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An electroless approach to atomic layer deposition on noble metal powders

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Division of Inorganic Chemistry
Chemistry of Materials
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Adsorbed layers (adlayers) on catalysts show enhanced properties

Electro-oxidation of formic acid on Pt catalyst

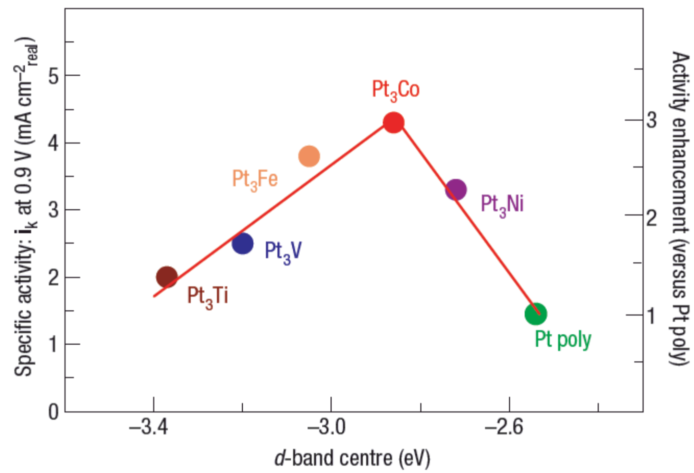
$HCOOH + ½ O_2$ → (active) $CO_2 + H_2O$

$HCOOH + ½ O_2$ → (poisoned) CO_2

- Adlayers such as Bi, Sb, As, Pd favor active pathway (reduce poisoning)

Oxygen reduction reaction on with bimetallic Pt catalysts

$$½ O_2 + 2 H^+ + 2 e^- \rightarrow H_2O$$



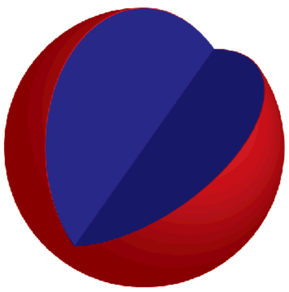
Hyunjoo Lee, Susan E. Habas, Gabor A. Somorjai, Peidong Yang, Journal of the American Chemical Society, 2008, 130, 5406-5407

Stamenkovic, V. R., Mun, B. S., Arenz, M., Mayrhofer, K. J. J., Lucas, C. A., Wang, G. F., Ross, P. N., Markovic, N. M., Nature Materials, 2007, 6, 241-247

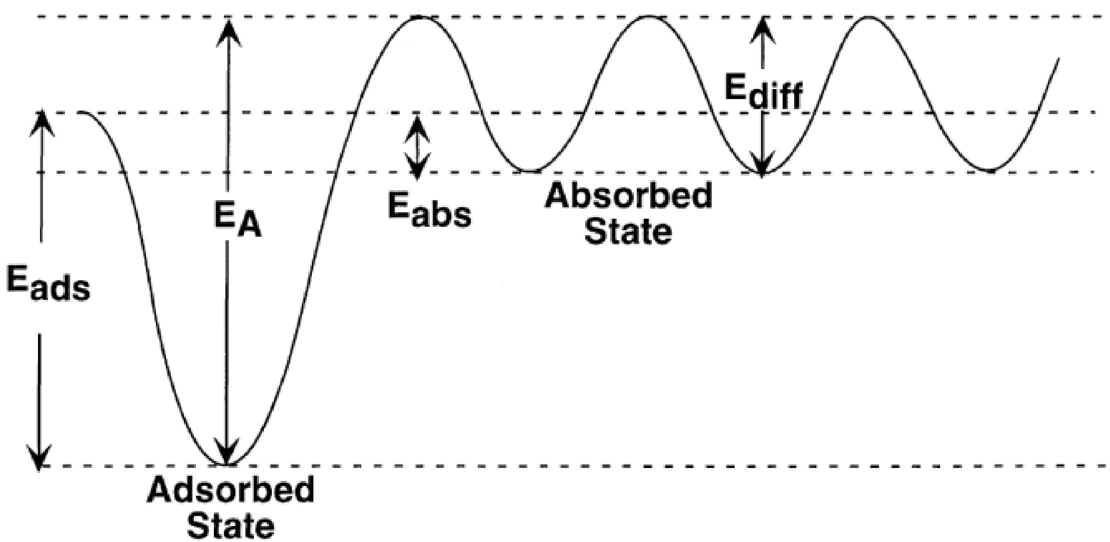
Surface modification should improve kinetics of hydriding and dehydriding Pd

$H_{2\,(g)} + Pd^0 \rightarrow PdH_x$ (X ~ 0.6)

- Surface Pd-H is very stable
- High surface site occupancy
- Large activation barrier
- Near-surface alloys destabilize surface hydrides
- May then improve absorption kinetics



Adsorbed hydride on Pd particle surface



Jeff Greeley and Manos Mavrikakis, J. Phys. Chem. B 2005, 109, 3460-3471

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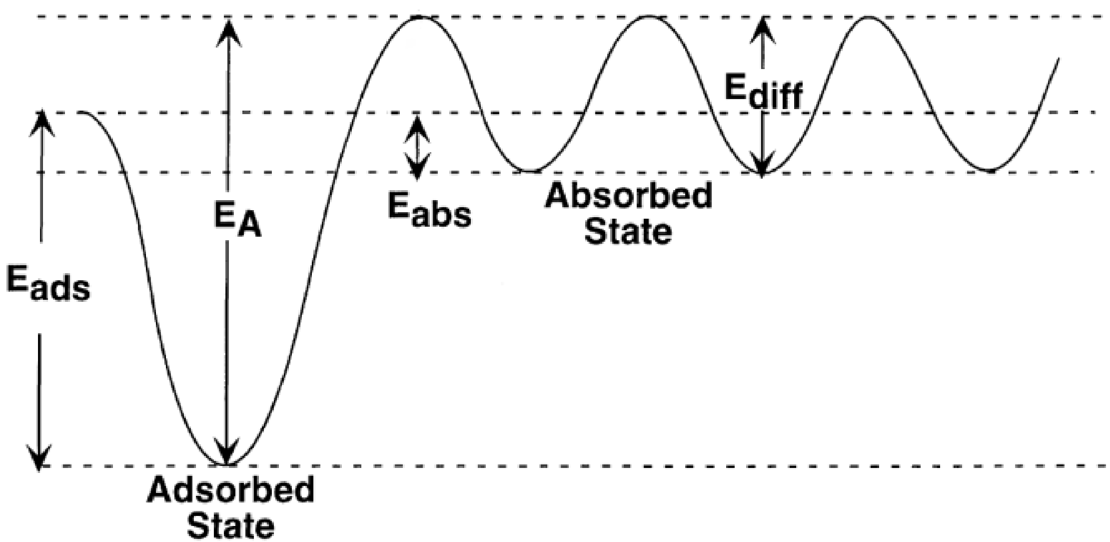

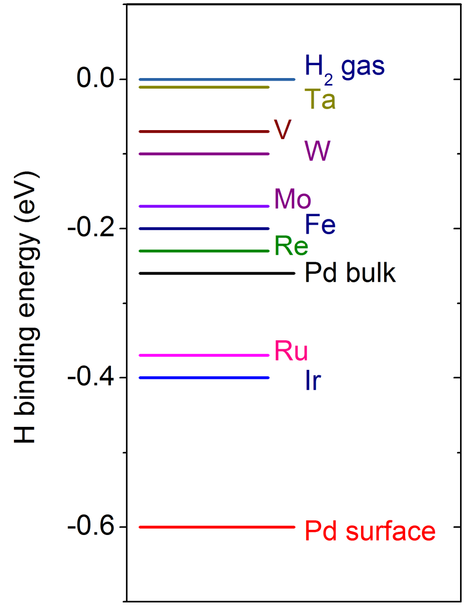

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Electroless Atomic Layer Deposition (EL-ALD)

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room temperature, “wireless”, amenable to “rough” surfaces with high surface area

Simple Apparatus for EL-ALD

- Pd powder suspended in electrolyte
- Reagent gas (1% H_2/N_2)/inert gas source
- Metal salt added by syringe
- Electrodes to measure progress of reaction

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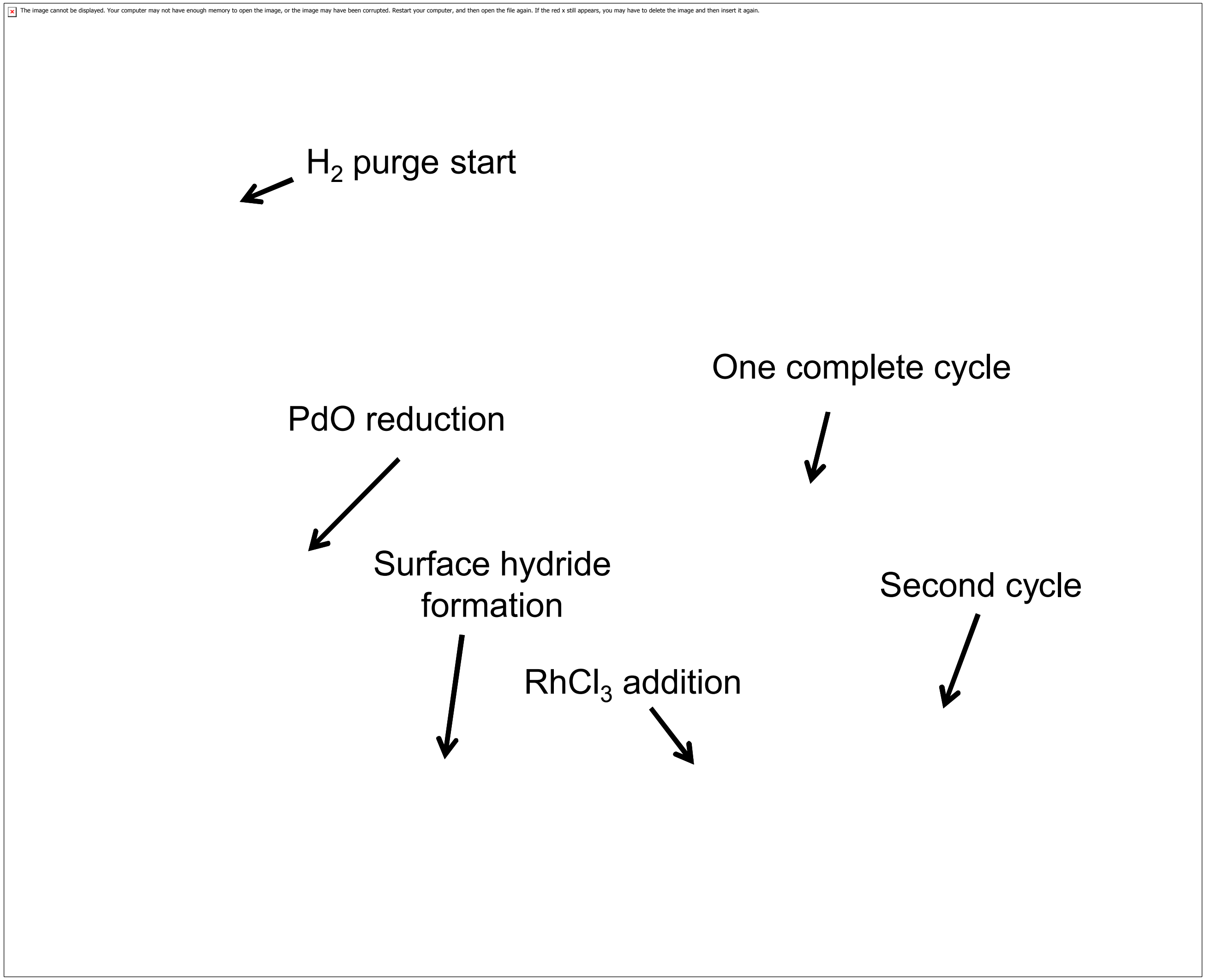
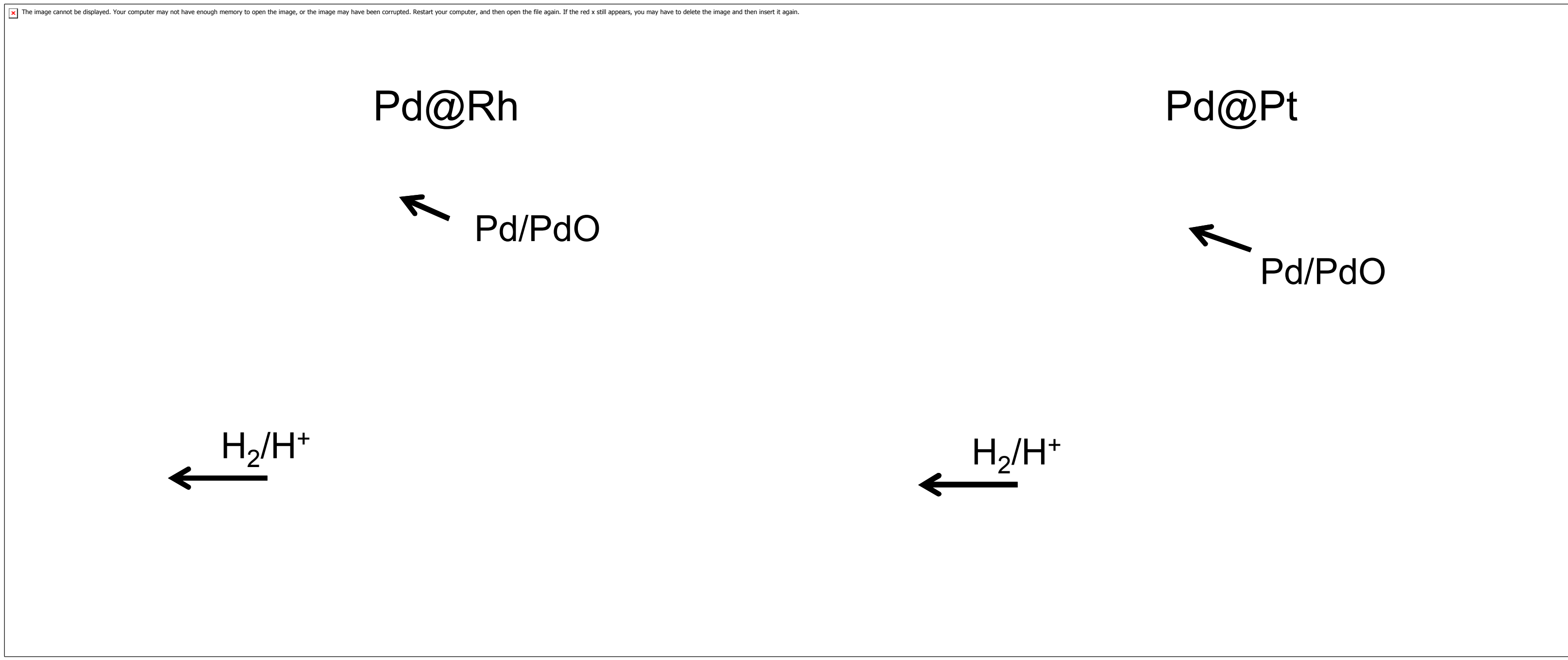
Monitor open circuit potential to follow reaction

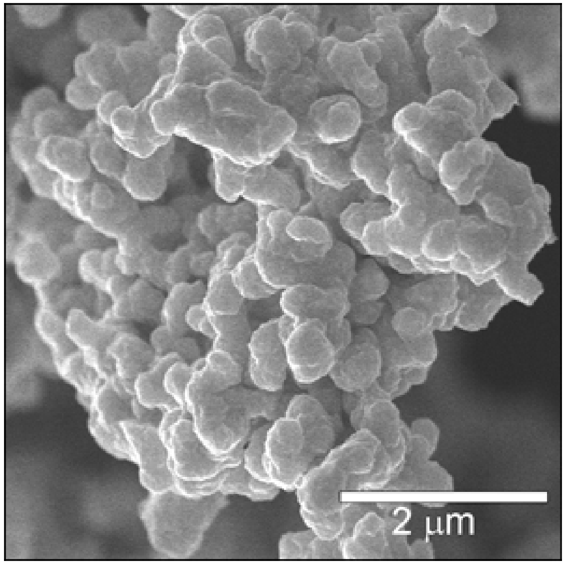


Cyclic voltammetry of Pd test wire before and after deposition of adlayer of Rh (left) and Pt (right)

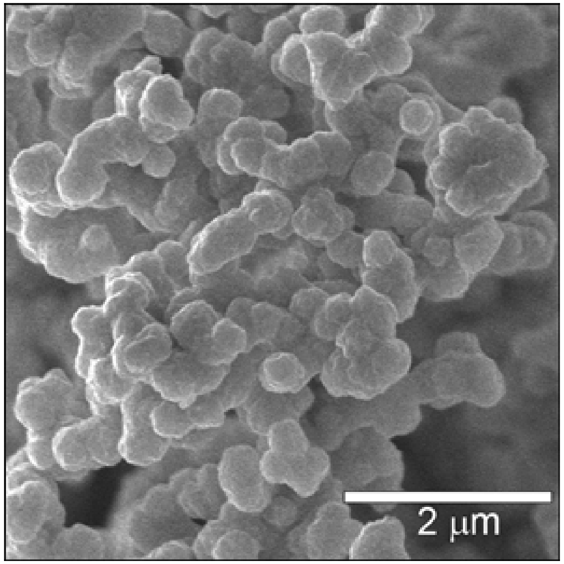


CV shows that adlayer blocks Pd/PdO redox couple and suggests improved hydride/dehydride kinetics

No change to particle morphology after two cycles of EL-ALD of Rh on Pd



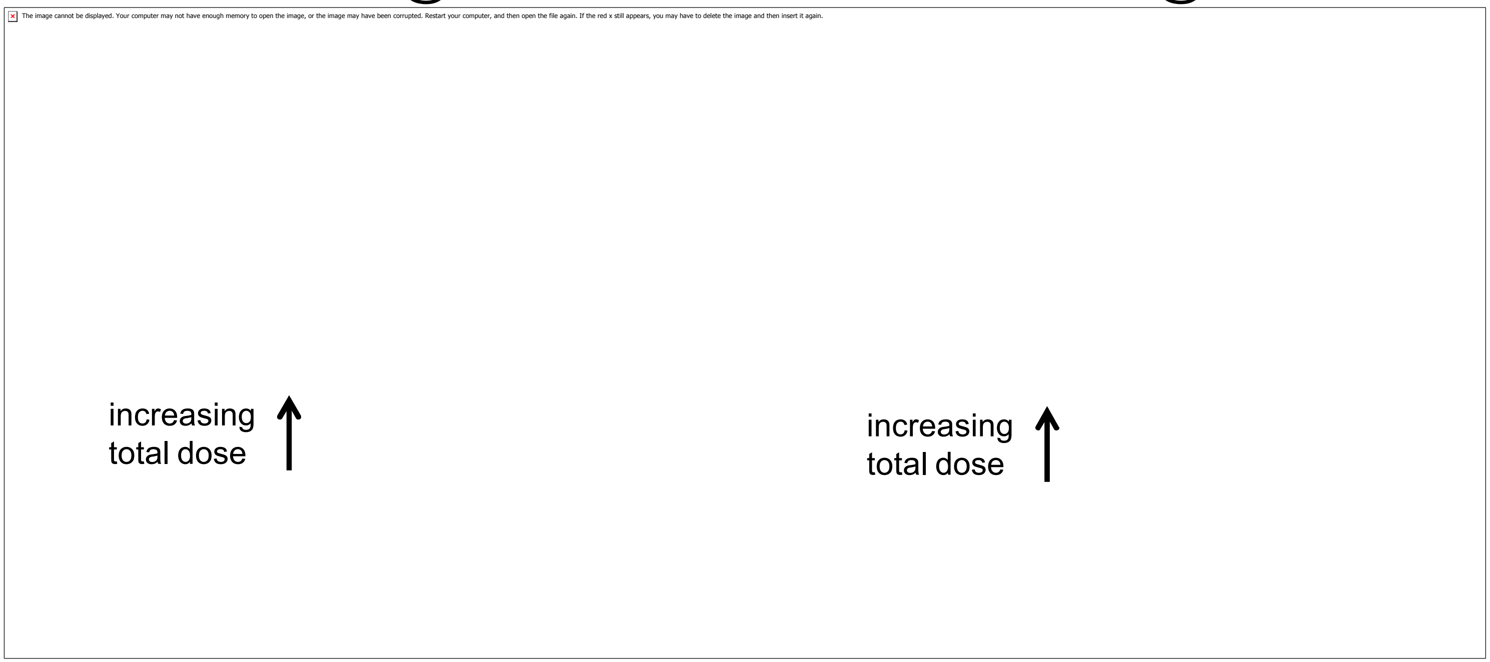
Pd powder before deposition



Pd powder after 2 cycles of EL-ALD

More cycles, more metal deposited (by X-ray Photoelectron Spectroscopy)

Pd@Rh Pd@Pt



Rh and Pt peaks normalized to Pd peak at 335 eV

STEM-EDS demonstrates conformal coating on Pd@Rh, 2 cycles

Atomic fraction Rh

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Atomic fraction Rh

STEM-EDS demonstrates conformal coating on Pd@Rh, 8 cycles as well, some thickness variation

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Atomic fraction Rh

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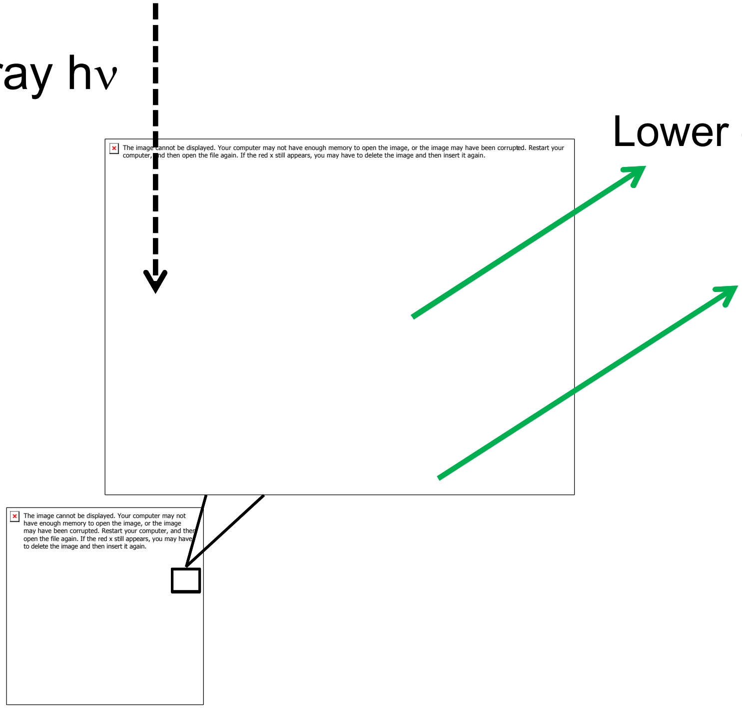
Energy Resolved Depth Profile (XPS)

At synchrotron, incident photon energy (hν) can be tuned, KE = hν - BE

X-ray hν



Lower energy photoelectrons are more surface sensitive

Higher energy photoelectrons travel farther

Lawrence Berkeley,
Advanced Light Source
Beamline 9.3.2

Energy Resolved Depth Profile (XPS)

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Spectra at three photon energies
demonstrate surface Rh enrichment

Some 3D growth and bare Pd indicated by simulated XPS depth profile

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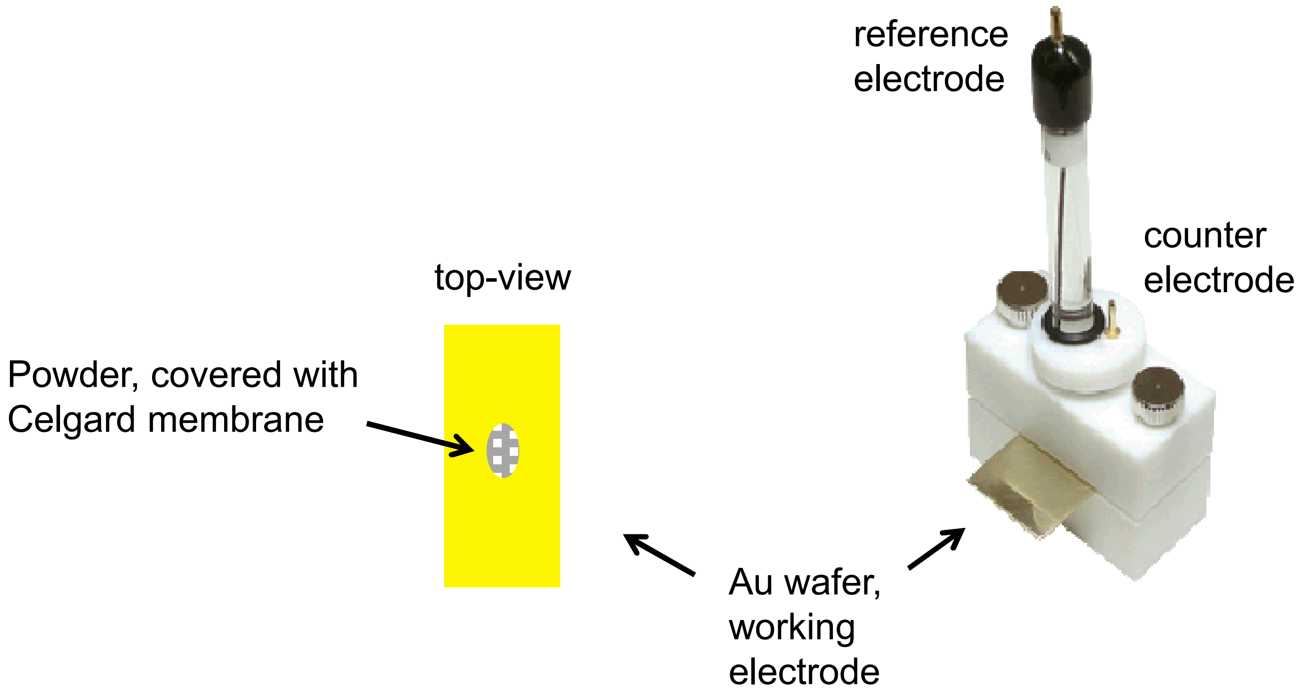
RMS Error in Rh atom % between experiment and simulation			
Pd	**4 Å layer**	**8 Å layer**	**RMSE**
0.24	-	0.76	3.6
0.23	0.05	0.72	3.8
0.23	0.07	0.70	4.0
0.21	0.14	0.65	4.3
0.14	0.46	0.40	6.7
0.05	0.95	-	11.4
-	1.00	-	11.8
-	-	1.00	19.4

Simulated* spectra with 4 & 8 Å Rh layers and 20 – 25% bare Pd

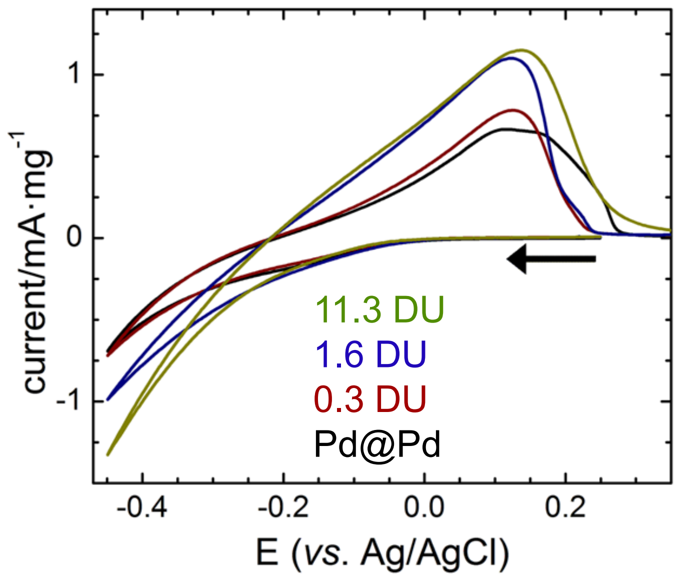
*Smekal, W. et *al*. Simulation of electron spectra for surface analysis (SESSA): a novel software tool for quantitative Auger-electron spectroscopy and X-ray photoelectron spectroscopy. Surf. Interface Anal. 2005, 37 (11), 1059-1067

Direct measurement of hydrogen desorption on powders

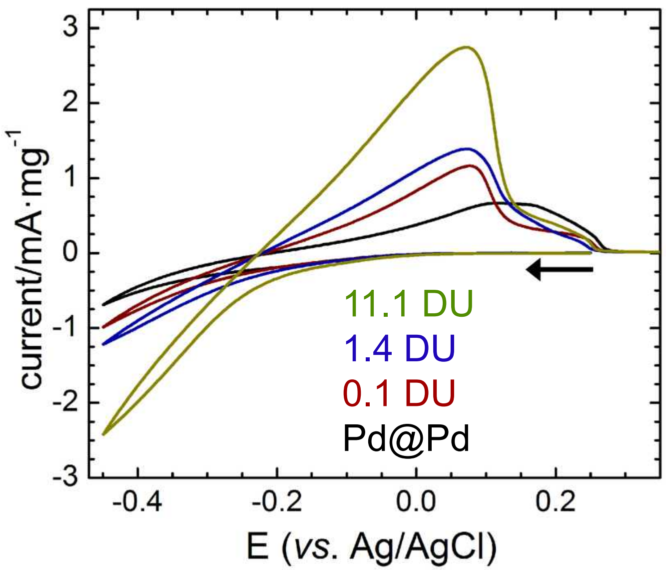


Direct measurement of hydrogen desorption on powders

Pd@Rh

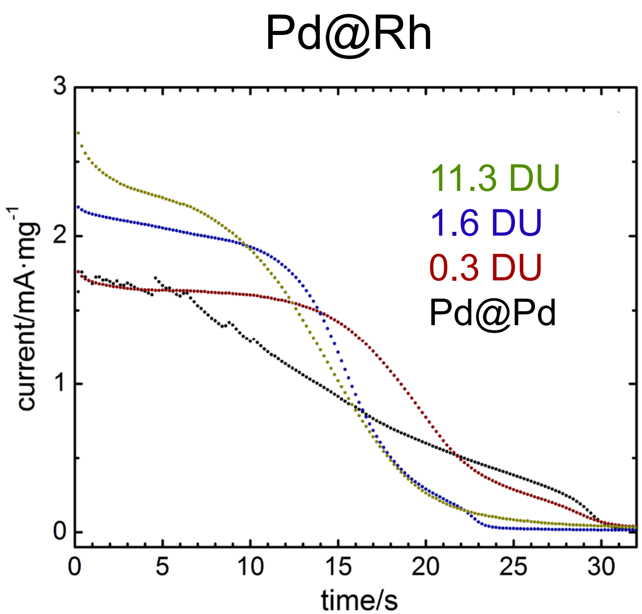


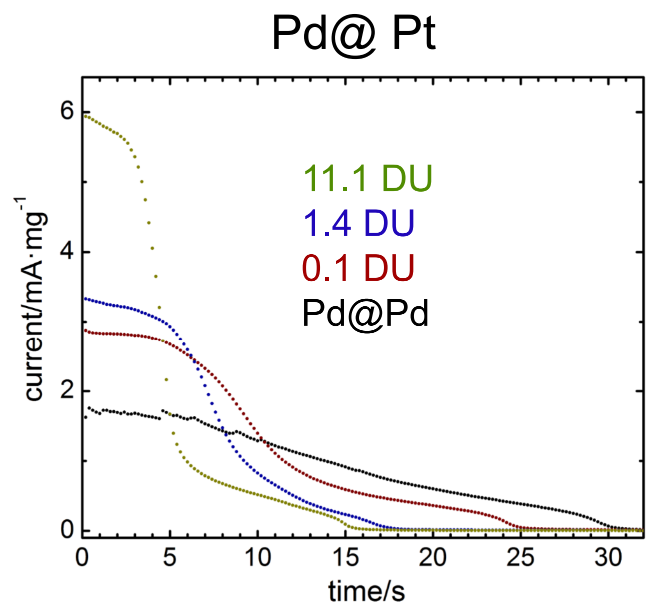
Pd@ Pt



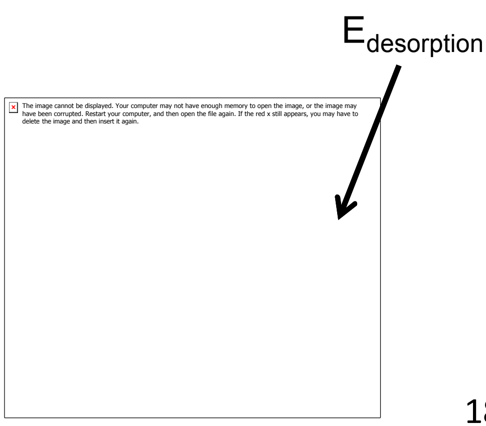
- Adlayer improves hydrogen absorption and desorption kinetics
- Greater effect with thicker layer

Direct measurement of hydrogen desorption on powders



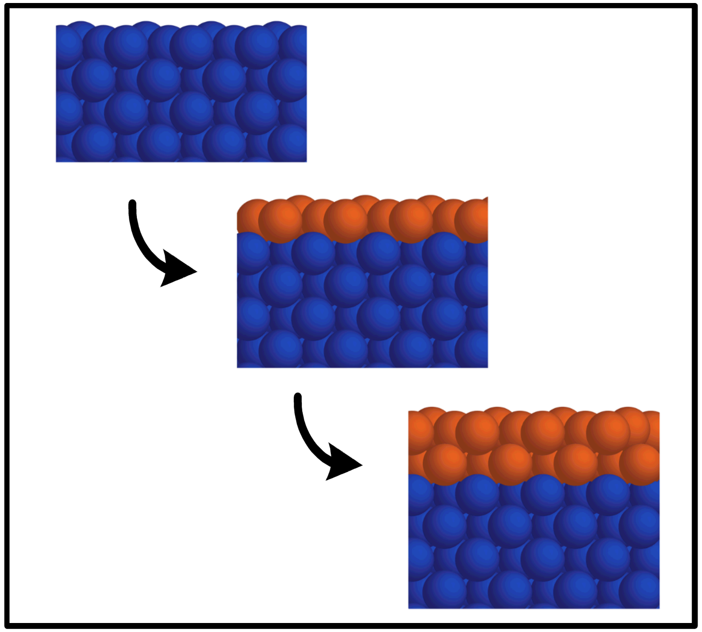


- Powders charged with H_2 by applying 1.5 mA for 60s
- Poised at 0.27 V vs. Ag/AgCl to desorb hydrogen (t_0)



Summary

- New strategy for large-scale deposition of adlayers on high surface area powders (Pd/C works too!)
- STEM-EDS shows a conformal adlayer can be formed
- STEM-EDS and ERXPS suggest nanometer-scale adlayers
- Powders show hydrogen adsorption and desorption kinetics



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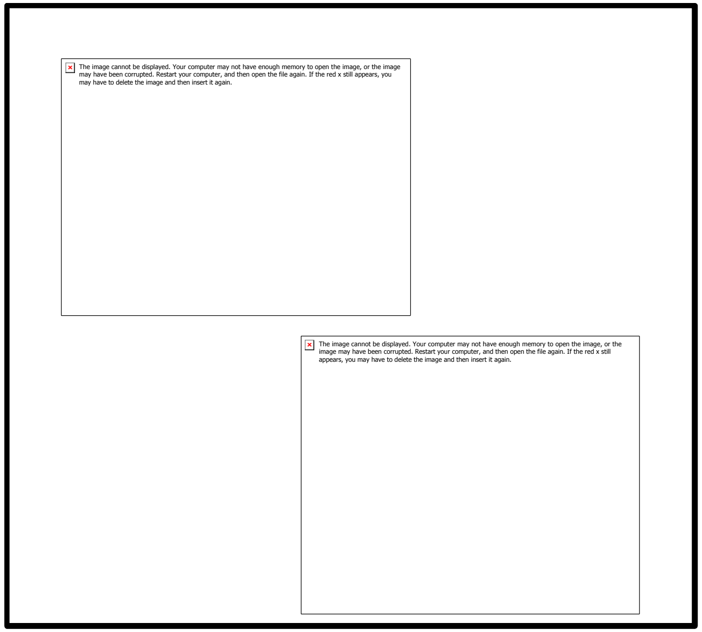

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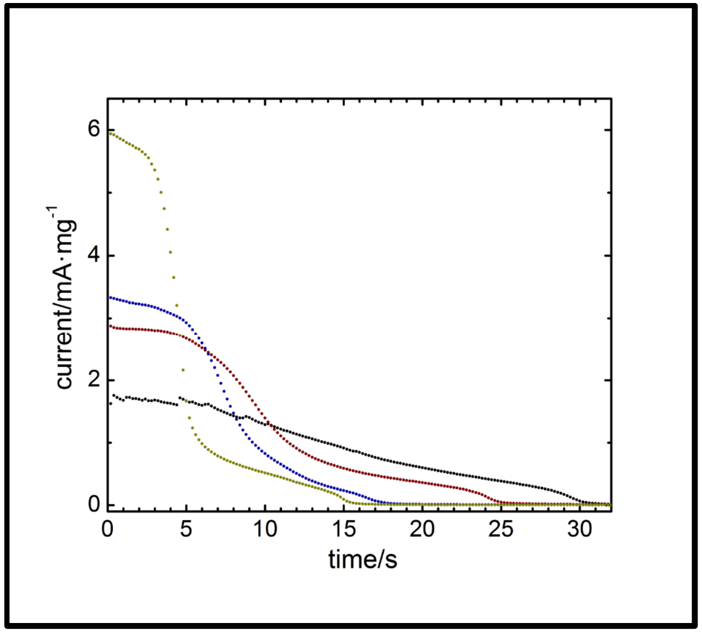
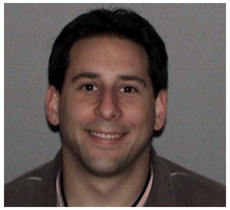


Acknowledgements

David Robinson
Project PI
Sandia



Josh Sugar
STEM-EDS

Professor John Stickney
Collaborator
University of Georgia

Farid El Gabaly
XPS

Sandia LDRD Program for funding

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