Research Article

Numerical Modeling of H_2 Molecule Formation within Near-surface Voids in Pd and Ni Metals in the Presence of Impurities

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Abstract

We have used density functional theory (DFT) to investigate crucial material parameters that can promote a low energy nuclear reaction (LENR). This approach significantly decreases the experimental burden involved into material fabrication and testing. It also provides the foundation for systematical study and optimization of important material properties. We focused on three characteristics to describe the LENR environment: (1) a high hydrogen isotope loading ratio, (2) the presence of dopants or impurities, and (3) material morphology. We chose two figures of merit to characterize those environments: hydrogen adsorption energy on metal surface and H_2 bond length. We showed that high hydrogen loading and the presence of impurities in Pd and Ni can lower the adsorption energy, thus increasing hydrogen surface mobility potentially improving the reaction rate. Another factor that would increase the fusion probability is the distance between two hydrogen atoms. We demonstrated that a hydrogen molecule can be formed in a near-surface void in Pd and Ni at the bond length of 0.70–0.74 Å.
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1. Introduction

Various aspects of the interaction between hydrogen isotopes and metals have been studied extensively because of the great technological role they play in hydrogen storage, gas separation/purification, catalyst design and energy applications. Numerous experimental studies that address the energetics and dynamics of hydrogen isotopes adsorption/absorption on metal surfaces and in bulk have been published. With the use of computational power, theoretical studies of metal hydrides have also contributed significantly to our understanding of the fundamental principles underlying hydrogen–metal interactions.

Deuterium and/or hydrogen loading in Pd and Ni materials under special conditions results in excess heat generation, transmutations and/or particle generation. This is known as low nuclear energy reaction (LENR) [1] . In our theoretical study we applied density functional theory (DFT) to investigate the properties of potentially active LENR materials. Our study does not explain or make any attempts to explain the theoretical basis for LENR, but rather we looked at a

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chemical environment that was reported to favor a reaction. We based our study on successful LENR reports that have been made available over the past 25 years [1–3]. We chose three factors that seemed to play a crucial role in obtaining positive experimental results. Those factors were (1) a high deuterium /hydrogen loading ratio when each Pd or Ni atom has at least one corresponding D or H atom within the fcc crystal lattice (loading ratio 1:1) [4,5]; (2) the presence of impurities introduced to Pd or Ni either intentionally (alloys, powdered additions to electrolyte) or unintentionally (doping by impurities from environment during the fabrication step or from electrolyte during the experiment) [6,7]; (3) and material morphology: cathode surface and bulk defects [8,9].

Hydrogen and deuterium systems are equivalent within a self-consistent DFT frame; therefore from this point forward we will leave out deuterium of our discussion and operate with hydrogen only with the validity of the results towards a deuterium system implied. We chose two figures of merit to evaluate the results of our simulations. The figures of merit were (1) hydrogen adsorption energy (E_{ads}), and (2) H_2 bond length — namely hydrogen–hydrogen (H–H) separation distance, which we studied in the manner proposed in Ref. [9].

In our simulations we targeted the systems that promote the reduction of E_{ads} and closer H–H separation distance. These systems include palladium and nickel hydrides, and their near-surface alloys (NSA). In NSAs the dopants are concentrated in a sub-layer, which allows a decrease in adsorption energy while keeping the H_2 dissociation barrier low [10]. Weaker binding of atomic hydrogen to the surface of the metal can make the subsequent surface reaction step easier. In the case of LENR we were interested in the type of reaction that would bring two hydrogen atoms as close to each other as possible, within the metal lattice frame, to increase the transmission probability and thus the fusion rate. The standard hydrogen bond length in a vacuum is 0.74 Å. When hydrogen is adsorbed in Pd the distance between two H atoms is equal to approximately 2.3 Å, or the distance between the two adjacent octahedral sites. The large separation makes these hydrogen atoms relatively isolated within the lattice frame. The conditions that favor closer H–H separation distances in bulk palladium were studied by Peter Hagelstein and others [9]. Their calculations predicted the hydrogen molecule formation inside Pd monovacancy at the bond length of 0.77 Å. In this manuscript we explore the conditions in a chemical environment which will reduce the H_2 bond length even further. Our analysis is applicable to H_2 formation in palladium and nickel hydrides inside near-surface voids in the presence of impurities.

2. Simulation Approach and Validation

The simulations were performed in a Quantum Espresso simulation package [11]. We used periodic self-consistent DFT calculations that have shown predictive results for similar transition metal systems [12,13]. The total energies were calculated within a generalized gradient approximation (GGA). The GGA was chosen over local density approximation (LDA) to assure good agreement between the calculated and experimentally measured hydrogen adsorption energies. All simulations were done for hydrogen, but the results of self-consistent energy calculations can be extended to deuterium systems as well.

The metal surface was modeled as a 3D set of periodically repeating multilayer slabs of bulk material at (100) crystal plane orientation. The convergence of a slab's potential energy as a function of its thickness was evaluated for 4, 6, 8 and 10-slab layer constructions in the manner described in [14]. Starting with 6-layer slabs and thicker, the formation energy converged. The 6-layer slab configuration was adopted for further simulations with implementation of 6 ×6×1 automatically generated k-point grid.

To avoid the interaction between periodically replicated slabs, we set the separation between the slabs to be 2.5 times larger than the lattice constants. For example, the Pd lattice constant in our model is 3.94 Å, which makes the vacuum gap in the slab construction to be 9.85 Å wide. The electron density falls off to near-vacuum level within 2 Å from the surface. Thus, the slabs were sufficiently separated and did not quantitatively affect surface processes.

We tested several models to verify that this simulation approach was sound and would give reasonable results for the system of interest. The immediate quantities of interest were binding energies and separation distances for simple

Table 1. Simulated configurations.

Dopant	Pd as a host	Ni as a host
F	Interstitial	Interstitial
O	Interstitial	Interstitial
Cl	Interstitial	Interstitial
C	Interstitial	Interstitial
Se	Interstitial	Substitutional
As	Interstitial	Substitutional
Li	Interstitial	Interstitial
B	Interstitial	Interstitial

molecules of H_2, PdH and Pd–H_2 complex. The binding energy for H_2 was found to be 4.97 eV at 0.75 Å separation (compare to known 4.52 eV at 0.74 Å). The binding energy for PdH was 2.12 eV at 1.57 Å separation (compare to 2.34 eV at 1.55 Å [15]). We found two stable states for Pd–H_2 complex in the manner described in [15,16]. For all three cases the results were in satisfying agreement with the referenced literature.

The next quantities we checked were the bulk lattice parameters for Pd and Ni and their hydrides. Based on our calculations the expansion of Pd lattice as a result of PdH formation is 4% from 3.94 to 4.10 Å (compare to 3.4% experimentally found 3.89 to 4.025 Å). For Ni to NiH transition the lattice expansion was found to be 7.8% from 3.46 to 3.73 Å (compare to 6% experimentally found 3.52–3.73 Å).

The last validation of our simulation approach was done for hydrogen adsorption energies on the surfaces of different metals and near-surface alloys (NSA). The calculations were done for Pd, Ni, Cu, and Pt. All three available adsorption sites were tested: four-folded, bridged and on-top. The upper two layers of the slab were relaxed in the direction perpendicular to the surface. After that, the atoms of the crystal lattice were fixed at their relaxed positions only hydrogen atom was allowed to move around the adsorption site in order to minimize the energy of the system. Hydrogen adsorption energy was calculated using the formula:

$$E_{\text{ads}} = E_{\text{surf+H}} - E_{\text{surf}} - \frac{1}{2}E_{H_2}.$$

The values reported in this paper are for four-folded adsorption sites only. The results are in good agreement with the experimental data and the other DFT studies [10].

In the near-surface configuration the dopants were included only in a sub-layer. The structures are described with the Y/X notation first introduced in Ref. [10], where X is a host and Y is a solute element.

The choice of interstitial versus substitutional configuration was justified by the energy minimization calculations. The configuration with lower total energy indicates the preferred system's state. The interstitial dopants were modeled using the expanded lattice parameter (4.10 Å for Pd and 3.73 Å for Ni). All simulated configurations and types of dopants are included in Table 1.

3. Results and Discussion

3.1. Role of hydrogen loading

As discussed in the introduction, hydrogen loading in palladium is known to decrease adsorption energy [17]. We replicated the calculations for the palladium surface and updated them with a similar study for Ni. Table 2 contains the hydrogen adsorption energy values for Pd and Ni materials loaded at different levels. The adsorption energy decreases with increases in the hydrogen loading.

Table 2. Hydrogen adsorption energy values for Pd and Ni hydrides.

Configuration	E_{ads} (eV)
Pure Ni	–0.684
Ni with one H atom in sub–layer*	–0.617
-Ni with 2 H atoms in sub–layer	–0.595
NiH fully loaded at 1:1 ratio	–0.592
NiH with additional H adsorbed in on–top position	–0.385
Pure Pd	–0.499
Pd with one H atom in sub-layer*	–0.397
Pd with 2 H atoms in sub-layer	–0.389
PdH fully loaded at 1:1 ratio	–0.382
PdH with additional H adsorbed in on-top position	–0.109

*Number of H atoms per unit cell. Unit cell consists of 12 host atoms: Pd or Ni.

The hydrogen adsorption energy was initially higher for pure Ni compared to pure Pd. E_{ads} decreased as increasing amount of hydrogen was absorbed in the metal. The adsorption process eventually stopped when the metal lattice was fully saturated with hydrogen and a hydrogen monolayer was formed on the surface.

3.2. Role of impurities

The inclusion of some dopants/impurities in the host metal lattice resulted in a similar hydrogenation effect: E_{ads} decreased in the presence of impurities. We modeled the presence of dopants in the metal lattice sub-layer in the manner described in [10]. The near-surface configuration can be experimentally achieved during the co-deposition of Pd in a heavy water-based electrolyte [18] or by a galvanic displacement of an add layer [19]. The E_{ads} values for Pd and Ni metals and their doped configurations are summarized in Table 3.

Table 3. Hydrogen adsorption energy for Pd and Ni slabs and their doped configurations.

Pure metal configuration	E_{ads} (eV)	Alloy configuration	E_{ads} (eV)
		H/Pd	–0.389
		O/Pd	–0.251
		C/Pd	–0.208
		Se/Pd	–0.160
Pd	–0.499	F/Pd	–0.243
		As/Pd	–0.083
		Cl/Pd	–0.070
		Li/Pd	–0.389
		B/Pd	–0.289
		H/Ni	–0.595
		O/Ni	–0.196
		C/Ni	–0.346
		Se/Ni	–0.614
		F/Ni	–0.274
Ni	–0.684	As/Ni	–0.482
		Cl/Ni	0.169
		Li/Ni	0.124
		B/Ni	–0.159
		Pd/Ni	–0.623
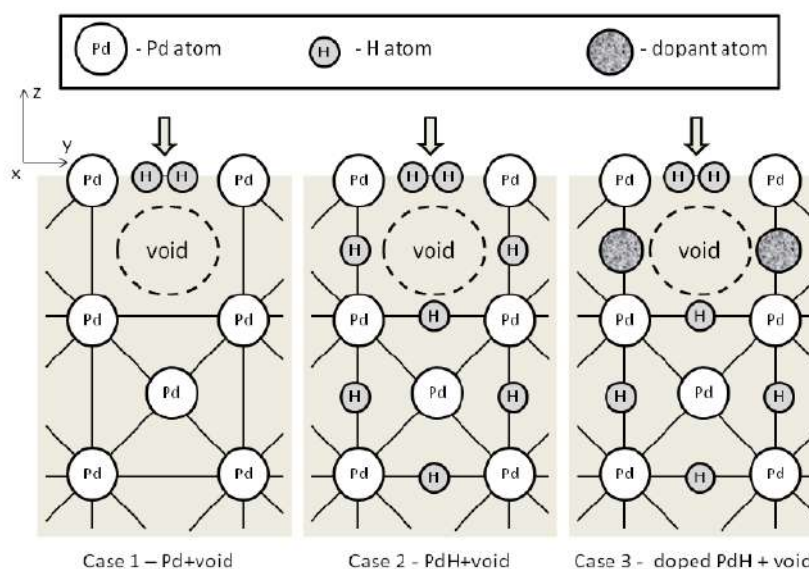
Figure 1. Pd slab with a void at a sub-layer. The hydrogen molecule is entering from the surface and traveling towards the void. Three cases represent: (1) undoped Pd, (2) PdH, and (3) doped PdH.

It follows from Table 3 that the E_{ads} for pristine metals is higher than for the doped material, meaning that hydrogen does not bind as strongly to the metal surface if near-surface impurities are present.

3.3. Role of vacancies

The near-surface void was modeled as an absence of the host atom in the sub-layer of a Pd or Ni slab. The hydrogen molecule entered the metal lattice through the four-fold adsorption site, penetrating the slab along the z-direction towards the void. At each point along the z-direction the H_2 molecule's z-coordinate was fixed, but the molecule was allowed to relax in the xy plane to minimize the total energy of the system. Figure 1 shows the 2D representation of the three different cases under investigation: (1) a pristine metal slab with the void, (2) a metal hydride slab with the void, and (3) a metal hydride slab with an interstitially doped sub-layer at the void.

We tested the verity of possible dopants or impurities that may be present in an experimental or industrial environment. Figure 2 shows the change in H–H separation as a function of the penetrating distance from the surface of Pd, PdH and F/PdH (fluorine atom as an interstitial dopant in PdH sub-layer).

The change in the electronic density as a result of hydrogenation promotes the formation of a hydrogen molecule inside the near-surface void at a 0.75 Å A separation distance. The same hydrogen molecule formed in pristine Pd metal will have a bond length of 0.80 Å. The presence of fluorine brings the electronic density even lower, reducing the separation distance to 0.74 Å. The calculations done for Ni showed a similar trend, with a minimum H–H separation distance of 0.70 Å inside the near-surface void in the presence of fluorine.

The H–H separation distances at the near-surface void were calculated for Pd and Ni metal slabs doped with F, O, Cl, Se, Rh, As, Li, and B. The results are summarized in Fig. 3. The impurities are arranged along the x-axis according to their electronegativity, with fluorine as the most electronegative element, and followed by the less electronegative dopants. Our calculations showed that the point of minimum H–H separation inside the crystal does not coincide with
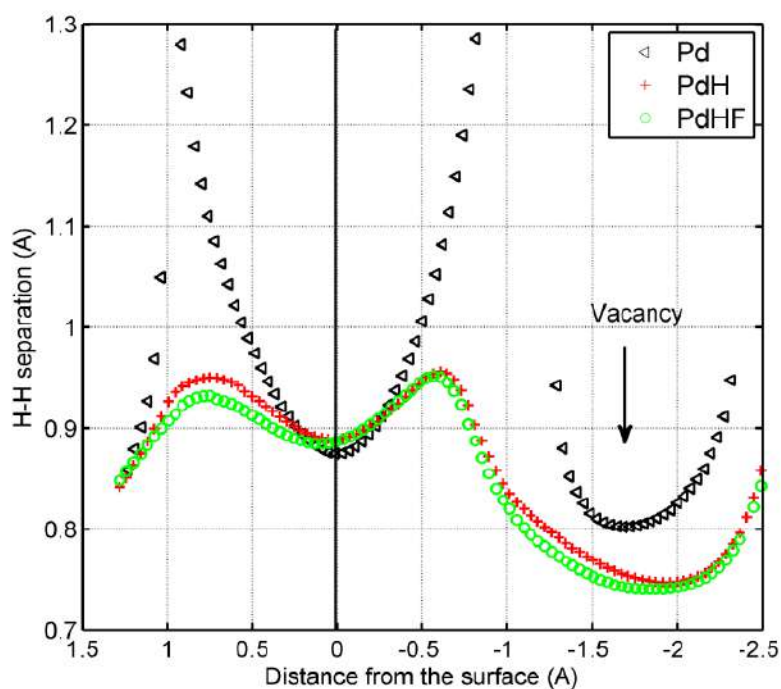
Figure 2. H–H separation as a function of the distance from the surface of the metal (located at zero). The positive values to the left correspond to the distances above the surface, while negative values to the right correspond to the distances beneath the surface. The vacancy is at -1.703 Å beneath the surface. Legend: *black* – pristine Pd metal (case I from Fig. 1), *red* – PdH (case II), *green* – PdH doped with F (case III).

the system total energy minimum. This means that this arrangement is not energetically preferable at the equilibrium state, and thus is unlikely. However, non-equilibrium processes such as mechanical stress of the crystal lattice due to hydrogen loading may promote a favorable environment for hydrogen molecule formation.

4. Conclusions

We investigated the mechanisms for hydrogen molecule formation in Pd and Ni within the near surface voids using the mean of the density functional theory. We used available experimental data to establish the important factors that are suggested to benefit LENR and modeled the chemical environment for those configurations. Those factors include: a high level of hydrogen loading, the presence of impurities and the presence of surface defects. Using adsorption energy as a figure of merit we demonstrated that a high level of hydrogen loading has an effect that is similar to the doping effect when hydrogen adsorption energy is reduced. Usually this implies the increase of a dissociation energy barrier. However, some near-surface alloy configurations offer a unique exception to this rule, providing both low adsorption energy and a low H_2 dissociation barrier. Weak binding of hydrogen to the surface can make the subsequent reaction steps easier. From the LENR point of view this could mean a monolayer of nearly free atomic hydrogen moving along the metal surfaces and encountering steps, dislocations or vacancies where the H_2 molecule can form at close separation distance. The near-surface void or vacancy could be a type of surface defect where two hydrogen atoms can bind together.
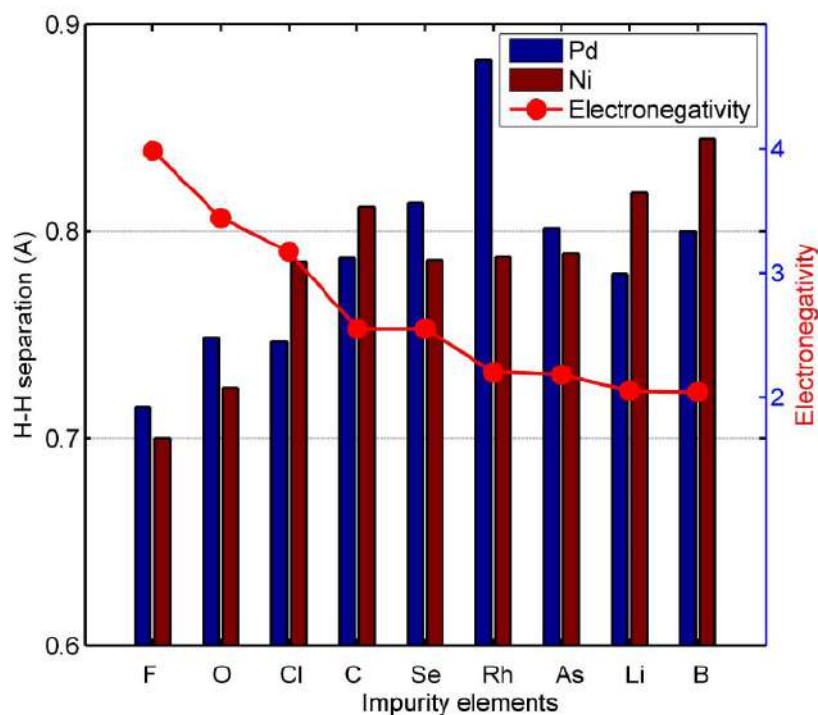
Figure 3. H–H separation at the near-surface void in the presence of different sub-layer impurities. Calculations were done for the Pd and Ni host structures using the procedure described in Section 2.

Since fusion probability depends strongly on the separation distance, we used H–H separation as another figure of merit to evaluate our model. The presence of hydrogen that has been absorbed in bulk changes the overall electronic density and allows the H_2 molecule to form a bond at shorter separation distance. This effect can be enhanced (and the separation reduced) through the introduction of high electronegative impurities.

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