Argonne NATIONAL LABORATORY

... for a brighter future

Pt nanoparticles for fuel cell applications: *In-situ* observation of electrocatalyst deterioration

Matt C. Smith

Hydrogen and Fuel Cell Materials Group

Argonne National Laboratory

Postdoc Seminar Series

Argonne National Laboratory

April 2nd

U.S. Department of Energy

UChicago ▸ Argonne LLC

Office of Science U.S. DEPARTMENT OF ENERGY

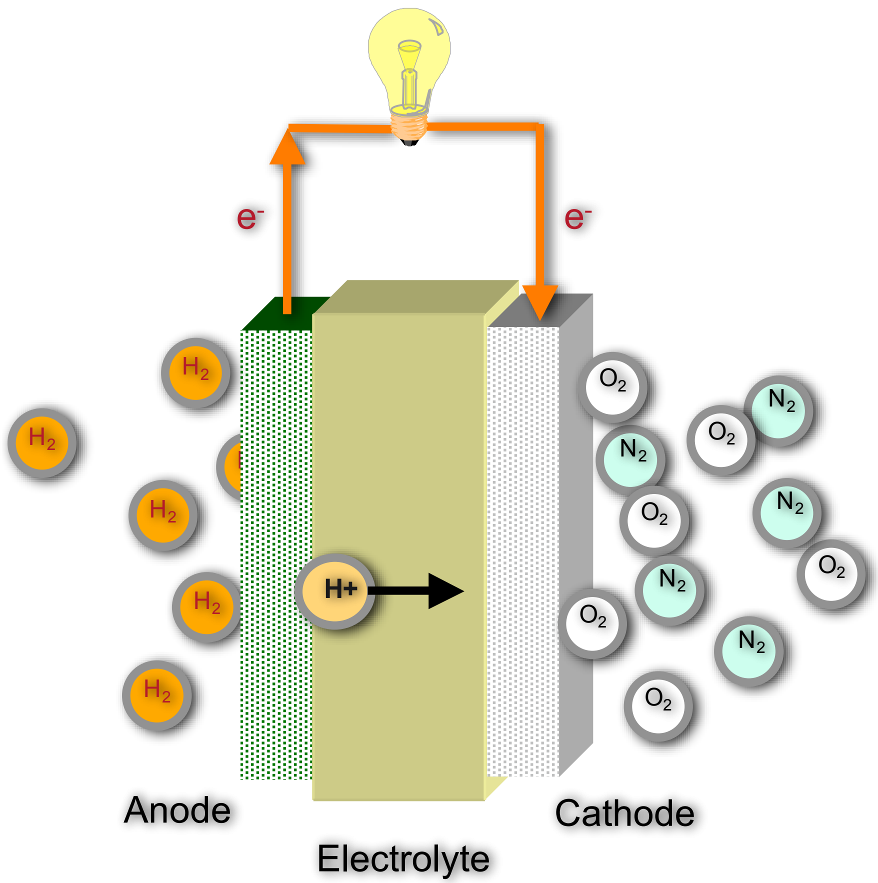
A U.S. Department of Energy laboratory managed by UChicago Argonne, LLC

What is a Fuel Cell?

- Electrochemical device that converts a fuel directly to electrical energy

$$H_2 + \frac{1}{2} O_2 = H_2O$$

$$E^\circ = 1.1 \text{ Volts}$$



Fuel Cell Types and Characteristics

Type	Features	Weaknesses
Alkaline (AFC) 25-100ºC	Used on Apollo and Space Shuttle Missions	Pt electrodes CO_2 intolerant
Phosphoric Acid (PAFC) 200ºC	First “commercial” units 200 kW units	Low CO tolerance (1-2%)
Polymer-Electrolyte (PEFC or PEM)	Quick start up Direct Methanol 60-90ºC	Very low CO tolerance High Materials Cost
Molten Carbonate (MCFC) 650ºC	2 MW units built Runs on Natural Gas	Molten electrolyte is corrosive
Solid Oxide (SOFC) 800-1000ºC	High Power Density Solid State Fuel flexible	High Temperature Slow start up

Polymer electrolyte fuel cells have been selected for automotive applications

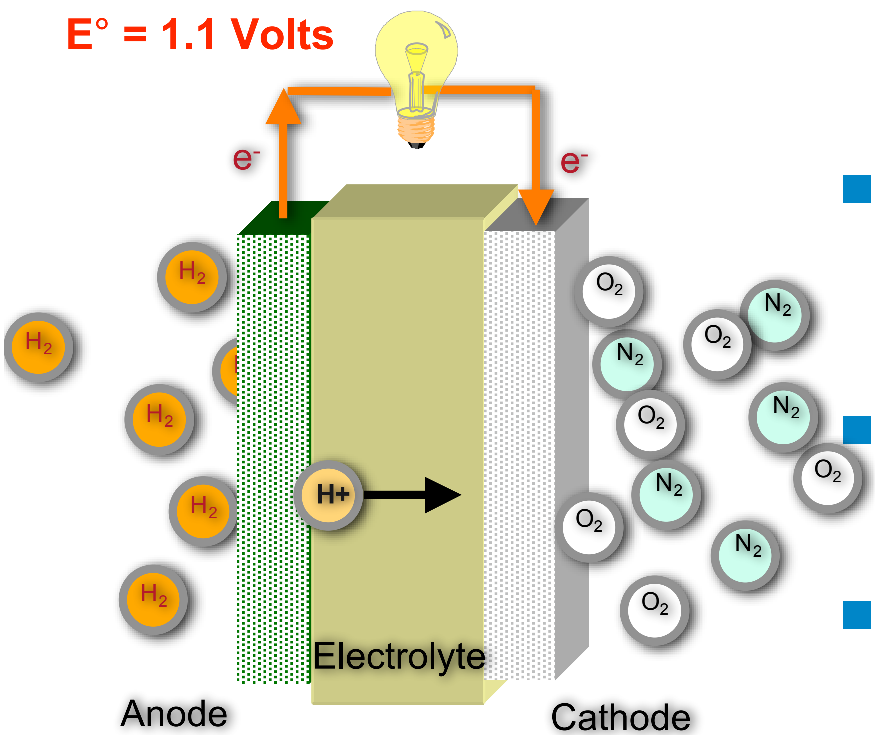
- Advantages
  - Low temperature operation (60-90°C)
  - Non-corrosive solid-state construction
  - Quick start-up time
- Challenges
  - Hydrogen storage
  - Low tolerance to impurities in the hydrogen fuel
  - Maintaining membrane's high proton conductivity
  - Cost of platinum catalyst, membrane production, and bipolar plate manufacturing
  - Durability of platinum catalyst and membrane

Pt Electrocatalyst Durability at the Cathode in Polymer Electrolyte Membrane Fuel Cells

- Cathode is responsible for the oxygen reduction reaction (ORR)
- ORR is limiting kinetic event (higher loadings of Pt required compared to anode)

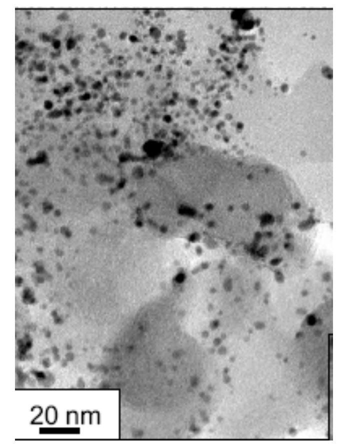
$H_2 + \frac{1}{2} O_2 = H_2O$

$E^\circ = 1.1$ Volts

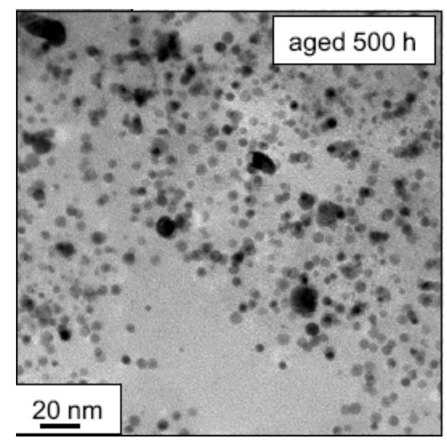


- Platinum cathode catalyst is not stable under long-term operation.
- Electrochemically active surface area decreases by ~1/3 in 1000 hours.
- Pt particles can coarsen 100 % in 500 hours
- Pt enrichment at membrane/catalyst interface

Fresh

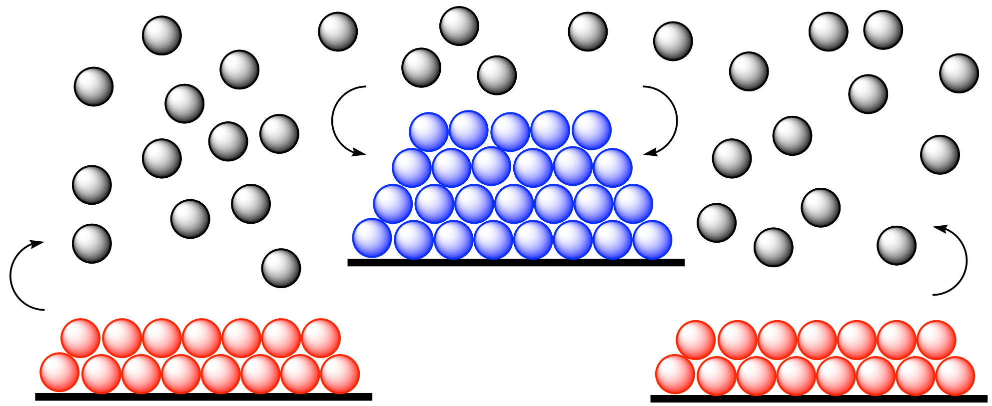


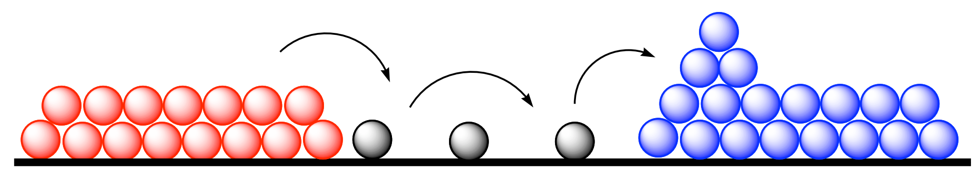
Aged 500 hrs



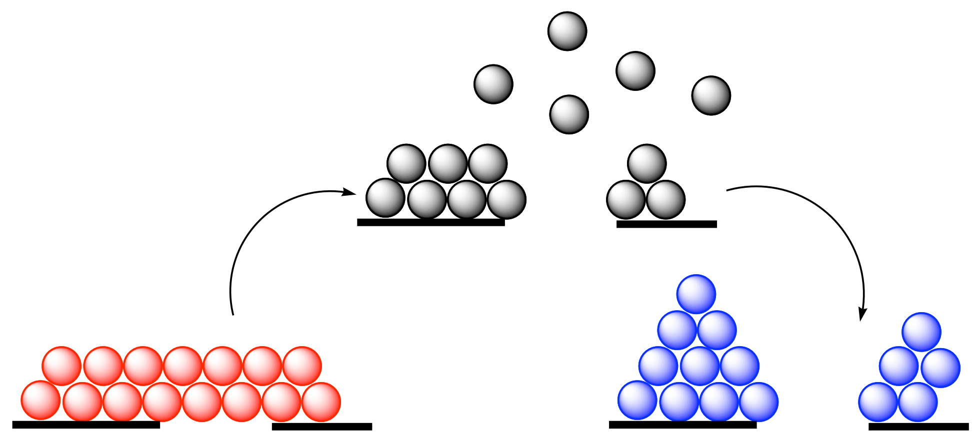
Pt Degradation Mechanism

- Pt dissolution of smaller particles and redepostion onto larger particles (3D)
- Pt coalescence *via* migration across support (2D)
- Erosion of [Carbon] support

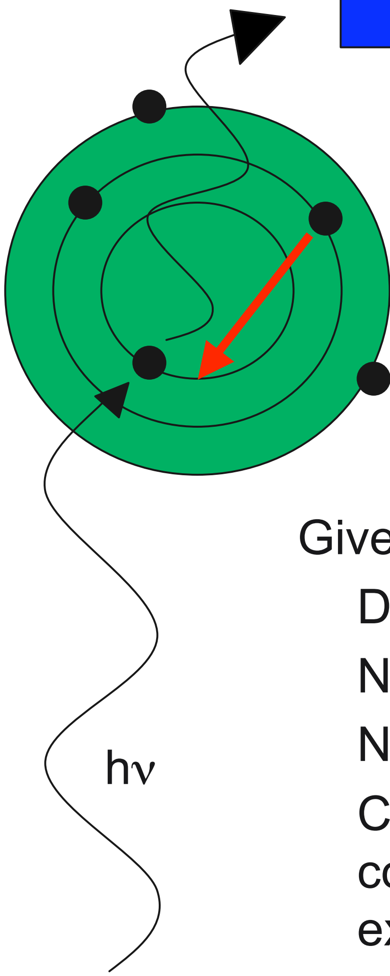


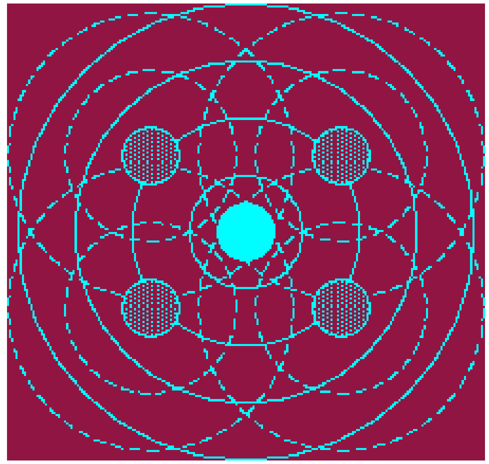


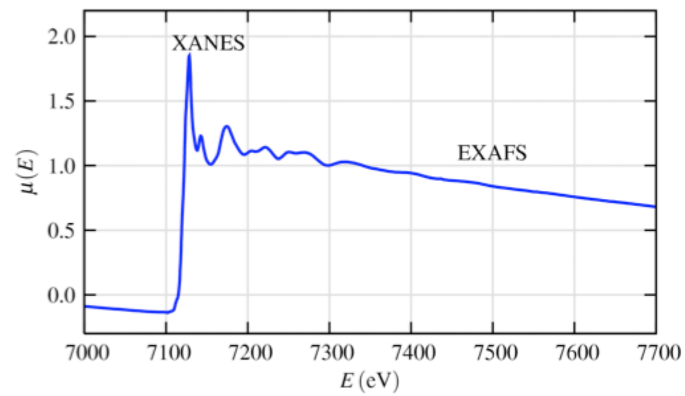
- Analysis is often *post mortem*
- X-rays offer non-interacting non-invasive *in-situ* spectroscopic study of the catalyst environment



X-ray Absorption Fine Structure (XAFS)



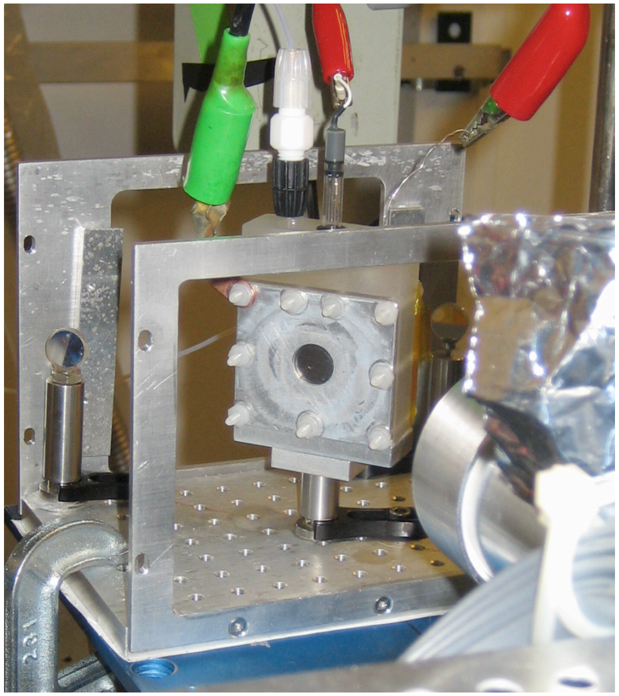


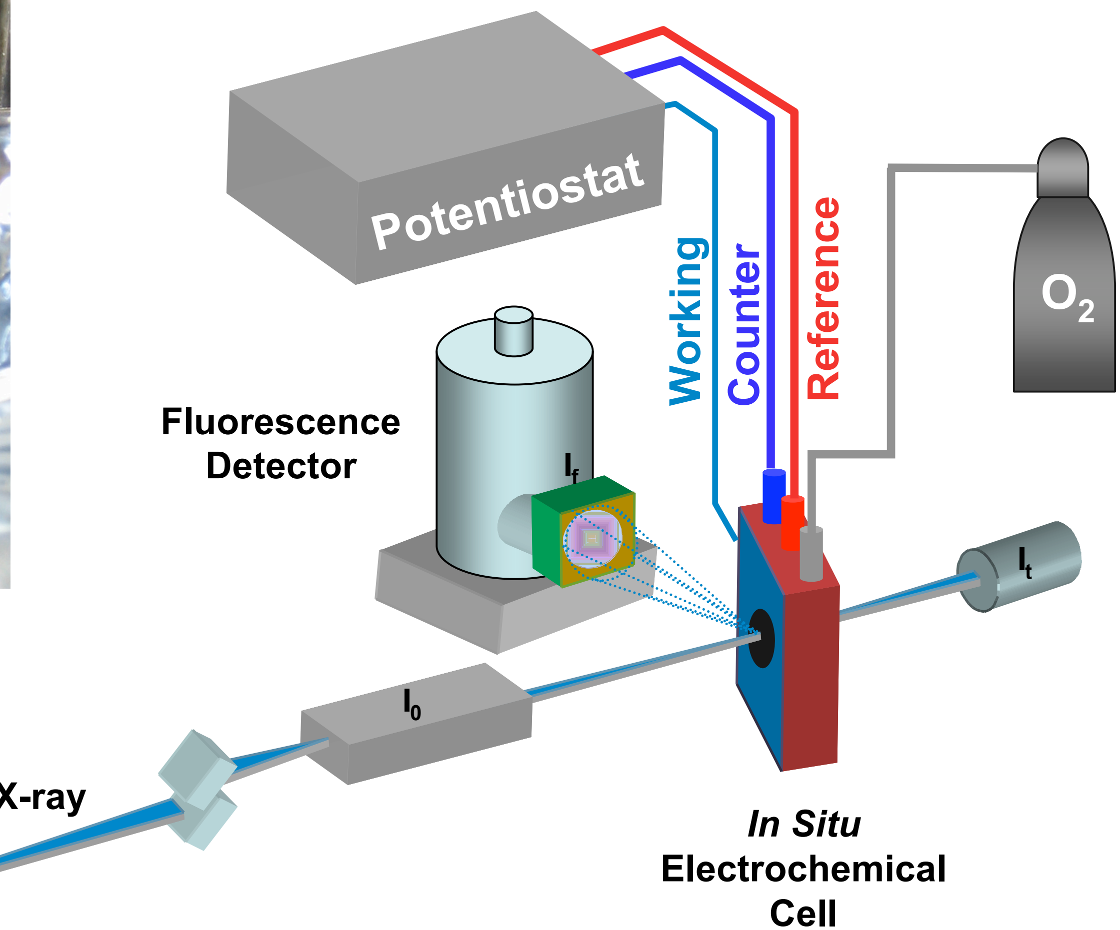


Gives information about:-

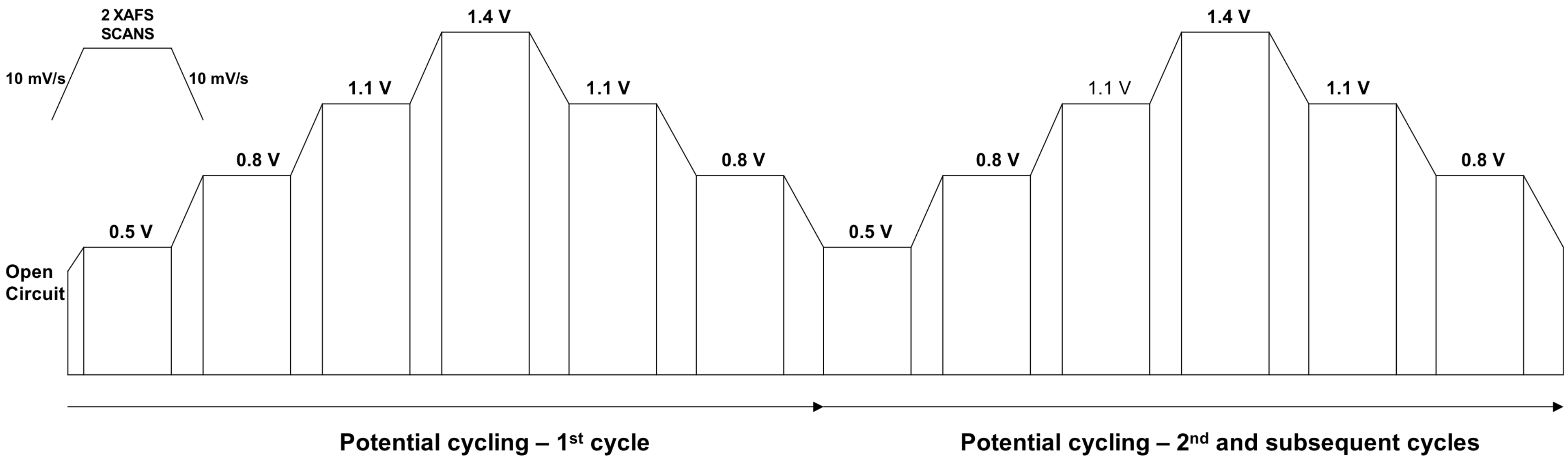
- Distances between atoms
- Number of neighbouring atoms
- Nature of neighbouring atoms
- Changes in central-atom coordination with changes in experimental condition
- Oxidation state of central atom

In-situ XAFS for Pt electrocatalysts in an Aqueous Cell

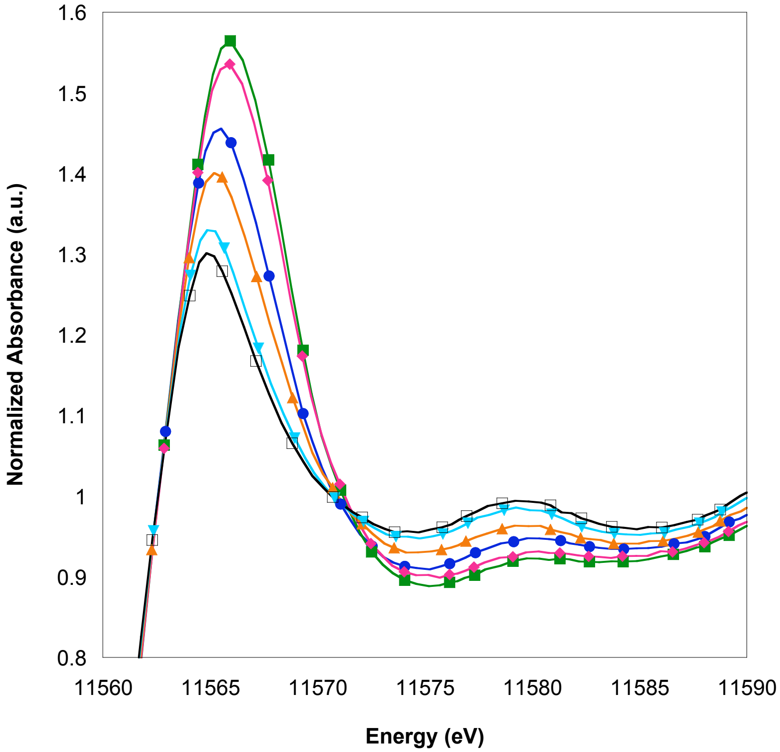


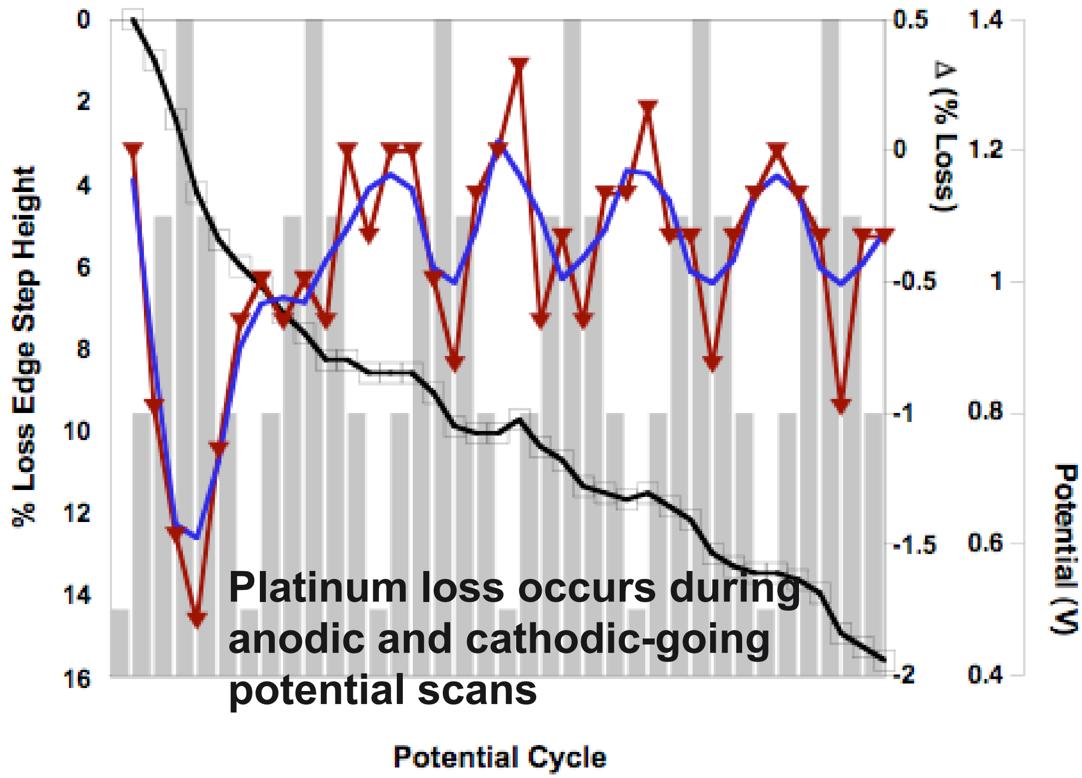


Pt/C electrocatalyst in an aqueous cell



Pt/C electrocatalyst in an aqueous cell

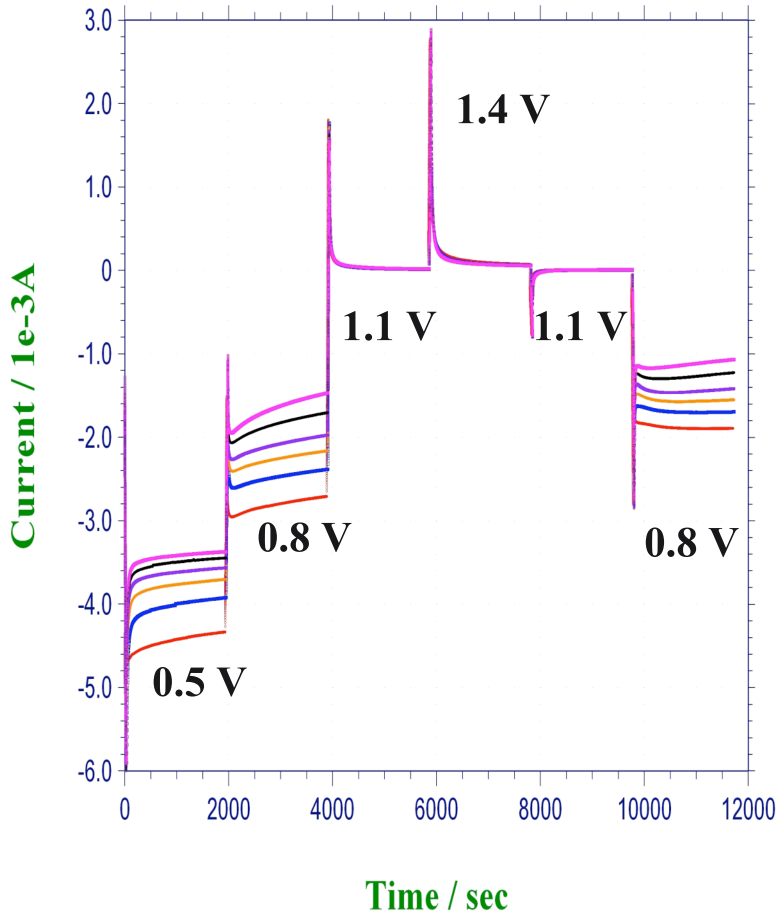


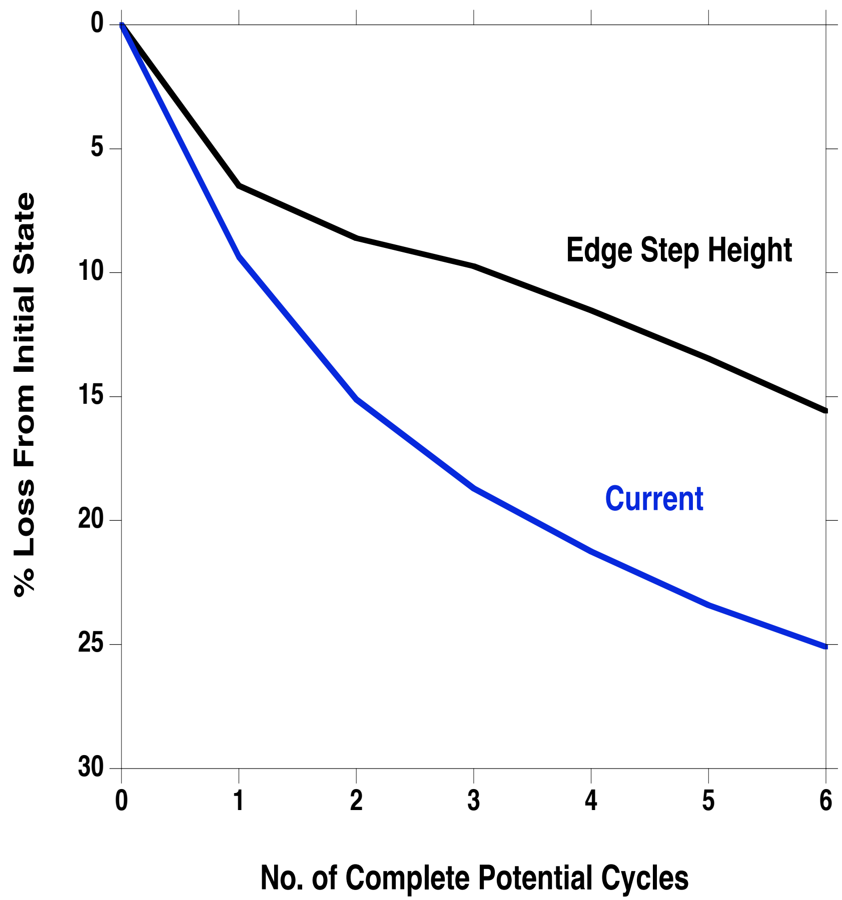


Pt L_3-edge XANES (0.5 V □; anodic 0.8 V ▼; anodic 1.1 V ▲; 1.4 V ◆; cathodic 1.1 V ■; cathodic 0.8 V ●).

Pt loss as a function of edge-step intensity (overall loss from initial point □; change in loss with potential step ▼ and weighted fit (—); potential is shown as grey histogram)

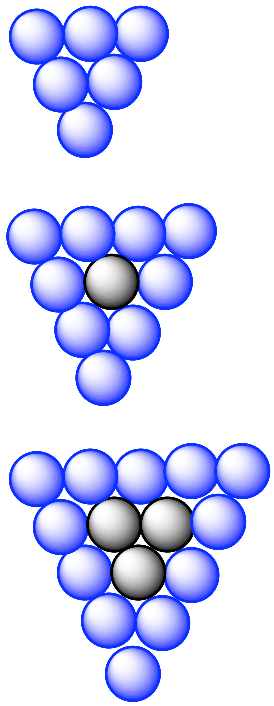
Current vs. Edge-Step



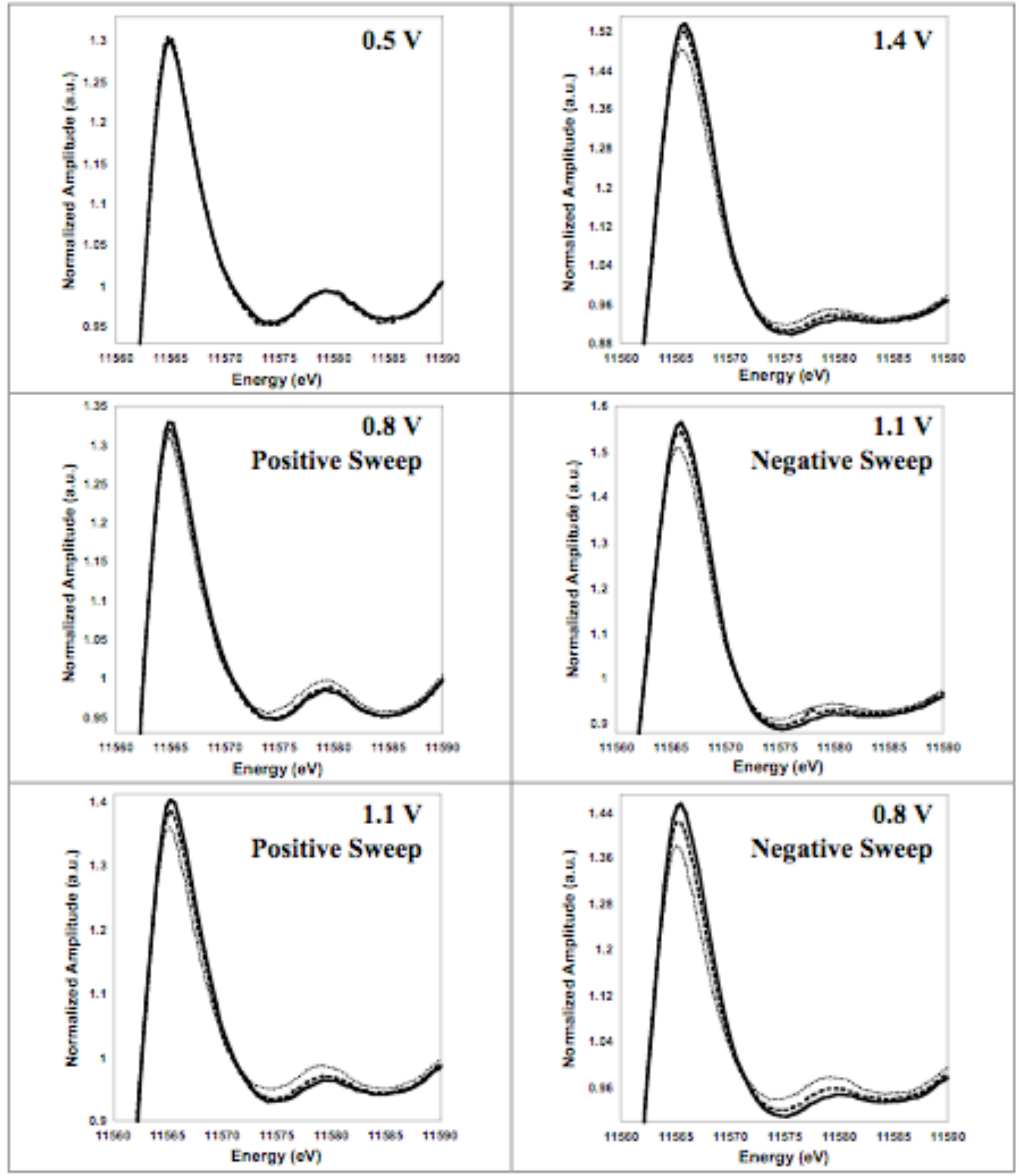


(Left) Current vs Time per cycle (Cycle 1 is orange and progesses thru to Cycle 6 – pink). (Right) Loss in current at 0.5 V compared to loss in edge-step height with respect to potential cycle.

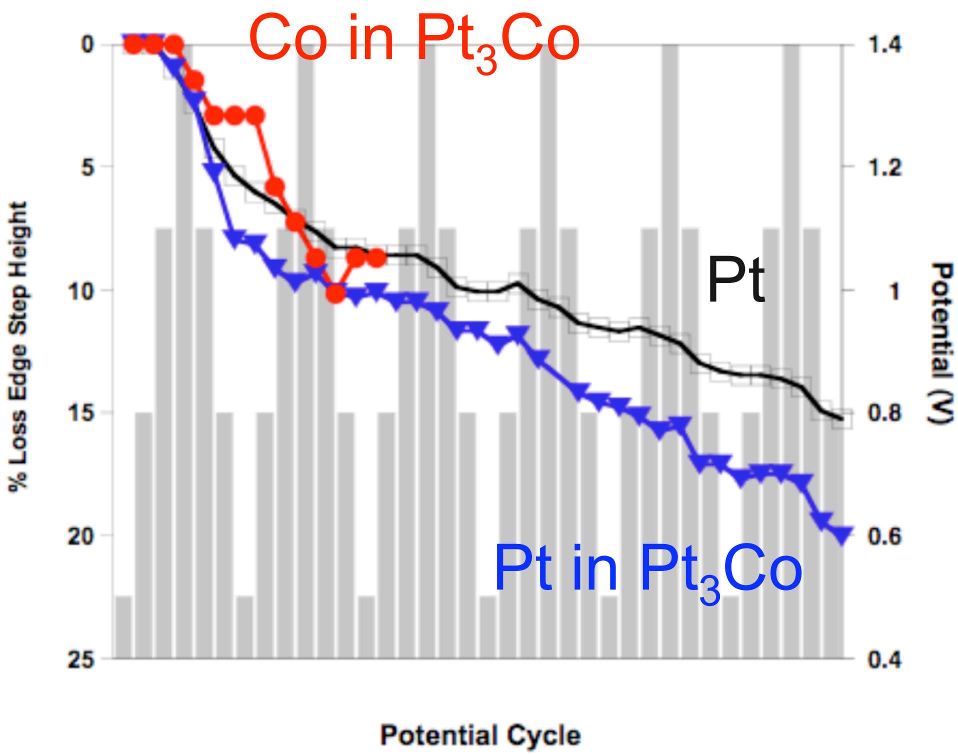
Size Agglomeration



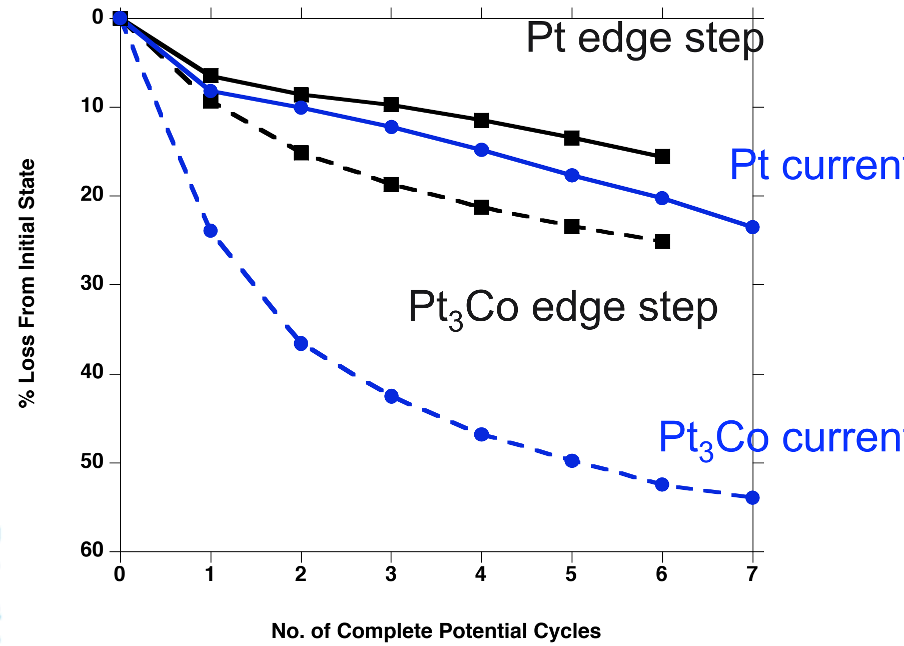
Normalized Pt L_3-edge XANES for Pt/C catalyst at different potentials. (Electrochemical cycle 1 (—), cycle 3 (•••), cycle 6 (• • •). Other cycles omitted for clarity)

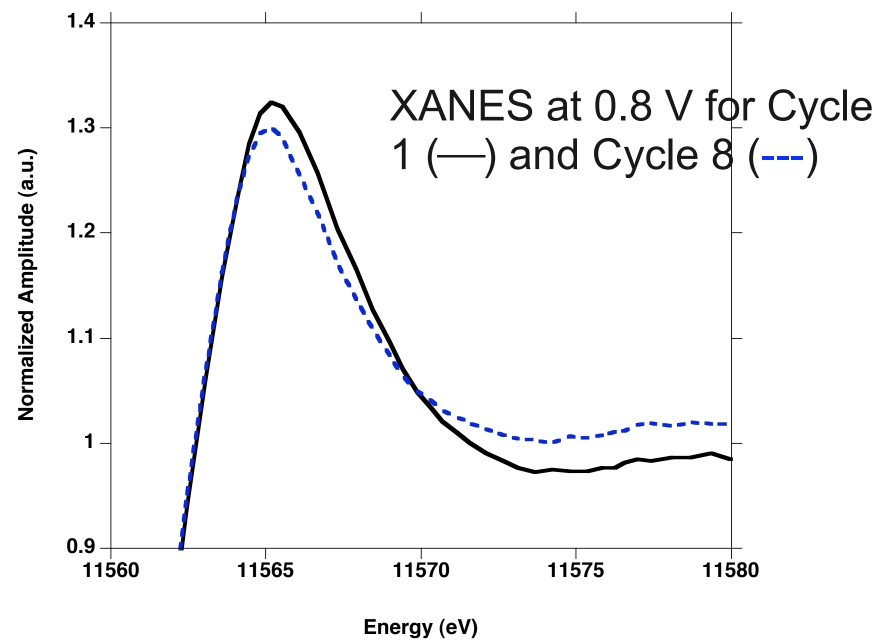


Pt_3Co/C

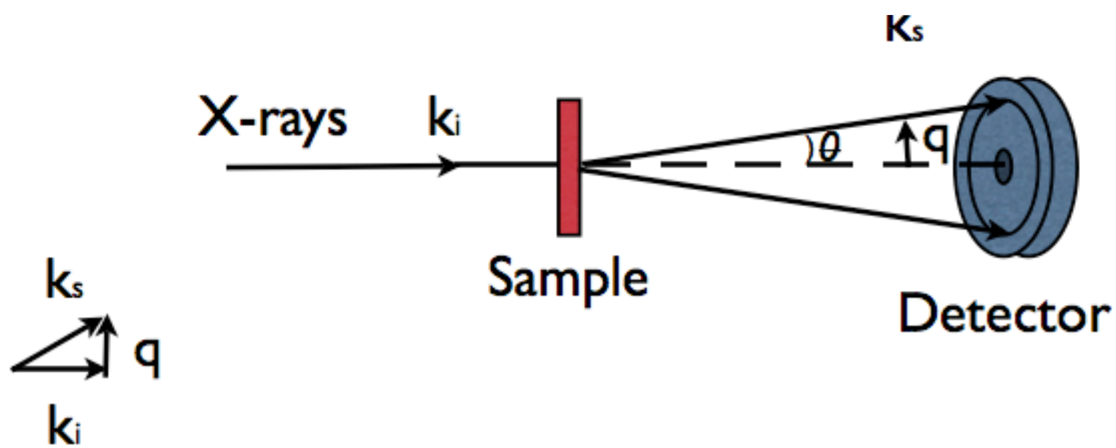


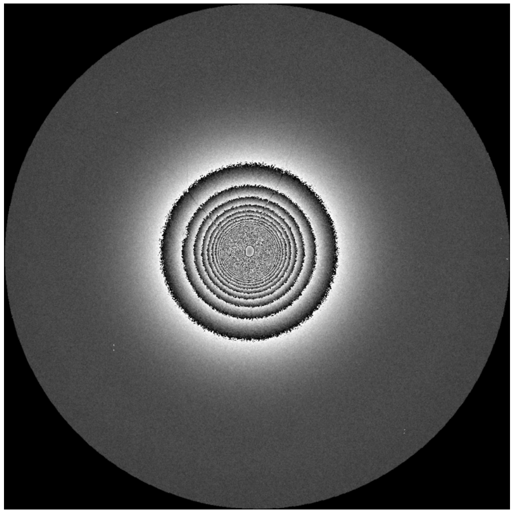
Pt loss as a function of edge step in Pt/C □; Pt_3Co/C ▼; and Co loss in Pt_3Co/C ● potential is shown as grey histogram).





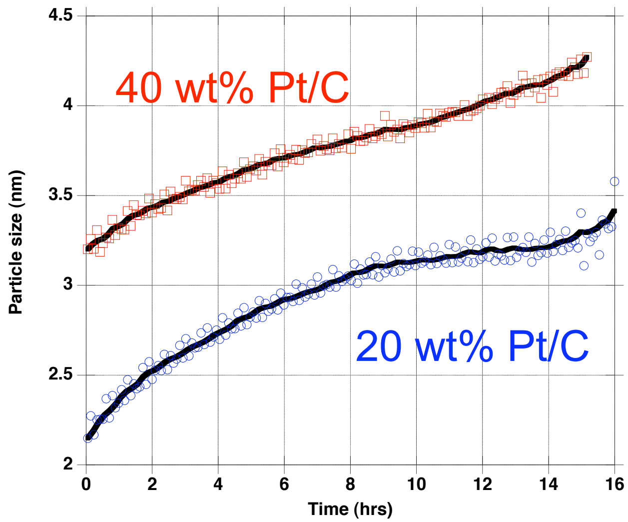
Small-Angle X-Ray Scattering (SAXS)

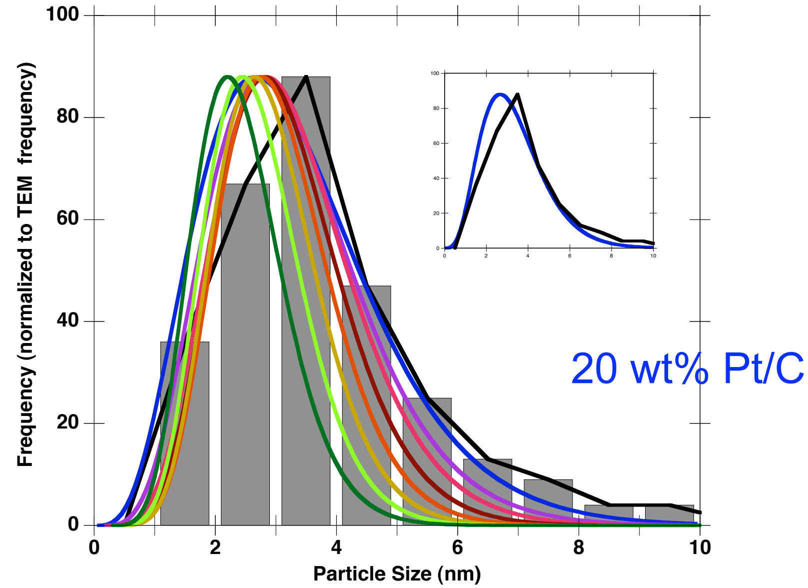


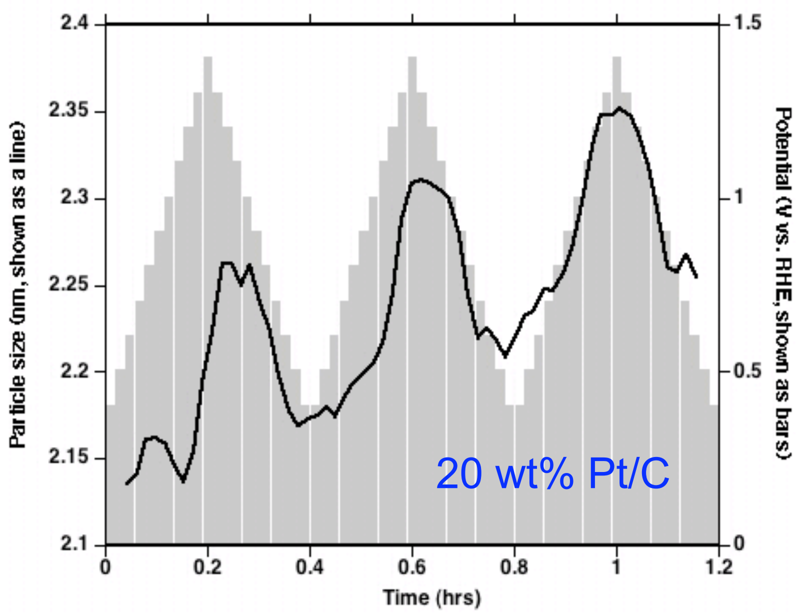


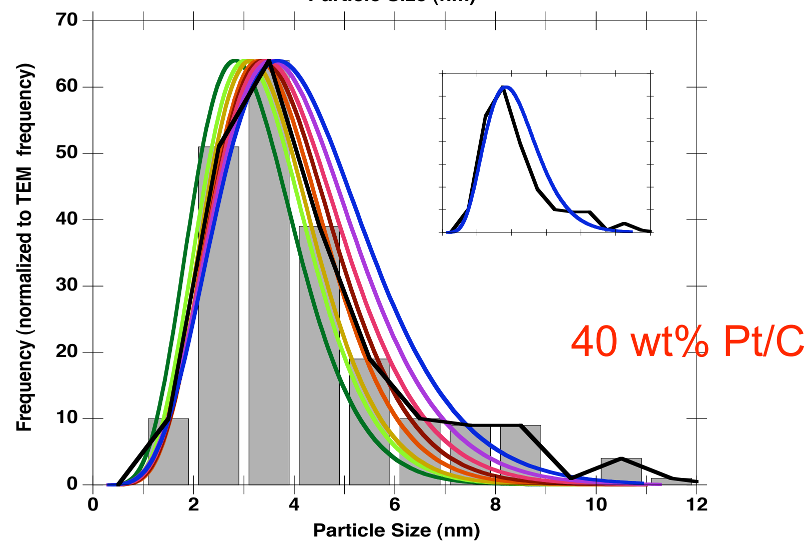
$$q = |\mathbf{q}| = \frac{4\pi}{\lambda}\sin(\theta / 2)$$

SAXS - Aqueous Cell









Summary

- Pt electrocatalyst loss and growth can be observed using x-ray spectroscopies
- Loss of Pt occurs during anodic and cathodic sweeps, but is greater during reduction, for Pt and Pt_3Co
- No evidence for Pt_3Co alloy being more stable than pure Pt under our aggressive conditions

Future Work

- Complete EXAFS analysis to provide full details on changing atomic environment - relate to mechanism and electrochemical dissolution data
- Analysis of *in-situ* working fuel cell XAFS data
- Fuel Cell SAXS

Acknowledgements

- CSE (ANL)
  - Debbie Myers
  - James Gilbert
  - Jeremy Kropf
  - Xiaoping Wang
  - Nancy Kariuki
  - Di-Jia Liu
  - Junbing Yang
  - Jennifer Mawdsley
  - Romesh Kumar
- APS (ANL)
  - Mali Balasubramanian
  - Sector 20 (PNC-CAT)
  - Nadia Leyaroskva
  - Sönke Seifert
  - Sector 12 (BESSRC-CAT)
- DOE,Office of Science, Basic Energy Science