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Hydrogen species within the metals: role of molecular hydrogen ion H_2^+

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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: $H_2 \rightleftharpoons (H_2^+)_{ad} + e^-$ and $(H_2^+)_{ad} \rightleftharpoons (H_2^+)_{ab} \rightleftharpoons 2(H^+)_{ab} + e^-$. 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.

Keywords: Hydrogen, molecular ion, adsorption, absorption, transition metals, inner surface, proton

1. Introduction

Hydrogen interaction with metals represents very wide and much investigated area of utmost technological importance^{1,2,3,4,5}. It is closely related with metallurgical processes, metal processing and their exploitation. All metals and their alloys which are widely used in engineering contain certain amount of hydrogen¹. 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^{6,7,8,9}. Nowadays, these issues are important in relation to hydrogen energy^{10,11,12,13,14}, fuel cells^{15,16}, high power metal-metal hydride electrochemical power sources¹⁷ and various nanotechnological processes¹⁸ used in hydrogen storage^{19,20,21,22,23,24,25} 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 co-

valent hydrides^{2,3,4,5}. However, the majority of transitional metals and their alloys do not form stable stoichiometric chemical compounds with hydrogen. Among them, such widely investigated metals as Pt, Pd, Ni and Ti¹. 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^{7,8,26,20}, 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 phase⁷. 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 properties¹ 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 suggested¹, 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

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proton state. So it was presumed that protons penetrate throughout the electronic shells of atoms in the form of proton gas¹. 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 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 palladium¹ 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 metals¹, 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:



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. $1/2D_{H_2} = 1/2 \cdot 453.6 \text{ kJ mol}^{-1} \approx 227 \text{ kJ mol}^{-1}$.

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., $\Delta G_H = 203.25 \text{ kJ mol}^{-1}$ ²⁹, since the standard potential of equation:



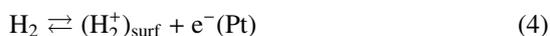
is $E_{H^+/H}^0 = -2.1 \text{ V}$ ³⁰.

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:

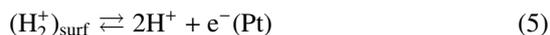


is $E_{2H^+/H_2}^0 = E_{SHE} = 0 \text{ V}$ and $\Delta G_{2H^+/H_2} = 0 \text{ kJ mol}^{-1}$, what means that ionization of H_2 molecule to $2H^+$ ions requires no input of energy at all. In theory, reaction (3) could go through the stage of H atoms formation, but this would involve great activation 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 far⁸. The bond energy between the two protons sharing one electron in H_2^+ makes $\sim 255 \text{ kJ mol}^{-1}$ ³². Quite recently, the electronic configurations of this molecular ion have attracted much attention, because mathematical modeling of such chemical bond is possible³³. In his recent review²⁰ Jena has described adsorbed molecule of quasi- H_2 with internuclear distance of $\sim 0.90 \text{ nm}$ 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:



and



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 $205.3 \text{ kJ mol}^{-1}$. The sum of the above indicated energy values, i.e., 255 kJ mol^{-1} and $205.3 \text{ kJ mol}^{-1}$, 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., $\Delta G_{H_2^+/H_2} \approx 0 \text{ kJ mol}^{-1}$. 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. 4,5) should also be in equilibrium at the same value of the potential, i.e., at $E = 0 \text{ V}$ (SHE) at a certain surface concentration of $(H_2^+)_{\text{surf}}$.

As demonstrated elsewhere³⁴, H_2^+ ions exist on Pt electrode surface in an adsorbed state within E range from $\sim 0.2 \text{ V}$ to $\sim -0.05 \text{ V}$ (SHE), surface concentration of $(H_2^+)_{\text{ad}}$ makes $\sim 0.7 \text{ nmol cm}^{-2}$ and these ions occupy all the 3-fold sites on Pt surface.

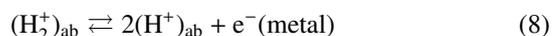
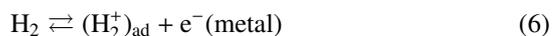
2.3. Steric factors and hindrance

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 $d \approx 10^{-8} \text{ nm}$, 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 should form on the inner surface of the lattice. As can be seen from Table 1 and Fig. 1, H atom can neither penetrate into metal lattice, nor fit in its tetrahedral site due steric constrains. Another particle, which can penetrate from outer surface into the lattice of Pt or other Pt group metals is hydrogen molecular ion H_2^+ . As it will be shown further this particle plays very important role in the processes of hydrogen interaction with inner surface of the metal phase.

2.4. The mechanism of H_2 interaction with transition metals

The interaction of H_2 with transition metals can be summarized by the following sequence of surface reactions:



with overall equation of dissociative ionization as follows:



here $(H_2^+)_{\text{ab}}$ should be regarded as $(H_2^+)_{\text{ad}}$ adsorbed on the inner surface of the lattice. Sequence of the equations 6-8 comprises the processes of dissociative ionization of H_2 on the outer surface of the electrode, absorption of H_2^+ ion and its further ionization within metal phase to adsorbed protons $(H^+)_{\text{ab}}$, which are located inside the volume of tetrahedral and octahedral voids within the metal phase (see Fig. 2). Overall reaction (eq. 9) reflects an interaction of H_2 with metal, which could be realized in a gas phase, in fact. Naturally, such interaction is possible only in the case when electrode surface is free from surface oxides or other adsorbed layers.

So, the essence of hydrogen interaction with transition metals is not adsorptive dissociation of H_2 molecule to adsorbed or chemisorbed H atoms, which requires large amount of energy, but dissociative ionization of H_2

Table 1: Dimensions of various species and Pt adsorption sites.

Particle or Site	Diameter (nm)	Literature
H ⁺ proton	10 ⁻⁸	ref. ³²
H atom	0.156	ref. ²⁹
H ⁻ hydride ion	~0.272	ref. ³²
H ₂ molecule	0.21–0.26	ref. ^{26,1}
H ₂ ⁺ molecular ion	width 0.03–0.04, length 0.106	ref. ³¹
H ₂ O molecule	0.22–0.27	ref. ³²
H ₃ O ⁺ hydrated proton	0.22–0.27	ref. ³²
Pt atom	0.138	ref. ³²
Pt[111] 3-fold site	~0.04	see Fig. 1
Pt[100] 4-fold site	~0.11	see Fig. 1

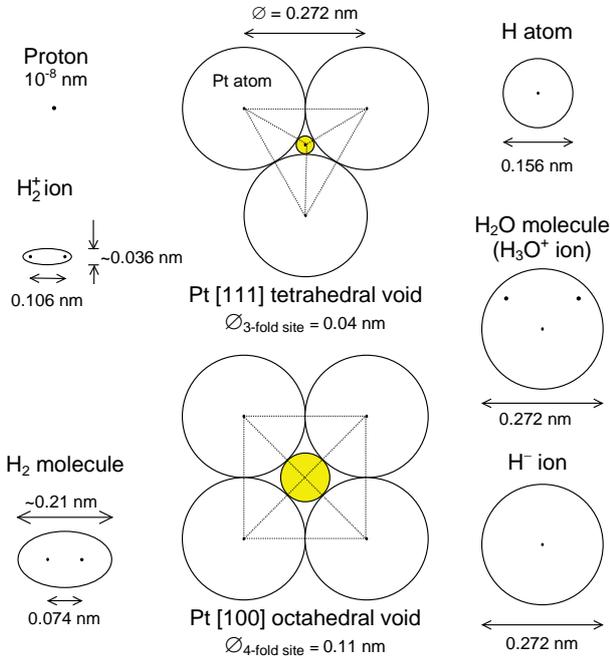
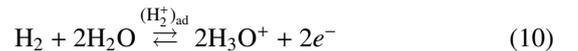


Figure 1: Steric hindrance on the surface of Pt. Relative sizes of various hydrogen species and 3-fold and 4-fold sites of Pt lattice (see, Table 1).

leading to formation of $(\text{H}_2^+)_{\text{ad}}$ and $(\text{H}_2^+)_{\text{ab}}$ ions adsorbed on the outer or inner surface of the electrode, respectively (Fig. 2). Consequently, H_2^+ ion represents a connecting link which combines the electrochemical behavior of outer and inner metal surface into integral whole and makes it possible to understand the well-known dependence of the physical and mechanical properties of the metal on the amount of hydrogen in it. As the size of H_2^+ ion is $\sim 10^6$ times larger than that of proton, the

presence of H_2^+ within metal lattice should inevitably block the shifting of atomic planes with respect to each other, thus causing the deterioration of metal plasticity and increase in fragility. Moreover, it becomes evident that general mechanism of H_2 interaction with the metals indicated is based on adsorptive interactions of H_2^+ and H^+ ions on both outer and inner surfaces of the metal, respectively. The adsorptive type of interaction is evidenced by the fact that, for instance, Pt group metals, i.e., Ru, Rh, Pd, Os, Ir and Pt in finely dispersed form (e.g. Pt black) absorb up to several hundred times more hydrogen than the same metals in their compact form¹. Since the inner surface of the metal is extremely large, not easily accessible and is never fully covered, no limits for solubility of hydrogen within metals, i.e., filling with H_2^+ and H^+ ions, have been established. It depends on the specific conditions of H_2 /metal interaction¹. The process of hydrogen diffusion throughout metal membranes also becomes clear. Since the overall reaction (9) is reversible, it is evident that H_{ab}^+ ions, which penetrate through the membrane, can reunite into H_2 molecule on the other side of it.

An important consequence of the proposed mechanism can be envisaged by an addition of 2 H_2O molecules to both sides of eq. 9. Such addition, which makes no difference from the thermodynamic point of view, would yield the following equation:



which reflects hydrogen oxidation and reduction reactions (HER and HOR) taking place on the outer surface of the electrode in aqueous solutions. The HOR (eq. 10) in aqueous medium also goes through the stage of $(\text{H}_2^+)_{\text{ad}}$ formation, i.e., eq. 6, and therefore the processes of absorption of this ion into electrode phase, as

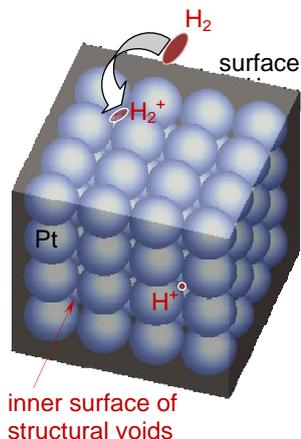
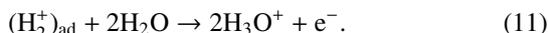


Figure 2: Visualization of the “inner” surface of structural voids of a cubic structure of platinum. The inner surface is accessible to $(\text{H}_2^+)_{\text{ad}}$ and $(\text{H}^+)_{\text{ab}}$ ions.

described by (eqs. 7, 8), are also possible, provided that electrode surface is free from oxides, like in the case of platinum³⁵. Further oxidation of $(\text{H}_2^+)_{\text{ad}}$ to H_3O^+ ions on the electrode surface proceeds according to the following overall reaction:



Proton, i.e., H^+ ion cannot exist on the electrode surface in aqueous medium because it hydrates immediately yielding H_3O^+ ion due to extremely large energy of hydration, which makes $\sim 750 \text{ kJ mol}^{-1}$.

From the above presented novel mechanism of hydrogen interaction with transition metals (eqs. 6- 9) it follows that adsorbed ionic pairs which form on the surface of metals during their interaction with H_2 can be treated as some kind of hydrogen metallides, i.e., $\text{H}_2^+ \cdot \text{Pt}^-$ and $\text{H}^+ \cdot \text{Pt}^-$, rather than chemisorbed metal hydrides as the commonly accepted approach postulates.

2.5. Some examples of H_2 interaction with transition metals

Nowadays, when interaction of H_2 with metals is discussed in scientific literature, it is always interpreted in terms of dissociative adsorption leading to formation of H atoms on the outer surface of the metal or to MH_x -type hydrides, if absorption is involved^{20,8,35,26}. It has been demonstrated, however, that under the conditions close to standard ones, the existence of H atoms adsorbed on or absorbed within the metals in both gaseous and aqueous media is neither thermodynamically (eq. 2) nor spatially possible (Fig. 1). Below are some examples of conventional treatment of H_2 interaction with

metals together with their novel interpretation in the light of conclusions of the presented mechanism.

2.5.1. Interaction with Pd, Pt, Ni, Ti, Zr, V, Nb, Ta

As far as interaction of hydrogen with transition metals is concerned, an exceptional metal in this regard is palladium¹. Under normal pressure of H_2 and room temperature it can absorb up to $\sim 10^3$ volumes of H_2 , what corresponds approximately to atomic ratio $\text{PdH}_{0.7}$ or to 8320 cm^3 of H_2 per 100 g of Pd. Maximum absorption is reached under high pressure of H_2 and it corresponds to 2800 volumes or $\text{PdH}_{2.2}$ or $\sim 2.33 \times 10^4 \text{ cm}^3$ $\text{H}_2/100 \text{ g Pd}$. In the case of Pt and Ni, H_2 absorption under normal conditions makes $1.1 - 1.9 \text{ cm}^3 \text{ H}_2/100 \text{ g Pt}$ and $3.3 - 15.4 \text{ cm}^3 \text{ H}_2/100 \text{ g Ni}$ ¹. As for Ti, following volumes of H_2 absorbed per 100 g of metal were reported: $50 - 100 \text{ cm}^3$ for compact metal, $280 - 330 \text{ cm}^3$ for metal in sponge form and $300 - 5300 \text{ cm}^3$ for Ti powder¹. Aside from Ti, very large amounts of H_2 , up to 10^4 cm^3 per 100 g of metal and more, can be absorbed by Zr, V, Nb and Ta¹. The latter facts are used as arguments to justify the adsorption of H atoms on metal surface in the case of HER and HOR^{6,7,8}. However, the fact that these metals can be saturated with hydrogen to a certain extent under specific conditions in gas phase does not necessarily mean that the layer of chemisorbed H atoms would exist on the surface of the metals in aqueous solution under standard conditions. As it has been demonstrated above, hydrogen can exist within these metals only in the form of $(\text{H}_2^+)_{\text{ab}}$ and H_{ab}^+ ions, whereas on the outer surface of the metal $(\text{H}_2^+)_{\text{ad}}$ ions prevail. In aqueous solutions with pH ranging from 0 to 14 and at $E \leq 0 \text{ V}$, Ti, Zr, Nb and Ta (RHE) are covered with layers of their surface oxides TiO_2 , ZrO_2 , Nb_2O_5 and Ta_2O_5 formed as a result of their interaction with H_2O molecules³⁰, because in this case chemical bonds between metal and O^{2-} ions are by far stronger than adsorptive bonds with $(\text{H}_2^+)_{\text{ad}}$, $(\text{H}_2^+)_{\text{ab}}$ and H_{ab}^+ ions.

2.5.2. Nanometric layers of YH_x , PdH_x , VH_x , TaH_x

From the viewpoint of H_2 interaction with metals, interesting results were reported by Broeder et al. in ref.¹⁸, where migration of hydrogen within 200 - 300 nm thick yttrium layer, formed on the surface of sapphire, was investigated. Yttrium surface was modified with locally formed Pd strips (electrodes) of $\sim 30 \text{ nm}$ width. Yttrium surface between the strips was oxidized, i.e., covered with isolating layer of Y_2O_3 , which prevented the interaction between Y and H_2 . Therefore H^+ ions (protons) could access the surface of yttrium and interact with it only through the layer of Pd. Yttrium with hydrogen forms ionic hydrides of YH_x

type, where x can vary between 0 and 3.0^{18,2}. As various yttrium hydrides exhibit different optical properties within the visible wavelength spectrum, it was possible to visualize the processes of hydrogen diffusion and migration within yttrium layer. It was shown that hydrogen particle in YH_x compound is charged negatively¹⁸, contrarily to PdH_x , VH_x , NbH_x and TaH_x compounds, where hydrogen species were found to have positive charge^{18,36,37}, as it should be expected according to the above presented concept of H_2 dissociative ionization. Negative charge implies formation of the hydride ion H^- , which cannot penetrate into Pd phase due to steric hindrance (Fig. 1). The H^- can be formed only at the Pd/Y interface as a result of hydrogen interaction with yttrium, because standard potential of the reaction:



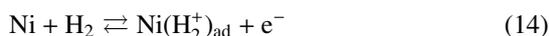
is $E_{H_2/2H^-}^0 = -2.25 \text{ V}^{30}$, whereas $E_{Y^{3+}/Y}^0 = -2.37 \text{ V}$. The values of standard potentials of ionization of all other above indicated metals are considerably more positive, therefore the formation of H^- is thermodynamically impossible and that is why the charge of H particle in the so-called hydrides PdH_x , VH_x , NbH_x and TaH_x was found positive^{18,36,37}.

2.5.3. Metal hydride electrodes

The so-called metal hydride electrodes (MH), which are used in both primary and secondary batteries, are also treated in literature⁸ as being the result of dissociative adsorption of hydrogen on metals and their alloys. Nickel metal hydride batteries (Ni-MH) can be taken as an example¹⁷. The AB_5 and AB_2 type metal alloys, which include very active metals such as La, rare earth elements: Ce, Nd, Pr, Gd, Y and also V, Ti, Zr, Al, Sr, Cr together with Ni or Co, are usually used as MH electrodes. Typical example is the $LaNi_5$ alloy. One can find in literature¹⁷, that the value of standard potential of MH electrode in alkaline medium irrespective of alloy composition is as follows:



The latter E value, however, corresponds to the value of the potential of standard hydrogen electrode at $pH = 14$. Thus it follows, that the so-called metal hydride electrodes are hydrogen electrodes, in fact. Equation 13 in the case of $LaNi_5$ electrode in alkaline medium should be written as follows:



This process (eq. 14) and not the reaction (13) determines the potential of the so-called metal hydride electrode. Nickel phase in this case serves as an electric

contact, since nickel in alkaline medium behaves like noble metal, i.e., water is not an oxidizer with respect to Ni. Lanthanum is the source of H_2 , as it slowly corrodes in aqueous medium, because its standard potential is $E_{La^{3+}/La}^0 = -2.52 \text{ V}$. Thus it turns out, that electrochemically active are not the H atoms adsorbed or absorbed by AB_5 and AB_2 type alloys, but molecular hydrogen, which evolves as a result of corrosive interaction between alloy's active component and aqueous electrolyte. Therefore, the operation time of MH electrodes in the so-called Ni-MH batteries is limited.

3. Conclusions

We show that interaction of H_2 with such transition metals as Pd, Pt, Ni, Ti, Zr, V, Nb, Ta in gaseous phase involves dissociative ionization of H_2 to $(H_2)_{ad}^+$, i.e., H_2^+ molecular ions adsorbed on the outer surface of the electrode. This processes is followed by absorption of $(H_2)_{ad}^+$ into the metal phase and further ionization of $(H_2)_{ab}^+$ to $(H^+)_{ab}$, i.e., absorbed protons. The main reason of such dissociative ionization of hydrogen molecules on a chemically clean metal surface is the high electron affinity of the metal. The mentioned hydrogen species represent the main form in which hydrogen can exist within the tetrahedral or octahedral voids of the discussed metals.

The presented mechanism is consistent with reported mechanical and optical properties of hydrogenated metals, can explain degradation of MH batteries, and formation of adsorbed hydrogen metallides of ionic pair type. The storage and production of hydrogen for energy applications are expected to benefit from a better understanding of the detailed steps and mechanisms of hydrogen evolution, oxidation and diffusion where the H_2^+ -ion is an intermediate. The energy efficiency of H_2 ionization on Pt surface is determined by the first principles and thermodynamics of the process and is an inviting feature to search for future energy solutions using hydrogen.

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