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# *Non-Platinum Bimetallic Cathode Electrocatalysts*

*Debbie Myers*

*Argonne National Laboratory*

*2007 DOE Hydrogen Program Review*

*Arlington, VA, May 15-18, 2007*



U.S. Department  
of Energy

UChicago ►  
Argonne<sub>LLC</sub>



A U.S. Department of Energy laboratory  
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Project ID:  
FCP28

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# Overview

## Timeline

- **Project start data:**  
January, 2007
- **Project end data:**  
December, 2010
- **Percentage complete:**  
10%

## Budget

- **Total project funding:**
  - DOE: \$5,434 K
  - Contractor share: \$172 K
- **Funding received for FY'07:**
  - DOE: \$945 K
  - Contractor share: \$29 K

## Barriers

- **Barriers addressed**
  - A. Durability
  - B. Cost
  - C. Electrode performance

## Partners

- William A. Goddard, III, California Institute of Technology (Caltech)
- John Regalbuto, University of Illinois at Chicago (UIC)
- Clemens Heske, University of Nevada at Las Vegas (UNLV)
- Karren More, Oak Ridge National Laboratory (ORNL)
- Piotr Zelenay, Los Alamos National Laboratory (LANL)

# Objectives

- Develop a non-platinum cathode electrocatalyst for polymer electrolyte fuel cells to meet DOE targets that:
  - Promotes the direct four-electron oxygen reduction reaction (ORR) with high electrocatalytic activity  
(**0.44 A/mg<sub>PGM</sub>; 720 μA/cm<sup>2</sup> @0.9 V<sub>iR-free</sub>**)
    - *O<sub>2</sub> reduction reaction (ORR) in acidic media*
      - *Two-electron transfer*  
$$\text{O}_2 + 2\text{H}^+ + 2\text{e}^- = \text{H}_2\text{O}_2$$
      - *Four-electron transfer*  
$$\text{O}_2 + 4\text{H}^+ + 4\text{e}^- = 2 \text{H}_2\text{O}$$
  - Is chemically compatible with the acidic electrolyte and resistant to dissolution  
(**<40% electrochemical area loss over 5000 h@≤80°C and 2000 h@>80°C**)
  - Is low cost (**\$5/KW, 0.3 mg PGM/cm<sup>2</sup>**)
- FY'07 Objective
  - Synthesize and evaluate the oxygen reduction activity and stability of nanoparticles of three palladium alloy systems

# Approach

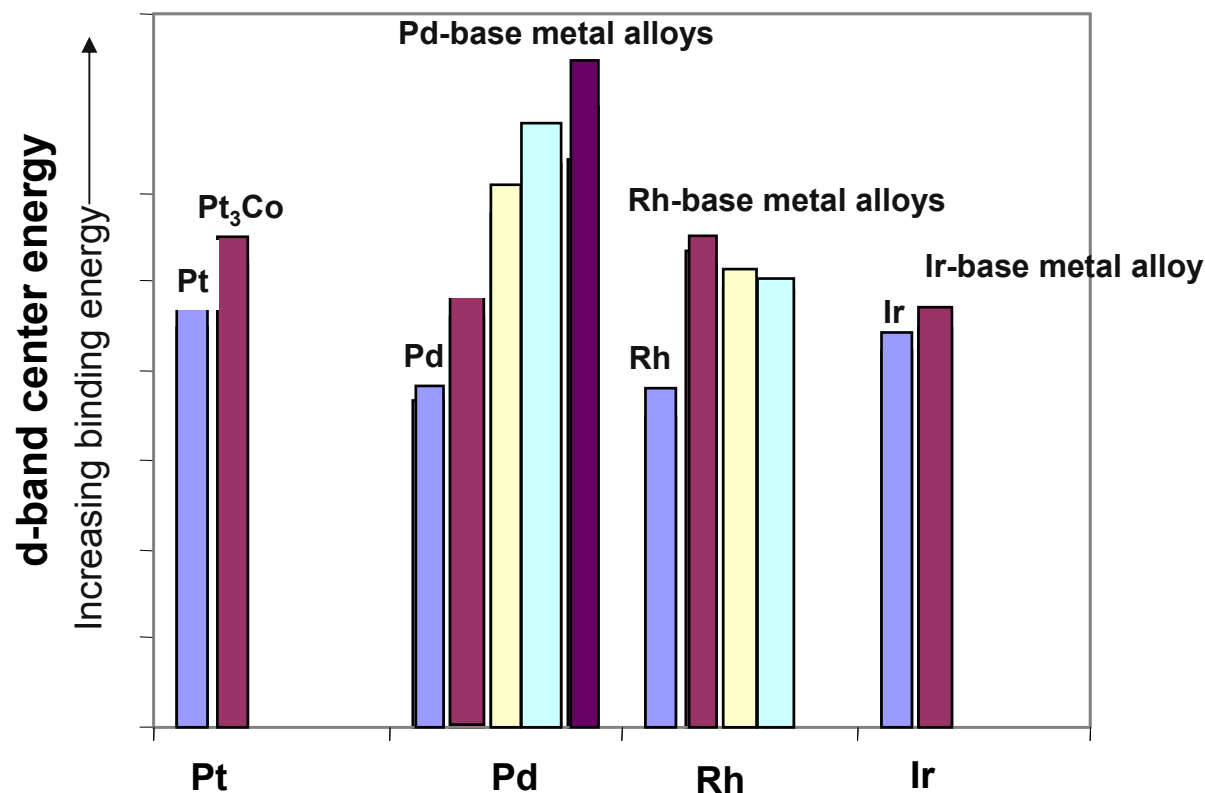
- Bimetallic systems (base metal-noble metal)
  - Surface segregation of minor noble metal component to form protective layer
  - Base metal component chosen to modify d-band center of noble metal making it more “Pt-like”
  - Choice of bimetallic systems is based on surface segregation energies and d-band center shift
  - Examples: Bimetallics of palladium, iridium, and rhodium
  
- How this project addresses the technical barriers
  - A. Durability: altering oxophilicity of catalyst to prevent oxidation-related degradation
  - B. Cost: lowering PGM loading by replacing PGM in electrocatalyst particle core with base metal
  - C. Electrode performance: modifying surface electronic properties to enhance ORR activity

## ***Noble metals were chosen based on stability and tendency to form surface “skins”***

- Noble metals are the most stable in acidic environment
  - Pd  $E^{\circ}$  for dissolution = 0.987 V
  - Rh  $E^{\circ}$  for dissolution = 0.76 V
  - Ir  $E^{\circ}$  for dissolution = 1.156 V
  - Pt  $E^{\circ}$  for dissolution = 1.188 V
- Base metals were chosen due to their ability to modify the electronic properties of the noble metal and for the tendency of the noble metal to form a protective skin on the noble metal-base metal alloy
- Tendencies of noble metals to segregate to the surface of base metal hosts have been calculated by J. Nørskov and co-workers [A.V. Ruban, H.L. Skriver, J.K. Nørskov, Phys. Rev. B, 59 (1999)15990.]

## The d-band centers of candidate noble metals can be shifted towards desired values by alloying with base metals

- There is a relationship between the d-band center of the metal and its ORR activity - Nørskov-Hammer theory and results of LBNL group
- Pt<sub>3</sub>Co has desirable d-band center and thus a high ORR activity (LBNL)

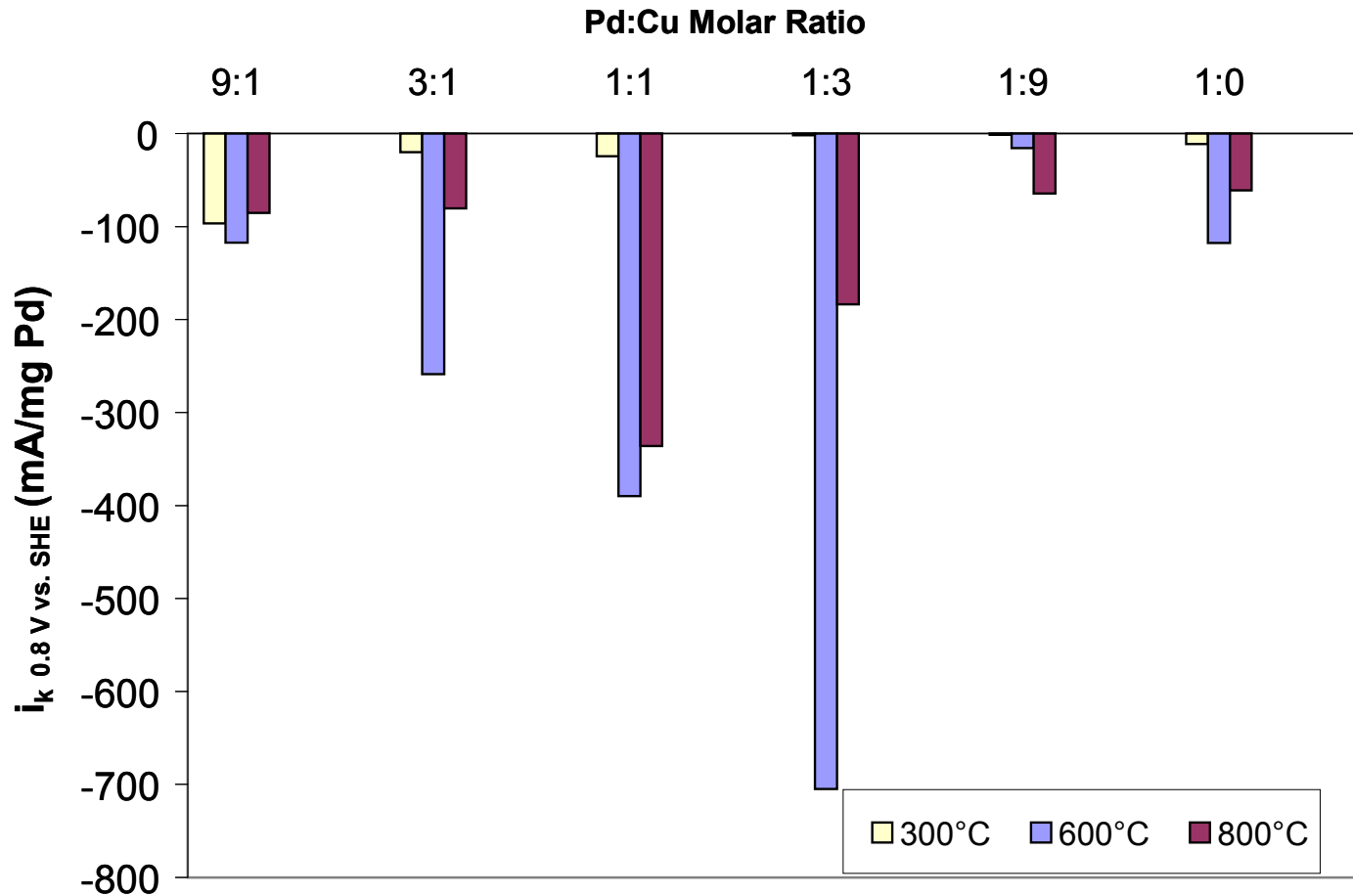


## Project tasks

- Perform computational studies to guide choice of systems and compositions (Caltech)
- Fabricate and characterize model systems-bulk electrodes to guide choice of systems and compositions (UNLV, Argonne)
- Synthesize nano-particles on high-surface-area carbon support (Argonne, UIC)
- Characterize nano-particle ORR activity, composition, electronic structure, and morphology (Argonne, ORNL, UNLV, UIC)
- Determine stability via dissolution measurements, mechanisms of degradation, and predict lifetime via modeling (Argonne)
- Fabricate, test, and characterize membrane-electrode assemblies with newly-developed electrocatalyst (LANL, ORNL)
  - determine performance and durability using accelerated test protocol

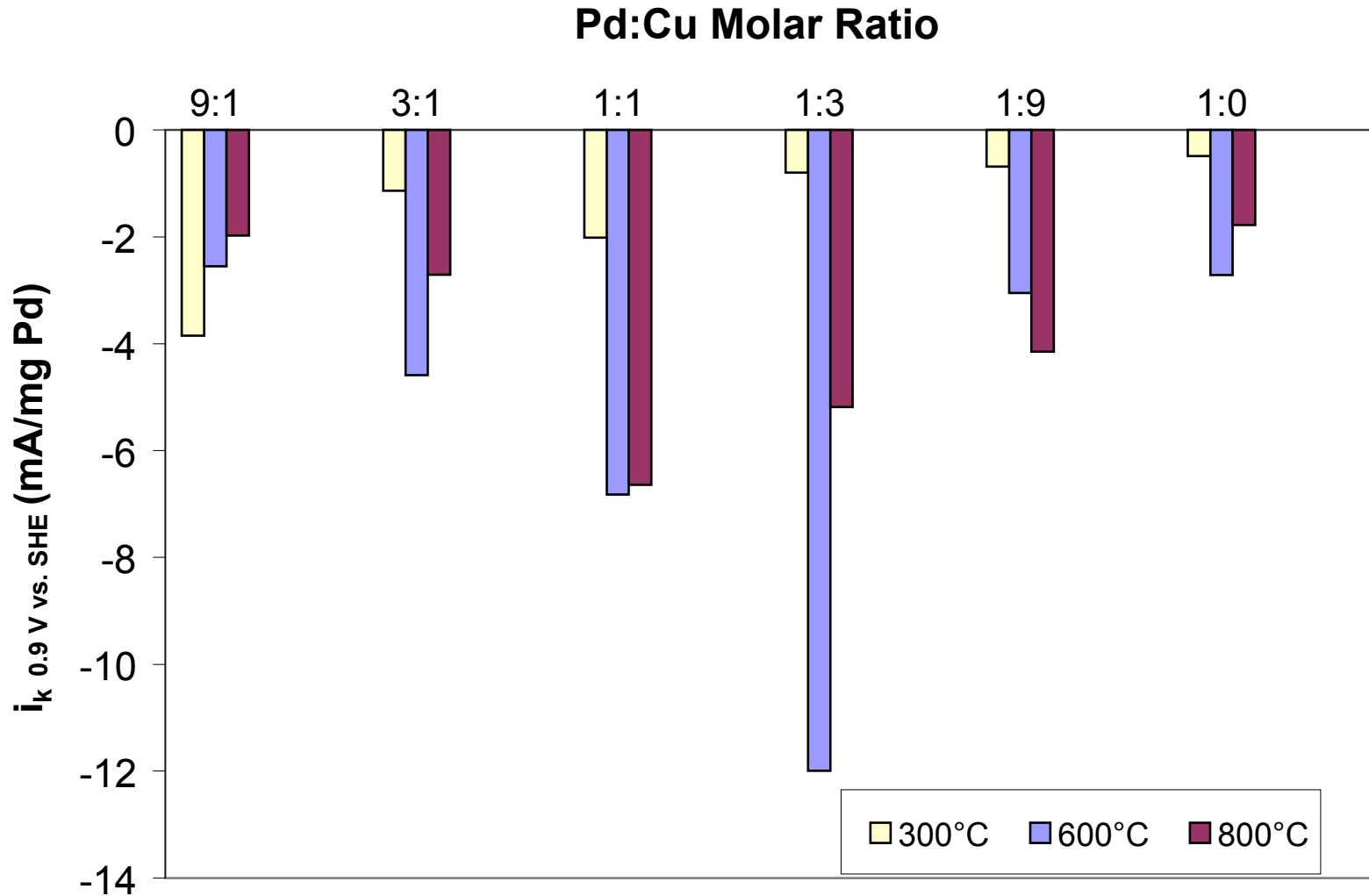
# Oxygen reduction activity is highly dependent on Pd:Cu ratio and post-deposition heat treatment (0.8 V, room temp.)

- Catalysts prepared by co-impregnation of Vulcan carbon with metal precursors and post-deposition heat treatment in a reducing atmosphere

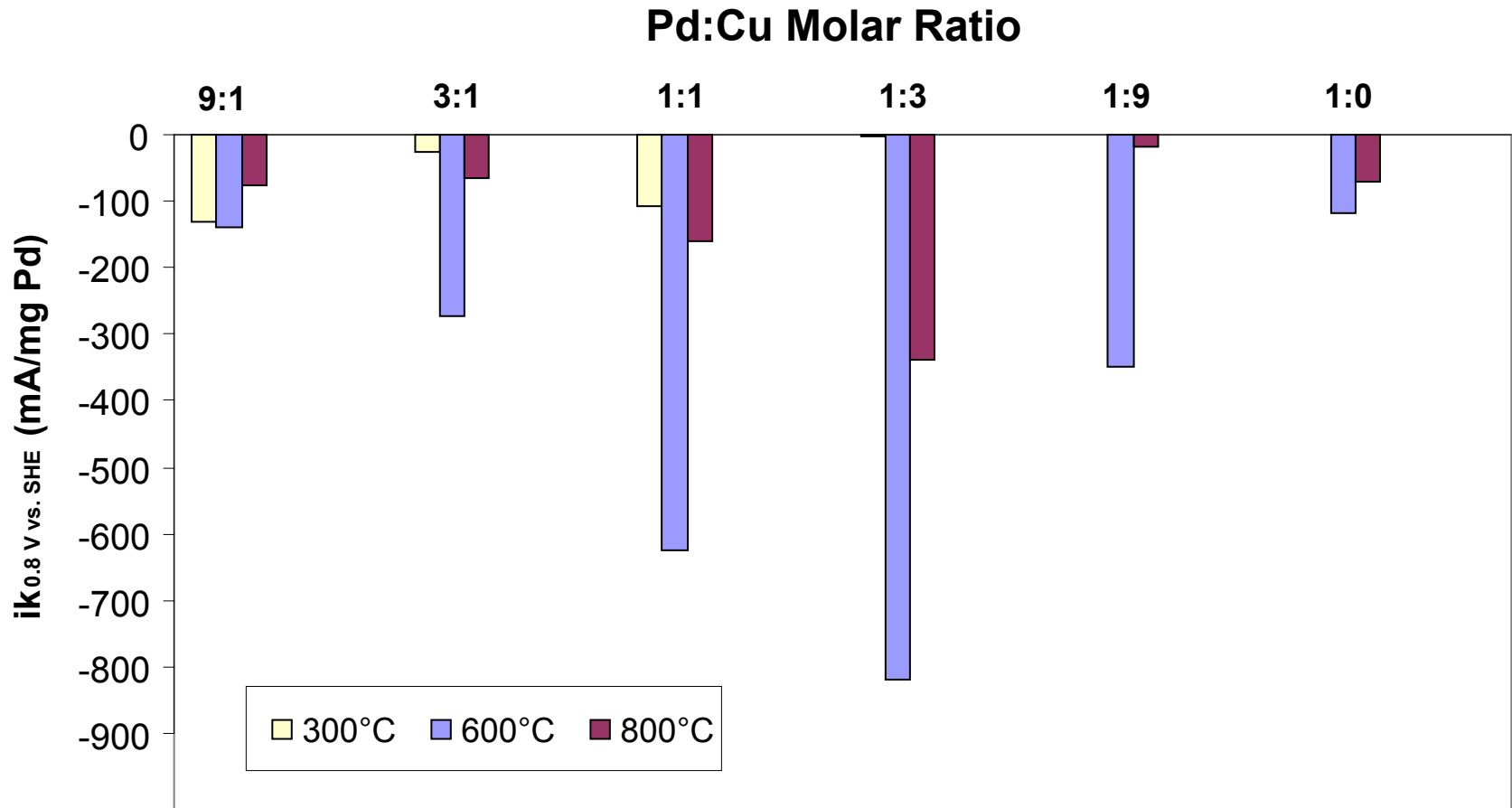




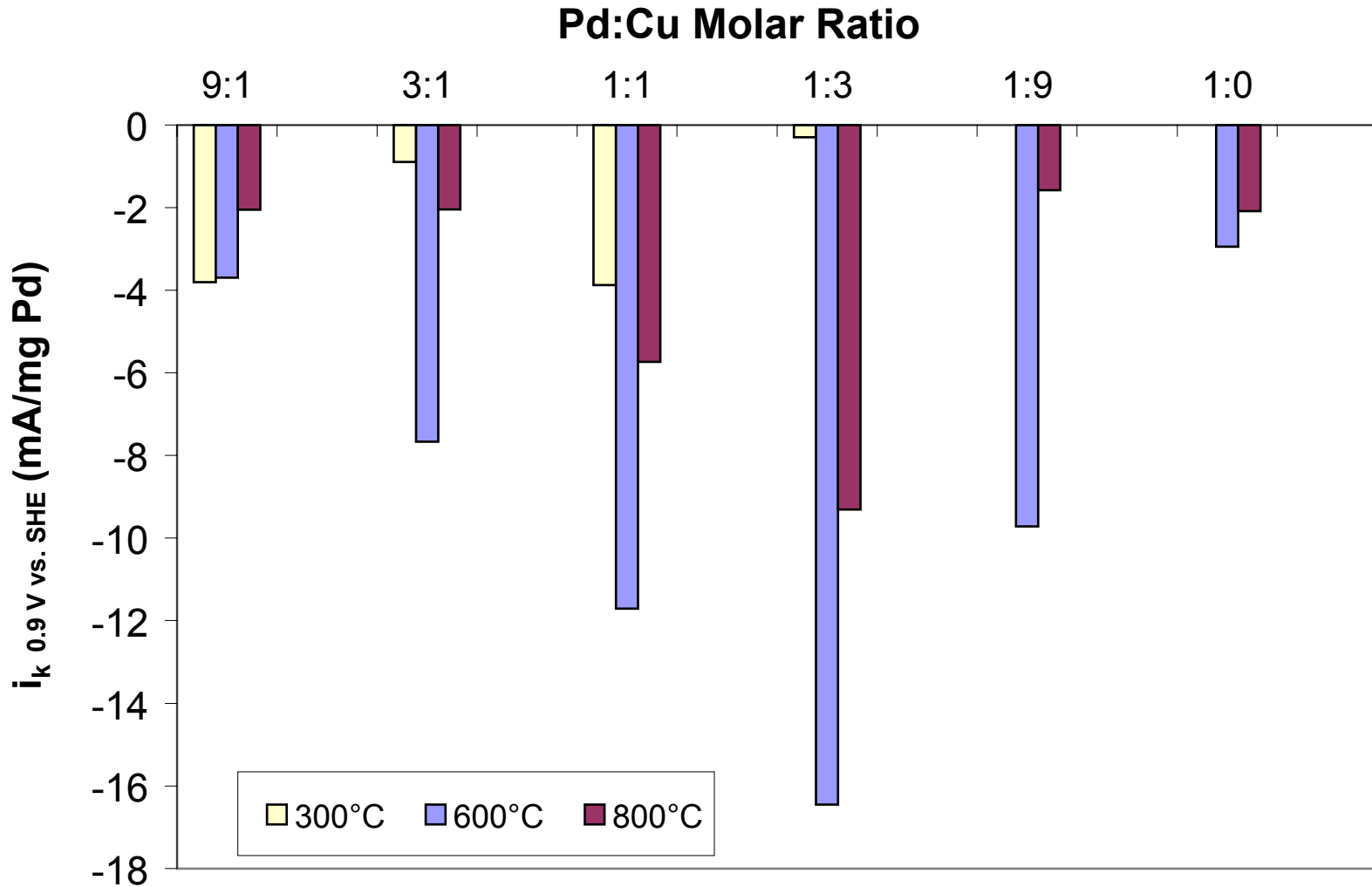
# Oxygen reduction activity is highly dependent on Pd:Cu ratio and post-deposition heat-treatment (0.9 V, room temp.)



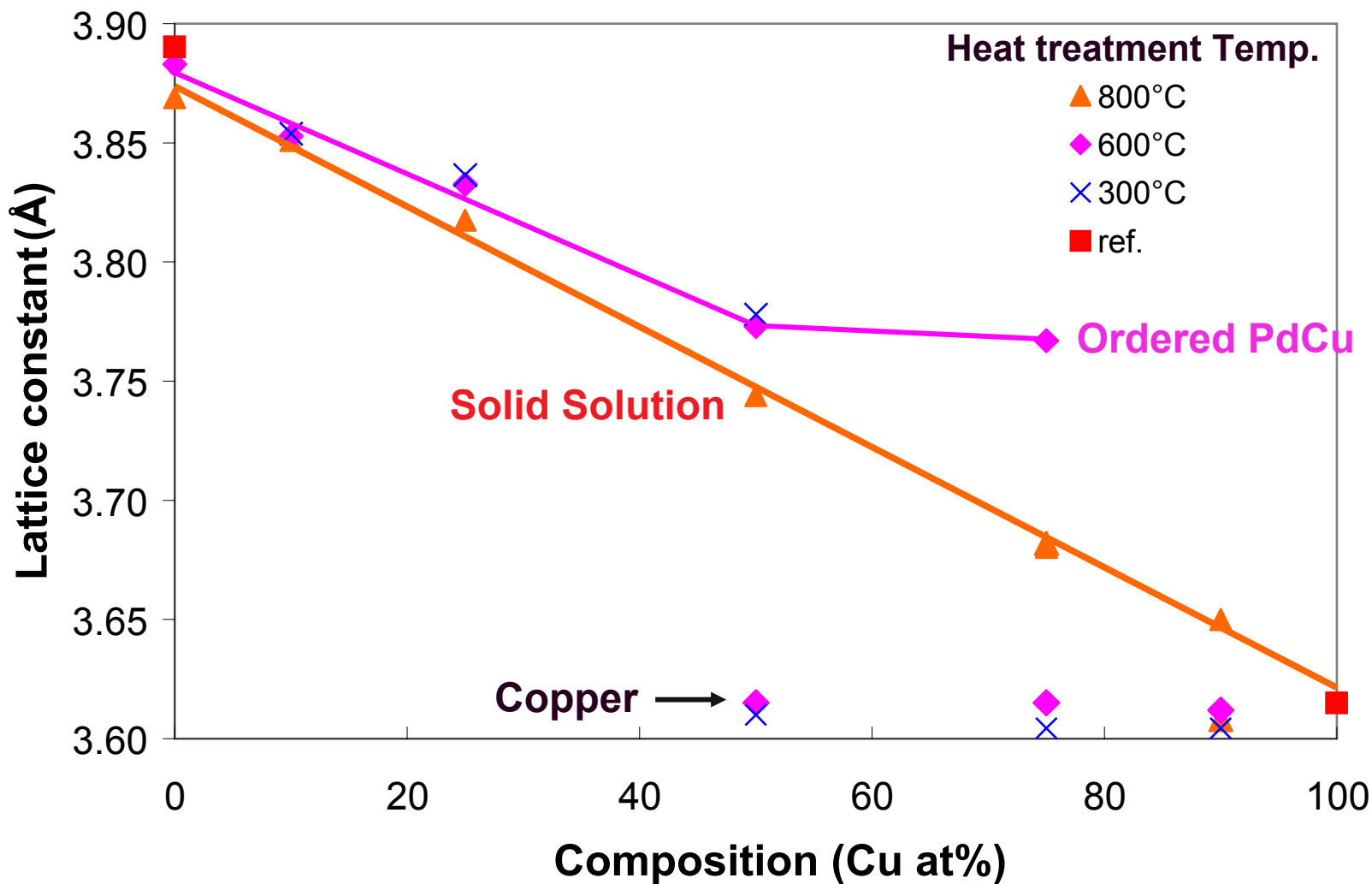
# Post-heat treatment acid treatment improved oxygen reduction activity of Pd:Cu catalysts (0.8 V, room temp.)



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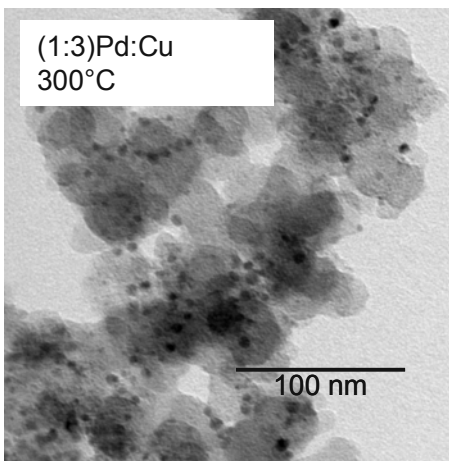


# Highest ORR activity was seen for catalysts showing formation of ordered PdCu phase

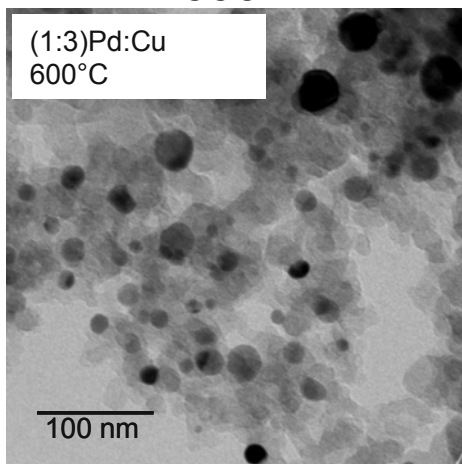


# Co-impregnation synthesis technique leads to large poly-disperse alloy particles

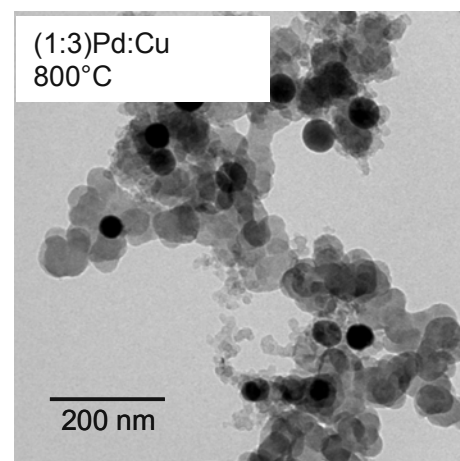
300°C



600°C



800°C



Pd: Cu Molar Ratio	Particle size (nm)		
	300°C	600°C	800°C
1:9	10.8 ± 2.1	17.2 ± 3.3	46.3 ± 11.2
1:3	8.1 ± 2.8	23.3 ± 8.3	55.0 ± 14.5
1:1	6.1 ± 1.6	21.0 ± 5.1	69.8 ± 18.1
3:1	9.1 ± 3.3	21.8 ± 5.5	68.3 ± 10.7
9:1	6.5 ± 1.8	21.9 ± 4.9	73.5 ± 15.4

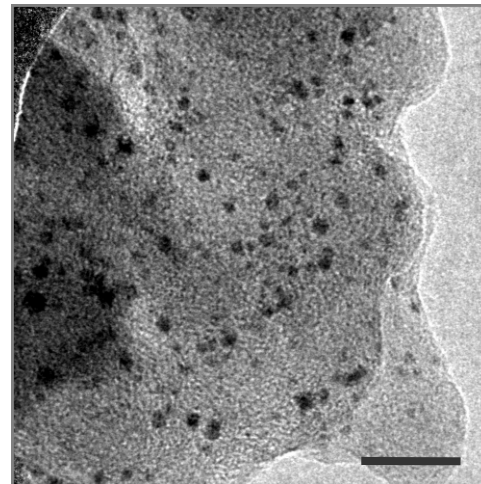
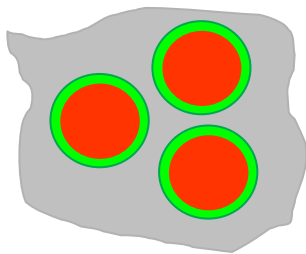
# Synthesis of nano-particle bimetallic carbon-supported electrocatalysts

## ■ Goals

- Achieve noble metal-base metal bimetallic core with noble metal skin
- Minimize particle size, maximize surface area/gram PGM
- Achieve uniform and controllable particle size and composition

## ■ Techniques

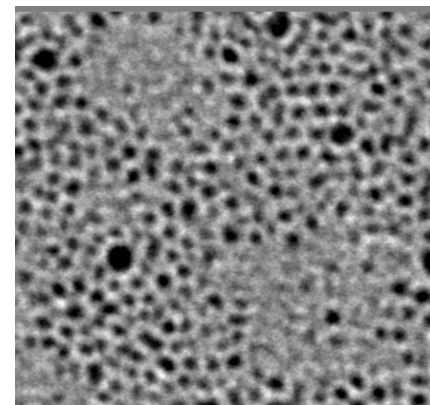
- Colloidal synthesis
- Strong electrostatic adsorption



20 nm

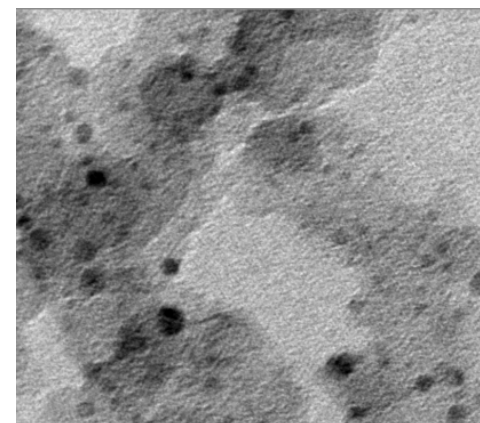
# *Single-phase colloidal technique is being developed to form mono-disperse bimetallic nano-particles (Argonne)*

- Chemical reduction of metal precursors in the presence of organic capping molecules (e.g., oleylamine and oleic acid)
  - ✓ capping molecules stabilize small particles, limit particle growth
- Pre-formed particles loaded on carbon support
  - ✓ capping molecules maintain particle dispersion
- Removal of capping molecules through thermal or electrochemical decomposition
  - ✓ capping molecules can be removed at moderate temperatures



50 nm

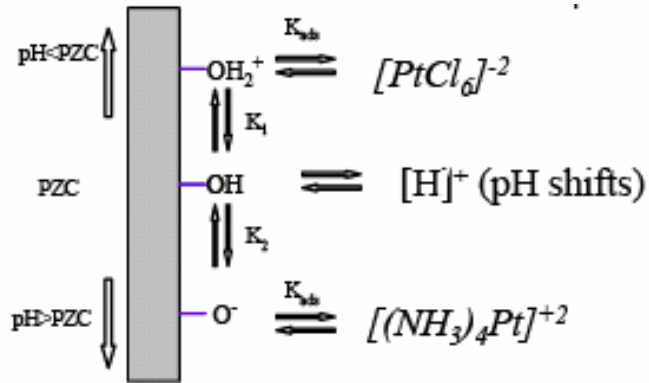
Unsupported Pd-Base Metal



50 nm

Pd-Base Metal/C

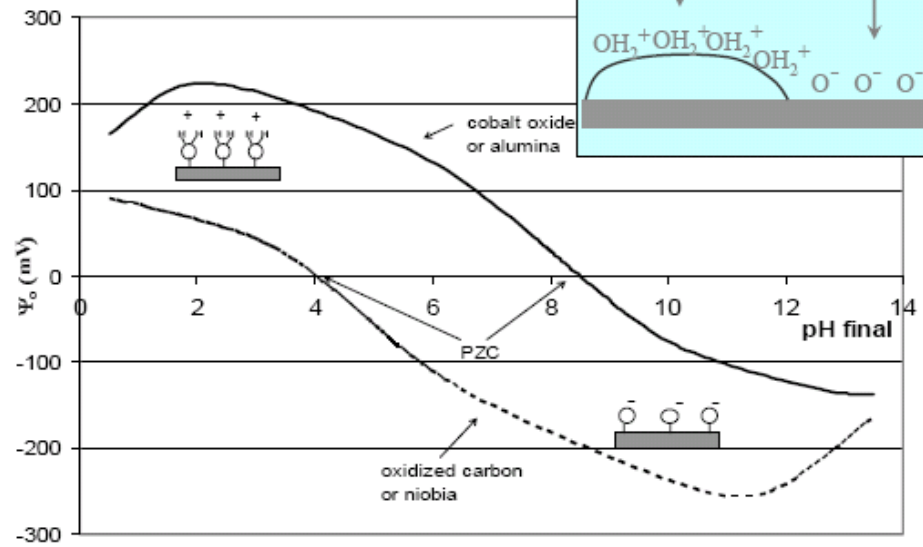
# Strong electrostatic adsorption technique for synthesis of core-shell bimetallic nano-particles (UIC)



- SEA technique has been demonstrated by UIC for Pt-Co bimetallics

- Impregnate at pH between pHs of zero charge (PZCs) for selective adsorption and formation of bimetallics

## SEA for Mixed Oxides, Bimetallics



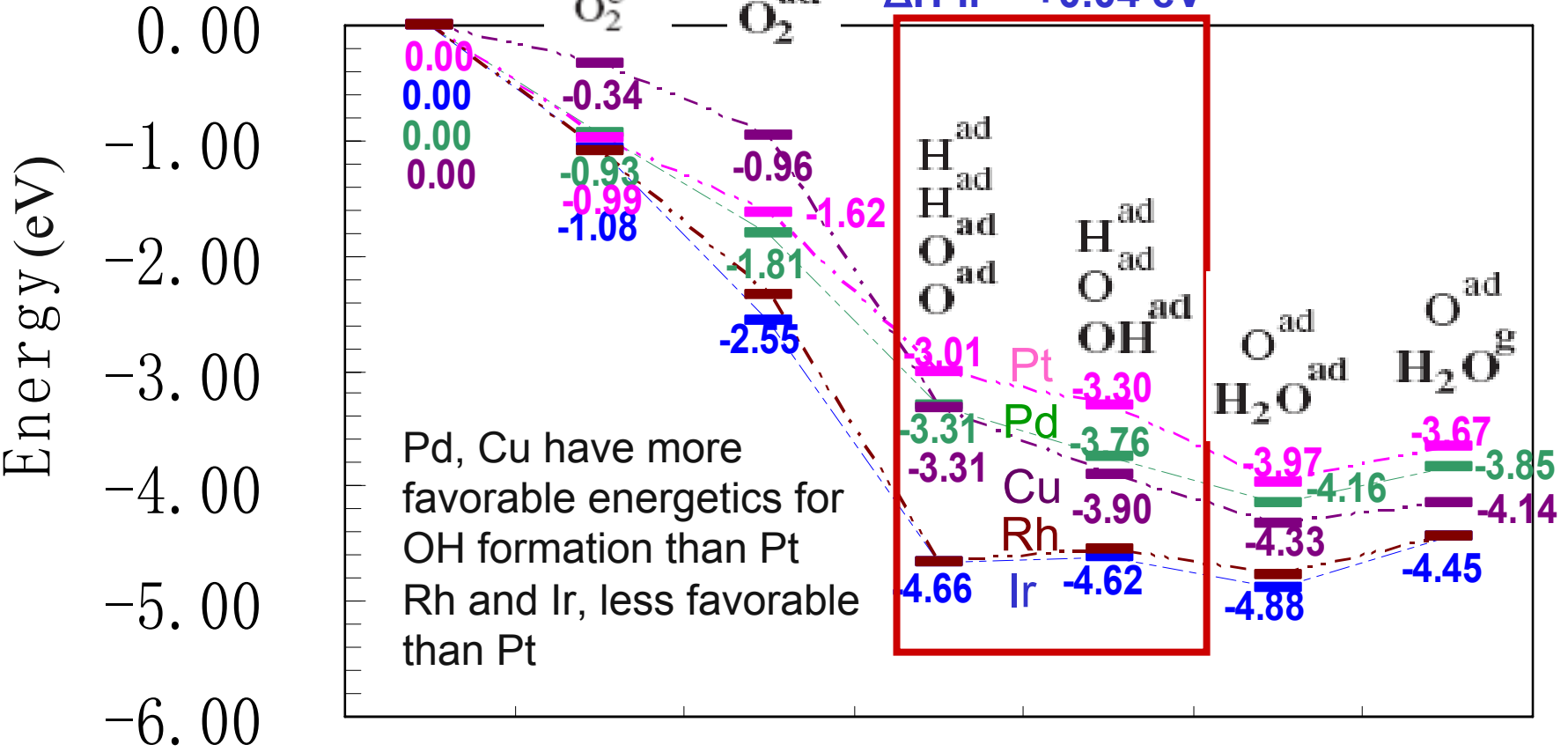


# *Computational analyses are being used to guide the choice of bimetallic systems and compositions (Caltech)*

- Quantum mechanical calculations
  - Detailed reaction mechanisms and rate-limiting processes
  - Binding energies and structures for possible intermediates (i.e., O, H, O<sub>2</sub>, H<sub>2</sub>, OH, OOH, H<sub>2</sub>O)
  - How alloying and nano-structure affect the ORR rates
- Large-scale molecular dynamics simulations using ReaxFF
  - Trends in chemisorption energies of oxygen-containing species
  - Effect of nano-particle size, alloying elements, surface defects and segregations, step edges, and kinks on the barriers and rates of the ORR

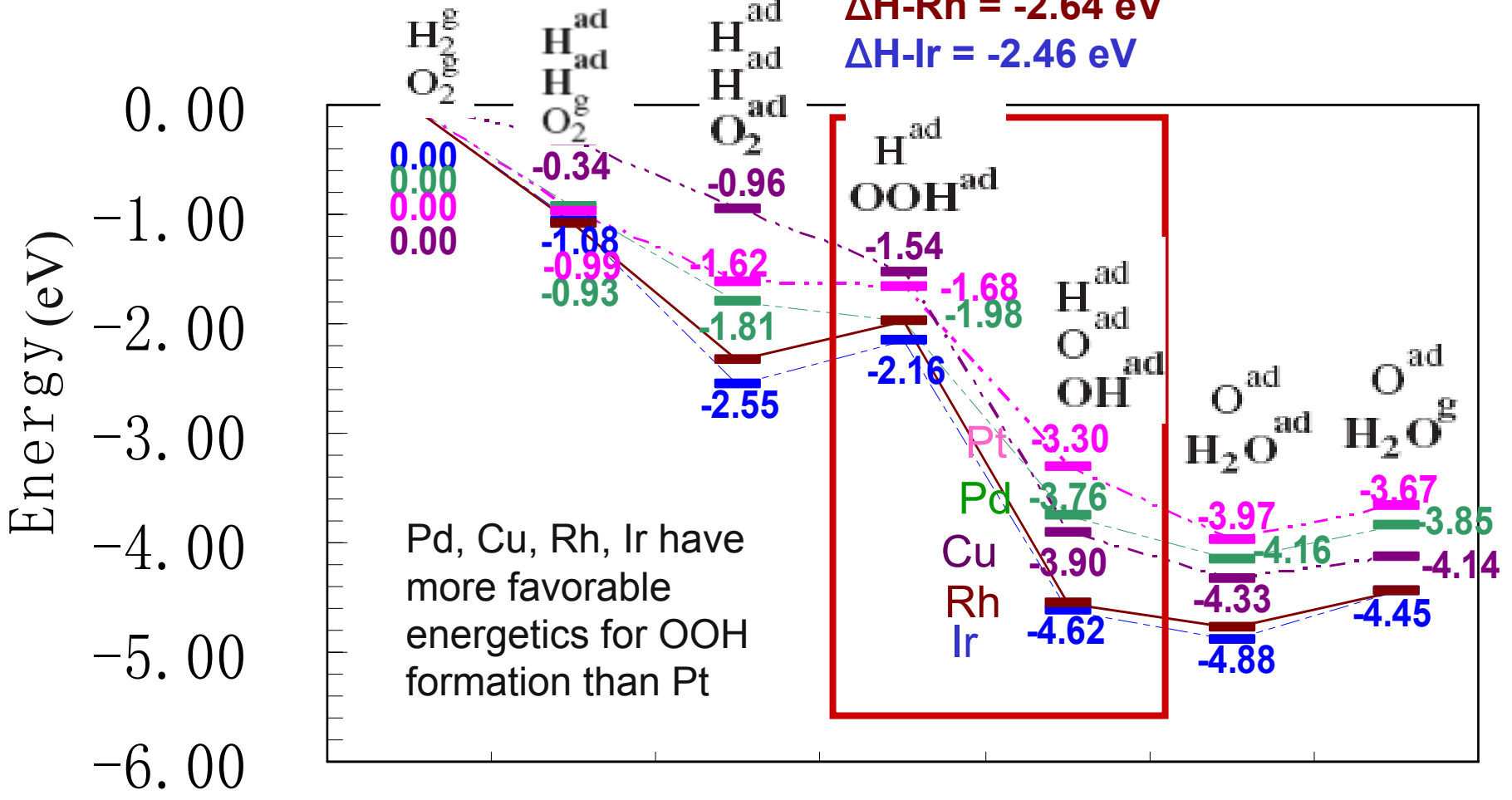
# Comparison of the energetics of O<sub>2</sub> reduction via OH formation on candidate metals (Caltech)

- $\Delta H\text{-Pt} = -0.29 \text{ eV}$
- $\Delta H\text{-Pd} = -0.45 \text{ eV}$
- $\Delta H\text{-Cu} = -0.59 \text{ eV}$
- $\Delta H\text{-Rh} = +0.08 \text{ eV}$
- $\Delta H\text{-Ir} = +0.04 \text{ eV}$



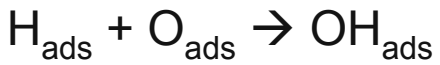
# Comparison of the energetics of O<sub>2</sub> reduction via OOH formation on candidate metals (Caltech)

$\Delta H\text{-Pt} = -1.62 \text{ eV}$   
 $\Delta H\text{-Pd} = -1.78 \text{ eV}$   
 $\Delta H\text{-Cu} = -2.36 \text{ eV}$   
 $\Delta H\text{-Rh} = -2.64 \text{ eV}$   
 $\Delta H\text{-Ir} = -2.46 \text{ eV}$

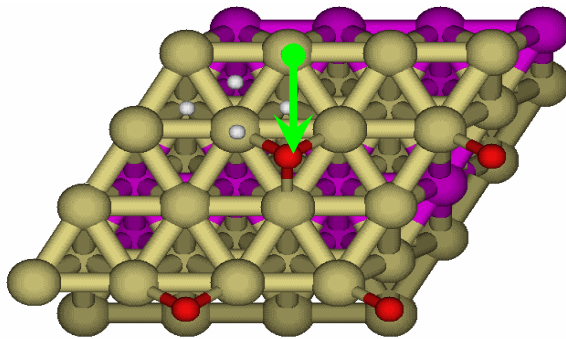


# Calculated barrier for OH formation is lowest on Pd (Caltech)

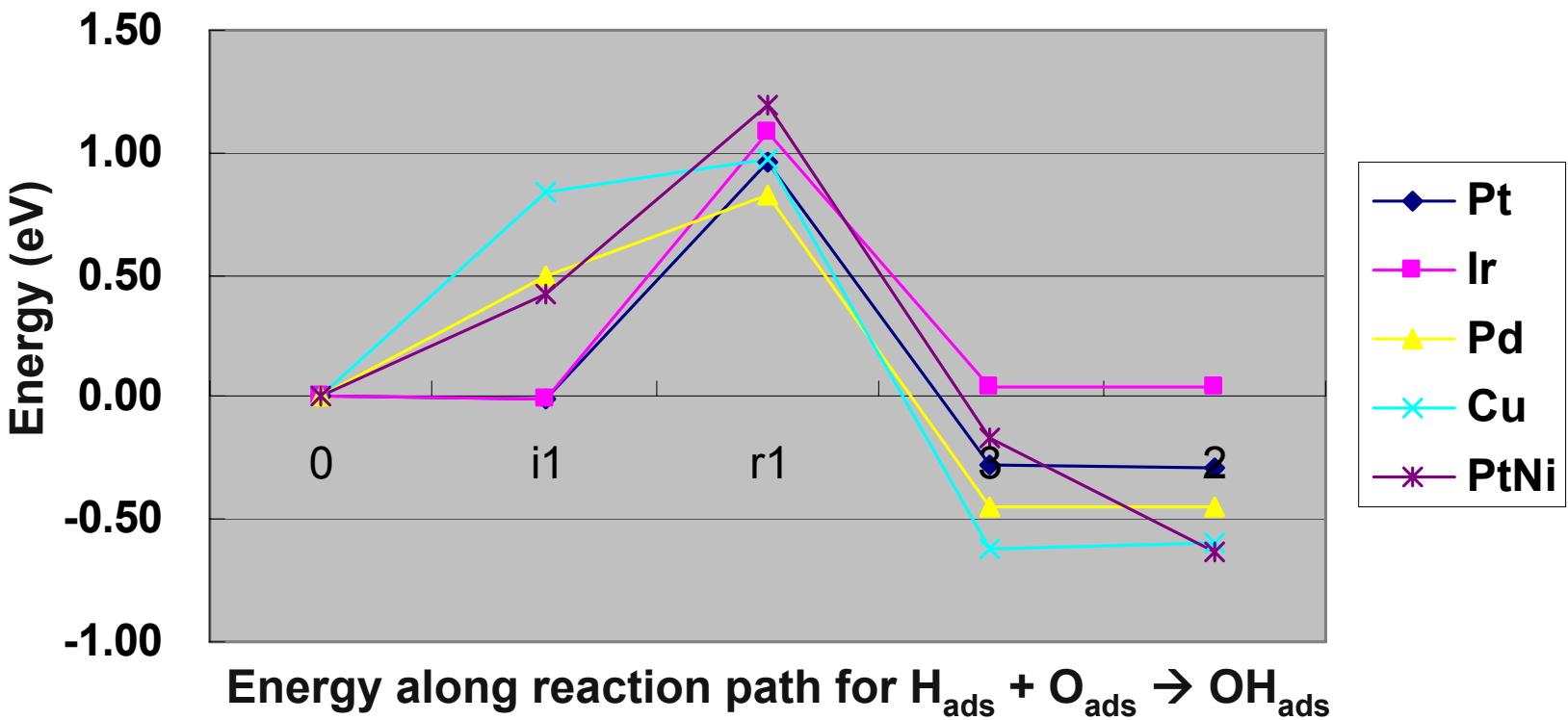
- Calculations on Pt indicate that the rate determining step is:



- Pd has the lowest barrier for this step compared to the pure metals Pt, Ir, and Cu and to Pt<sub>3</sub>Ni alloy (along  $\mu_{2/3}$ )

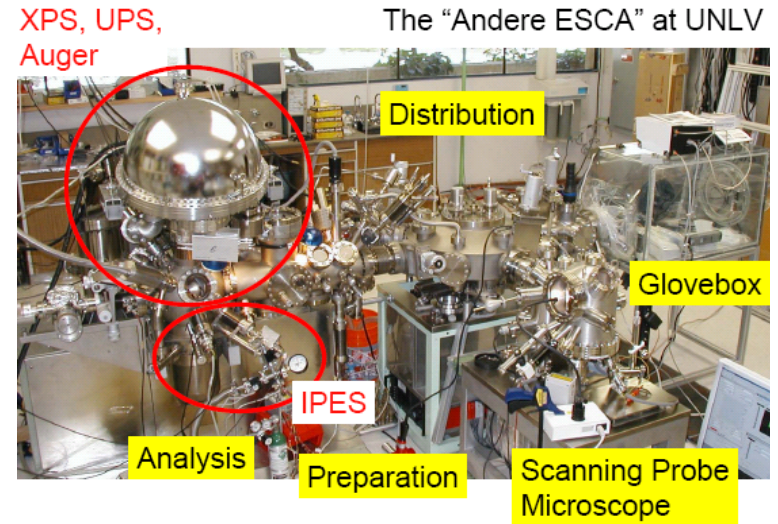


Pathway for Pt<sub>3</sub>Ni alloy



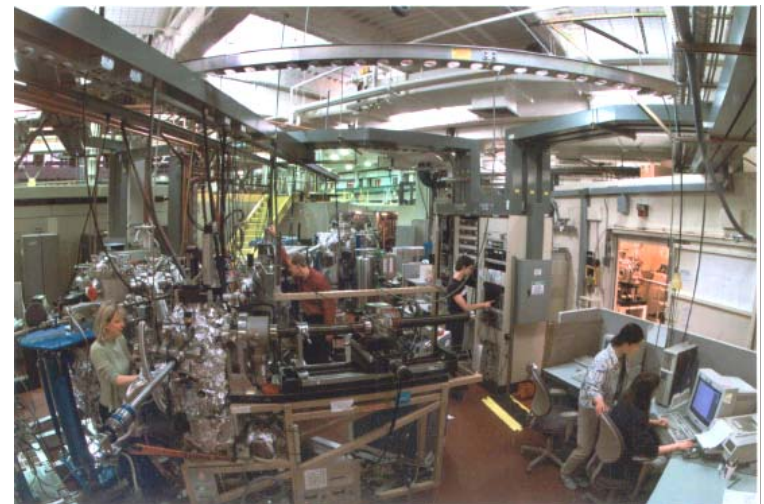
# Model systems (bulk electrodes) will be used to guide the choice of bimetallic systems (UNLV)

- Used to establish relationship between physicochemical properties and ORR activity
- Model systems
  - Fabrication by e-beam evaporation
  - Surface composition verification by XPS
- Electronic characterization (UPS, IPES, STS, KPFM)
  - Energy of d-band
  - Density of occupied and unoccupied electronic states
- Oxygen reduction activity, reaction mechanism, and stability
  - Electrochemical measurements via hanging meniscus technique
  - Post-test spectroscopic and microscopic characterization to determine changes in composition, morphology, and electronic properties



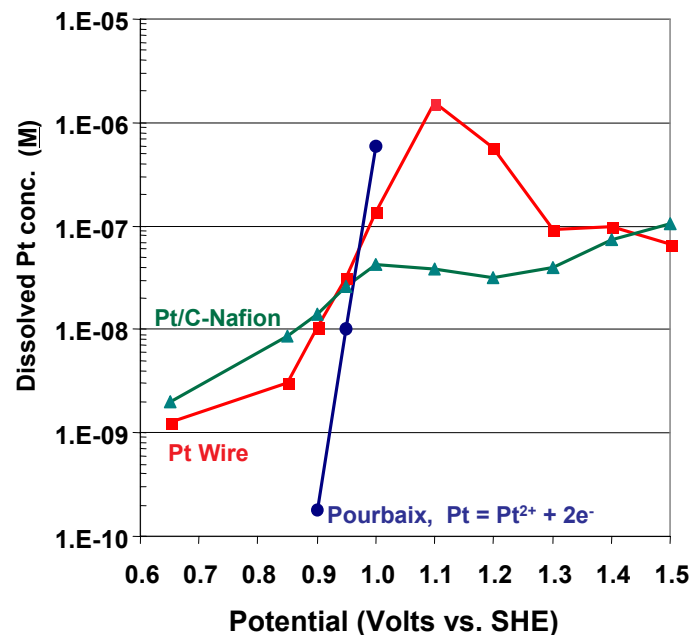
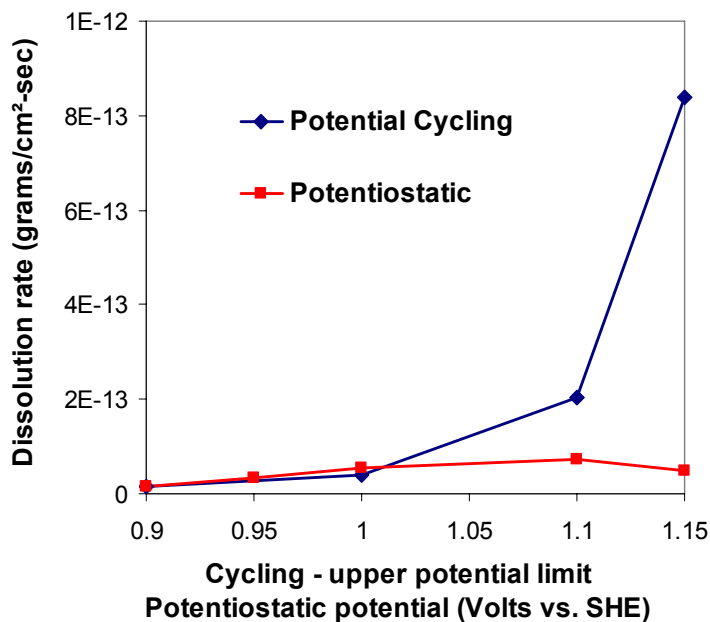
# Catalyst activity and structural characterization of carbon-supported nano-particle catalysts

- Determine oxygen reduction activity and reaction mechanism (4 e- or 2 e-)
  - Thin-film rotating ring-disk technique
- Verify that desired structures, compositions, and particles sizes are obtained
  - TEM, EDAX, XRD, XAS, XPS, XES, IR of adsorbed CO
- Characterize nano-particle electronic structure
  - Soft X-ray and UV spectroscopies



# Accelerated durability testing of carbon-supported nanoparticle catalyst

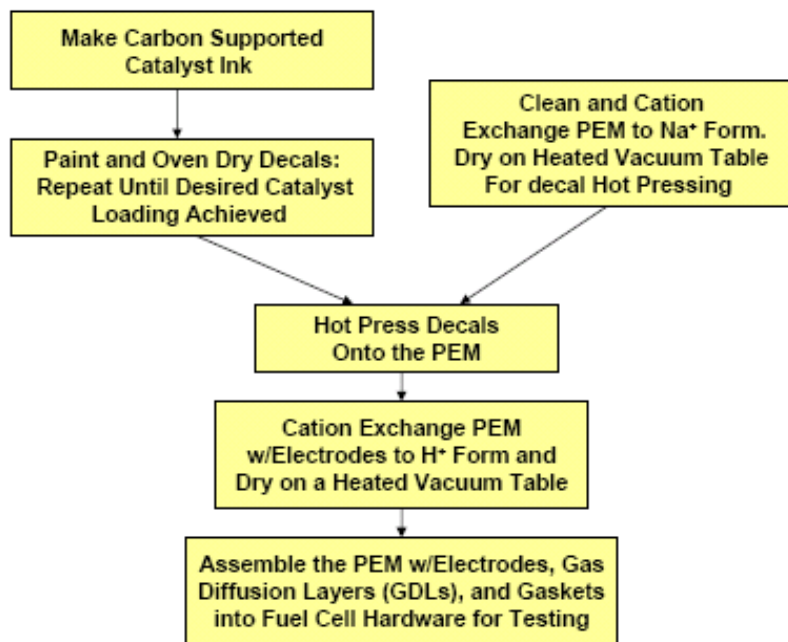
- Potentiostatic and potential cycling dissolution rates
- Equilibrium concentration of dissolved metallic components of electrocatalysts
- Mechanism of dissolution reaction via rotating ring-disk experiments
- Modeling of performance degradation (beginning with Pt/C commercial electrocatalyst)



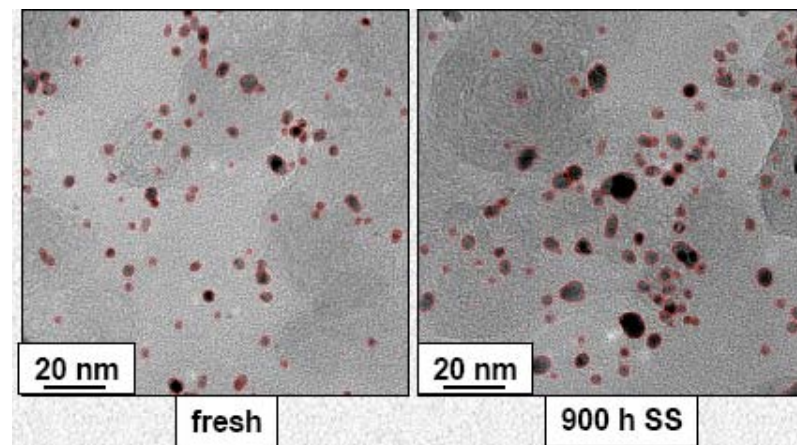
# Electrocatalysts that pass activity and durability screening tests will be tested in MEAs

- Membrane-electrode assembly fabrication, testing, and characterization
  - MEA fabrication
  - MEA performance and durability testing
    - Pre- and post-test analyses using TEM, XRD, and SAXS

## LANL H<sub>2</sub>-Air MEA Fabrication Procedure



## ORNL TEM analyses of LANL MEA





## Summary of Progress

- Milestone (12/07): Synthesize and evaluate the oxygen reduction reaction (ORR) activity and stability of nano-particles of three palladium alloy systems with goals of:
  - specific activity:  $720 \mu\text{A}/\text{cm}^2$ ; mass activity:  $0.44 \text{ A}/\text{mg}$  (@900 mV<sub>iR-free</sub>); volumetric activity:  $>130 \text{ A}/\text{cm}^3$  (@800 mV<sub>iR-free</sub>)
- Progress:
  - Synthesized a series of carbon-supported Pd-Cu catalysts via co-impregnation; determined the effect of Pd:Cu ratio, post-deposition heat treatment temperature, and acid treatment on the phases formed, particle size, particle size distribution, and ORR activity
    - *Highest room temperature ORR mass activity observed:*  
 $0.82 \text{ A}/\text{mg Pd}$  (800 mV);  $0.016 \text{ A}/\text{mg Pd}$  (900 mV)
  - Formed palladium-copper alloy on carbon support with smaller particle size and narrower size distribution using colloidal technique
  - Synthesized 1-3 nm Pd particles on various high surface area carbon supports using the strong-electrostatic adsorption technique
  - Calculated the energetics of the oxygen reduction reaction on candidate noble metals and copper

## Future work

### ■ Remainder of the first year

- Synthesize and fully characterize two additional palladium-base metal systems
- Utilize electrochemical methods for removing the capping agents from the carbon-supported colloidal bimetallics to retain small particle size during capping agent removal
- Form carbon-supported palladium-base metal nano-particles using the strong electrostatic adsorption technique
- Complete calculation of the reaction step barriers in the oxygen reduction reaction
- Calculate the thermodynamically favorable alloy atomic structure
- Determine the effect of temperature treatment on the surface segregation of alloy components from bulk electrodes
- Fully characterize the electronic structure of Pd-Cu bulk electrodes

### ■ Next year

- Explore three iridium-base metal systems and fabricate and test MEAs using promising palladium-base metal catalysts

## *Team members*

- Argonne National Laboratory: Xiaoping Wang, Nancy Kariuki, Suhas Niyogi, Bilge Yildiz, and Jennifer Mawdsley
- California Institute of Technology: William A. Goddard, III, Boris Merinov, Yao Sha, and Ted Yu
- University of Illinois at Chicago: John R. Regalbuto and Lawrence DSouza
- University of Nevada, Las Vegas: Clemens Heske, Timo Hofmann, and Lothar Weinhardt
- Los Alamos National Laboratory: Piotr Zelenay
- Oak Ridge National Laboratory: Karren More