

Electrode Stability

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Project ID # FC 17



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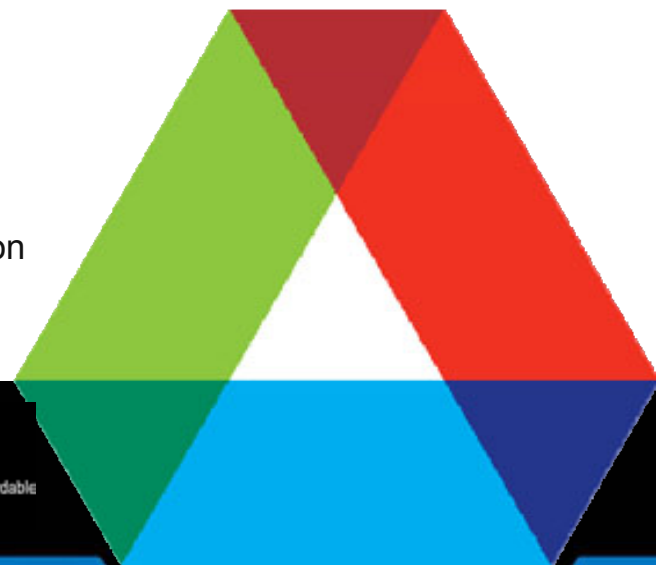
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Overview

Timeline

- Formal project start data: October FY'06
- Project end data: Open
- Percentage complete: n/a

Budget

- Total funding: (\$500 K)
- Funding for FY06: \$350 K

Barriers

- Barriers addressed
 - A. Durability
 - C. Electrode Performance

Interactions

- Oak Ridge and Los Alamos National Laboratories
- Regularly providing updates and soliciting feedback from the FreedomCAR Fuel Cell Technical Team
- Collaborations with Argonne's BES-funded groups on characterization



Objective

- Elucidate rates and mechanisms of loss of electrochemically active surface area (EASA) of polymer electrolyte fuel cell platinum electrodes
 - Proposed mechanisms of EASA loss
 - *Platinum dissolution and re-deposition to form larger particles*
 - *Platinum dissolution with loss of platinum into the membrane, GDL, product water, or other electrochemically inaccessible portion of the MEA*
 - *Particle migration and coalescence or transport of neutral Pt on support*
 - *Loss of electrochemically accessible Pt due to restructuring of electrode layer (e.g., loss of contact with proton-conducting phase) or impurity adsorption*

Approach

- Determine mechanisms and rates of Pt dissolution
 - Dissolution measurements as a function of
 - *Dissolution time*
 - *Potential*
 - *Type of electrolyte (adsorbing and non-adsorbing)*
 - *Form of Pt electrode and alloying (Pt wire, Pt/C, Pt₃Co/C)*
 - *Potential cycling*
 - *Temperature*
 - Mechanism of the platinum dissolution reaction using RRDE
- Determine particle size, oxidation state, and distribution of platinum
 - *Quantifying the extent of platinum loss in membrane-electrode assemblies using electrochemical and ex situ analyses*
 - *In situ X-ray fluorescence and wide-angle diffraction studies of membrane-electrode assemblies*

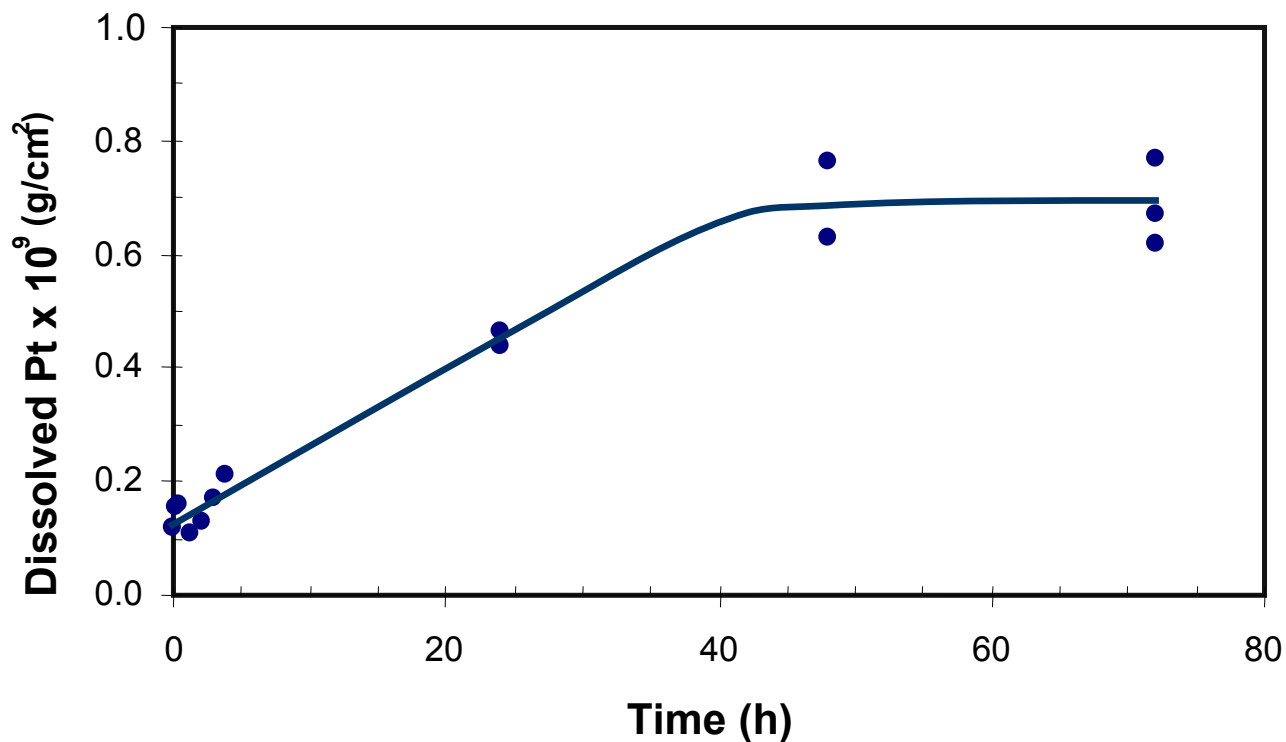
Progress vs. FY '06 Milestones

- Determine effect of potential and potential cycling on dissolution of Pt and Pt-Co supported on carbon (06/06)
 - Polycrystalline Pt for baseline performance
 - *Completed study of dissolution behavior as a function of both potential and potential cycling*
 - Pt/C
 - *Completed determination of effect of potential and determined particle size change*
 - *Potential cycling study is near completion*
 - Pt-Co/C
 - *In progress*
- Determine effect of temperature on dissolution of Pt and Pt-Co supported on carbon (09/06)
 - Design and construction of test apparatus for elevated temperatures is underway



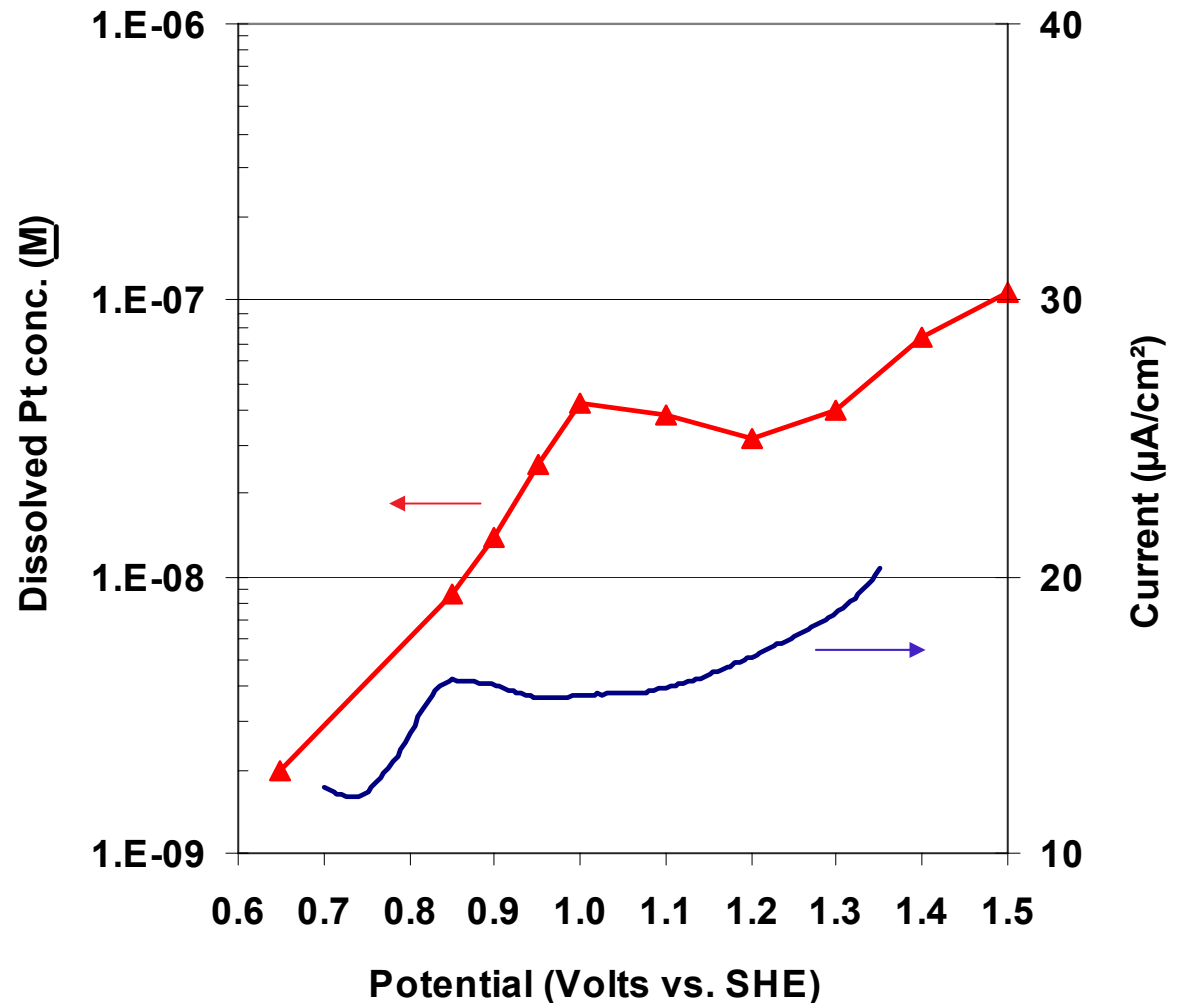
Pt dissolution at 0.90 V reached equilibrium in >48h

- 10 wt% Pt/C supported on carbon cloth (E-Tek), imbibed with Nafion[®] in 0.57 M HClO₄
- Pt wire - similar behavior



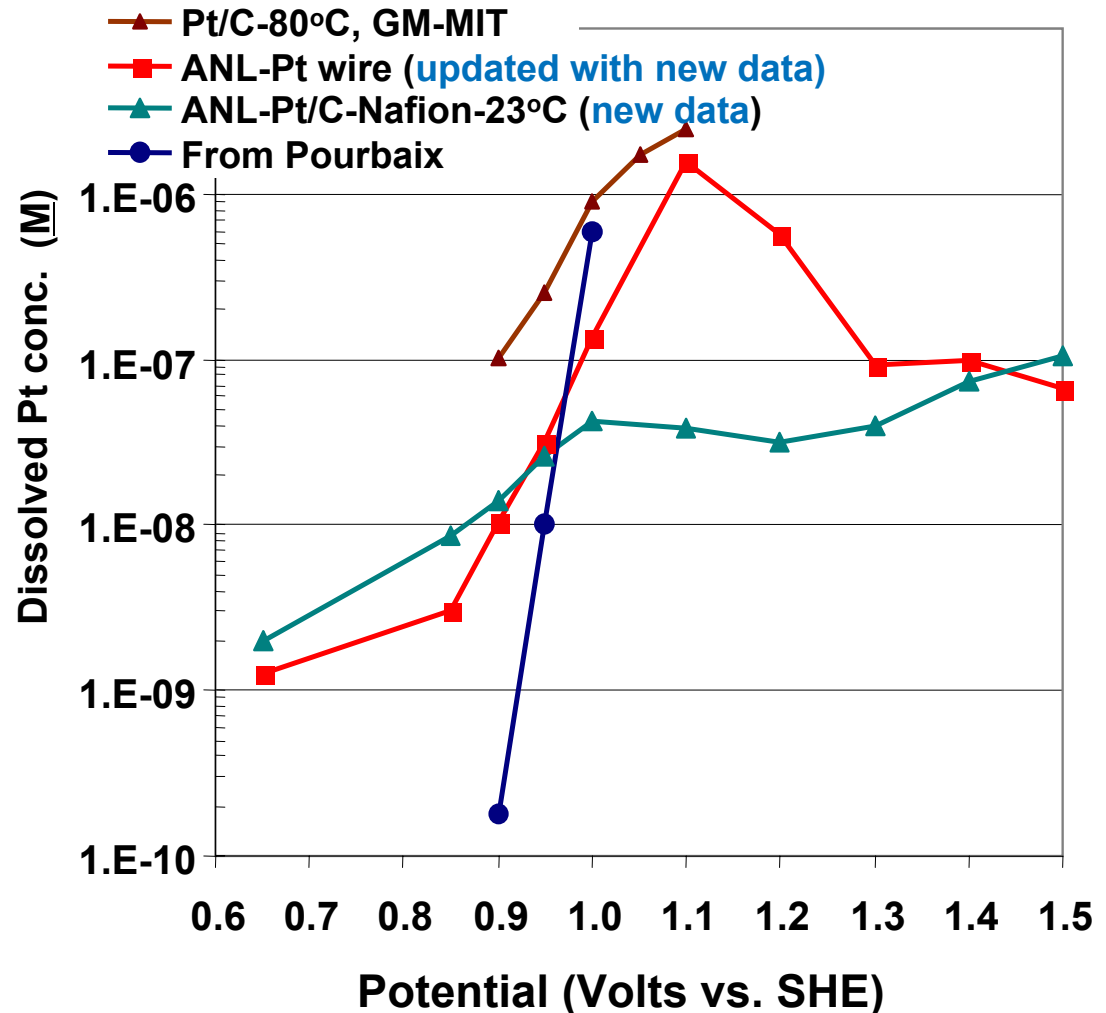
Dissolution behavior indicates that Pt/C is not passivated at >1.2 V

- Concentration of dissolved Pt correlates with the current-potential behavior
- There exists a potential shift between the concentration and current-potential curves

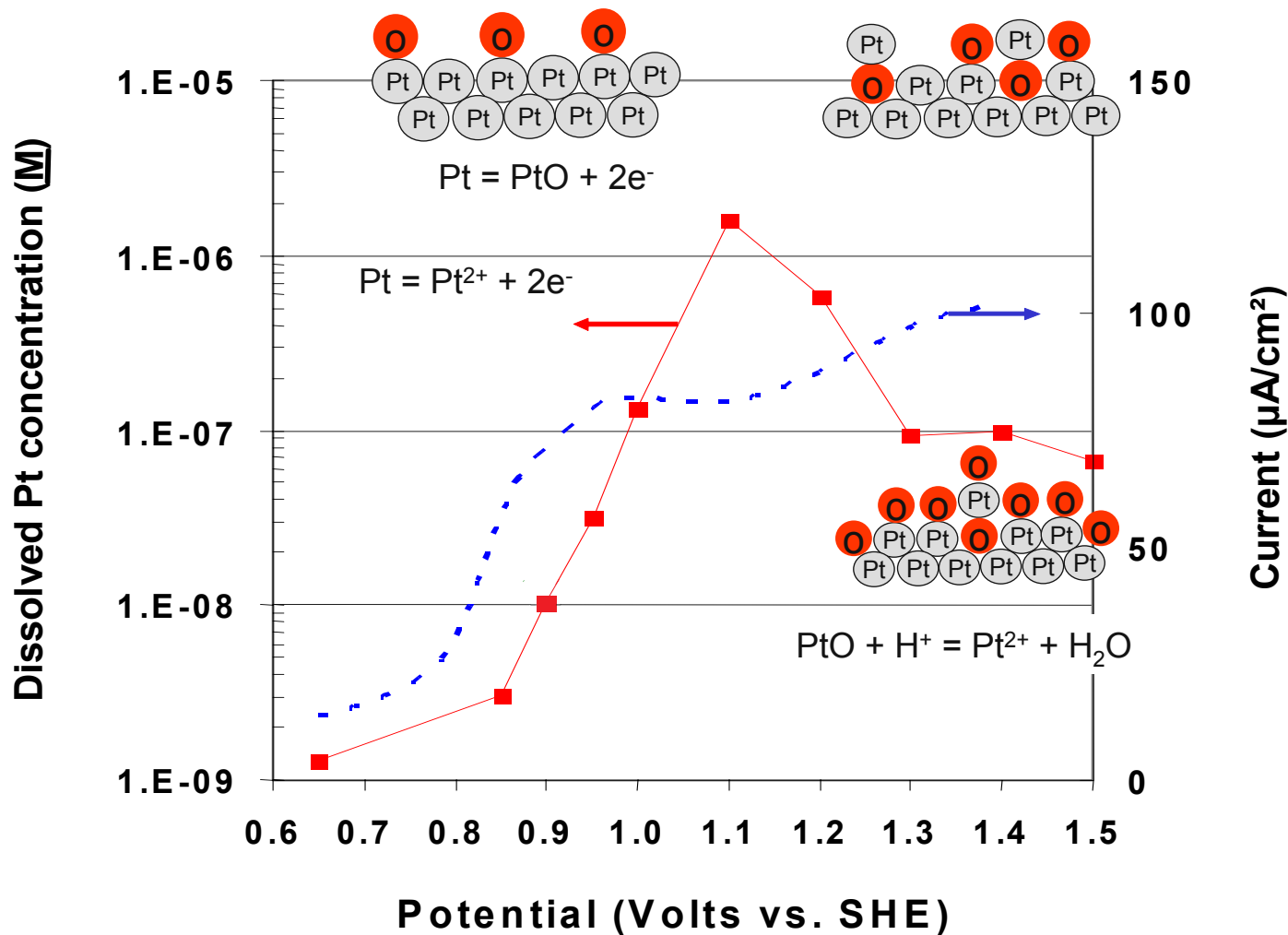


Equilibrium concentration of dissolved Pt depends on potential

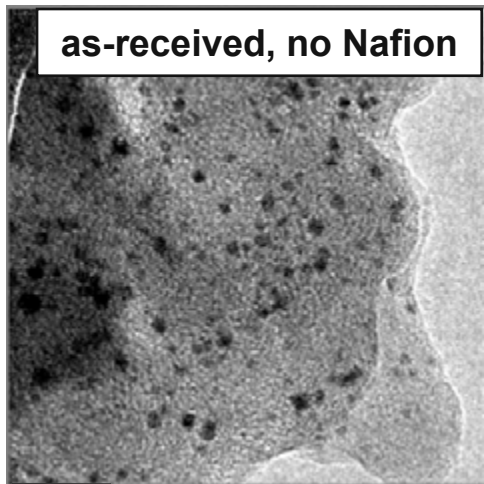
- Dissolved Pt equilibrium concentration
 - Less dependent on potential than predicted by Pourbaix diagram (in agreement with GM-MIT, Pt/C data)
 - Higher than predicted by Pourbaix diagram at < 0.95 V, less at > 0.95 V
- Both polycrystalline Pt and Pt/C showed a maximum Pt equilibrium concentration, at 1.1 V and 1.0 V, respectively
- At >1.2 V, dissolved Pt concentration decreases for polycrystalline Pt, but continues to increase for Pt/C



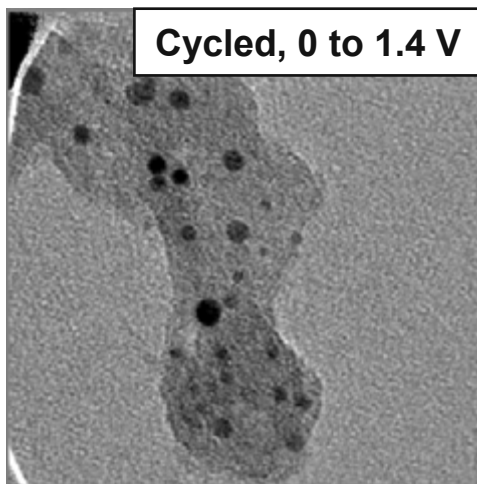
Polycrystalline Pt dissolution behavior explained by complex oxide layer formation



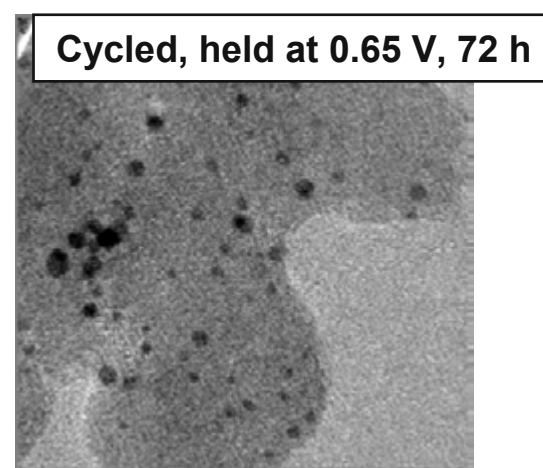
TEM analysis shows growth of Pt particles most significant during electrode prep or cycling pre-treatment



20 nm

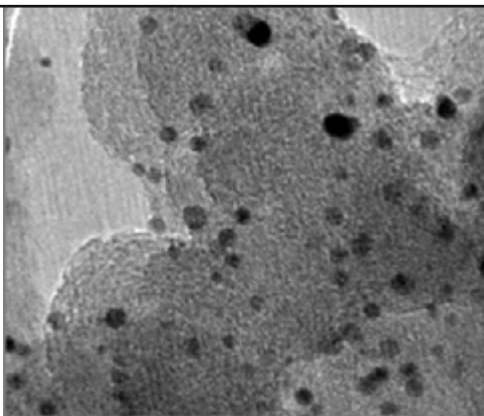


20 nm



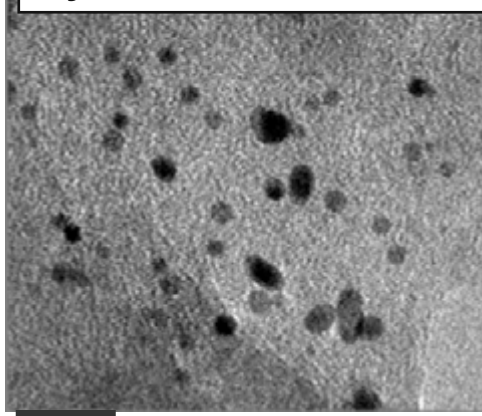
20 nm

Cycled, held at 0.9 V, 467 h



20 nm

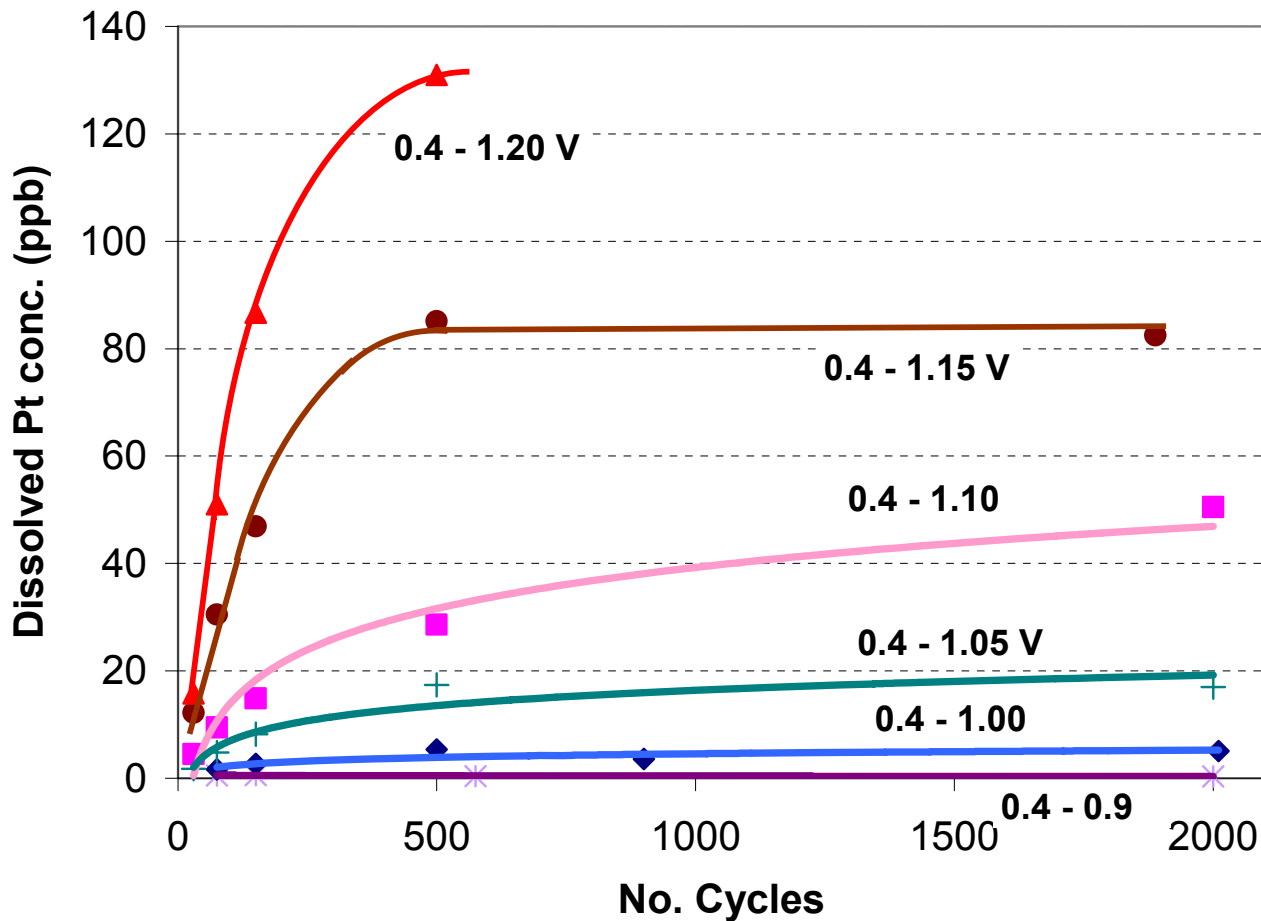
Cycled, held at 1.4 V for 72 h



20 nm

- *As-received*: 1-3 nm, 5 nm
- All other samples:
 - Increase in Pt size
 - 2-5 nm, 10 nm
- No strong effect of potential hold on particle growth

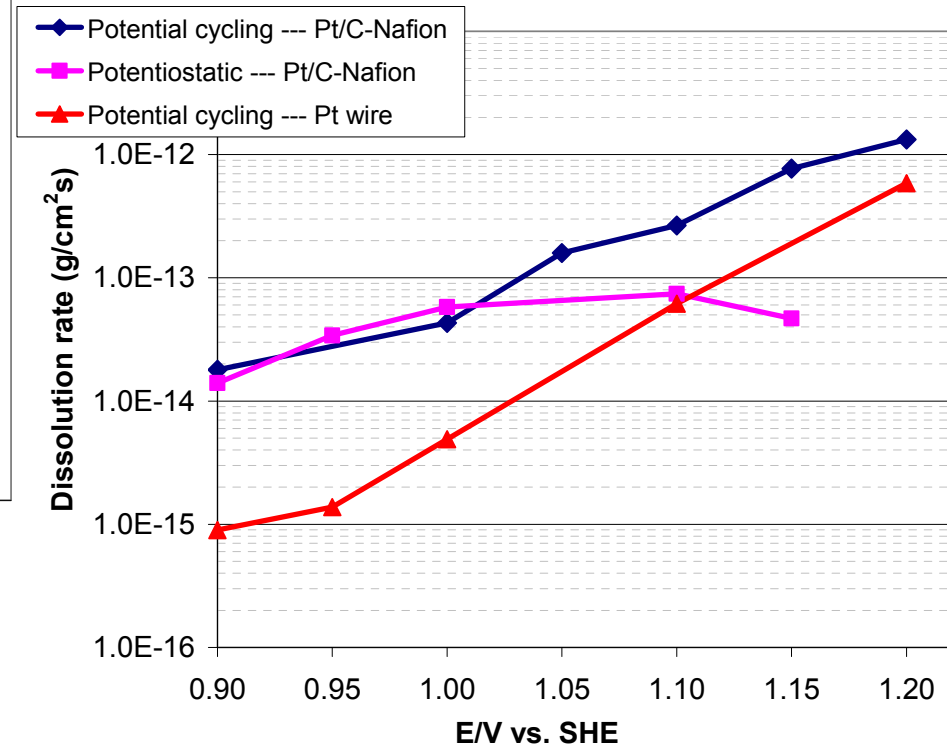
The upper limit of potential cycling strongly affects the rate of Pt dissolution



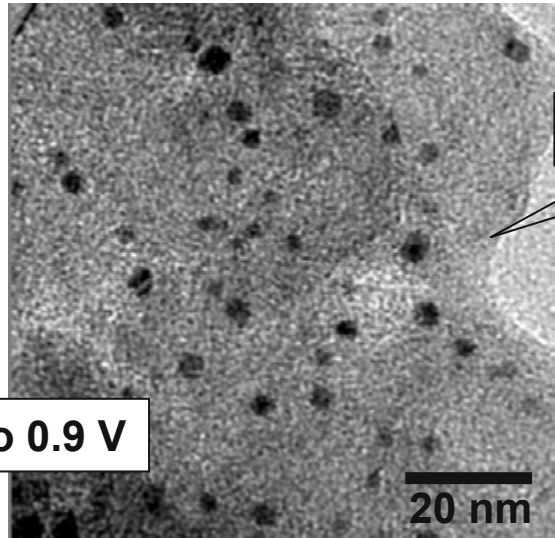
- Dissolved Pt conc.
 - Approaches steady-state value
 - Increases with the upper limit potential
- 10% Pt/C-Nafion
- 0.57 M HClO₄
- Room temperature
- 10 mV/s

Pt dissolution rate is accelerated by potential cycling to >1.0 V

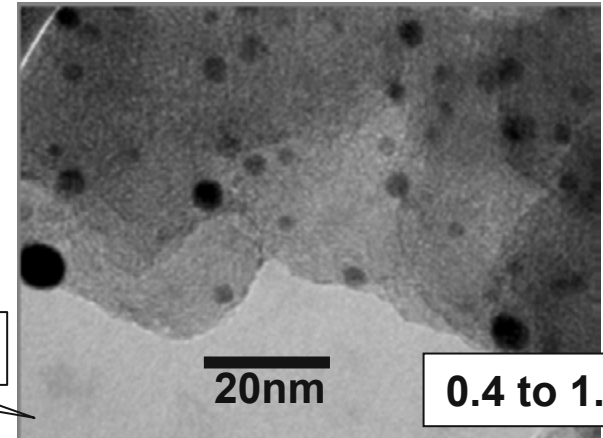
- Dissolution rate for potential cycling: Pt/C >> Pt wire



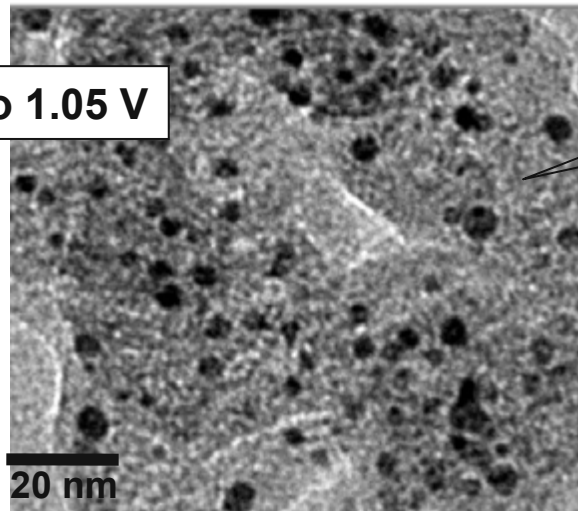
Potential cycling to higher potentials showed more extensive Pt particle growth



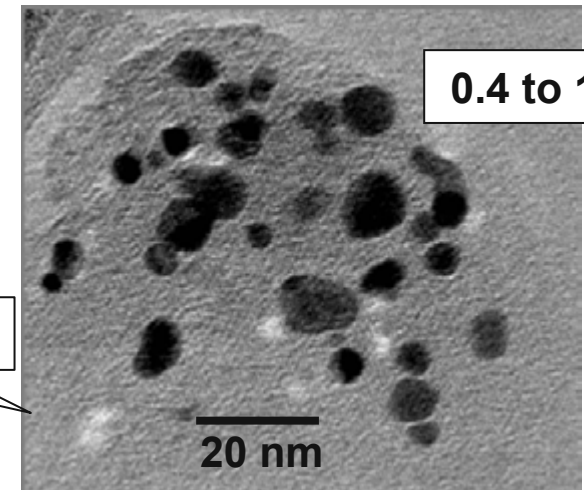
• 2 to 4 nm, 6 nm



• 2 to 6 nm, 8 nm



• 2 to 5 nm, 6 nm



• 2 to 6 nm, 10 nm

Summary

- Under potentiostatic conditions
 - Dissolved Pt equilibrium concentration is less dependent on potential than predicted by Pourbaix diagram (in agreement with GM-MIT data)
 - Dissolved Pt equilibrium concentration is higher than predicted by Pourbaix diagram at < 0.95 V, less at > 0.95 V
 - Both Pt wire and carbon-supported Pt nanoparticles (Pt/C) showed a maximum Pt equilibrium concentration, at 1.1 V and 1.0 V, respectively
 - At > 1.2 V, dissolved Pt concentration decreases for Pt wire, but continues to increase for Pt/C
 - The dissolution rates at 0.9 V for Pt wire and Pt/C are comparable

Summary (cont.)

■ Under potential cycling conditions

- Pt/C: concentration of dissolved Pt increased with increasing upper potential limit
- Pt/C and Pt wire: higher dissolution rate with increasing upper potential limit

■ Potential Cycling vs. Potentiostatic

- Dissolution rate increased with the upper limit potential for potential cycling, but showed a maximum for potentiostatic condition
- At > 1.02 V, higher dissolution rate for potential cycling than for potentiostatic condition
- At < 1.02 V, lower dissolution rate for potential cycling than for potentiostatic condition
- Pt/C yielded much higher Pt dissolution rates than Pt wire

Response to FY '05 Reviewers' Comments

- “Project should expand to include drier conditions and polymer electrolyte interface“
- “Probably needs to find ways to do this with more realistic conditions next”
 - These will be addressed in the second phase of the project
 - *Membrane-electrode assemblies*
 - *In sulfonic acid medium*
- “Extrapolations of the present corrosion results for real systems are required”
 - Work scope will include a modeling effort to correlate Pt dissolution data with published single cell and stack data (e.g., LANL data)

Future work

- Pt/C high surface area electrode (E-Tek) in HClO_4
 - Finish determining potential cycling effect with higher upper-limit potentials (1.3 – 1.5 V)
 - *TEM for Pt particle size and support change*
 - Effect of atmosphere (air and hydrogen)
 - Effect of temperature (room temperature to 120°C)
- $\text{Pt}_3\text{Co}/\text{C}$ high surface area electrode (Tanaka) in HClO_4
 - Potential (0.65-1.4 V)
 - Potential cycling (0.4 V to 1.4 V)
 - Atmosphere (air and hydrogen)
 - Temperature (room temperature to 120°C)
- Particle size, oxidation state, and distribution of platinum in MEA under varied experimental conditions (e.g, potentiostatic, potential cycling, different atmosphere, and temperature)



Acknowledgments

- Jennifer Mawdsley and Nancy Kariuki for TEM work
- Y. Tsai and Argonne's Analytical Chemistry Laboratory for ICP-MS analyses

Publications/Presentations

- “Effect of Voltage on Dissolution of Pt, Relevance to Polymer Electrolyte Fuel Cells”, Xiaoping Wang, Romesh Kumar, and Deborah J. Myers, *Electrochem. and Solid-State Letters*, 9 (5), A225-A227 (2006)
- “Fundamental Studies of Platinum Electrocatalyst Degradation”, Xiaoping Wang, Deborah J. Myers, and Romesh Kumar, Fuel Cell Durability 2005, Washington, DC, December 8-9, 2005
- “Polymer Electrolyte Fuel Cell Cathode Electrocatalysts”, Xiaoping Wang, Romesh Kumar, and Deborah J. Myers, Poster and Abstract, 2005 Fuel Cell Seminar, Palm Springs, CA, November 14-18, 2005