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V.S. Protsenko^a, *D.O. Makhota*^a, *T.E. Butyrina*^a, *S.A. Korniy*^b, *F.I. Danilov*^a**ANODIC SURFACE TREATMENT OF NICKEL IN EUTECTIC IONIC LIQUIDS BASED ON CHOLINE CHLORIDE FOR ELECTROCHEMICAL POLISHING AND ENHANCEMENT OF ELECTROCATALYTIC ACTIVITY IN HYDROGEN EVOLUTION REACTION**^a Ukrainian State University of Chemical Technology, Dnipro, Ukraine^b Karpenko Physico-Mechanical Institute of the NAS of Ukraine, Lviv, Ukraine

The paper reports the impact of anodic potentiostatic treatment of nickel in two representatives of a new type of eutectic ionic liquids (deep eutectic solvents), ethaline and reline, which are eutectic mixtures of choline chloride with ethylene glycol and urea, respectively. The influence of anodic treatment on surface morphology, roughness coefficients, and electrocatalytic activity towards the hydrogen evolution reaction is characterized. It is demonstrated that the current densities of nickel anodic dissolution in reline are approximately an order of magnitude lower than in ethaline under all other identical conditions. Significant differences in the kinetics of nickel anodic dissolution and passivation during anodic polarization in ethaline and reline have been established, which may be attributed to both a substantial difference in the viscosity of these solvents and differences in the chemical nature and composition of the ions present in them. It is found that anodic treatment in ethaline, at certain potentials, results in electrochemical polishing of the surface, confirmed by a decrease in measured roughness coefficients, while anodic treatment in reline does not allow effective electropolishing and only surface etching (increase in roughness coefficients) is observed. Anodic potentiostatic treatment of nickel in both investigated deep eutectic solvents at specific electrode potential values significantly enhances the electrocatalytic activity of the surface towards the hydrogen evolution reaction in an alkaline environment. This finding can be utilized in the development of electrocatalytic materials for the electrolytic synthesis of green hydrogen.

Keywords: nickel, anodic treatment, deep eutectic solvent, surface morphology, electropolishing, electrocatalysis, hydrogen evolution reaction.

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Introduction

The development of new highly active electrocatalysts for the electrolytic synthesis of hydrogen is one of the primary goals in modern electrochemical materials science [1]. Nickel and nickel-containing electrode materials meet most of the requirements imposed on electrocatalysts for water electrolysis: they are inexpensive, readily available, and corrosion- and mechanically resistant under operating conditions. Nickel catalysts exhibit high activity for both the cathodic hydrogen evolution reaction and the anodic

oxygen evolution reaction [2]. However, the challenge of enhancing the electrocatalytic activity of nickel and nickel-containing electrocatalysts remains relevant. One effective approach to address this challenge is electrochemical surface modification. In our previous studies, it has been demonstrated that the activity of electrocatalysts based on nickel-copper alloy can be increased through their electrochemical anodic treatment in electrolytes based on a new type of eutectic ionic liquids, known as deep eutectic solvents (DESS) [3,4]. Currently, DESS are considered highly promising

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Anodic surface treatment of nickel in eutectic ionic liquids based on choline chloride for electrochemical polishing and enhancement of electrocatalytic activity in hydrogen evolution reaction

media for various applications in a range of processes and technologies, serving as an alternative to traditional aqueous solutions and organic solvents [5].

While it was previously established that the anodic potentiostatic treatment of nickel-copper alloy in the so-called ethaline (a typical representative of DESs, a eutectic mixture of ethylene glycol and choline chloride) under certain electrolysis conditions allows for electrochemical surface polishing and reducing the overpotential for hydrogen evolution in 1 M NaOH aqueous solution, questions remained unanswered regarding the impact of anodic treatment of «pure» nickel in DESs on its surface morphology and electrocatalytic behavior. This particular set of questions is addressed in the present study. The anodic treatment of nickel was investigated in both ethaline and reline (another typical representative of DESs, which is a eutectic mixture of urea and choline chloride).

Experimental

The procedure for preparing the ethaline and reline solvents, which are eutectic mixtures of choline chloride (33.33 mol.%) with ethylene glycol or urea, respectively (66.67 mol.%), involved thorough mixing of the components on a magnetic stirrer at a temperature of approximately 70°C until the formation of a homogeneous clear liquid [3–5]. The residual water content, determined by the Fischer method, did not exceed 1%.

Nickel samples were prepared from nickel foil (99.9% Ni) with a thickness of 1 mm, and the surface area subjected to anodic treatment was 1 cm². Before electrochemical treatment, the nickel samples were degreased with a water suspension of MgO, thoroughly rinsed in distilled water, and dried in a stream of air. Electrochemical investigations were conducted using a Potentiostat/Galvanostat/ZRA Reference 3000 (Gamry, USA) in a glass electrochemical cell at a temperature of 25°C. For anodic potentiostatic treatment in ethaline and reline, and recording the corresponding voltammetric responses of nickel anodic dissolution, a graphite counter electrode and a silver reference electrode were used. In the study of the electrocatalytic activity of the DES-treated nickel samples in a 1 M NaOH aqueous solution (temperature 25°C), a platinum counter electrode and a saturated silver chloride reference electrode were used. When processing the obtained dependences in coordinates of Tafel equation, the potentials were converted to the standard hydrogen electrode scale.

The Zeiss EVO 40XVP scanning electron microscope with an integrated energy-dispersive X-ray analyzer Oxford INCA Energy 350 was employed to evaluate the surface morphology of the samples and the chemical composition of their surfaces.

The roughness coefficient was measured using the Surface Roughness Tester SRT 6210 (China).

Results and discussion

For the evaluation of the behavior of a nickel electrode under conditions of its anodic polarization in ethaline and reline, respective cyclic voltammograms were obtained (Figs. 1 and 2). As observed, on the anodic polarization curve of nickel in ethaline, a clear current peak is formed at potentials around 0.5–0.6 V (versus the Ag reference electrode). With further anodic polarization, a decrease in current is observed (passivation), and upon reaching a potential of approximately 1.8–2.0 V, the anodic current starts to increase again. It is noteworthy that on the reverse scan (to the cathodic side), there is no appearance of the current peak of anodic dissolution at 0.5–0.6 V, which is clearly evident in the previous anodic scan. Interestingly, upon the addition of some nickel (II) chloride to ethaline, the anodic currents at all regions (metal dissolution peak on the curve and in the passive state region) noticeably decrease (Fig. 1, curve 2). It is worth mentioning that the obtained polarization curve 1 in Fig. 1 closely coincides with the curve presented in the previous publication by Abbott et al. [6].

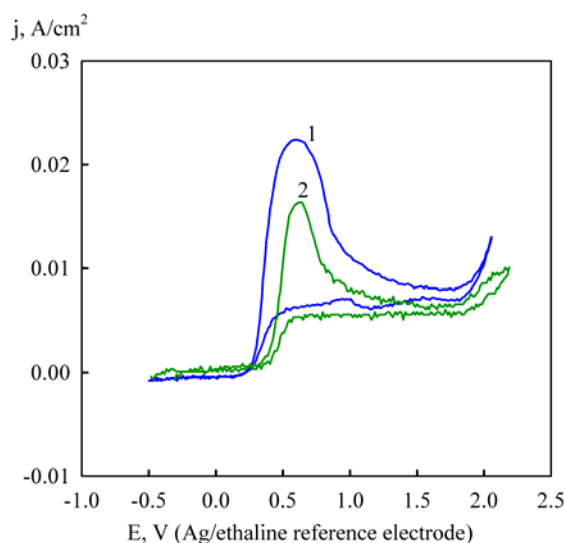


Fig. 1. Cyclic voltammograms depicting the anodic behavior of nickel in ethaline (1) and in ethaline+0.5 mol/dm³ NiCl₂·6H₂O (2). Potential scan rate: 200 mV/s

The reduction in the current density of nickel anodic dissolution after reaching its maximum (peak) value can be explained by the phenomenon known as salt-induced passivation. This involves the formation of a film in the near-electrode layer and directly on the electrode surface containing poorly soluble compounds of nickel chloride salt [3,7]. The formation of such a viscous film on the surface significantly

reduces the diffusion rate of the dissolution stages and partially blocks the electrode surface, resulting in a decrease in the anodic current of metal dissolution. Additionally, this phenomenon contributes to the electrochemical polishing of the metal surface. Within this explanation, the reduction in nickel dissolution currents upon the addition of Ni(II) salt to ethaline (Fig. 1, curve 2) is entirely logical, as it creates conditions where the saturation of the surface layer (attainment of the salt solubility product) is achieved at lower rates of electrochemical metal dissolution. Small oscillations in the current, noticeable in the voltammograms after reaching the peak current value (i.e., when the film of poorly soluble salts on or near the surface has already formed), also support the proposed mechanism, as such oscillations are often observed in polarization curves under conditions of forming a new blocking phase on the electrode surface.

The voltammogram characterizing the process of nickel anodic dissolution in reline (Fig. 2) noticeably differs from the curve obtained in ethaline. Firstly, the maximum current densities for nickel dissolution in reline are approximately an order of magnitude smaller than those in ethaline. This difference can be attributed to the significantly higher viscosity of reline compared to ethaline (750 cP and 37 cP at 25°C, respectively [5]). Since lower solvent viscosity in reline implies more significant diffusion limitations regarding the transport of electrolyte components participating in the anodic dissolution reaction (such as chloride ions, for instance), lower electrode reaction rates are evidently realized in such a system compared to ethaline.

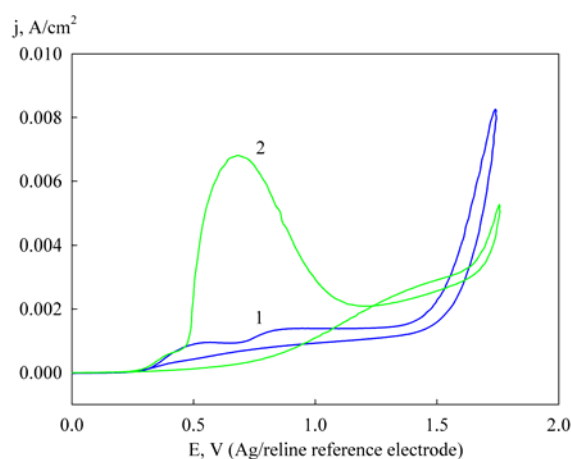


Fig. 2. Cyclic voltammograms depicting the anodic behavior of nickel in reline (1) and in reline+0.5 mol/dm³ NiCl₂·6H₂O (2). Potential scan rate: 200 mV/s

It is important to note the splitting of the peak of the nickel anodic dissolution current with the

formation of weakly pronounced maxima at potentials approximately 0.5 V and 0.8–0.9 V (Fig. 2, curve 1). The splitting of the peak of the nickel anodic dissolution current in reline during anodic potential sweep was previously observed in the work of Abbott et al. [8]. Ali et al. [9] also revealed two separated peaks of nickel anodic dissolution in reline. In the mentioned studies, the formation of two anodic peaks was explained by the formation on electrode surface two types of nickel structures with different surface morphologies, which were electrochemically deposited during the previous cathodic potential scan. However, in our case, experiments were conducted directly on an electrode made of nickel foil under conditions where electrochemical deposition from the solution could not occur. Therefore, we consider it more plausible to assume that the first of the peaks of the current is due to the two-electron reaction $\text{Ni}(0) \rightarrow \text{Ni}(\text{II}) + 2e$, while the second is induced by the one-electron reaction of further oxidation $\text{Ni}(\text{II}) \rightarrow \text{Ni}(\text{III}) + e$. The possibility of the latter reaction was indicated in the work [8]. Additional evidence supporting this hypothesis is the noticeable increase in the maximum (peak) dissolution current upon the addition of additional Ni(II) salt to reline (Fig. 2, curve 2). In this case, the current increase may be associated with the fact that both Ni(II) ions formed at the initial stage of anodic dissolution and those diffusing to the electrode surface from the bulk solution participate in the electrooxidation reaction of Ni(II) to Ni(III). However, even in the case of nickel dissolution in reline, the occurrence of salt-induced passivation cannot be ruled out (as observed in ethaline), since reverse scans of the voltammetric curves in Fig. 2 show a significant reduction in the anodic dissolution current across the entire range of electrode potentials studied.

The observed differences in the anodic behavior of nickel in ethaline and reline are evidently associated not only with differences in the physicochemical properties of these solvents (primarily viscosity) but also with variations in the composition and structure of nickel-containing species present in these systems. For instance, research conducted using fast atom bombardment mass spectrometry (FABMS) [8] revealed that nickel (II) ions in ethaline are mainly present in the form of complex anions NiCl_3^- and Ni_2Cl_5^- , while only NiCl_3^- ions exist in reline. However, in the ethaline environment, the formation of nickel (II) chelate complexes with ethylene glycol NiEG_2^{2+} is also possible [10]; it is evident that such complexes cannot be formed in the reline solvent, either in the bulk solution or on the electrode surface during the anodic dissolution process. On the other

hand, there are certain differences in the structure of chloride-containing particles, which likely participate in the anodic process: in ethaline, ChCl_2^- ions are present, but $\text{Cl}\cdot\text{EG}^-$ ions are entirely absent, while in reline, the presence of a considerable amount of complex ions $\text{Cl}\cdot\text{urea}^-$ is documented, and ChCl_2^- ions are present in small quantities [8]¹.

Thus, the differences in the chemical composition of various types of DESs, their physicochemical properties, the nature and composition of ions present in them, define the specificity and significant distinctions in the anodic behavior of nickel in the investigated solvents.

For further investigation of the impact of anodic treatment in DESs on various properties of the nickel surface, potentiostatic treatment of Ni samples was conducted for 2.5 hours at specific values of the electrode potential selected at different characteristic regions of the obtained voltammograms: at 1.5, 1.8, and 2.0 V for ethaline and at 0.5, 1.0, and 1.7 V for reline. The current transients recorded at the chosen potentials indicate that after a certain transient period (approximately 500–2000 s), the anodic treatment current density becomes nearly stationary (Fig. 3). Notably lower anodic dissolution current densities of nickel in the reline solvent compared to ethaline are evident, which correlates well with the differences in current densities on the voltammograms in Figs. 1 and 2. Oscillations are also observed in the current transients, especially in the curves recorded in reline.

Figure 4 characterizes changes in surface morphology occurring during the anodic treatment of nickel in ethaline and reline solvents. On the surface of the nickel foil before anodic treatment, individual

defects are visible in SEM images, and the presence of crystals with well-defined facets is not observed (Fig. 4,a). Anodic treatment in ethaline results in the formation of star-shaped asymmetric crystals, present against a relatively smooth and defect-free background (Fig. 4,b,c), with the portion of the leveled surface increasing with the elevation of the anodic treatment potential. Treatment of nickel in ethaline at a potential of 2.0 V leads to electrochemical polishing of the metal, confirmed not only by microscopic surface morphology examination (Fig. 4,g) but also by visual observation and measurement of the roughness coefficient (Table 1) [11].

Anodic treatment of nickel in reline at relatively low anodic potentials does not lead to the formation of specific morphological structures on the surface (Fig. 4,d,e), and only slight metal polishing is observed (a negligible decrease in the roughness coefficient, as shown in Table 1). At the highest of the applied potentials (1.7 V), etching of individual crystals from the surface occurs, resulting in the formation of pits (cavities), consequently increasing the roughness coefficient (Table 1). Thus, anodic treatment of Ni in the two investigated DESs with different chemical compositions has varying effects on changes in surface morphology: surface modification in ethaline allows for electrochemical polishing, while treatment in reline induces surface etching only. These differences are likely attributed to the previously mentioned distinctions in the kinetics of nickel anodic dissolution in ethaline and reline.

It should be noted that X-ray spectroscopic electron probe microanalysis showed that under any regime of anodic treatment of the investigated samples

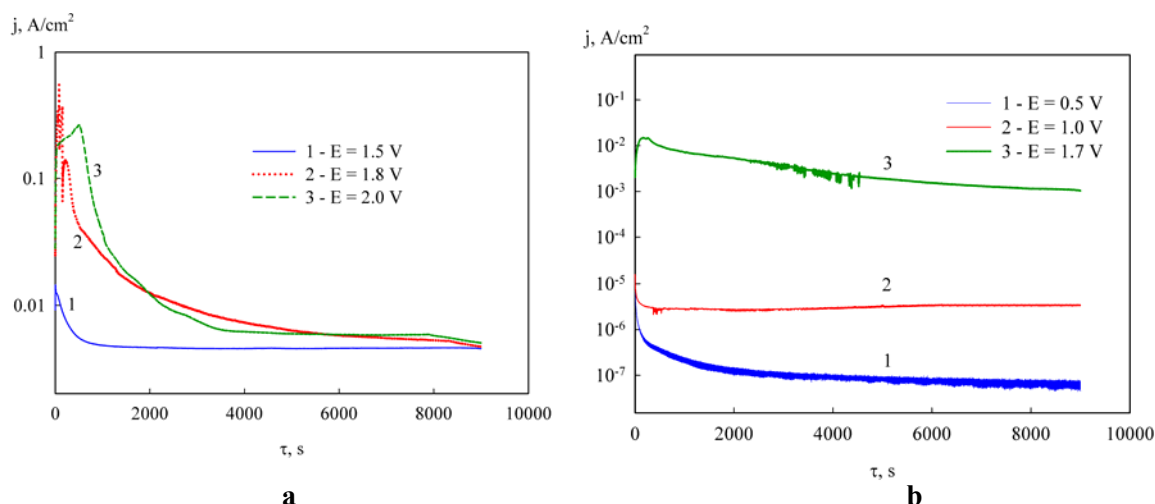


Fig. 3. Current transients during potentiostatic treatment of nickel in ethaline (a) and reline (b) at certain values of the electrode potential (indicated on the plots)

¹ The designations Ch and EG refer to the choline cation and ethylene glycol molecule, respectively.

in DESs, nickel is the dominant component on the surface. Other elements (oxygen, nitrogen, and chlorine) are present in trace amounts within the margin of error of the method. Therefore, the anodic treatment does not lead to the formation of passivating oxide films on the surface, which is expected given the high concentration of chloride ions in the electrolyte, typically inhibiting the passivation of the metal surface through the formation of oxide layers.

Table 1
Effect of anodic treatment of nickel (150 min at 25°C) in DESs on the roughness coefficient (R_a) of the surface

Type of DES	Treatment potential, V (vs. Ag reference electrode)	R_a , μm
–	– (without treatment)	0.72
ethaline	1.5	0.53
	1.8	0.47
	2.0	0.43
reline	0.5	0.68
	1.0	0.63
	1.7	0.84

It is well-known that anodic modification of the metal surface can influence the electrocatalytic activity of the surface [3,4]. Considering that nickel is one of the most promising and active electrocatalysts for the electrochemical generation of green hydrogen [1], we determined the kinetic parameters of the hydrogen evolution reaction in a 1 M NaOH aqueous solution on a nickel surface before and after its anodic potentiostatic treatment in ethaline and reline solvents. The corresponding polarization dependences are shown in Fig. 5, and the kinetic parameters of the hydrogen evolution reaction calculated by the data processing in the coordinates of Tafel equation are systematized in Table 2. The obtained results indicate that the anodic treatment of nickel in ethaline and reline

significantly affects the overpotential of the cathodic hydrogen evolution reaction, Tafel constants, exchange current density, and apparent transfer coefficient.

The mutual arrangement of the polarization curves shown in Fig. 5 and the determined values of the overpotential for hydrogen evolution at a current density of 0.1 A/cm² suggest that at high current density (relatively high overpotential), the anodic treatment of nickel in ethaline reduces electrocatalytic activity at a treatment potential of 1.5 V but significantly enhances it at treatment potentials of 1.8 and 2.0 V. Thus, the formation of areas with a smoothed (electropolished) surface on the sample (Fig. 4) contributes to the increase in electrocatalytic activity, probably due to the increased surface concentration of active catalytic sites. However, anodic treatment of nickel in ethaline also leads to a certain decrease in the Tafel slopes (i.e., an increase in apparent transfer coefficients). As a result, as shown in Fig. 6,a, at low overpotentials, the Tafel lines intersect for samples obtained at different anodic treatment potentials in a DES. Therefore, the calculated exchange current density values determined by extrapolation to $\eta=0$ do not correlate with the described influence of the anodic treatment potential in ethaline on electrocatalytic behavior at sufficiently high current densities. Furthermore, it follows from the calculated j_0 values that anodic treatment results in a reduction of electrocatalytic activity (clearly, this conclusion is only valid for the region of low overpotentials of hydrogen evolution near the equilibrium potential).

The data regarding the impact of nickel anodic treatment in reline on the kinetics of hydrogen evolution (Fig. 5,b) indicate that, in the region of relatively high current densities (i.e., high overpotentials), applying treatment potentials of 0.5 and 1.0 V results in a decrease in electrocatalytic activity (increased overpotential), while applying a

Table 2
Effect of anodic treatment of nickel (150 min at 25°C) in DESs on the kinetic parameters of hydrogen evolution reaction in 1 M NaOH*

Type of DES	Treatment potential, V (vs. Ag reference electrode)	$\eta_{0.1}$, mV	–a, V	–b, V	j_0 , A/cm ²	α
–	– (without treatment)	–330	0.463	0.128	$2.4 \cdot 10^{-4}$	0.46
ethaline	1.5	–340	0.463	0.121	$1.5 \cdot 10^{-4}$	0.49
	1.8	–292	0.401	0.107	$1.8 \cdot 10^{-4}$	0.55
	2.0	–291	0.295	0.112	$2.3 \cdot 10^{-4}$	0.53
reline	0.5	–382	0.563	0.174	$5.8 \cdot 10^{-4}$	0.34
	1.0	–386	0.550	0.164	$4.4 \cdot 10^{-4}$	0.36
	1.7	–210	0.509	0.296	$1.9 \cdot 10^{-2}$	0.20

Note: * – overpotential of hydrogen evolution at a current density of 0.1 A/cmI; a and b are the Tafel constants; j_0 is the exchange current density; α is the transfer coefficient.

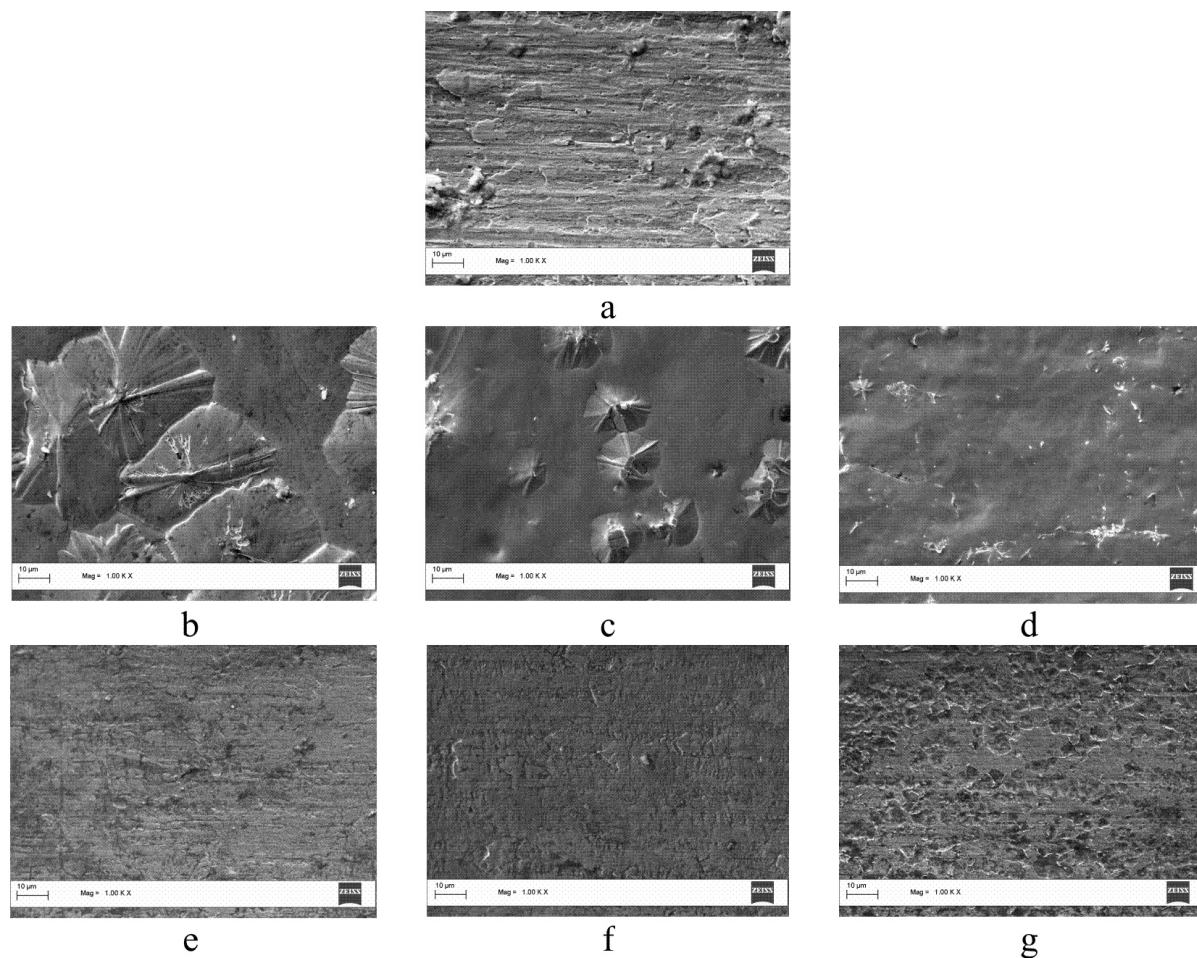


Fig. 4. SEM images of the surface of Ni samples: before treatment in DES (a), after treatment in ethaline (b–d), and reline (e–g) at anodic potentials (V): 1.5 – b; 1.8 – c; 2.0 – d; 0.5 – e; 1.0 – f; 1.7 – g

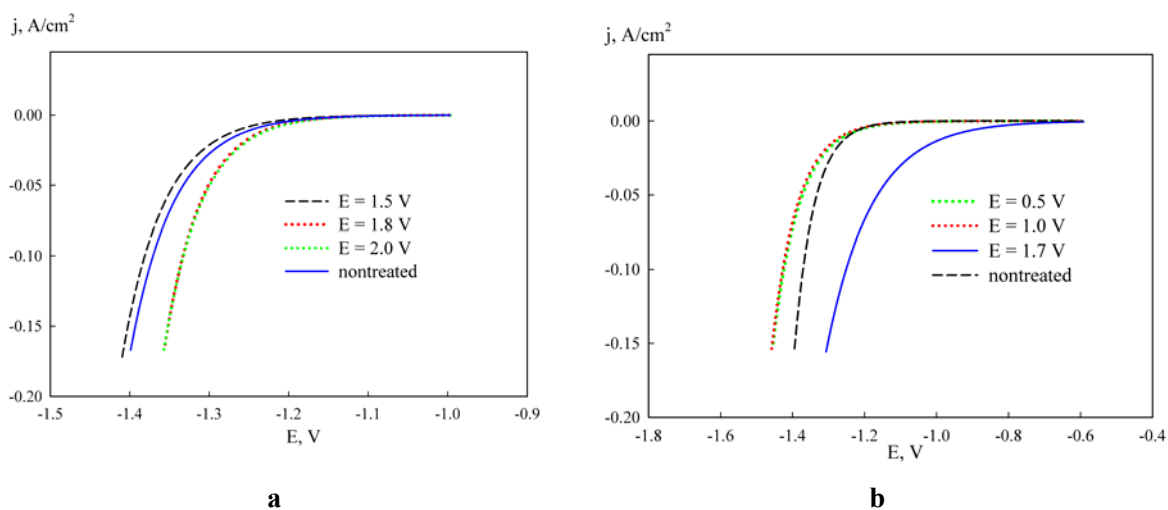


Fig. 5. Polarization curves of hydrogen evolution in a 1 M NaOH solution on the Ni surface before electrochemical treatment and after anodic treatment in ethaline (a) and reline (b) at different applied anodic potentials (indicated in the figure). The curves for potentials of 1.8 V and 2.0 V in Fig. 5,a and the curves for potentials of 0.5 V and 1.0 V in Fig. 5,b practically overlap

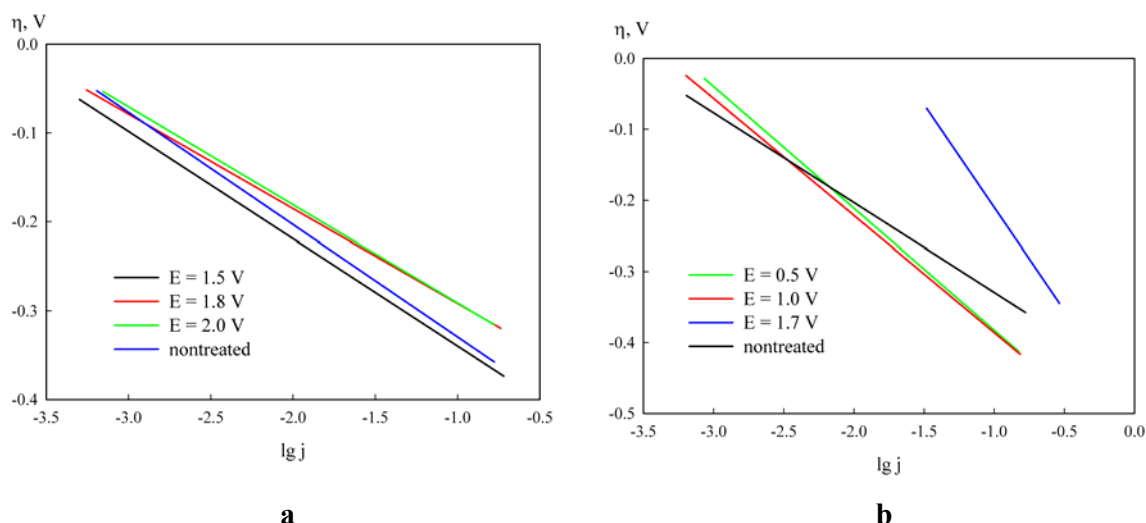


Fig. 6. Polarization curves plotted in Tafel equation coordinates for the hydrogen evolution reaction in a 1 M NaOH solution on the Ni surface before electrochemical treatment and after anodic treatment in ethaline (a) and reline (b) at different applied anodic potentials (Fig. 5)

treatment potential of 1.7 V, on the contrary, leads to a significant increase in electrocatalyst activity (a noticeable decrease in overpotential). The latter effect is likely associated with the pronounced etching of the nickel surface (Fig. 4,g). Similar to the case of treatment in ethaline, the anodic etching of Ni in the reline solvent also alters the Tafel slopes (and thus the apparent transfer coefficients). However, in this case, there is a tendency for an increase in Tafel slopes compared to the untreated surface. Consequently, due to the different slopes, the Tafel lines (Fig. 6,b) also intersect. Thus, in the case of anodic treatment in reline, changes in the calculated exchange current densities (at $\eta=0$) do not correlate with the observed influence of the anodic treatment potential of the metal in ethaline on electrocatalytic behavior at sufficiently high current densities (i.e., at significant deviations from the equilibrium potential).

As known, the Tafel slope in the electrochemical hydrogen evolution reaction (i.e., the value of the apparent transfer coefficient) is determined by the mechanism of this process. It is widely accepted that hydrogen evolution on metallic nickel in an alkaline aqueous solution occurs through the Volmer-Heyrovsky mechanism [2], where the rate-determining step is considered to be the stage (1):



where H^\bullet represents the adsorbed hydrogen atom.

If we consider that the energy barrier in the rate-determining step of the charge transfer (1) is

symmetric (the true transfer coefficient is close to 0.5), theoretical elementary calculations show that at a temperature of 298 K, the Tafel slope should be 118 mV/dec [12]. The observed deviations from this value and changes in the Tafel slope after the anodic treatment of nickel in DESs obviously do not indicate fundamental changes in the mechanisms of the process and/or asymmetry of the energy barrier. Perhaps, such deviations in Tafel slopes are due to the microheterogeneity of the electrode surface (the simultaneous presence of active sites on the surface with different adsorption energies, which, as shown in ref. [13], can be the cause of corresponding changes in the apparent transfer coefficient). In addition, it has been previously established [14] that the formation of microdomains of oxide films on the surface of metals (which is not excluded after anodic etching of the metal) leads to an increase in Tafel slopes compared to theoretically calculated values. Currently, it is challenging to detail the nature of these changes in the state of the electrocatalyst's surface and the redistribution of microdomains with different electrocatalytic activity due to the anodic treatment of nickel in ethaline and reline.

The analysis of data regarding electrocatalytic activity, presented in Table 2, vividly underscores the conclusion already made in the literature that there is no single and unambiguous quantitative criterion for electrocatalytic activity [15]. In particular, there are no correlations between trends in changes in the overpotential of the electrode process at a certain value of the cathodic current and the values of the Tafel slope «a» and exchange current densities. Bockris [15] noted that although, for example, exchange current

density may seem theoretically flawless as a quantitative characteristic of the kinetics of any electrochemical reaction, comparing the kinetic capabilities of several electrocatalysts using the value of j_0 is correct only under the condition of identical or close Tafel slopes. If the apparent Tafel slopes of two electrochemical reactions (or the same reaction occurring on the surfaces of different electrocatalysts) do not coincide, then the exchange current density cannot be used to assess electrocatalytic activity (more precisely, it can only be used for the region of very low polarizations). As seen from our data, the overpotential value for a specific chosen current density and/or Tafel slope «a» are also not explicit quantitative characteristics of the electrocatalyst's activity given the presence of intersection points of Tafel lines due to differences in Tafel slopes. Such ambivalence is a consequence of the common drawback of all mentioned quantitative criteria of electrocatalytic activity: they characterize the behavior of the electrocatalyst and the course of the electrochemical reaction only for a specific value of electrode potential or current density. Obviously, the development of new integral criteria of electrocatalytic activity that would assess the behavior not at a specific «point» but over a sufficiently wide working range of electrode polarization and/or current density is crucial. This is important for advancing the theory of modern electrocatalysis and will be addressed in our future publications.

Conclusions

1. This study provides a comparative analysis of the influence of anodic treatment of nickel in two types of DESs (ethaline and reline) at different applied potentials on surface morphology, roughness coefficients, and electrocatalytic activity towards the hydrogen evolution reaction for the first time.

2. Significant differences were identified in the kinetics of anodic dissolution and passivation of nickel during anodic polarization in ethaline and reline. These differences may arise from substantial variations in the viscosity of these solvents and differences in the chemical nature and composition of ions present in them. It is noteworthy that the anodic dissolution current densities of nickel in reline are approximately an order of magnitude lower than in ethaline under otherwise identical conditions. 3. Variations in the kinetics and mechanism of Ni anodic behavior lead to different types of microprofile evolution on the surface: anodic treatment in ethaline at specific potentials results in electrochemical surface polishing (confirmed by roughness coefficient measurements), whereas anodic treatment in reline does not allow for effective electropolishing and only surface etching and roughness increase are observed.

4. Anodic potentiostatic treatment of nickel in both investigated DESs at specific electrode potentials significantly enhances the electrocatalytic activity of the surface towards the hydrogen evolution reaction in an alkaline medium. This feature can be utilized for controlled manipulation of the electrocatalytic behavior of materials used in the electrolytic synthesis of green hydrogen.

5. The obtained data further emphasize the fact that well-known quantitative criteria of electrocatalytic activity (exchange current density, Tafel constants, overpotential values at arbitrarily chosen current density, etc.) are not unequivocal and universal. Thus, there is a highlighted need for further development of new integral criteria of electrocatalytic activity covering specific ranges of electrode polarization or current density.

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АНОДНЕ ОБРОБЛЕННЯ ПОВЕРХНІ НІКЕЛЮ В ІОННИХ РІДИНАХ НА ОСНОВІ ХОЛІН ХЛОРИДУ ДЛЯ ЕЛЕКТРОХІМІЧНОГО ПОЛІРУВАННЯ ТА ПІДВИЩЕННЯ ЕЛЕКТРОКАТАЛІТИЧНОЇ АКТИВНОСТІ У РЕАКЦІЇ ВИДІЛЕННЯ ВОДНЮ
В.С. Проценко, Д.О. Махова, Т.Є. Бутуріна, С.А. Корній, Ф.Й. Данилов

У роботі досліджено вплив анодного потенціостатичного оброблення нікелю в двох представниках нового типу іонних рідин – низькотемпературних евтектичних розчинників – ethaline і reline (евтектичні суміші холін хлориду з етиленгліколем і карбамідом, відповідно). Охарактеризовано вплив анодного оброблення на поверхневу морфологію, коефіцієнти шорсткості та електрокаталітичну активність стосовно реакції виділення водню. Показано, що густини струму анодного розчинення нікелю в reline приблизно на порядок менші, ніж в ethaline за всіх інших однакових умов. Встановлені суттєві відмінності у кінетиці анодного розчинення і пасивації нікелю при анодній поляризації в ethaline та reline, що можуть бути обумовлені як суттєвою різницею у в'язкості цих розчинників, так і у відмінностях у хімічній природі і складі іонів, що в них присутні. Виявлено, що анодне оброблення в ethaline за певних потенціалів приводить до електрохімічного полірування поверхні, що підтверджено зменшенням вимірних коефіцієнтів шорсткості, тоді як анодне оброблення в reline не дозволяє проводити ефективне електрополірування і спостерігається лише розтравлювання поверхні (зростання коефіцієнтів шорсткості). Анодне потенціостатичне оброблення нікелю в обох досліджених низькотемпературних евтектичних розчинниках за певних значень електродних потенціалів дозволяє помітно підвищити електрокаталітичну активність поверхні стосовно реакції виділення водню у водному лужному середовищі, що може бути використано при розробці електрокаталітичних матеріалів для електролітичного синтезу «зеленого» водню.

Ключові слова: нікель, анодне оброблення, низькотемпературний евтектичний розчинник, поверхнева морфологія, електрополірування, електрокаталіз, реакція виділення водню.

ANODIC SURFACE TREATMENT OF NICKEL IN EUTECTIC IONIC LIQUIDS BASED ON CHOLINE CHLORIDE FOR ELECTROCHEMICAL POLISHING AND ENHANCEMENT OF ELECTROCATALYTIC ACTIVITY IN HYDROGEN EVOLUTION REACTION
V.S. Protsenko^{a,*}, *D.O. Makhota*^a, *T.E. Butyrina*^a,
S.A. Korniy^b, *F.I. Danilov*^a

^a Ukrainian State University of Chemical Technology, Dnipro, Ukraine

^b Karpenko Physico-Mechanical Institute of the NAS of Ukraine, Lviv, Ukraine

* e-mail: Vprotsenko7@gmail.com

The paper reports the impact of anodic potentiostatic treatment of nickel in two representatives of a new type of eutectic ionic liquids (deep eutectic solvents), ethaline and reline, which are eutectic mixtures of choline chloride with ethylene glycol and urea, respectively. The influence of anodic treatment on surface morphology, roughness coefficients, and electrocatalytic activity towards the hydrogen evolution reaction is characterized. It is demonstrated that the current densities of nickel anodic dissolution in reline are approximately an order of magnitude lower than in ethaline under all other identical conditions. Significant differences in the kinetics of nickel anodic dissolution and passivation during anodic polarization in ethaline and reline have been established, which may be attributed to both a substantial difference in the viscosity of these solvents and differences in the chemical nature and composition of the ions present in them. It is found that anodic treatment in ethaline, at certain potentials, results in electrochemical polishing of the surface, confirmed by a decrease in measured roughness coefficients, while anodic treatment in reline does not allow effective electropolishing and only surface etching (increase in roughness coefficients) is observed. Anodic potentiostatic treatment of nickel in both investigated deep eutectic solvents at specific electrode potential values significantly enhances the electrocatalytic activity of the surface towards the hydrogen evolution reaction in an alkaline environment. This finding can be utilized in the development of electrocatalytic materials for the electrolytic synthesis of green hydrogen.

Keywords: nickel; anodic treatment; deep eutectic solvent; surface morphology; electropolishing; electrocatalysis; hydrogen evolution reaction.

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