

Article

Electrochemical Corrosion Behavior of Ni–TiO₂ Composite Coatings Electrodeposited from a Deep Eutectic Solvent-Based Electrolyte

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Abstract: The need to develop new electrochemical energy storage and conversion devices requires the creation of new, available, low-cost and high-performance electrocatalytic materials, which can be produced as coatings by electrodeposition technique. The electrodeposited composite coatings based on nickel seem to be very promising in this context. We studied the corrosion resistance of electrocatalytic Ni–TiO₂ composite coatings fabricated by electrodeposition method using a plating solution based on deep eutectic solvents, a new environmentally friendly and affordable type of room-temperature ionic liquids. We investigated the corrosion behavior of Ni and Ni–TiO₂ coatings (5 and 10 wt.% of TiO₂) in a 3% NaCl aqueous solution as a corrosive medium. The corrosion parameters were determined by linear voltammetry and electrochemical impedance spectroscopy. It was established that the inclusion of titania particles in the Ni matrix and an increase in their content in the coating leads to a shift in corrosion potential towards positive values, a decrease in corrosion current density and an increase in polarization resistance. The observed effects of improving the corrosion resistance of coatings are associated with the barrier action of particles of the dispersed phase and the formation of corrosion microcells contributing to the inhibition of local corrosion.

Keywords: composite coating; Ni–TiO₂ film; electrodeposition; deep eutectic solvent; corrosion characteristic



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1. Introduction

The development of up-to-date electrochemical energy storage and conversion devices requires the creation of new, available and high-performance materials with enhanced electrocatalytic activity [1,2]. Although electrocatalysts based on noble metals show high electrocatalytic activity, they are very expensive, and therefore the development of noble-metal-free electrocatalysts is a very topical issue in electrochemical materials science [3–5]. Among the great variety of different prospective electroactive materials, nickel and nickel-containing alloys and composites attract special attention [6–8] because they combine high catalytic activity with relatively low cost, stability, versatility (for instance, they are able to operate both as cathode and anode electrocatalysts), high corrosion and mechanical resistance, and the ability to synthesize and restore worn electrodes in such a simple and flexible method as electrolytic deposition from solutions. Moreover, nickel even in its oxidized form can be used as an oxygen evolution catalyst [9,10].

The nickel-based electrocatalytic coatings can be easily prepared by the electrodeposition method using various kinds of plating electrolytes [6,7]. Ni-containing plating baths based on deep eutectic solvents (DESs) attract special attention. DESs are a novel kind of room-temperature ionic liquids, characterized by a wide electrochemical window, high fluidity and electroconductivity, negligible volatility, non-flammability, cheapness,

affordability and environmental safety [11–14]. Due to their numerous advantages, electrochemical systems based on the application of DESs seem to be very promising in different electrochemical processes, especially in deposition of metals, alloys and composites [11]. In particular, it has been shown that nickel and composite nickel–titania coatings, electrochemically fabricated using DES-based electrolytes, demonstrate high electrocatalytic activity towards the reaction of hydrogen evolution in an alkaline solution [15–17]. It should be noted that DESs show higher viscosity than aqueous electrolytes, thereby hindering the sedimentation and aggregation of disperse particles and having a favorable effect on the electrochemical synthesis of composite electrodeposits [16,17]. Thus, the deposition of composite nickel–titania coatings using DES-assisted electrochemical systems has a number of distinct advantages over “common” aqueous plating solutions [18–20].

Evidently, the study of the corrosion resistance of an electrocatalytic material is an integral part and mandatory stage of the development of any electrocatalyst [21], since the rate of corrosion destruction largely determines the duration of its uninterrupted operation. The electrochemical corrosion behavior of nickel–titania layers electrodeposited using DES-assisted plating baths has not yet been described in the literature. Therefore, this work was devoted to elucidating the features and patterns of electrochemical corrosion of composite coating Ni–TiO₂ electrodeposited from DES-based colloidal solutions. By using the linear voltammetric method and electrochemical impedance spectroscopy technique, we established that the improvement in the corrosion stability of composite Ni–TiO₂ films compared to “pure” Ni coatings is associated with the barrier action of dispersed particles and the appearance of a large number of corrosion microcells.

2. Materials and Methods

The so-called ethaline was used in this study as a basis for the preparation of electrolytes for the deposition of nickel and nickel–titania coatings. Ethaline, as a typical representative of DESs, is a mixture of choline chloride and ethylene glycol (the mole ratio being 1:2, respectively), and its detailed preparation is available in the literature [22,23]. To obtain a Ni(II)-containing plating solution, NiCl₂·6H₂O (1 mol dm^{−3}) was dissolved in the synthesized DES under heating (343 K) and stirring, and water (6 mol dm^{−3}) was added, the presence of which helps to reduce the viscosity, increase the electrical conductivity of the system and increase the content of the titania particulates in the formed deposits [16]. TiO₂ was introduced into the plating bath as nanopowder Degussa P 25 (containing mainly anatase, average particle size being 25 nm [24]). To ensure uniform distribution of colloidal particles in the solution and to prevent aggregation, the solution was subjected to ultrasonic treatment for one hour (340 W dm^{−3}, 22.4 kHz).

Electrodeposition of coatings in galvanostatic mode (10 mA cm^{−2}) was performed on samples made of copper foil ($S = 1 \text{ cm}^2$) that were degreased and activated in a solution of hydrochloric acid. Nickel plates served as a counter electrode. During electrodeposition, the plating solution was thermostated (313 K) and agitated by means of a magnetic stirrer (500 rpm). The duration of deposition (1.6 h) was selected so that the coating thickness was about 20 μm.

Corrosion parameters of coatings were evaluated by linear voltammetry and electrode impedance spectroscopy. The corrosive medium was a 3% NaCl water solution at the temperature of 298 K under natural aeration. Electrochemical studies were conducted using a Potentiostat Reference 3000 (Gamry, Warminster, PA, USA). The counter electrode in these experiments was a platinum mesh. The saturated Ag/AgCl-electrode served as a reference electrode, all potentials being converted into the scale of a standard H₂ electrode. The electrode impedance was measured at a steady state after 30 min of exposure of the test electrode in a corrosive environment. In preliminary experiments, we found that this duration of exposure is sufficient to establish a virtually stationary value of the corrosion potential. The electrode impedance was determined in the AC frequency range of 10⁵ to 10^{−2} Hz, the amplitude being 0.005 V.

A scanning electron microscope Zeiss EVO 40XVP was utilized to characterize the surface morphology of the electrodeposited coatings. Energy-dispersive X-ray spectroscopy technique was applied to establish the chemical composition of the electrochemically synthesized coatings.

3. Results

3.1. Electrodeposition of Composite Nickel–Titania Coatings

As follows from the experimental data (Figure 1), the percentage of the TiO_2 dispersed phase in the resulting composite coatings grows with an increase in the weight content of titanium dioxide in the plating solution. However, when a certain threshold concentration is reached, a limit value of TiO_2 content in the coating is reached, which is about 10 wt.% at the applied current density of 10 mA cm^{-2} . This dependence is typical of many types of electrodeposited composites [25,26]; it is explained by the fact that the adsorption of a dispersed phase on the surface of a deposited film, which precedes the introduction of these particles into the coating, obeys the Langmuir type isotherm equation [16].

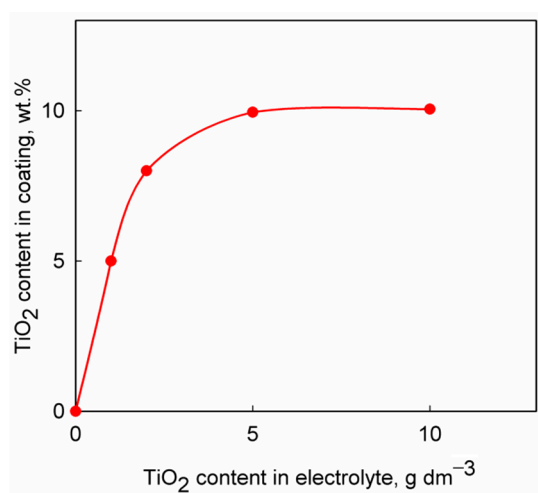


Figure 1. Variation in the content of titania in composite coatings with TiO_2 concentration in the colloidal plating solution.

Earlier, it was shown [22] that the maximum available concentration of TiO_2 particles in the nickel–titania composite films electrodeposited from ethaline-assisted plating systems without the addition of H_2O is no more than 2.35 wt.%. The data obtained in this work exhibit that the addition of H_2O to the colloidal solution allows growing the content of the dispersed phase in composites layers and, consequently, their electrocatalytic activity [16]. For further studies of corrosion characteristics, three following coatings were selected that differ in the concentration of the disperse phase: “pure” nickel layers and composite films with a content of dispersed oxide phase of 5 and 10 wt.%. These coatings are designated as Ni, Ni– TiO_2 (5%) and Ni– TiO_2 (10%), respectively. Figure 1 shows that the electrodeposits with such compositions can be prepared from electrolytes with the titania content of 0, 1 and 10 g dm^{-3} , respectively.

Figure 2 demonstrates typical SEM images and EDX spectra of the coatings under consideration. The surface of the nickel coating is formed of spheroids with a diameter of ca. $5\text{--}15 \mu\text{m}$ (Figure 2a). A network of cracks can also be detected on the surface. When titania particulates are embedded in the nickel matrix, an appreciable smoothing of the surface profile is observed, and the size of the spheroids forming the metal layer decreases (Figure 2b,c). The number and thickness of cracks also decrease. The surface of electrodeposits with the maximum content of the dispersed phase Ni– TiO_2 (10%) is rather uniform. It should be noted that no dispersed phase particles were detected in SEM microphotographs, probably owing to the nanoscale dimensions of these particulates. However, the presence of titanium dioxide in coatings is convincingly evidenced by the

registered EDX spectra, which detect peaks of Ti and O in a quantitative ratio close to the stoichiometric composition of TiO_2 (Figure 2d).

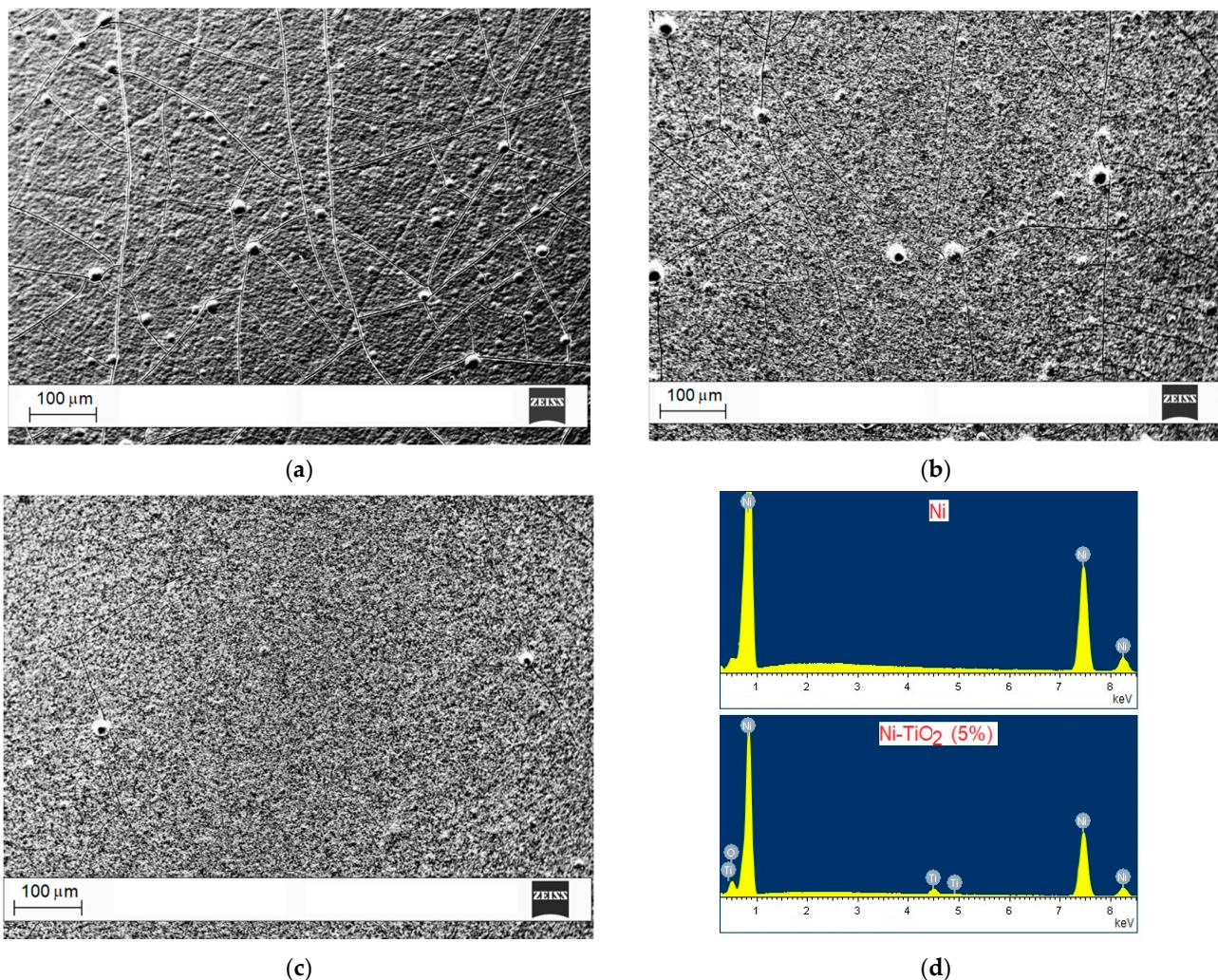


Figure 2. (a–c) SEM microphotographs of coatings electrodeposited from electrolytes based on ethaline: (a) Ni, (b) Ni-TiO₂(5%) and (c) Ni-TiO₂(10%); (d) typical EDX spectra of Ni and Ni-TiO₂(5%) coatings.

3.2. Corrosion Performance of Composite Nickel–Titania Coatings

Polarization curves characterizing the corrosion behavior of nickel and nickel–titania electrodeposits in a corrosive medium of 3% NaCl are demonstrated in Figure 3, and the corresponding corrosion characteristics (E_{corr} are the corrosion potentials, j_{corr} are the corrosion current densities, and β_a are the Tafel slopes of anodic segments of j vs. E curves) are summarized in Table 1. Let us note that the corrosion current density was found by extrapolation of Tafel dependences plotted for the anodic sections to the experimentally measured corrosion potentials (i.e., OCPs). The obtained data show that the corrosion potential increases and the corrosion current density decreases when TiO_2 particles are included in the nickel matrix when their content increases. The obtained results are generally consistent with those relating to the corrosion behavior of composite nickel–titania coatings reported previously for aqueous deposition electrolytes [27–29]. For instance, the calculated values of anodic Tafel slopes (β_a) are similar to those determined previously for the corrosion of Ni and its composites electrochemically deposited from common Watts nickel plating baths [30].

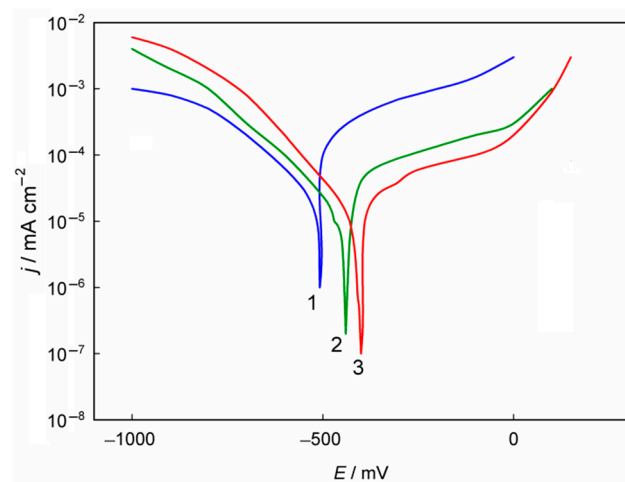


Figure 3. Polarization curves characterizing electrochemical behavior of Ni (1), Ni-TiO₂(5%) (2) and Ni-TiO₂(10%) (3) coatings in a 3% NaCl aqueous solution. Potential scan rate was 1 mV s⁻¹.

Table 1. Corrosion parameters of nickel and nickel–titania coatings in a 3% NaCl water solution determined from the results of potentiodynamic measurements.

Coating Type	E_{corr} (mV)	j_{corr} (mA cm ⁻²)	β_a (mV dec ⁻¹)
Ni	−508	9.31×10^{-6}	110
Ni-TiO ₂ (5%)	−451	3.45×10^{-6}	113
Ni-TiO ₂ (10%)	−408	1.28×10^{-6}	112

To gain more detailed information on the features of corrosion destruction of nickel and nickel–titania coatings deposited from an ethaline-based solution, spectra of electrochemical impedance were recorded at a stationary corrosion potential (Figure 4a). The obtained Nyquist diagrams resemble compressed semicircles, indicating that the rate of an electrode process is governed by the stage of charge transfer and the corrosion reaction occurs on an inhomogeneous surface. Given these circumstances, an equivalent circuit including polarization resistance (R_{ct}), constant phase element (with two parameters, Q and n) and ohmic drop in the solution (R_s) was used to quantify the data of electrochemical impedance measurements (Figure 4b) [23,31]. The defined parameters of individual elements in the equivalent circuit are given in Table 2.

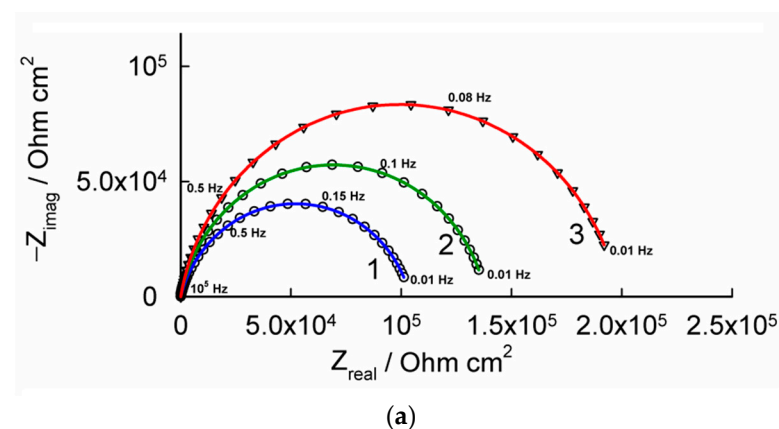


Figure 4. (a) Nyquist plots characterizing corrosion of Ni (1), Ni-TiO₂(5%) (2) and Ni-TiO₂(10%) (3) coatings in a 3% NaCl aqueous solution at 298 K; (b) adopted equivalent circuit.

Table 2. Parameters of equivalent circuit calculated according to the adopted equivalent circuit for corrosion of nickel and nickel–titania electrodeposited films in a 3% NaCl water solution at 298 K.

Coating Type	Parameters of Equivalent Circuit			
	R_s (Ω)	R_{ct} ($k\Omega\text{ cm}^2$)	$Q \times 10^6$ ($\Omega^{-1}\text{ s}^n\text{ cm}^{-2}$)	n
Ni	8.3	104.1	8.64	0.84
Ni–TiO ₂ (5%)	8.2	138.4	7.32	0.88
Ni–TiO ₂ (10%)	8.4	198.7	7.17	0.89

4. Discussion

A reduction in the corrosion current density and a growth in the corrosion potential, resulting from the introduction of the TiO₂ dispersed phase into the nickel matrix (Table 1), suggest an increase in the corrosion stability of composite coatings as compared to “pure” Ni electrodeposits. Discussing the reasons for the observed growth in corrosion resistance of coatings, it should be noted that, first of all, TiO₂ particles, filling pores and cracks in the coating and partially blocking the active metal surface, protect the metal surface from contact with aggressive media and thus help to reduce the rate of anodic dissolution of nickel and its corrosion destruction [27–29]. In addition, it should be borne in mind that titanium dioxide particles cannot be considered completely inactive from an electrochemical point of view. The introduction of the dispersed phase of TiO₂ particulates in the coating stimulates the formation of a large number of surface corrosion microcells, in which nanoparticles of titanium dioxide are cathode regions and Ni matrix regions act as an anode (standard potential of the Ti(IV)/Ti(III) couple is more positive than that of the Ni(II)/Ni(0) couple) [27]. This phenomenon results in a positive shift in the corrosion potential and prevention of localized corrosion.

The polarization resistance (R_{ct}) of the corrosion dissolution determined from the electrochemical impedance measurements increases with embedding the colloidal TiO₂ particulates in the metal matrix and with increasing their content in the composite from 5 to 10 wt.% (Table 2). It should be observed that the polarization resistance of the electrochemical process is given as follows [32]:

$$R_{ct} = \lim_{\omega \rightarrow 0} R(Z_f), \quad (1)$$

where $R(Z_f)$ is the real part of faradaic impedance Z_f at the frequency tending to zero.

The value of R_{ct} is associated with the Faraday current of an electrochemical process [33]. A decrease in the value of R_{ct} indicates the acceleration of the charge transfer.

Thus, the data obtained indicate an increase in corrosion stability of electrodeposits. Probably, this is caused by the partial overlap of the TiO₂ nanoparticles with the active centers on the surface of the metal, which are subject to corrosion dissolution.

Another element of the adopted equivalent circuit, the constant phase element, implies that its electrochemical impedance is determined by the following equation [34]:

$$Z_{CPE} = [Q(j\omega)^n]^{-1}, \quad (2)$$

where Q is a coefficient relating to the electrode capacity, $j = \sqrt{-1}$ is the imaginary unit, $\omega = 2\pi f$ is the angular frequency and n is a dimensionless parameter.

It is known that increasing the value of Q suggests that the exposed coating area is expanded [35]. Very low values of the capacitive parameter Q (compared to the “classical” capacity of the double layer on the mercury electrode) are characteristic of corrosion of nickel and its composites in NaCl solution; they can be ascribed to the existence of a thin dense oxide layer with low dielectric constant on the metal surface [30].

As far as the dimensionless exponent n is concerned, its value commonly varies in the range of 0 to 1 [36,37]. If $n = 0$, then the constant phase element describes an ideal resistor,

and if $n = 1$, then the constant phase element implies an ideal capacitor. As follows from the experimental data (Table 2), there is a decrease in the capacitive parameter Q and an increase in the dimensionless value n , which characterizes the degree of geometric and energy inhomogeneity of the surface, with an increase in the concentration of titania in the electrodeposited composite film. This conclusion well correlates with leveling the surface profile observed in the SEM study (Figure 2a–c). All these observations taken together convincingly testify to the smoothing of the surface profile and homogenization of the electrode surface. Evidently, these factors contribute to lowering the rate of corrosion processes.

A thorough analysis of the reason for the high anticorrosion behavior of the electrodeposited TiO_2 nanoparticle reinforced Ni coatings [27] allowed establishing that the incorporated TiO_2 particulates improve corrosion stability via three main mechanisms. First of all, these particulates provide inert physical barriers preventing the contact between the corrosive environment and the metal surface. In addition to a barrier effect, dispersion of titania nanoparticles in the nickel metal matrix leads to the appearance of corrosion microcells, in which the titania particulates serve as the cathode and the regions of the metal matrix act as the anode. Since the nanoparticles of a dispersed phase in these corrosion microcells are evenly spaced in the metal matrix, this contributes to the homogenization of the surface state and deceleration of local corrosion. Finally, the presence of titania nanoparticles increases the length of current paths during electrochemical corrosion of a metal substrate as compared with pure Ni coatings. Obviously, all these mechanisms should be implemented in the case under consideration, providing increased corrosion resistance of Ni– TiO_2 composite coatings fabricated using DES-based solutions.

5. Conclusions

It was determined that the inclusion of TiO_2 particulates in the Ni matrix during electrochemical deposition from the deep eutectic solvent ethaline leads to enhanced corrosion resistance of coatings: there is a reduction in the corrosion current density and a growth in the polarization resistance. Our findings clearly show that in the series of coatings Ni, Ni– TiO_2 (5%) and Ni– TiO_2 (10%), deposited from a DES-assisted plating bath, there is an increase in corrosion resistance to electrochemical corrosion in aggressive environments of 3% aqueous solution of NaCl.

Thus, nickel–titania composite coatings fabricated from DES-based colloidal solutions not only show previously established enhanced electrocatalytic activity towards the electrode reactions occurring during water electrolysis, but also exhibit increased corrosion resistance compared to “pure” nickel, thereby ensuring high stability and service life. These results allow us to conclude that the composite nickel–titania deposits produced via DES-assisted plating processes demonstrate tremendous potential for real applications as electrocatalysts in “green” hydrogen energy.

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References

1. Grigoriev, S.A.; Fateev, V.N.; Bessarabov, D.G.; Millet, P. Current status, research trends, and challenges in water electrolysis science and technology. *Int. J. Hydrogen Energy* **2020**, *45*, 26036–26058. [\[CrossRef\]](#)
2. Kovač, A.; Paranos, M.; Marciuš, D. Hydrogen in energy transition: A review. *Int. J. Hydrogen Energy* **2021**, *46*, 10016–10035. [\[CrossRef\]](#)
3. Mohammed-Ibrahim, J.; Sun, X. Recent progress on earth abundant electrocatalysts for hydrogen evolution reaction (HER) in alkaline medium to achieve efficient water splitting—A review. *J. Energy Chem.* **2019**, *34*, 111–160. [\[CrossRef\]](#)
4. Safizadeh, F.; Ghali, E.; Houlachi, G. Electrocatalysis developments for hydrogen evolution reaction in alkaline solutions—A review. *Int. J. Hydrogen Energy* **2015**, *40*, 256–274. [\[CrossRef\]](#)
5. Jamesh, M.I. Recent progress on earth abundant hydrogen evolution reaction and oxygen evolution reaction bifunctional electrocatalyst for overall water splitting in alkaline media. *J. Power Source* **2016**, *333*, 213–236. [\[CrossRef\]](#)
6. Vij, V.; Sultan, S.; Harzandi, A.M.; Meena, A.; Tiwari, J.N.; Lee, W.G.; Yoon, T.; Kim, K.S. Nickel-based electrocatalysts for energy related applications: Oxygen reduction, oxygen evolution, and hydrogen evolution reactions. *ACS Catal.* **2017**, *7*, 7196–7225. [\[CrossRef\]](#)
7. Li, R.; Li, Y.; Yang, P.; Wang, D.; Xu, H.; Wang, B.; Meng, F.; Zhang, J.; An, M. Electrodeposition: Synthesis of advanced transition metal-based catalyst for hydrogen production via electrolysis of water. *J. Energy Chem.* **2021**, *57*, 547–566. [\[CrossRef\]](#)
8. Gong, M.; Wang, D.Y.; Chen, C.C.; Hwang, B.J.; Dai, H. A mini review on nickel-based electrocatalysts for alkaline hydrogen evolution reaction. *Nano Res.* **2016**, *9*, 28–46. [\[CrossRef\]](#)
9. Fruehwald, H.M.; Moghaddam, R.B.; Melino, P.D.; Ebraldizze, I.I.; Zenkina, O.V.; Easton, E.B. Ni on graphene oxide: A highly active and stable alkaline oxygen evolution catalyst. *Catal. Sci. Technol.* **2021**, *11*, 4026–4033. [\[CrossRef\]](#)
10. Juodkazis, K.; Juodkazyte, J.; Vilkauskaitė, R.; Jasulaitiene, V. Nickel surface anodic oxidation and electrocatalysis of oxygen evolution. *J. Solid State Electrochem.* **2008**, *12*, 1469–1479. [\[CrossRef\]](#)
11. Smith, E.L.; Abbott, A.P.; Ryder, K.S. Deep eutectic solvents (DESs) and their applications. *Chem. Rev.* **2014**, *114*, 11060–11082. [\[CrossRef\]](#) [\[PubMed\]](#)
12. Zhang, Q.; Vigier, K.D.O.; Royer, S.; Jérôme, F. Deep eutectic solvents: Syntheses, properties and applications. *Chem. Soc. Rev.* **2012**, *41*, 7108–7146. [\[CrossRef\]](#) [\[PubMed\]](#)
13. Hansen, B.B.; Spittle, S.; Chen, B.; Poe, D.; Zhang, Y.; Klein, J.M.; Horton, A.; Adhikari, L.; Zelovich, T.; Doherty, B.W.; et al. Deep eutectic solvents: A review of fundamentals and applications. *Chem. Rev.* **2021**, *121*, 1232–1285. [\[CrossRef\]](#) [\[PubMed\]](#)
14. Abbott, A.P.; Edler, K.J.; Page, A.J. Deep eutectic solvents—The vital link between ionic liquids and ionic solutions. *J. Chem. Phys.* **2021**, *155*, 150401. [\[CrossRef\]](#)
15. Wang, S.; Zou, X.; Lu, Y.; Rao, S.; Xie, X.; Pang, Z.; Lu, X.; Xu, Q.; Zhou, Z. Electrodeposition of nano-nickel in deep eutectic solvents for hydrogen evolution reaction in alkaline solution. *Int. J. Hydrogen Energy* **2018**, *43*, 15673–15686. [\[CrossRef\]](#)
16. Protsenko, V.S.; Bogdanov, D.A.; Korniy, S.A.; Kityk, A.A.; Baskevich, A.S.; Danilov, F.I. Application of a deep eutectic solvent to prepare nanocrystalline Ni and Ni/TiO₂ coatings as electrocatalysts for the hydrogen evolution reaction. *Int. J. Hydrogen Energy* **2019**, *44*, 24604–24616. [\[CrossRef\]](#)
17. Protsenko, V.S.; Butyrina, T.E.; Bobrova, L.S.; Danilov, F.I. Preparation and characterization of Ni–TiO₂ composites electrodeposited from an ethylene glycol-based deep eutectic solvent. *Mater. Today Proc.* **2022**, in press. [\[CrossRef\]](#)
18. Thiemi, D.; Bund, A. Characterization of electrodeposited Ni–TiO₂ nanocomposite coatings. *Surf. Coat. Technol.* **2008**, *202*, 2976–2984. [\[CrossRef\]](#)
19. Chen, W.; He, Y.; Gao, W. Electrodeposition of sol-enhanced nanostructured Ni–TiO₂ composite coatings. *Surf. Coat. Technol.* **2010**, *204*, 2487–2492. [\[CrossRef\]](#)
20. Chen, W.; Gao, W. Sol-enhanced electroplating of nanostructured Ni–TiO₂ composite coatings—The effects of sol concentration on the mechanical and corrosion properties. *Electrochim. Acta* **2010**, *55*, 6865–6871. [\[CrossRef\]](#)
21. Khan, M.A.; Zhao, H.; Zou, W.; Chen, Z.; Cao, W.; Fang, J.; Xu, J.; Zhang, L.; Zhang, J. Recent progresses in electrocatalysts for water electrolysis. *Electrochem. Energy Rev.* **2018**, *1*, 483–530. [\[CrossRef\]](#)
22. Danilov, F.I.; Kityk, A.A.; Shaiderov, D.A.; Bogdanov, D.A.; Korniy, S.A.; Protsenko, V.S. Electrodeposition of Ni–TiO₂ composite coatings using electrolyte based on a deep eutectic solvent. *Surf. Eng. Appl. Electrochem.* **2019**, *55*, 138–149. [\[CrossRef\]](#)
23. Danilov, F.I.; Protsenko, V.S.; Kityk, A.A.; Shaiderov, D.A.; Vasil'eva, E.A.; Kumar, U.P.; Kennady, C.J. Electrodeposition of nanocrystalline nickel coatings from a deep eutectic solvent with water addition. *Prot. Met. Phys. Chem. Surf.* **2017**, *53*, 1131–1138. [\[CrossRef\]](#)
24. Ohtani, B.; Prieto-Mahaney, O.O.; Li, D.; Abe, R. What is Degussa (Evonik) P25? Crystalline composition analysis, reconstruction from isolated pure particles and photocatalytic activity test. *J. Photochem. Photobiol. A* **2010**, *216*, 179–182. [\[CrossRef\]](#)
25. Low, C.T.J.; Wills, R.G.A.; Walsh, F.C. Electrodeposition of composite coatings containing nanoparticles in a metal deposit. *Surf. Coat. Technol.* **2006**, *201*, 371–383. [\[CrossRef\]](#)
26. Walsh, F.C.; Larson, C. Towards improved electroplating of metal-particle composite coatings. *Trans. IMF* **2020**, *98*, 288–299. [\[CrossRef\]](#)
27. Shao, W.; Nabb, D.; Renevier, N.; Sherrington, I.; Fu, Y.; Luo, J. Mechanical and anti-corrosion properties of TiO₂ nanoparticle reinforced Ni coating by electrodeposition. *J. Electrochem. Soc.* **2012**, *159*, D671–D676. [\[CrossRef\]](#)

28. Baghery, P.; Farzam, M.; Mousavi, A.B.; Hosseini, M. Ni-TiO₂ nanocomposite coating with high resistance to corrosion and wear. *Surf. Coat. Technol.* **2010**, *204*, 3804–3810. [[CrossRef](#)]
29. Mohajeri, S.; Dolati, A.; Ghorbani, M. The influence of pulse plating parameters on the electrocodeposition of Ni-TiO₂ nanocomposite single layer and multilayer structures on copper substrates. *Surf. Coat. Technol.* **2015**, *262*, 173–183. [[CrossRef](#)]
30. Szczygiel, B.; Kolodziej, M. Corrosion resistance of Ni/Al₂O₃ coatings in NaCl solution. *Trans. IMF* **2005**, *83*, 181–187. [[CrossRef](#)]
31. Danilov, F.I.; Tsurkan, A.V.; Vasil'eva, E.A.; Protsenko, V.S. Electrocatalytic activity of composite Fe/TiO₂ electrodeposits for hydrogen evolution reaction in alkaline solutions. *Int. J. Hydrogen Energy* **2016**, *41*, 7363–7372. [[CrossRef](#)]
32. Macdonald, D.D. Review of mechanistic analysis by electrochemical impedance spectroscopy. *Electrochim. Acta* **1990**, *35*, 1509–1525. [[CrossRef](#)]
33. Yao, Z.; Jiang, Z.; Xin, S.; Sun, X.; Wu, X. Electrochemical impedance spectroscopy of ceramic coatings on Ti-6Al-4V by micro-plasma oxidation. *Electrochim. Acta* **2005**, *50*, 3273–3279. [[CrossRef](#)]
34. Rammelt, U.; Reinhard, G. On the applicability of a constant phase element (CPE) to the estimation of roughness of solid metal electrodes. *Electrochim. Acta* **1990**, *35*, 1045–1049. [[CrossRef](#)]
35. He, D.; Li, G.; Shen, D.; Guo, C.; Ma, H.; Cai, J. Effect mechanism of ultrasound on growth of micro-arc oxidation coatings on A96061 aluminum alloy. *Vacuum* **2014**, *107*, 99–102. [[CrossRef](#)]
36. Sayar, P.N.; Bahrololoom, M.E. Comparison of anodic dissolution, surface brightness and surface roughness of nanocrystalline nickel coatings with conventional decorative chromium coatings. *J. Appl. Electrochem.* **2009**, *39*, 2489–2496. [[CrossRef](#)]
37. Kaseem, M.; Yang, H.W.; Ko, Y.G. Toward a nearly defect-free coating via high-energy plasma sparks. *Sci. Rep.* **2017**, *7*, 2378. [[CrossRef](#)]