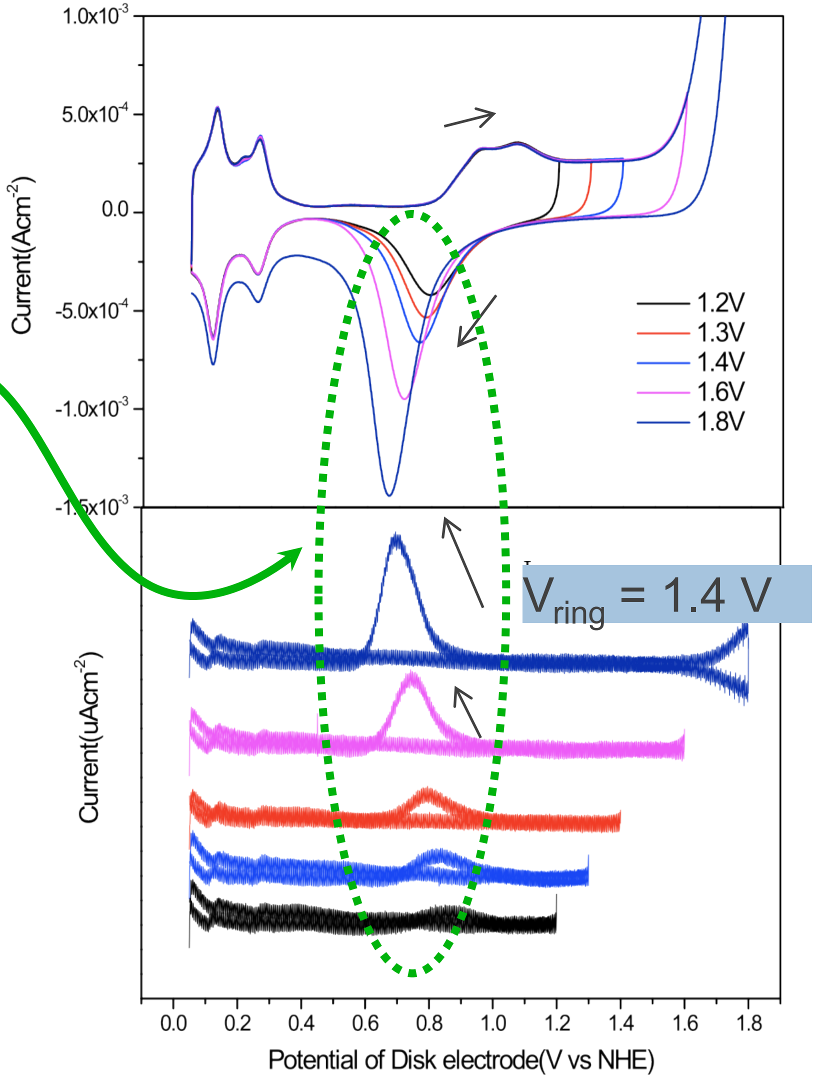
Technical Progress (Task 5)
Catalyst dissolution modeling

Developing mathematical model to explain key phenomena previously identified in our lab:

1) Hydrogen adsorption region appears to stabilize surface
2) Release of electrochemically-active species on oxide reduction peak







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

- **Establishing and participating in "Durability Working Group"**

- **Collaborators outside of DOE H_2 Program**
  - Dane Morgan (UW-Madison) is collaborating with Peter Strasser (Univ. Houston) 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 the DOE-BES Hydrogen Fuel Initiative

Proposed Future Work for FY10-11

- Task 1 (JMFC)
  - Supply MEAs and powders to project partners using prepared Pt_3Co/C alloys with 3-4nm, 5-7nm and 10-12nm particle sizes,
  - Prepare PtCo/C and $PtCo_3/C$ materials,
  - Explore preparation of Pt_3Y/C catalyst.
- Task 2 (UTRC)
  - Post-test electron probe microanalysis of Pt/C cathodes from parametric and particle size studies,
  - Further Pt/C parametric or particle size studies to verify trends,
  - Parametric and particle size studies of Pt_3Co/C in 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)
  - ASAXS and TEM characterization of pre- and post-test Pt/C MEAs
  - Completion of SAXS data analysis from aqueous cell tests
  - *In situ* ASAXS/X-ray absorption characterization of Pt/C MEAs
- Task 5 (UW and UT-Austin)
  - Modeling of aqueous cell and MEA mean particle size and particle size distribution evolution with cycling
  - Further development of Kinetic Monte Carlo (KMC) model of Pt alloy nano-particles under fuel cell conditions,
  - Construction of a realistic Hamiltonian for the KMC that can describe the physics of alloy systems and parameterization for Pt-Co,
  - Use KMC simulation to predict how de-alloying occurs in nano-particles (de-alloying rate, the formation of pores, and the stability of core-shell and acid-leached structures),
  - Complete cyclic voltammetry 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 (e.g., particle size and oxophilicity).

Accomplishments:

- Quantified Pt/C catalyst performance loss in a fuel cell as a function of initial Pt particle size and various cell parameters (RH, temp., upper potential limit, cycling protocol)
- Developed a Kinetic Monte Carlo code which can predict Pt nano-particle evolution under fuel cell conditions
- Acquired *in situ* aqueous cell ASAXS data during potential cycling as a function of initial Pt particle size (four initial particle sizes)

Collaboration:

- Project team of JMFC, UTRC, MIT, UT-Austin, and UW-Madison
- Establishing/participating in “Durability Working Group”

Future Work:

- Characterize Pt dissolution as a function of particle size for Pt and Pt_3Co
- Quantify Pt_3Co catalyst performance loss in a fuel cell as a function of initial particle size and cell parameters
- Extend Kinetic Monte Carlo code development to alloy nano-particles
- Develop model for Pt nano-particle voltammetry, including states of oxide as a function of potential to predict Pt dissolution rates