

Electrochemical Synthesis of Ni/TiO₂ Composite Coatings from Deep Eutectic Solvent and Electrocatalytic Characteristics of Deposits

V. S. Protsenko^{a, *}, T. E. Butyrina^a, D. A. Bogdanov^a, S. A. Korniy^{a, b}, and F. I. Danilov^a

^a *Ukrainian State University of Chemical Engineering, Dnipro, 49005 Ukraine*

^b *Karpenko Physicomechanical Institute, National Academy of Sciences of Ukraine, Lviv, 79060 Ukraine*

**e-mail: Vprotsenko7@gmail.com*

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Abstract—Kinetics of electrodeposition of composite Ni/TiO₂ coatings was studied using the electrolyte based on a deep eutectic solvent (DES) containing choline chloride, ethylene glycol, water additive, and nickel chloride. Degussa P 25 nanopowder was used as a dispersed phase in the electrolyte (1–10 g/dm³). The developed electrolyte allows depositing composite coatings with the content of titanium dioxide reaching ~10 wt %. The electrolytic deposition of the composite was shown to obey Guglielmi's kinetic model. The main parameters of codeposition of TiO₂ particles into a nickel matrix were determined in the framework of this kinetic model. The codeposition of titanium dioxide was found to inhibit the reaction of the nickel ions' discharge. Electrocatalytic properties of the prepared composite Ni/TiO₂ coatings were evaluated with respect to the hydrogen evolution reaction in an aqueous alkaline solution. A noticeable improvement in the electrocatalytic activity was observed when titanium dioxide particles were introduced into an electrodeposited nickel matrix.

Keywords: electrodeposition, nickel, titanium dioxide, composite coating, deep eutectic solvent, electrocatalysis, hydrogen evolution reaction

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INTRODUCTION

Electrolytic deposition of composites is an effective approach to the fabrication of the coatings with improved physicochemical and operational characteristics [1, 2]. Among various types of composites, which can be accessed through electrodeposition, the nickel-based coatings are of particular interest. On the one hand, this is caused by the ability to codeposit the particles of disperse phase that are different in chemical composition and microstructure along with the nickel matrix; on the other hand, the Ni-based composite coatings provide high corrosion resistance, increased hardness and wear resistance, and high electrocatalytic activity [3–23].

Electrolytic composite coatings containing the disperse phase of titania in the nickel matrix are of particular interest [14–23] because the incorporation of TiO₂ particles in the coating results not only in the increase in microhardness, wear resistance, and corrosion resistance but also renders the surface photo-induced hydrophilicity, photocatalytic activity, and self-healing ability [18, 19] as well as electrocatalytic activity with respect to hydrogen and oxygen electro-evolution reactions during electrolysis of water [20–23].

Aqueous suspension electrolytes are conventionally used for electrodeposition of Ni/TiO₂ composite

coatings [14–20]. Even though aqueous nickel-plating electrolytes possess a number of evident advantages (low cost and availability), their drawbacks include aggregation and sedimentation instability: in aqueous dispersion medium, the particles of the disperse phase aggregate relatively quickly and further precipitate under gravity force. These effects complicate the stable work of colloidal electrolyte and decrease the content of TiO₂ in deposit and worsen some characteristics of the formed coatings.

The systems based on so-called deep eutectic solvents (DES) could represent an alternative to aqueous electrolytes for deposition of nickel-containing composite coatings [5–8, 21–23]. DES is a specific class of ionic liquids, which represents eutectic mixtures of various inorganic and organic components, in which there is electrolytic dissociation of components and a drastic decrease in melting point (as compared to melting points of individual components) due to the interaction between particles (formation of hydrogen bonds and/or donor-acceptor interactions) [24, 25]. In the literature, such advantages of DES-based electrolytes as wide “electrochemical window” (the range of potentials of electrochemical stability), high solubility of metal salts, relatively high electrical conductivity, negligibly low saturation vapor pressure, availability, low cost, and ecological safety are mentioned [24].

At present, DES-based electrolytes are considered as a promising type of electrochemical systems for the preparation of various types of electroplatings [26–28]. In particular, a higher viscosity (as compared to aqueous systems) provides an increased aggregation and sedimentation stability of DES-based colloidal systems, which significantly facilitates the problem of electrodeposition of composite coatings [28].

We earlier showed the possibility of electrodeposition of nickel–titania composites from DES-based electrolyte [21]. An increase in the microhardness and corrosion resistance upon incorporation of particles into the nickel matrix deposited from DES was mentioned, and photocatalytic properties of the composites were also characterized. However, the coatings described in [21] contained no more than 2.35 wt % TiO₂, which restricted the potential modification of characteristics of deposits. It was later discovered that the content of titania particles could be significantly increased up to 10 wt % in the nickel matrix with the introduction of a particular amount of water into the DES-based electrolyte [22]. The coatings with Ni/TiO₂ composite deposited from DES-based electrolyte containing water additive displayed increased electrocatalytic activity in cathode hydrogen evolution reactions and anode oxygen evolution reactions during electrolysis of aqueous alkaline solutions [22, 23]. However, many aspects of electrochemical synthesis of such coatings, as well as their characteristics, were hardly investigated. In this work, kinetic principles were characterized and a possible mechanism of electrochemical synthesis of Ni/TiO₂ coatings in the electrolyte described in [22, 23] was considered. In addition, using the electrochemical impedance spectroscopy, hydrogen evolution process on electrodeposited Ni/TiO₂ composites was investigated in detail, which is of not only fundamental but also applied interest in context of the development of new, high-performance and available methods for hydrogen production for hydrogen energy [29].

PROCEDURE OF EXPERIMENT

To deposit metal coatings, the electrolyte based on eutectic mixture of choline chloride and ethylene glycol at a 1 : 2 molar ratio was used. Nickel ions were added to electrolyte by dissolving solid salt of NiCl₂·6H₂O; in this case, the concentration of Ni(II) was always 1 mol/dm³. In some cases, water was added to the electrolyte. In most experiments, the electrolyte containing 15 mol/dm³ of water was used to deposit composite coatings (here and elsewhere, numbers indicate the total amount of water added to electrolyte with crystallhydrate of nickel salt (6 mol/dm³) and introduced separately).

The disperse phase of titania was added to the electrolyte in the form of Degussa P 25 nanopowder (major fraction is 25 nm; the mixture of anatase and

rutile is at the 80 : 20 weight ratio, respectively). To provide uniform bulk distribution of colloidal particles, the electrolyte was exposed to ultrasonication in a UZDN-A ultrasound disperser for 1 h (22.4 kHz, 340 W/dm³).

We previously described a procedure for preparation of electrolyte in detail in [21–23].

During the study of kinetics of preparation of coatings and evaluation of their electrocatalytic properties, deposition was performed on a gold plate with the surface area of 1 cm². Before each experiment, the electrode surface was etched for several minutes in hydrochloric acid solution, thoroughly washed with distilled water, and dried. Nickel-soluble anodes were used for electrodeposition.

Electrolysis was carried out in a usual glass thermostated cell at 313 K in galvanostatic mode at a cathode current density from 1 to 3 A/dm³ at continuous stirring of electrolyte using magnetic stirrer (500 rpm). The time of experiments was chosen in such a way that the thickness of the deposit would be about 20 μm.

Surface morphology of the obtained composite deposits was evaluated by scanning electron microscopy (SEM) using a Zeiss EVO 40XVP scanning electron microscope in secondary-electron detection mode. Chemical composition of the coatings was determined using energy-dispersive X-ray analysis (EDX) on a built-in Oxford INCA Energy 350 device. The weight fraction of the disperse phase of TiO₂ in composite coating was calculated from the experimental content of titanium in deposit assuming the stoichiometric ratio of titanium to oxygen in the oxide. For control in some cases, the content of disperse phase in the coating was evaluated by chemical analysis, according to which the deposits were quantitatively dissolved in acid and, then, the obtained solution was analyzed on the content of nickel ions (photometry with dimethylglyoxime indicator). The mass of titania in the coating was then determined as the difference between the total mass of deposit and the determined mass of “pure” nickel. Notably, the results of determination of the TiO₂ content in the composite coating obtained on the basis of EDX spectroscopy data and chemical analysis coincide within experimental error.

To record X-ray diffractograms, a DRON-3.0 diffractometer with monochromatic CoK_α radiation was used.

To record current–voltage dependences and measure electrochemical impedance, a Potentiostat/Galvanostat Reference 3000 potentiostat (Gamry) was employed. To measure and compensate for ohmic component of potential, the automatic compensator built in the potentiostat was employed. In the experiments with three-electrode cell, electrode compartments were separated by a porous glass diaphragm. Reference electrodes were represented by silver reference quasi-electrode (during polarization studies in

DES-based electrolyte) or saturated silver-chloride electrode (during the study of electrocatalytic characteristics of the coatings in aqueous solution). In the latter case, the potentials were calculated on the scale of standard hydrogen electrode.

During the study of the kinetics of hydrogen evolution on the obtained composite coatings, dissolved atmospheric oxygen was firstly evacuated by bubbling of purified electrolytic hydrogen through electrolyte.

During measurement of electrochemical impedance, a platinum grid represented auxiliary electrode, the surface area of which was much larger than that of the working electrode. Electrochemical impedance measurements were carried out under potentiostatic conditions in the frequency range of 0.01 Hz to 100 kHz at the amplitude of sinusoidal component of potential of 5 mV. The data were processed using Elchem Analyst software package.

RESULTS AND DISCUSSION

Kinetics of Electrodeposition of Composite Coating of Ni/TiO₂

The Ni/TiO₂ composite coatings, the deposition of which from the DES-based electrolyte was described in [21], included less than 2.35 wt % of titania. As follows from the data of Fig. 1, additional water in electrolyte could notably increase the content of dispersed phase in the composite (up to ≈10 wt %). Relatively low content of TiO₂ particles incorporated into the deposit in DES-based electrolyte at a low water content is rationalized in [21] by the increased viscosity of these ionic liquids (as compared to conventional aqueous solutions). Each particle of disperse phase in colloidal electrolyte is coated by a thin layer, which should be removed upon incorporation into the growing metal deposit. In addition, the analogous layer of solution should be removed from the surface of the nickel matrix during incorporation of the particles of the disperse phase in it. A relatively high viscosity of DES-based electrolytes determines the demand to consume particular time and energy to destruct compact and viscous film on the surface of the particles of electrodeposited matrix, which prevents incorporation of particles into the coating and ultimately determines low content of the disperse phase in the deposited composite.

Additional water decreases the viscosity of electrolyte (one example is that the viscosity of the nickel-plating electrolyte without additional water is ~59 mPa s at 313 K, while it decreases to ~18 mPa s at additional water with the content of 9 mol/dm³ [22]). A decrease in viscosity accelerates destruction of the films of solution, which should be removed from the electrode surface, and particles upon their incorporation in the composite coating. In addition, a decrease in viscosity obviously accelerates convective-diffusion mass transfer of the particles of the disperse phase. All

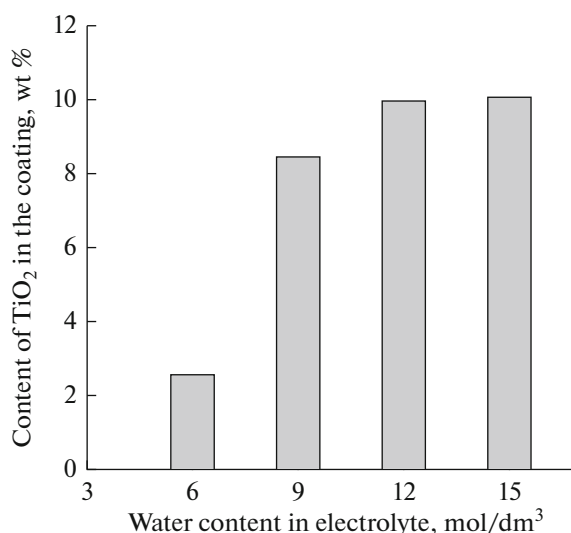


Fig. 1. Effect of water content in electrolyte on the content of disperse phase of TiO₂ in the coating. The concentration of titania particles in electrolyte is 5 g/dm³ and current density is 1 A/dm².

these effects ultimately increase the content of the disperse phase of TiO₂ in electroplated coatings.

It should be noted that DES-based electrolytes are characterized by high aggregation and sedimentation stability. One example is that we did not observe features of coagulation and sedimentation after mixing of electrolyte and its maintenance over 3–4 h.

In further experiments on the deposition of composite coatings, the electrolyte containing 15 mol/dm³ water was used.

Figure 2 shows the dependence of the content of titania particles in electrodeposited composite on the concentration of disperse phase in electrolyte at different current density values. It is clear that the content of titania particles in electrolyte increases with an increase in their concentration and reaches a limiting value. An increase in the current density in the studied range decreases the content of the disperse phase in the composite coating. Such dependences are often observed during electrodeposition of various composites [1, 2, 30–33]; their form allows us to suggest that kinetics of deposition of the particles of disperse phase into metallic matrix follow the model suggested by Guglielmi [34].

This model is based on the considering the stepwise adsorption of the particles of disperse phase on the electrode surface during their incorporation into the growing metal coating. At the first stage, particles are adsorbed reversibly on the electrode providing a sufficiently high surface coverage (so-called loose adsorption). At the second stage, metal ions, which are adsorbed on the surface of particles immobilized on the electrode, are discharged. As a result, there is a destruction of solvate shells and the particles of

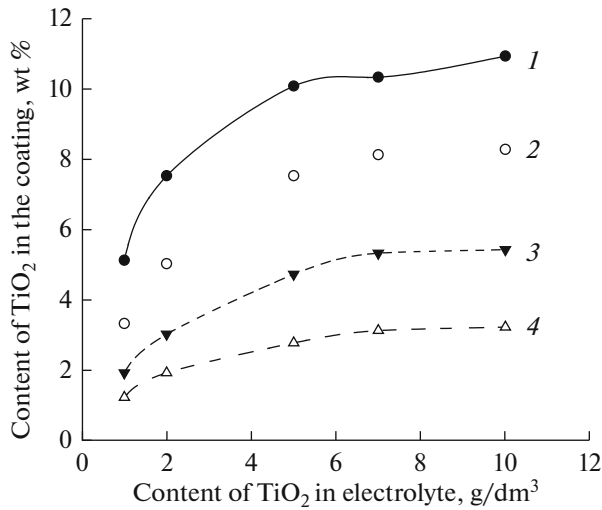


Fig. 2. Effect of concentration of titania in electrolyte on the content of TiO₂ in composite coatings electrodeposited at various current density values (A/dm²): (1) 1.0, (2) 1.5, (3) 2.0, and (4) 3.0.

disperse phase after irreversible adsorption are entrapped by the growing metal matrix (so-called strong adsorption) [34]. In the considered model, Langmuir-type adsorption isotherm is suggested, which determines experimentally observed achievement of some limiting value of the content of disperse phase in the coating with an increase in its concentration in electrolyte (Fig. 2).

It should be noted that the Guglielmi model was often used to interpret experimental data on the deposition of composite coatings of different composition and nature [1, 2, 35].

The main equation of the Guglielmi theory, which describes the dependence of the content of disperse phase in the composite on electrodeposition conditions, is as follows [34]:

$$\frac{C}{\alpha} = \frac{Mi_0}{nF\rho_m v_0} e^{(A-B)\eta} \left(\frac{1}{k} + C \right), \quad (1)$$

where C is the volume fraction (in percent) of particles in suspension (or sol), α is the volume fraction of particles in the composite coating, M is atomic mass of metal, i_0 is the exchange current density of metal deposition, n is the number of electrons in the equation of electrochemical electrodeposition reaction, F is Faraday number, ρ_m is the density of metal, η is overvoltage of electrochemical metal deposition reaction, A is the constant in the kinetic equation of electrochemical reaction $i = i_0 e^{A\eta}$, k is the adsorption coefficient (constant of adsorption equilibrium in the Langmuir-type equation), and B and v_0 are the constants describing the kinetics of incorporation of the particles of nonmetallic phase into the composition

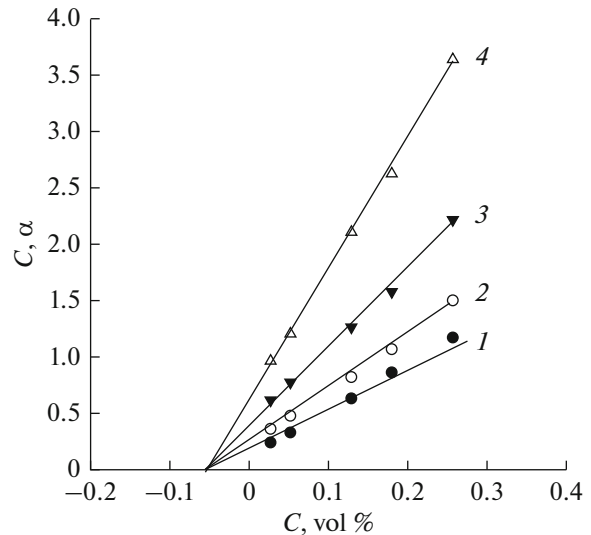


Fig. 3. Dependences $\frac{C}{\alpha} = f(C)$ for Ni/TiO₂ composite coatings electrodeposited at various current density values (A/dm²): (1) 1.0, (2) 1.5, (3) 2.0, and (4) 3.0.

coating and analogous to A and i_0 constants for electrochemical process.

As follows from Eq. (1), the dependences plotted in $\frac{C}{\alpha} = f(C)$ coordinates and obtained at different current density values should represent the family of lines that pass through the point with $\left(-\frac{1}{k}, 0\right)$ coordinates upon intersection with the x axis. Figure 3 demonstrates the data from this work plotted in test coordinates of $\frac{C}{\alpha} = f(C)$. It is clear that the dependences are linear and intersect at one point on x axis, which, on the one hand, could state that the Guglielmi model adequately describes the kinetics of codeposition of nickel and TiO₂ particles from the considered DES-based electrolyte and, on the other hand, provides the ability to determine the adsorption coefficient k graphically, which was 17.5.

It is interesting to compare the obtained value with the one previously calculated by Guglielmi for the deposition of Ni/TiO₂ composite coating from aqueous electrolyte: $k = 5.3$ [34]. It follows that there is a stronger adsorption of TiO₂ particles on the surface of growing nickel coating upon deposition from the DES-based electrolyte under study as compared to aqueous solution. The oxide particles of the disperse phase apparently compete less with water molecules in DES (even in the presence of a particular amount of added water) during adsorption on the surface of deposited hydrophilic nickel. Consequently, with other conditions being equal, employment of DES-based electrolytes could produce the composite coat-

Table 1. Surface coverage of the nickel matrix with titania particles during electrodeposition of composite coating due to weak (σ) and strong (θ) adsorption

Current density, A/dm ²	Concentration of TiO ₂ particles in electrolyte, vol %									
	0.026		0.051		0.128		0.179		0.256	
	σ	θ	σ	θ	σ	θ	σ	θ	σ	θ
1.0	0.279	0.109	0.398	0.156	0.552	0.203	0.600	0.208	0.640	0.218
1.5	0.290	0.072	0.421	0.107	0.584	0.156	0.631	0.168	0.679	0.170
2.0	0.300	0.042	0.441	0.066	0.622	0.101	0.672	0.113	0.724	0.115
3.0	0.305	0.027	0.452	0.042	0.650	0.061	0.706	0.068	0.761	0.070

ings with a larger content of the disperse phase, which is their advantage over conventional aqueous electrolytes.

Guglielmi's kinetic model suggests that the Langmuir adsorption isotherm can be written here as follows [34]:

$$\sigma = \frac{kC}{1 + kC}(1 - \theta), \quad (2)$$

where σ is the surface coverage of the growing metal matrix by the particles of the disperse phase due to weak adsorption (first stage) and θ is the surface coverage due to strong adsorption (second stage).

The surface coverage due to weak adsorption was evaluated using Eq. (2) with Guglielmi's assumption that the surface coverage due to strong adsorption is close to the volume fraction of the particles of the disperse phase in the composite coating (that is, $\theta \approx \alpha$) [34]. As follows from the results of calculations (Table 1), the surface coverage by particles due to weak adsorption is much higher than their bulk concentration in the composite deposit at all current density values and concentrations of TiO₂ in electrolyte. Thus, only a small part of weakly adsorbed particles is incorporated into the formed composite.

Table 2 shows the results of calculations of the slope ($\tan\phi$) of linear plots in $\frac{C}{\alpha} = f(C)$ coordinates for different current density values (Fig. 3). The following equation was previously derived for these dependences [34]:

$$\log(\tan\phi) = \log \frac{Mi_0 B/A}{nF\rho_m v_0} + \left(1 - \frac{B}{A}\right) \log i. \quad (3)$$

According to Eq. (3), the dependence plotted in $\log(\tan\phi) = f(\log i)$ coordinates is linear (Fig. 4) and its slope is $\left(1 - \frac{B}{A}\right)$. Because the ascending line was obtained (slope is +0.516), $(1 - B/A) > 0$, that is, $B < A$.

The same inequality was established during the study of electrodeposition of Ni/TiO₂ composite coating from aqueous suspension electrolyte [34] and it is typical of the processes in which the content of the

disperse phase in composite decreases with an increase in the current density (Fig. 2).

In addition to determining the quantitative patterns of codeposition of the particles of disperse phase upon formation of composite coating, it is interesting to reveal the character of the effect of adsorption of TiO₂ particles on the surface on the rate of electrochemical discharge of nickel ions. As follows from the data of Fig. 5, there is a significant shift of polarization curve with the incorporation of titania into the DES-based electrolyte, which characterizes nickel electrodeposition, into more negative potentials. This fact indicates the inhibition of discharge reaction of nickel ions by TiO₂. In this case, the degree of inhibition increases with an increase in the concentration of titania in electrolyte (and, consequently, on the cathode surface). In our opinion, partial hindrance of the electrode surface by the adsorbed particles of the disperse phase is the main reason for the observed inhibition of metal deposition.

X-ray diffractograms of the composite coatings of Ni/TiO₂ deposited from DES-based electrolyte show the reflexes of face-centered cubic lattice of nickel (diffraction peaks of (111), (200), (220), (311), and (222) planes), as well as reflexes of TiO₂ (anatase) (Fig. 6).

The surface of Ni/TiO₂ composite coatings obtained from the DES-based electrolyte is formed from a large number of spheroid crystallites of nickel with a small number of cracks (Fig. 7). Energy-dispersive X-ray analysis of the composition of surface layers

Table 2. Dependence of slope of lines plotted in $\frac{C}{\alpha} = f(C)$ coordinates on the density of deposition current

Current density, A/dm ²	$\tan\phi$
1.0	3.44
1.5	4.82
2.0	6.99
3.0	11.60

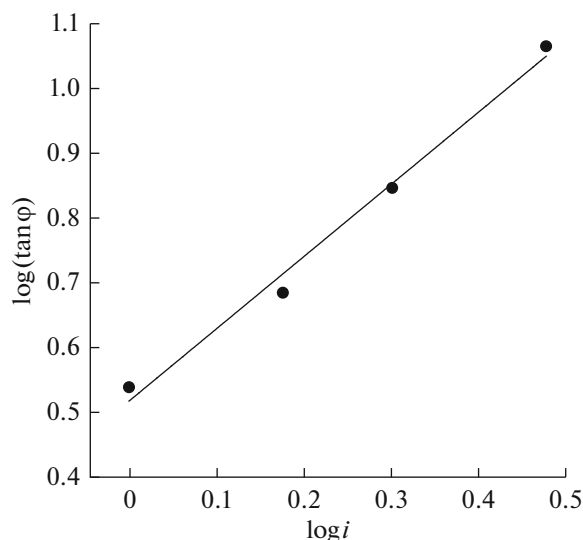


Fig. 4. Dependence in coordinates $\log(\tan \varphi) = f(\log i)$.

of composite coating showed the presence of such elements as nickel, titanium, and oxygen (Fig. 8).

Electrocatalytic Characteristics of Ni/TiO₂ Composite Coating in Hydrogen Evolution Reaction

It is known that electrodeposited nickel and its composites can be successfully used as electrocatalysts during electrocatalytic hydrogen production from aqueous alkaline solutions [36–38].

During incorporation of titania particles into the nickel matrix deposited from the DES-based electrolyte, polarization curves of hydrogen evolution on the obtained composite coatings shift towards more positive potential values (Fig. 9), which indicates the acceleration of the electrochemical reaction. The obtained dependences are rectified well in Tafel coordinates, from which the constants in the Tafel equation were calculated (a and b) as well as exchange current density (i_0) and transfer coefficients (α) of hydrogen evolution reaction (Table 3). It is evident that an increase in the exchange current density with the incorporation of TiO₂ particles into the nickel matrix indicates electrocatalytic effect.

It is considered that the mechanism of electrochemical evolution of hydrogen in aqueous alkaline

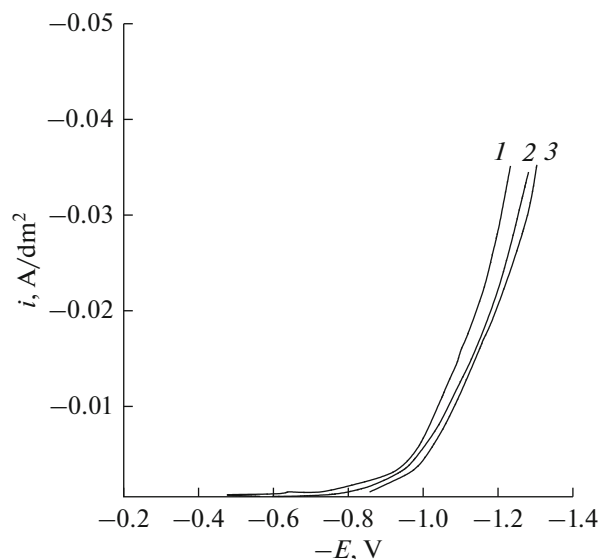
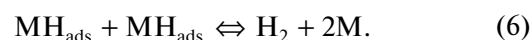


Fig. 5. Polarization curves recorded on nickel electrode in DES-based electrolyte at various contents of TiO₂ (g/dm³): (1) 0, (2) 5, and (3) 10. The potential scanning rate is 10 mV/s.

solutions involves several elementary steps [38]: hydrogen electro-reduction from water molecules with the formation of adsorbed hydrogen atoms (reaction (4), Volmer stage), electrochemical desorption (reaction (5), Heyrovsky stage), and so-called chemical desorption (reaction (6), Tafel stage).



Calculated values of the Tafel slope close to 120 mV (that is, transfer coefficients are about 0.5) indicate that the discharge step (4) is the rate-determining step of hydrogen evolution reaction, which is followed by the electrochemical desorption stage (5) [38, 39].

However, the method of polarization curves could not provide detailed information on the reasons for the change of electrocatalytic properties of the coating. Therefore, electrochemical impedance spectroscopy was employed in this work. Impedance measurements were carried out in 1 M NaOH solution at two values of hydrogen overvoltage: $\eta = -50$ mV and $\eta = -100$ mV

Table 3. Kinetic parameters of hydrogen evolution reaction on the coatings of nickel and Ni/TiO₂ composites in 1 M NaOH at 298 K

Electrode	a , V	b , V	i_0 , A/cm ²	α
Ni	-0.480	-0.128	1.78×10^{-4}	0.46
Ni/TiO ₂ (2 g/dm ³ TiO ₂ in electrolyte)	-0.412	-0.124	4.76×10^{-4}	0.48
Ni/TiO ₂ (5 g/dm ³ TiO ₂ in electrolyte)	-0.363	-0.122	1.06×10^{-3}	0.48

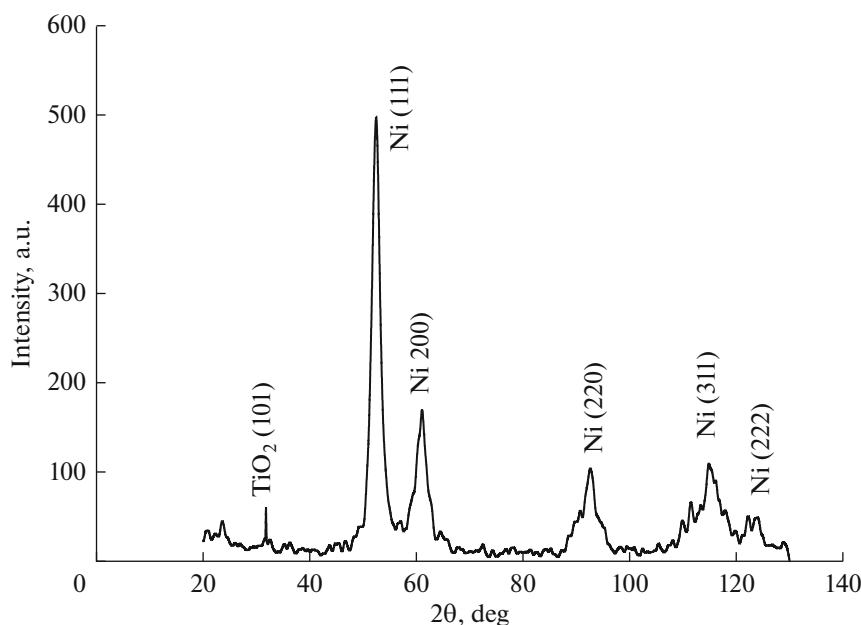


Fig. 6. X-ray diffractogram of Ni/TiO₂ composite coating deposited from DES-based electrolyte containing 5 g/dm³ TiO₂.

(equilibrium potential of hydrogen electrode was calculated according to Nernst equation based on the data on pH of electrolyte).

The obtained Nyquist plots (Fig. 10) represent deformed semi-circles, which indicate that the electrochemical process is controlled by the charge transfer stage and occurs on the nonuniform electrode surface. Such behavior can be described by the so-called constant-phase element (CPE) [40]. The equivalent electric circuit given in the inset of Fig. 10 was used for modeling. This equivalent circuit involves ohmic resistance of solution (R_s), polarization resistance of electrochemical reaction (R_{ct}), and constant-phase element (CPE).

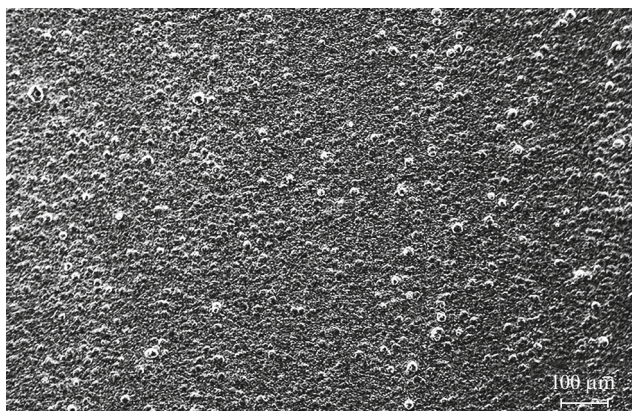


Fig. 7. SEM micrograph of the surface of Ni/TiO₂ composite coating deposited from DES-based electrolyte and containing 5 g/dm³ TiO₂.

It is known that the impedance of constant-phase element is determined as follows [41]:

$$Z_{CPE} = [Q(j\omega)^n]^{-1}, \quad (7)$$

where Q is a constant, $j = \sqrt{-1}$ is imaginary unit, ω is the angular frequency of alternating current, and n is the dimensionless empirical exponent caused by non-uniform electrode surface.

Experimental data in Fig. 10 are shown by points, while solid lines were obtained by approximation using the considered equivalent electric circuit. Calculated kinetic parameters are given in Table 4.

It should be considered during analysis of the obtained data that polarization resistance of electrochemical reaction (R_{ct}) can be considered as the parameter that unambiguously characterizes kinetic

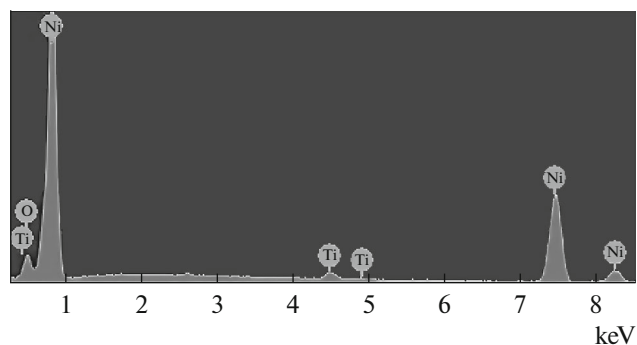


Fig. 8. Energy-dispersive X-ray spectrum of the surface of Ni/TiO₂ composite coating deposited from DES-based electrolyte and containing 5 g/dm³ TiO₂.

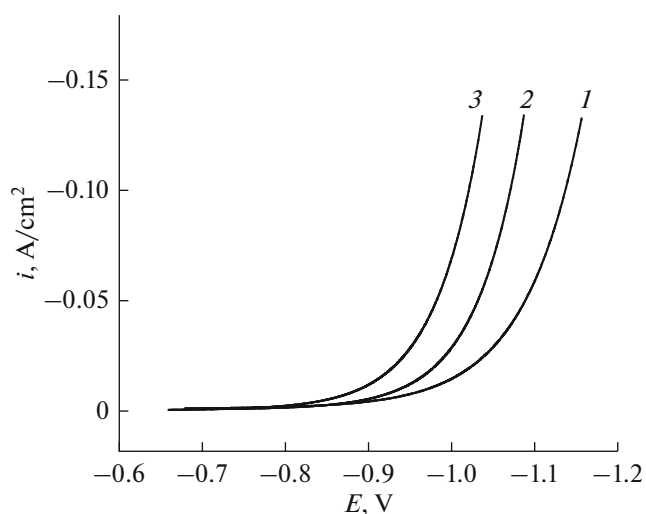


Fig. 9. Polarization curves of hydrogen evolution in 1 M NaOH at 298 K on the surface of electrocatalysts deposited from DES-based electrolytes: (1) nickel, (2) Ni/TiO₂ composite coating from electrolyte containing 2 g/dm³ TiO₂, and (3) Ni/TiO₂ composite coating from electrolyte containing 5 g/dm³ TiO₂. The potential scanning rate is 10 mV/s.

possibilities of electrochemical process. As could be anticipated, an increase in the cathode polarization decreases polarization resistance due to the decrease in the activation barrier of charge transfer. With other conditions being equal, incorporation of titania parti-

cles into the nickel matrix notably decreases the polarization resistance, which agrees well with the described increase in the exchange current density (Table 3) and confirms the increase in electrocatalytic activity of Ni/TiO₂ composite deposits as compared to that of nickel coating.

The dimensionless exponent n in Eq. (7) characterizes the degree of energy and geometrical heterogeneity of the electrode surface. In the case of “perfectly smooth” uniform surfaces (e.g., for the surface of liquid mercury electrode), $n = 1$. With an increase in the degree of surface heterogeneity, this parameter decreases. As follows from these data, the surface of nickel and nickel/titania electrodes is nonuniform ($n < 1$) and the degree of heterogeneity increases with the incorporation of TiO₂ particles into the metallic matrix (a decrease in n is observed).

Multiplier Q in Eq. (7) is often associated with the capacity of the double electric layer. For this reason, the change of parameter Q characterizes a corresponding change of the true electrode surface area (more specifically, the surface area available for electrochemical reaction). Comparing Q values for nickel and nickel/titania composite deposited from DES-based electrolyte, it can be stated that the highest values of Q correspond to lowest empirical constants n . Analysis of the data could state that an increase in the true area of electrode surface upon incorporation of titania particles into the nickel matrix (there is an increase in Q) is relatively low and certainly could not be the only reason for a significant decrease in the rate of hydro-

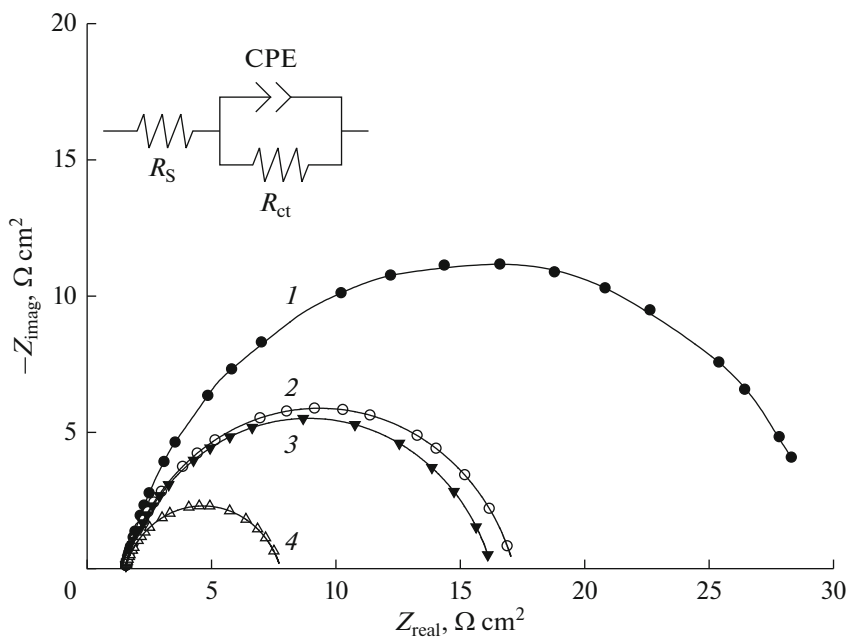


Fig. 10. Nyquist plots for hydrogen evolution reaction in 1 M NaOH at 298 K on the surface of electrocatalysts deposited from DES-based electrolytes: (1, 2) nickel and (3, 4) Ni/TiO₂ composite coating from electrolyte containing 5 g/dm³ TiO₂. Measurements were performed at the overvoltage of cathode hydrogen evolution (mV) of (1, 3) 50 and (2, 4) 100.

Table 4. Calculated parameters of electrochemical impedance of hydrogen evolution reaction on coatings with nickel and Ni/TiO₂ composites in 1M NaOH at 298 K

Electrode	Overvoltage η , mV	Parameters			
		R_s , Ω	R_{ct} , $\Omega \text{ cm}^2$	$Q \times 10^6$, $\Omega^{-1} \text{ cm}^2$	n
Ni	-50	1.5	28.4	114.5	0.848
	-100	1.5	15.6	125.6	0.816
Ni/TiO ₂ (5 g/dm ³ TiO ₂ in electrolyte)	-50	1.5	14.4	158.3	0.808
	-100	1.5	6.2	171.4	0.790

gen evolution reaction (that is, a decrease in polarization resistance). Thus, the discovered electrocatalytic effect of the Ni/TiO₂ composite coating is true and determined not only by the simple increase in the electrode surface area but also an increase in the concentration of active sites on the catalyst surface and/or increase in their activity.

Electrocatalytic effect of titania particles incorporated into the electrodeposited metal matrix is associated with the formation of additional active centers consisting of titania TiO₂ and its protonated forms on the electrode surface, in which redox pairs TiO₂ \leftrightarrow Ti₂O₃ \leftrightarrow TiOOH are realized [42–46]. It is known that the presence of redox couples on the electrode surface with metal ions in intermediate oxidation levels enhances electrocatalytic activity [47]. In addition, it was mentioned that, in spite of a relatively low electrocatalytic activity of titania, it can interact with the Fermi level of nickel due to its clear semiconductor properties and enhance its electrocatalytic activity [20].

CONCLUSIONS

(1) It has been shown that the composite coatings of Ni/TiO₂ containing up to 10 wt % titania can be deposited from deep eutectic solvent (eutectic mixture of choline chloride and ethylene glycol) containing 1 M NiCl₂·6H₂O and added water (total content is 15 mol/dm³), as well as disperse phase of TiO₂ (up to 10 g/dm³ of Degussa P 25 nanopowder). Experimental data on the dependence of the content of the particles of disperse phase in the coating on their concentration in electrolyte and current density are described well by the kinetic model suggested by Guglielmi. In this case, the adsorption coefficient $k = 17.5$ is much larger than the value previously calculated for the deposition of Ni/TiO₂ composite from aqueous electrolyte ($k = 5.3$). The latter indicates a stronger adsorption of TiO₂ particles on the surface of growing nickel coating upon deposition from DES-based electrolyte (as compared to aqueous systems). In this case, adsorption of titania particles on the surface leads to the inhibition of nickel ions' discharge.

(2) With experimental data of linear voltammetry and electrochemical impedance spectroscopy, we have shown that there is notable increase in the electrocatalytic activity of the coatings obtained upon incorporation of the particles of disperse phase of TiO₂ into the nickel matrix deposited in the DES-based electrolyte during cathode hydrogen evolution reaction in alkaline aqueous solution. An increase in the electrocatalytic activity is caused not only by the increase in the true area of electrode surface but also an increase in the concentration of active sites due to the formation of additional surface redox couples with titanium ions at intermediate oxidation states.

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CONFLICT OF INTEREST

The authors declare that they have no conflicts of interest.

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