Role of dopants in deuterium loading during electrochemical experiment

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Abstract

Density functional theory was applied to study the hydrogen/deuterium evolution reaction on the palladium surface. High deuterium loading ratio (> 0.9) has been identified as a necessary condition for initiating low energy nuclear reaction in palladium material [1],[2]. However, electrochemical loading of deuterium to the concentrations above 0.75 has its own challenges. While loading concentrations above 0.95 have been reported, the mechanism responsible for such elevated loading levels is still unknown. Our recent experiments gave an indication that the use of certain dopants modifies the process of deuterium adsorption on palladium surfaces. Such modifications promote deuterium loading to higher concentrations. We provide a detailed explanation on how the presence of dopants changes the activation overpotential and alter the deuterium escape kinetics during the evolution reaction.

- [1] E.Storms, The science of low energy nuclear reaction, Singapore: World Scientific Publishing Co. Pte. Ltd., 2007
- [2] M.McKubre, S.Crouch-Baker, R.C. Rocha-Filho, S.I.Smedley, and F.L.Tanzella, "Isothermal flow calorimetric investigation of D/Pd and H/Pd systems", J.Electroanal.Chem, vol 368, p55, 1994

Deuterium loading in Pd
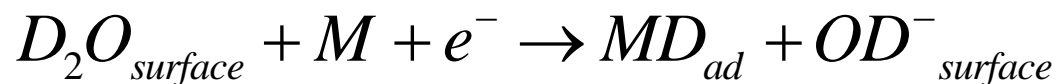
Source of deuterium: (1) D_2, (2)D_2O, (3)OD

100% deuterium loading in bulk palladium is possible when deuterium
surface coverage is maintained at 100% - not the case under standard conditions
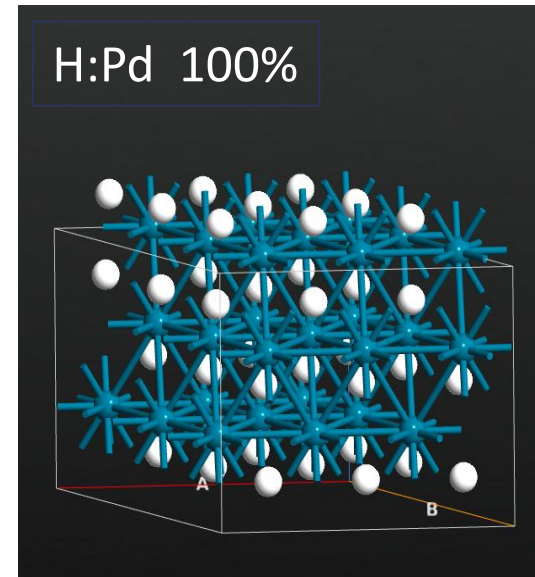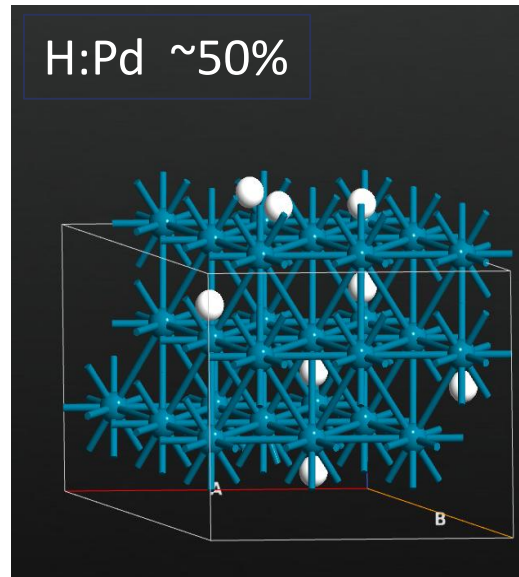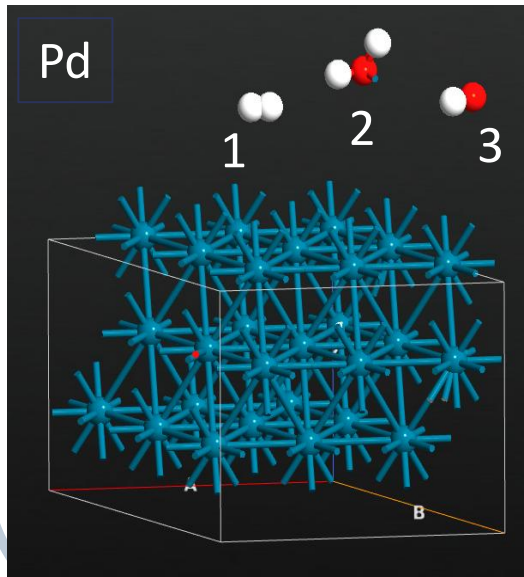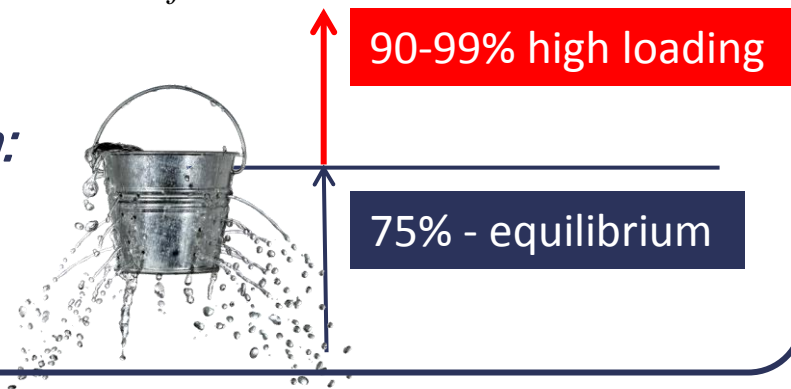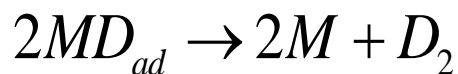
Electrochemical loading

Deuterium evolution reaction in base solution:

*Deuterium provided to the surface through Volmer reaction:*

$$D_2O_{surface} + M + e^- \rightarrow MD_{ad} + OD^-_{surface}$$

Deuterium is leaving the surface through Tafel reaction:

$$2MD_{ad} \rightarrow 2M + D_2$$

90-99% high loading

75% - equilibrium

We can fill up only 75% of a "leaky bucket", which is consistent with equilibrium deuterium pressure at max R/R_0 of the Baranowski curve, unless we modify the electrochemical environment!

Electrochemical loading
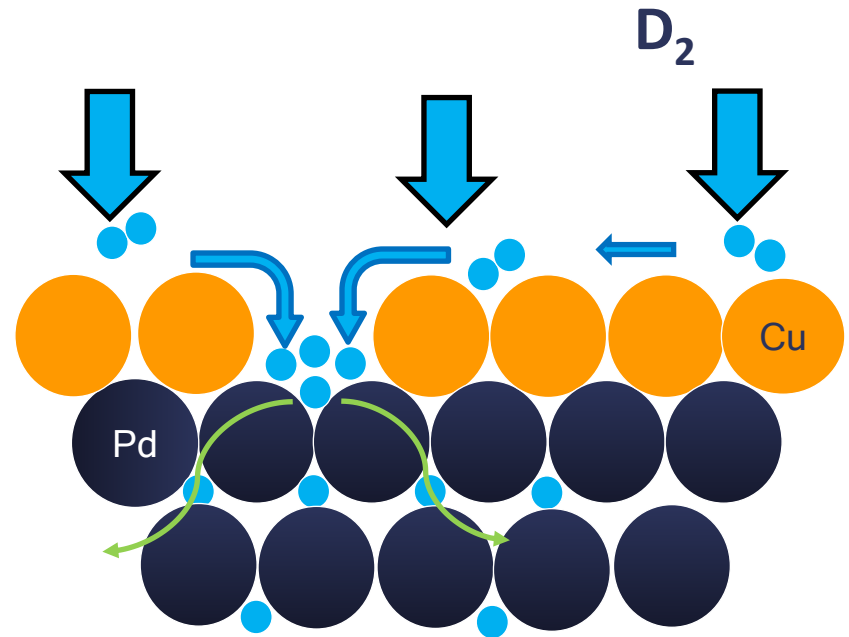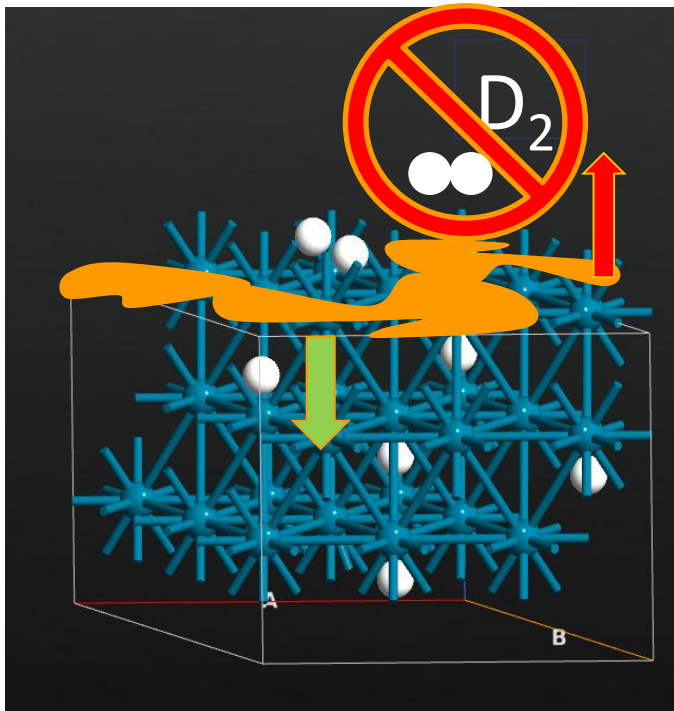
Presence of impurities focuses more current through exposed Pd area which will deliver more deuterium to the surface where it gets absorbed,
while D_2 desorption is suppressed over the covered areas.

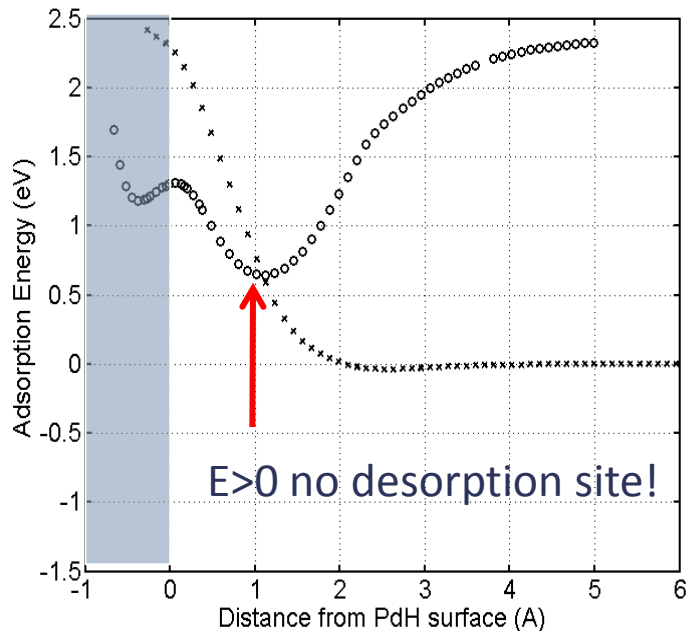# Why the desorption is suppressed? Density Functional Theory calculations

Calculations on the Lennard-Jones Potential deuterium adsorption/desorption at (100) crystallographic plane for PdD and PdD covered with copper and lead films:

Palladium Deuteride

Desorption site
E<0

D

D$_2$

Physiosorption site
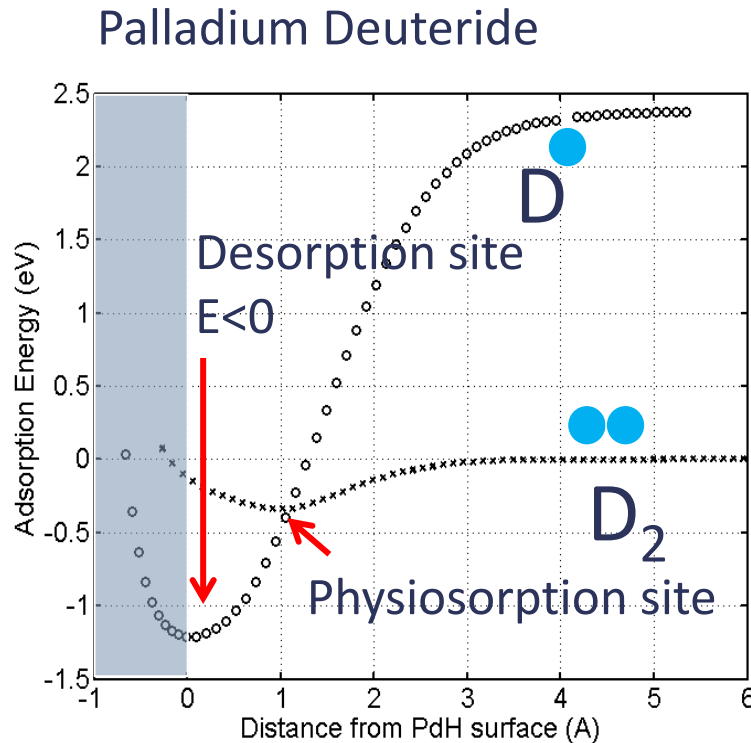
- In PdD deuterium will occupy the adsorption sites on the surface and then desorb as a D$_2$ molecule (Tafel reaction)

Why the desorption is suppressed?

Monolayer of Lead (Pb) over PdD

Monolayer of Copper (Cu) over PdD

E>0 no desorption site!

E< 0: Desorption site exists, but at higher energy and further distance from the surface
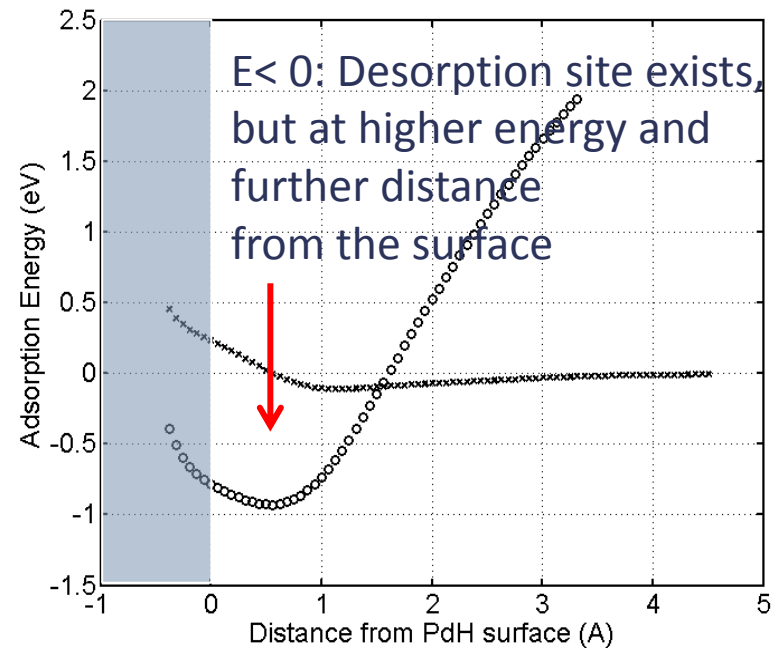
- E(PdD) < E(Cu on PdD) < E(Pb on PdD)
- Cu or Pb film has weak or no deuterium desorption sites, thus , D_2 desorption from surface (Tafel reaction) is suppressed

Conclusions

- Non-uniform coating of Pd surface

    - Modifies the desorption path → disables Tafel reaction

    - Increases current density through Pd islands → increases H/D coverage and promotes high levels of bulk loading

- Density Functional Theory simulations

    - Explains the energetics of adsorption/desorption process on modified surfaces

    - Provides the framework for screening additional materials Fe, Ag, Zn, Bi, Ti, W, In, Mo, Sn, Si and Al (including oxides)

- Future work

    - Photolithographic patterning of the surface which will control the size of the exposed palladium islands