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Article

Atoms *vs.* ions: intermediates in reversible electrochemical hydrogen evolution reaction

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Abstract: We present a critical analysis of the mechanism of reversible hydrogen evolution reaction based on thermodynamics of hydrogen processes considering atomic and ionic species as intermediates. Clear distinction between molecular hydrogen evolution/oxidation (H_2ER and H_2OR) and atomic hydrogen evolution/oxidation (HER and HOR) reactions is made. It is suggested that the main reaction describing reversible H_2ER and H_2OR in acidic and basic solutions is: $H_3O^+ + 2e^- \xrightleftharpoons{(H_2^+)_{ad}} H_2 + OH^-$, which proceeds via the formation of hydrogen molecular ion as intermediate and its potential is E^0 = 0.414 V (at the standard Hydrogen electrode SHE scale). We analyse experimentally reported data with models which provide *quantitative* match (R.J.Kriek et al., Electrochem. Sci. Adv. e2100041 (2021)). The experimentally observed slope of $\lg(Current)$ vs. *Potential* equal to $\approx$ 30 mV/dec corroborates the presented model of H_2ER/H_2ER based on $H_2{}^+$ as intermediate.

Keywords: H_2ER, H_2OR, HER, HOR, hydrogen, hydrogen molecular ion $H_2{}^+$, reversible process

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1. Introduction

Hydrogen is the most abundant element in the universe and the main source of energy. Water, H_2O, is essential to life on Earth and is a source of H_2, which can be generated by water splitting. To produce green fuel H_2 from water and sea water electrolysis using solar/renewable power is a required technological step, which was considered expensive a decade ago [1]. To make it practical, exact mechanisms and reactions with detailed steps and intermediates should be revealed and optimised for the highest efficiency. As recently highlighted [2], there is no quantitatively satisfactory understanding of the hydrogen evolution and oxidation reactions (HER & HOR) despite abundant studies in electrochemistry, electro- and photo-catalytic water splitting. Electrochemical evolution of hydrogen can take place on the surface of various metals, semiconductor oxides, sulfides as well as other electrically conducting surfaces. Therefore various issues related with hydrogen evolution reaction are thoroughly analyzed in the scientific literature [3–7]. Starting from the first studies on this subject [8–10] it was assumed that reduction of H^+ ions, either from H_2O molecules or H_3O^+ ions, proceeds step-wise with formation of hydrogen atoms adsorbed on the electrode surface, H_{ad}, which later are desorbed via Heyrovsky or Tafel reactions. H_{ad} atoms are considered as intermediates of H_2 evolution process. Various states such as H_{top}, H_{bridge} and $H_{terminal}$ (according to H-atom position), which differ in their bond strength with the electrode surface are considered [4]. Such treatment of hydrogen evolution mechanism is commonly acknowledged and applied for interpretation of various electrocatalytic as well as photoelectrochemical processes taking place on different substrates [11].

It is generally accepted that electrochemical hydrogen evolution reaction occurring in acidic aqueous solutions is described by: $2H_3O^+ + 2e^- \overset{H_{ad}}{\rightleftharpoons} H_2 + 2H_2O$, whereas the one proceeding in neutral or alkaline medium is: $2H_2O + 2e^- \overset{H_{ad}}{\rightleftharpoons} H_2 + 2OH^-$. It is considered that cathodic and anodic halves of these reactions proceed step-wise via formation of H_{ad} atoms adsorbed on the electrode surface as intermediates. These adatoms are removed from the surface during the cathodic process via chemical Tafel or electrochemical Heyrovski reactions. The above described mechanism of H_2 evolution process is, however, contradictory, as elaborated further. Firstly, the energy of interaction between H atom and Pt electrode surface under standard conditions at E = 0 V (SHE) is evaluated to be up to 50 kJ mol^{-1} [4]. Taking into consideration the fact that $E^0_{H^+/H}$ = −2.106 V [12], the energy of H_{ad} interaction with surface, required to compensate such depolarization, should be ΔG = 203 kJ mol^{-1}. Such energy is typical to chemisorption, rather than adsorption. Thus, hydrogen atoms are considered to be adsorbed, whereas the indicated values of interaction energy are by far too high for adsorptive interaction. If chemisorption took place, the formation of surface hydrides should occur on the electrode surface, but this is not the case for platinum group metals. Another contradiction is related with the existence of standard hydrogen electrode (SHE). Recently, in many publications the values of electrochemical potential are given versus convenient reference hydrogen electrode (RHE) scale [13]. The very existence of such reference electrode implies that reversible two-electron transfer process ($2H^+ + 2e^- \rightleftarrows H_2$) with Nernstian shift of $\frac{dE^0}{d(pH)} = \frac{2.3RT}{F} = 0.059$ V is feasible on Pt electrode surface under certain conditions. If so, then what is the real mechanism of hydrogen evolution reaction?

This work presents counter arguments for the commonly accepted treatment of hydrogen evolution reaction as well as arguments supporting the alternative concept of this process. This revisiting view is mandated by recent experimental study which can only explain Pt deposition on a carbon electrode via $H_2{}^+$ mediation [14].

2. Mechanisms of H and H_2 evolution/oxidation reactions

2.1. Thermodynamics of H atom formation

The energy of chemical bond in H_2 molecule is ΔH = 453.6 kJ.mol^{-1}, or $\frac{1}{2}D_{H_2} \approx 226.8$ kJ.mol^{-1} if calculated per one atom [15]. In electrochemistry, usage of ΔG is more appropriate, since $\Delta G = -nFE^0$ and $\Delta G = \Delta H - T\Delta S$, where G, H and S are the thermodynamic functions (Gibbs free energy, Enthalpy and Entropy, respectively), E^0 is the standard potential, T is the absolute temperature and n is the number of electrons transferred in the reaction. From the electrochemical point of view, the standard potential of the so-called Volmer reaction involving the transfer of the first electron:

$$H^+ + e^- \rightleftarrows H, \tag{1}$$

is $E^0_{H^+/H}$ = −2.106 V (SHE) [12]. The transfer of the second electron as well as formation of H_2 molecule occurs in Heyrovsky step:

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

the standard potential of which is $E^0_{H,H^+/H_2}$ = 2.106 V (SHE) [12], i.e. exactly the same number with an opposite sign. Formal summing of the eqs. 1 and 2 yields the well-known summary equation

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

with the value of standard potential $E^0_{2H^+/H_2}$ = 0 V (SHE). In other words, formation of H_2 molecule fully compensates the electrochemical energy ΔG = -nF$E^0_{H^+/H}$ = 406.4 kJ.mol^{-1}, consumed for the formation of 2 moles of H atoms. Under standard conditions the actual onset of hydrogen evolution on the surface of platinum group metals is observed at $E = 0$ V (SHE). Thermodynamically, the transfer of the first electron at $E = 0$ V (SHE) to form H atom should require adequate energetic compensation. It is well-known that in case there is a chemical interaction between the electrode surface and the discharging particle, the electrode process becomes depolarized. The effect is called underpotential deposition or UPD and the extent of depolarization depends on the energy of interaction. In order to depolarize the first electron transfer process from E^0 = -2.106 V (SHE) to E^0 = 0 V (SHE), the energetic effect of such UPD should be as large as ΔG = 203.2 kJ mol^{-1}. In the case of anodic hydrogen oxidation reaction on Pt, occurring at even more positive potentials, i.e. within 0 - 0.5 V (SHE), the energy of interaction between H atom and Pt surface can reach 260 kJ mol^{-1} according to the literature [3,16–19].

2.2. Depolarization of H_2 evolution due to hydrogen molecular ion $H_2{}^+$ formation

First of all, it should be admitted that depolarization of the process can be conditioned by any kind of interaction of the discharging particle with ions or atoms present in its close proximity. In aqueous solutions there are two particles which can directly take part in H_2 evolution process, i.e. H_2O molecule and H_3O^+ ion. We hypothesize that the main particle irrespective of solution pH is hydronium ion H_3O^+. In neutral and alkaline solutions hydronium ion can be produced by dissociation of water molecules according to reaction:

$$2H_2O \rightleftarrows H_3O^+ + OH^- \tag{4}$$

Reaction (4) is fast, because the energy of H-OH bond disruption is compensated by the energy of hydration of formed H_3O^+ ions. According to literature [4], the activation energy of reaction (4) is about 75 kJ mol^{-1}, which is not high. This reaction explains why kinetics of hydrogen evolution reaction in alkaline solutions is more sluggish [4].

As shown in our previous studies [20,21], the transfer of the first electron during electrochemical discharge of H_3O^+ ion should lead to formation of molecular hydrogen ion $H_2{}^+$, whereas the transfer of second electron should yield H_2 molecule. An important property of $H_2{}^+$ ion is the $H - H^+$ bond energy, which according to the literature [22] is ΔH^0_{298} = 255.7 kJ mol^{-1}. The latter value is close to the amount of energy ΔG^0 = 203.2 kJ mol^{-1} required to depolarize the discharge of H^+ ion from E^0 = -2.106 V (SHE) to E^0 = 0 V (SHE). The processes occurring at $E = 0$ V (SHE) can be described by the following sequence of electrochemical reactions:

$$H_3O^+ + e^- \rightleftarrows (H_2{}^+)_{ad} + OH^- (rds) \tag{5}$$

$$(H_2{}^+)_{ad} + e^- \rightleftarrows H_2. \tag{6}$$

Overall reaction:

$$H_3O^+ + 2e^- \rightleftarrows H_2 + OH^-. \tag{7}$$

Reaction (5) is reversible rate determining step. Both processes (5) and (6) are fast and reversible and proceed simultaneously, therefore the overall two-electron process (7) describes redox processes occurring within certain rate limits on Pt surface in reversible hydrogen electrode (RHE) and determines the magnitude of exchange current, i_o, as well as E of the process. Anodic oxidation of H_2 proceeds according to reaction (6) and leads to formation of $(H_2{}^+)_{ad}$ rather than *via* the dissociation to H_{ad} atoms.

If reaction (4) is taken into account, the sum of the equations (4) and (7) yields the summary equation of reversible hydrogen evolution process:

$$2H_2O + 2e^- \xrightleftharpoons{(H_2^+)_{ad}} H_2 + 2OH^-. \tag{8}$$

Thus, molecular hydrogen ion $(H_2{}^+)_{ad}$ should be considered as intermediate in hydrogen evolution process instead of H_{ad} atom. Actually, molecular hydrogen ion is the precursor of H_2 molecule, for the formation of which the energy of H^+ ion hydration equal to 432 kJ.mol^{-1} [23] is consumed. H_3O^+ ion accommodates two H^+ ions, which upon addition of two electrons can be used for the formation of H_2 molecule. The potential limits of $(H_2{}^+)_{ad}$ existence on the electrode surface are restricted to $E = \pm\frac{2.3RT}{F}$ V (SHE). Within these limits, hydrogen evolution and oxidation reactions proceed reversibly. When cathodic current significantly exceeds the magnitude of exchange current of reaction (7), i.e. when $i \gg i_0$, transition to irreversible H_2 evolution occurs with slope $\frac{dE}{d\lg i} = \frac{2.3RT}{\alpha F} = 120$ mV, given that $\alpha = 0.5$. In such case the transfer of first electron becomes hindered (eq. (5)), whereas the transfer of second one proceeds instantaneously. In the case of hydrogen evolution on Pt electrode, the decrease of slope $\frac{dE}{d\lg i}$ to attain values $\frac{2.3RT}{F} \approx 60$ mV and $\frac{2.3RT}{2F} \approx 30$ mV as the potential approaches $E = 0$ V (SHE), demonstrates the transition towards conditions where the process proceeds reversibly. If there is any hindrance which limits the access to electrode surface for H_3O^+ ions, the slope $\frac{dE}{d\lg i}$ as well as the overvoltage of HER, η_{H_2} will decrease due to large i_0.

It is noteworthy, that no additional chemical energy except for that resulting from the bond formation between H atoms, is required for eqs. (5) and (6). On the contrary, the postulation of the bond between H_{ad} and the surface of platinum group metal acknowledges the need for additional interaction, which inevitably should have an adverse effect on the kinetics of H_2 molecule formation and its detachment from the electrode surface. Since the existence of reversible hydrogen electrode is an experimentally established fact, the E range above $E^0 = 0$ V (SHE), i.e. the so-called hydrogen UPD region, should, in fact, be related with anodic oxidation of H_2, rather than reduction of H^+ ion to H_{ad} atom. In our previous study [21] on the basis of precise analysis of microgravimetric and coulombmetric data reported in [24] it was demonstrated that the current peaks observed in the voltammograms of Pt electrode in 0.5 M H_2SO_4 within the above mentioned E range between 0 V and 0.5 V (SHE) are related with reversible adsorption/desorption of the products of anodic oxidation of H_2 molecule, i.e. $(H_3O^+)_{ad}$ and $(H_2{}^+)_{ad}$ (see Fig. 2(b) for a detailed account of processes). The energy of adsorptive interaction of these surface compounds with electrode surface was evaluated to be -25.1 kJ/mol and -11.6 kJ/mol, respectively. These values are by far less than 203.2 kJ/mol required for the underpotential formation of chemisorbed H_{ad} atom at $E = 0$ V (SHE). In fact, formation of H_{ad} as intermediate in the reduction of H^+ could be hypothesized only in the cathodic range, i.e. at $E < 0$ V (SHE). Thus, there is a profound contradiction between chemisorptive interaction, which could justify the formation of H atom at $E \leq 0$, and postulated adsorptive interaction deemed to stabilize H_{ad} on the electrode surface. In other words, the chemisorption as a prerequisite for the formation of hydrogen atom is replaced by adsorption. Schematic representation of the above discussion is shown in Fig. 1. Formation of surface hydrides (denoted as H_{hydr} in Fig. 1) can also depolarize the discharge of hydrogen ions (for details, see Appendix A in ref. [25]).

2.3. Kinetics and pH-dependence of E in the case of reversible H_2 evolution/oxidation processes

In modern handbooks one can find two hydrogen evolution equations for aqueous solutions:

$$2H_3O^+ + 2e^- \rightleftarrows H_2 + 2H_2O \tag{9}$$

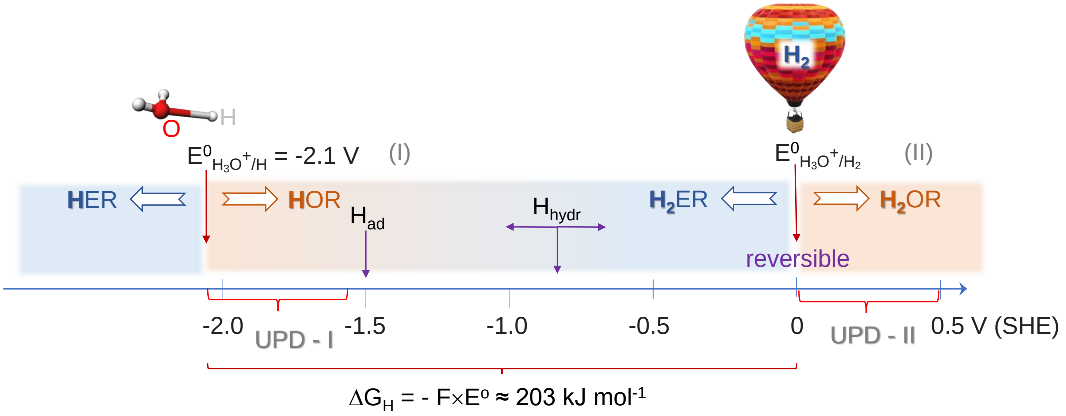

Figure 1. Thermodynamics of atomic and molecular hydrogen in H_2O (under standard conditions). The underpotential deposition (UPD - II) region corresponds to adsorption (weak) of H_3O^+ and $H_2{}^+$. The molecular hydrogen evolution and oxidation reactions (H_2ER/H_2OR) for H_2 are reversible on a Pt electrode at E = 0 V (SHE).

with $E^0 = 0$ V (SHE) for acidic medium and

$$2H_2O + 2e^- \rightleftarrows H_2 + 2OH^- \tag{10}$$

with $E^0 = -0.848$ V (SHE) for alkaline medium. Both the above reactions are composite and can be subdivided into the steps as follows. For the acidic conditions[1]:

$$H_3O^+ + 2e^- \rightleftarrows H_2 + OH^-, \tag{7}$$

$$OH^- + H_3O^+ \rightleftarrows 2H_2O \tag{11}$$

and for the alkaline conditions:

$$2H_2O \rightleftarrows OH^- + H_3O^+, \tag{11}$$

$$H_3O^+ + 2e^- \rightleftarrows H_2 + OH^-. \tag{7}$$

Thus, the equation 7 is the same for all media, because the process is the same irrespective of solution pH. The processes of water dissociation (eq. (11)) either precede or follow the electrochemical act (eq. (7)), thus, in fact, there is one ion H_3O^+ or OH^- participating in the two-electron transfer process.

The Nernst equation for reaction 7 is as follows:

$$E = E^0 + \frac{RT}{2F} \times \ln\left(\frac{c_{H_3O^+}}{p_{H_2} c_{OH^-}}\right), \tag{12}$$

where $E^0 = -0.414$ V (SHE) at $c_{H_3O^+} = c_{OH^-} = 10^{-7}$ mol l^{-1}, $E^0 = 0$ V (SHE) at $c_{H_3O^+} = 1$ mol l^{-1} and $E^0 = -0.826$ V (SHE) at $c_{OH^-} = 1$ mol l^{-1}, given that $p_{H_2} = 1$ atm. If $\left[c_{H_3O^+} \times c_{OH^-}\right] = K_w = 10^{-14}$, then eq. (12) can be written as:

$$E - E^0 = \frac{RT}{F} \ln c_{H_3O^+} = -2.3\frac{RT}{F} \times pH \tag{13}$$

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[1] note, the same reactions are numbered by the number which was the first time encountered, however, it is repeated where required for clarity and methodology of discussion/analysis

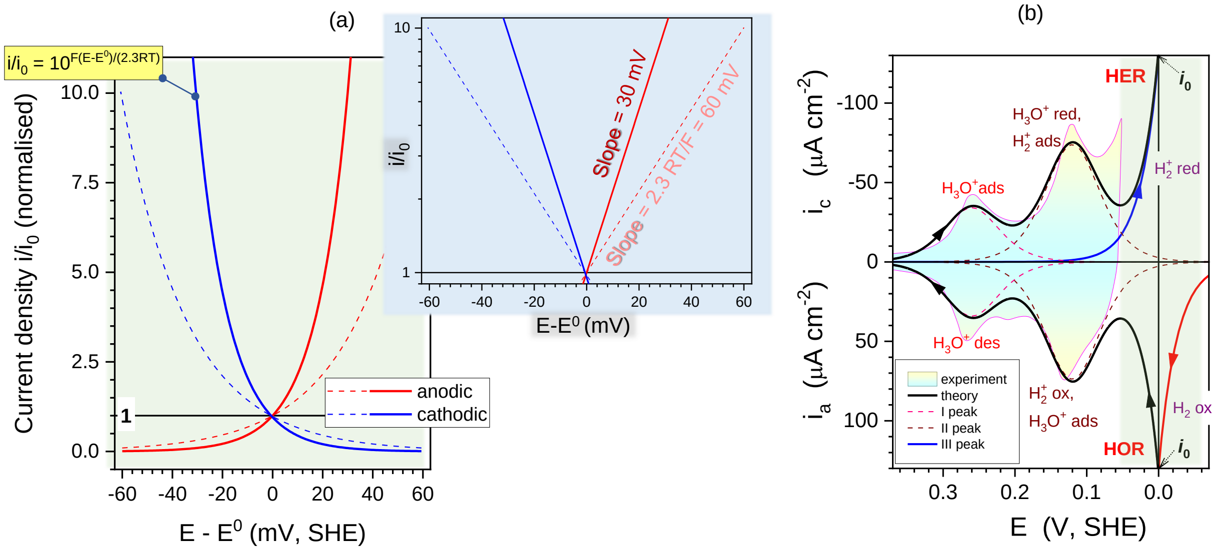

Figure 2. Analysis based on the Nernst equation for reaction (7). (a) The reversible polarization curves on Pt modelled for one- (dashed trace) and two-electron (solid trace) transfer processes. The right-inset shows log-lin presentation of the same graph to reveal linear slope; i_0 is the exchange current. In experiments [26, 27] the slope of 30 mV/dec was determined (solid lines). (b) Surface processes (adopted from [20]): adsorption and red/ox reactions of ions H_3O^+ and $H_2{}^+$ on Pt.

or

$$c_{H_3O^+} = \exp\left(\frac{F(E-E^0)}{RT}\right) \tag{14}$$

and the time derivative is

$$\frac{dc_{H_3O^+}}{dt} = \exp\left(\frac{F(E-E^0)}{RT}\right), \tag{15}$$

because $(e^x)' = e^x$ and $1/\lg(e) \equiv \ln(10) = 2.303$. On the other hand, it is known that:

$$i = nF \times \frac{dc}{dt}, \tag{16}$$

where n is the number of electrons transferred per one mole and

$$\lg i = \lg(nF) + \lg\left(\frac{dc}{dt}\right) \tag{17}$$

Combination of eqs. 17 and 15 yields:

$$\lg i = const + \frac{F(E-E^0)}{RT}\lg e = const + \frac{F(E-E^0)}{2.3RT}, \tag{18}$$

where $const = \lg(nF)$. From eq. (18) it follows that:

$$d\lg i = \frac{FdE}{2.3RT}, \text{ or } \frac{dE}{d\lg i} = \frac{2.3RT}{F} \approx 60\text{ mV/dec}. \tag{19}$$

Combination of equations 15 and 16 yields the expression for reversible polarization curves:

$$i = nF\exp\frac{F(E-E^0)}{RT}, \text{ or } i_0 = nF\exp\frac{FE^0}{RT} \tag{20}$$

or

$$i_0 = nF\exp\frac{FE^0}{RT} \tag{21}$$

These polarization curves for the anodic and cathodic processes are shown in Figure 2 (a), whereas Figure 2 (b) depicts polarization curves of surface electrochemical processes, taking place on Pt electrode surface in the so-called hydrogen UPD region at $E > 0$ V (SHE).

Equality $\left[c_{H_3O^+} \times c_{OH^-}\right] = K_w = 10^{-14}$ means that OH^- ion formed in reaction (7) will react with H_3O^+ yielding $2\,H_2O$ and vice versa in the anodic reaction. Consequently, in the case of reversible process, in accordance with eq.(9), where the formal ratio of H_3O^+ to electron is 1:1, Nernst slope of $\frac{dE}{d\lg(i)} = \frac{2.3RT}{F} \approx 60$ mV/dec and $\frac{dE}{dpH} \approx 60$ mV/pH should be observed. However, if due to some reason the concentration (or activity) of OH^- ions is not decreasing as a result of its interaction with H_3O^+ (e.g. OH^- adsorption on the electrode surface, formation of (hydr)oxides ($MeOH \rightleftarrows Me^+ + OH^-$) or due to some hindrance of their transport at rough nanostructured surfaces), the rate of anodic half-reaction (7) as well as i_0 will increase and the path (7) will become dominant. The Nernst equation for reaction (7), when c_{OH^-} = const and $p_{H_2} = 1$ atm can be written as:

$$E = E^0 + \frac{RT}{2F} \times \ln\left(\frac{c_{H_3O^+}}{p_{H_2}c_{OH^-}}\right) = const + \frac{2.3RT}{2F}\lg c_{H_3O^+} = const - \frac{2.3RT}{2F}pH \tag{22}$$

Consequently:

$$\frac{dE}{dpH} = -\frac{2.3RT}{2F} \approx 30 \text{ mV/pH unit} \tag{23}$$

It can also be shown that $\frac{dE}{d\lg i} = \frac{2.3RT}{2F} \approx 30$ mV/dec (detailed derivation of kinetic equations for the case when c_{OH^-} = const is presented in Appendix 3.

Thus in the case of reversible process, the slope $\frac{dE}{d\lg(c)} = \frac{2.3RT}{F}$ is equal to the slope $\frac{dE}{d\lg(i)}$. The E limits of the process reversibility are $\pm\frac{2.3RT}{nF}$, whereas i should not exceed $10 \times i_0$ (Fig. 2(a)). As one can see from the above discussion, in the case of reversible H_2 energy process (denoted as H_2ER and H_2OR in Fig. 1), only those H_2O molecules which are contained in H_3O^+ ion can participate in electrochemical reduction reaction. Other H_2O molecules participate only in chemical processes of neutralization or dissociation (eq.(11)). This, however, does not imply that they cannot be electrochemically reduced on the surface under an adequate overvoltage via formation of hydrides, or be reduced chemically to H_2 via the reactions with various electrochemically-produced metal oxide or sulfide surface species. These processes should be analyzed taking into consideration specific conditions of their occurrence and are outside the scope of the present paper.

3. Conclusions

We postulate that reversible electrochemical hydrogen evolution occurring in acidic, neutral and alkaline aqueous solutions can be described by one common reaction: $H_3O^+ + 2e^- \overset{(H_2^+)_{ad}}{\rightleftarrows} H_2 + OH^-$, the potential of which is given by the Nernst equation: $E = E^0 + \frac{2.3RT}{2F} \times \lg\left(\frac{c_{H_3O^+}}{c_{OH^-}}\right)$, where $E^0 = -0.414$ V. The peculiar features of this reaction are as follows: (i) it involves transfer of two electrons per one H_3O^+ ion, (ii) the precursor of H_2 molecule in a form of intermediate $(H_2{}^+)_{ad}$ ion is formed after the transfer of the first electron already, whereas the transfer of second electron leads to formation of H_2 molecule. The energy of chemical bond between H atom and H^+ ion within molecular hydrogen ion ${H_2}^+$ is ΔH = 255 kJ mol^{-1}, which fully accounts for the above indicated hydrogen UPD phenomenon. The energy of hydration which is conserved within H_3O^+ ion is consumed for the formation of bond in H_2 molecule. Considering that $\left[c_{H_3O^+} \times c_{OH^-}\right] = K_w$, transformation of the above Nernst equation yields standard formal slopes of $\frac{dE}{dpH} = \frac{dE}{dlgi} = \frac{2.3RT}{F} = 59$ mV/dec. However, if the condition of $c_{H_3O^+} = const$ or $c_{OH^-} = const$ is fulfilled, the indicated slopes become twice less. The values of $\frac{2.3RT}{2F} \approx 30$ mV/dec found experimentally [5,26,27] in the case of reversible hydrogen evolution process serve as a proof of the alternative mechanism presented herein. Presented analysis is further supported by recent experimental results of Pt electrodeposition and HER [14] which are explained by the mechanism involving formation of ${H_2}^+$ as intermediate in reversible hydrogen evolution on Pt. It is demonstrated that formation of H_{ad} as intermediate is thermodynamically and kinetically unfavourable process.

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Appendix

Actual slope $\frac{dE}{dpH} \approx 30$ mV/dec, though formal one, considering the reaction (11) would be 60 mV/dec ($K_w = c_{H_3O^+} \times c_{OH^-} = 10^{-14}$ for bulk process).

From eq. (22) it follows that $\lg c_{H_3O^+} = \frac{(E-const)2F}{2.3RT}$ or $\ln c_{H_3O^+} = \frac{(E-const)2F}{RT}$. Then $c_{H_3O^+} = \exp(\frac{(E-const)2F}{RT})$ and $\frac{dc_{H_3O^+}}{dt} = \exp(\frac{(E-const)2F}{RT})$, since $(e^x)' = e^x$.

If $i = nF \times \frac{dc}{dt}$, then $\lg i = \lg(nF) + \lg(dc/dt)$, $\lg(dc/dt) = \exp(\frac{(E-const)2F}{2.3RT})$ and $\lg i = const + \exp(\frac{(E-const)2F}{RT})$ and $d\lg i = \frac{2F}{2.3RT}dE$, which yields $\frac{dE}{d\lg i} = \frac{2.3RT}{2F} \approx 30$ mV/dec.

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