

Electrochemical Analysis of Palladium Cathodes towards the Advancement of Reproducibly High H/Pd Loading Ratios

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Abstract

Motivation:

- A strong correlation has been found between surface impurities and H/Pd (D/Pd) loading. Impurities that promote increased loadings are referred to as “promoter” impurities.
- Therefore, it is important to understand the effects of these impurities since it is believed there is a higher probability of observing the Fleischmann-Pons Effect when D/Pd>0.9.
- It is also important to determine how pure Pd in a pure electrolyte theoretically behaves, and whether it would be possible to achieve high loading in such a configuration.

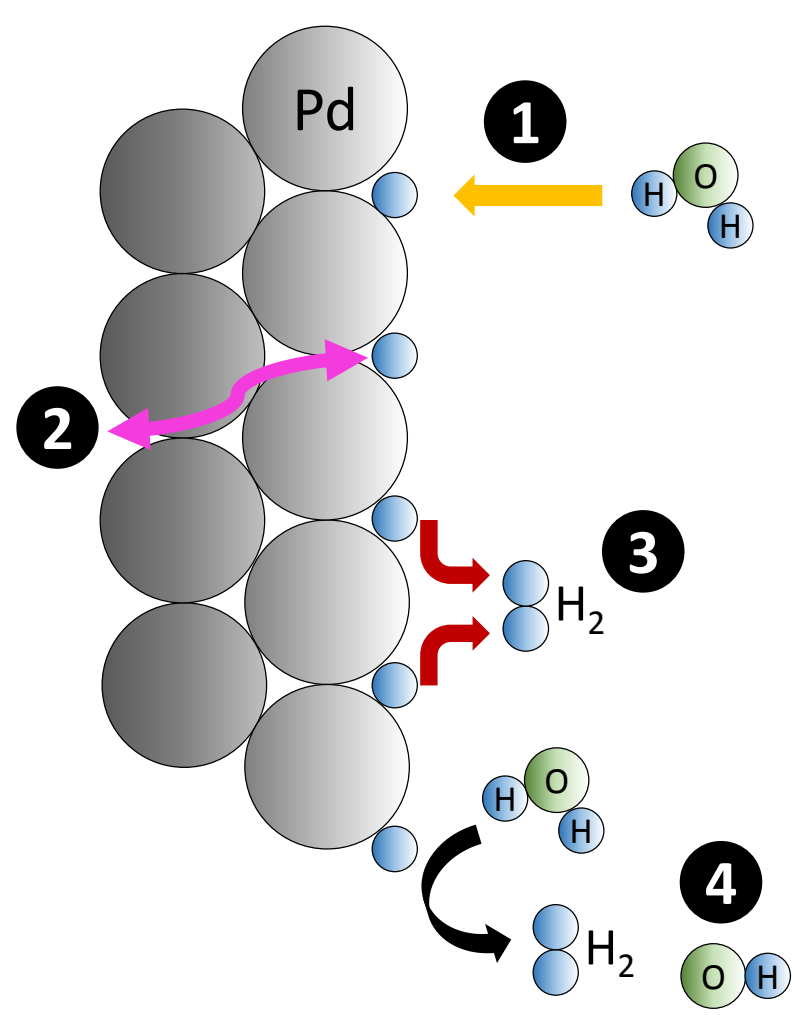
Experimental Approach:

- We are studying the electrochemical properties of surface impurities and how they affect loading/de-loading behavior using impedance spectroscopy (EIS) and chronopotentiometry (CP). Unless otherwise noted, experiments were performed in 0.1 M LiOH in H₂O.
- Copper was chosen as the investigated impurity for the bulk of this work since numerous experiments indicated it to be beneficial toward high loading, and it is easy to electrodeposit and study with electrochemical techniques. Approximately 9 mass equivalent monolayers (ML) – a total mass of roughly 70 µg and charge of about 3.8 mC cm⁻² – of Cu was electrodeposited using 0.5 mM CuSO₄.
- Our group is also currently investigating the effects of Pb, Sn, Zn, Bi, Ni, Fe, and more.

Conclusions:

- The results of our work suggest the surface impurities are the primary aspect controlling the loading, whereas crystal orientation, grain size, crack formation, etc. appear to be secondary effects (see also O. Dmitriyeva and D. Knies presentations).

Reaction Mechanisms



In alkaline solutions:

- 1) $\text{H}_2\text{O} + \text{M} + \text{e}^- \leftrightarrow \text{M-H}_{\text{ad}} + \text{OH}^-$ (Volmer)
- 2) $\text{M-H}_{\text{ad}} \leftrightarrow \text{M-H}_{\text{ab}}$ (Absorption)
- 3) $2\text{M-H}_{\text{ad}} \leftrightarrow 2\text{M} + \text{H}_2$ (Tafel)
- 4) $\text{H}_2\text{O} + \text{M-H}_{\text{ad}} + \text{e}^- \leftrightarrow \text{M} + \text{H}_2 + \text{OH}^-$ (Heyrovsky)

Note: The mechanisms are the same for H and D

Important Equation:

Simplified Butler-Volmer relationship (Mechanism (1)):

$$J_{\text{Tot}} = \sum_j J_{0j} (e^{\beta f \eta} - e^{-(1-\beta) f \eta})$$

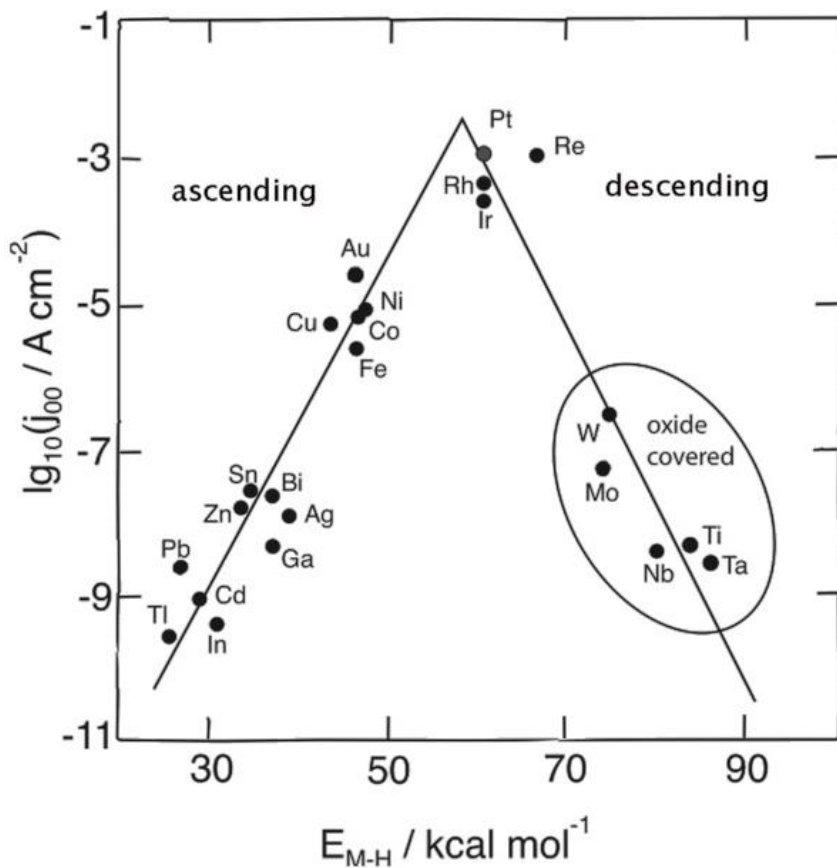
J_{Tot} = Total current density [A cm⁻²]
 J_0 = Exchange current density [A cm⁻²]
 β = Symmetry coefficient
 $f = F/RT$ [V⁻¹]
 η = Overpotential [V]

Effects of Surface Impurities

Increased H/Pd (D/Pd) Loading

High D/Pd loading suggested to increase probability of observing excess heat [1]

“Volcano Plot” showing exchange current densities (j_{00}) for the hydrogen evolution reaction (HER) on various materials [2]. Pd (not shown) is near Pt.



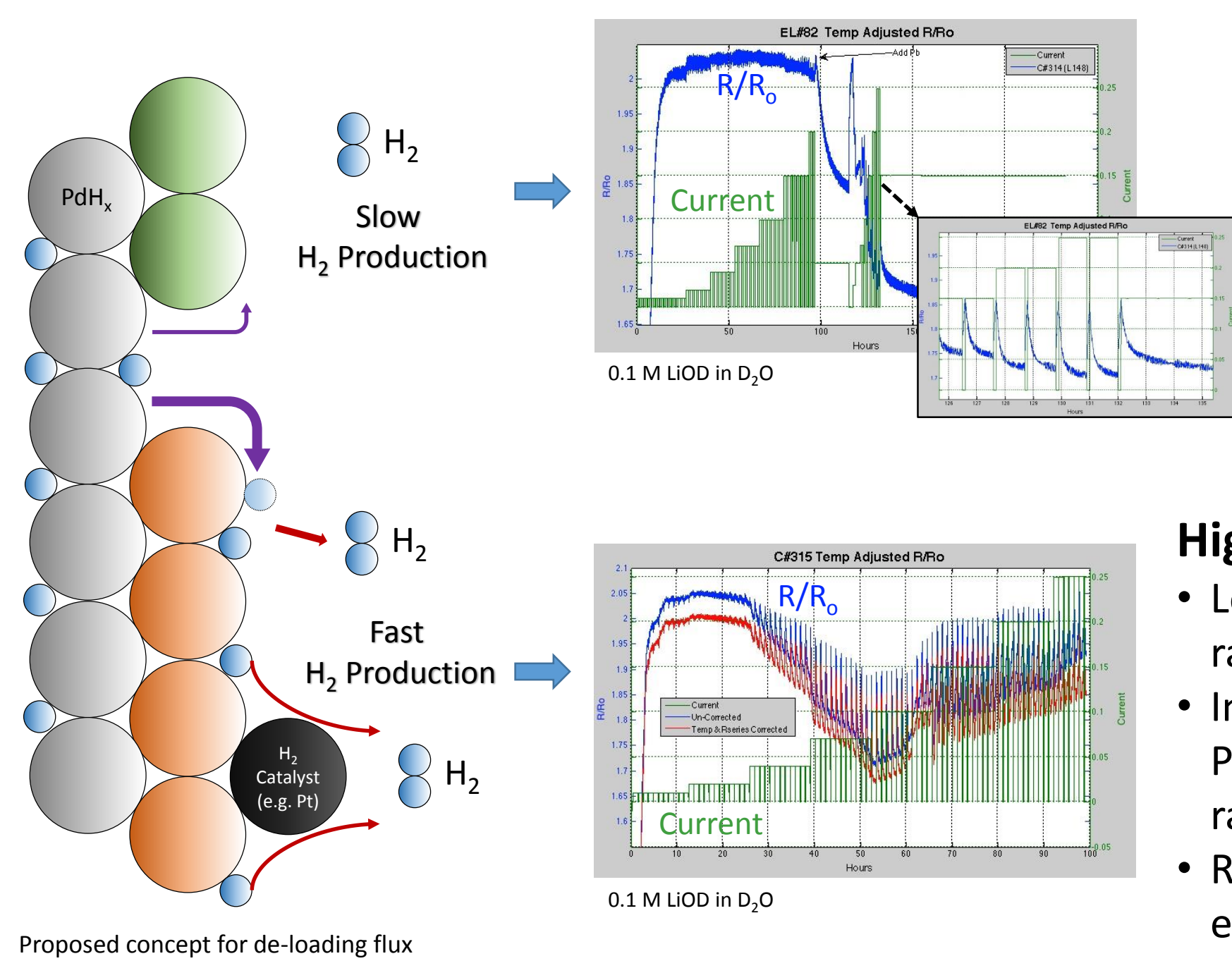
Pd + “Promoter” Impurities

- Current from Volmer reaction focused on exposed Pd due to higher exchange current density (E.C.D.)
 - Increased overpotential needed to achieve same current
 - Rate of H₂ production (specifically from (3)) reduced
 - Hydrogen chemical potential enhanced by adjacent impurities [3]
- We believe some or all of these characteristics play a role in the observed increase in the H/Pd or D/Pd ratio**

High- and Low-Flux De-Loading

High D flux also suggested to increase probability of observing excess heat [1]

- Open circuit interruptions during galvanostatic loading protocol used to test the D flux (how fast D can enter/leave the Pd).



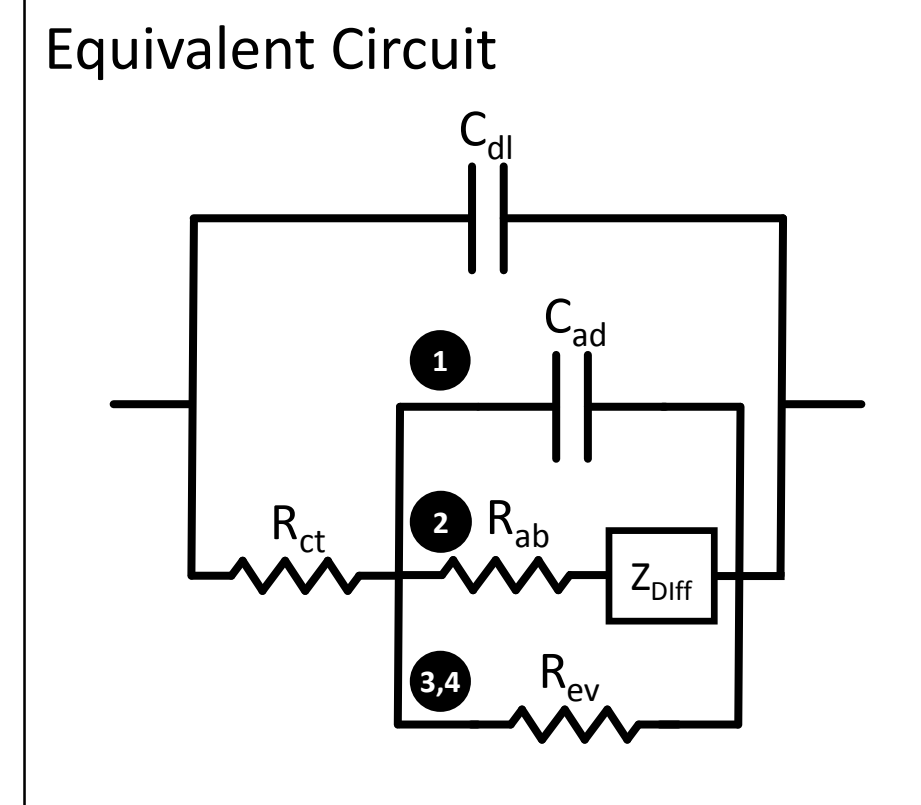
Low Flux “Promoter” Impurities

- Loaded cathodes de-load slowly
- Indicative of slower hydrogen spill-over from PdH (PdD) to impurity surface resulting in slower H₂ production
- Note: Rate is also dependent on H or D/Pd loading

High Flux “Promoter” Impurities

- Loaded cathodes de-load to equilibrium rapidly
- Indicative of fast hydrogen spill-over from PdH (PdD) to impurity surface resulting in rapid H₂ production
- Rate of H₂ production possibly also enhanced by H₂ recombination catalyst, e.g. Pt [4]

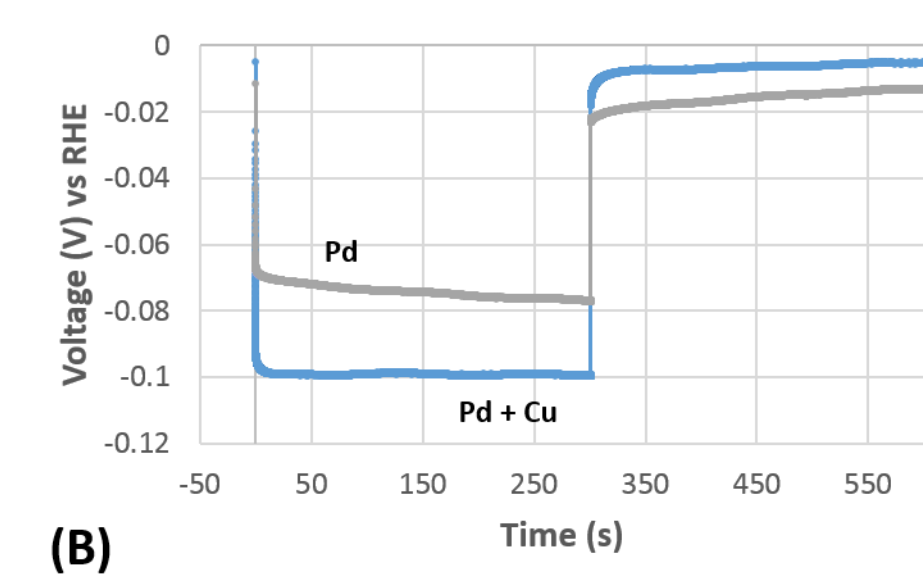
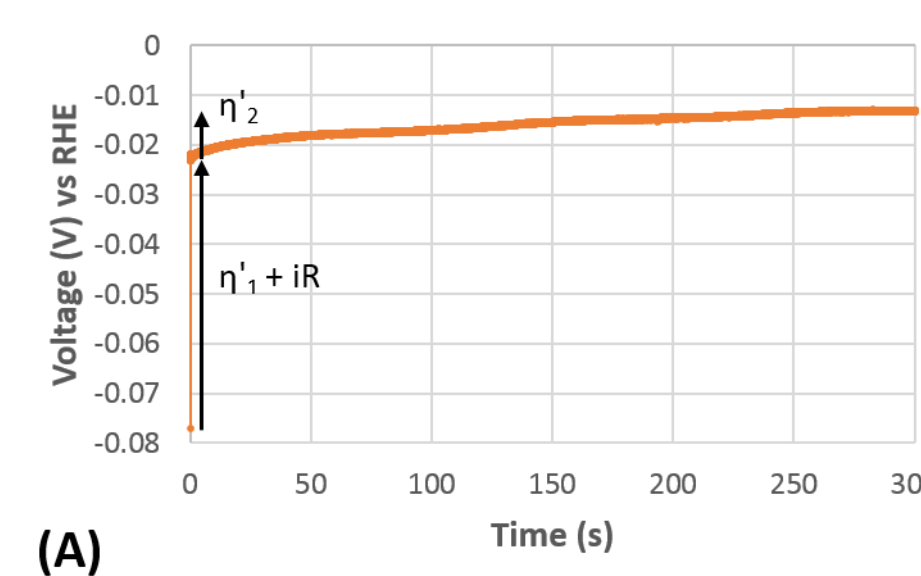
Electrochemical Impedance Spectroscopy



- Impedance data was fitted from 30 kHz to 100 mHz at DC voltages ranging from 0.5 to -0.2 V with a 25 mV signal amplitude. The analysis was performed by fitting the impedance data to the equivalent circuit provided above at each DC voltage point.

- (A) Cu deposition increased the double-layer capacitance (C_{dl}), and thus surface area, by about a factor of two.
- (B) Due to the poor H coverage on Cu at these potentials, the adsorbed capacitance (C_{ad}) is much smaller than before deposition.
- (C) Since $J_{0(\text{Cu})} \ll J_{0(\text{Pd})}$, the Cu-blocked sites increase the charge transfer resistance (R_{ct}).
- (D) The low H coverage on Cu decreases the rate of H₂ evolution, as shown by a significant increase in R_{ev} .

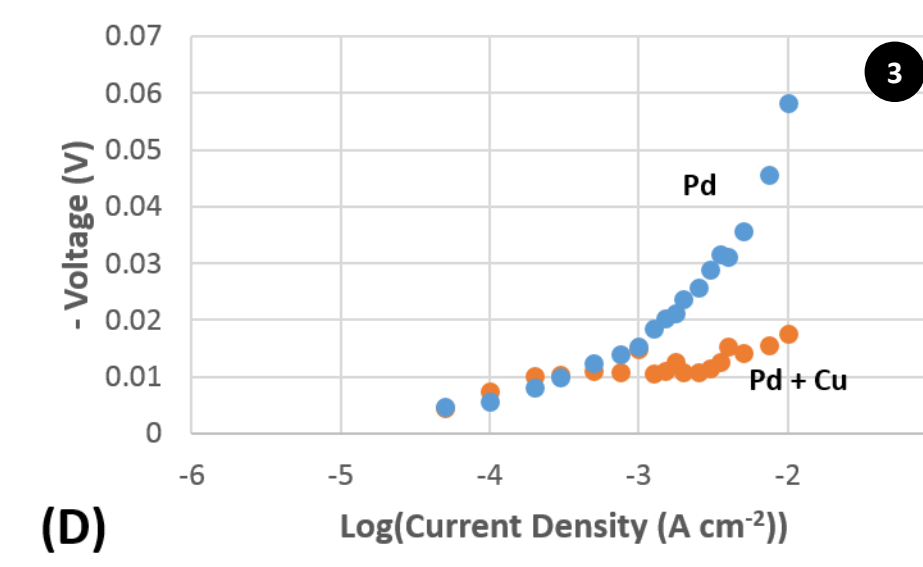
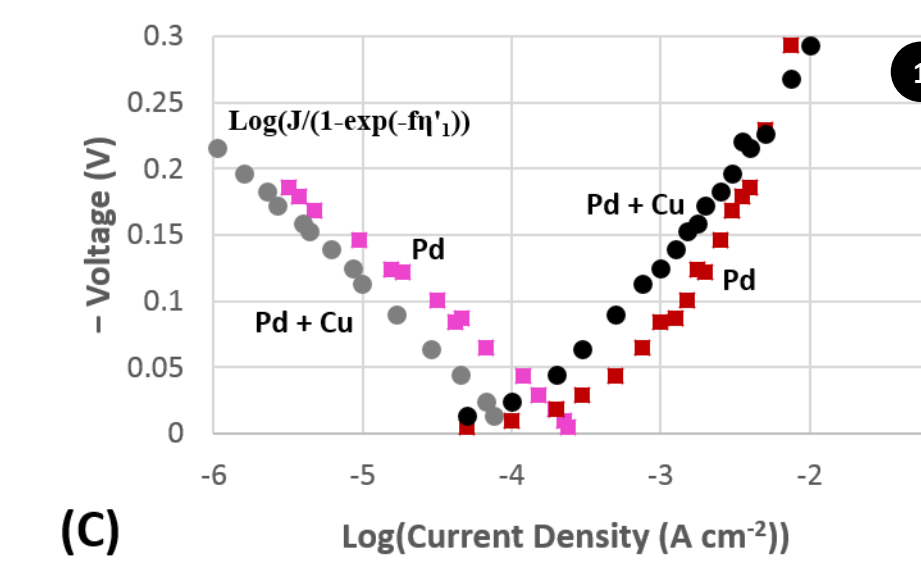
Chronopotentiometry



A H(D) loaded Pd foil is unique in that constant current and open circuit (OC) tests can be used to separate reactions (1) and (3). [5,6]

(A) A constant current is applied, followed by an OC. The initial rapid drop in voltage ($\eta'_1 + iR$) is related to reaction (1). The slowly decaying drop (η'_2) is associated with reaction (3).

(B) Typical potential response from 3 mA stimulus followed by OC for a Pd foil and Pd foil after Cu deposition.



(C) η'_1 vs. current density and η'_1 vs. $\ln\left(\frac{J}{1-e^{-f\eta'_1}}\right)$ to find the Volmer E.C.D. (j_{0v}) and change in charge transfer coefficient (β) by rearranging the Butler-Volmer equation to:

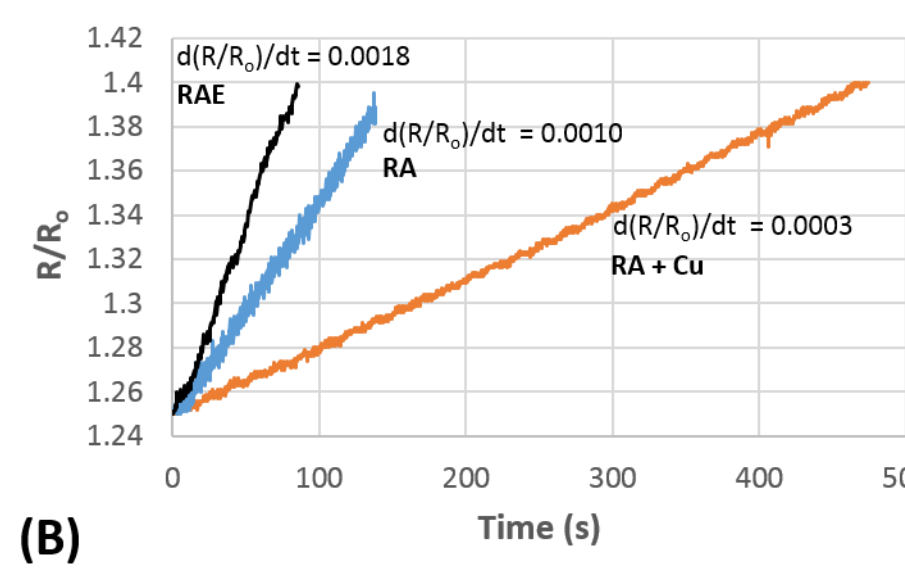
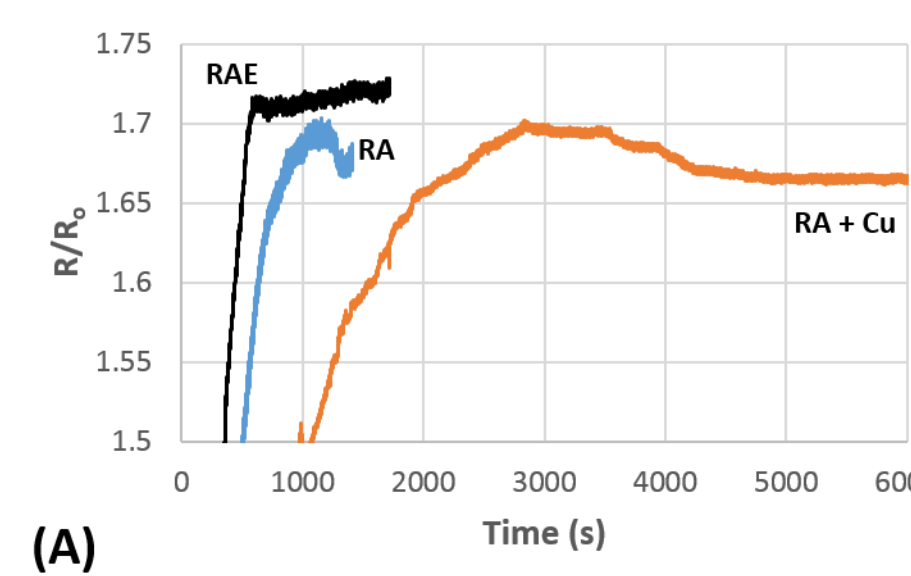
$$\ln\left(\frac{J}{1-e^{-f\eta'_1}}\right) = \ln(j_{0v}) + \beta f \eta'_1$$

j_{0v} (intercept) decreases, and $d\beta/d\eta'_1$ decreases from ~1.4 to ~1.1 after Cu deposition.

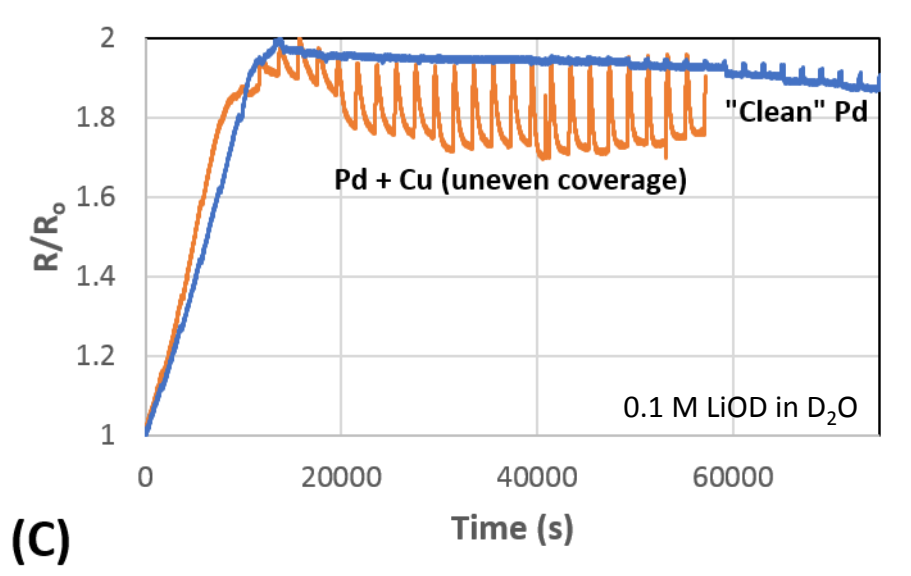
(D) η'_2 vs. current density for Pd and Pd + Cu showing significant changes in the Tafel reaction pathway.

Loading Results

This Work:



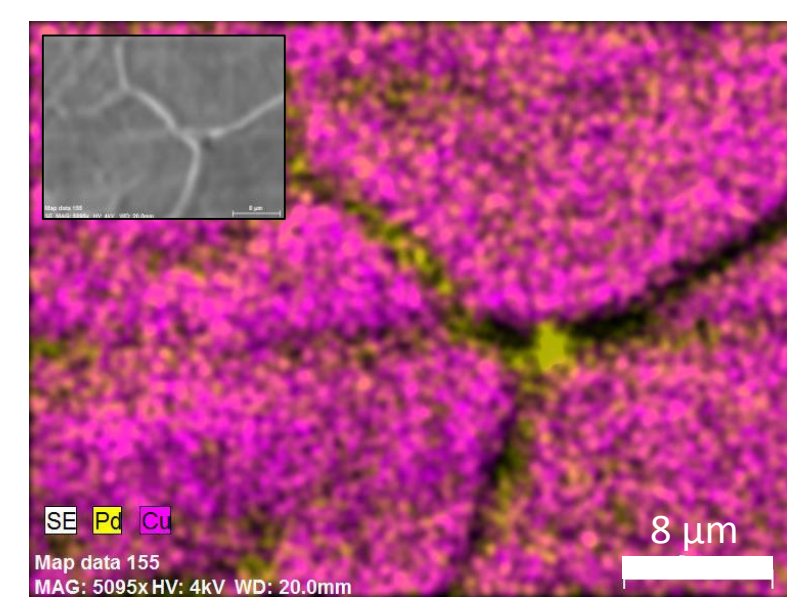
Other Cu Coating Attempt:



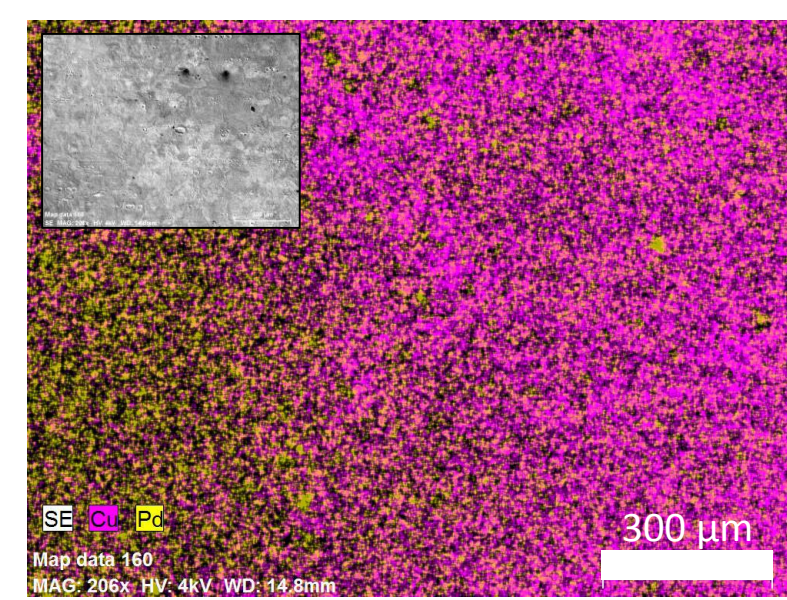
- (A) The Cu deposited on the Pd (RA + Cu) was relatively uniform, and resulted in very little loading change from the foil prior to Cu deposition (RA). Interestingly, after Aqua Regia etching (RAE), the foil loaded less (initial surface impurities affected loading).
- (B) Despite a somewhat uniform and thick (~9 ML) Cu layer, the loading rate is only ~3x lower than prior to deposition, since the current is now focused on the exposed Pd ($J_{0(\text{Pd})} \gg J_{0(\text{Cu})}$). The low loading rate correlates well with the observed electrochemical trends – i.e. increased R_{ct} (EIS) and decreased j_{0v} (CP).
- (C) In another attempt, a very uneven Cu deposition (see below) strongly affects the loading and de-loading behavior of the foil.

Future Work

Impurity Coverage Matters



Somewhat uniform coverage:
No significant change in loading



Uneven coverage (note scale):
D/Pd = 0.87 → D/Pd = 0.93
R/R₀ = 1.87 → R/R₀ = 1.71

Initial studies imply that impurity coverage matters – good coverage affects loading less than bad coverage.

- Further investigate how uniform or uneven impurity coverage affects electrochemical properties and loading.
- Develop methods for controlled deposition (will depend on surface structure).
- Take measurements in split cell to prevent Pt deposition during tests.
- Different types of impurities are currently under investigation.

Conclusions

- Surface impurities clearly affect the total H adsorption coverage, H₂ evolution rate, and rate of absorption and desorption. Electrochemical measurement techniques, such as EIS and Chronopotentiometry, are very useful techniques in investigating the surface reactions and effects of impurities.
- As once proposed,[1] a thin film or some amount of surface coverage of impurities appears to be a simple answer to the question, “How do you reproducibly achieve high D/Pd loading ratios?”
- Whether or not it is the *only* way is another issue, and stresses the importance of performing experiments in configurations that are as clean as possible (e.g. no copper leads, solder joints, or exposed bolts, even in the electrolytic cell headspace).

References:

- [1] M. C. H. McKubre, et al. “New Hydrogen Energy Research at SRI.” ICCF-6 NHE Session, 1996.
- [2] P. Quaino, et al. *Beilstein J. Nanotechnol.* **5**, 2014, 846–854
- [3] B. E. Conway, G. Jerkiewicz. *J. Electroanal. Chem.*, **357**, 1993, 47–66
- [4] M. D. Marcinkowski, et al. *Nature Materials*. **12**, 2013, 523–528
- [5] T. Maoka, M. Enyo. *Electrochimica Acta*. **26**(5), 1981, 607–614
- [6] T. Green, D. Britz. *J. Electroanal. Chem.* **412**, 1996, 59–66.