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V.N. Nikitenko [1], E.A. Babenkov [1], O.L. Bersirova [1, 2], V.S. Kublanovsky [1]

ELECTROCATALYTIC REDUCTION OF WATER CLUSTERS ON BINARY ALLOYS OF MOLYBDENUM WITH IRON SUBGROUP METALS IN AN ALKALINE MEDIUM

[1] V.I. Vernadskyi Institute of General and Inorganic Chemistry of National Academy of Sciences of Ukraine
32–34 Academician Palladin Ave., Kyiv, 03142, Ukraine, E-mail: kublan@ukr.net
[2] Department of Physical Chemistry, Vilnius University
24 Naugarduko Str., LT-03225, Vilnius, Lithuania

The total reorganization energy of the system and its components, the solvent reorganization energy and the transformation energy of reactants (water clusters $[(H_2O)_nOH]^-$), during electrocatalytic hydrogen evolution on binary alloys of molybdenum with iron subgroup metals (Fe, Co, Ni) in an alkaline medium (30 wt. % NaOH solution) have been calculated.

The calculated values of the solvent reorganization energy and the reorganization energy of water clusters are in agreement with the Marcus – Dogonadze – Kuznetsov theory. The dependence of the total reorganization energy of the system, the solvent reorganization energy, and the reorganization energy of discharging species (water clusters) on the electrolyte temperature has been calculated. It was shown that the total reorganization energy of the system and the activation energy of the electron-transfer reaction of electrocatalytic hydrogen evolution (HER) on binary alloys of molybdenum with iron subgroup metals in an alcaline vedium (30 wt. % NaOH solution) decrease linearly with increasing electrolyte temperature in the following order: Fe-54 at. % Mo > Ni-54 at. % Mo > Co-52 at. % Mo.

The temperature dependences of the water cluster discharge reorganization energy and the activation energy on binary molybdenum alloys are linear and intersect in the boiling point region of 30 wt. % NaOH solution 384.7 K. At this temperature, the electrode process is limited by the diffusion of regenerating water clusters to the electrode surface. The calculated diffusion activation energy A_d is 9.9 kJ·mol^{-1}. The value of the system reorganization energy λ_t is 39.8 kJ·mol^{-1}, which is consistent with the theory of Markus – Dogonadze – Kuznetsov. Electrocatalytic activity of binary alloys of molybdenum with iron subgroup metals at 30 wt. % NaOH solution at this temperature is maximum and does not depend on the nature of the alloy.

***Keywords**: binary alloys Co-Mo, Ni-Mo, Fe-Mo, hydrogen evolution reaction, water clusters, system reorganization energy, electrocatalysis*

INTRODUCTION

The reorganization energy of the system and the activation energy of the stages of the electrochemical process are the fundamental energy characteristics of the electrochemical reaction. The study of the energy characteristics of the electrochemical process, their relationship with the kinetic parameters is of scientific interest, since it expands the understanding of the elementary act of electron transfer and the mechanism of the electrode process.

The consideration of the electrocatalytic reduction of water clusters on alloys in an alkaline medium is an important aspect in the development of the theory of electrocatalysis and requires detailed study. Thus, of considerable scientific interest is the study of the relationship between the total reorganization energy of the system and its components, the solvent reorganization energy and the reorganization energy of discharging species (water clusters), and the parameters of electrocatalysis during hydrogen evolution on electrolytic alloys of refractory metals (Mo, W, Re) with iron subgroup metals.

As a model system, promising for practical application in electrocatalysis, in particular, as a cathode material in the electrolysis of water [1–3], we chose the process of electrocatalytic reduction of water clusters on binary superalloys of molybdenum with iron subgroup metals (Fe, Co, Ni) in an alkaline medium.

THEORETICAL PART

Electrochemical processes refer to heterogeneous chemical reactions that occur at the electrode-electrolyte interface and are accompanied by charge transfer through this interface.

Modern ideas are based on the fact that the electrochemical reaction proceeds only through the transition state, which corresponds to the smallest amount of energy expended. The value of the energy of the transition state – the activation energy - depends in the general case on several energy characteristics, namely: a change firstly in solvation energy during the transition from reactants to the transition state (outer-sphere reorganization energy of the solvent λ_s); secondly, in the energy required to change the nuclear coordinates of the coordination ion during the transition to the transition state (inner-sphere reorganization energy of the coordination ion, the energy of formation of the electrochemically active complex λ_c); thirdly, in the difference in the equilibrium energies of the reactants and reaction products (change in the Gibbs free energy ΔG_{if}, thermal effect of the electrochemical reaction).

In modern theories of electron transfer, the main role in the formation of the Franck-Condon barrier is played by the total reorganization energy of the system (λ_t), which consists of the solvent reorganization energy (λ_s) and the inner-sphere reorganization energy of the reacting complex ion (λ_c):

$$\lambda_t = \lambda_c + \lambda_s . \tag{1}$$

During the heterogeneous reduction of ions, the solvent is repolarized and the parameters of the inner sphere of the discharging ion are retuned.

It is known that, in the general case, the value of the total reorganization energy of the system (λ_t) is determined by the nature of the solvent, the radius of reactant, the change in its charge, the stability constant of the complex ion, and the temperature of the solution. In the general form, the total reorganization energy of the system (λ_t) is related to the activation energy of the electron-transfer reaction of the electrochemical process (A_0) by the Marcus equation [4, 5]:

$$A_0 = W_{ox} + \frac{[(\lambda_s + \lambda_c) + (nF\Delta E + W_{red} - W_{ox})]^2}{4\lambda_t}, \tag{2}$$

where A_0 is the activation energy of the elementary act of slow discharge (electron-transfer reaction); ΔE – reaction overpotential; W_{ox} and W_{red} are the work (energy) of approach of reactants to the electrode surface and removal of the cathodic reaction product from the electrode surface, respectively.

Under the conditions of high ionic strength of the solution (30 wt. % NaOH), the work of approach $W_{ox} = qF\psi'$, where ψ' is the potential of the diffusion portion of the electrical double layer; q is the charge of reactants, which is much less than the total energy of system reorganization ($W_{ox} << \lambda_t$), since the potential of the diffusion portion of the double electrical layer, ψ', under these conditions is close to zero (~ 0.001 mV). $W_{ox} << 4\ \mathrm{kJ \cdot mol^{-1}}$ [5, 6], and this value can be neglected in comparison with the values of the activation energy of the elementary act of slow discharge (electron-transfer reaction), A_0, and the total energy of system reorganization, λ_t.

Considering that the difference between the works of approach of the reactant to the electrode surface (W_{ox}) and removal of the cathodic reaction product (W_{red}) is equal to the thermal effect of the electrochemical reaction, ΔG_{if} (free energy):

$$\Delta G_{if} = W_{red} - W_{ox} , \tag{3}$$

and the sum of the solvent reorganization energy (λ_s) and the inner-sphere reorganization energy of the reacting complex ion (λ_c), according to equation (1), is equal to the total system reorganization energy (λ_t), we obtain:

$$A_0 = \frac{(\lambda_t + nF\Delta E + \Delta G_{if})^2}{4\lambda_t} . \tag{4}$$

At the equilibrium state of the system and the reaction overpotential equal to zero ($\Delta E = 0$), equation (4) takes the classical form:

$$A_0 = \frac{(\lambda_t + \Delta G_{if})^2}{4\lambda_t} . \tag{5}$$

To calculate the total reorganization energy of the system, as follows from Eq. (5), the values of the activation energy of the electron-transfer reaction and the thermal effect of the reaction are required.

The magnitude of the thermal effect of an electrochemical reaction can be determined based on the laws of thermodynamics and the Thomson principle [5, 7].

Based on the laws of thermodynamics, the change in the free energy of the process, $\Delta G_{p,T,}$

according to the Gibbs–Helmholtz equation [5, 7] is:

$$\Delta G_{p,T} = -\Delta G_{if} + T\left(\frac{\partial \Delta G_{p,T}}{\partial T}\right)_{p,T}, \qquad (6)$$

where $\left(\frac{\partial \Delta G_{p,T}}{\partial T}\right)_{p,T}$ is the thermochemical coefficient at constant pressure and temperature.

As applied to electrochemical processes, using the Thomson principle [5, 7]:

$$-\Delta G_{p,T} = nFE_r, \qquad (7)$$

where E_r is the equilibrium (stationary) potential of the electrode in the system under study, it can be shown that the thermal effect of the reaction, ΔG_{if} , according to equations (6) and (7), is [5, 7]:

$$\Delta G_{if} = nFE_r - nFT\left(\frac{\partial E_r}{\partial T}\right)_{p,T}. \qquad (8)$$

The values of the activation energy of the electron-transfer reaction are determined, as a rule, in “Arrhenius” coordinates from the “linear” dependence of the logarithms of exchange currents on the reciprocal temperature according to the following equation:

$$A_o = -2.303R\left(\frac{\partial(\lg j_0)}{\partial(1/T)}\right)_{\Delta E=0}. \qquad (9)$$

We considered a method for calculating the total reorganization energy of the system, as well as obtaining information about the solvent reorganization energy and the reorganization energy of discharging species using the example of electrocatalytic hydrogen evolution on binary alloys of molybdenum with iron subgroup metals in an alkaline solution of NaOH, based on the mechanism of their discharge [5].

The most effective and controllable way to obtain high-quality coatings of binary and ternary alloys of molybdenum and tungsten with iron subgroup metals is the deposition of complex compounds of these metals from aqueous electrolytes, in particular, from monoligand and polyligand (pyrophosphate, citrate, pyrophosphate-citrate) electrolytes [8–17].

In this work, we studied the energy characteristics of the electrochemical evolution of hydrogen on binary alloys of molybdenum with metals of the iron subgroup (Fe, Co, Ni) obtained from a polyligand highly concentrated ammonium acetate electrolyte developed and presented in [18], as effective electrolyte in terms of obtaining alloys with a high molybdenum content that are promising for electrocalysis.

The aim of the work was to study the total energy of reorganization of the system and its components – the energy of solvent reorganization and the reorganization energy of the inner coordination sphere – of reactants during electrocatalytic hydrogen evolution (HER) on binary Co-Mo, Ni-Mo, Fe-Mo alloys of constant composition (atomic ratio [Mo]:[M] = 1:1) in an alkaline medium.

In [18], in the study of electrocatalytic hydrogen evolution on Fe-54 at. % Mo, Ni-54 at. % Mo, and Co-52 at. % Mo alloys obtained from a polyligand ammonium-acetate electrolyte, the values of the activation energy of the electron-transfer reaction, A_0, were calculated in a 30 wt. % NaOH solution. It has been found that the activation energy of the electron-transfer reaction in the reaction under study decreases in the following order: Fe-Mo > Ni-Mo > Co-Mo.

The experimental data necessary for calculating the total energy of system reorganization during the electrocatalytic reduction of water clusters on binary molybdenum alloys were taken from [18].

The equilibrium potential of the electrode E_r in the system under study was calculated from the equation:

$$E_r = -\left(\frac{2.303RT}{F}\right)pH. \qquad (10)$$

The slope of the rectilinear plot of $E_r = f(T)$ is $-2.98\cdot10^{-3}$ V·deg^{-1}.

It should be emphasized that the value of the equilibrium potential of the hydrogen electrode can be calculated using the Nernst equation and does not depend on the electrode material. However, the electrode material affects not only the rate of achievement of equilibrium between various forms of hydrogen on the electrode surface, but also the magnitude of exchange current.

RESULTS AND DISCUSSION

Since the plots of $\lg j_0 = f(1/T)$, as can be seen from Fig. 1, are not, strictly speaking, “linear”, then, consequently, the values of the activation energy of the electron-transfer reaction are not average values in the temperature range under study. The $\partial(\lg j_0)/\partial(1/T)$ slope values for the Fe–Mo, Ni–Mo, and Co–Mo molybdenum alloys, as follows from Fig. 1, and, consequently, the values of A_o change, that is, they gradually decrease with increase in the electrolyte temperature from 298 to 338 K.

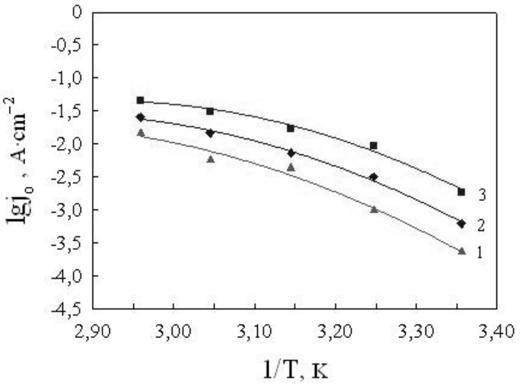

Fig. 1. Arrhenius plots for the electrocatalytic reduction of water clusters in the binary alloys Fe-Mo (▲– *1*); Ni-Mo (◆ – *2*) and Co-Mo (■ – *3*) at 30 wt. % NaOH solution

The values of the activation energy of the electron-transfer reaction of electrocatalytic hydrogen evolution on binary molybdenum alloys were determined from equation (9), taking into account the plots of $\lg j_o = f(1/T)$ shown in Fig. 1, as follows. The values of the $\partial(\lg j_0)/\partial(1/T)$ slopes were calculated by the method of continuous (stepwise) differentiation of curves (Fig. 1, curves 1–3) and then were chosen at the points corresponding to the values of experimental temperatures. The values of the activation energy of the electron-transfer reaction of the electroreduction of water clusters on the molybdenum alloys Fe-Mo, Ni-Mo, and Co-Mo in a 30 wt. % NaOH solution, calculated by this method, are presented in Fig. 2.

The values of the activation energy of the electron-transfer reaction, as can be seen from Fig. 2, decrease almost linearly with increasing electrolyte temperature and change in the series of binary alloys of molybdenum with iron subgroup metals in the following order: Fe-54 at. % Mo > Ni-54 at. % Mo > Co-52 at. % Mo. The magnitude of A_o is related to the activity of the electrode surface. The lowest activation energy value for the Co-Mo alloy indicates a greater activity of the surface of this alloy in the series of alloys of molybdenum with iron subgroup metals in the reaction of electrocatalytic reduction of water clusters.

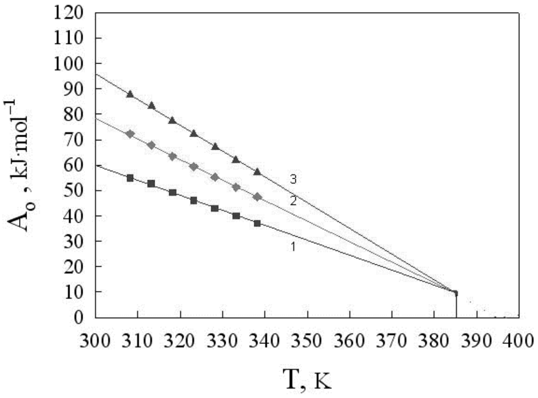

Fig. 2. Dependence of the activation energy of the electron-transfer reaction of the electrocatalytic reduction of water clusters on the binary alloys Co-Mo (■ – *1*), Ni-Mo (◆ – *2*), Fe-Mo (▲ – *3*) in a 30 wt. % NaOH solution on temperature

The coordinates of the point of intersection of the linear plots of $A_o = f(T)$, as can be seen from Fig. 2, are: “T” (384.7±0.5) K; “A_o” (9.9±0.7) kJ·mol^{-1}.

The value of activation energy of 9.9 kJ·mol^{-1} is equal to the value of diffusion activation energy A_d. Therefore, at the boiling point of the 30 wt. % NaOH solution 384.7 K, the electrode process is controlled by the diffusion of the reducing water clusters to the electrode surface. The results obtained (Fig. 2) allow us to conclude that at this temperature, the electrocatalytic activity of binary alloys of molybdenum with iron subgroup metals in an alkaline solution of NaOH is a maximum and does not depend on the nature of the alloy.

The values of the thermal effect of the reaction of electrocatalytic hydrogen evolution on binary alloys of molybdenum with metals of the iron subgroup in a 30 wt. % NaOH solution, calculated from equation (8) depending on the temperature, are given in Table 2.

Based on the obtained values of the activation energy of the electron-transfer reaction and the thermal effect of the reaction, the values of the total reorganization energy of the electrocatalytic reduction of water clusters on binary molybdenum alloys at different temperatures were calculated from equation (5). The calculated values of λ_t are given in Table and in Fig. 3.

The values of λ_t , as follows from Fig. 3, decrease linearly with increasing electrolyte temperature and change in the series of binary molybdenum alloys in the following order: Fe-54 at. % Mo > Ni-54 at. % Mo > Co-52 at. % Mo.

The electrocatalytic activity of the Co-Mo alloy, as follows from the results obtained, is higher compared to the binary alloys Ni-Mo and Fe-Mo, *i.e.*, the values of the activation energy of the electron-transfer reaction and the total reorganization energy of the system are smaller for the Co-Mo alloy in the entire range of temperatures under study.

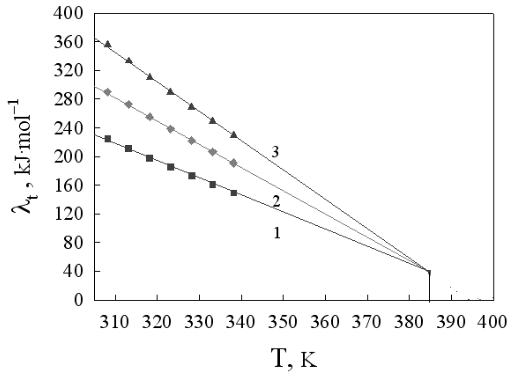

Fig. 3. Dependence of the total reorganization energy of the electrocatalytic reduction of water clusters on Co-Mo (■ – *1*), Ni-Mo (◆ – *2*) and Fe-Mo (▲ – *3*) alloys in a 30 wt. % NaOH solution on temperature

Table. Energy parameters of the electrocatalytic reduction of water clusters on binary alloys of molybdenum with iron subgroup metals in a 30 wt. % NaOH solution

T, K	$1/T \times 10^3$, K^{-1}	$-E_r$, V	ΔG_{if}, $kJ \cdot mol^{-1}$	λ_t, $kJ \cdot mol^{-1}$			λ_c, $kJ \cdot mol^{-1}$	λ_s, $kJ \cdot mol^{-1}$		
				Co-Mo	**Ni-Mo**	**Fe-Mo**		**Co-Mo**	**Ni-Mo**	**Fe-Mo**
308	3.2452	0.9084	0.57	224.75	290.16	355.62	87,8	136.95	202.36	267.82
313	3.1934	0.9232	0.57	211.48	272.66	333.35	89.2	122.28	183.46	244.15
318	3.1432	0.9379	0,58	198.14	255.07	310.98	90.6	107.54	164.47	220.38
323	3.0945	0.9527	0.59	185.64	238.60	290.03	92.0	93.64	146.60	198.03
328	3.0474	0.9674	0.60	173.10	222.07	269.02	93.5	79.60	128.57	175.53
333	3.0017	0.9821	0.61	161.29	206.50	249.21	94.9	66.39	111.60	154.31
338	2.9573	0.9969	0.62	149.55	191.02	229.54	96.3	53.25	94.73	133.24

It should be noted that all plots of the reorganization energy of the water discharge system, as well as the activation energy on binary molybdenum alloys, are linear and intersect at one point. The coordinates of the intersection point of the linear plots of the reorganization energy of the system under study (Fig. 3) are: "T", (384.8±0.5) K and "λ_t", (39.8±0.9) kJ·mol^{-1}.

The boiling point of the 30 wt. % NaOH solution, according to literature data [19], is 387.2 K, *i.e.*, it practically corresponds to the "T" coordinate of the point of intersection of the plots of activation energy on molybdenum alloys versus temperature (Fig. 2). The activation energy value of 9.9 kJ·mol^{-1} indicates that the process at this temperature is controlled by the diffusion of reducing ions to the electrode surface and, therefore, the electrocatalytic effect is no longer observed.

This statement is true, as follows from Fig. 3, also in relation to the value of the total reorganization energy of the system, which at the boiling point of the solution does not depend on the nature of the binary molybdenum alloy and is (39.8±0.9) kJ·mol^{-1}. This minimum value of λ_t is consistent with the theory of Markus – Dogonadze – Kuznetsov [5, 20]. Consequently, the electrocatalytic activity of binary alloys of molybdenum with metals of the iron subgroup in an alkaline medium, as follows from the data presented in Fig. 3, is a maximum and does not depend on the nature of the alloy, since λ_t has a minimum and constant value of 39.8 kJ·mol^{-1}.

The electrochemically active form of particles (EAC), which are directly involved in the electron-transfer reaction during the electrocatalytic evolution of hydrogen on binary alloys of molybdenum with metals of the iron subgroup in a 30 wt. % NaOH solution, are water clusters $[(H_2O)_nOH]^-$ ($n = 1$ or 2 depending on the concentration in the NaOH solution). The mechanism of the electrocatalytic reduction of water clusters $[(H_2O)_nOH]^-$ under these conditions [5] can be represented by the equations (11)–(20).

The discharge of water clusters in an alkaline medium passes through the stage of adsorption (solvent reorganization):

$$[HO{-}H\cdots OH]^- \rightleftarrows [HO{-}H\cdots OH]^-_{ads}, \tag{11}$$

and reorganization of the discharging species of the system (electrochemically active ion, transition state):

$$[HO{-}H\cdots OH]^-_{ads} \rightleftarrows [H_2O]_{ads} + [OH]^-. \tag{12}$$

This is followed by the mechanism of stepwise discharge of water clusters on molybdenum and metals of the iron subgroup (Fe, Co, Ni), which is described by the following equations:

On molybdenum

$$Mo{-}H_2O_{ads} + \bar{e} \rightleftarrows MoH_{ads} + OH^- \tag{13}$$

$$MoH_{ads} + H_2O + \bar{e} \rightarrow MoH_{2ads} + OH^- \tag{14}$$

emission (diffusion into the bulk solution) of elemental hydrogen:

$$MoH_{2ads} \rightleftarrows Mo + H_2. \tag{15}$$

On metals (M = Fe, Co, Ni)

$$M{-}H_2O_{ads} + \bar{e} \rightarrow MH_{ads} + OH^- \tag{16}$$

$$MH_{ads} + H_2O + \bar{e} \rightleftarrows MH_{2ads} + OH^- \tag{17}$$

$$MH_{2ads} \rightleftarrows M + H_2. \tag{18}$$

The surface diffusion of hydrogen atoms also occurs on the electrode surface (spillover effect):

$$MH_{ads} + MoH_{ads} \rightarrow MH_{2ads} + Mo. \tag{19}$$

The overall reaction of the electrocatalytic reduction of water clusters on molybdenum alloys in an alkaline medium (30 wt. % NaOH solution) can be expressed by the following equation:

$$2[H_2O\cdots OH]^-_{ads} + 2\bar{e} \rightleftarrows H_2 + 4OH^-. \tag{20}$$

Based on the mechanism of the electrode process, it can be considered that the energy of reorganization of water clusters $[(H_2O)_nOH]^-$ during the electrocatalytic evolution of hydrogen on binary molybdenum alloys in a 30 wt. % NaOH solution is approximately equal to the free energy (change in isobaric potential, $\Delta G_{p,T} = -2.303RT\,\lg(K_W/[OH]^-)$) [20] of the dissociation reaction of water molecules and does not depend on the nature of the binary alloy. The calculated values of λ_c at different temperatures of the electrolyte under study are given in Table.

The values of the solvent reorganization energy in the system under study at different electrolyte temperatures were calculated from Eq. (1) based on the values of the total system reorganization energy and the reorganization energy of water clusters (Table). The calculated values of the solvent reorganization energy for binary molybdenum alloys are shown in Fig. 4.

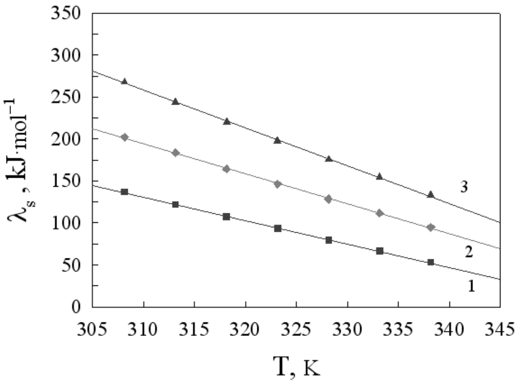

Fig. 4. Dependence of solvent reorganization energy during the electrocatalytic reduction of water clusters on the binary alloys Co-Mo (■ – *1*), Ni-Mo (◆ – *2*) and Fe-Mo (▲ – *3*) in a 30 wt. % NaOH solution on temperature

According to the Dogonadze-Kuznetsov theory [5, 21], the total energy of the system reorganization is equal to or greater than the thermal effect of the reaction, that is, $|\lambda_t \geq \Delta G_{if}|$. The activation energy of the electron-transfer reaction is determined mainly by the interaction of reactants with the solvent and rearrangement of the reacting complex ion (in this case, a water cluster).

The energy of solvent reorganization lies within 50÷150 kJ·mol^{-1}, and the reorganization energy of the inner coordination sphere (transformation of reactants) of a discharging complex ion is within 10÷200 kJ·mol^{-1} [5, 21].

As follows from the results obtained, the calculated values of the solvent reorganization energy (Fig. 4) and the reorganization energy of water clusters (Table) are in agreement with the Marcus – Dogonadze – Kuznetsov theory [5, 21].

CONCLUSIONS

The total reorganization energy of the system and its components, the solvent reorganization energy and the transformation energy of reactants (water clusters $[(H_2O)_nOH]^-$), during electrocatalytic hydrogen evolution on binary alloys of molybdenum with iron subgroup metals in a 30 wt. % NaOH solution have been calculated.

The calculated values of the solvent reorganization energy and the reorganization energy of water clusters are in agreement with the Marcus – Dogonadze – Kuznetsov theory.

A dependence of the total reorganization energy of the system, the solvent reorganization energy, and the reorganization energy of discharging species (water clusters) on the electrolyte temperature has been found. It has been shown that the total reorganization energy of the system and the activation energy of the electron-transfer reaction of electrocatalytic hydrogen evolution on binary alloys of molybdenum with iron subgroup metals in an alkaline medium (30 wt. % NaOH solution) decrease with increasing electrolyte temperature in the following order: Fe-54 at. % Mo > Ni-54 at. % Mo > Co-52 at. % Mo.

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Електрокаталітичне відновлення кластерів води на бінарних сплавах молібдену з металами підгрупи заліза в лужному середовищі

В.М. Нікітенко, Є.А. Бабенков, О.Л. Берсірова, В.С. Кублановський

Інститут загальної та неорганічної хімії ім. В.І. Вернадського Національної академії наук України
просп. Академіка Палладіна, 32/34, Київ, 03142, Україна, kublan@ukr.net
Department of Physical Chemistry, Vilnius University
Naugarduko Str., 24, LT-03225, Vilnius, Lithuania

Метою роботи було дослідження фундаментальних енергетичних характеристик (енергії реорганізації системи, енергії активації та їхніх складових) електрохімічного процесу, їхнього зв’язку з кінетичними параметрами на прикладі реакції електрокаталітичного виділення водню (РВВ) на бінарних сплавах молібдену з металами підгрупи заліза (Fe, Co, Ni) в лужному середовищі. Дані дослідження являють науковий інтерес, оскільки розширюють наші уявлення про елементарний акт переносу електрона, механізм та природу електрокаталітичних процесів. В роботі в рамках теорії Маркуса розраховано повну енергію реорганізації системи, її складові – енергію реорганізації розчинника та енергію перебудови реагуючих кластерів води при електрокаталітичному виділенні водню (РВВ) на бінарних сплавах молібдену з металами підгрупи заліза (Fe, Co, Ni) в 30 ваг. % розчині NaOH. Обчислені значення енергії реорганізації розчинника та енергії реорганізації кластерів води узгоджуються з теорією Маркуса –Догонадзе –Кузнецова. Розраховано залежність повної енергії реорганізації системи, енергії реорганізації розчинника та енергії реорганізації кластерів води, що розряджаються, від температури електроліту. Показано, що повна енергія реорганізації системи та енергія активації реакції переходу електрокаталітичного виділення водню (РВВ) на бінарних сплавах молібдену в 30 ваг. % розчині NaOH лінійно зменшуються із підвищенням температури електроліту в ряду:

Fe-54 ат. % Mo > Ni-54 ат. % Mo > Co-52 ат. % Mo. Показано, що залежності енергії реорганізації розряду кластерів води та енергії активації від температури на бінарних сплавах молібдену лінійні й перетинаються в області температури кипіння 30 ваг. % розчину NaOH 384.7 K. При даній температурі електродний процес лімітується дифузією кластерів води, що відновлюються, до поверхні електрода. Обчислене значення енергії активації дифузії A_d дорівнює 9.9 кДж·моль$^{-1}$. Значення енергії реорганізації системи λ_n складає 39.8 кДж·моль$^{-1}$, що узгоджується з теорією Маркуса –Догонадзе –Кузнецова. Електрокаталітична активність бінарних сплавів молібдену з металами підгрупи заліза в 30 ваг. % розчині NaOH при даній температурі максимальна й не залежить від природи сплаву.

***Ключові слова**: бінарні сплави Co-Mo, Ni-Mo, Fe-Mo, реакція виділення водню (РВВ), кластери води, енергія реорганізації системи, електрокаталіз*

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