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Functionalization of Metal Surfaces using Hydride Intermediates

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U.S. DEPARTMENT OF ENERGY

NNSA National Nuclear Security Administration

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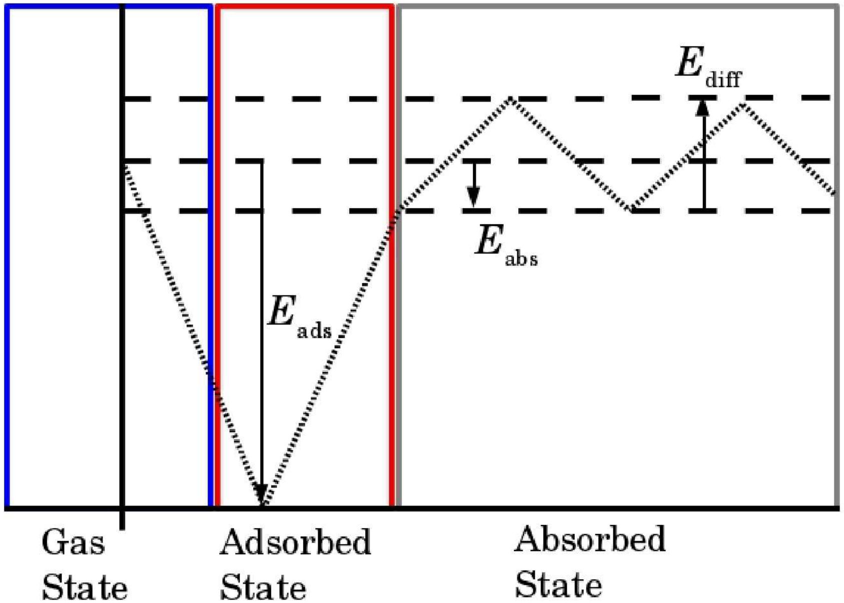
Outline

- Goal: improve hydrogen reaction kinetics at surfaces
- Strategy: Use H surface reactivity to modify composition
  - Atomic-layer electroless deposition
    - Pd powder substrates
    - Pd film substrates
    - Pt powder substrates
- Strategy: Use H surface reactivity to modify surface area
  - Growth of nanoporous Pd on Pd by bulk hydriding
- Solution-phase path to surface and bulk hydriding

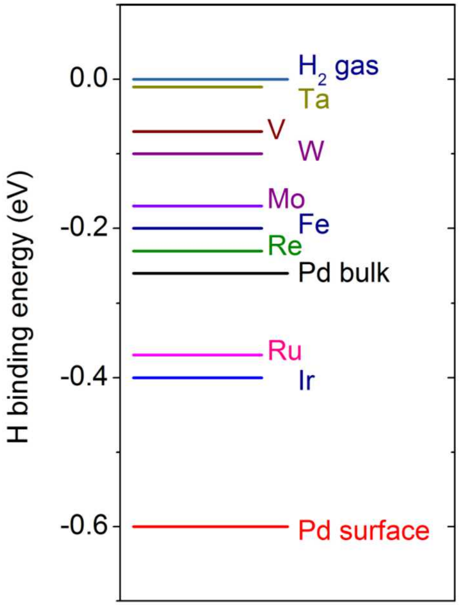
Surface modification should improve kinetics of hydriding and dehydriding Pd

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

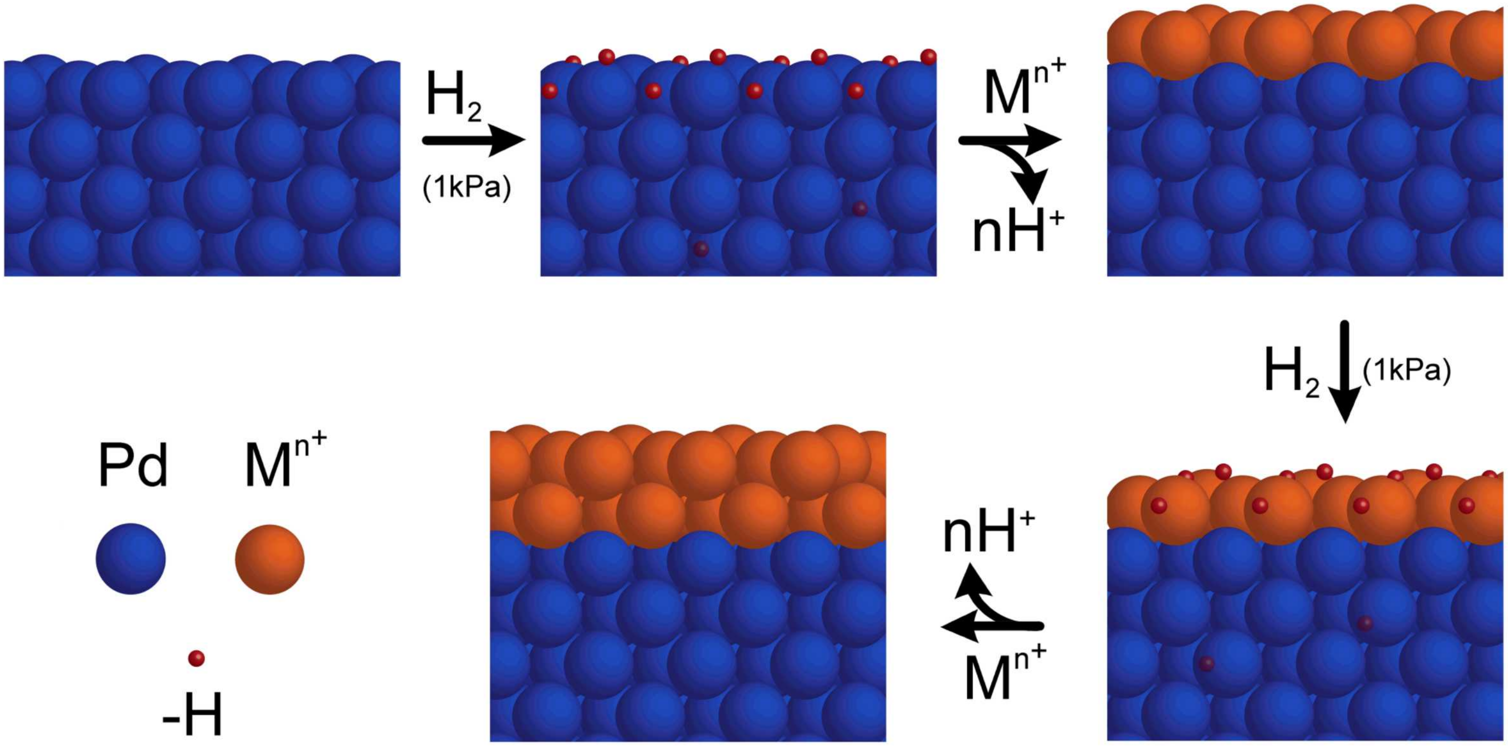


M. Salloum, S.C. James, D. B. Robinson. Chem Eng Sci. 2014 10.1016/j.ces.2014.09.001



J. Greeley, M. Mavrikakis. J. Phys. Chem. B 2005, 109, 3460-3471

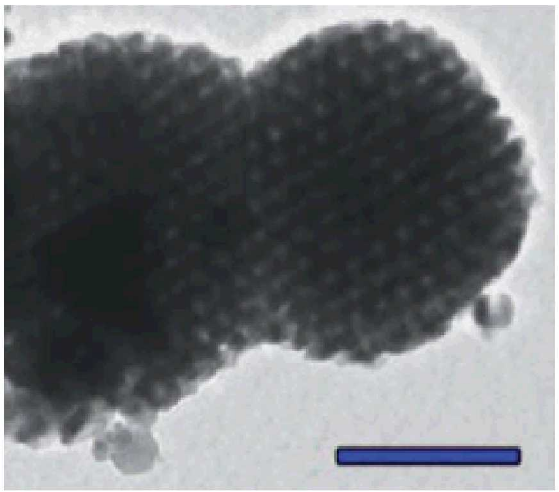
Atomic-Layer Electroless Deposition (ALED)



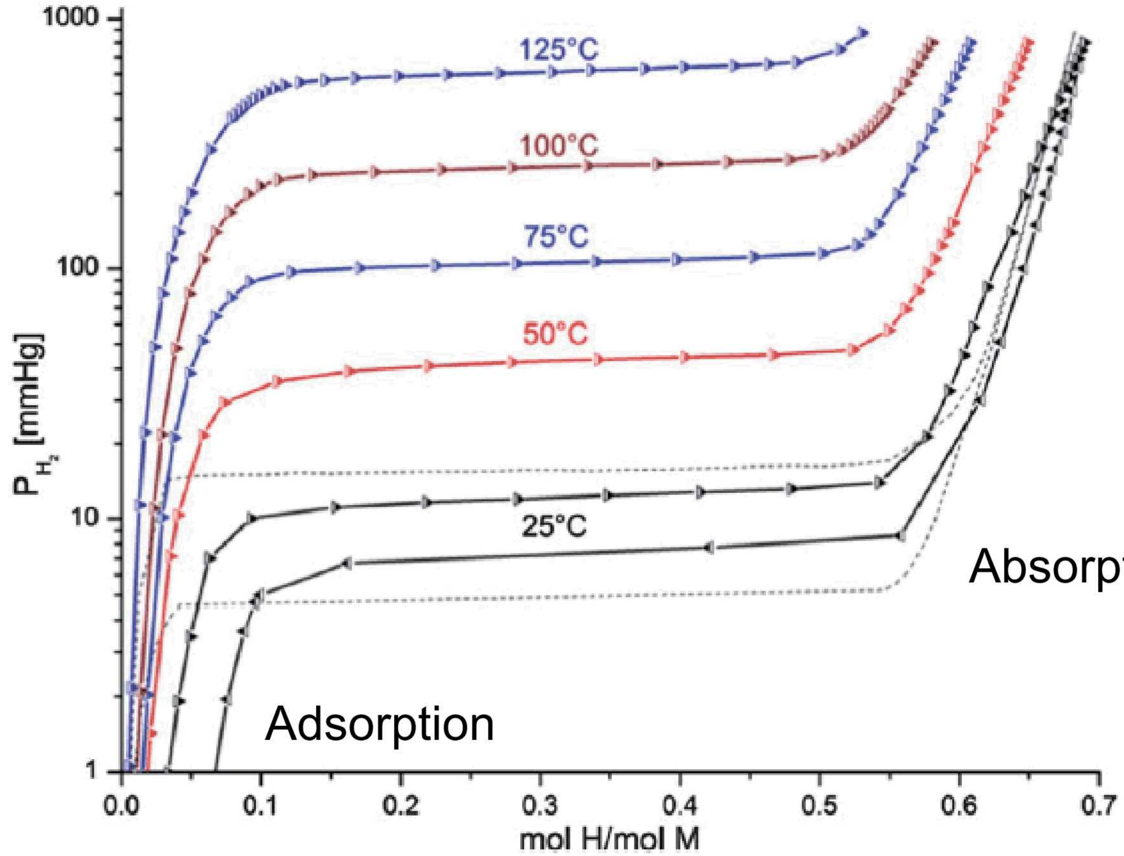
Scalable, room temperature, works with insulating support, applies to “rough” surfaces with high surface area

Patrick J. Cappillino et al., Langmuir 30 (2014) 4820 10.1021/la500477s

Absorption of H_2 gas by Pd



100 nm



Absorption

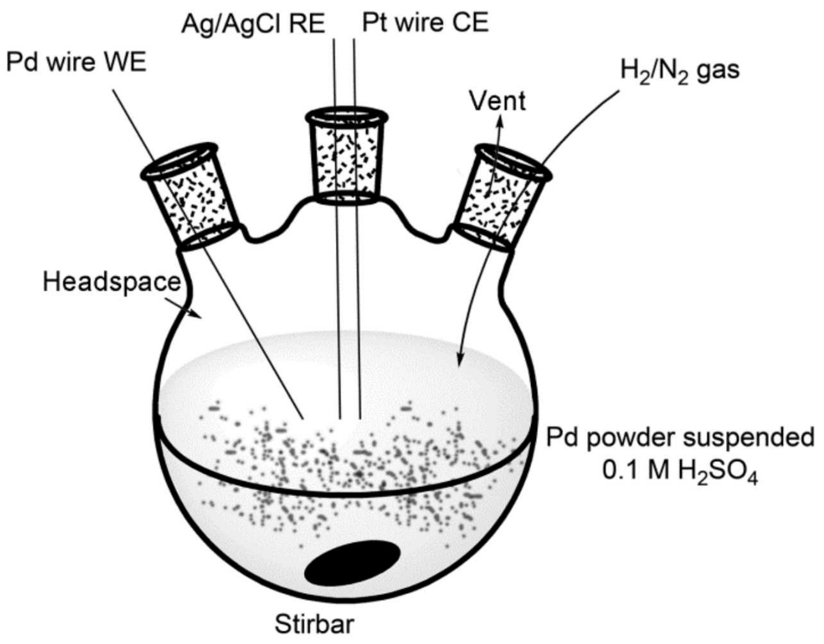
Adsorption

P. J. Cappillino et al.,
J. Mater. Chem. A 2013, 1, 602
10.1039/C2TA00190J

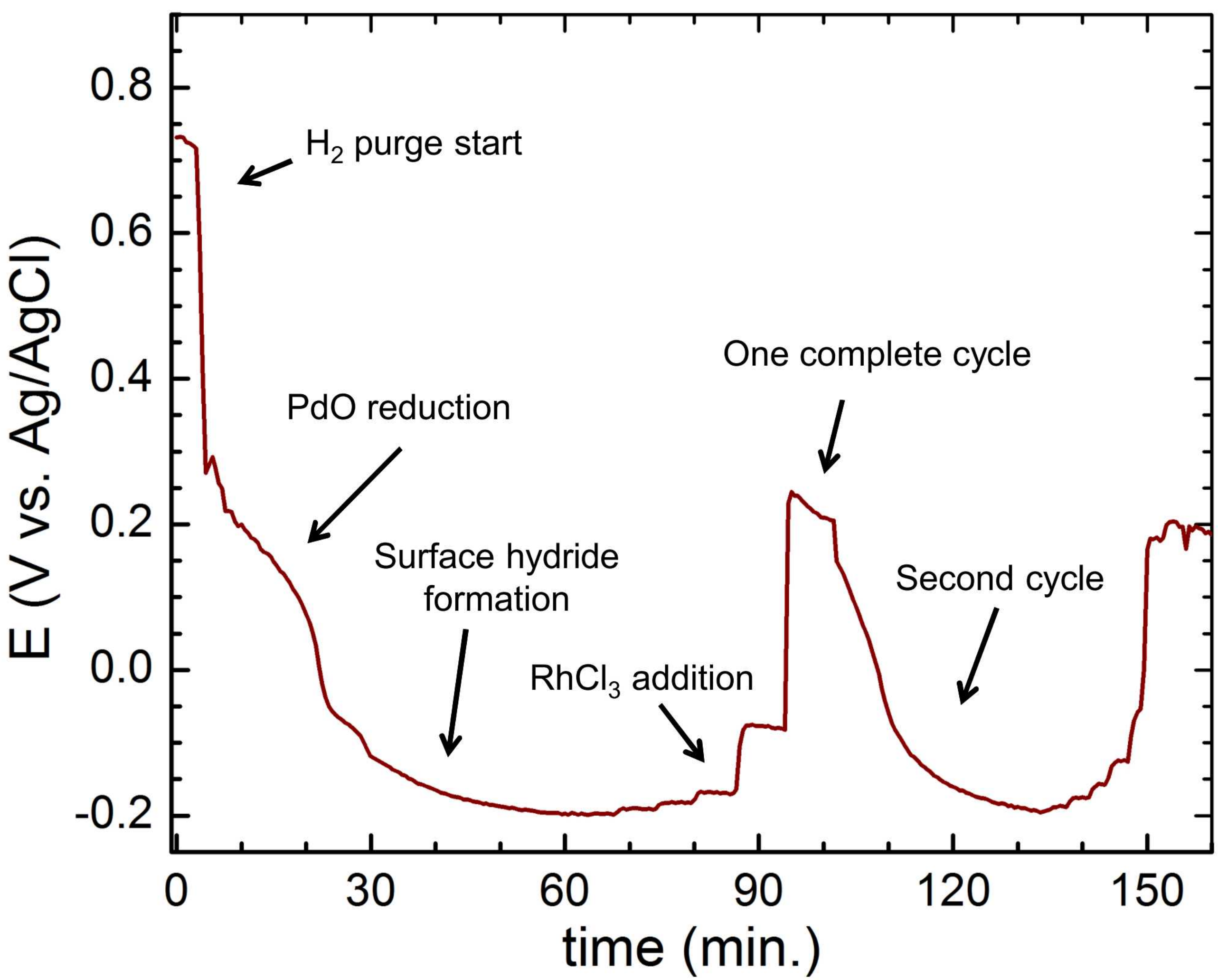
Only surface, dilute bulk hydride below a transition pressure

Simple Apparatus for ALED

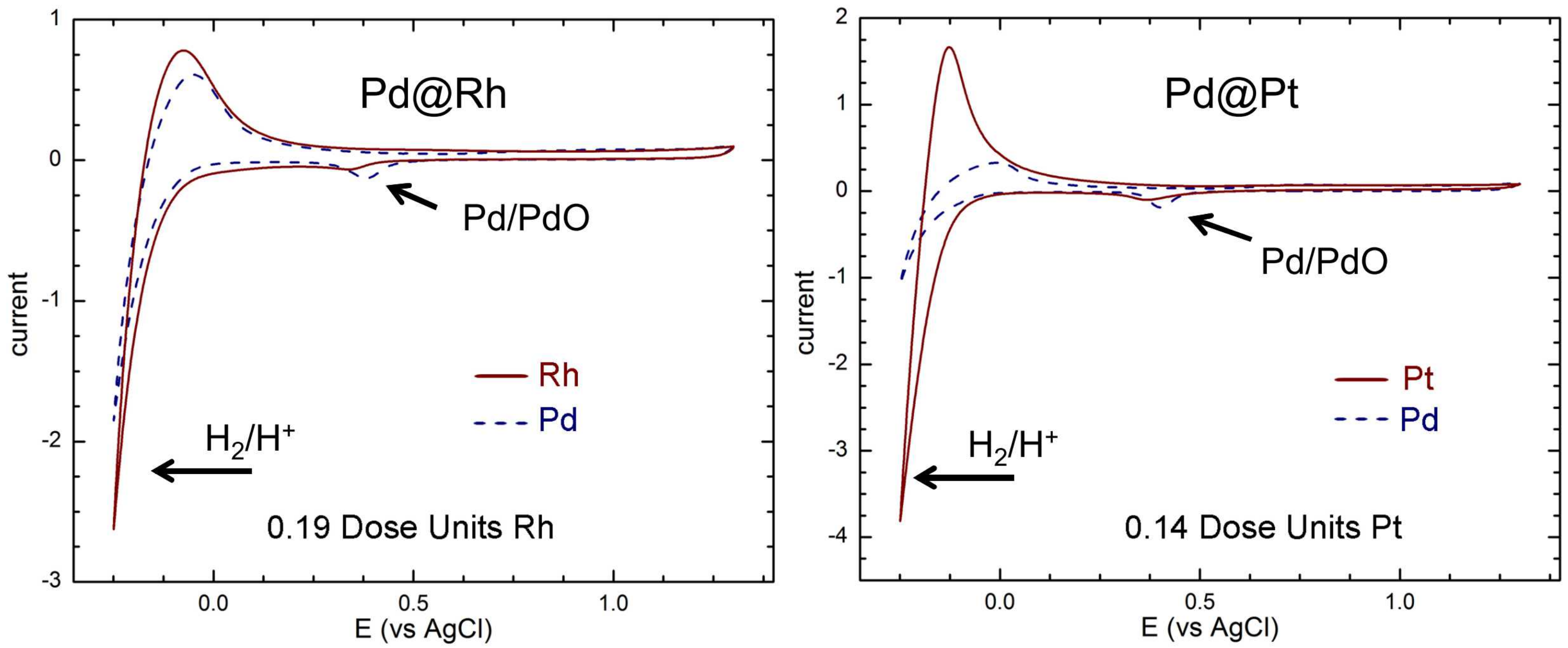
- Pd powder suspended in electrolyte
- Reagent gas (1% H_2/N_2)/inert gas source
- Metal salt solution added by syringe
- Electrodes to measure progress of reaction



Monitor open circuit potential to follow reaction



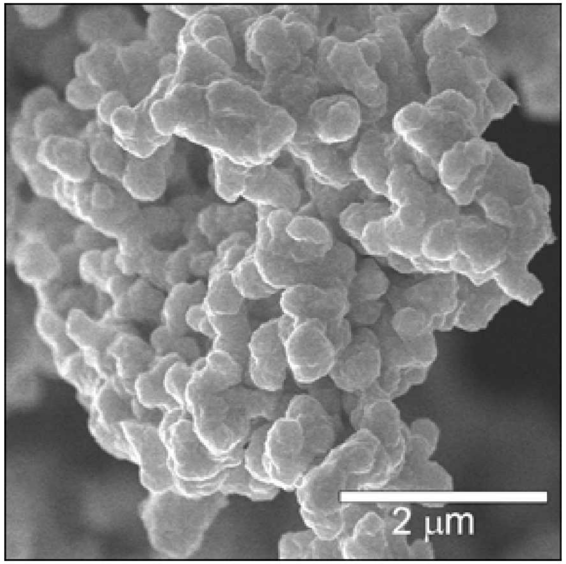
Cyclic voltammetry of Pd test wire before and after deposition of adlayer of Rh (left) and Pt (right)



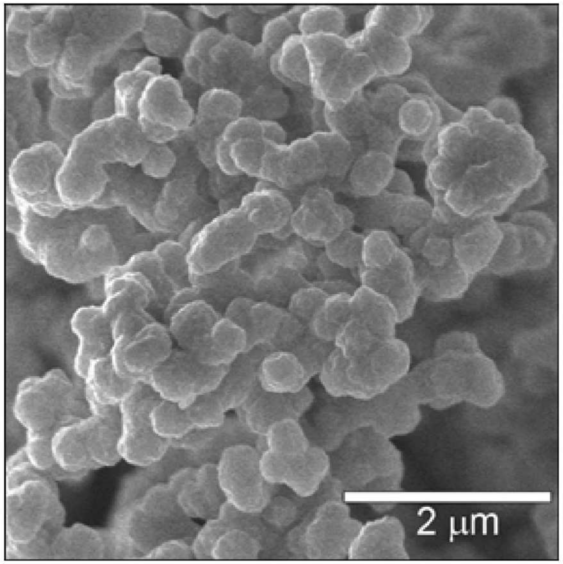
CV shows that adlayer inhibits surface Pd/PdO redox couple and suggests improved hydride/dehydride kinetics.

“Dose Unit” is approximately one metal ion introduced per surface metal atom.

No change to particle morphology after two cycles of ALED of Rh on Pd

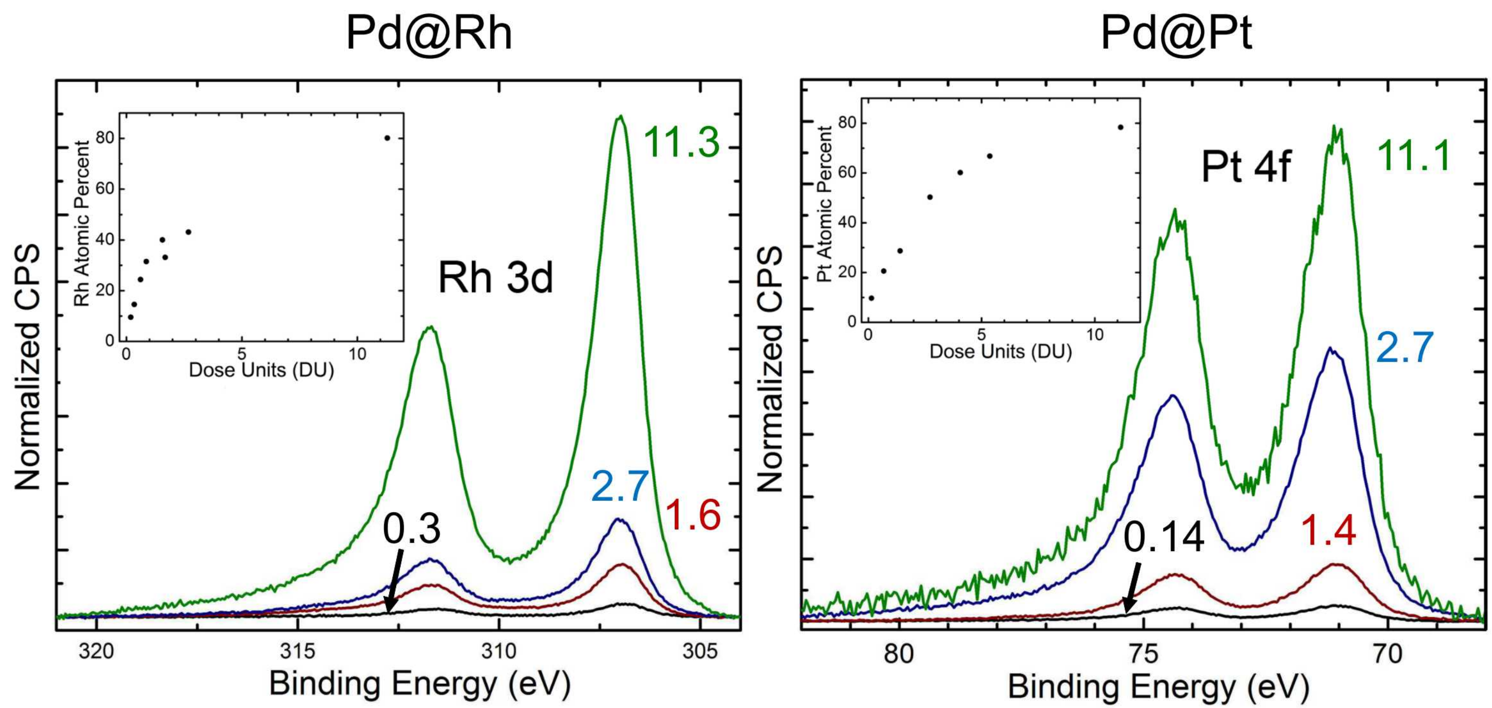


Pd powder before deposition



Pd powder after 2 cycles of ALED

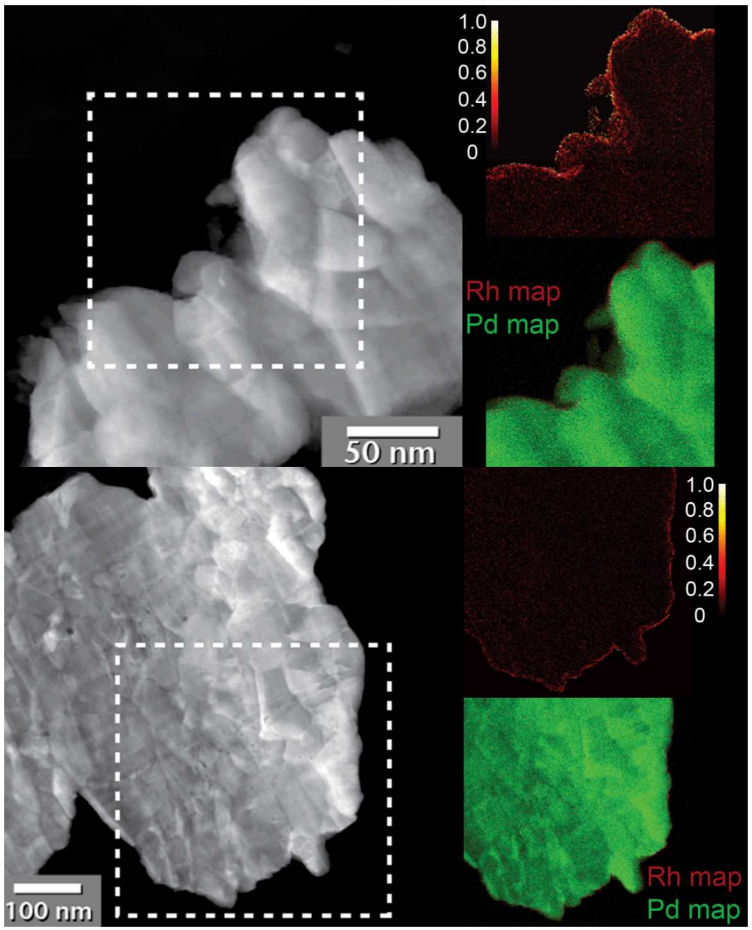
More cycles, more metal deposited (by X-ray Photoelectron Spectroscopy)



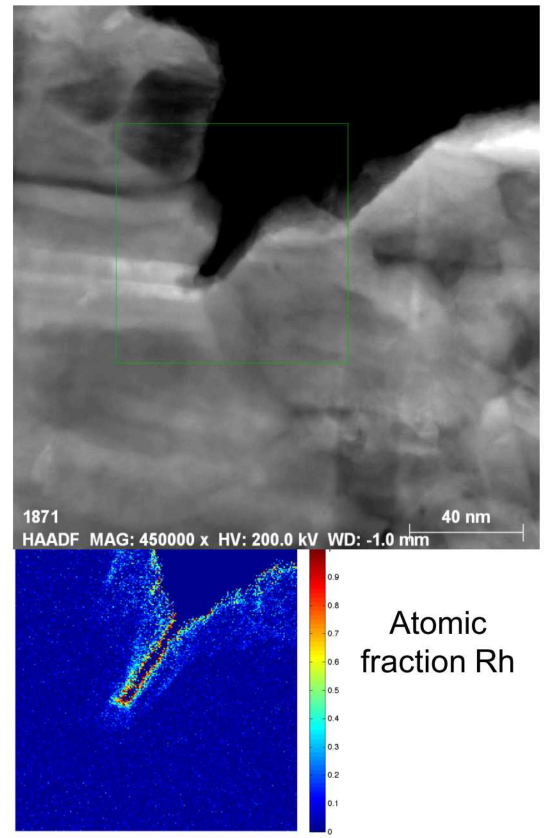
Rh and Pt peaks normalized to Pd peak at 335 eV
Numbers on curves indicate dose units

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

Atomic fraction Rh



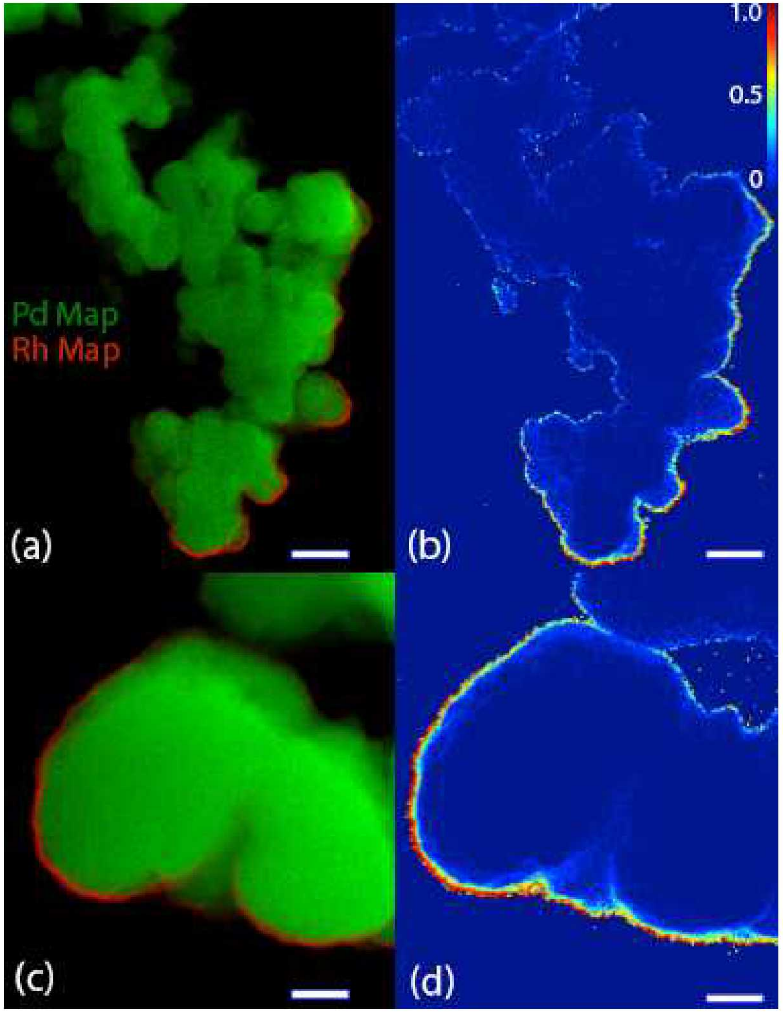
Atomic fraction Rh



Atomic fraction Rh

Coating is present in narrow regions

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

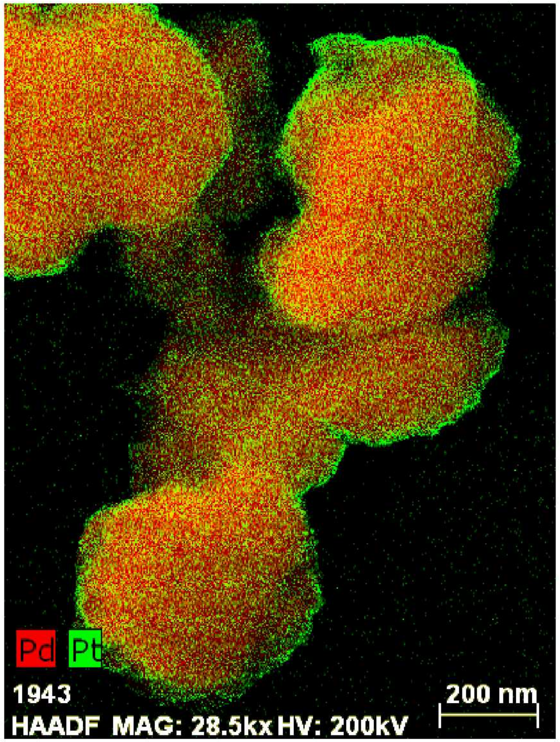


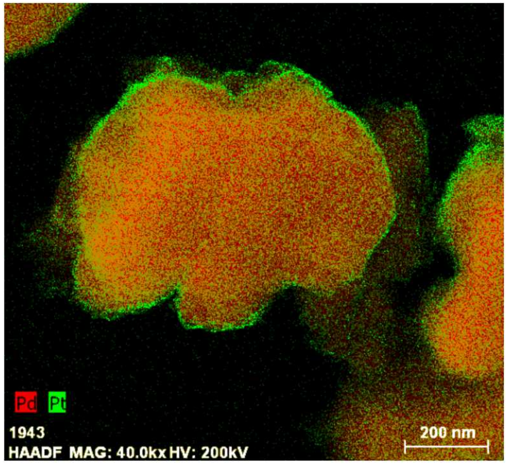
Atomic fraction Rh

500 nm

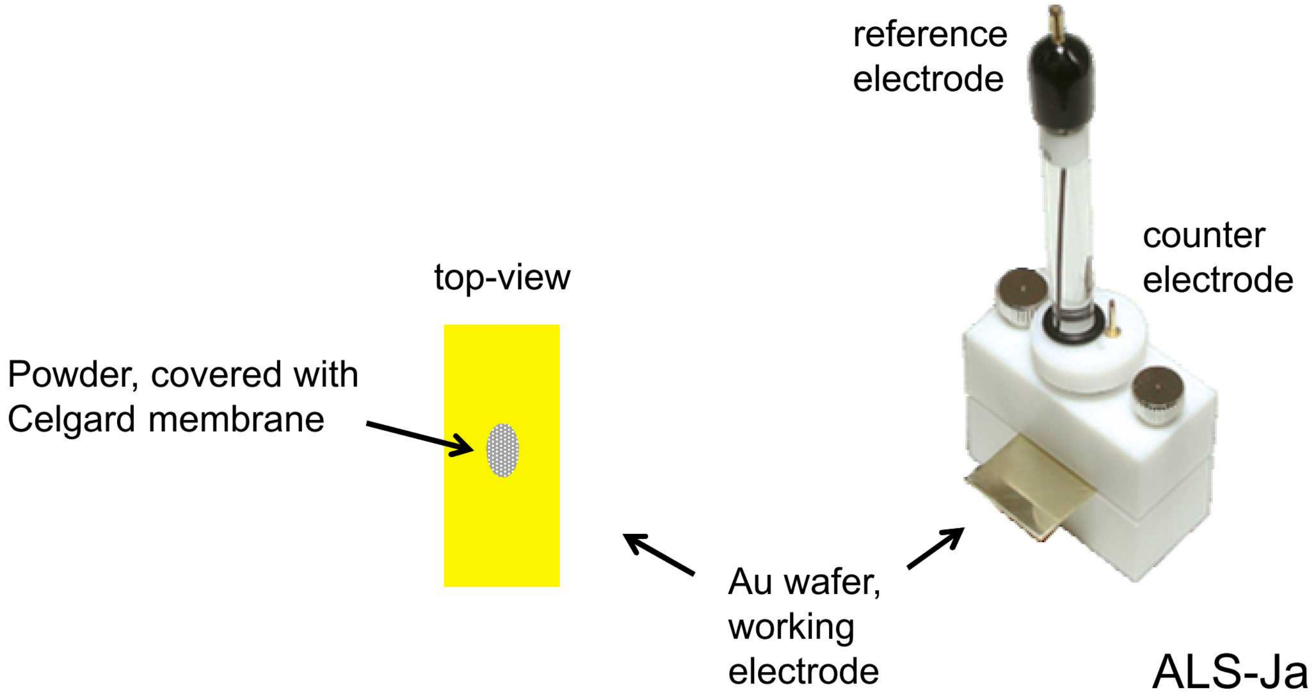
150 nm

STEM-EDS demonstrates conformal coating on Pd@Pt, 1 cycle



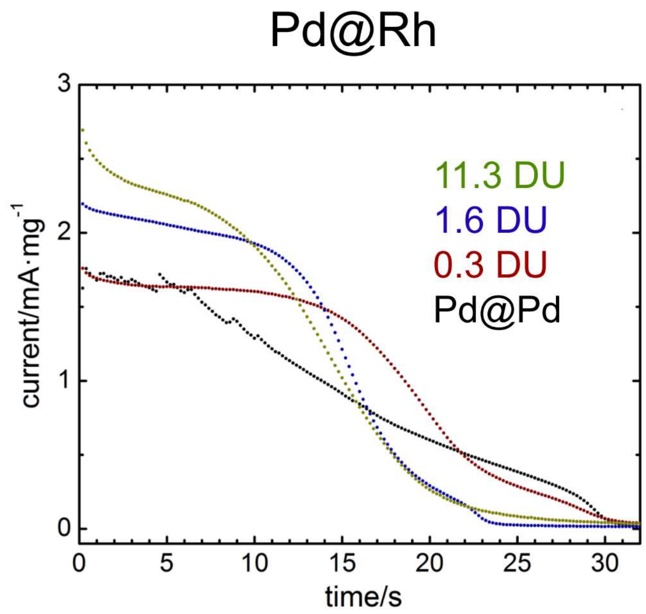


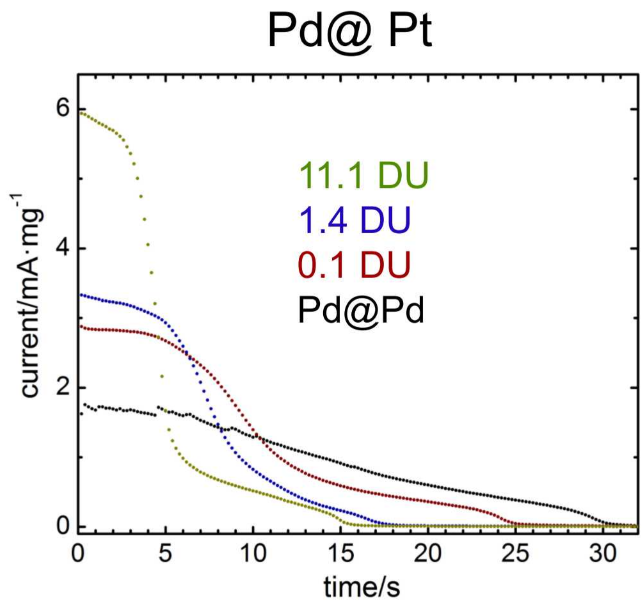
Direct measurement of hydrogen desorption on powders



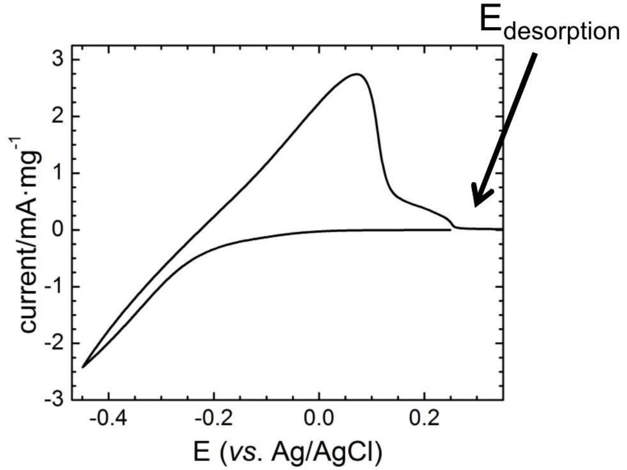
ALS-Japan
Plate material
evaluating cell

Hydrogen desorption from powders

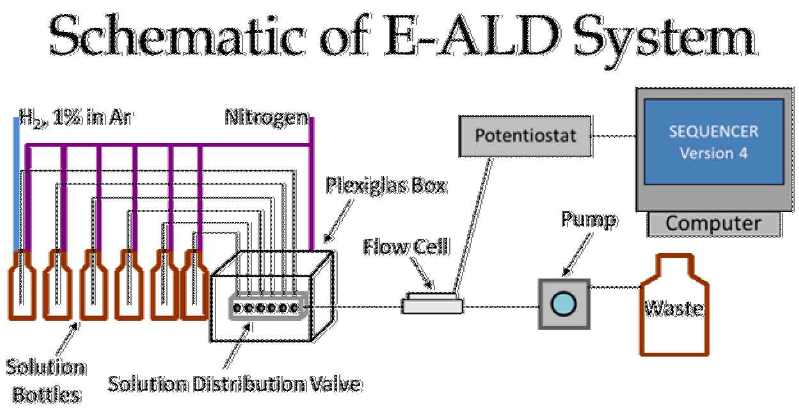


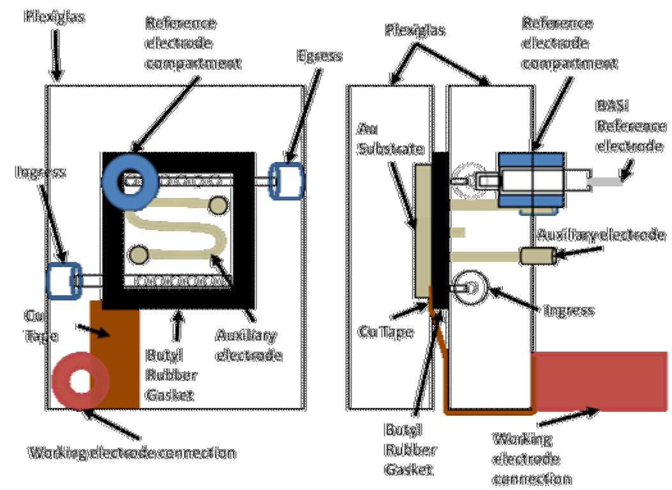


- Powders charged with H_2 by applying 1.5 mA for 60s
- Poised at 0.27 V vs. Ag/AgCl to desorb hydrogen (t_0)
- More adlayer metal yields faster dehydriding in this dose range
- Pt adlayer yields faster dehydriding kinetics than Rh



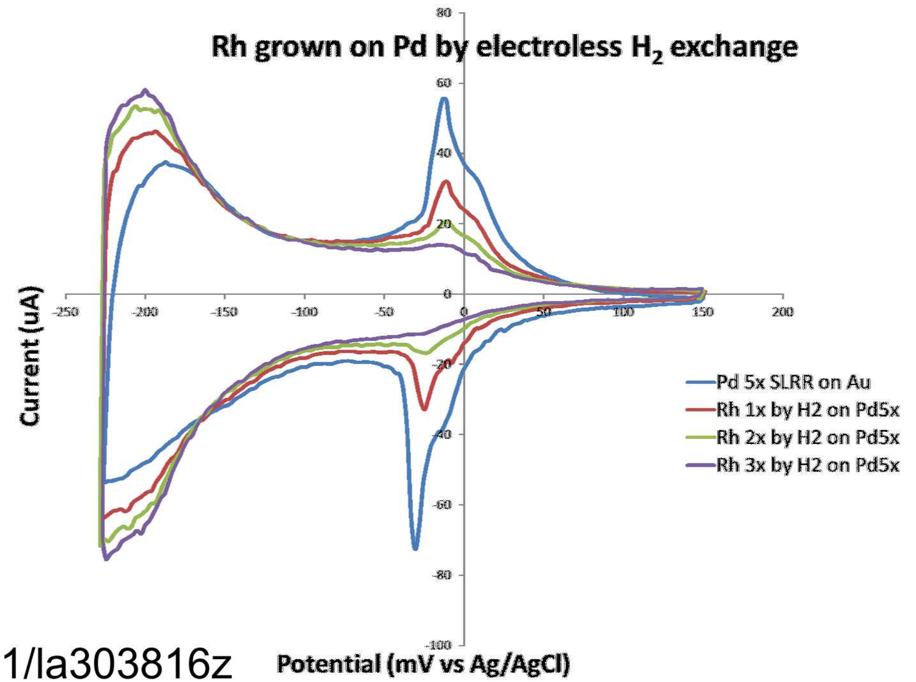
ALED on thin films





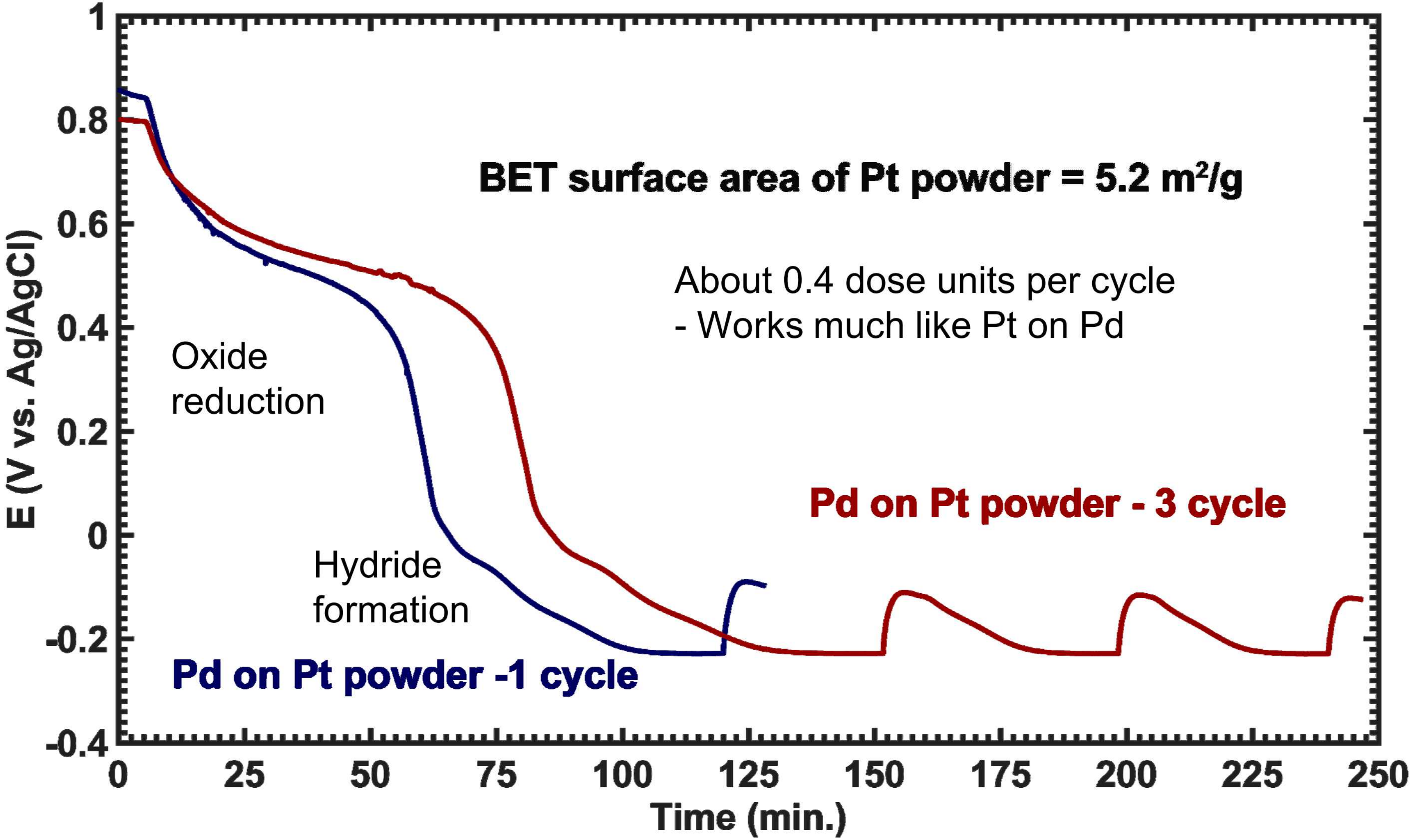
Reagents:
0.1 mM $RhCl_3$ 10mM HCl 100mM H_2SO_4
0.1 mM $PdCl_2$ 50mM HCl
2 mM $CuSO_4$ in 100 mM H_2SO_4
0.1 M H_2SO_4 blank

Grow Pd on Au by E-ALD*
Similar amounts bulk, surface hydride
Rh suppresses surface H peak (-50 mV),
Improves hydrogen desorption kinetics

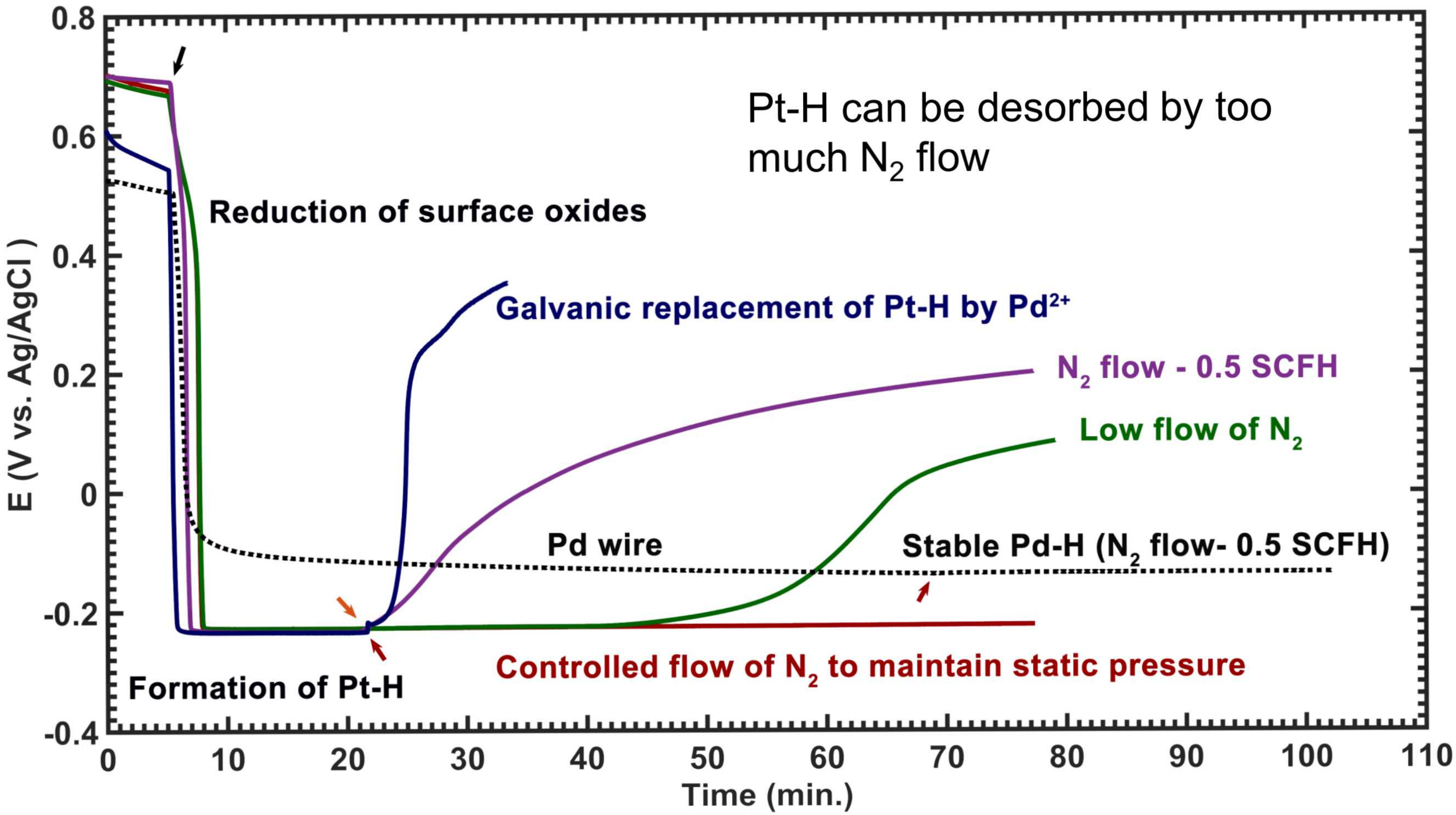


*Sheridan et al., Langmuir 2013, 29, 1592 10.1021/la303816z

Pd on Pt powder



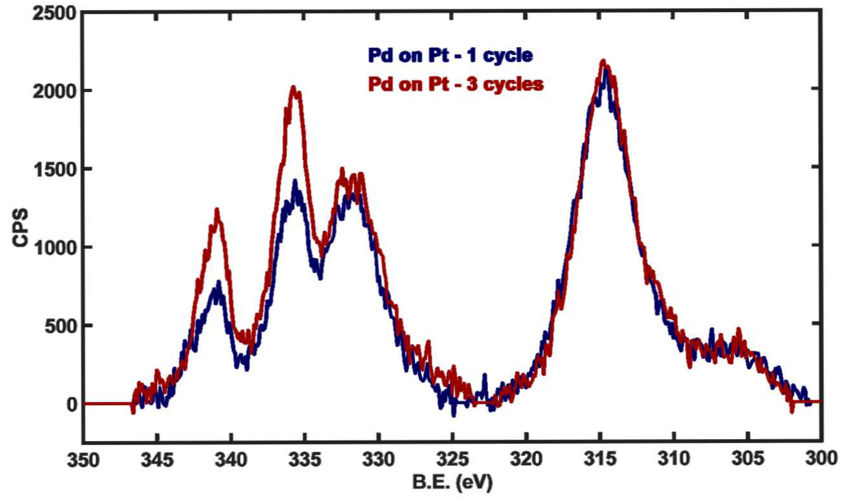
Pt surface hydride stability



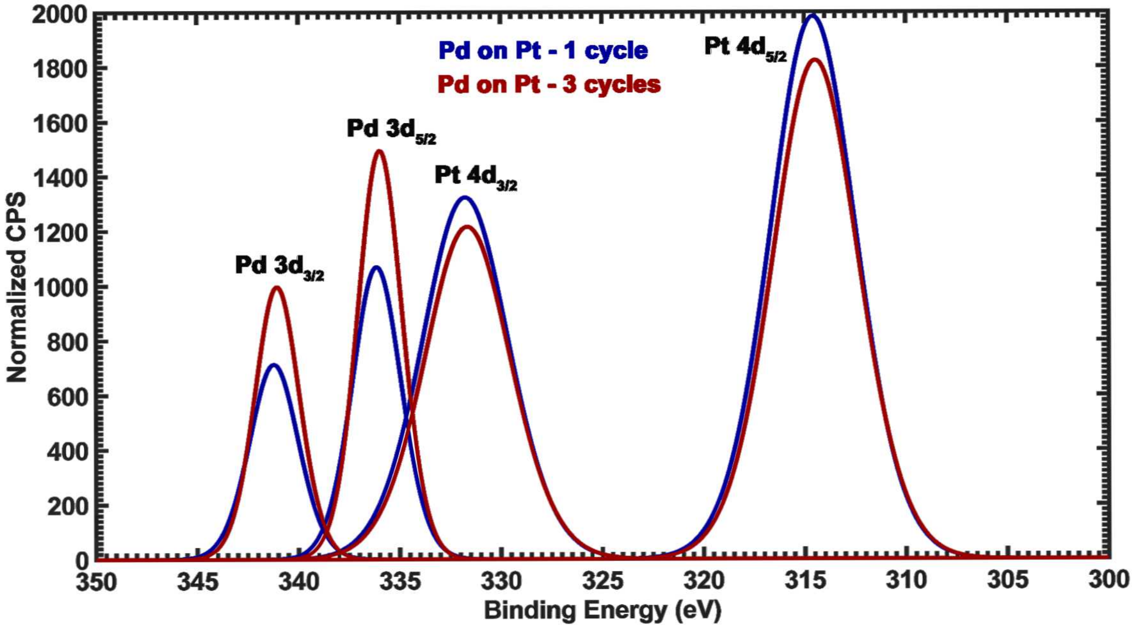
Pd on Pt powder XPS

Surface Pd increases with increasing number of cycles

Raw spectı

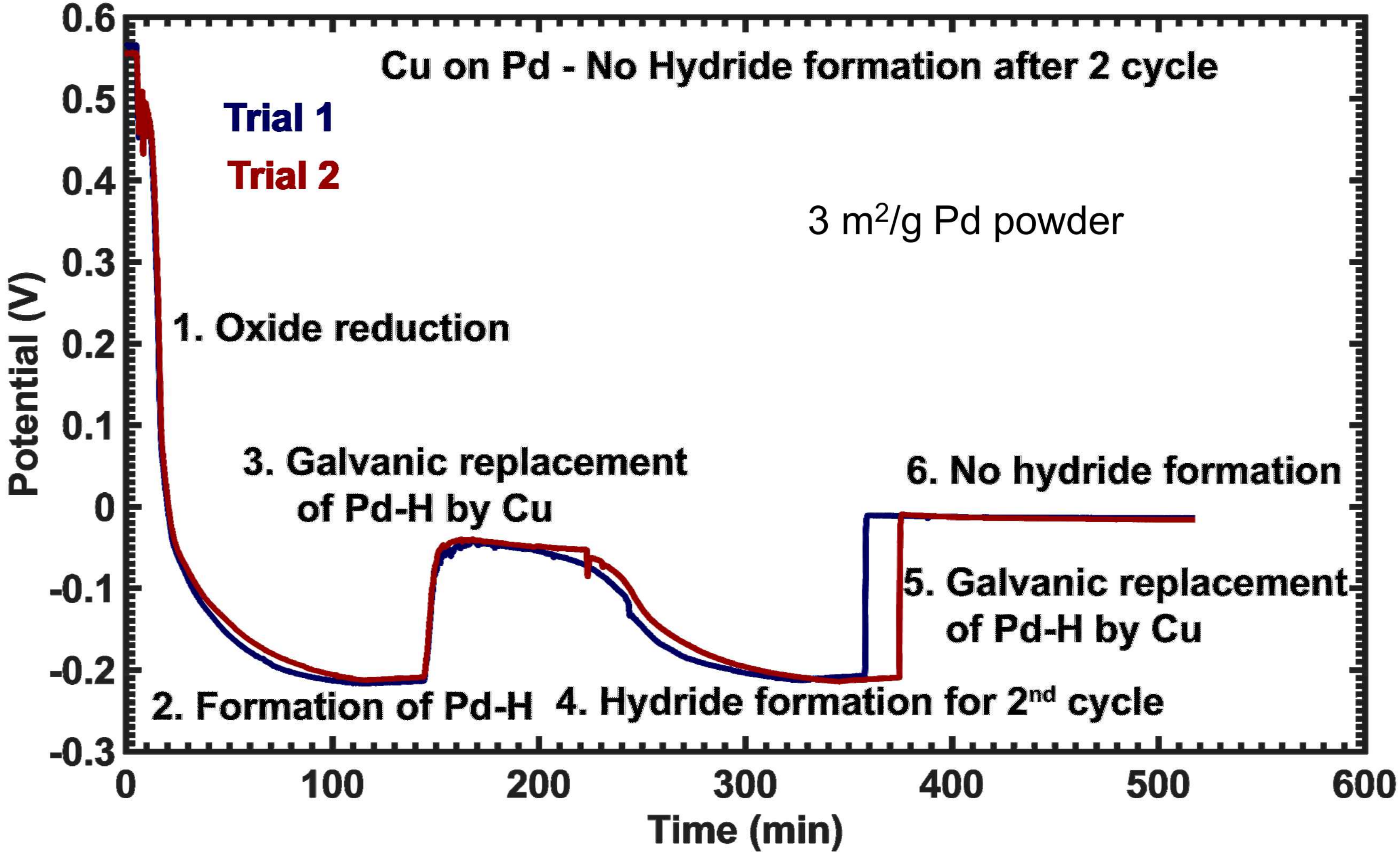


Background-corrected Gaussian fits



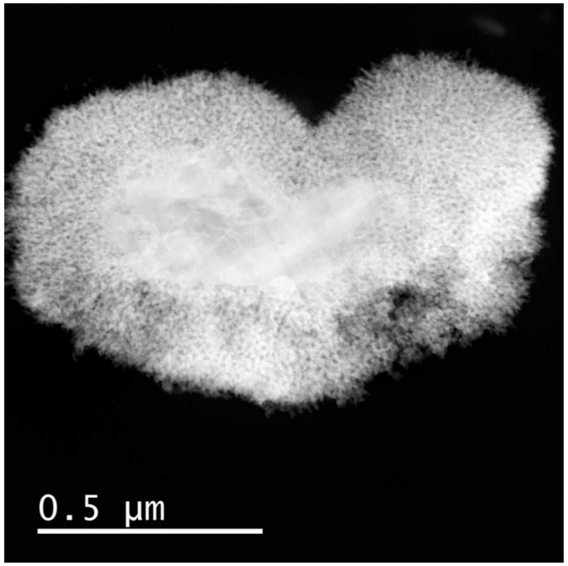
Sample	% Pd
1-cycle	23
3-cycle	29

ALED of Cu onto Pd powder



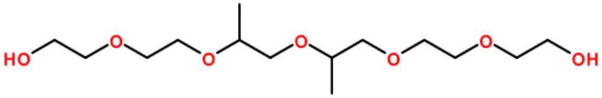
Iterative Electroless Nanoporous Pd

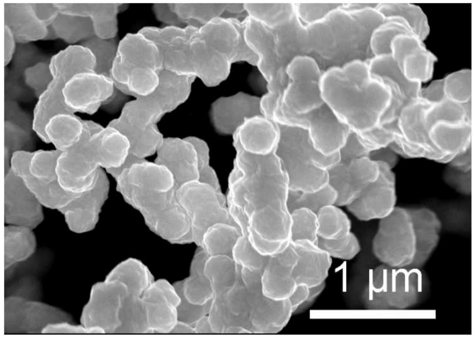
- Stepwise growth of nanoporous Pd with dilute micelle former
  - Place Pd film or powder in vented fritted tube
  - Flow H_2 (or dilute H_2)
  - $Pd + H_2 \rightarrow PdH_{0.6}$
  - Purge headspace with N_2
  - Add aqueous Pd^{2+}, Pluronic F127, dilute HCl
  - $PdH_{0.6} + Na_2PdCl_4 + F127 \rightarrow$ porous Pd + HCl
  - Drain, repeat as desired, rinse

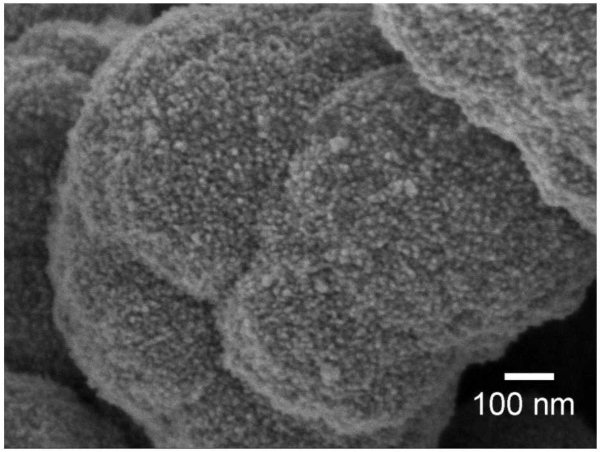


1 cycle

Pluronic F127 micelle former
$EO_{101}\ PO_{56}\ EO_{101}$
where $EO_2PO_2EO_2$ is :





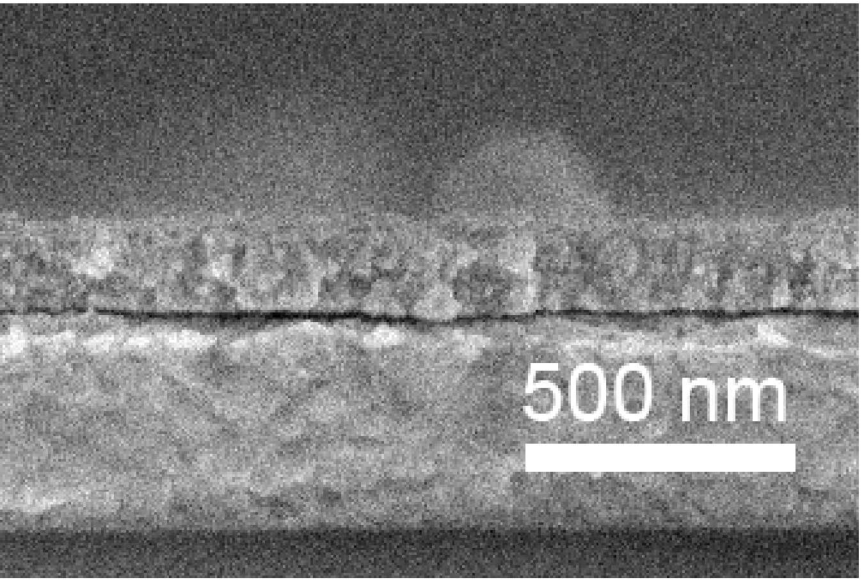


Film thickness vs. cycle number

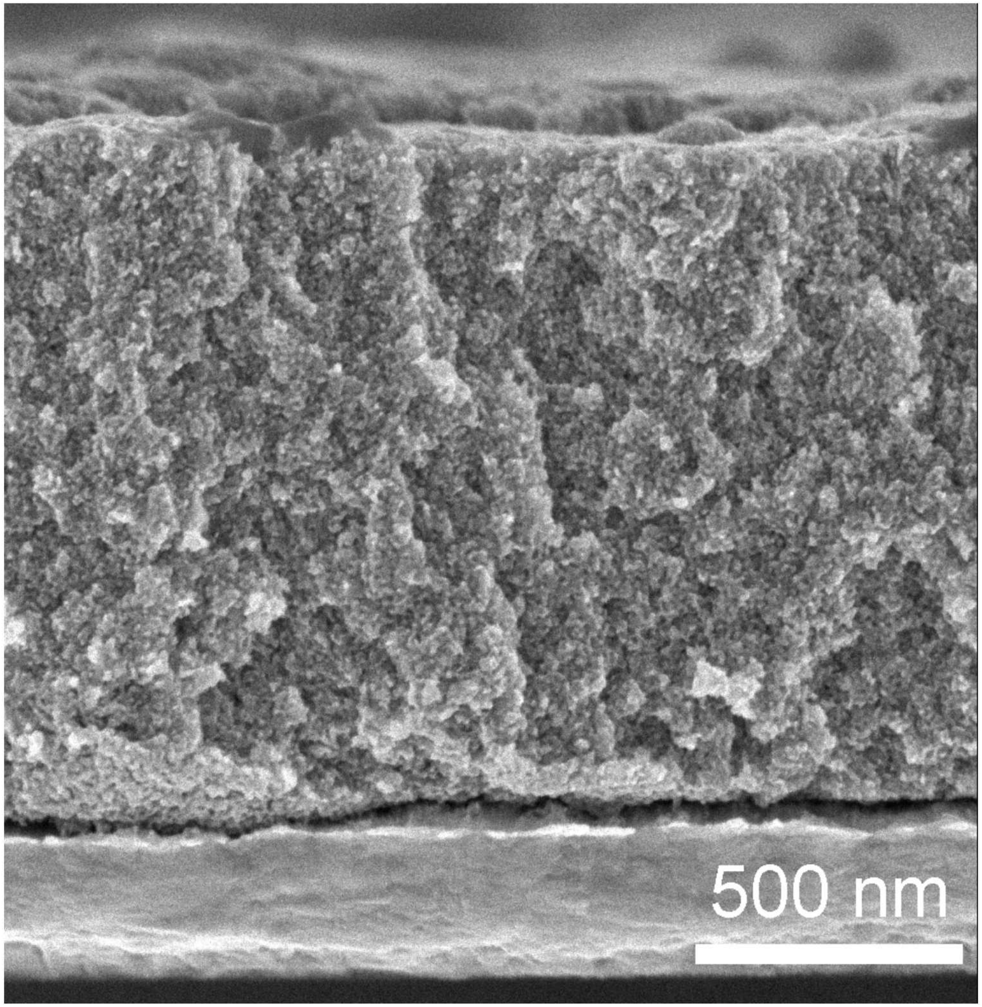
Film ideally grows exponentially

~ $(d_0/\phi) \times 1.3^n$
d_0 = initial film thickness
ϕ = porosity
n = number of cycles

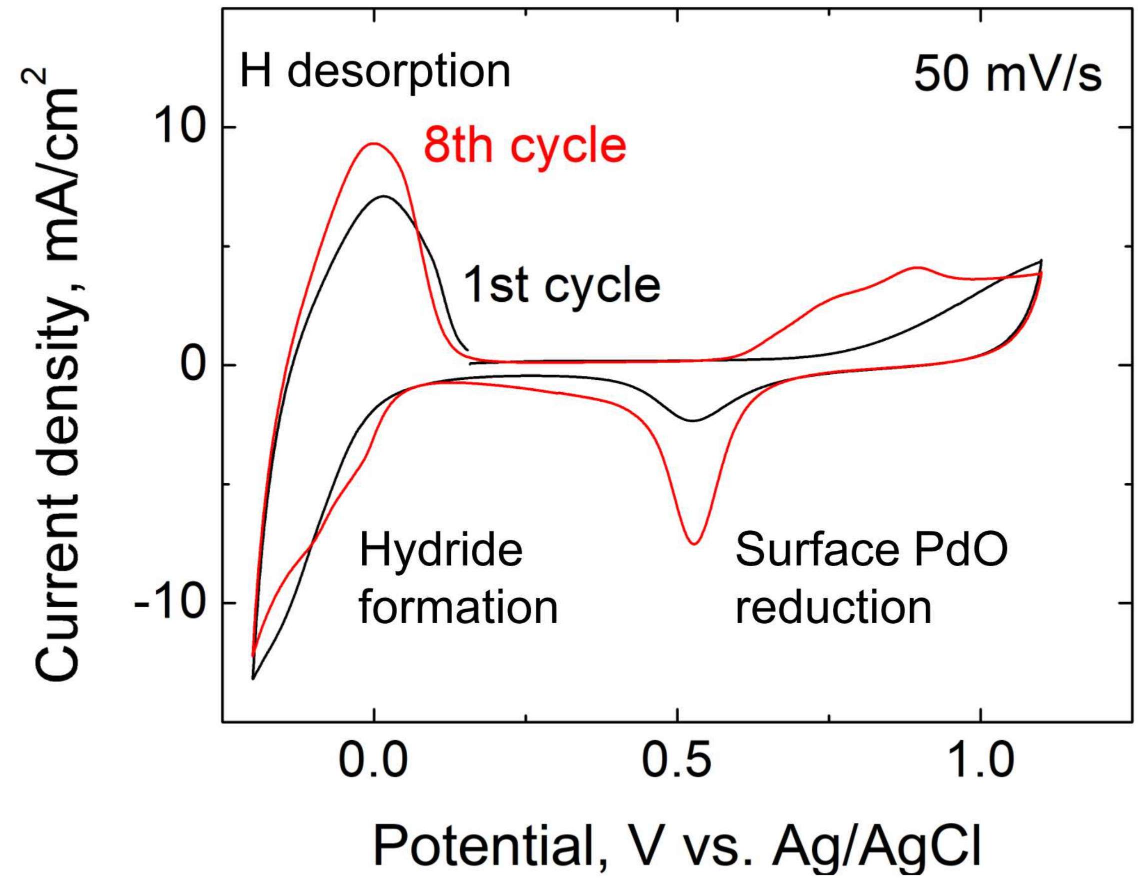
1 cycle



3 cycles

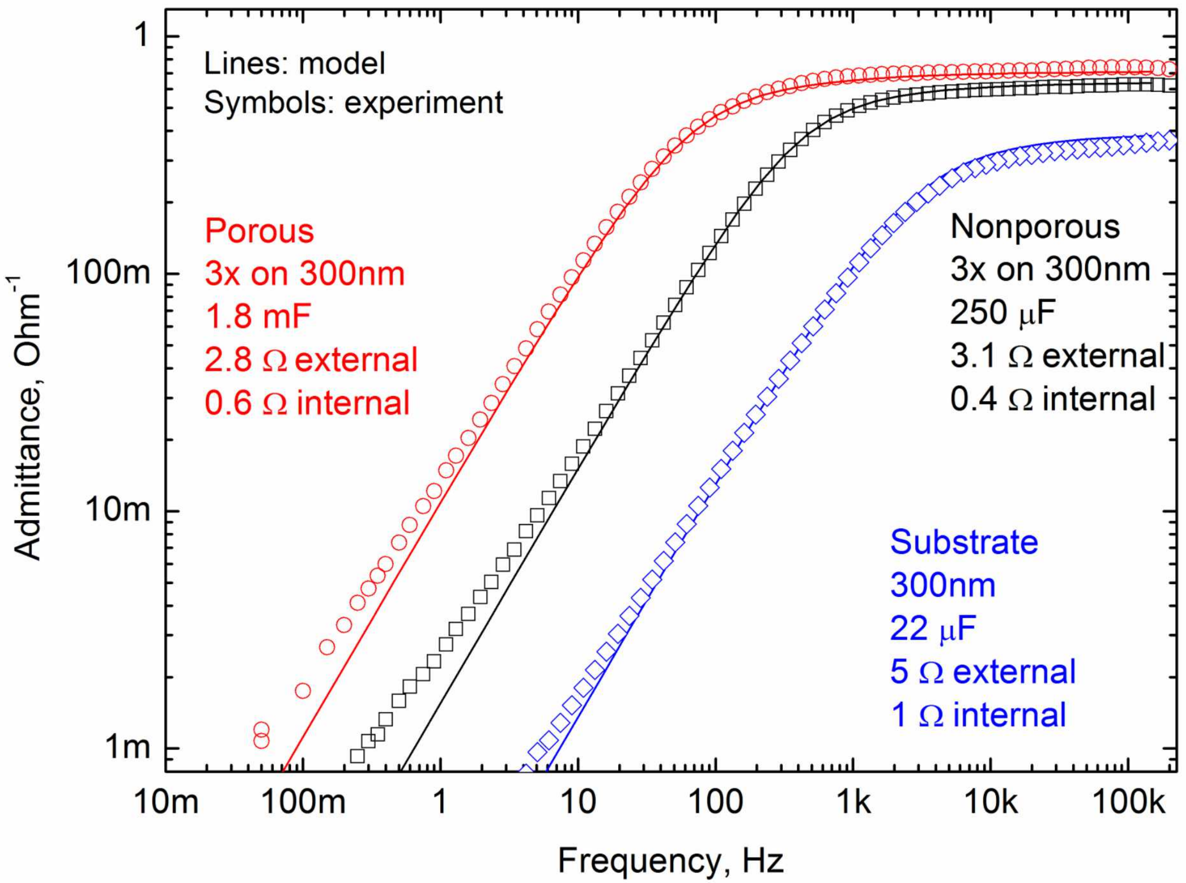


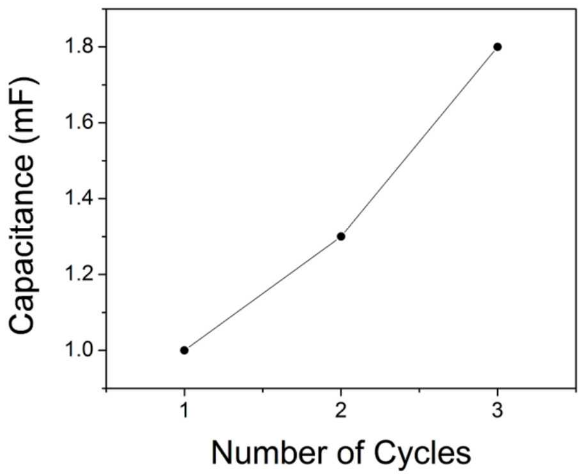
Cyclic voltammetry of porous Pd film



300 nm thick Pd film sample after 1 growth cycle in 2 M H_2SO_4
Surface redox cycles help clean Pd surface, including within pores

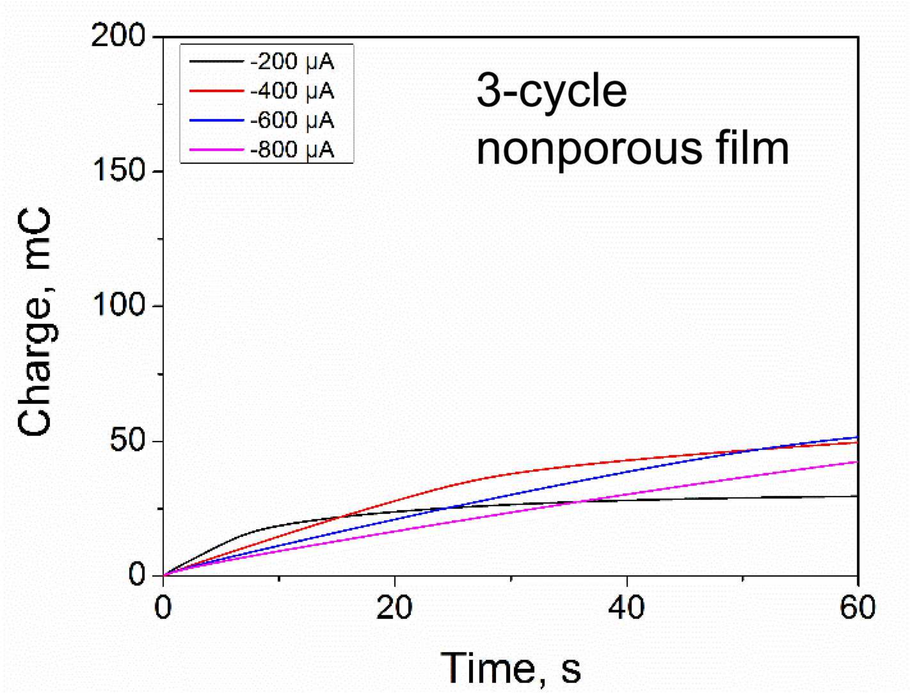
Admittance of porous film

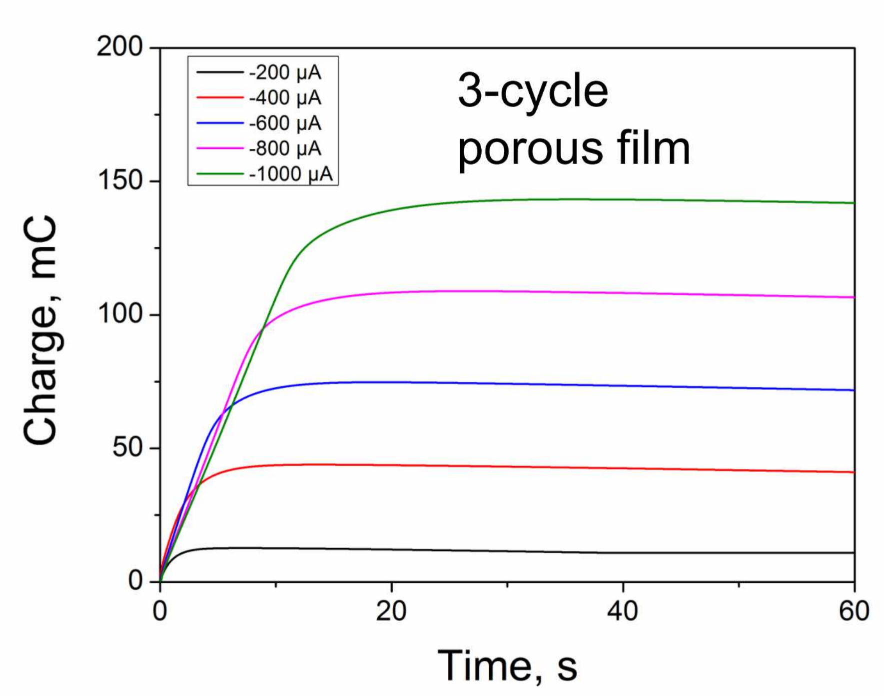




Admittance at 0.2 V vs Ag/AgCl, 10 mV zero to peak, 2 M H_2SO_4.
Modeled as RC transmission line with external resistance.
Porous layer has highest capacitance, increasing with number of cycles.

H_2 desorption kinetics

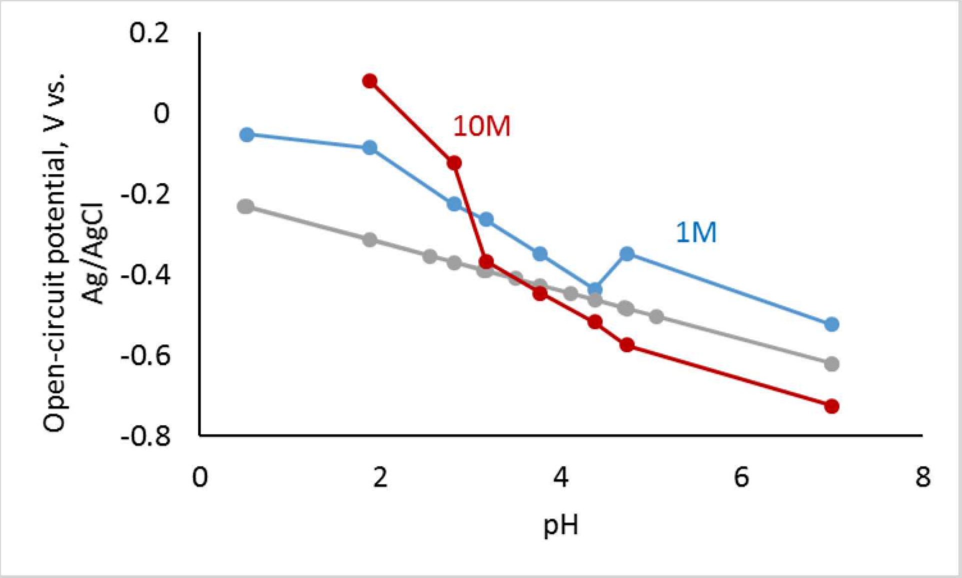




Samples charged with H_2 at given current for 180 s in 2M H_2SO_4
Discharged at 50 mV vs. Ag/AgCl

Porous film discharges more quickly and efficiently.

Pd hydride formation without H_2



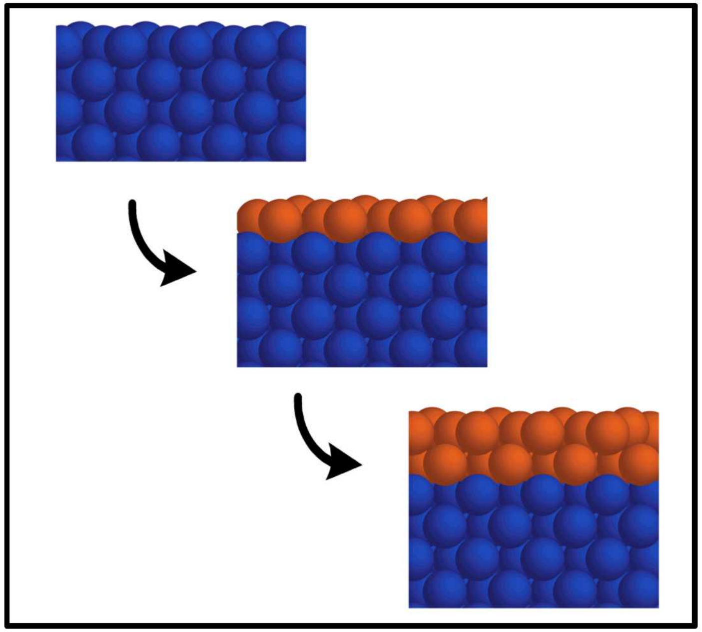
Formic acid/K formate mixtures tunably form surface, bulk hydride vs. pH, concentration. (pKa is 3.77)

Straight gray line is expected open-circuit potential for a Pd hydride electrode.

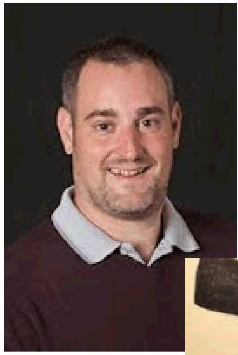
L.D. Burke, F.A. Lewis, C. Kemball. “The Formation of Palladium Hydride by Reaction of Formic Acid at Palladium Electrodes.” J. Catalysis 1966, 5 (3) 539-542
10.1016/S0021-9517(66)80074-X

Summary

- Hydrogen chemistry provides versatile methods to modify the composition and area of noble metal surfaces.
- STEM-EDS and XPS show conformal nm-scale adlayers can be formed from surface hydrides
- SEM and STEM show µm-scale porous layers can be formed from bulk hydrides
- Products show improved hydrogen adsorption and desorption kinetics



Contributors and Acknowledgements



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