

Non-Platinum Bimetallic Cathode Electrocatalysts



... for a brighter future

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U.S. Department
of Energy

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Overview

Timeline

- Project start data: January, 2007
- Project end data: December, 2010
- Percentage complete: 65%

Budget

- Total project funding:
 - DOE: \$5,434 K
 - Contractor share: \$172 K
- Funding received in FY'08:
 - DOE: \$1480 K
 - Contractor share: \$42 K
- Funding for FY'09:
 - DOE: \$1350 K
 - Contractor share: \$40 K

Barriers

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

Partners

- California Institute of Technology (Caltech)
- University of Illinois at Chicago (UIC)
- University of Nevada at Las Vegas (UNLV)
- Oak Ridge National Laboratory (ORNL)
- Los Alamos National Laboratory (LANL)
- Lead Lab: Argonne

Objectives

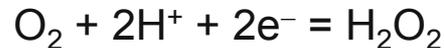
■ Develop a non-platinum cathode electrocatalyst for polymer electrolyte fuel cells to meet DOE targets that:

- Promotes the direct four-electron oxygen reduction reaction (ORR) with high electrocatalytic activity

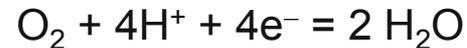
(*0.44 A/mg_{PGM}; 720 μA/cm² @0.9 V_{iR-free}*)

- *O₂ reduction reaction (ORR) in acidic media*

- *Two-electron transfer*



- *Four-electron transfer*



- 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/cm²*)

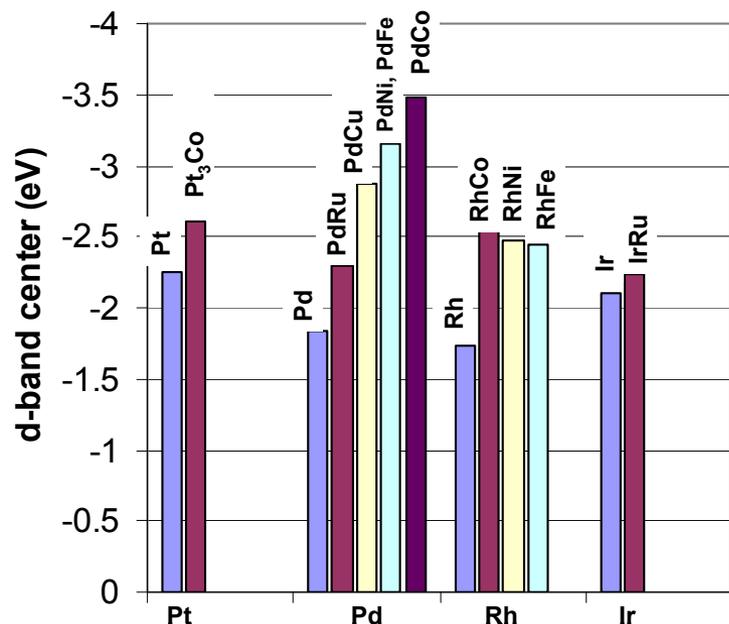
■ Objective in the past year:

- Optimize ORR activity and stability of Pd-Cu nano-particles; study correlation between Pd-Cu electronic structure and activity; perform MEA tests
- Synthesize and evaluate the oxygen reduction activity and stability of nano-particles of one palladium alloy system and two rhodium alloy systems (Pd-Co, Rh-Co, and Rh-Fe)

Approach

■ Bimetallic systems (base metal-noble metal)

- Surface skin of minor noble metal component over noble metal-base metal alloy particle interior to form protective layer
- Base metal component chosen to modify electronic properties of noble metal making it more “Pt-like”
- Initial choice of bimetallic systems based on published surface segregation energies and d-band center shifts (A.V. Ruban, H.L. Skriver, J.K. Nørskov, Phys. Rev. B, 59 (1999)15990.; A. Ruban, B. Hammer, P. Stoltze, H.L. Skriver, and J.K. Nørskov, J. Mol. Catal. A 115 (1997) 421.)



Noble Metal Segregation		
Ir	Rh	Pd
Ru, moderate	Fe, strong Co, strong Ni, moderate	Ru, very strong Cu, moderate Ni strong Fe, very strong Co, strong

How this project addresses the DOE barriers

■ A. Durability:

- Altering oxophilicity of catalyst to prevent oxidation-related degradation
 - ***Alloying Pt and Pd with base metals decreases their oxophilicity***
[e.g., V. Stamenkovic, B. Mun, K. Mayrhofer, P. Ross, N. Markovic, J. Rossmeisl, J. Greeley, and J. K. Nørskov, *Angew. Chem. Int. Ed.*, 45, 2897 (2006).; M. Shao, P. Liu, J. Zhang, and R. Adzic, *J. Phys. Chem. B*, 111, 6772 (2007).]
 - ***Alloying Pt with base metals results in improved resistance to electrochemically-active surface area loss*** [e.g., studies by GM, Johnson Matthey, UTC and others]
 - ***Computational studies have shown that alloying with base metals can increase the dissolution potential of surface noble metals***
[J. Greeley and J.K. Nørskov, "Electrochemical dissolution of surface alloys in acids: Thermodynamic trends from first-principles calculations", *Electrochim. Acta* 52 5829 (2007).]

■ 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
 - ***Studies on Pt alloys have shown a correlation between surface valence band energy and ORR activity***

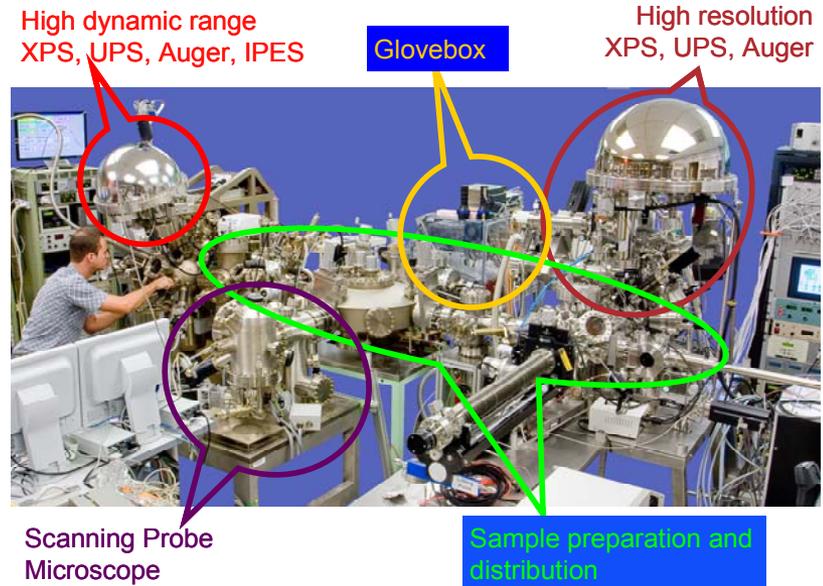
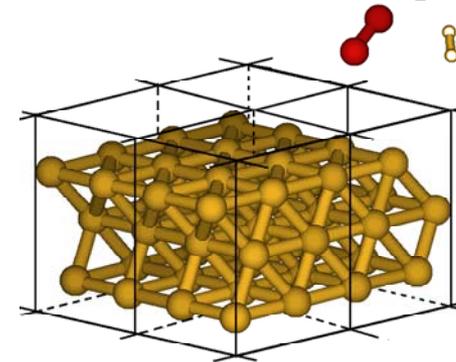
[e.g., V. Stamenkovic, B. Mun, K. Mayrhofer, P. Ross, N. Markovic, J. Rossmeisl, J. Greeley, and J. K. Nørskov, *Angew. Chem. Int. Ed.*, 45, 2897 (2006).]

Project tasks

- Computational studies (Caltech)
 - Guide choice of systems and compositions (beyond systems from Norskov et al. calc.)
 - Quantum mechanical and large scale molecular dynamics for reaction pathways, kinetics, and preferred catalyst structures
- Model systems: bulk electrode fabrication and characterization (UNLV, Argonne)
 - Guide choice of systems and compositions
- Nano-particle synthesis on high-surface-area carbon support (Argonne, UIC)
 - Impregnation (screening)
 - Colloidal (controlled composition)
 - Strong-electrostatic adsorption
- Nano-particle characterization (Argonne, ORNL, UNLV, UIC)
 - ORR activity and stability screening (rotating ring-disk technique), composition, electronic structure, and morphology
- Membrane-electrode assembly fabrication and testing (LANL, ORNL)
 - Performance and durability using accelerated test protocol



ORR intermediates: H, O, OH, O₂, OOH, H₂O

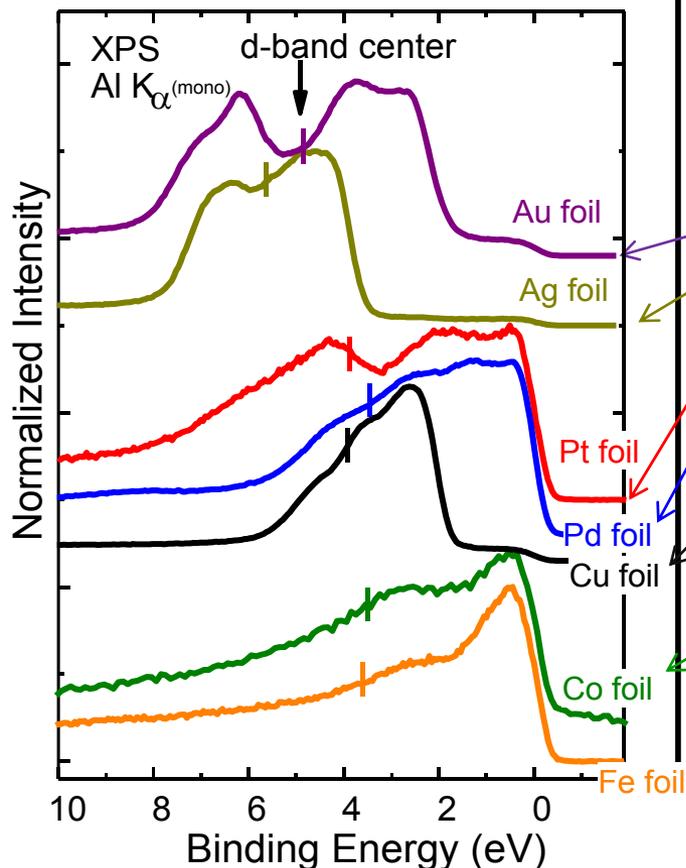


UNLV

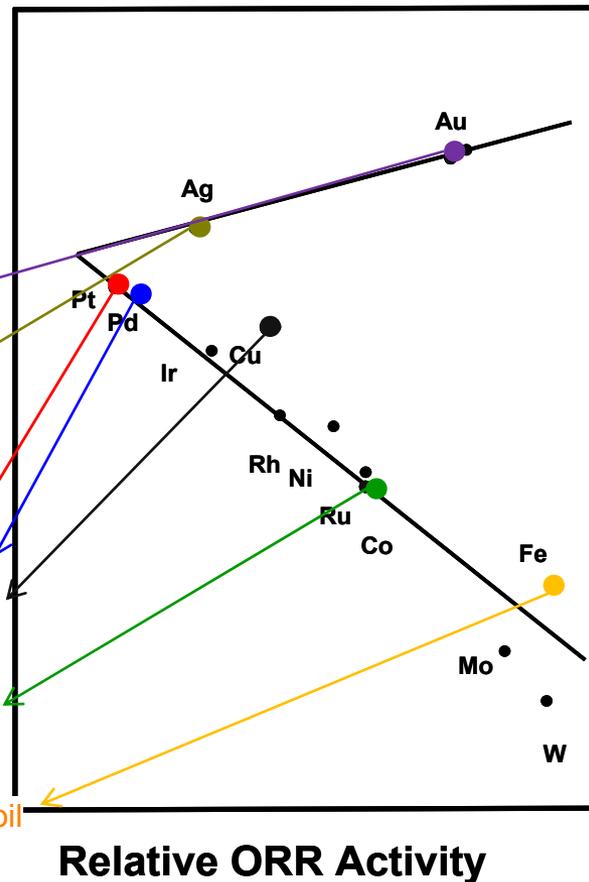
D-band center and ORR activity

- Pt and Cu have similar d-and centers, but ORR activity and overall density of states (DOS) differ significantly
 - D-band center does not adequately reflect valence band (VB) structure and interaction of metal with oxygen
 - Spectral distribution (DOS vs energy) needs to be analyzed to determine if catalyst has a “Pt-like” electronic structure

Measured DOS in the valence band



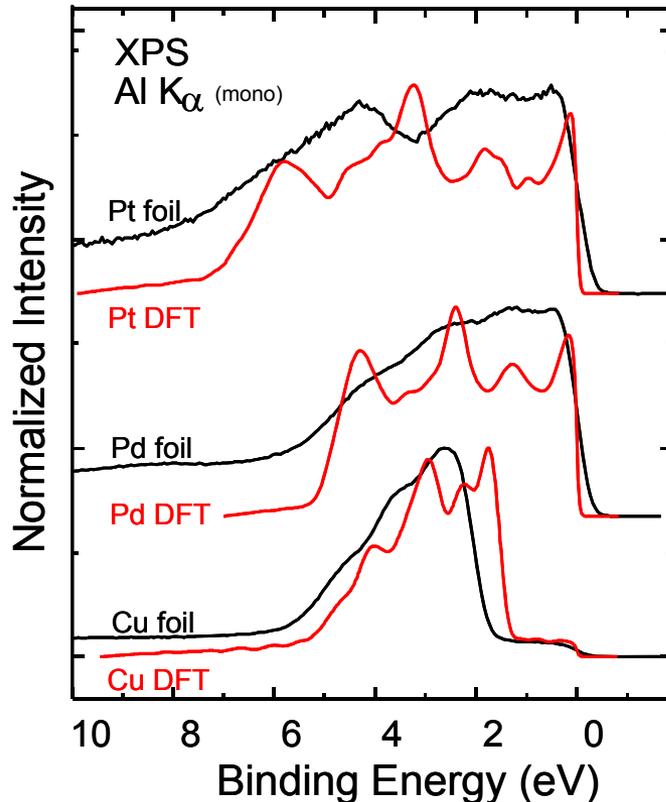
Trends in oxygen reduction activity



Adapted from J. Nørskov et al., *J. Phys. Chem. B* **108** (2004) 17886.

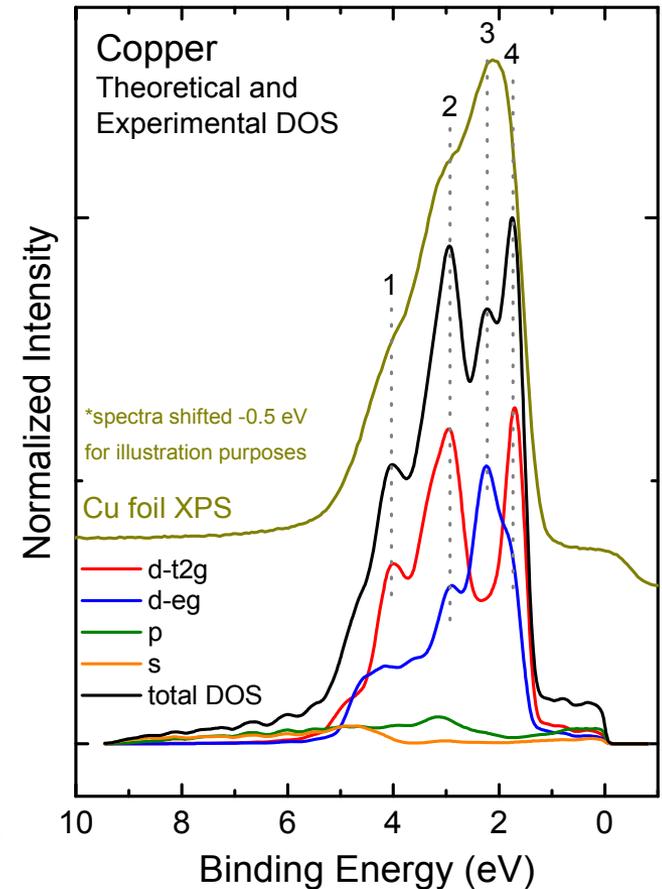
Calculated and experimental density of states

- DOS calculations provide insight into the relative strength of the different contributions to the overall DOS
- First step towards analysis of contributions to valence band structure and involvement of various states in the ORR



- Theoretical and experimental VB structures show similarities in the overall spectral shape – final state effects are responsible for the observed differences

Theoretical DOS calculation using Gaussian basis set, DFT (PBE) and periodic code, modified for instrumental broadening and Fermi distribution



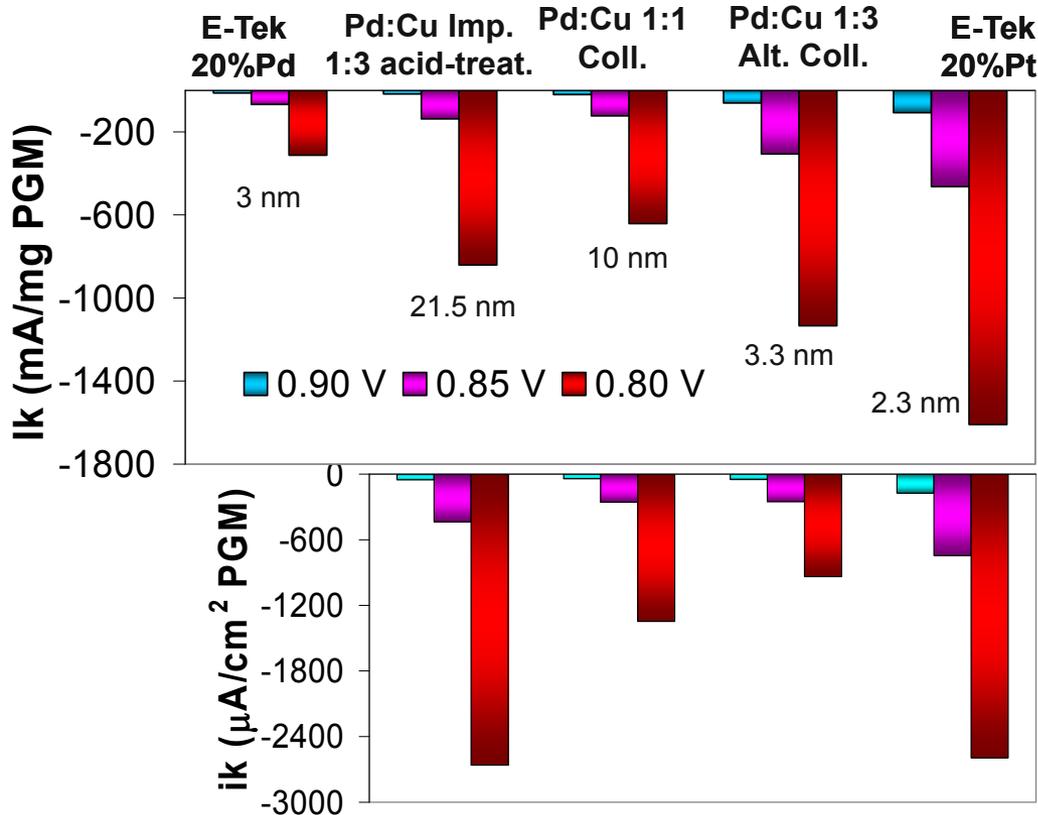
- Spectral features in the measured DOS (1-4) are correlated with peaks in the DOS of the individual wave functions

Summary of nanoparticle systems studied this year

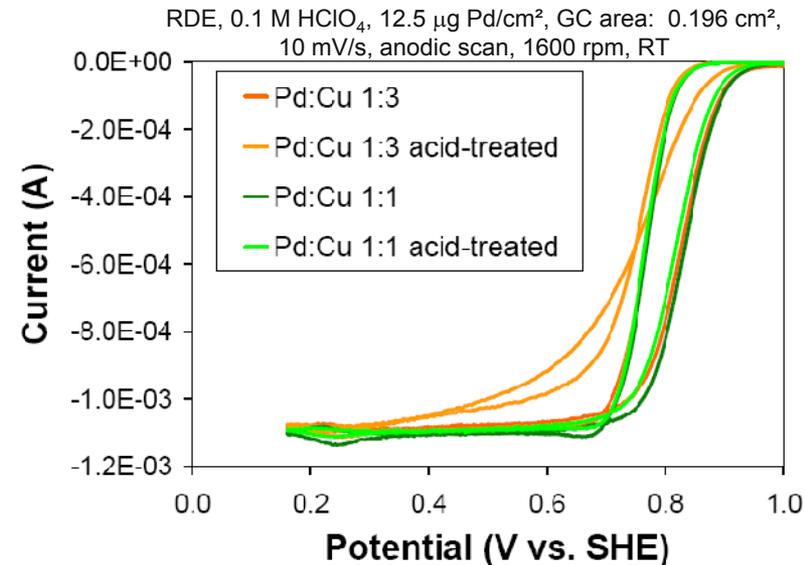
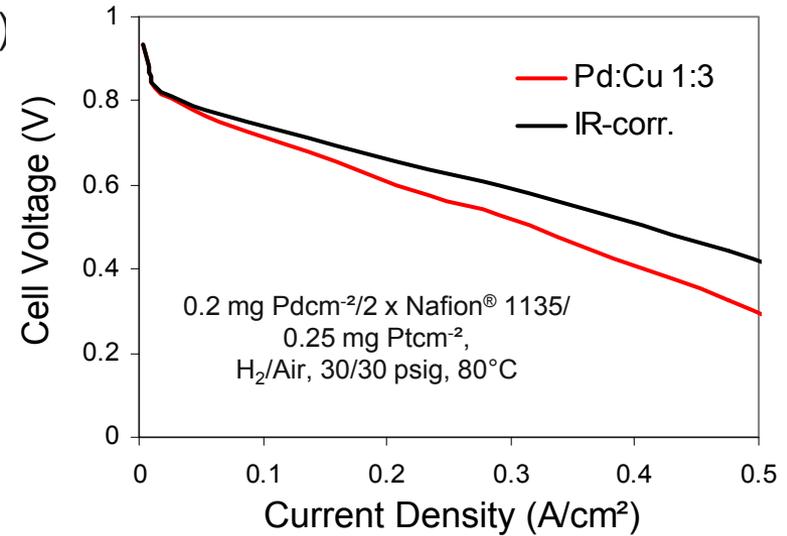
Technique	Impregnation				Colloidal				Core-shell structure synthesis	
System	Pd-Cu	Pd-Co	Rh-Co	Rh-Fe	Pd-Fe	Pd-Cu-Ni	Pd-W	Pd-Mo-Ni	Pd@1:1PdCu	Pd@1:3PdCu
PGM loading (wt%)	10, 20 30	20, 25	2-22	2-22	10	20 13	20	27, 28 20, 11	10, 16, 23, 26	9, 11, 17, 19, 21, 26, 31
Composition PGM:BM1:BM2 molar ratio	25:75 33:67 40:60 50:50	80:20 67:33 50:50	90:10 75:25 50:50 25:75 10:90	90:10 75:25 50:50 25:75 10:90	63:27	50:50 25:75 64:18:18 33:60:7	75:25	67:33 69:31 55:45 33:14:53	63:37 64:36 73:26 76:24	67:33 70:30 72:28 73:27 74:26 77:23 81:19
PGM precursor	chloride nitrate	acac	nitrate	nitrate	acac	acetate acac	chloride	acac	1:1 Pd:Cu alloy particles acetate amine	1:3 Pd:Cu alloy particles acetate amine
BM precursor	chloride nitrate	acac	nitrate	nitrate	carbonyl	acetate acac	tungstate	carbonyl acac		
Post-deposition heat treatment temperature (°C)	400	415	300 400 470 550 650 700	250 400 500 550 650	500	500 550	500 700	550 700 570	80 180 200 500	80 180 200 500
Heat treatment atmosphere	4% H ₂ pure H ₂	4% H ₂	4% H ₂ pure H ₂	4% H ₂ pure H ₂	4% H ₂	4% H ₂	4% H ₂	4% H ₂ pure H ₂	Vacuum 4%H ₂	Vacuum 4%H ₂

Summary of Palladium-Copper nano-particle activity and stability

- Highest area-specific ORR activity: acid-treated Pd:Cu showing Pd-rich shell on Pd:Cu 1:1 core (21 nm)
- Pd:Cu 1:1 is more stable than Pd:Cu 1:3 (aqueous tests)
- MEA testing confirmed instability of Pd:Cu 1:3; Pd:Cu 1:1 MEA testing is underway

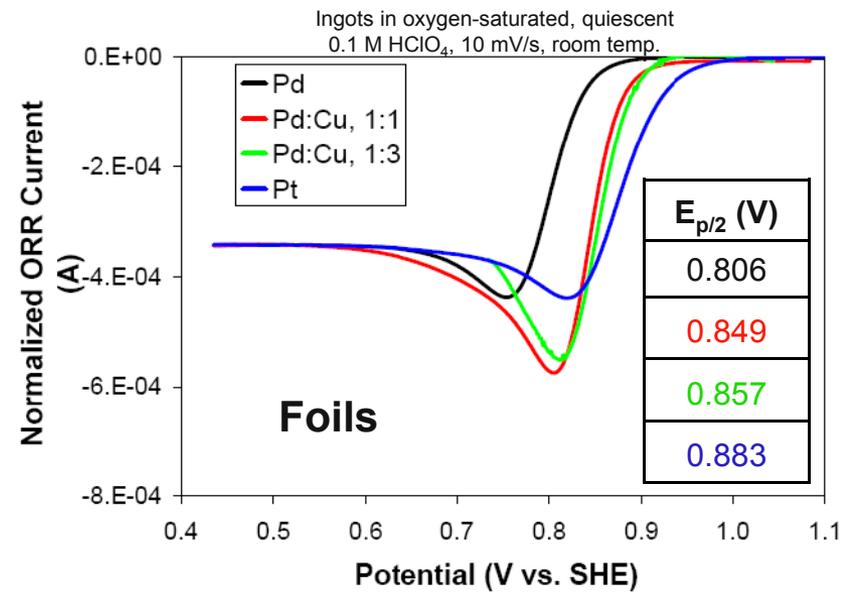
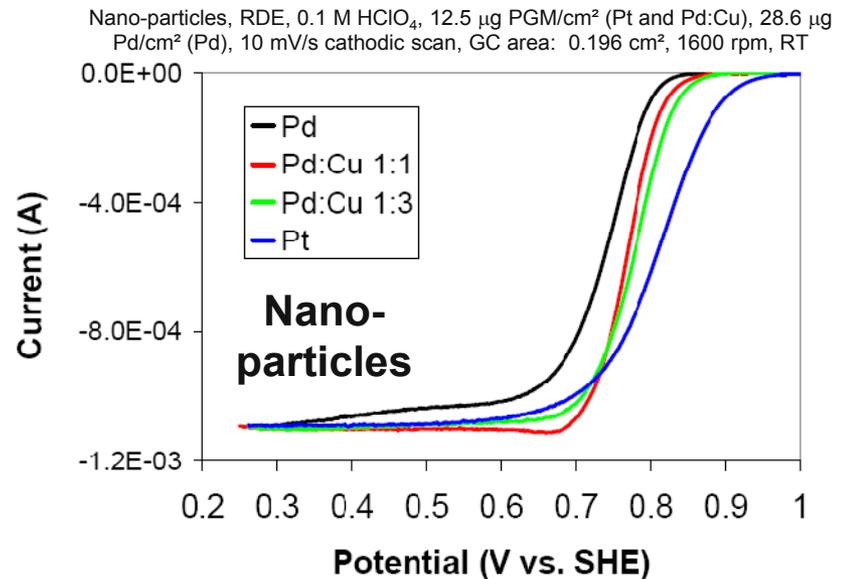
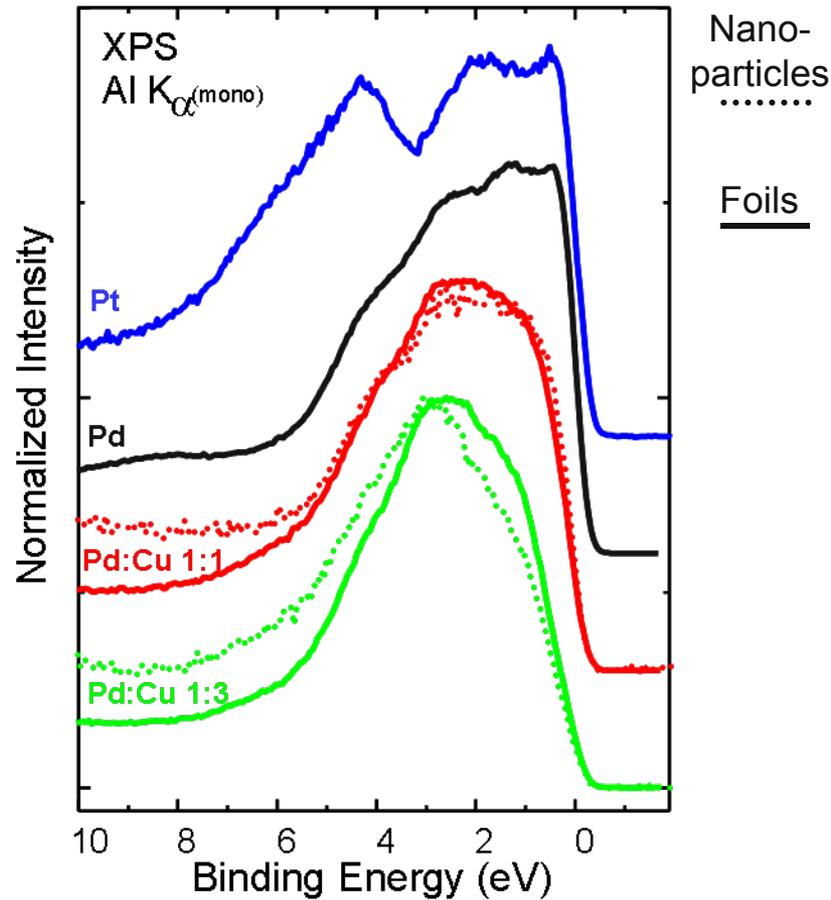


PdCu₃ on Vulcan XC-72: 8.9 wt% Pd; 15.5 wt% Cu



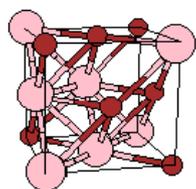
Palladium-Copper model systems and nano-particles

- Bulk alloys and nano-particles have very similar ORR activity (rel. to Pt) and similar DOS
- DOS of Pd-Cu alloys show shift to higher binding energies and are dominated by contribution from Pd

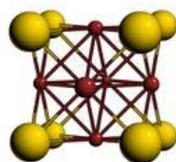


Computational results for Palladium-Copper alloy system

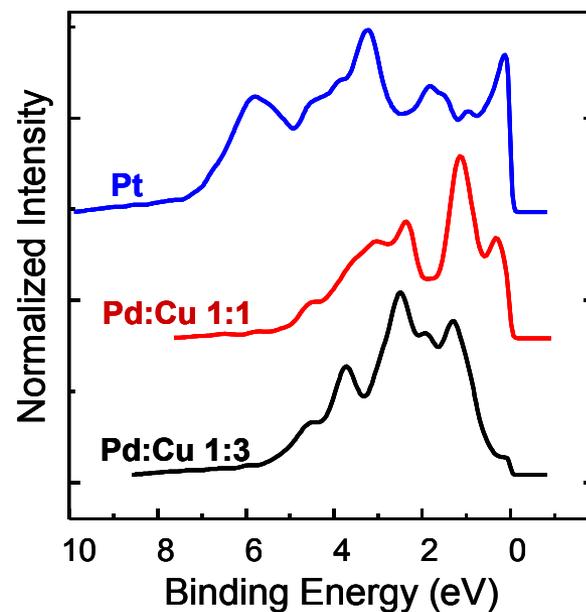
- Pd:Cu 1:1 has a higher density of states near the Fermi energy than Pd:Cu 1:3 (as observed experimentally)
- “Non-layered” Pd:Cu 1:1 shows lowest barrier for ORR



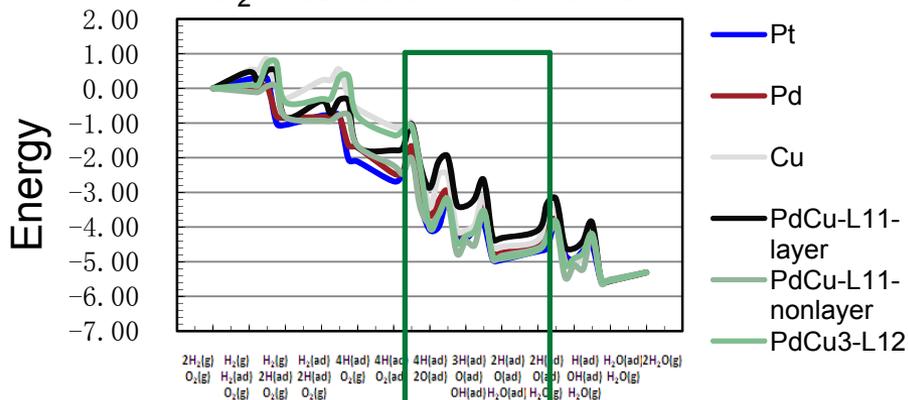
*PdCu: L1₁



*PdCu₃: L1₂

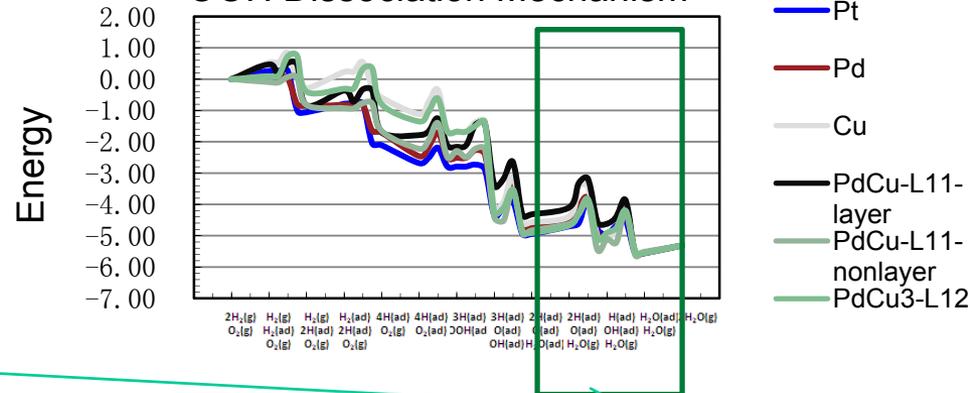


O₂ Dissociation Mechanism



Reduced OH formation barrier (~0.33 eV) for non-layered PdCu

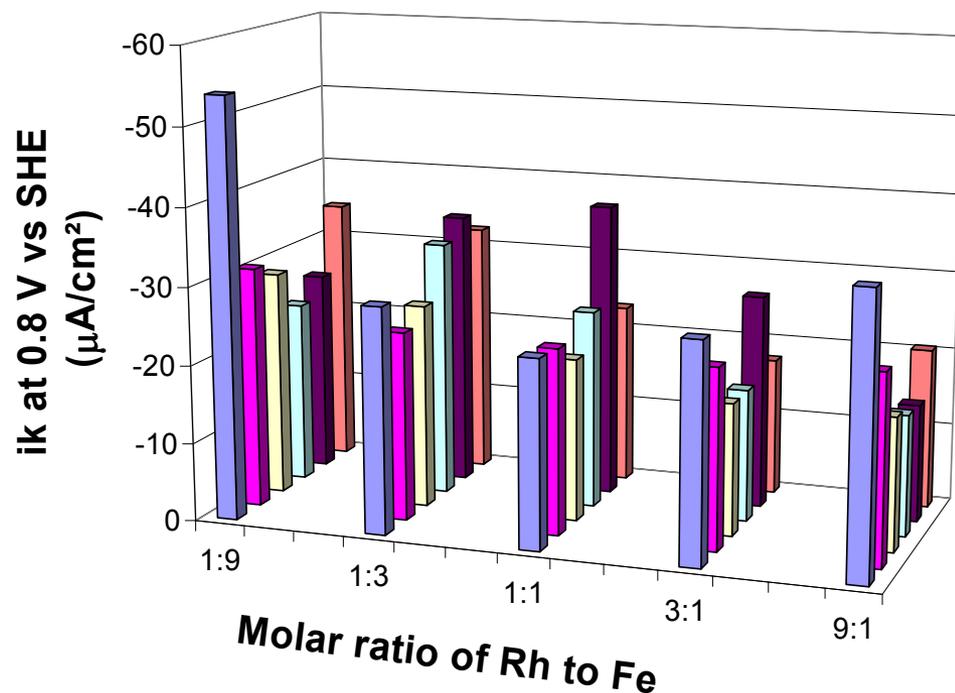
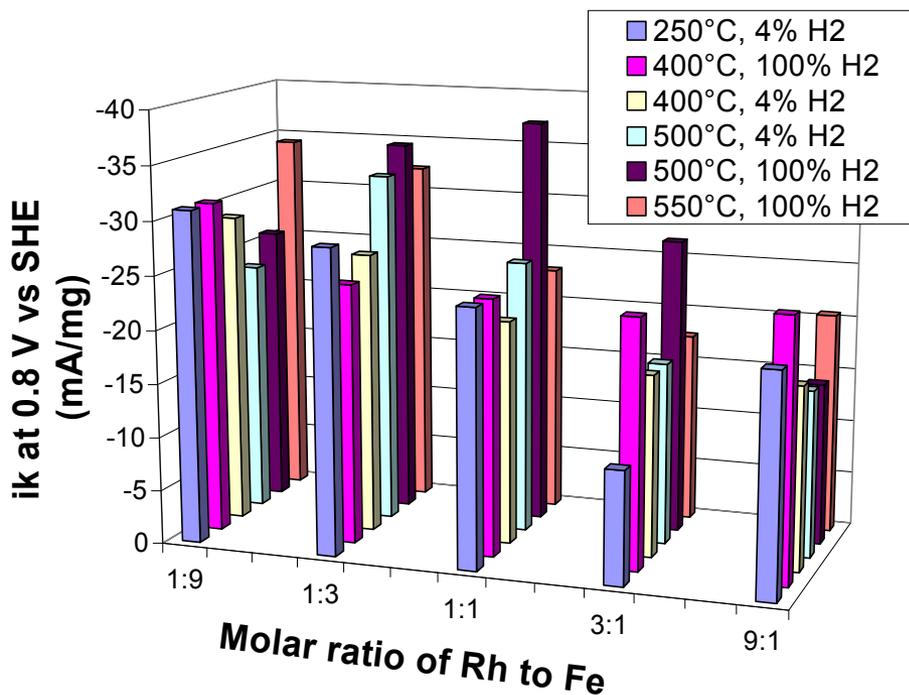
OOH Dissociation Mechanism



Rate-determining step: water formation

Summary of Rhodium-Iron alloy ORR activity

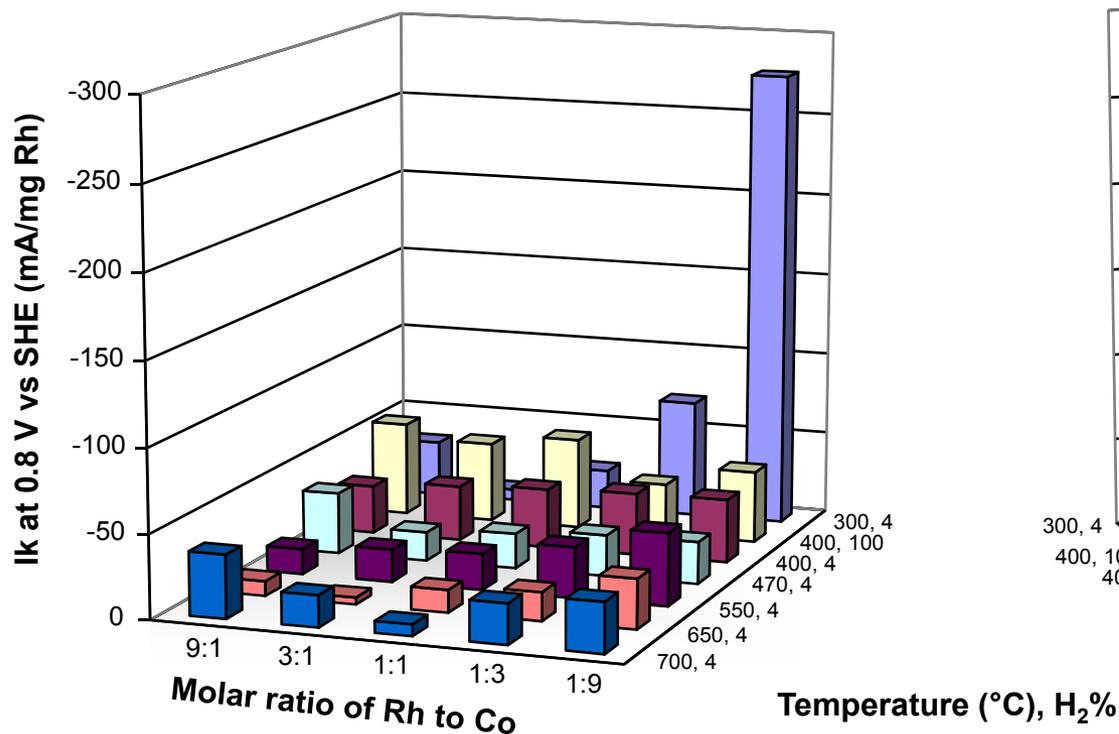
- Rh to Fe molar ratio varied from 1:9 to 9:1; Vulcan XC72-supported nanoparticles synthesized via co-impregnation of nitrate precursors
- Post-deposition heat treatment in 4% hydrogen or 100% hydrogen at 250°C to 550°C
- Highest ORR mass activity observed: 37 mA/mg Rh (@ 0.8 V, room temp.)
- Highest ORR area specific activity observed: 53 $\mu\text{A}/\text{cm}^2$ (@ 0.8 V, room temp.)



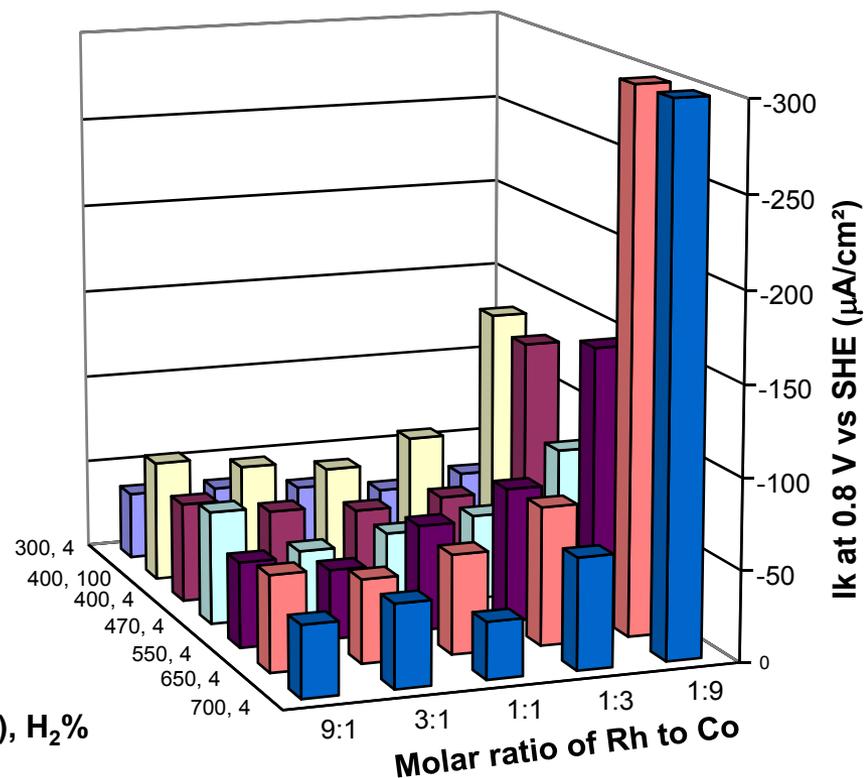
Summary of Rhodium-Cobalt alloy ORR activity

- Rh to Co molar ratio varied from 1:9 to 9:1; Vulcan XC72-supported nanoparticles synthesized via co-impregnation of nitrate precursors
- Post-deposition heat treatment in 4% H₂ or 100% H₂ at 300°C-700°C
- Highest ORR mass activity observed: 275 mA/mg Rh (@ 0.8 V, room temp.)
- Highest ORR area specific activity observed: 290 $\mu\text{A}/\text{cm}^2$ (@ 0.8 V, room temp.)

Mass activity at 0.8 V vs SHE



Area specific activity at 0.8 V vs SHE



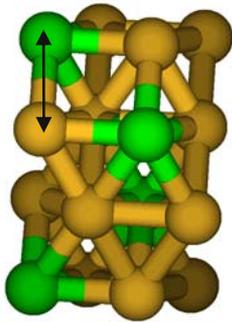
What next? Calculations of transition metal alloy surface segregation

- The goal of these DFT slab calculations is to find binary alloys favoring surface segregation of the noble metal

	3	4	5	6	7	8	9	10	11	12
	3B	4B	5B	6B	7B	8B	8B	8B	1B	2B
	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd
	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg
	Ac	Rf	Db	Sg	Bh	Hs	Mt			

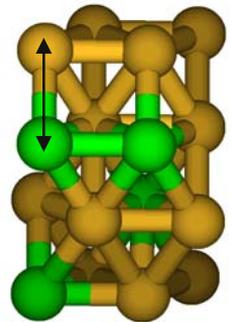
Blue Box – Noble Metals Studied

Red Box – Solute Metals Studied



75-75-75-75%

“Surface Uniform” Case



100-50-75-75%

“Surface Segregated” Case

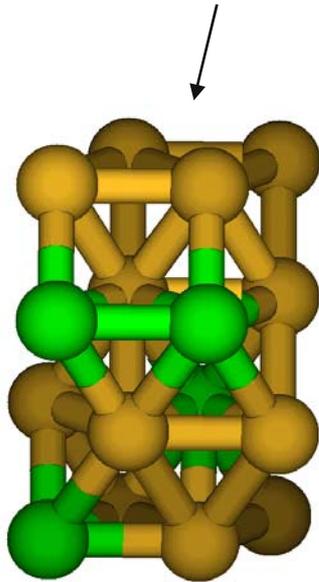
Noble Metal
Solute Metal

Energy difference between surface segregated and surface uniform

Solute \ Noble	Pd (eV)	Pt (eV)	Rh (eV)
Co	-0.41	-0.49	
Ir	-0.76	-0.57	
Mo	-1.23	-1.00	
Ni		-0.43	
Os		-1.32	-0.91
Ta	-0.33		
Tc	-0.74	-1.03	-0.56
Re	-2.09	-1.69	-0.85
Rh	-0.47	-0.39	
Ru	-0.88	-0.83	-0.56
W	-1.99	-1.37	

What next? Surface d-band Center of Pt, Pd and Rh alloys

- Initial choices based on d-band center until full VB structure calculations are completed
- The d-band center of the surface noble metal in 3:1 (noble:base molar ratio) alloys was calculated



Gold – Noble Metal
Green – Solute Metal

- Of the noble metal alloys, Pd-Mo, Pd-Re, Pd-Ta, and Pd-W have desirable d-band centers closest to that of Pt

Solute\ Noble	Pd	Pt	Rh
Ag	-1.59	-2.17	-1.85
Au	-1.61	-2.18	-1.88
Cd	-1.66	-2.24	-1.70
Co	-2.08	-2.76	-2.17
Cr	-2.11	-2.73	-2.26
Cu	-1.92	-2.58	-2.11
Fe	n/a	-2.72	-2.10
Hg	-1.57	-2.13	-1.69
Ir	-2.03	-2.65	-2.24
Mn	-1.98	-2.65	-2.16
Mo	-2.25	-2.83	-2.26
Nb	n/a	-2.79	-2.10
Ni	-2.03	-2.69	-2.19
Os	n/a	-2.76	-2.27
Pd	-1.82	-2.44	-2.04
Pt	-1.83	-2.47	-2.09
Re	-2.28	-2.85	-2.31
Rh	-1.95	-2.59	-2.16
Ru	-2.11	-2.68	-2.23
Sc	-2.12	-2.52	-1.77
Ta	-2.44	-2.85	-2.13
Tc	-2.21	-2.79	-2.29
Ti	n/a	-2.78	-2.10
V	n/a	n/a	-2.26
W	-2.39	-2.95	-2.27
Y	-1.97	-2.23	-1.59
Zn	-1.89	-2.58	-1.91
Zr	-2.25	-2.55	-1.86

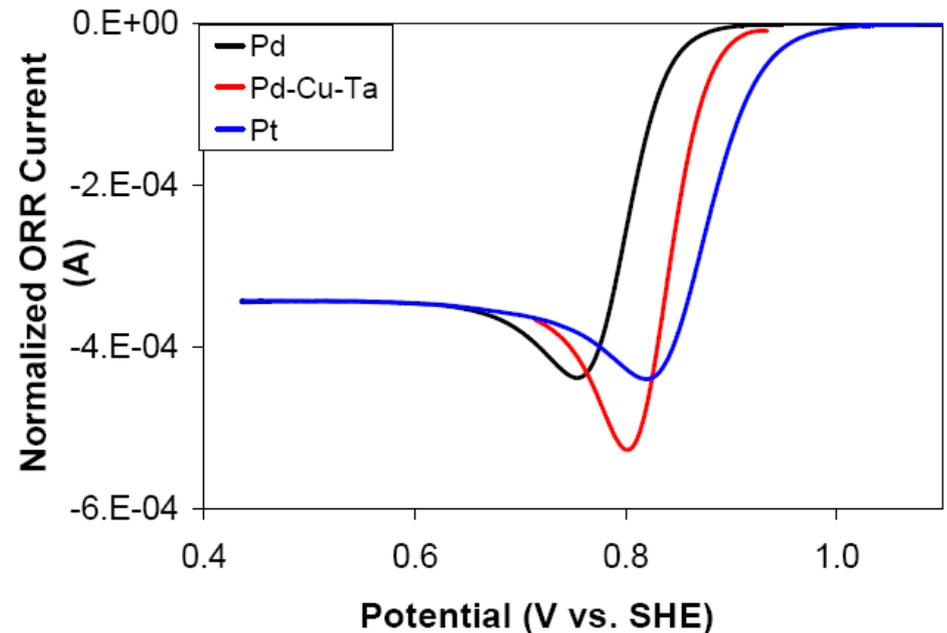
Summary of new systems currently being studied

- Binary systems identified as having promising surface segregation and electronic structure properties

- Pd-Mo
- Pd-Re
- Pd-Ta
- Pd-W

- Ternary systems to enhance activity and stability of highest activity binary system identified to date

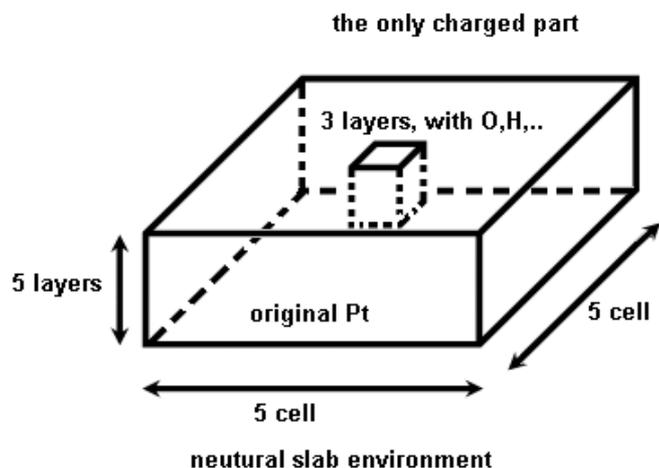
- Pd-Cu-Mo
- Pd-Cu-W
- Pd-Cu-Re
- Pd-Cu-Ta
- Pd-Cu-Ni



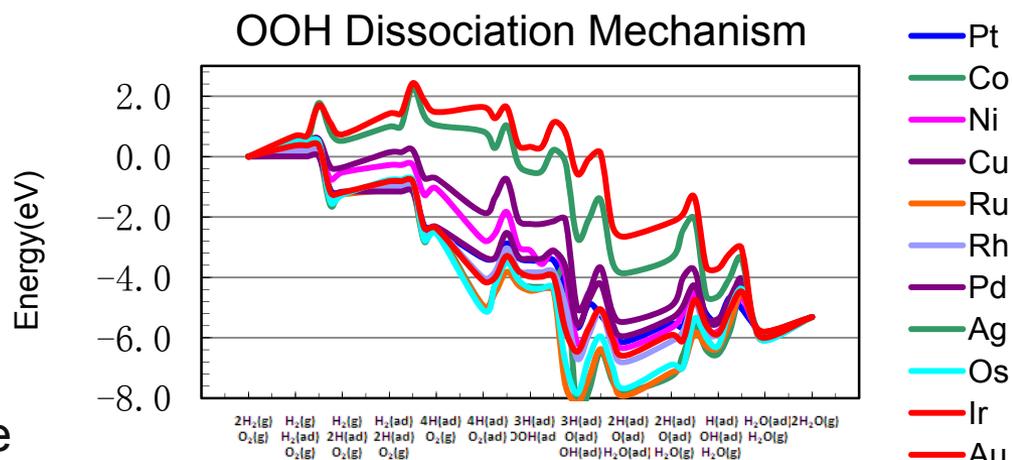
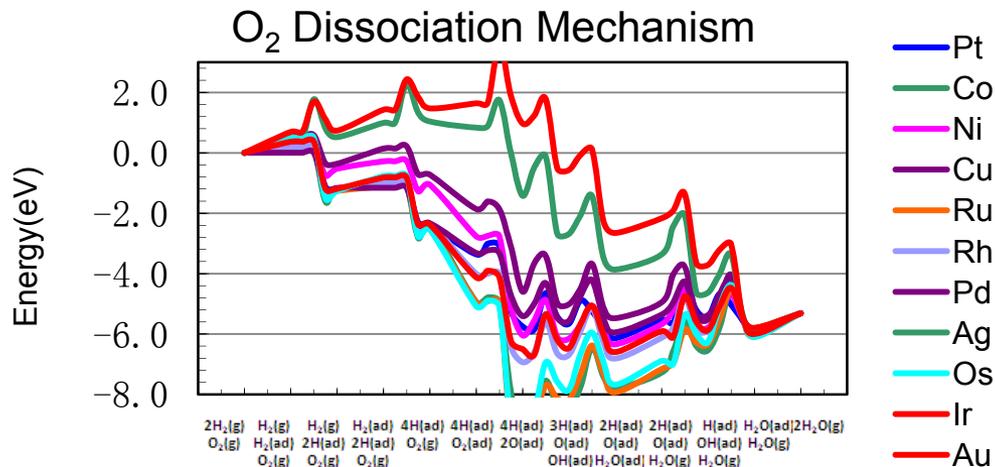
Ongoing computational studies - solvent effect on ORR

Continuum model

- Poisson Boltzmann
- UFF radii
- Charge from slab calculations



- Solvent helps dissociate O_2 and OOH
- OH and OOH formation become more difficult in the presence of solvent
- OH formation becomes dominant barrier for both mechanisms



Milestones/Summary of Progress

- Synthesize and evaluate the oxygen reduction reaction (ORR) activity and stability of nano-particles of with goals of specific activity: $720 \mu\text{A}/\text{cm}^2$; mass activity: $0.44 \text{ A}/\text{mg PGM}$ (@ $900 \text{ mV}_{\text{iR-free}}$)
 - Milestone (09/08): one palladium alloy system (Pd-Co) and two rhodium alloy systems (Rh-Fe and Rh-Co)✓
 - Milestone (09/09): one rhodium-base metal alloy system and two iridium-base metal alloy systems (on-going; milestone and focus changing based on recent computational results)
- Progress:
 - Synthesized and tested the ORR activity of palladium-cobalt, rhodium-cobalt, and rhodium-iron alloy nanoparticle systems
 - Highest room temperature nanoparticle ORR specific and mass activity observed:
 - **$95 \mu\text{A}/\text{cm}^2$** for Pd:Cu 1:1 by co-impregnation; 20 nm (900 mV; room temperature)
 - **$0.06 \text{ A}/\text{mg Pd}$** for Pd:Cu 1:3 by alternative colloidal; 3.3 nm (900 mV; room temperature)

Milestones/Summary of Progress (continued)

- Determined that Cu modifies the electronic structure of Pd and correlated that modification with ORR activity
- Tested PdCu₃ electrocatalyst in MEAs
- Developed capability to calculate the full valence band structure of pure metals and alloys and correlated the calculated structure of Pt, Pd, and Pd-Cu alloys with experimentally-determined structure
- Correlated Pd-Cu nano-particle ORR activity and electronic structure with model systems
- Using computational studies, identified several Pd alloys favoring noble metal surface segregation
- Identified several non-Pt systems having d-band centers similar to Pt's (as a first approximation for choice of systems with desirable electronic structures)
- Fabricated model systems of binary and ternary Pd alloys identified as promising in computational effort

On-going and future work (FY'09 and FY'10)

■ Computational analyses

- Based on DFT calculations, determine complete energetics for the ORR on Pd-Mo, Pd-Re, Pd-Ta, and Pd-W alloys
- In cooperation with experimentalists (UNLV) continue to determine alloy electronic structures using density of states (DOS) analysis
- Investigate solvation effect for the ORR on Pd-based alloys
- Continue developing ReaxFF reactive force field for the ORR on relevant alloys

■ Model systems

- Characterize ingots of Pd-Mo, Pd-Re, Pd-Ta, and Pd-W binaries and Pd-Cu-Mo, Pd-Cu-W, Pd-Cu-Re, Pd-Cu-Ta, and Pd-Cu-Ni ternaries with varying Pd to base metal ratios
 - *ORR activity, electronic structure, and surface composition as a function of annealing temperature*

■ Nano-particle fabrication, activity, and stability characterization

- *Testing of Pd:Cu 1:1 nano-particle catalyst activity and stability in MEA*
- *Synthesis of alloy and core/shell Pd-Cu, Pd-Mo, and Pd-W catalysts using strong-electrostatic adsorption technique*
- *Fabricate Pd-Cu-M ternaries and Pd-M binaries using colloidal techniques*