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VANADIUM-CONTAINING COATINGS: FUNCTIONAL PROPERTIES

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The synthesis of new electrode materials that reduce the cost of electrochemically produced hydrogen is a relevant modern research direction. Such materials should have catalytic activity for the hydrogen evolution reaction, corrosion resistance, sufficient microhardness, long service life, and low cost. These properties can be expected for alloys of iron-group metals with vanadium. A cobalt–vanadium coating was electrodeposited from a complex citrate electrolyte under stationary electrolysis conditions. X-ray dispersive spectrometry results indicate that the resulting coating contains 0.7–1.5 wt.% vanadium. It was found that the overpotential of the hydrogen evolution reaction on a cathode with the Co–V coating is 0.1 V lower, and the exchange current density is higher than on the cobalt-coated electrode. This indicates the electrocatalytic activity of the vanadium-containing material in the hydrogen evolution reaction. The microhardness of the Co–V coating is also 100–150 kg/mm^2 higher than that of the cobalt-coated electrode. An increase in the vanadium content improves the coating corrosion resistance compared to pure cobalt, as evidenced by a decrease in the corrosion current. Therefore, electrodes with Co–V coating can be recommended as cathodes for electrochemical hydrogen production.

Keywords: Co–V coating, electrocatalytic activity, overpotential, microhardness, corrosion resistance.

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Introduction

Hydrogen energy is based on hydrogen utilization as a fuel to produce energy. Hydrogen can be produced in various ways. One of the principles of Green Chemistry postulates the requirement to use technologies and substances that are least toxic to humans and more environmentally benign [1,2]. Following it, hydrogen obtained by aqueous solutions electrolysis is considered the most environmentally friendly. However, the cost of producing such hydrogen is higher than producing hydrogen from fossil raw materials. Therefore, it is relevant to develop new electrode materials that can reduce the cost of hydrogen produced in this way.

Electrochemical hydrogen production widely involves cathode materials that have catalytic properties for the hydrogen evolution reaction (HER). Such materials should also have a long service life, corrosion and wear resistance, and low cost. All that should reduce energy consumption for this process and the cost of produced hydrogen.

High values of catalytic activity can be expected for alloys of elements located on opposite sides of the trend line dependence of the hydrogen exchange current on «metal–hydrogen» and «metal–oxygen» bond energy difference [3]. These alloys include iron

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periodic group metals alloys with vanadium, molybdenum and tungsten [4,5]. Deposition of such coatings can be carried out in stationary or pulsed electrolysis modes using electrolytes containing complex or simple ions [6–8]. For instance, electrodeposition of iron periodic group metals (Fe, Co, Ni)–vanadium alloys can be performed from aqueous citrate and tartrate solutions [9,10]. Addition of aqueous NH_3(aq.) to citrate solutions and rising solution pH from 5.5 to 7 results in increased vanadium deposit content up to 4 wt.% in Fe–V, Ni–V, and Co–V alloys. In general, the amount of vanadium that could be co-deposited with the iron group metal increased as follows: Ni<Fe<<Co [11].

Vanadium has high corrosion resistance in fresh and sea water, in dilute solutions of sulfuric and hydrochloric acids, and in salts and alkali solutions. Vanadium is used as an alloying additive in the smelting for creating wear-resistant, corrosion-resistant, heat-resistant steels, also eliminating their brittleness.

Taking into account the aforementioned properties of vanadium, for the electrolytically produced vanadium-containing alloys, it is possible to predict their catalytic activity in the HER, corrosion resistance, and increased microhardness.

The functional properties of a cobalt-vanadium alloy coating, which is envisioned to be used as a cathode material in the hydrogen electrochemical production, were investigated in this work.

Experimental

The cobalt-vanadium alloy coatings were deposited in a citrate electrolyte containing ($mol{\cdot}dm^{-3}$): 0.4 $Na_3C_6H_5O_7{\cdot}2H_2O$, 0.1 $CoSO_4{\cdot}7H_2O$, and 0.2 $VOSO_4$. Electrodeposition was carried out at $35–40^0$C and pH 3–3.5 using a cobalt anode, via the galvanostatic mode with a current density of 5–15 $A{\cdot}dm^{-2}$. The obtained coatings thickness was 9–12 μm. Before electrodeposition, the surface of steel electrodes with area of 2 cm^2 was polished and degreased.

The chemical composition of the coatings was determined via the energy-dispersive X-ray spectroscopy results, using an Oxford INCA Energy 350 microanalyzer integrated into the scanning electron microscope system (SEM).

Electrolysis in galvanostatic mode was performed using a stabilized DC power supply B5-47. Polarization dependences were obtained using MTech PGP-550M potentiostat. Platinum was used as the counter electrode. The saturated silver/silver chloride electrode was used as reference electrode. The values of the electrode potentials were recalculated against the standard hydrogen electrode.

Corrosion research and electrocatalytic properties of the obtained Co–V coating for the HER were determined in a solution of 2.5 M NaOH [5,11], which is used for the industrial electrochemical production of hydrogen.

The analysis of the Co–V electrolytic coatings catalytic activity was carried out using the exchange current density (j_0) indicator of the HER, since this value does not depend on the electrode potential. For this purpose, sections of the cathodic polarization dependence linearized in Tafel coordinates were extrapolated in the range of potentials 200–300 mV away from the equilibrium one. The Tafel constant b was determined by the slope of the linear Tafel dependences [12].

The obtained coatings corrosion resistance was evaluated by the polarization dependence analysis, which includes the cathodic and anodic voltammograms recording in the corrosion potential zone. Corrosion current density (j_{cor}) was determined by the extrapolation of partial anodic and cathodic dependencies linear sections in Tafel coordinates $\lg j$ vs. ΔE [13].

Determination of microhardness according to the Vickers method was carried out by indenting a diamond pyramid with a square base and an angle at the top of 136^0, using a hardness tester PMT-3.

Results and discussion

The variety of vanadium ionic forms in solutions leads to the formation of a large number of compounds with other metals, where the ratio of metals to vanadium varies significantly. In addition to that, vanadium ions are known for their ability to form complex compounds with inorganic and organic ligands.

Introducing vanadium(V) oxide into a solution of sodium citrate results in the formation of a yellow solution containing vanadate ions, which includes pentavalent vanadium. Over time, the color changed to green and then to dark blue, which may indicate the reduction of vanadium(V) compounds to vanadium(III) with the formation of vanadium(III) complex ions $[V(C_6H_5O_7)_2]^{3-}$. This solution of mentioned vanadium (III) complex ion oxidizes by air to form oxovanadium(IV) citrate complexes $[VO(C_6H_5O_7)_2]^{4-}$ [7].

To prepare the citrate electrolyte, vanadyl sulfate $VOSO_4$ was used instead of vanadium(V) oxide V_2O_5 [2], which allows preparing an electrolyte with a high content of vanadyl ions due to the higher solubility of vanadyl sulfate accelerating complexation with citrate ions. Oxovanadium(IV) citrate complexes $[VO(C_6H_5O_7)_2]^{4-}$ are formed immediately after adding vanadyl sulfate to a sodium citrate solution. Treating the resulting solution with cobalt sulfate leads to the electrolyte containing both cobalt and oxovanadium(IV) citrate complexes. This electrolyte is easier to prepare and stable during operation. The use of vanadyl sulfate also allows obtaining the coatings with high vanadium content [7].

The resulting electrodeposited coatings have a proper and targeted quality: uniform, microcrystalline, light-gray, semi-shiny, rough (Fig 1,a).

The vanadium content in coatings is in the range of 0.7−1.5 wt.%. The maximum vanadium content (1.5 wt.%) in the coating is observed at cathodic current density j_k=10 A·dm^{-2} (Fig. 2).

Cathodic polarization curves of hydrogen evolution on the electrodes with the Co coating and with the Co−V coating, respectively, are shown in Fig. 3. Hydrogen evolution begins at more positive potential values (−0.95÷−1.0 V) on the Co−V coated electrodes than on the Co coated electrode (−1.15 V). Increasing vanadium content in the coating leads to a shift in the hydrogen evolution potential towards more positive values (Fig. 3). The polarization of HER on electrodes with Co−V coating is 0.15−0.2 V less as compared with the Co-coated electrode.

Analysis of the polarization dependences linearized in the Tafel coordinates (Fig. 4) allows determining the kinetic parameters of the HER for the electrodes studied (Table 1).

The values of the exchange current density (j_0) and the Tafel equation coefficients (*a, b*) reflect the impact of the electrode nature on the reaction kinetics. Therefore, the decrease in overpotential of the HER on Co−V alloy coating is explained by the presence of vanadium (value of *a*). In addition, increasing the vanadium content in the coating leads to a greater reduction of the HER overvoltage.

The value of the coefficient *b* for the cobalt-vanadium alloy is close to the «common» value of the coefficient for cobalt in an alkaline environment (*b*=0.14), which indicates that the HER on the alloy studied occurs according to the Volmer-Heyrovsky mechanism with a slow discharge stage.

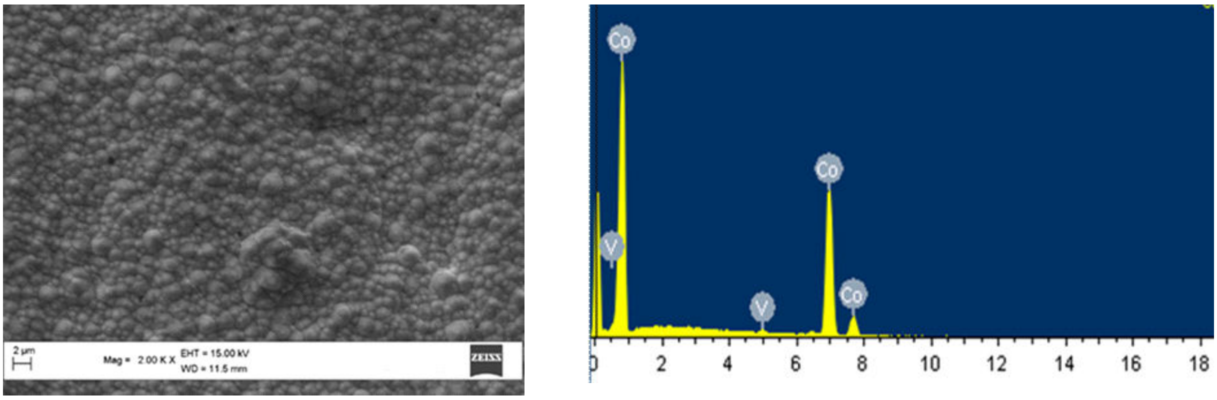
The value of j_0 for the electrodes with Co−V coating indicates a higher activity of these materials in comparison with the cobalt-coated electrode. The obtained values of overvoltage and current exchange for a cobalt-vanadium coating with a vanadium content in the range of 0.7−1.5 wt.% are close to the values of the corresponding parameters for a platinum electrode in alkaline solutions (Table 1), which confirms their competitiveness over platinum electrodes and the possibility of using them as low-cost electrocatalytic materials in the electrolytic hydrogen production.

Hardness measurements show that the microhardness of the coating obtained is 100−150 kg·mm^{-2} higher than that of cobalt electroplated from a sulfate solution (Fig. 5). It can be concluded that higher indicators of microhardness for cobalt−vanadium alloys compared to cobalt coating are achieved due to the formation of intermetallic compounds and a more perfect relief [14].

Table 1

Kinetic parameters of the HER

Electrode materials	Vanadium content, wt.%	*a*, V	*b*, V	$-\lg j_0$, A·cm^{-2}
Pt	–	–0.31	–0.100	3.1
Co	–	–0.60	–0.140	4.3
Co coating	–	–0.61	–0.120	5.1
Co–V coating	0.7	–0.58	–0.140	4.1
	1.5	–0.50	–0.141	3.5



a b

Fig. 1. Surface morphology (a) and X-ray spectrum (b) of cobalt−vanadium coating with vanadium content 0.75 wt.%

The increased vanadium corrosion resistance in a various environment is associated with the protective oxide films formation on its surface. The results of the Co–V alloys corrosion-electrochemical behavior studies demonstrate that vanadium content increase leads to better coating corrosion resistance compared to pure cobalt material. Increase of vanadium content in the alloy shifts corrosion potential to the negative side, decreases the corrosion current which leads to a decrease in the corrosion rate.

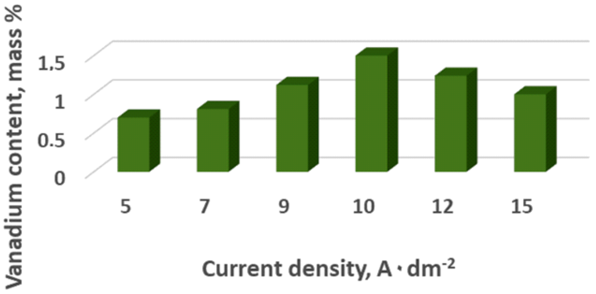


Fig. 2. Dependence of the vanadium content in the alloys on the current density

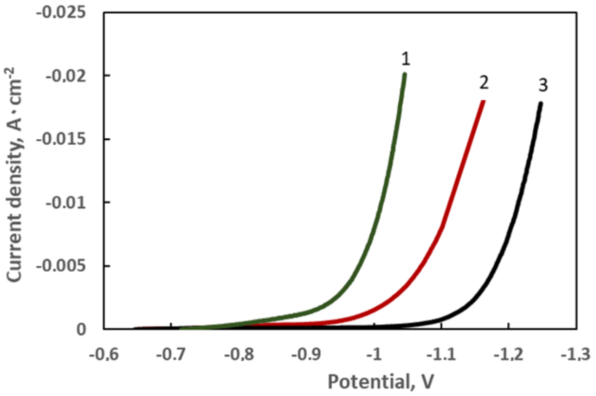


Fig. 3. Cathodic polarization curves of hydrogen evolution for electrodes with coating: 1 – Co–$V_{1.5}$; 2 – Co–$V_{0.7}$; 3 – Co

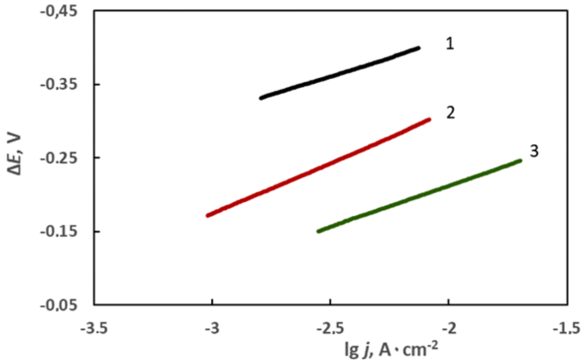


Fig. 4. Dependence of overpotential on the logarithm of current density for electrodes with coating: 1 – Co; 2 – Co–$V_{0.7}$; 3 – Co–$V_{1.5}$

The corrosion potential shifts to the negative side due to the cathodic reaction inhibition in an alkaline environment as a consequence of the alloys surface passivation by low-soluble cobalt hydroxides limiting the depolarizer's access to the electrode surface [13,14] (Table 2).

Albeit vanadium is a relatively expensive element, its addition in small quantities provides a significant improvement of the alloy protective properties.

In conclusion, the aforementioned studies confirmed the predicted functional properties of the cobalt–vanadium alloy coating. Electrodes with such a coating can be recommended as potential cathodes for the electrochemical production of hydrogen, bringing reduction in energy and material cost for this process.

Conclusions

1. Cobalt–vanadium coating is electrodeposited from a complex citrate electrolyte via stationary electrolysis modes. The resulting coating contains 0.7–1.5 wt.% vanadium.

2. The overpotential of the hydrogen evolution reaction on the cathodes with Co–V coating is lower, and the exchange current value is higher than on the cobalt coated electrode, that indicates higher

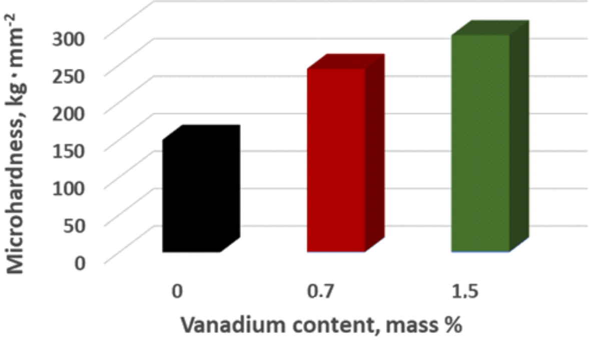


Fig. 5. Dependence of the microhardness of Co–V coating on vanadium content

Table 2

Corrosion indicators of steel and coatings studied

Coating composition	Vanadium content, wt.%	E_{cor}, V	lg j_{cor}, A·cm^{-2}
Steel	–	–0.32	–2.80
Co	–	–0.61	–4.10
Co–V	0.7	–0.65	–4.25
	1.5	–0.70	–4.50

electrocatalytic activity of this material in the hydrogen evolution reaction.

3. The microhardness of the coating obtained is also higher than for cobalt electroplated from a sulfate solution.

4. An increase in the vanadium content increases the coating corrosion resistance compared to pure cobalt: the decrease of the corrosion current value leads to a decrease in the corrosion rate.

5. Electrodes with Co–V coating can be recommended as cathodes for the electrochemical hydrogen production to help reduce the cost of this process.

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ВАНАДІЙВМІСНІ ПОКРИТТЯ: ФУНКЦІОНАЛЬНІ ВЛАСТИВОСТІ

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Синтез нових електродних матеріалів, що знижують вартість електрохімічно виробленого водню, є актуальним напрямом сучасних досліджень. Такі матеріали мають володіти каталітичною активністю у реакції виділення водню, корозійною стійкістю, достатньою мікротвердістю, тривалим ресурсом експлуатації та низькою вартістю. Очікується, що перелічені властивості притаманні сплавам металів залізної групи з ванадієм. Кобальт-ванадієве покриття було електроосаджене з комплексного цитратного електроліту за умов стаціонарного електролізу. За результатами рентгенівської дисперсної спектрометрії встановлено, що одержане покриття містить 0,7–1,5 мас.% ванадію. Встановлено, що перенапруга реакції виділення водню на катоді з покриттям Co–V на 0,1 В менша, а густина струму обміну вища, ніж на катоді з кобальтовим покриттям. Це вказує на електрокаталітичну активність ванадійвмісного матеріалу у реакції виділення водню. Мікротвердість покриття Co–V також на 100–150 кг/мм^2 вища, ніж у кобальтового покриття. Збільшення вмісту ванадію підвищує корозійну стійкість покриття порівняно з чистим кобальтом, про що свідчить зменшення корозійного струму. Отже, електроди з покриттям Co–V можуть бути рекомендовані як катоди для електрохімічного виробництва водню.

Ключові слова: Co–V покриття; електрокаталітична активність; перенапруга; мікротвердість; корозійна стійкість.

VANADIUM-CONTAINING COATINGS: FUNCTIONAL PROPERTIES

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Keywords: Co–V coating; electrocatalytic activity; overpotential; microhardness; corrosion resistance.

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