Regularities of cathodic hydrogen evolution at an electrolytic Co-V alloy and its components

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ABSTRACT

The regularities of cathodic hydrogen evolution from a 30 % KOH solution at an electrolytic Co-V alloy, an electrolytic cobalt coating as well as at cobalt and vanadium with smooth surface in the temperature range 25-85 °C have been studied. The Co-V alloy and cobalt coating were deposited on stainless steel from a nonaqueous electrolyte. It has been found that at the least negative potentials and with the lowest overpotential hydrogen evolves at the Co-V alloy. The exchange currents and real activation energies of hydrogen evolution at the investigated electrodes as well as the Tafel coefficients have been determined. On the basis of an analysis of the angular Tafel coefficient values, it has been shown that the rate of cathodic hydrogen evolution at cobalt and cobalt coating is controlled by the rate of formation of adsorbed hydrogen atoms while at vanadium and electrolytic Co-V alloy by the rate of their electrochemical desorption.   © 2014 Trade Science Inc. - INDIA

KEYWORDS

Hydrogen evolution;
Co-V alloy and compo-
nents;
Alkaline solution.

INTRODUCTION

Hydrogen production from water by the electrolysis of alkaline solution has a number of obvious advantages over other known methods. These advantages are the high purity of produced hydrogen, easy availability and low cost of raw material (water), simplicity of the manufacturing scheme and high operational reliability of electrolyzers, ecologically useful by-product (oxygen). The main disadvantage of the electrochemical method of hydrogen production, which limits its wide application, is high electrical energy consumption for its realization. The cost of used electrical energy is 70 % of the prime cost of electrolytic hydrogen[1]. Therefore, electrolysis as a method of hydrogen production is employed only when high-purity hydrogen is needed, and there are sources of low-price electrical energy.

The quantity of electrical energy required for carrying out electrolysis is determined by the value of voltage across the terminals of operating electrolyzer, which includes several components and is determined from a formula:

$$U = E_a - E_c + I \cdot \Sigma R = U^o + |\eta_a| + |\eta_c| + I \cdot \Sigma R \qquad (1)$$

where E_a and E_c are the anode and cathode potentials respectively, I is the value of current flowing through the electrolyzer, ΣR is the total ohmic resistance, U^o is the theoretical value of water decomposition voltage, η_a and η_c are the overpotentials of the anodic and cathodic processes respectively[2-4]. It follows that a potential way of decreasing the electric energy consumption for hydrogen production from water by the electrolysis is the reduction of U^o, η_a, η_c and ΣR.

The theoretical (thermodynamic) value of water decomposition voltage is 1.23 V at 25 °C and a pressure of 1 atm[1]. It can be reduced by increasing the electrolyte temperature; other electrolysis conditions do not affect the U^o value. Therefore, the possibilities of reducing U by decreasing U^o are limited.

According to[4], the ΣR quantity comprises the following constituents:

$$\Sigma R = R_e + R_m + R_b + R_c \qquad (2)$$

where R_e, R_m, R_b and R_c are the ohmic resistance of the electrolyte, membrane, gas bubbles formed on the cathode and anode and the metallic elements of the electrical circuit over which current is fed to the to the electrodes respectively. For electrolyzer of definite design, the R_m and R_c quantities are practically constant and have a small value. The ohmic resistance of the electrolyte depends on its composition and inter-electrode spacing. Besides, hydrogen and oxygen bubbles, which form on the cathode and anode respectively, disperse into the electrolyte, which leads to an increase in R_e.

The ΣR value is greatly affected by the gas bubbles that are retained on the surface of the electrodes since they do not conduct current and block a large part of the surface of the electrodes. To accelerate the removal of hydrogen and oxygen bubbles from the surface of the electrodes, various (magnetic, ultrasonic, super gravity) external fields can be used[4-6], but to establish such fields, considerable material and power costs are required.

A promising way of decreasing the electrolyzer voltage in the electrolysis of alkaline solution is the use of electrodes with the low value of cathodic hydrogen evolution and anodic oxygen evolution overpotential. The values of cathodic and anodic overpotential at preset current and electrolyte temperature are determined by the nature and condition of the electrode surface[1,2,7,8]. Platinum metals (Pt, Pd) have the lowest η_a and η_c values, electrode polarization depending largely upon the electrode surface condition. However, expensive platinum metals are used as electrode materials in electrochemical hydrogen production only in exceptional cases. The electrodes made of iron family metals as well as of their alloys and composite materials are of much greater practical importance[2,3,9-12]. The iron family metals have η_a and η_c values which are slightly larger than those of the platinum metals, but they are much cheaper and corrosion resistant in alkaline solution.

The increase of the catalytic activity of electrodes based on iron family metals in cathodic hydrogen evolution and anodic oxygen evolution processes and the development of their surface were the aim of many investigations. The analysis of them is not the subject of the present paper. Note, however, that nickel cathodes, which are widely used in the electrolysis of KOH solution, are deactivated during the first tens of hours of electrolysis, which manifests itself by a decrease in hydrogen evolution current at fixed potential. As was shown Refs[13,14], however, the addition of V_2O_5 to the alkaline solution to a vanadium content of 200 mg$\cdot$L^{-1} leads to the *in situ* reactivation of nickel cathodes practically to the initial state; in the opinion of the authors of this paper, this results from the formation of a vanadium-containing spongy hydroxide coating on the surface of the electrodes.

The authors of Ref[15] managed to greatly increase the activity of nickel cathodes in the reaction of hydrogen evolution at it from an alkaline solution after the electrodeposition of cobalt and vanadium particles on the nickel surface. As a result of this modification, the electrode surface roughness increased by a factor of over 10, which led to a five-fold increase in apparent exchange current. The use of surface-modified nickel cathodes for the electrolysis of alkaline solution allowed reducing the electrolyzer voltage and electric energy consumption by 10-15 %.

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In this work, to develop electrodes with high electrocatalytic activity in the reaction of cathodic hydrogen evolution from alkaline solution we have carried out systematic comparative studies of the regularities of cathodic hydrogen evolution from a 30 % KOH solution at the following electrodes: polished vanadium and cobalt, as well as electrolytic cobalt coating and electrolytic Co-V alloy deposited on stainless steel from a nonaqueous electrolyte.

EXPERIMENTAL

Plate-like vanadium electrodes 3 mm in thickness and 10 mm in width were cut out from cylindrical ingots of electron beam melted VnM-1 vanadium (TU 48-4-272-73). To make smooth cobalt cathodes, K0 electrolytic sheet cobalt (GOST 123-2008) with a cobalt content of not fewer than 99.98 % was used. 10×10 mm^2 electrodes with current leads 2 mm in width were cut out from this cobalt. The obtained vanadium and cobalt electrodes were mechanically mirror-finished and degreased in ethyl alcohol or acetone.

Electrodes made of 12Kh18N10T stainless sheet steel (GOST 5949-75, analog of AISI 321) in the form of strips 10 mm in width and 1 mm in thickness were also mechanically polished and electrochemically degreased in a solution containing 20 g·L^{-1} Na_2CO_3 and 20 g·L^{-1} Na_3PO_4 before depositing a cobalt or Co-V alloy on them. The degreasing conditions were as follows: cathodic current density 30 mA·cm-2, solution temperature 50 °C, duration 2 min. A circular platinum anode was used. The degreasing was conducted with washing the steel electrodes with twice distilled water.

Electrolytic cobalt coating and Co-V alloy were cathodically deposited on the surface of prepared steel electrodes from solutions of cobalt and vanadium acetylacetonate complexes in a formamide-dimethylformamide mixture. The acetylacetonate complexes $Co(C_5H_7O_2)_2$ and $V(C_5H_7O_2)_2$ were obtained from aqueous solutions of $CoSO_4$ and VSO_4. Vanadium (II) sulfate was synthesized from vanadyl sulfate by the procedure described in[16]. To the $CoSO_4$ and VSO_4 solutions was added a 25 % ammonia solution, and the precipitated hydroxides $Co(OH)_2$ and $V(OH)_2$ were quickly filtered off. The $V(OH)_2$ was filtered under argon. The newly precipitated cobalt and vanadium hydroxides were dissolved in acetylacetone, and the precipitated cobalt and vanadium acetylacetonates were filtered off and placed in a desiccator, containing silica gel and filled with argon (99.993 % Ar, GOST 10157-79).

A cobalt coating was deposited on steel electrodes from an electrolyte of the following composition (wt %): formamide, 70.4; dimethylformamide, 23.1; tetrabutylammonium chloride, 3.9 and $Co(C_5H_7O_2)_2$, 2.6. To deposit a Co-V alloy, an electrolyte containing (wt %): formamide, 68.6; dimethylformamide, 22.6; tetrabutylammonium chloride, 3.8; $Co(C_5H_7O_2)_2$, 2.5 and $V(C_5H_7O_2)_2$, 2.5 was used.

Cobalt and the Co-V alloy were deposited in a cell with thermostating jacket; the cathode and anode chambers of the cell were separated by a porous glass diaphragm. A 20×20 mm^2 platinum plate was used as the anode. The duration of deposition was 20-30 min at a cathodic current density of 2.5-5.0 mA·cm^{-2} and an electrolyte temperature of 25 °C. Current in the deposition of coatings and degreasing of steel electrodes was preset by means of a B5-49 dc supply. The electrodes coated with cobalt and Co-V alloy were washed in a formamide-dimethylformamide mixture and dried in a desiccator.

To study the surface morphology of the obtained cathode deposits, a REM-101 scanning electron microscope was used. The quantitative composition of the surface layer of the deposited cobalt and Co-V alloy was determined by Auger spectroscopy. The spectra were recorded by means of a JEOL JAMP-10S spectrometer from a 10 μm^2 portion of the surface. The effective depth of analysis was about 2 nm.

Before polarization measurements, the nonworking surface of the prepared electrodes was insulated with epoxy resin. The geometric area of the working surface of the electrodes under investigation was 1 cm^2. The polarization curves (PCs) of cathodic hydrogen evolution from a 30 % KOH solution at vanadium, cobalt and steel coated with cobalt

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and Co-V alloy were recorded using a PI-50-1 potentiostat, a PR-8 programmer and a laboratory LKD-4 X-Y recorder. Potentiodynamic mode was employed; the potential scan rate was 2 mV·c⁻¹. The PCs were recorded in a commonly used 0.1 L glass cell with thermostating jacket, Luggin capillary and glass diaphragm between the cathode and anode chambers. A 20×20 mm² platinum plate was used as the counter electrode; the current lead was a platinum wire. The working electrode potential was measured relative to a saturated silver-chloride reference electrode and converted to hydrogen scale.

The polarization curves were recorded cyclically from the stationary potential of unpolarized working electrode to the preset potential (forward PCs) and back to the initial potential (reverse PCs). To reduce surface oxides and stabilize the surface of the electrodes, three cyclic cathodic PCs were recorded sequentially, and the kinetic parameters of hydrogen evolution were determined from the data of third curves. The cathode current density was calculated on the basis of the geo-metric area of the working surface of the electrodes.

To prepare an alkaline solution, analytically pure KOH and water twice distilled in a quartz distiller were used. The required solution temperature in the cell in polarization measurements and cobalt and Co-V alloy deposition was maintained by means of a U-10 thermostat. To deaerate the catholyte, high-purity argon was used in all cases.

RESULTS AND DISCUSSION

Figure 1 shows micrographs of the surface of cathode deposits of cobalt and Co-V alloy deposited on a steel electrode. It can be seen that the obtained coatings have a very developed micro- and nanostructured surface.

The quantitative composition of the surface layers of the coatings was determined by the analysis of their Auger spectra see Figure 2. From the results of a quantitative analysis given in TABLE 1 it follows that the main elements on the cobalt coating surface are, be-
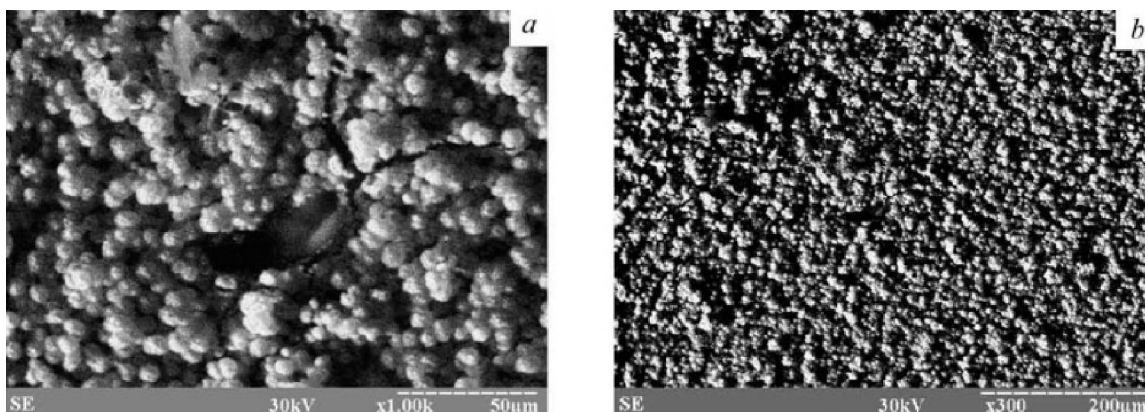

Figure 1 : Micrographs of the surface of an electrolytic cobalt coating *(a)* **and a Co-V alloy** *(b)*
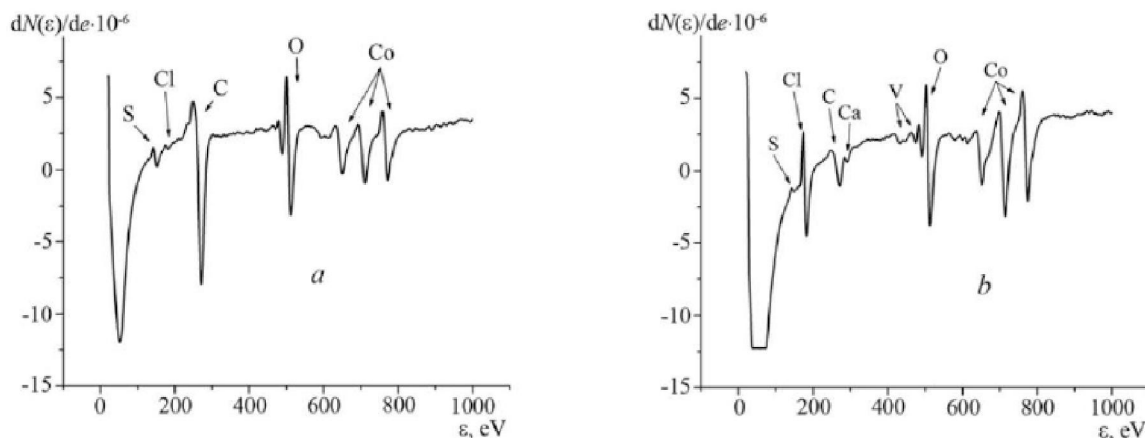

Figure 2 : Auger spectra of the surface of an electrolytic cobalt coating *(a)* **and a Co-V alloy** *(b)*

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TABLE 1 : Quantitative composition of the surface layer of an electrolytic cobalt coating and a Co-V alloy

Coating	Content, at. %							
	S	Cl	C	Ca	N	V	O	Co
Co	2.17	0.38	47.60	–	0.72	–	25.66	23.47
Co-V	0.40	11.03	10.36	1.54	–	4.37	29.56	42.74

sides cobalt, oxygen and carbon. The surface layer of the obtained Co-V alloy contains a large amount of oxygen, chlorine and carbon. Obviously, the surface of the cobalt coating and electrolytic Co-V alloy oxidizes in air. The presence of carbon and chlorine in the surface layer indicates that the constituents of the electrolytes used for the deposition of coatings are held by the developed surface of coatings.

Figure 3 shows forward and reverse cathodic PCs obtained in an alkaline solution at 40 °C on smooth vanadium and cobalt electrodes, as well as on steel electrodes cathodically coated with cobalt and Co-V alloy. The collocation of the PCs obtained at the other electrolyte temperatures was the same. It follows from Figure 3 that cathodic hydrogen evolution at smooth vanadium electrode takes place at the most negative potentials. The hydrogen evolution potentials (E) at cobalt, especially at electrolytic cobalt coating, are much more positive than at smooth vanadium. The addition of vanadium to the cobalt coating allowed obtaining an electrode which is much more active in the cathodic 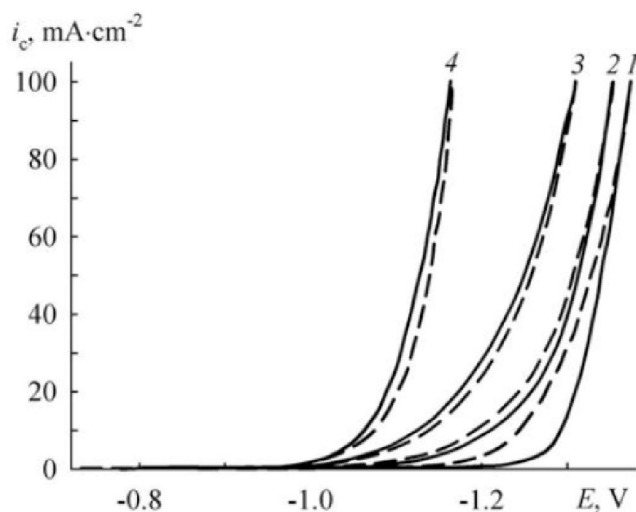hydrogen evolution reaction than the other investigated electrodes. Hydrogen evolved at this electrode at the least negative potentials. At a current density of 100 mA·cm^{-2} and an electrolyte temperature of 40 °C, the hydrogen evolution potential at electrode coated with Co-V alloy is 0.146, 0.190 and 0.211 V less negative than at cobalt-coated electrode and smooth cobalt and vanadium electrodes respectively.

Between the forward and reverse PCs obtained on a vanadium electrode, a considerable hysteresis is observed in the low current density range; this indicates changes in the surface properties of this electrode during measurements, which are apparently caused by the great tendency of vanadium to hydrogen absorption. The potentials of reverse PC are more positive than those of forward PC. It follows that cathodic hydrogen evolution at vanadium increases its activity in this electrode process, which may be due to the loosening of the electrode surface caused by hydrogen incorporation into the vanadium lattice. The forward and reverse PCs obtained on a smooth cobalt electrode are arranged analogously, but the hysteresis value is much smaller than between the PCs for vanadium electrode.

Between the forward and reverse curves obtained on electrodes coated with electrolytic cobalt and Co-V alloy, a small hysteresis was also detected, but the potentials of reverse PCs are more negative than those of forward PCs. Obviously, the reduction of the surface cobalt oxide and formation of a more homogenous and less active surface as a result of this have a determining effect on the surface activity of these electrodes.

It is characteristic that the stationary potentials of unpolarized electrodes (E_{st}) depended differently on temperature. When the temperature was raised, E_{st} of smooth vanadium and cobalt electrodes shifted towards more negative values (from -0.731 V at 25 °C to -0.834 V at 85 °C in the case of vanadium electrode and from -0.745 V at 25 °C to -0.878 V at 85 °C in the case of cobalt electrode), whereas E_{st} of steel electrodes with electrolytic coatings shifted towards less negative value (from -0.874 V at 25 °C to -0.842 V at 85 °C in the case of cobalt-coated electrode and from -0.868 V at 25 °C to -0.861 V at 85 °C in the case of electrode coated with Co-V alloy).

To study in greater detail the kinetics and mechanism of cathodic hydrogen evolution at the investigated

Figure 3 : Polarization curves of hydrogen evolution from a 30 % KOH solution (40 °C) at smooth vanadium (*1*), smooth cobalt (*2*), an electrolytic cobalt coating (*3*) and a Co-V alloy (*4*)

electrodes, polarization curves obtained at different temperatures were plotted in Tafel coordinates. The calculated equilibrium potential value of hydrogen electrode at pH 14, 25 °C and the partial hydrogen pressure of 1 atm. is -0.828 V, which is close to the experimental stationary values of the unpolarized electrodes investigated in this work. Therefore, E_{st} values were used to calculate the values of hydrogen evolution overpotential at the investigated electrodes from the formula:

$$\eta_c = E_i - E_{st} \qquad (3)$$

where E_i is polarized-electrode potential. It has been found that at the current density of 100 mA·cm^{-2} and electrolyte temperature of 40 °C, the hydrogen evolution overpotential at electrode coated with Co-V alloy is -0.296 V, which is 0.132, 0.283 and 0.322 V lower than at cobalt-coated electrode and smooth cobalt and vanadium electrodes respectively. It follows that the cathodes coated with electrolytic Co-V alloy are most promising among the investigated electrodes for electrochemical hydrogen production from water with low electrical energy consumption.

Figure 4 shows $\eta_c - \lg i_c$ plots, obtained on the investigated electrodes at several alkaline solution temperatures. It can be seen that raising the temperature leads to an increase in the rate of hydrogen evolution at all electrodes.

The kinetic parameters of hydrogen evolution at these electrodes (Tafel coefficients a and b, exchange current density i_o and real activation energy A_o at zero overpotential), calculated on the basis of $\eta_c - \lg i_c$ plots are listed in TABLE 2. To calculate exchange current densities, we put to zero the overpotential in the equations describing the straight line portions of the $\eta_c - \lg i_c$ plots. The real activation A_o was calculated on the basis of plots of exchange current density against temperature.

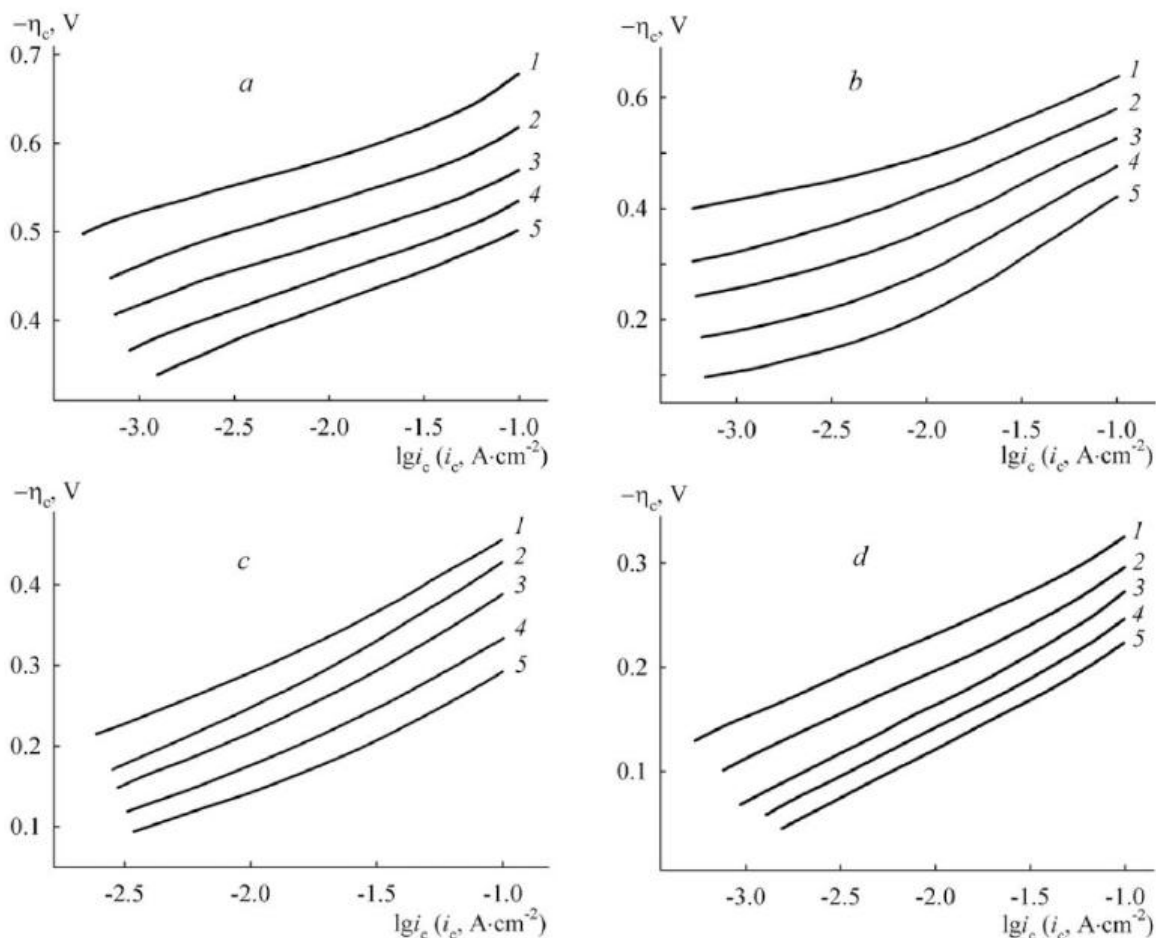The values of the Tafel coefficient a in the case of cathodic hydrogen evolution at the electrode coated

Figure 4 : Tafel plots for hydrogen evolution from a 30 % KOH solution at smooth vanadium (*a*), smooth cobalt (*b*), an electrolytic cobalt coating (*c*) and a Co-V alloy (*d*) at the temperatures (°C): (*1*) 25, (*2*) 40, (*3*) 55, (*4*) 70, (*5*) 85

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TABLE 2 : Kinetic parameters of hydrogen evolution at smooth vanadium and cobalt, an electrolytic cobalt coating and a Co-V alloy

Parameter	Electrode	Temperature, °C				
		25	40	55	70	85
$-a$, V	V smooth	0.713	0.669	0.626	0.601	0.576
	Co smooth	0.777	0.731	0.694	0.672	0.635
	Co coating	0.606	0.593	0.545	0.479	0.424
	Co-V coating	0.394	0.369	0.354	0.329	0.310
$-b$, V·dec^{-1}	V smooth	0.064	0.068	0.071	0.075	0.079
	Co smooth	0.144	0.151	0.165	0.193	0.216
	Co coating	0.155	0.172	0.164	0.152	0.141
	Co-V coating	0.081	0.085	0.091	0.093	0.094
i_o, A·cm^{-2}	V smooth	$7.40 \cdot 10^{-12}$	$1.32 \cdot 10^{-10}$	$6.22 \cdot 10^{-10}$	$1.02 \cdot 10^{-8}$	$5.37 \cdot 10^{-8}$
	Co smooth	$3.89 \cdot 10^{-6}$	$1.44 \cdot 10^{-5}$	$6.19 \cdot 10^{-5}$	$3.31 \cdot 10^{-4}$	$1.15 \cdot 10^{-3}$
	Co coating	$2.18 \cdot 10^{-4}$	$5.51 \cdot 10^{-4}$	$7.48 \cdot 10^{-4}$	$9.31 \cdot 10^{-4}$	$1.41 \cdot 10^{-3}$
	Co-V coating	$1.31 \cdot 10^{-5}$	$4.86 \cdot 10^{-5}$	$1.82 \cdot 10^{-4}$	$3.01 \cdot 10^{-4}$	$5.12 \cdot 10^{-4}$
A_o, kJ·mol^{-1}	V smooth			131.0		
	Co smooth			85.6		
	Co coating			25.4		
	Co-V coating			54.7		

with Co-V alloy are much smaller than in all other investigated cases, indicating a higher catalytic activity of this electrode.

The largest exchange current density values have been obtained in the case of hydrogen evolution at the cobalt-coated electrode (see TABLE 2). The exchange current density of the electrode coated with Co-V allot is slightly lower than i_o of the cobalt-coated electrode and slightly higher than i_o of smooth cobalt electrode. The closeness of the i_o values of these three electrodes with obvious difference in their real surface areas is most likely due to the fact that the developed surface of electrodes with electrolytic coatings is accessible to a lesser extent to cathodic hydrogen evolution than the smooth cobalt surface. On the surface of rough electrodeposits, much more formed gaseous hydrogen is retained than on the smooth cobalt surface; this results in additional blocking of the surface of deposits and in a decrease in the area of their active surface, on which water molecules are discharged. The exchange current of smooth vanadium electrode is much lower than that of the other investigated electrodes.

The values of the real activation energy of hydrogen evolution at the investigated cathodes are also widely different see TABLE 2. The largest A_o value was es-

tablished in the case of hydrogen evolution at a smooth vanadium cathode. The lowest activation energy is required for hydrogen evolution at cobalt-coated cathode. The A_o value of hydrogen evolution at the cathode coated with Co-V alloy is between its values in the case of hydrogen evolution at smooth cobalt cathode and at cobalt-coated cathode.
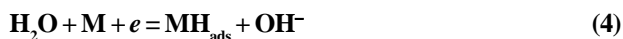
According to the obtained i_o and A_o values, cobalt-coated electrode has the highest catalytic activity in the cathodic hydrogen evolution reaction among the investigated electrodes. In the work[15], the surface of nickel cathodes was activated by electrodepositing cobalt and vanadium, and the regularities of cathodic hydrogen evolution at the obtained electrodes from a 1M KOH solution were studied. Having compared the values of exchange current density and the angular Tafel coefficient b, the authors of[15] found that Ni-Co and Ni-Co-V electrodes are much more active in the hydrogen evolution reaction than polished nickel, Ni-Co being slightly more active than Ni-Co-V. It should be noted, however, that the exchange current values obtained both by us and in the work[15] are apparent since the geometric but not active surface area of the electrodes was used to calculate them.

The real saving of electric energy in the case of ca-

thodic hydrogen evolution is achieved if depolarization and decrease in the overpotential of the electrode processes take place as a result of electrode surface modification. As was shown above, in the case of hydrogen evolution at the investigated electrodes, the least negative potentials and lowest overpotentials at the same current densities were obtained when an electrode coated with electrolytic Co-V alloy was used.

The value of angular Tafel coefficient is also often regarded as a measure of the electrolytic activity of the electrode material: the lower the *b* value, the higher the activity of the material[17-19]. The lowest values of angular Tafel coefficient were established in the case of hydrogen evolution at smooth vanadium cathode see TABLE 2. The *b* values, which characterize hydrogen evolution at the cathode coated with Co-V alloy, are slightly larger than those in the case of hydrogen evolution at smooth vanadium, but much smaller than those in the case of hydrogen evolution at smooth cobalt and cobalt-coated electrode. At 70 and 85 °C, a decrease in *b* values in going from smooth cobalt to electrodes coated with cobalt and Co-V alloy is observed, which corresponds to decrease in the values of hydrogen evolution potentials and overpotentials at these electrodes. However, the lowest values of angular Tafel coefficient persist when the hydrogen evolves at the smooth vanadium cathode in spite of the highest values of hydrogen evolution potential and overpotential at this electrode as well as the lowest i_o and the largest A_o values.

Obviously, the rate of cathodic hydrogen evolution at the investigated electrodes is controlled by the rate of different stage of this process. It is known from literature data that the mechanism of cathodic hydrogen evolution from water may comprise the following stages:

$$H_2O + M + e = MH_{ads} + OH^- \qquad (4)$$
$$MH_{ads} + MH_{ads} = H_2\uparrow + 2M \qquad (5)$$
$$MH_{ads} + H_2O + e = H_2\uparrow + OH^- + M, \qquad (6)$$

where M is the electrode material. According to this mechanism, the discharge of water molecule occurs on the cathode surface as a result of attachment of one electron and leads to the formation of an adsorbed hydrogen atom and OH- ion (reaction (4), Volmer reaction). Then adsorbed hydrogen atoms can quickly recombine by the reaction (5), which is called Tafel reaction, or be desorbed by the electrochemical reaction (6) called Heyrovsky reaction[7,8].

The large values of angular Tafel coefficient established by us in the case of hydrogen evolution at smooth cobalt and cobalt-coated electrode (see TABLE 2) indicate that the rate of the electrode process at these electrodes is determined by the rate of the electrochemical stage of the formation of adsorbed hydrogen atoms in accordance with the reaction (4). If a linear Langmuir isotherm is used to describe adsorption and it is taken into account that activity of water in alkaline solution is practically unity, then the kinetic equation describing the rate of the slow stage and hence of the whole cathodic hydrogen evolution process may be represented as:

$$i_c = \vec{i}_4 = \vec{k}_4(1-\theta)a_{OH^-}^{-1}\exp\left(-\frac{\alpha_4 F\eta_c}{RT}\right) \qquad (7)$$

where $\vec{k}_4$ is the rate constant of the forward reaction (4), θ is electrode surface coverage by adsorbed hydrogen atoms, a_{OH^-} is the activity of OH- ions, α_4 is electron transfer coefficient in the forward reaction (4), *F* is Faraday constant, *R* is universal gas constant, *T* is absolute temperature. The Langmuir isotherm is suitable for the description of adsorption at the boundary values of electrode surface coverage by adsorbed particles (($\theta < 0.2$ and $\theta > 0.8$)[20]. Taking the logarithm of Eq. (7) yields a $\eta_c - \lg i_c$ Tafel plot, whose slope is:

$$b = -2.303\frac{RT}{\alpha_4 F} \qquad (8)$$

The *b* values calculated from formula (8) are equal to the experimental values if the α_4 values are in the ranges 0.33-0.42 and 0.33-0.46 in the case of smooth cobalt and cobalt-coated electrode respectively see TABLE 2.

When water molecules are discharged on smooth vanadium cathode and on cathode coated with Co-V alloy, the rate-determining step of the electrode process is apparently the electrochemical desorption of adsorbed hydrogen atoms by the reaction (6). This is possible if the end product (gaseous hydrogen) is formed by a recombination reaction (5) very slowly or is not formed at all by this reaction, and the reaction (4) occurs readily. At mean θ values ($0.2 \le \theta \le 0.8$), when the Temkin isotherm is suitable for the description of adsorption[20], the rate equation of the forward reaction (6) is of the form:

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$$\vec{i}_6 = \vec{k}_6 \theta a_{OH^-}^{-1} p_{H_2}^{-1} \exp(-\frac{\alpha_6 F\eta_c}{RT}) \exp[\delta f(\theta)] \qquad (9)$$

where $\vec{k}_6$ is the rate constant of the forward reaction (6), p_{H_2} is the partial pressure of gaseous hydrogen, α_6 is electron transfer coefficient in the forward reaction (6), δ is a coefficient having the significance of symmetry factor in the adsorption process $(0 < \delta < 1)$, f (θ) is a function characterizing variation in the free energy of adsorption with θ. The activity of water was taken to be unity.

The fast previous stage of formation of adsorbed hydrogen atoms may be regarded as equilibrium stage. The rate of the forward and reverse reactions of the MH_{ads} formation stage may be represented as:

$$\vec{i}_4 = \vec{k}_4 (1-\theta) a_{OH^-}^{-1} \exp(-\frac{\alpha_4 F\eta_c}{RT}) \exp[-\delta f(\theta)] \qquad (10)$$

$$\vec{i}_4 = \vec{k}_4 \theta a_{OH^-} \exp[\frac{(1-\alpha_4)F\eta_c}{RT}] \exp[(1-\delta)f(\theta)] \qquad (11)$$

where $\vec{k}_4$ is the rate constant of the reverse reaction (4). Proceeding from the equilibrium condition of this stage, $\vec{i}_4$ and $\vec{i}_4$ were equated, and the following expression for exp[f (θ)] was obtained:

$$\exp[f(\theta)] = K_4 \frac{1-\theta}{\theta} a_{OH^-}^{-2} \exp(-\frac{F\eta_c}{RT}) \qquad (12)$$

where K_4 is the equilibrium constant of the reaction (4).

The activity of OH⁻ ions changes negligibly during the electrolysis of a 30 % KOH solution, therefore it can be combined with the equilibrium constant into one constant. At the mean values of electrode surface coverage by adsorbed hydrogen atoms, the factor $(1 - \theta)/\theta$ H" 1. Subject to these conditions, expression (12) simplifies to:

$$\exp[f(\theta)] = K_4' \exp(-\frac{F\eta_c}{RT}) \qquad (13)$$

where $K_4' = K_4 a_{OH^-}^{-2}$. It follows from Eq. (13) that the function f (θ) can be expressed in term of the overpotential of the electrode process:

$$f(\theta) = \ln K_4' - \frac{F\eta_c}{RT} \qquad (14)$$

Substituting the expression for f (θ) into Eq. (9) yields the following kinetic equation describing the hy-

drogen evolution rate when the rate-determining step is the electrochemical desorption of hydrogen atoms:

$$i_c = \vec{i}_6 = \vec{k}_6' \theta p_{H_2}^{-1} \exp[-\frac{(\alpha_6 + \delta)F\eta_c}{RT}] \qquad (15)$$

where $\vec{k}_4'$ is a constant which combined all constants. According to this equation, the slope of the Tafel portions of the corresponding polarization curves is determined from the formula:

$$b = -2.303 \frac{RT}{(\alpha_6 + \delta)F} \qquad (16)$$

In order that the results of calculation of the angular coefficient *b* from this formula may agree with its experimental values it is necessary that the values of the sum $\alpha_6 + \delta$ should be in the ranges 0.900-0.925 and 0.715-0.756 in the case of hydrogen evolution at vanadium and Co-V alloy respectively, which is quite possible in the studied potential and current density ranges. Hence it can be stated that the mechanism of hydrogen evolution at such electrodes is stepwise, and that the rate of the electrode process is determined by the rate of the electrochemical desorption of adsorbed hydrogen atoms.

SUMMARY

The paper presents results of comparative studies of the regularities of cathodic hydrogen evolution from a 30 % KOH solution at an electrolytic Co-V alloy, an electrolytic cobalt coating and at cobalt and vanadium with smooth surface at 25-85 °C. The Co-V alloy and cobalt coating were deposited on stainless steel from a nonaqueous electrolyte. It has been found that hydrogen evolves at Co-V alloy at the least negative potentials and with the lowest overpotential. The apparent exchange current densities and real activation energies of hydrogen evolution at the investigated electrodes as well as the Tafel coefficients *a* and *b* have been determined On the basis of an analysis of angular Tafel coefficient values it has been shown that the rate of cathodic hydrogen evolution at smooth cobalt and cobalt coating is controlled by the rate of formation of adsorbed hydrogen atoms and at smooth vanadium and electrolytic Co-V alloy by the rate of their electrolytic desorption.

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CONCLUSIONS

1. Cathodic hydrogen evolution from alkaline solution at electrolytic alloy deposited on steel from a non-aqueous electrolyte takes place at less negative potentials and at much lower overpotentials than at its components. Therefore, electrodes coated with this alloy have promise in reducing electrical energy consumption in the electrolysis of alkaline solution.

2. The smallest values of the Tafel coefficient *a* have been determined in the case of hydrogen evolution at Co-V alloy, while the highest values of exchange current and the lowest values of real activation energy have been estimated when hydrogen evolved at cobalt coating.

3. The angular Tafel coefficient *b* has lower values in the case of hydrogen evolution at smooth vanadium and Co-V alloy than in the case of its evolution at smooth cobalt and cobalt coating. The obtained values of the coefficient *b* can be explained if it is assumed that the rate-determining step of hydrogen evolution at smooth vanadium and Co-V alloy is the electrochemical formation of adsorbed hydrogen atoms, and that in the case of hydrogen evolution at smooth cobalt and cobalt coating, the rate of the electrode process is determined by the rate of electrochemical desorption of hydrogen atoms.

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