

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

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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



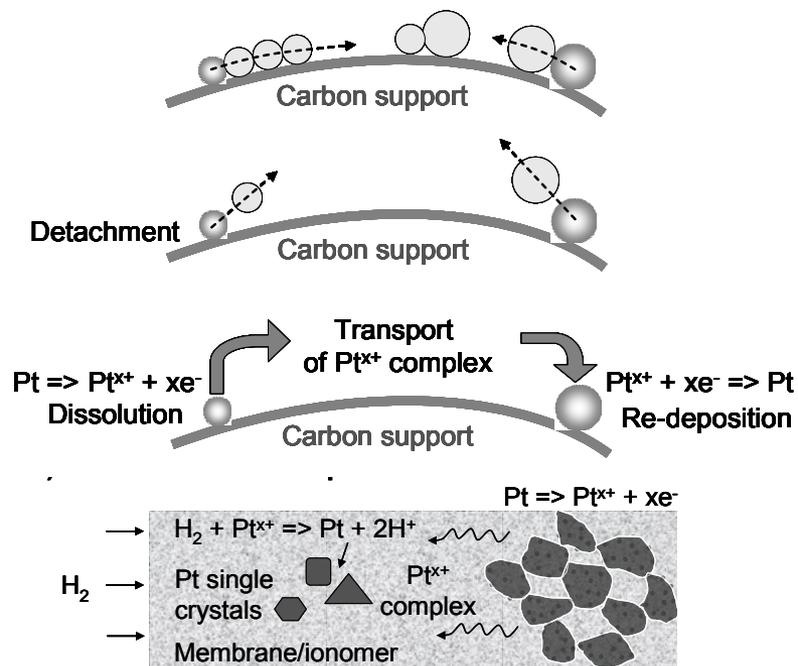
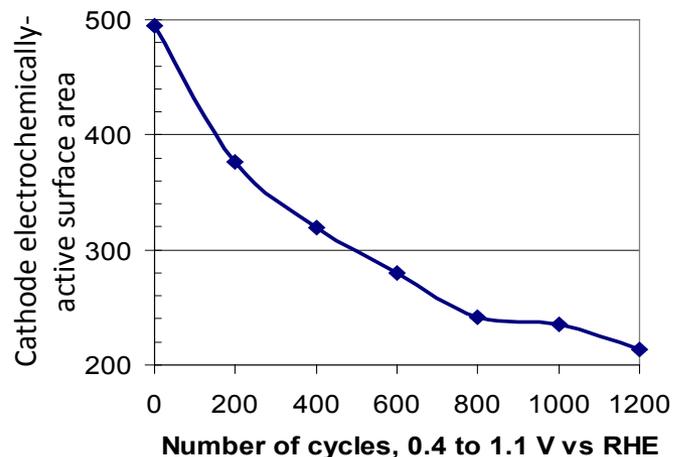
# Relevance

## 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 ( $\leq 80^\circ\text{C}$ ) and 2,000 hours ( $> 80^\circ\text{C}$ )
  - $\leq 40\%$  loss of initial catalytic mass activity;
  - $< 30$  mV loss at  $0.8 \text{ A/cm}^2$



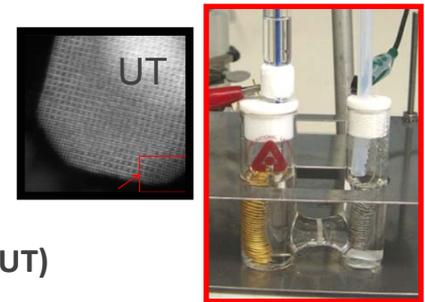
Y. Shao-Horn et al., *Topics in Catalysis*, **46** (2007) 285–305.

# 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)

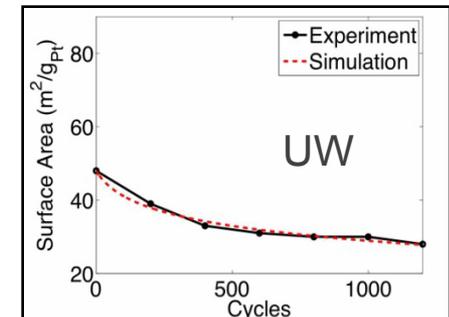
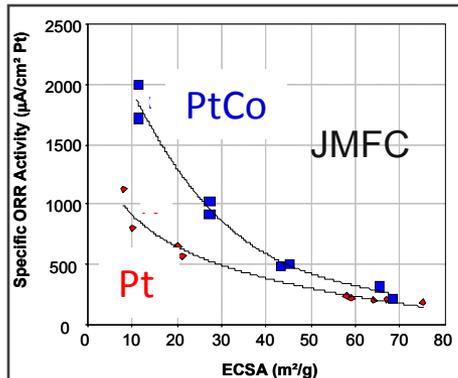


ANL



## 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
<b>Task 1. Catalyst and Membrane-Electrode Assembly Fabrication</b>												
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												
<b>Task 2. Cell degradation studies/single cell cycling/parametric aging studies</b>												
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												
<b>Task 3. Mechanisms of catalyst degradation and underlying physicochemical catalyst properties responsible for degradation</b>												
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												
<b>Task 4. Ex situ microscopic and X-ray scattering characterization of catalysts and MEAs</b>												
4.1 Optical microscopy, aberration-corrected STEM and high-resolution TEM w/ EDAX, EELS, XPS												
4.2 Small angle X-ray scattering												
<b>Task 5. Modeling</b>												
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

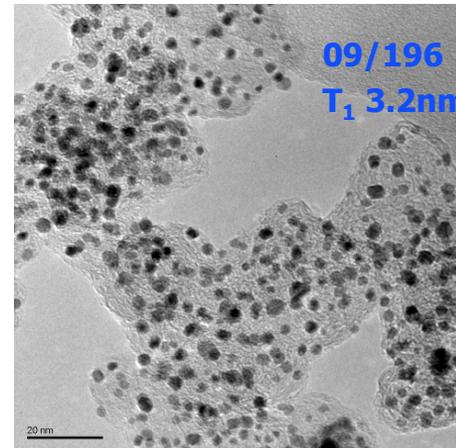
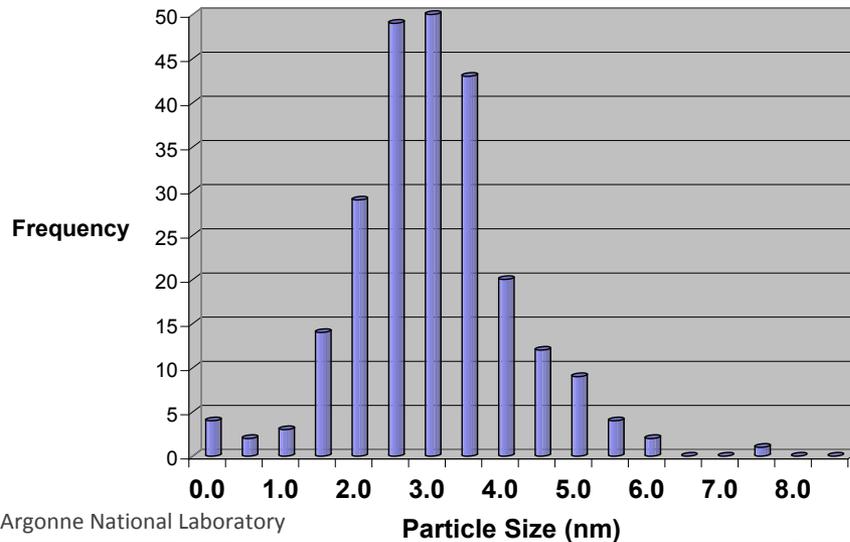
## Milestones and Go/No-Go Decision Point

- 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<sub>4</sub> 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/cm<sup>2</sup> 09/152 in anode and 0.2 mg Pt/cm<sup>2</sup> of 09/152-204 in cathode,
- Multiple MEAs with 09/196 catalyst in cathode supplied to UTRC for parametric studies.

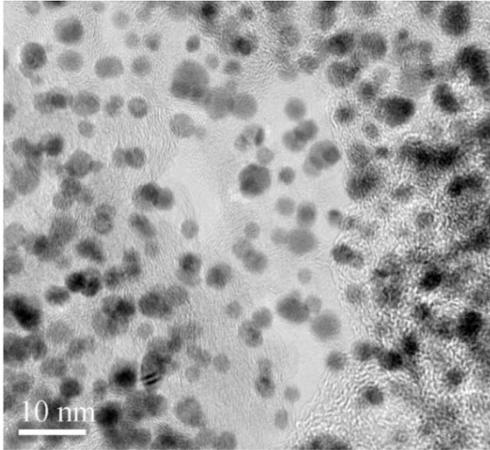
Code	Annealing conditions	Pt (%)	CO area (m <sup>2</sup> g <sup>-1</sup> -Pt)	TEM Mean particle size (nm)	
09/152	As-prepared	35.6	96	1.9	
09/196	T <sub>1</sub>	40.7	63	3.2	Benchmark
09/203	T <sub>2</sub>	40.2	26	7.1	
09/204	T <sub>3</sub>	40.9	11	12.7	



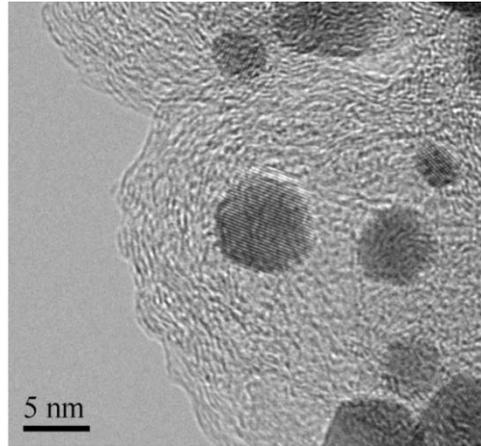
# Technical Progress (Task 4)

## TEM characterization: Pt nanoparticles

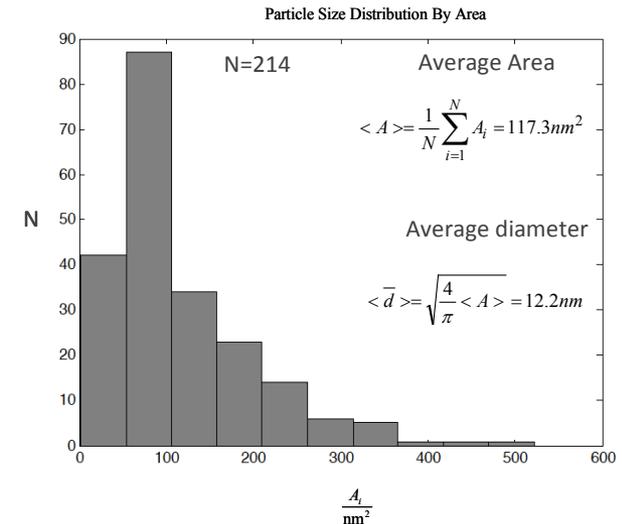
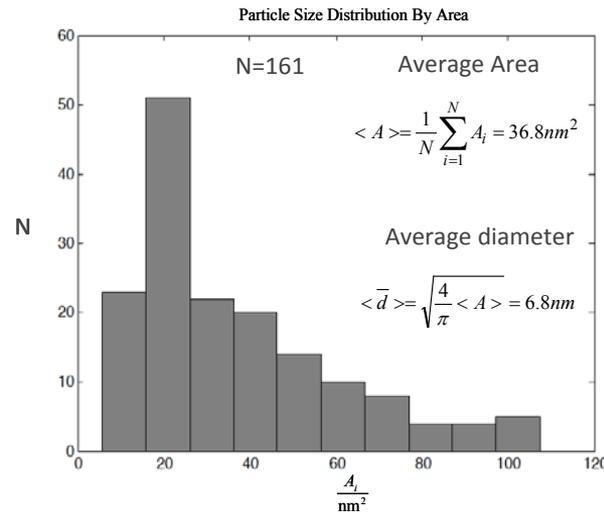
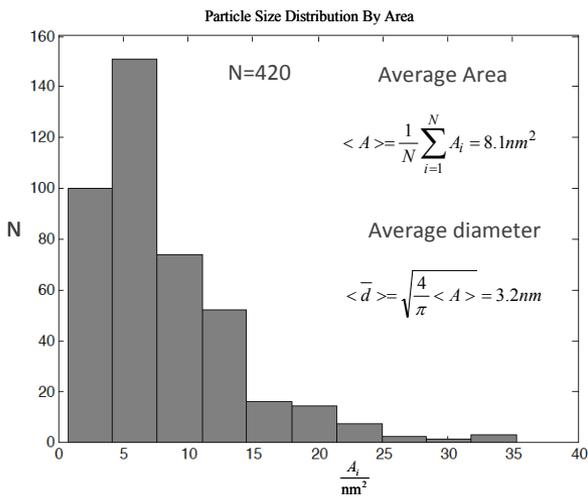
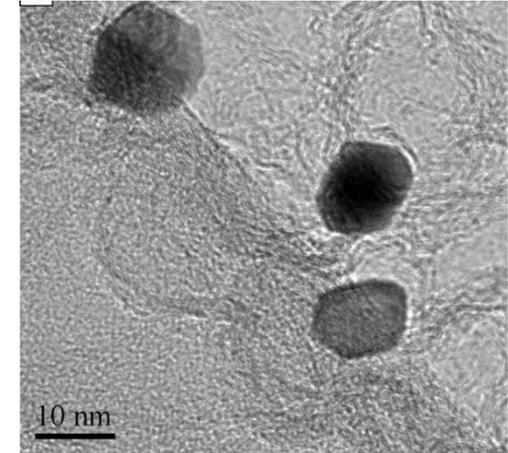
09/196



09/203



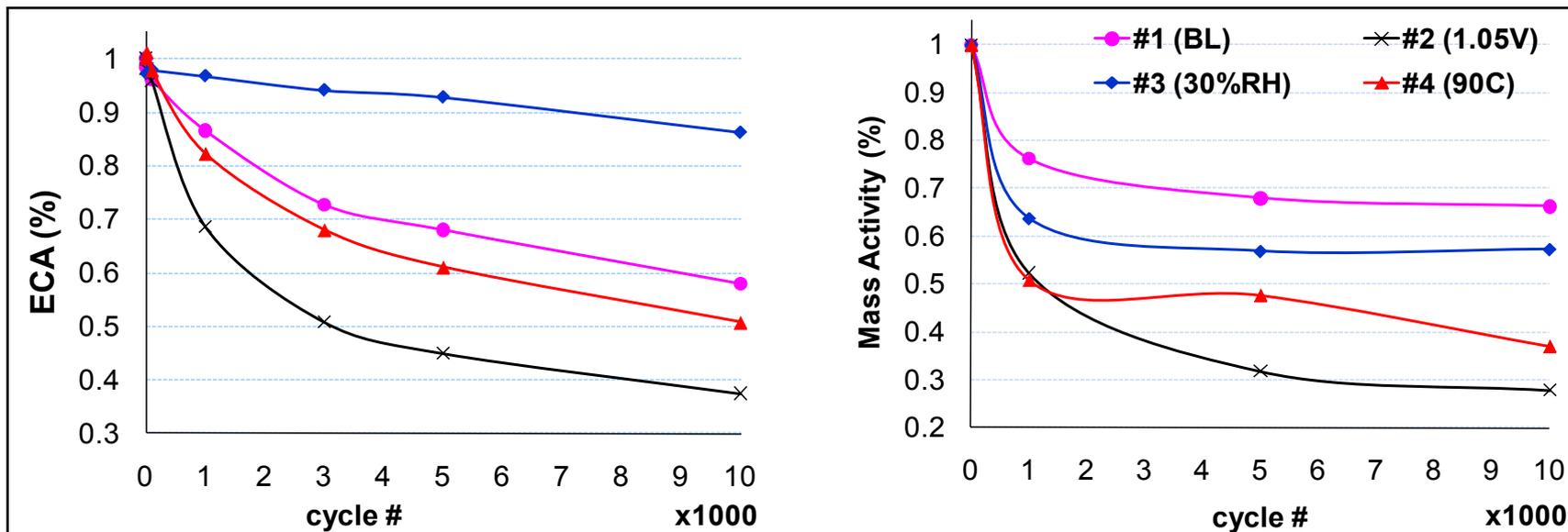
09/204



# Technical Progress (Task 2.1)

## Parametric studies of benchmark Pt catalyst

Cell #	Potential cycle
#1 (BL)	<ul style="list-style-type: none"><li>• Square wave potential cycle: 10s at 0.4V, 10s at 0.95V (20s / cycle)</li><li>• Cell Temperature: 80°C</li><li>• Relative Humidity: Anode / Cathode = 100% / 100%</li><li>• Fuel/Oxidant : 4%N<sub>2</sub> at 500 sccm and N<sub>2</sub> at 500 sccm</li><li>• Pressure: Atmospheric pressure</li></ul>
#2 (1.05V)	<ul style="list-style-type: none"><li>• Square wave potential cycle: 10s at 0.4V, 10s at 1.05V (20s / cycle)</li><li>• All other parameters were same as cell #1</li></ul>
#3 (30%RH)	<ul style="list-style-type: none"><li>• Relative Humidity: Anode / Cathode = 30%RH / 30%RH</li><li>• All other parameters were same as cell #1</li></ul>
#4 (90C)	<ul style="list-style-type: none"><li>• Cell Temperature: 90°C</li><li>• All other parameters were same as cell #1</li></ul>



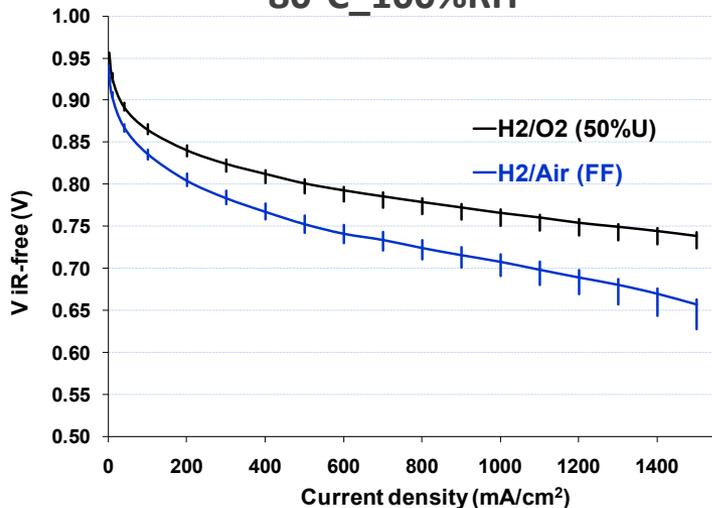
- Increasing upper limit of voltage cycling increases cathode catalyst surface area and mass activity loss
- Low inlet RH decreases cathode catalyst degradation
- Increased cell temperature increases cathode catalyst degradation

# Technical Progress (Task 2.1)

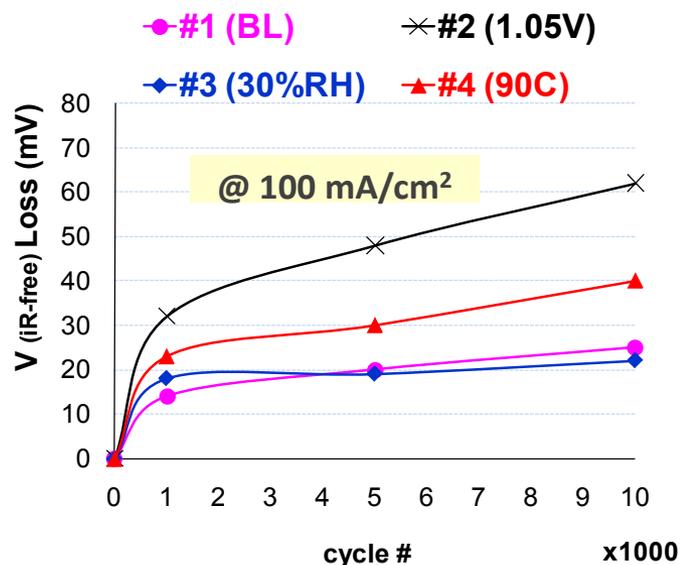
## Parametric studies of benchmark Pt catalyst

### Initial Polarization Curves

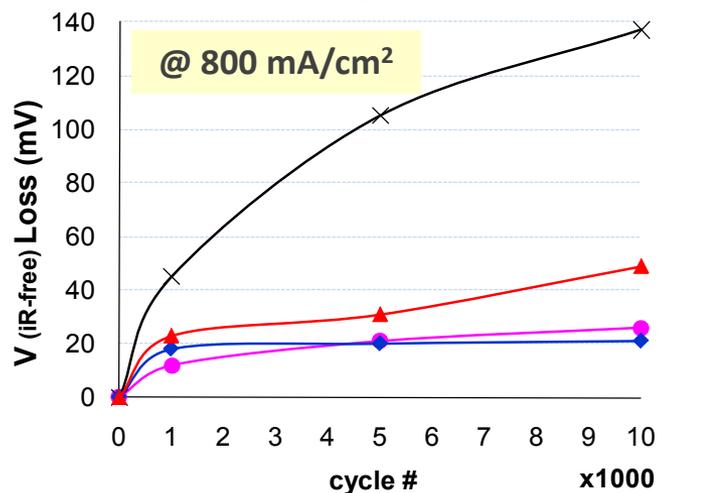
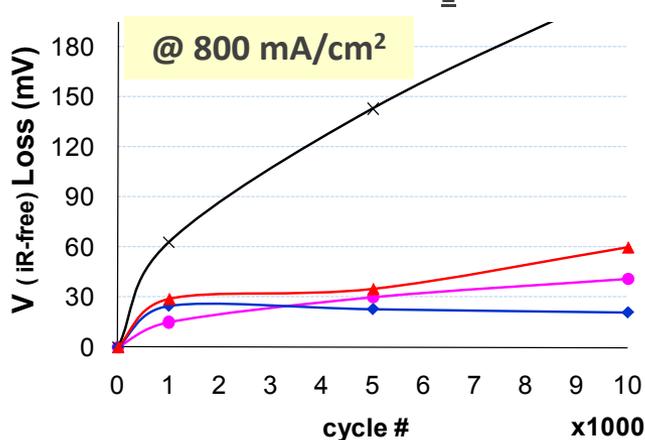
80°C\_100%RH



### Performance Loss H<sub>2</sub>/O<sub>2</sub>



### Performance Loss H<sub>2</sub>/Air



- Cycling to high potentials effects cathode transport losses

# Technical Progress (Task 2.1)

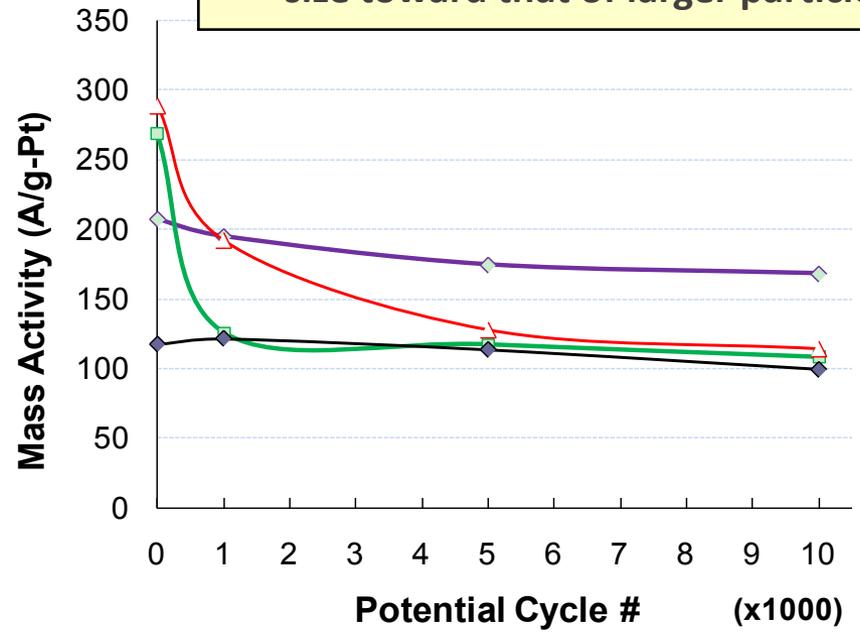
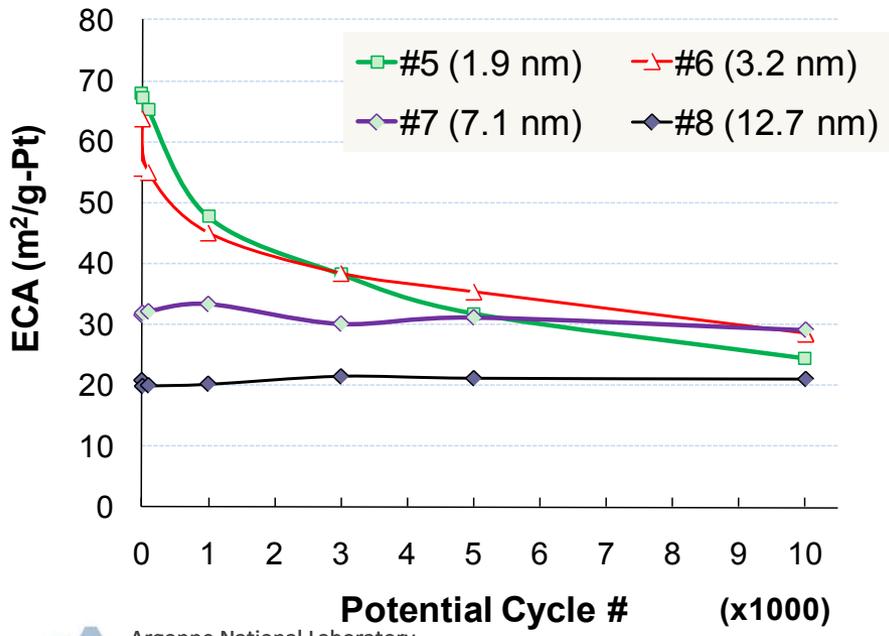
## Particle size studies

Cell #	Particle size	Cathode CCM code	Cathode loading (mg-Pt/cm <sup>2</sup> )	Anode loading (mg-Pt/cm <sup>2</sup> )
#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 °C
- Fuel/Oxidant : 100% RH H<sub>2</sub> at 100 sccm and 100% RH N<sub>2</sub> at 50 sccm
- Pressure: Atmospheric

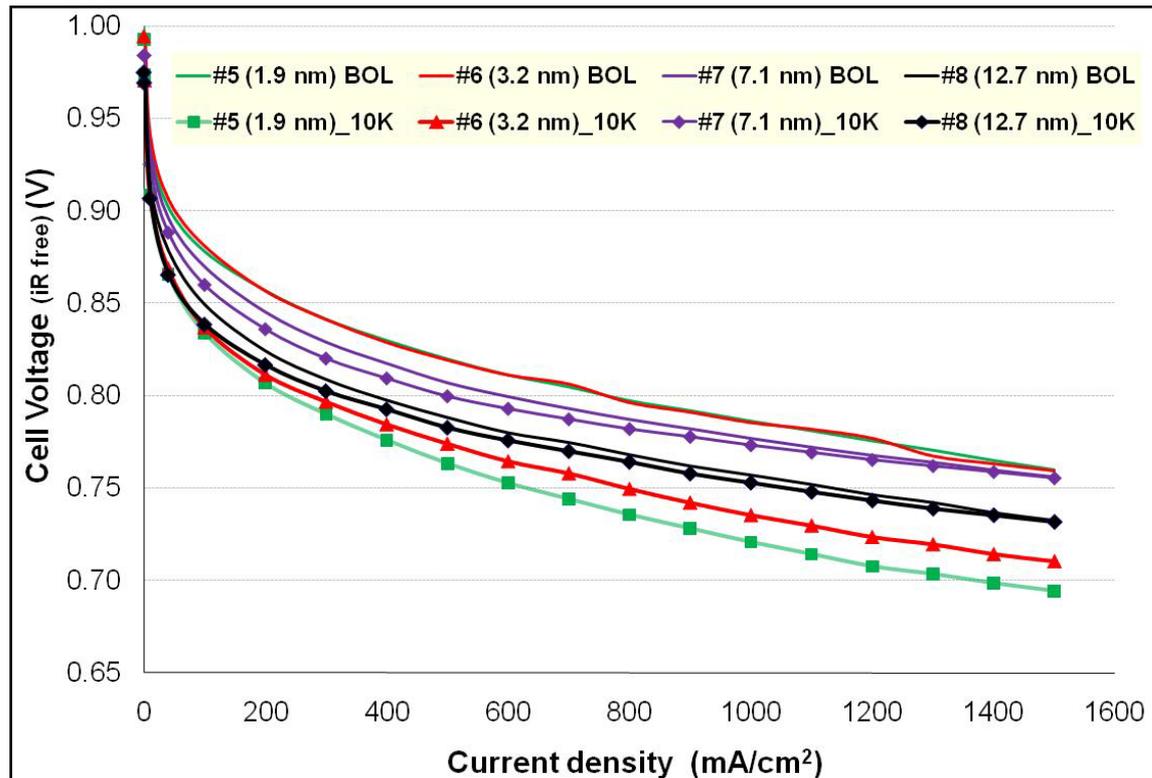
**■ Cycling to 1.0 V has minimal impact on catalysts with large initial particle size (7.1 and 12.7 nm)**  
**■ Cycling degrades performance of catalysts with small initial particle size toward that of larger particles**



# Technical Progress (Task 2.1)

## Particle size studies

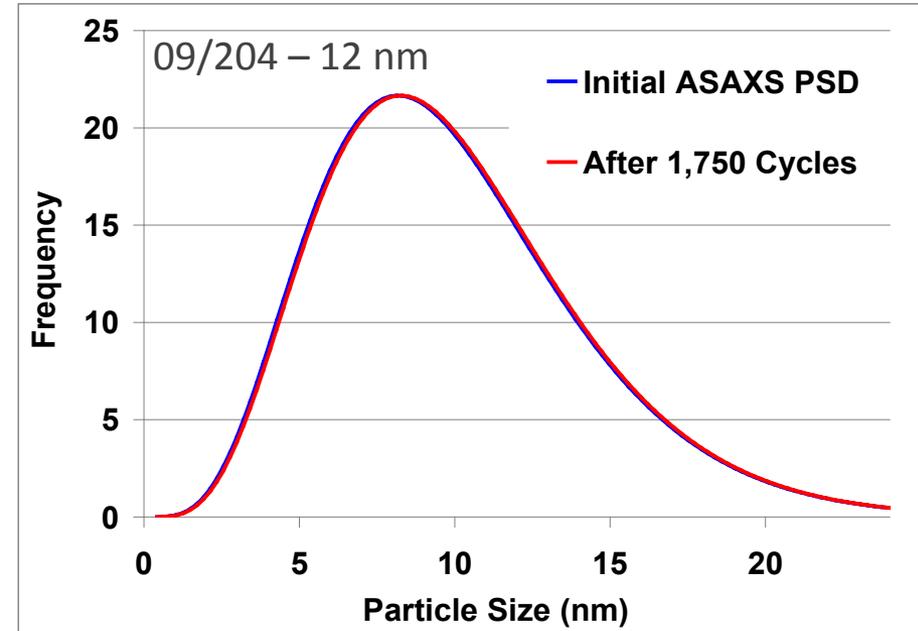
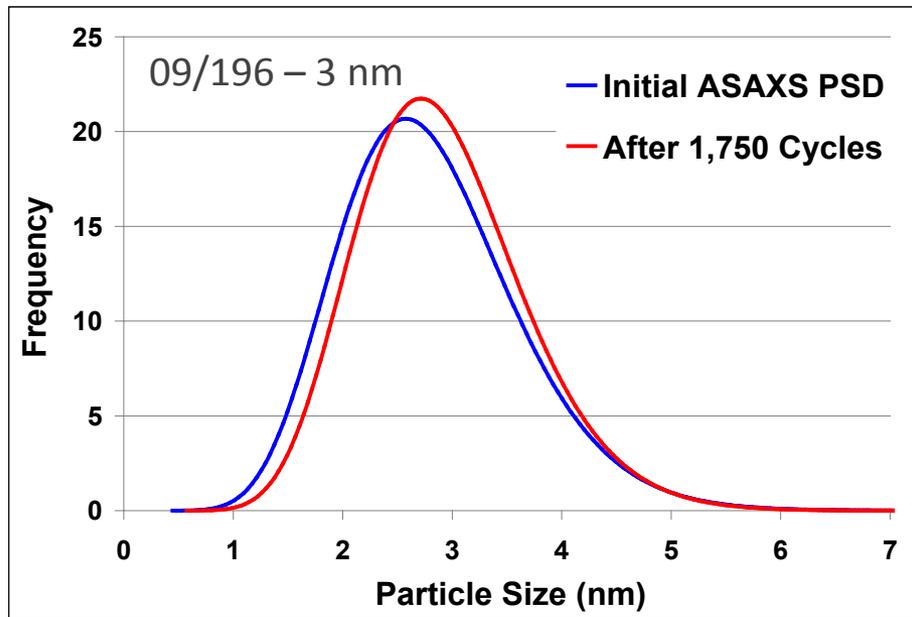
Polarization curves Initial & After 10K Potential Cycles, 80°C\_100%RH\_H<sub>2</sub>/O<sub>2</sub>  
(50% utilization)



- 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<sub>2</sub> 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 *in situ* analysis of catalyst/Nafion<sup>®</sup> composite electrodes in 0.1 M HClO<sub>4</sub>
  - DOE cycling protocol: 0.6 to 1.0 V, 50 mV/s triangle wave

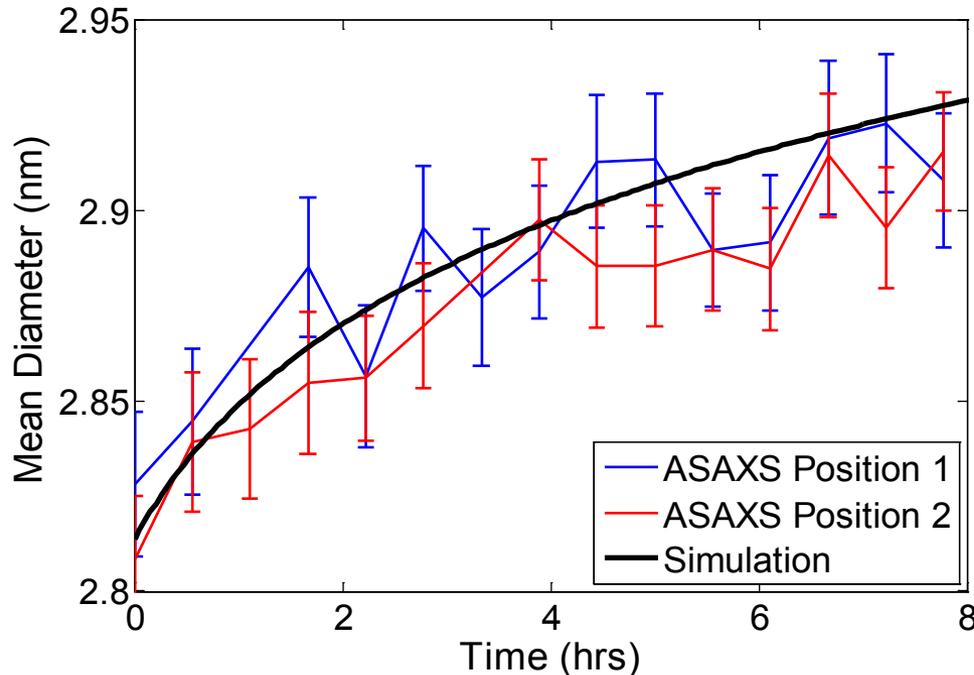


- Particles of ~ 3 nm show growth and narrowing of distribution over 1,750 cycles
- Particles of ~12 nm show no growth or change in distribution over 1,750 cycles

# 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<sub>4</sub>, 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

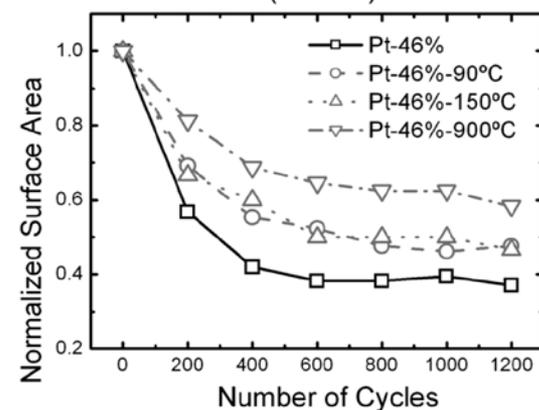
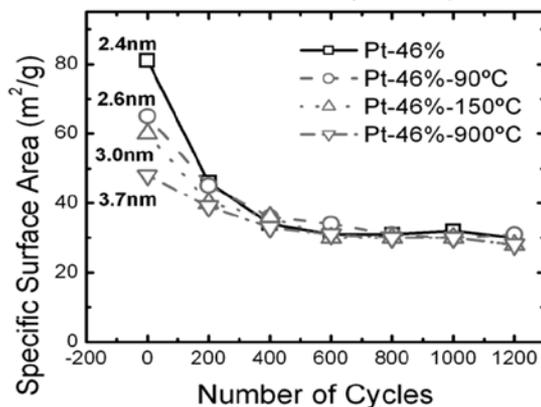
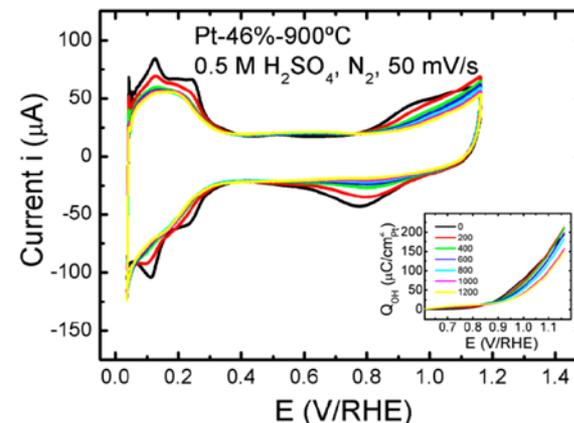
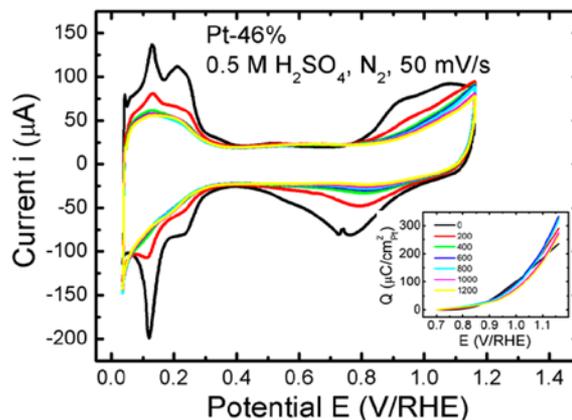
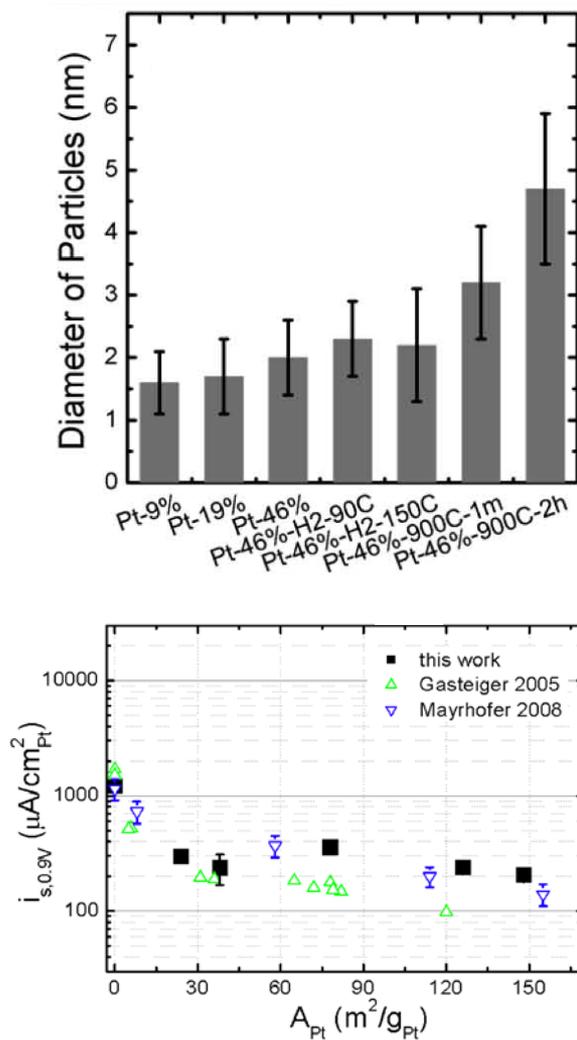
- Identifies loss mechanisms (dissolution vs. coarsening)
- Determines thermodynamic parameters that govern coarsening

### 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



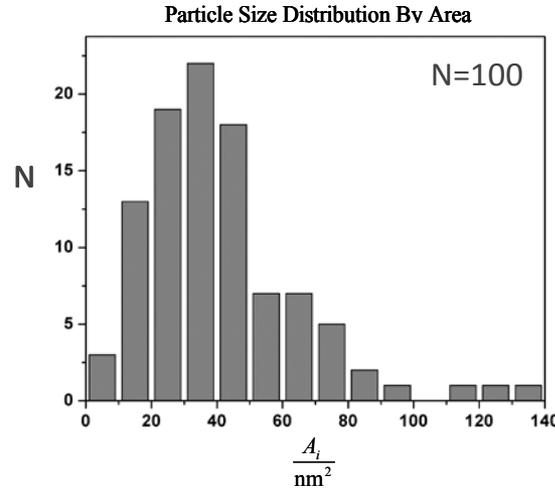
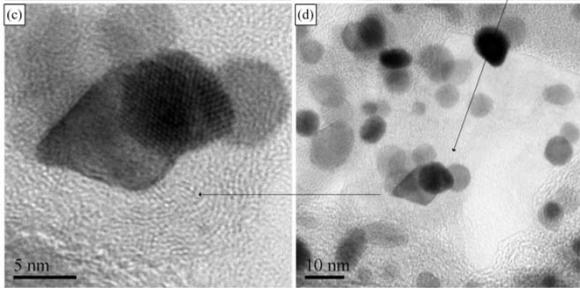
- Cycling causes Pt catalysts to evolve to identical specific surface areas, independent of initial particle size
- Data shown on this slide are for TKK catalysts
- Measurements on JMFC catalysts are in progress



UT Austin

# Technical Progress (Task 4)

## Preliminary/initial exploration of Pt-Sc

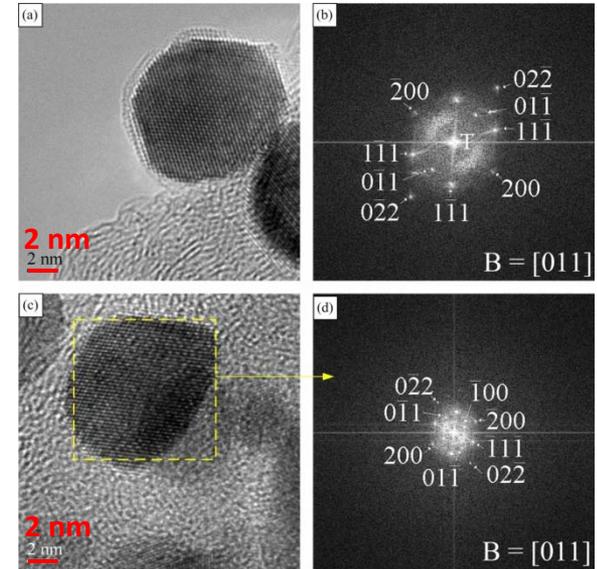


Average Area

$$\langle A \rangle = \frac{1}{N} \sum_{i=1}^N A_i = 41.2 \text{ nm}^2$$

Average diameter

$$\langle \bar{d} \rangle = \sqrt{\frac{4}{\pi} \langle A \rangle} = 7.2 \text{ nm}$$



- We are exploring  $\text{Pt}_3\text{Sc}$  and  $\text{Pt}_3\text{Y}$  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

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

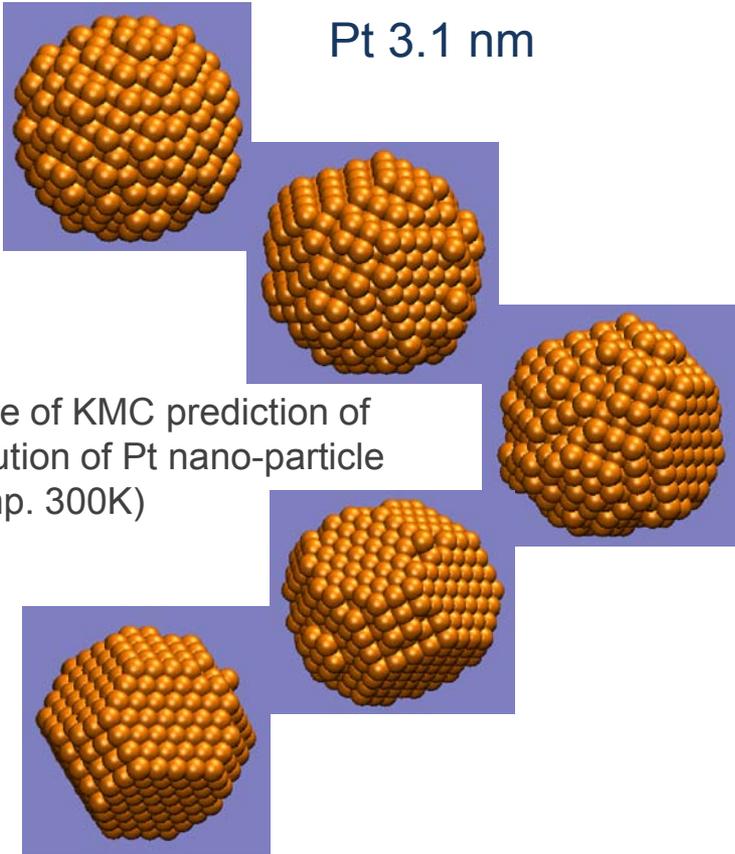
\*J. Greeley, I. E. L. Stephens, A. S. Bondarenko, T. P. Johansson, H. A. Hansen, T. F. Jaramillo, J. Rossmeisl, I. Chorkendorff and J. K. Nørskov, Nature Chemistry 1, 552 - 556 (2009).



# Technical Progress (Task 5)

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

Pt 3.1 nm



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

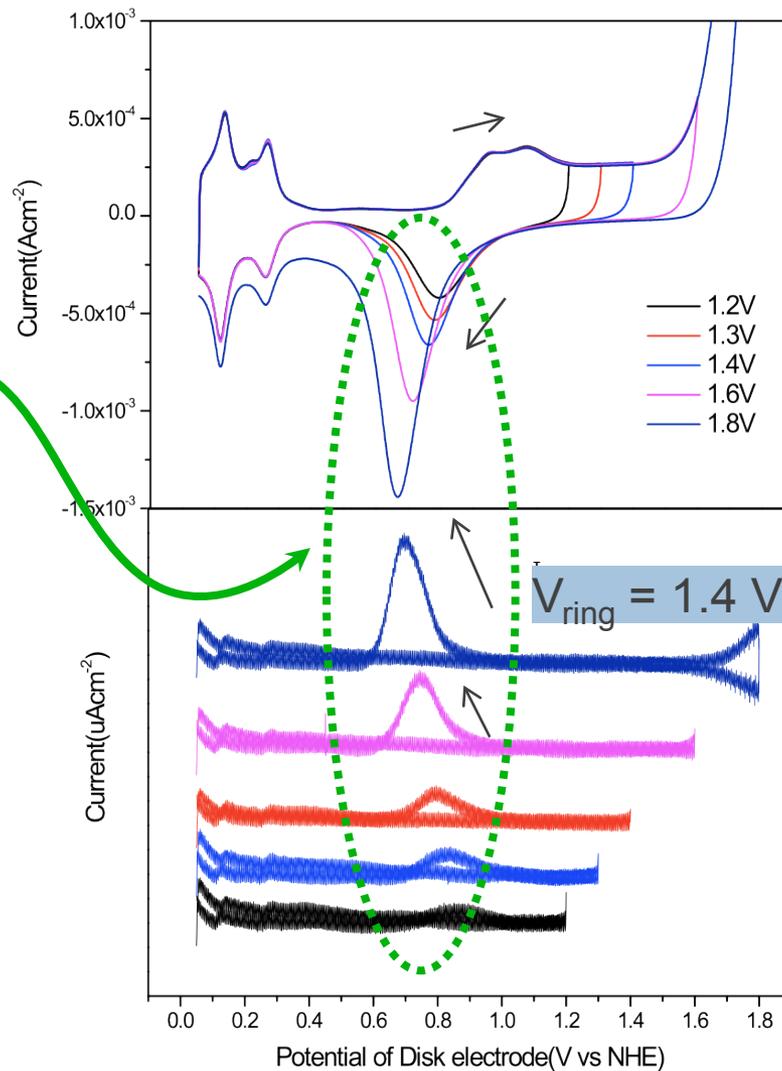
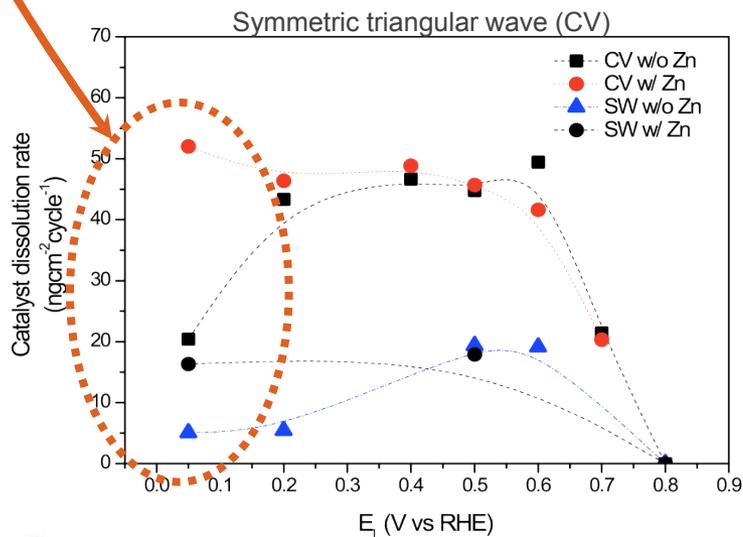
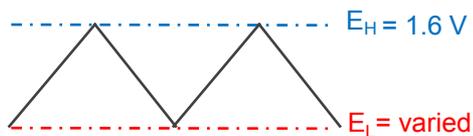
- **Results**
  - Developed a KMC code which can predict Pt nano-particle evolution under fuel cell conditions
- **Impact**
  - KMC tool will identify causes of stability/instability in nano-particle alloys
- **Future Goals**
  - Extend KMC code to predict *alloy* nano-particle evolution under fuel cell 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<sub>2</sub> 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<sub>2</sub> 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<sub>3</sub>Co/C alloys with 3-4nm, 5-7nm and 10-12nm particle sizes,
  - Prepare PtCo/C and PtCo<sub>3</sub>/C materials,
  - Explore preparation of Pt<sub>3</sub>Y/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<sub>3</sub>Co/C in MEAs.
- Task 3 (ANL and MIT)
  - Pt dissolution rates for Pt/C and Pt<sub>3</sub>Co/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<sub>3</sub>Co/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<sub>3</sub>Co
- Quantify Pt<sub>3</sub>Co 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

