

Chemical Enhancement of Surface Kinetics in Hydrogen Storage Media

David B. Robinson, George M. Buffleben, Scott C. James, Kevin F. McCarty,
Sandia National Laboratories;
Leah B. Sheridan, Daniel K. Gebregziabiher, John L. Stickney, U. of Georgia

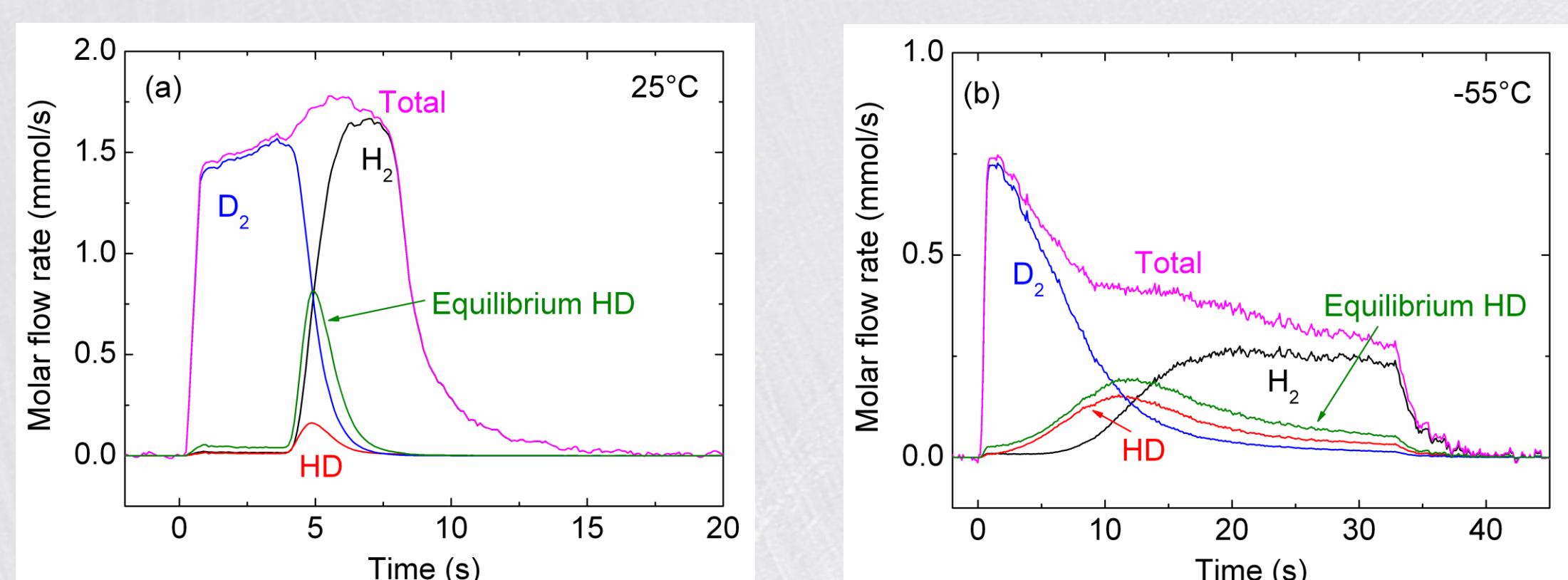


Nuclear Weapons EAB Review

Problem

Hydrogen isotopes can be stored compactly and safely as metal hydrides. We want to elute the stored isotope quickly, with minimal mixing with the eluent.

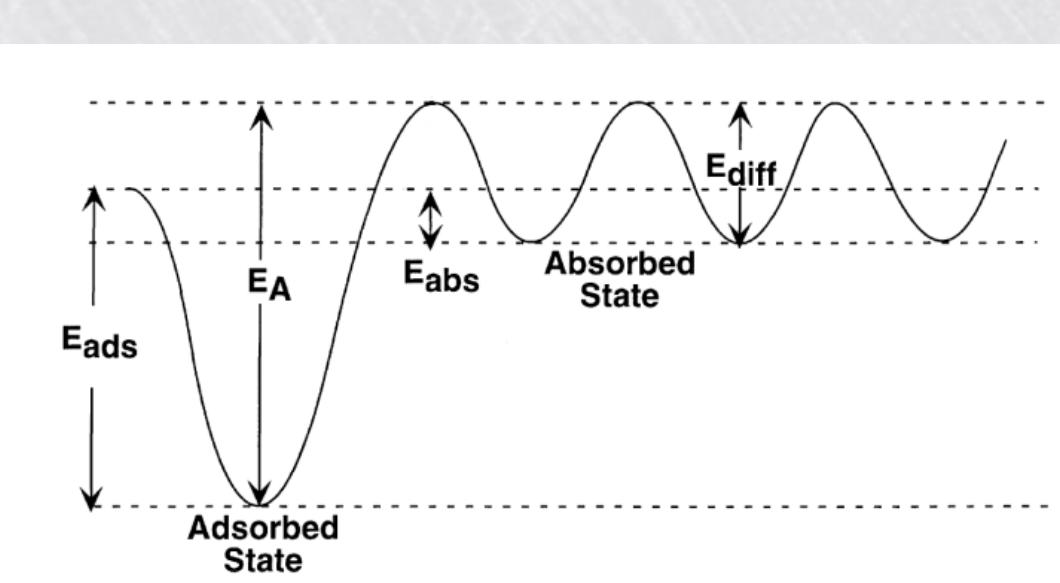
- Elution is limited by surface kinetics and/or bulk diffusion
- Less than equilibrium amount of HD is evidence of this
- Slow bulk transport (D oozing out) causes broad HD peak when cold, but still not enough HD is seen.



Approach

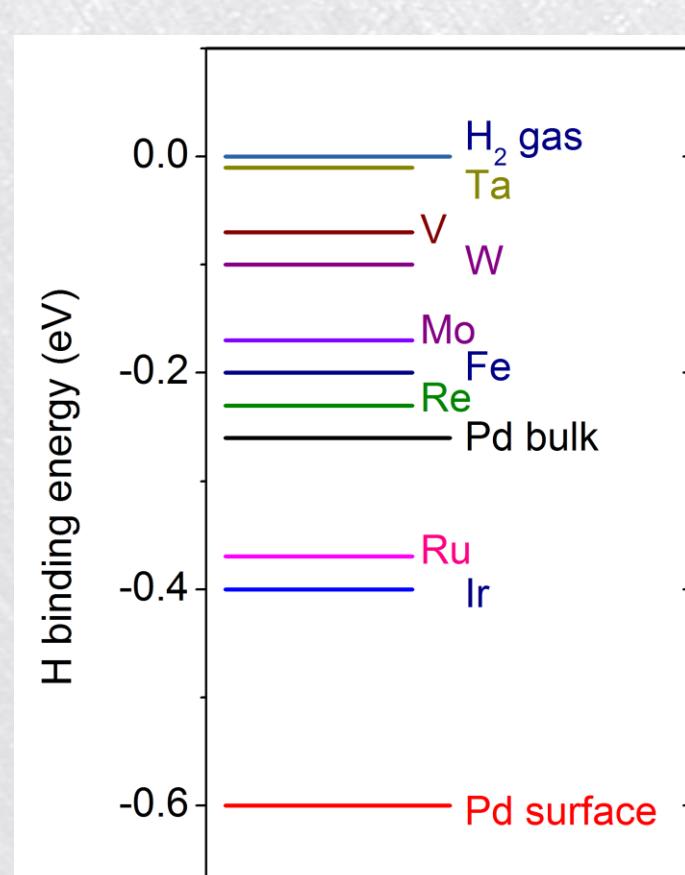
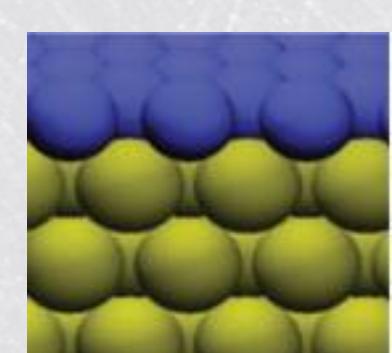
Hypothesis

H/D/T transport is slowed by formation of a highly occupied, stable Pd surface hydride.



Ward & Dao, J. Membr. Sci 153 211

Submonolayers or monolayers of other elements on Pd surface destabilize the surface hydride.

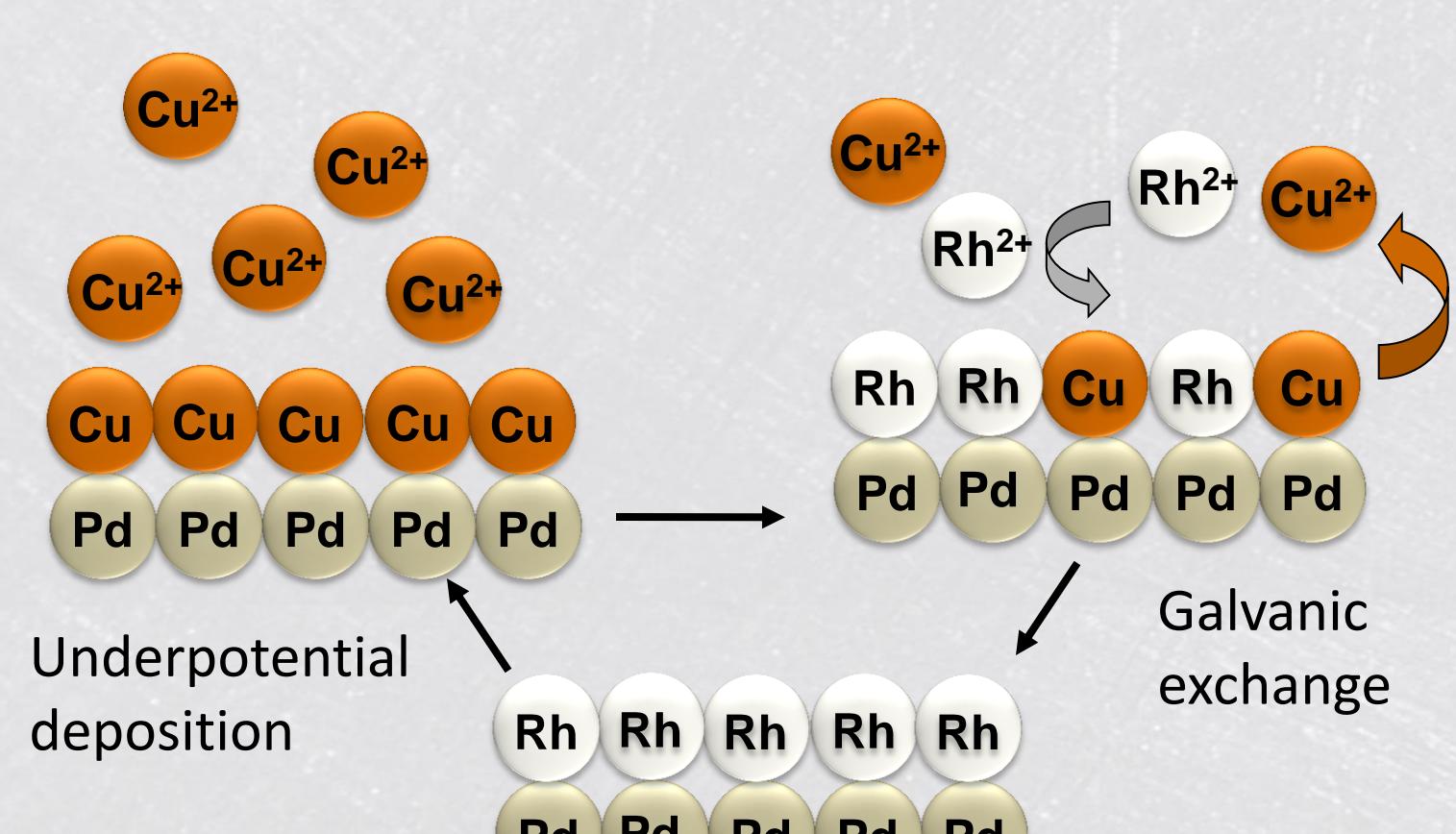


Greeley & Mavrikakis, J. Phys. Chem. B 109 3460

If the surface hydride binding energy nearly matches that of the bulk, exchange will be faster.

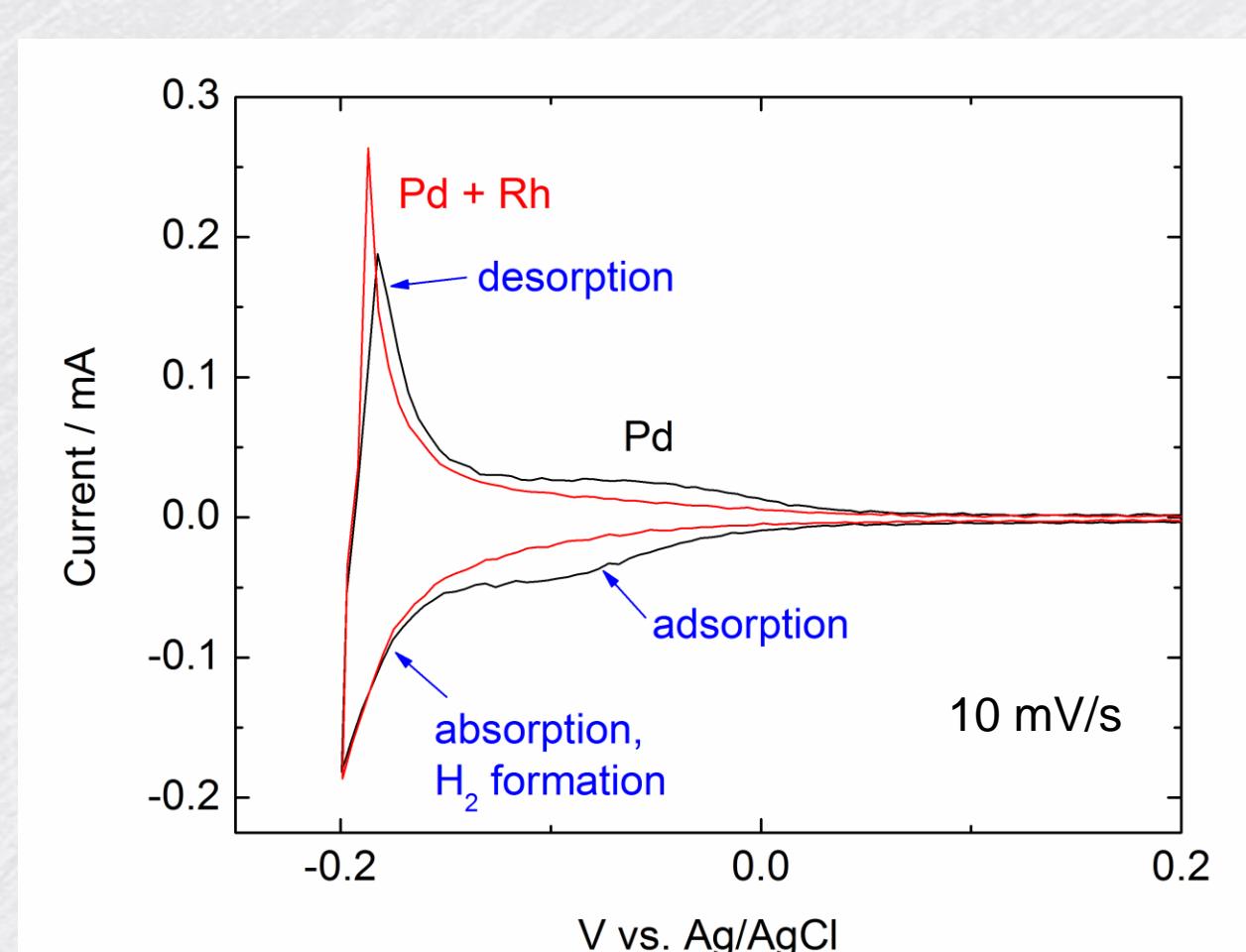
Method

We use electrochemical atomic layer deposition to apply these layers, and to create Pd thin film test samples. We are building a reactor to apply the method to bulk powders. Hydride uptake and release rates can be measured electrochemically.



Results

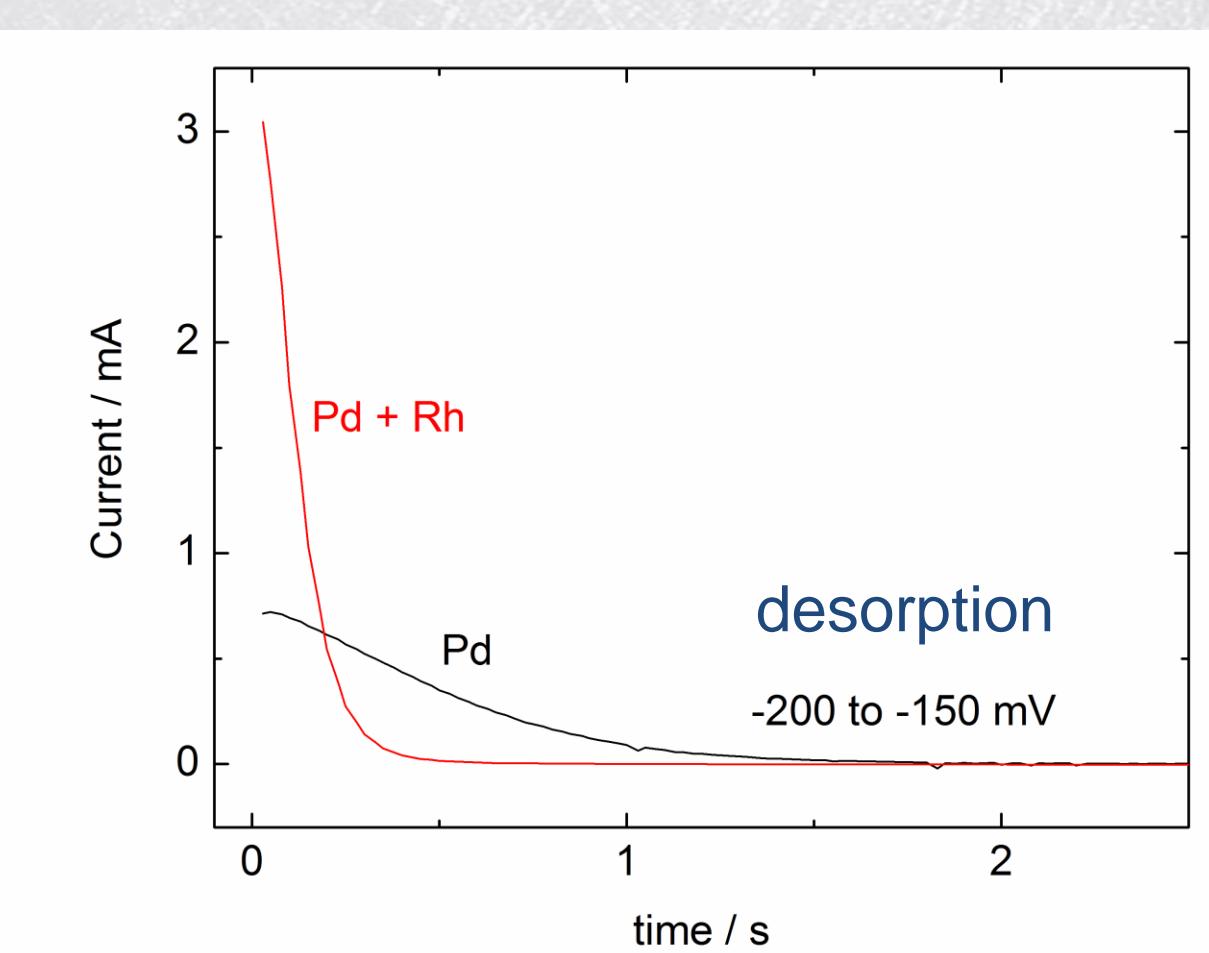
Electrochemical measurement of hydride formation



Sweeping the electrode potential negatively in 0.1M H₂SO₄ first causes H⁺ to reductively adsorb as a surface hydride, and then absorb as a bulk hydride. H₂ may also form. Sweeping positively causes bulk hydride to oxidatively desorb as H⁺, and the surface hydride comes off later.

The sample with a Rh layer shows suppressed surface hydride formation, and faster desorption kinetics, supporting our hypothesis.

Uptake and release rates



Reaction rates are more directly measured through small but abrupt potential steps. Desorption from Pd is clearly faster when the Rh coating is present.

Significance

A simple chemical modification of a Pd surface can significantly improve kinetics of hydride uptake and release. While we must still demonstrate this for gas-phase reactions instead of electrochemically, and for powders instead of films, it promises to be a convenient way to gain a significant improvement in performance of metal hydride storage materials.

These materials are especially important in the Department of Energy's management of tritium and its decay product, helium-3. These isotopes are important in the maintenance of the nuclear weapons stockpile and in the detection of smuggled radioactive materials.