

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

Xiaoping Wang, Debbie Myers, Nancy Kariuki,  
Ramachandran Subbaraman, Rajesh Ahluwalia, and Xiaohua Wang  
Argonne National Laboratory

IEA Annex 22 Spring Workshop  
Graz University of Technology  
Graz, Austria

July 4-5, 2011

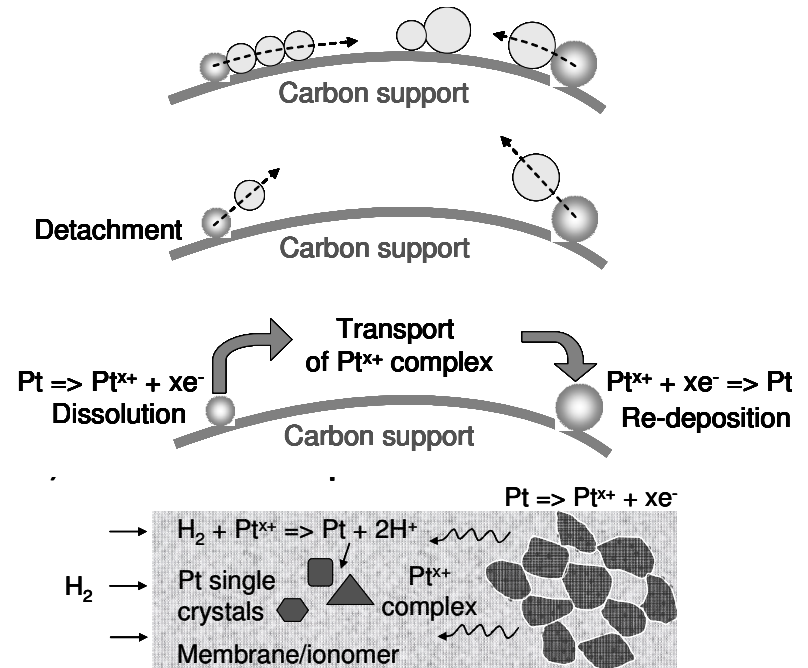
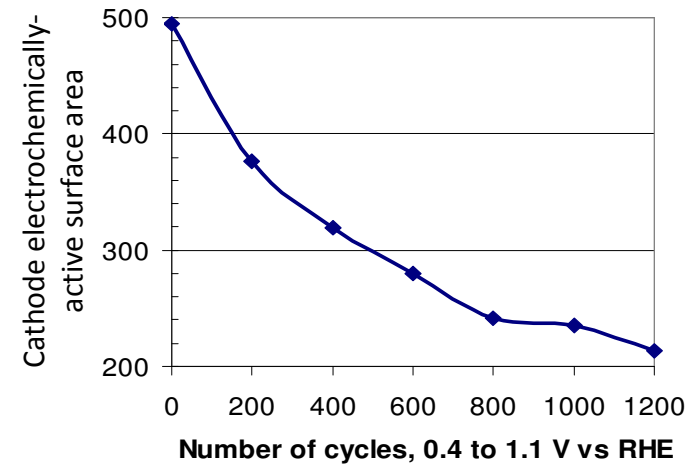
The submitted manuscript has been created by UChicago Argonne, LLC, Operator of Argonne National Laboratory (“Argonne”). Argonne, a U.S. Department of Energy Office of Science laboratory, is operated under Contract No. DE-AC02-06CH11357. The U.S. Government retains for itself, and others acting on its behalf, a paid-up nonexclusive, irrevocable worldwide license in said article to reproduce, prepare derivative works, distribute copies to the public, and perform publicly and display publicly, by or on behalf of the Government.

# Collaborators

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

# Objectives

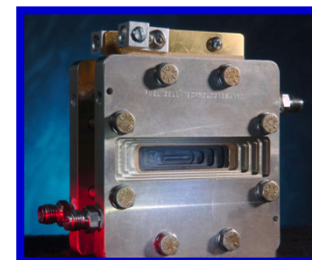
- Understand the role of cathode electrocatalyst degradation in the long-term loss of PEMFC performance
- Establish dominant catalyst and electrode degradation mechanisms
- Identify key properties of catalysts and catalyst supports that influence and determine their degradation rates
- Quantify the effect of cell operating conditions, load profiles, and type of electrocatalyst on the performance degradation
- Determine operating conditions and catalyst types/structures that will mitigate performance loss and allow PEMFC systems to achieve the DOE lifetime 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;  $< 30\text{ mV}$  loss at  $0.8\text{ A/cm}^2$



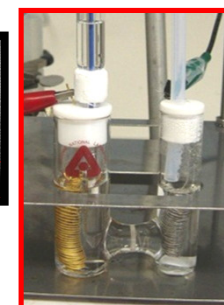
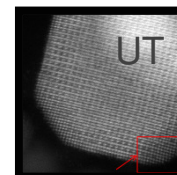
Y. Shao-Horn et al., *Topics in Catalysis*, **46** (2007) 285–305.

# Approach

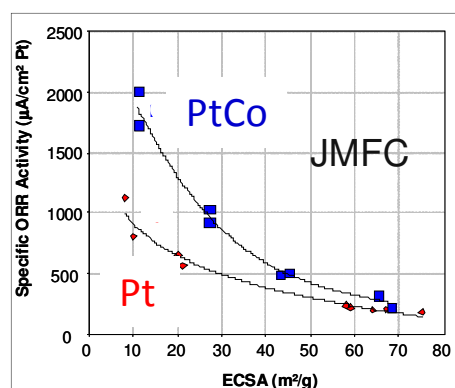
- **Methods for identifying the degradation modes and factors contributing to degradation**
  - **Systematic cell degradation tests (JMFC and UTRC)**
  - ***In situ* and *ex situ* structural characterization of the catalyst (ANL and UT)**
    - Small angle X-ray scattering, X-ray absorption spectroscopy, 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)



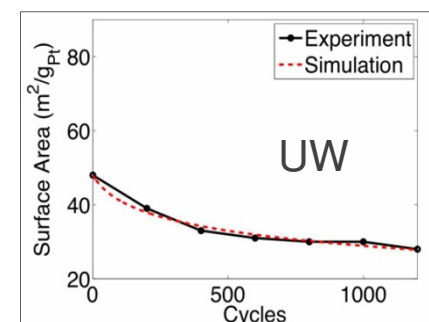
ANL



## ■ 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

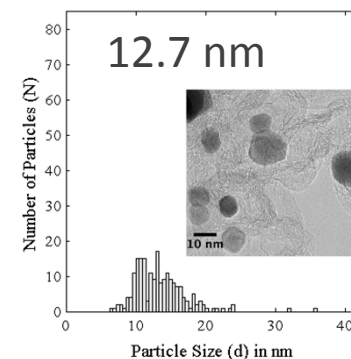
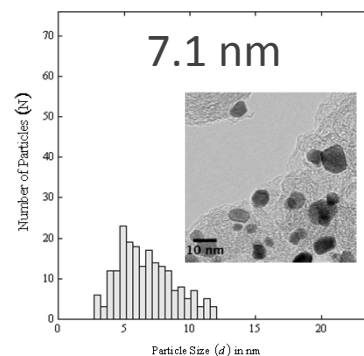
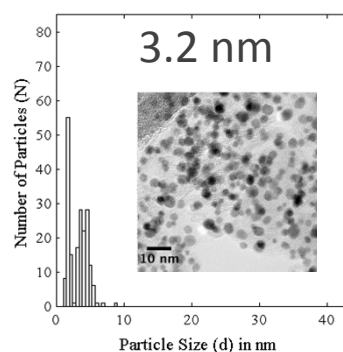
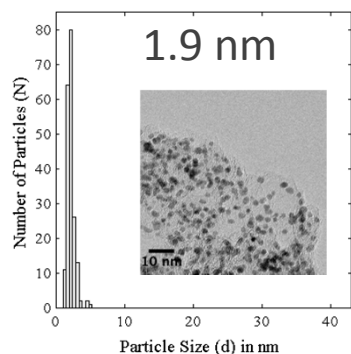


# Pt and Pt<sub>3</sub>Co nanoparticle catalysts with varied Particle Size

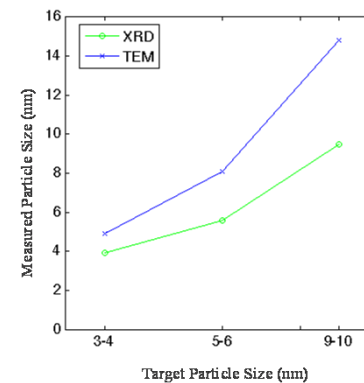
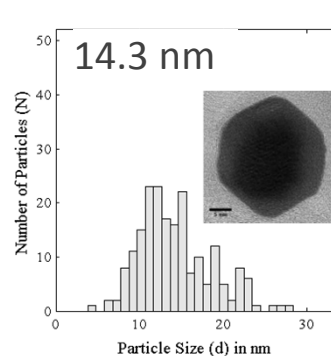
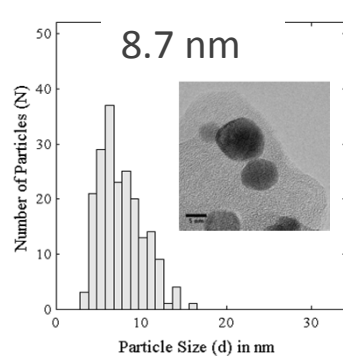
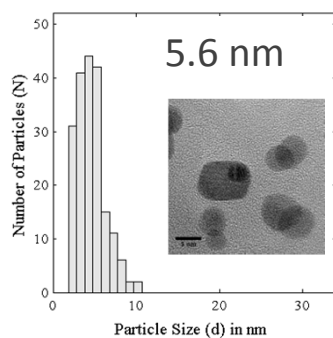


UT Austin

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



## 40 wt% Pt<sub>3</sub>Co/Ketjen: three particle sizes (5.6, 8.7, 14.3 nm)



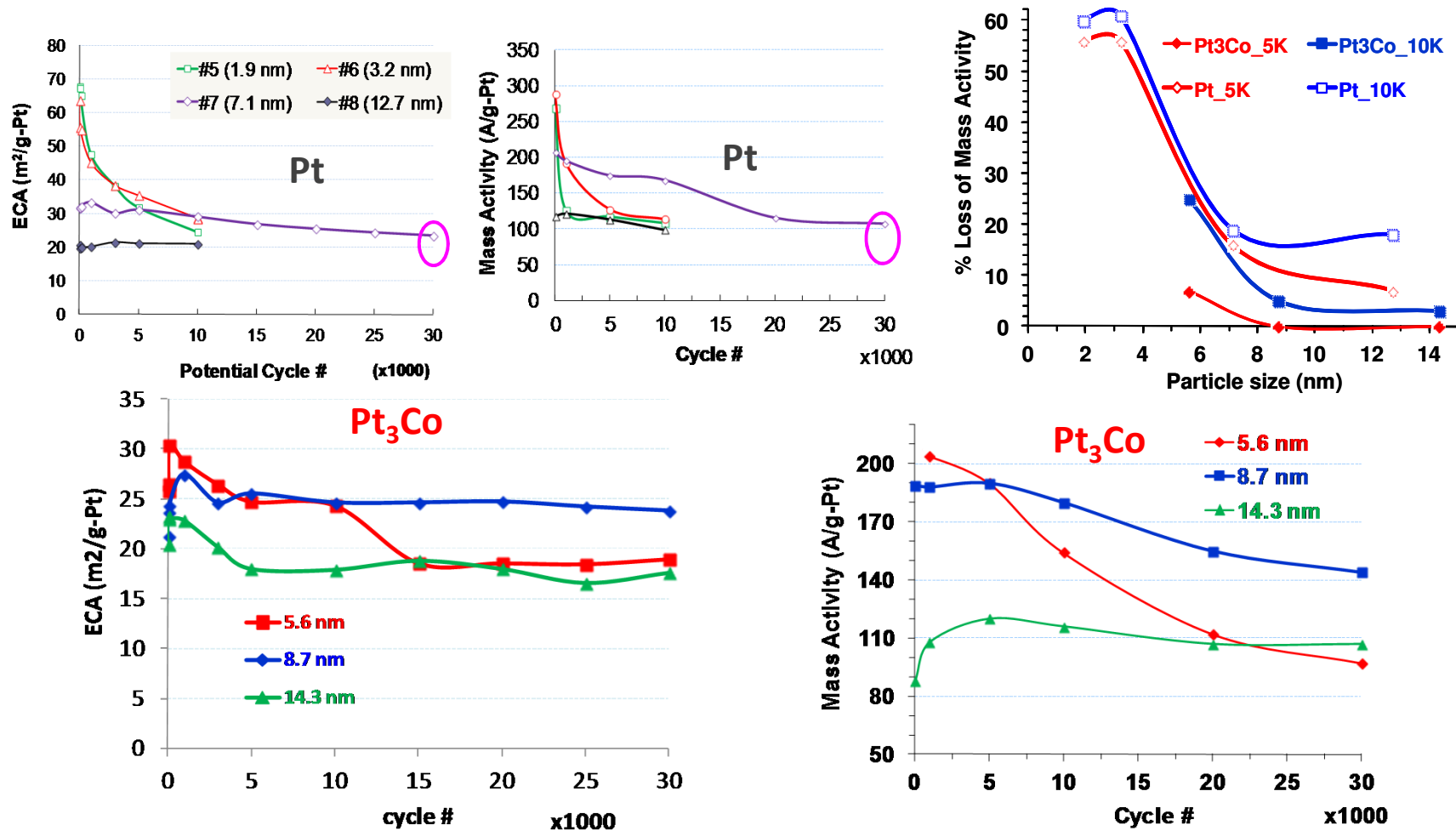
## Particle size studies of Pt and Pt<sub>3</sub>Co in single fuel cells

### ▪ 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

Cathode Cat.	TEM Mean Particle size (nm)	Cathode loading (mg-Pt/cm <sup>2</sup> )	Anode loading (mg-Pt/cm <sup>2</sup> )
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 <sub>3</sub> Co	5.6	0.23	0.20
Pt <sub>3</sub> Co	8.7	0.22	0.20
Pt <sub>3</sub> Co	14.3	0.22	0.20

# Particle size studies --- ECA and mass activity change with cycling

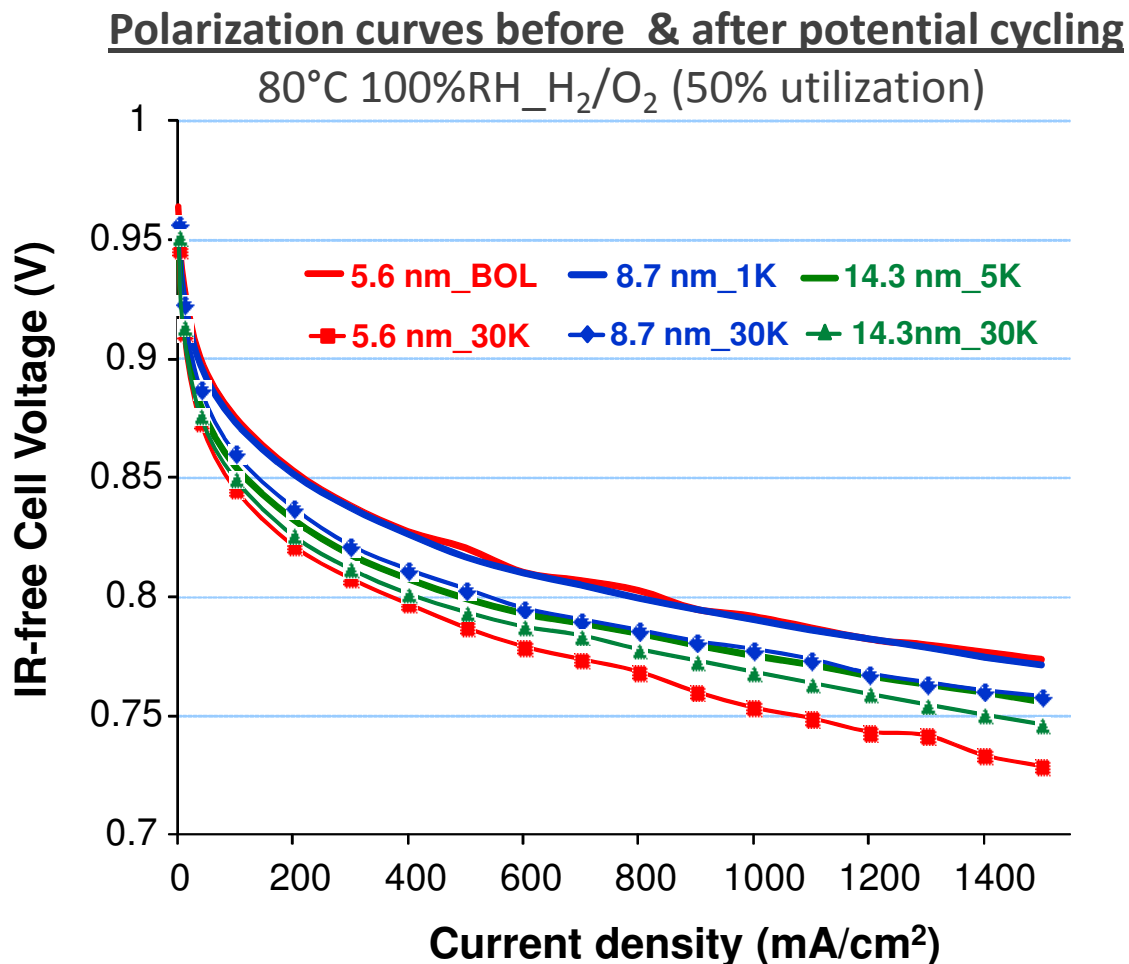


- Cycling to 1.0 V has minimal impact on catalysts with large initial particle size
- Cycling degrades performance of catalysts with smaller initial particle size toward that of larger particles
- Similar decay trends observed for Pt 7.1 nm and Pt<sub>3</sub>Co 5.6 nm; Pt 12.7 nm and Pt<sub>3</sub>Co 8.7 nm
- Mass activity decay of the Pt<sub>3</sub>Co cells is lower than Pt cells over the range of particle sizes

Argonne National Laboratory



## Particle size studies --- cell performance change with cycling for Pt<sub>3</sub>Co catalyst

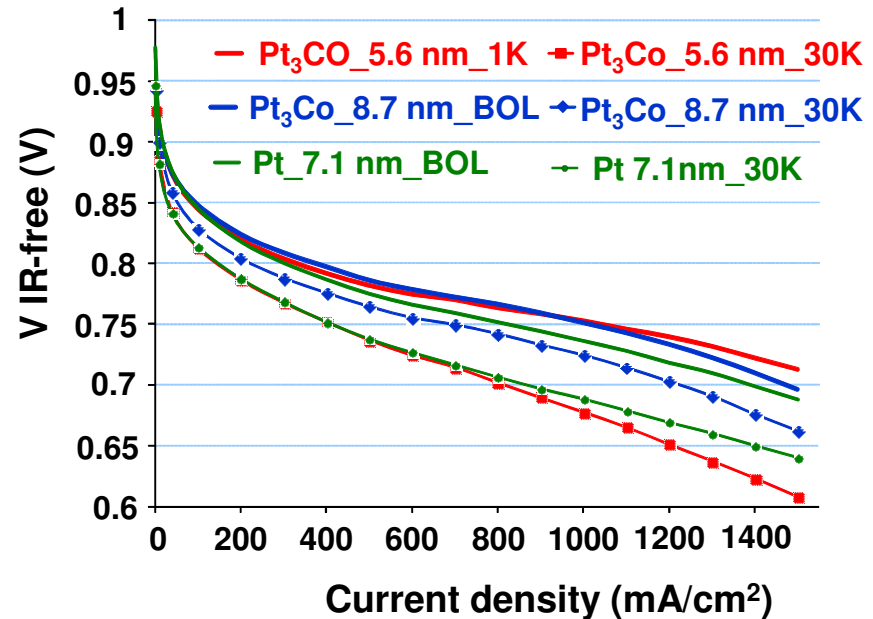
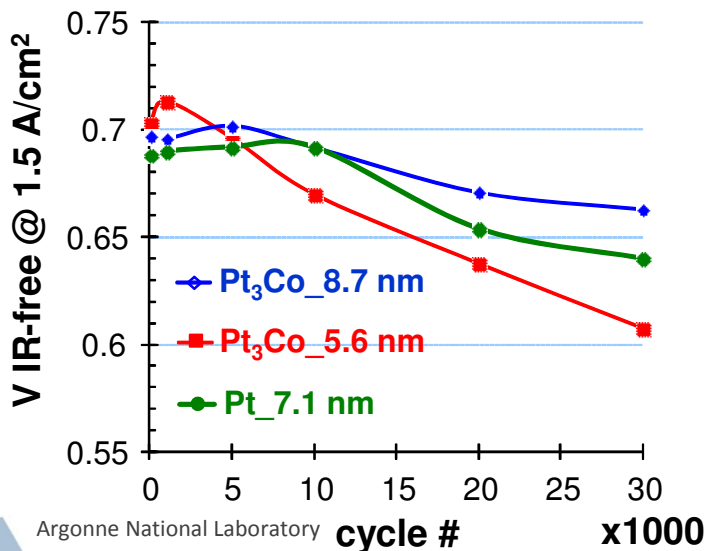
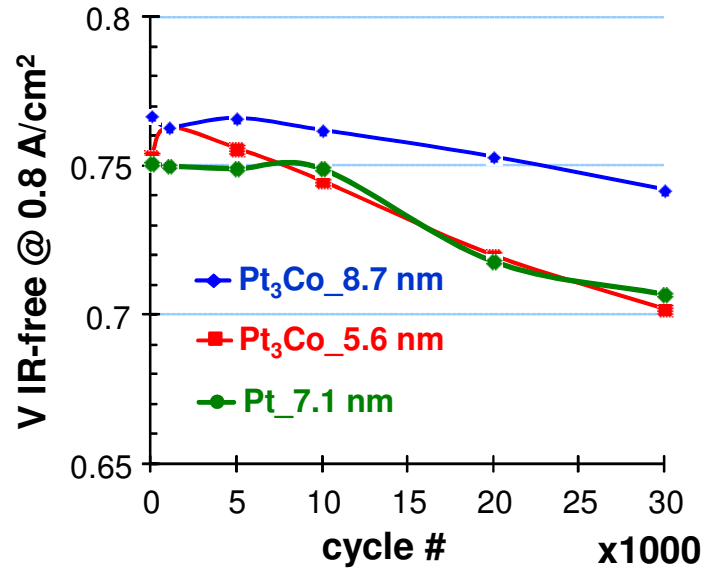


- Beginning of life performance of MEAs with smaller cathode catalyst particle size (5.6 nm) is highest, but voltage cycling degrades performance to below that of MEAs with larger initial particle size
- MEAs with large cathode catalyst particles (14.3 nm) show minimal O<sub>2</sub> performance degradation over 30,000 cycles



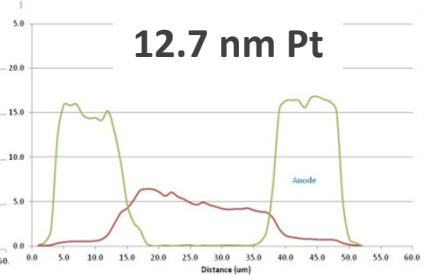
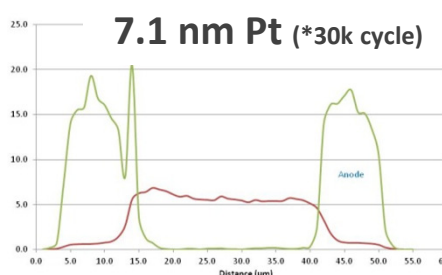
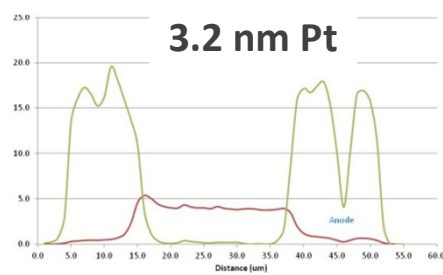
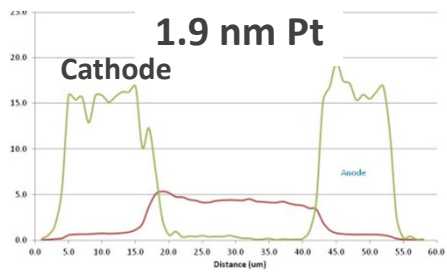
# Particle size studies --- IR-free cell performance of Pt<sub>3</sub>Co in comparison with Pt

- air, fixed flow, Pt and Pt<sub>3</sub>Co cathode catalysts

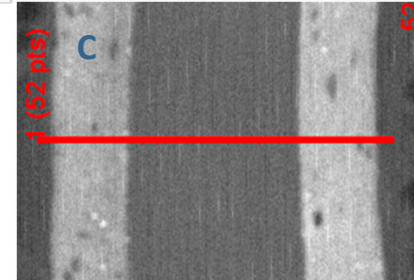
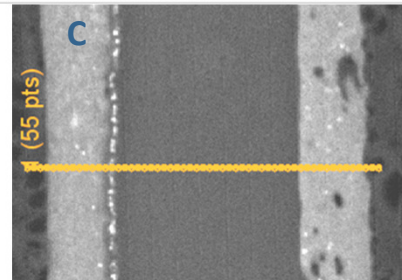
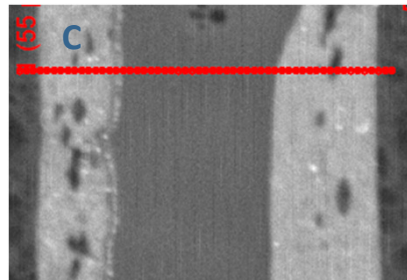
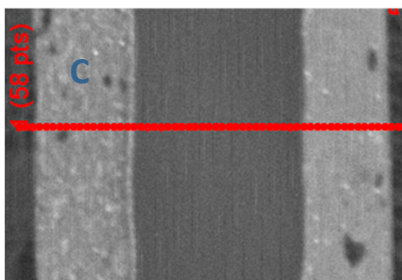


- Initial IR-free performance of 8.7 nm Pt<sub>3</sub>Co cell is the best and exceeds Pt performance
- IR-free decay rate of 8.7 nm Pt<sub>3</sub>Co cell is lower than 7.1 nm Pt cell
- Difference between IR-free performance after 30,000 cycles of 8.7 nm Pt<sub>3</sub>Co and 7.1 nm Pt decreases with increasing current density

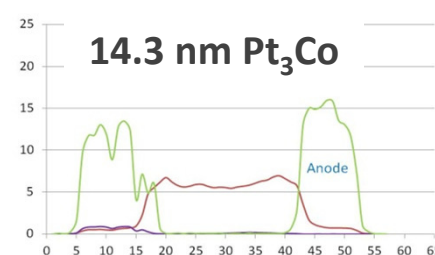
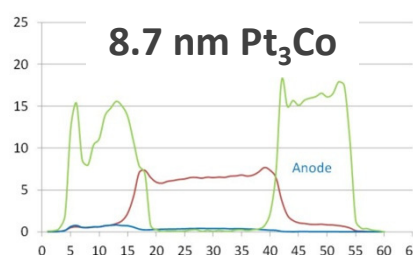
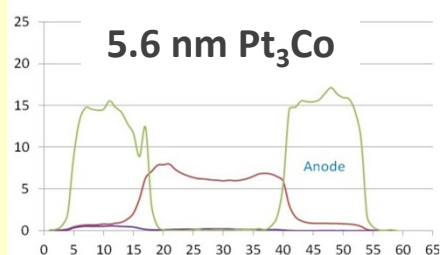
# Particle size studies --- structural change of cathode layer with cycling for Pt and Pt<sub>3</sub>Co catalysts



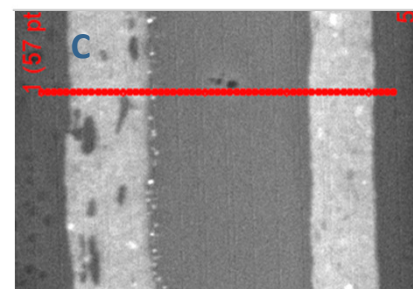
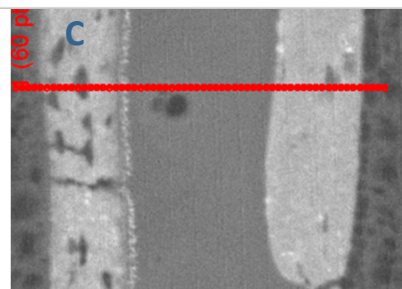
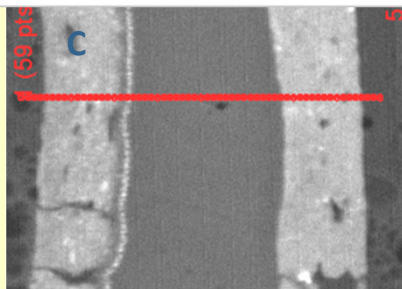
Middle



- Lower Pt content observed in membrane with larger initial Pt particle sizes

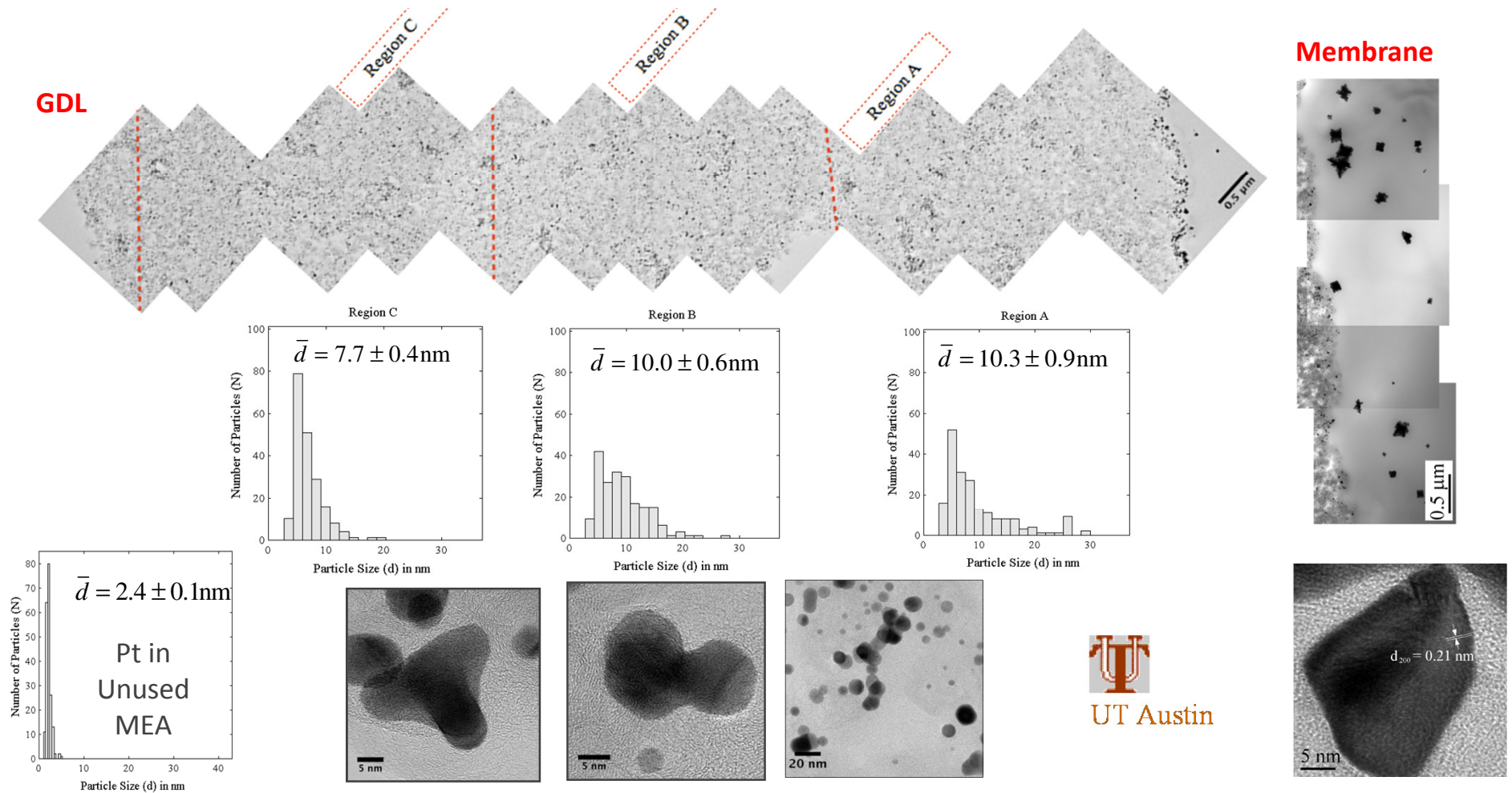


- In general, change in electrode thickness with cycling increases with decreasing particle size



# Particle size study --- Pt catalyst degradation mechanisms

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



- 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



## Particle size study --- Pt catalyst degradation mechanisms

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

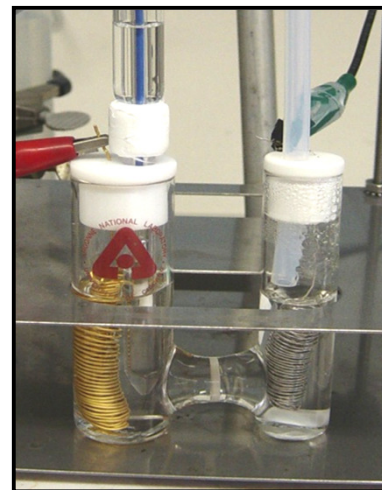
Initial mean particle dia. (nm)	Initial ECA (m <sup>2</sup> /g)	Final ECA (m <sup>2</sup> /g)	Final particle dia. in three regions (nm)	ECA estimated from average dia. (m <sup>2</sup> /g)
2.4 ± 0.1	67.9	24.5	A: 10.3±0.9 B: 10.0 ±0.6 C: 7.7 ±0.4	30
3.4 ±0.2	55.7	28.7	A: 9.8±0.5 B: 9.1 ±0.5 C: 9.4 ±0.5	30
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
13.8 ± 0.6	20.8	21.0	A: 16.6 ±2.2 B: 13.4 ± 0.6 C: 14.5 ± 0.7	20

- Three smallest particle sizes evolve to approximately the same average particle size (9.5 nm) after extended potential cycling
- 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)

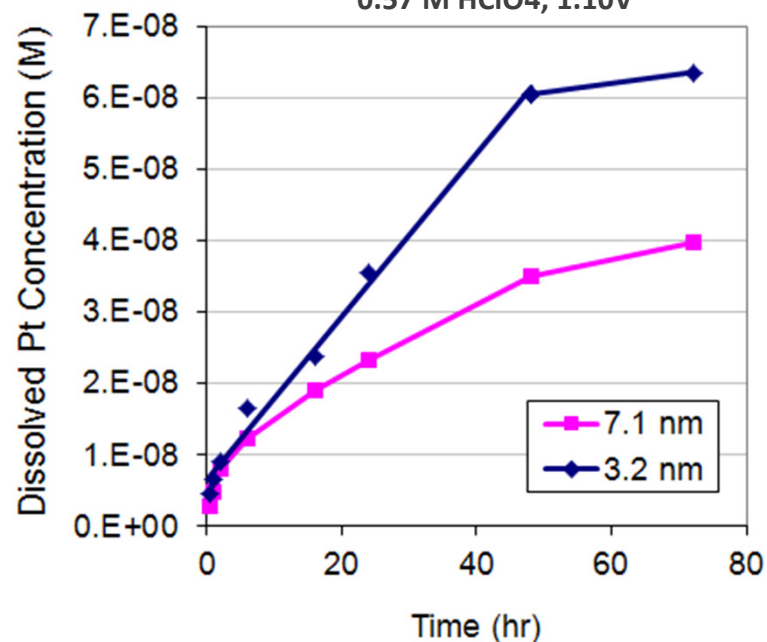


## Particle size studies --- aqueous dissolution behavior

- Potentiostatic dissolution of Pt catalyst layer on GDL with varied particle sizes
- Dissolution experiments performed in an H-cell to isolate working electrode
  - Pt loading: 0.3-0.4 mg Pt/cm<sup>2</sup>
  - Electrolyte: 0.57 M HClO<sub>4</sub> or 0.5 M H<sub>2</sub>SO<sub>4</sub>
  - Room temperature
  - Counter electrode: gold wire
  - ECA range: 30-40 cm<sup>2</sup>
  - Potential holding: up to 72 h
  - Dissolved metal (Pt and Au) concentrations in the working and counter/reference electrode compartments determined using ICP-MS (Det. Lim.: 1 ppt)

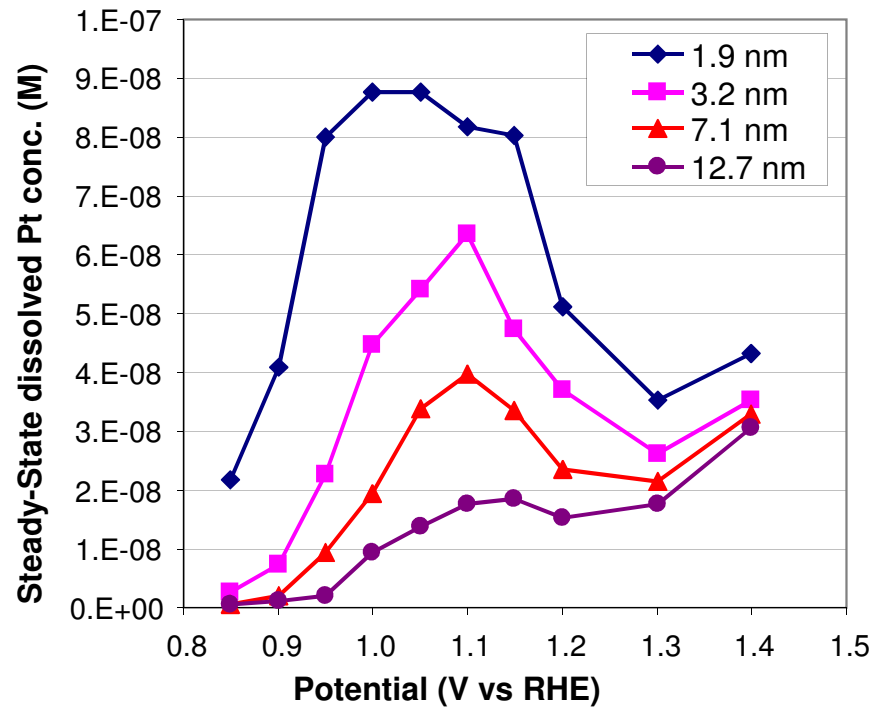


Time effect of Pt dissolution  
0.57 M HClO<sub>4</sub>, 1.10V

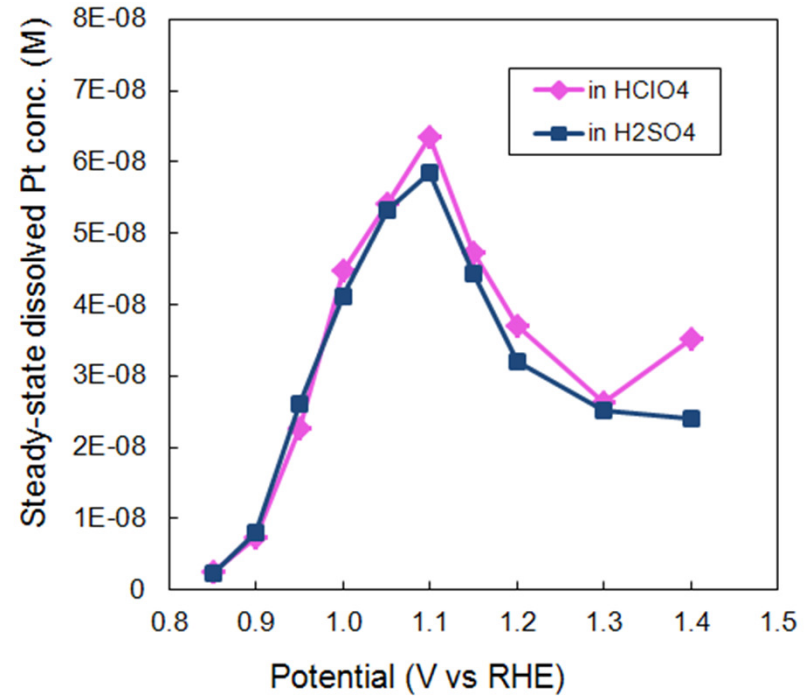


# Particle size studies --- aqueous Pt dissolution

## Particle size dependence of Pt dissolution

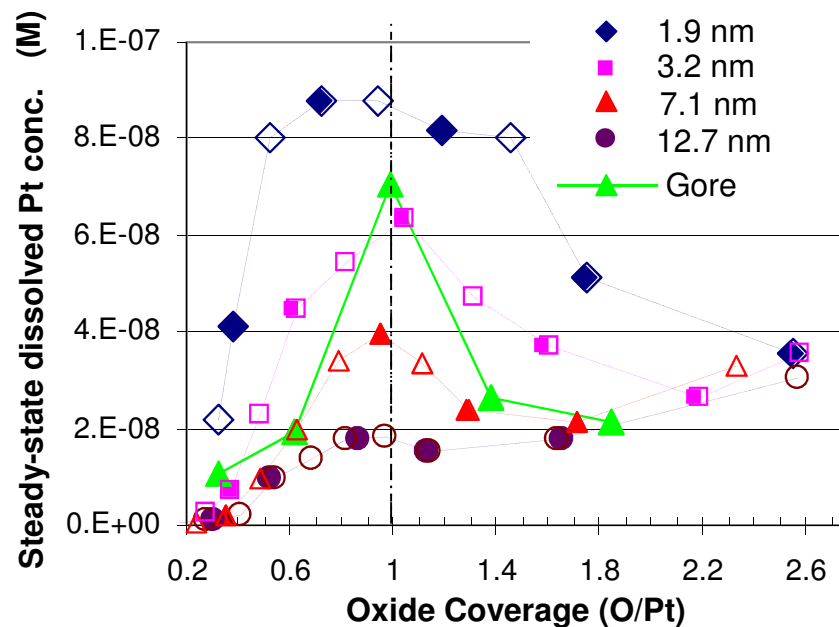
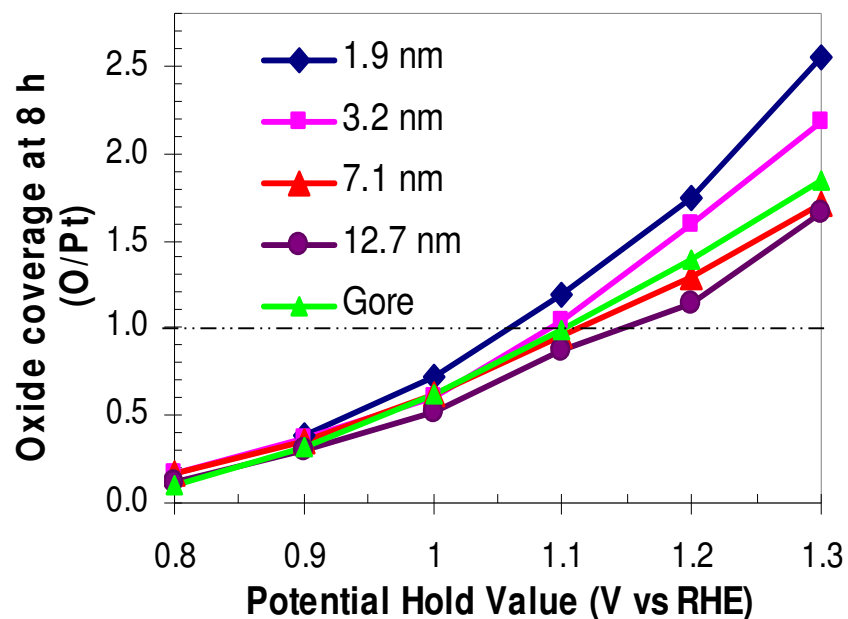


## Dissolution in different electrolyte, 3.2 nm



- Steady-state dissolved Pt concentration increased with decreasing mean particle size
- No significant difference in the steady-state dissolved Pt concentration in the different electrolytes

## Pt particle size study --- correlation between Pt dissolution and oxide coverage



- 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

## Parametric studies of Pt and Pt<sub>3</sub>Co catalysts in single fuel cells

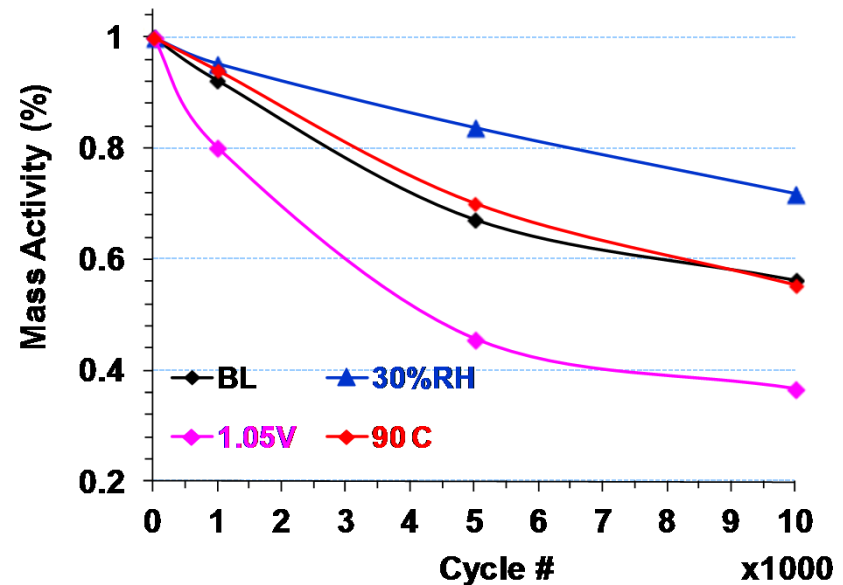
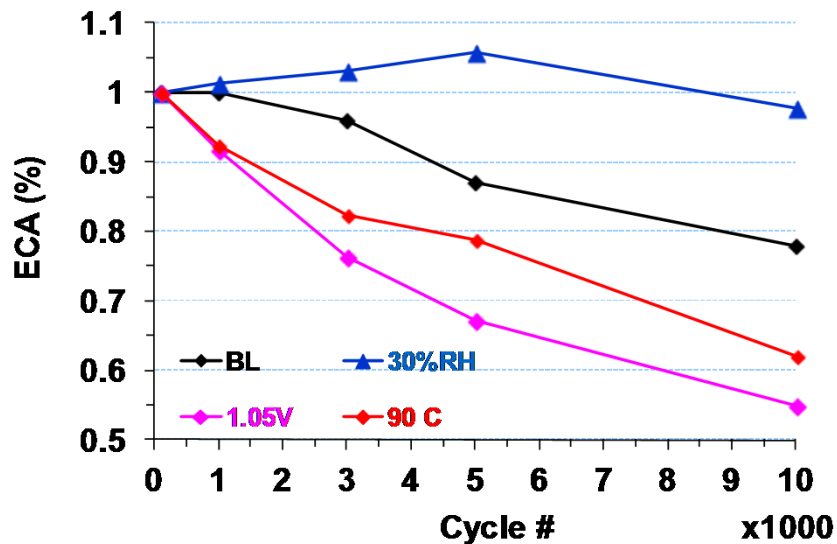
- Effect of upper potential limit, relative humidity, temperature
- Pt: 3.2 nm mean particle size; Pt<sub>3</sub>Co: 5.6 nm mean particle size

Cell ID	Potential cycle
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>• Humidity: Anode = Cathode = 100% RH</li> <li>• Fuel/Oxidant : 0.5 SLPM 4%H<sub>2</sub> / 0.5 SLPM N<sub>2</sub></li> <li>• Pressure: Atmospheric pressure</li> </ul>
1.05V	<ul style="list-style-type: none"> <li>• Square wave potential cycle: <b>10s at 0.4V, 10s at 1.05V (20s / cycle)</b></li> <li>• All other parameters same as BL</li> </ul>
30%RH	<ul style="list-style-type: none"> <li>• Humidity: <b>Anode = Cathode = 30%RH</b></li> <li>• All other parameters same as BL</li> </ul>
90 °C	<ul style="list-style-type: none"> <li>• Cell Temperature: <b>90°C</b></li> <li>• All other parameters same as BL</li> </ul>



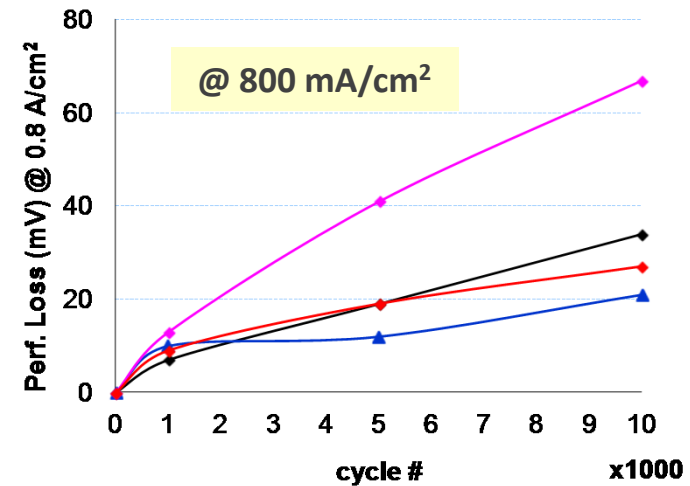
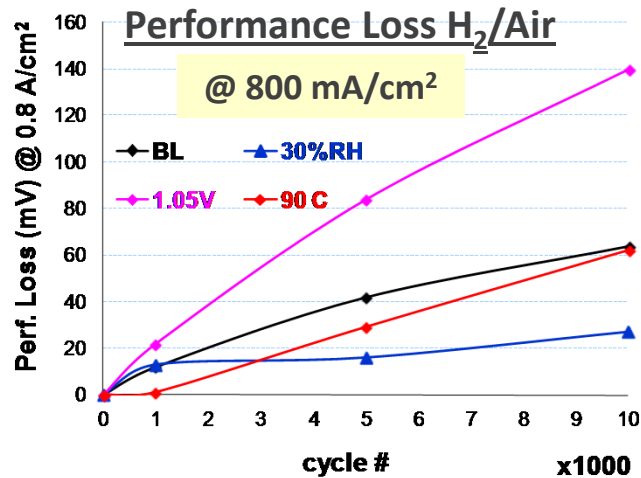
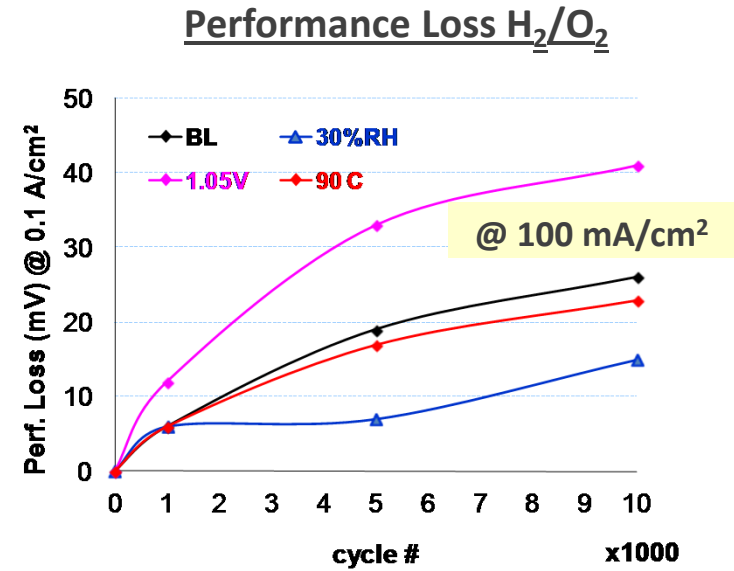
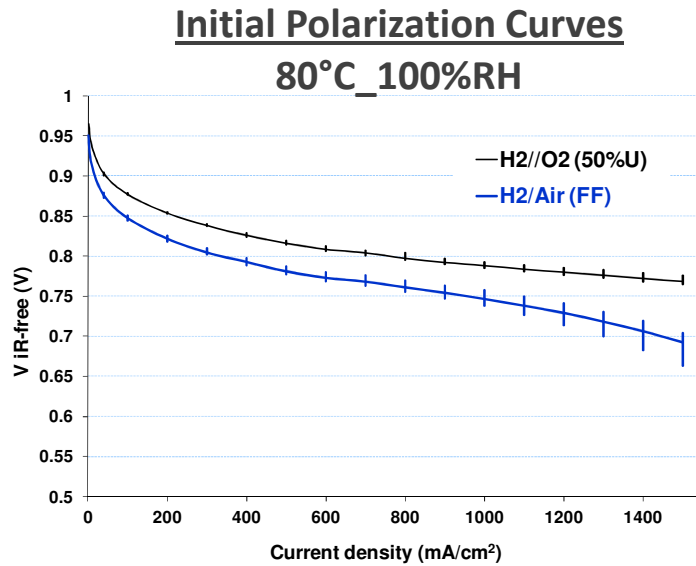
# Parametric studies of Pt<sub>3</sub>Co catalyst (5.6 nm)

Cell #	Potential cycle
#11 (BL)	<ul style="list-style-type: none"> <li>Square wave potential cycle: 10s at 0.4V, 10s at 0.95V (20 s / cycle)</li> <li>Cell Temperature: 80°C</li> <li>Humidity: Anode = Cathode = 100% RH</li> <li>Fuel/Oxidant : 0.5 SLPM 4%H<sub>2</sub> / 0.5 SLPM N<sub>2</sub></li> <li>Pressure: Atmospheric</li> </ul>
#12 (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 same as #11</li> </ul>
#13 (30%RH)	<ul style="list-style-type: none"> <li>Humidity: Anode = Cathode = 30%RH</li> <li>All other parameters same as #11</li> </ul>
#14 (90 °C)	<ul style="list-style-type: none"> <li>Cell Temperature: 90°C</li> <li>All other parameters same as #11</li> </ul>



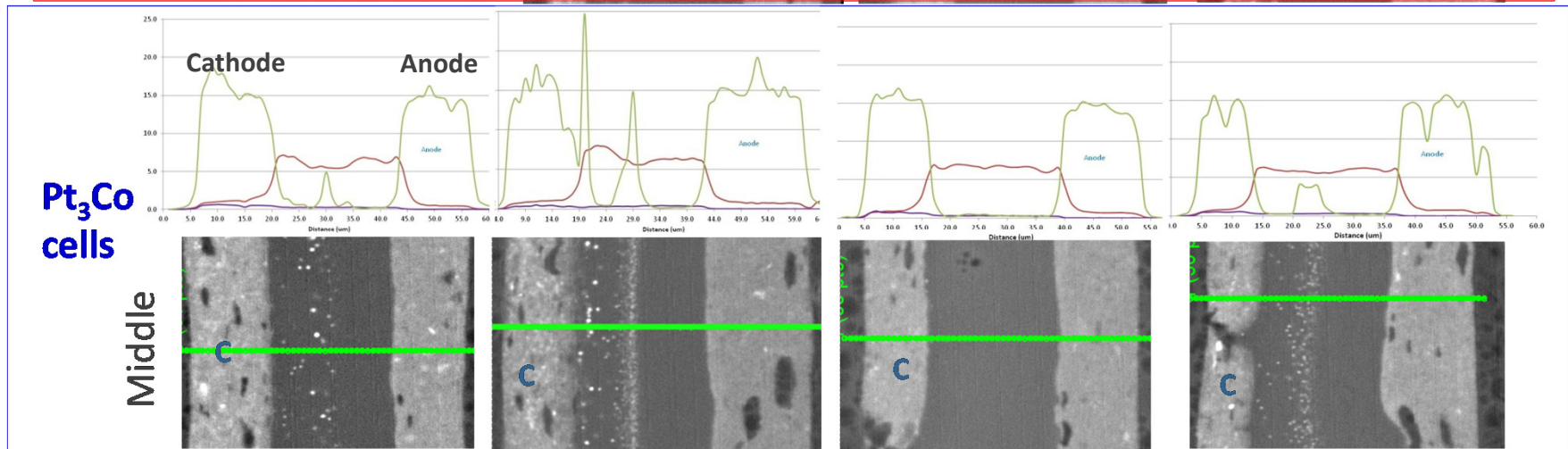
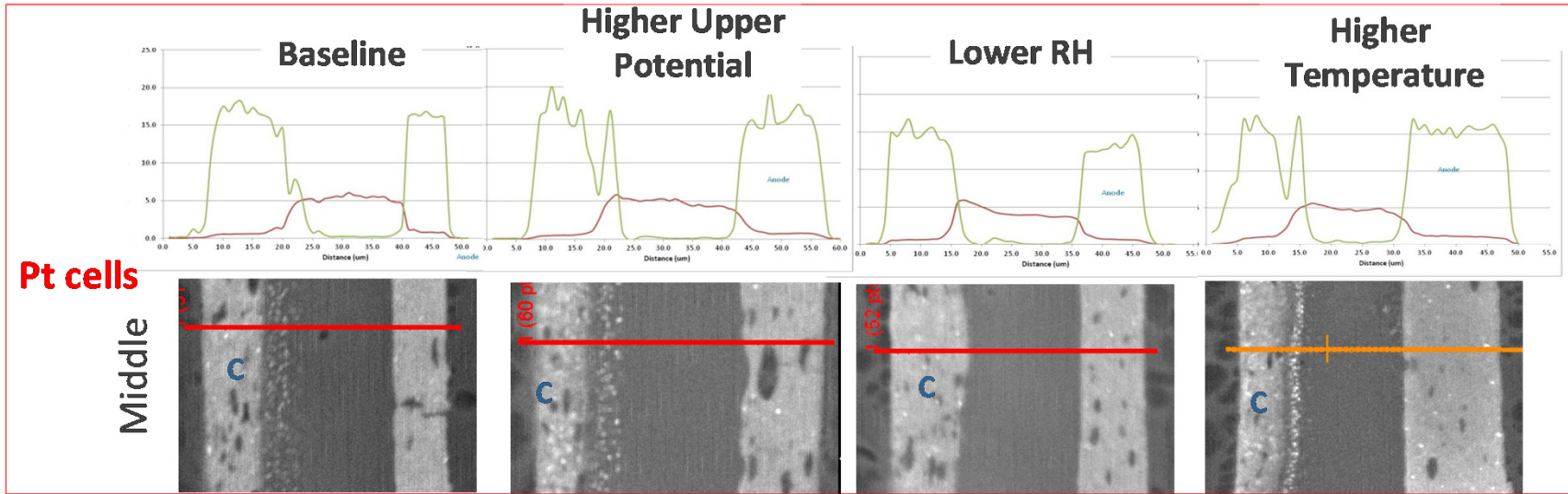
- Increasing upper limit of voltage cycling increases cathode catalyst surface area and mass activity loss
- Low inlet RH decreases cathode catalyst degradation

# Parametric studies of Pt<sub>3</sub>Co catalyst (5.6 nm)



- Cycling to high potentials significantly affects cathode transport losses

# 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



# Summary

- Increasing upper limit of voltage cycling increases loss of cathode catalyst surface area and mass activity
- Low inlet RH decreases cathode catalyst degradation
- Initial performance: Pt<sub>3</sub>Co-based MEAs showed better BOL performance than Pt-based MEAs (~ 20 mV in H<sub>2</sub>/O<sub>2</sub> or ~ 15 mV in H<sub>2</sub>/Air @ 1 A/cm<sup>2</sup>)
- Performance degradation: At high currents, the performance loss depends on catalyst particle size, no statistically meaningful difference was observed between Pt MEAs and Pt<sub>3</sub>Co MEAs
- ECA loss: Depends on catalyst particle size, no statistically meaningful difference was observed between Pt MEAs and Pt<sub>3</sub>Co MEAs
- Mass activity loss: Depends on catalyst particle size, the mass activity of Pt-based MEAs is less stable than Pt<sub>3</sub>Co-based MEAs
- The trends of migration of Pt into the membrane are the same for Pt and Pt<sub>3</sub>Co 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 temperature cycled cell
  - Pt MEA (7.1 nm) has a higher Pt content in the membrane than Pt<sub>3</sub>Co MEAs (5.6 nm & 8.7 nm) after 30,000 triangle cycles; more tests are needed to quantify Pt loss
- Pt dissolution depends strongly on potential and time of potential hold, Pt particle size, and oxide formed on the Pt surface

# Acknowledgments

- **Nancy Garland, Technology Development Manager,  
US DOE Fuel Cell Technologies Program**
- **Yifen Tsai, Argonne's Analytical Chemistry Laboratory**
- **Stacy DeCrane and Tammi Nowicki, Kettering University**