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# Hydrogen species within the metals: Role of molecular hydrogen ion $H_2^+$

Kęstutis Juodkazis [a,*], Jurga Juodkazytė [a], Asta Grigucevičienė [a], Saulius Juodkazis [b]

[a] Center for Physical Sciences and Technology, Institute of Chemistry, A. Goštauto 9, LT-01108, Vilnius, Lithuania
[b] Centre for Micro-Photonics, Faculty of Engineering and Industrial Sciences, Swinburne University of Technology, Hawthorn, VIC, 3122, Australia

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ABSTRACT

Novel mechanism of hydrogen interaction with transition metals via stepwise reversible dissociative ionization of $H_2$ molecule is proposed instead of a commonly accepted dissociative adsorption. It involves ionization of $H_2$ to molecular ion $(H_2^+)_{ad}$ on the outer surface of metal phase, its subsequent absorption and dissociation within the metal phase into $(H^+)_{ab}$ ions, i.e., absorbed protons, as described by: $H_2 \rightleftarrows (H_2^+)_{ad} + e^-$ and $(H_2^+)_{ad} \rightleftarrows (H_2^+)_{ab} \rightleftarrows 2(H^+)_{ab} + e^-$. Absorption here is treated as adsorption on the inner surface of the tetrahedral and octahedral voids within metal lattice. The mechanism is based on the first principles and explains consistently the dependence of mechanical properties of metals on the amount of absorbed hydrogen as well as the mechanism of hydrogenation and hydrogen transport through the metals. The proposed dissociative ionization mechanism is well supported by thermodynamic and steric arguments. In the case of noble metals the presented mechanism carries versatile character as it is valid for both gaseous phase and aqueous solutions.

## 1. Introduction

Hydrogen interaction with metals represents very wide and much investigated area of utmost technological importance [1–5]. It is closely related with metallurgic processes, metal processing and their exploitation. All metals and their alloys which are widely used in engineering contain certain amount of hydrogen [1]. Traditionally, the problems of $H_2$ interaction with metals are analyzed in such areas as electrochemistry and catalysis in relation to hydrogen evolution and oxidation reactions (HER and HOR), reduction and hydrogenation of metals, as well as other electrochemical processes [6–9]. Nowadays, these issues are important in relation to hydrogen energy [10–14], fuel cells [15,16], high power metal-metal hydride electrochemical power sources [17] and various nanotechnological processes [18] used in hydrogen storage [19–25] and production of solar batteries, displays, light emitting diodes and micro-electro-mechanical systems (MEMS).

The variety of hydrogen–metal compounds is very broad encompassing ionic (salt type), metallic and covalent hydrides [2–5]. However, the majority of transition metals and their alloys do not form stable stoichiometric chemical compounds with hydrogen. Among them, such widely investigated metals as Pt, Pd, Ni and Ti [1]. In this case, the interactions such as $H_2$ adsorption, absorption, hydrogenation, hydrogen diffusion within the metal phase, influence of hydrogenation on a metal structure, physical and chemical properties become important.

According to the accepted concept of hydrogen interaction with metals [7,8,20,26], a dissociative adsorption of hydrogen on a metal surface takes place and results in chemical splitting of the $H_2$ molecule into two H atoms chemisorbed on the surface. These atoms can be further absorbed into metal or alloy phase [7]. Such concept was formulated on the basis of early electrochemical studies of HER and HOR [27,28]. On the other hand, investigations of the influence of hydrogenation on metals properties [1] have long ago led to a conclusion that hydrogen within metals should exist in the ionized state, because its transport through metals can be controlled with a help of electric field. It was suggested [1], that the experimental facts acquired by then can be understood and explained only on the basis of a single assumption that hydrogen in metals stays in as the $H^+$ ion, i.e., in a proton state. So it was presumed that protons penetrate throughout the electronic shells of atoms in the form of proton gas [1]. This conclusion, however, failed to draw proper attention of scientists.

As it will be shown further, on the basis of the first principles as well as the analysis of surface steric hindrance effects, we propose that molecular hydrogen undergoes reversible dissociative ionization on metal surface, resulting in formation of hydrogen molecular ion $(H_2^+)_{ad}$, which can be absorbed into metal phase, or, in other words, adsorbed on the inner surface of metal lattice. Within metal phase this ion can further ionize to $(H^+)_{ab}$ ions, i.e., absorbed protons. The present study is a discussion paper and critical analysis

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[*] Corresponding author.
E-mail addresses: kesjuod@ktl.mii.lt (K. Juodkazis), jurgajuod@chi.lt (J. Juodkazytė).

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of the published accounts. All the experimental data referred in the text are taken from available literature.

## 2. Analysis and discussion

### 2.1. The specifics of hydrogen interaction of with metals

We have chosen for our analysis the most popular case of hydrogen interaction with transition metals, platinum group metals among them, which do not form chemically stable stoichiometric hydrides. This interaction is unique due to identical phenomena observed in the case of different metals. Hydrogen concentration, which can be expressed in atomic, mass, volume % and, most often, in $cm^3$ per 100 g of metal can vary within a very wide range, depending on the technique of metal processing, state of the matter (liquid, powder or monolith) and external conditions such as temperature and partial pressure ($T, p_{H_2}$). Interaction of hydrogen with metals can be either exothermic or endothermic. At $p_{H_2} = const$ the concentration of hydrogen within certain metal can either increase or decrease depending on temperature. Augmentation of $p_{H_2}$ and temperature usually leads to an increase in hydrogen concentration within metals, whereas under vacuum conditions dehydrogenation proceeds. The most interesting, however, is the fact that while concentration of $H_2$ in metal varies within very wide range, it practically does not change the parameters of metal crystal lattice. For example, in palladium [1] the crystal cell dimensions remain the same even when ratio between Pd and H atoms is 1:1, i.e., the concentration of hydrogen atoms amounts to ~50 at.%. Physical and mechanical properties of metals, such as plasticity, fragility and relative elongation are reversibly dependent on the amount of hydrogen within metal. Mechanical properties deteriorate with increase of hydrogen concentration, but they are fully recovered when the amount of hydrogen is reduced to its initial value. It is practically impossible to remove hydrogen from the metal phase completely. It is interesting to note that solubility of hydrogen in metal always increases considerably upon transition from solid to liquid phase and, in general, changes significantly with changes in metal structure. During investigations of hydrogen solubility in metals [1], even in the case of exothermic interaction, no insertion of H atoms in or between the sites of crystal lattice was observed, i.e., no indications of solid insertion solutions formation were found.

### 2.2. The concept of $H_2$ dissociative ionization

Thermodynamically, for $H_2$ molecule to dissociate into two chemisorbed H atoms as described below:

$$H_2 \rightleftarrows 2H_{ad} \tag{1}$$

the energy of such dissociative chemisorption for each atom should be no less than half of the bond energy between H atoms in $H_2$ molecule, i.e., $1/2D_{H_2} = 1/2 \times 453.6\,\mathrm{kJ\,mol^{-1}} \approx 227\,\mathrm{kJ\,mol^{-1}}$.

According to the accepted concept [7,8,26], the required energy is derived from chemisorption of H atoms on a metal surface. Judging from the amount of energy indicated above, such chemisorption should lead to the formation of chemically stable surface hydrides. However, the experimentally measured energetic effects of $H_2$ interaction with metals in gaseous phase are significantly smaller and usually do not exceed 100 kJ $mol^{-1}$ [26]. In the case of Pt, for instance, the reported value was 41.2 kJ $mol^{-1}$ [8], which is typical for heat of adsorption. Electrochemical formation of H atom from $H^+$ ion on the electrode surface also requires very large amount of energy, i.e., $\Delta G_H = 203.25\,\mathrm{kJ\,mol^{-1}}$ [29], since the standard potential of equation:

$$H^+ + e^- \rightarrow H \tag{2}$$

is $E^0_{H^+/H} = -2.1\,\mathrm{V}$ [30].

On the other hand, it is well known [6,30] that the standard potential of the overall reaction describing electrochemical processes of reversible hydrogen electrode:

$$2H^+ + 2e^- \rightleftarrows H_2, \tag{3}$$

is $E^0_{2H^+/H_2} = E_{SHE} = 0\,\mathrm{V}$ and $\Delta G_{2H^+/H_2} = 0\,\mathrm{kJ\,mol^{-1}}$, what means that ionization of $H_2$ molecule to $2H^+$ ions requires no input of energy at all. In theory, reaction (3) could go through the stage of H atoms formation, but this would involve great activation energy, as mentioned above. It is logical to suppose, that oxidation of $H_2$ molecule to $H^+$ ions (Eq. (3)) could proceed through the stage of such intermediate, where chemical bond between the two protons in $H_2$ molecule would be partly preserved, what would lead to a significantly lesser amount of energy. The only such intermediate in Eq. (3) can be a hydrogen molecular ion $H_2{}^+$ [31] the role of which in electrochemistry was somehow overlooked so far [8]. The bond energy between the two protons sharing one electron in $H_2{}^+$ makes ~255 kJ $mol^{-1}$ [32]. Quite recently, the electronic configurations of this molecular ion have attracted much attention, because mathematical modeling of such chemical bond is possible [33]. In his recent review [20] Jena has described adsorbed molecule of quasi-$H_2$ with internuclear distance of ~0.90 nm instead of 0.76 nm. In our view, this quasi-molecule should be the molecular ion $H_2{}^+$, where distance between protons is 0.106 nm [31]. If so, the stages of reaction (3) in the case of platinum should be as follows:

$$H_2 \rightleftarrows (H_2{}^+)_{surf} + e^-(Pt) \tag{4}$$

and

$$(H_2{}^+)_{surf} \rightleftarrows 2H^+ + e^-(Pt) \tag{5}$$

Index “surf” here denotes the surface nature of the process. The feasibility of the first step (Eq. (4)) should be determined by the electron affinity of the metal, which in the case of platinum is as high as 205.3 kJ $mol^{-1}$ [29]. The sum of the above indicated energy values, i.e., 255 kJ $mol^{-1}$ and 205.3 kJ $mol^{-1}$, equals the value of bond energy in $H_2$ molecule. Thus, it follows that ionization of $H_2$ molecule to $H_2{}^+$ ion (Eq. (4)) on Pt surface requires no additional energy, similarly to (Eq. (3)), i.e., $\Delta G_{H_2{}^+/H_2} \approx 0\,\mathrm{kJ\,mol^{-1}}$. Consequently, dissociation of $H_2{}^+$ to $2H^+$ ions (Eq. (5)) should proceed without consumption of energy as well, i.e., $\Delta G_{2H^+/H_2{}^+} \approx 0$. If reversible overall electrochemical reaction (Eq. (3)) is in equilibrium at a certain value of the potential, then all the intermediate stages of this reaction (Eqs. (4) and (5)) should also be in equilibrium at the same value of the potential, i.e., at $E = 0$ V (SHE) at a certain surface concentration of $(H_2{}^+)_{surf}$.

As demonstrated elsewhere [34], $H_2{}^+$ ions exist on Pt electrode surface in an adsorbed state within $E$ range from ~0.2 V to ~ −0.05 V (SHE), surface concentration of $(H_2{}^+)_{ad}$ makes ~0.7 nmol $cm^{-2}$ and these ions occupy all the 3-fold sites on Pt surface.

### 2.3. Steric factors and hindrance

Let us check compliance of the above listed arguments with the steric factors on surfaces of metals for several different species. Dimensions of various hydrogen species are listed in the Table 1, while their relative sizes together with dimensions of Pt atoms and tetrahedral and octahedral sites of Pt lattice are shown in Fig. 1. As one can see, only protons, i.e., not hydrated $H^+$ ions with $d \simeq 10^{-8}$ nm, can freely penetrate into the Pt lattice through the tetrahedral sites and, hence, can migrate into the bulk of metal under influence of concentration or electric field gradients. However, penetration of proton into lattice, or, to be more precise, into metal phase is possible only when its charge is compensated by an electron, i.e., adsorbed or absorbed proton–electron ionic pair