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The influence of anodic potentiostatic treatment of nickel surface in deep eutectic solvents, ethaline and reline (eutectic mixtures of choline chloride with ethylene glycol and urea, respectively), on the electrocatalytic activity in the electrochemical reactions of oxygen evolution and urea oxidation in an aqueous alkaline medium (1 M NaOH) was investigated for the first time. It was shown that, depending on the chosen treatment potential and the nature of the eutectic solvent used, a significant increase in the rate of the studied processes was observed. Specifically, after anodic treatment of nickel under certain conditions, the polarization of the oxygen evolution reaction at a current density of 0.1 A/cm<sup>2</sup> could be reduced by approximately 150–200 mV, and the maximum current density of urea oxidation could be increased by an order of magnitude (from 0.012 A/cm<sup>2</sup> to 0.131 A/cm<sup>2</sup> at a urea concentration of 0.33 mol/dm<sup>3</sup> in alkaline solution). The observed increase in electrocatalytic activity after anodic treatment of nickel in deep eutectic solvents is likely related to changes in surface morphology patterns and the nature and concentration of relevant electroactive sites on the electrode surface. The results obtained in this work can be used for the development of highly efficient electrode materials for green hydrogen energy.

**Keywords:** deep eutectic solvent, nickel, potentiostatic anodic treatment, electrocatalytic behavior, oxygen evolution reaction, urea oxidation reaction, hydrogen energy.

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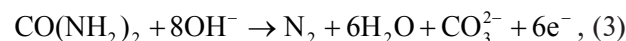
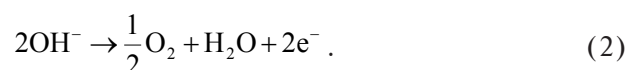
**Introduction**

A crucial task in the development of modern green hydrogen energy is the reduction of energy consumption in the hydrogen synthesis process (reaction (1)) through water electrolysis:



A possible solution is to replace the anodic oxygen evolution reaction (reaction (2), which has a relatively high standard equilibrium potential of +1.23 V and significant polarization) with another oxidation process of an organic compound with better energy parameters [1,2]. In particular, the use of the urea (CO(NH<sub>2</sub>)<sub>2</sub>) oxidation reaction (reaction (3)) [3–7] appears very promising, as its standard

equilibrium potential in an alkaline medium is only –0.852 V [8].



However, a significant obstacle to replacing the coupled oxygen evolution reaction with the urea electrooxidation reaction in the cathodic synthesis of hydrogen is the considerable polarization of this multi-step electrode process [3–5]. Therefore, considerable attention is currently being devoted to developing methods to enhance the electrocatalytic activity of electrode materials, particularly those based on nickel,

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*Influence of anodic treatment of nickel in deep eutectic solvents on electrocatalytic activity in oxygen evolution and urea oxidation reactions*

for the anodic oxidation of urea [6].

In the context of the above, it seemed interesting and promising to explore the influence of anodic treatment of nickel surfaces on the electrocatalytic activity in the urea electrooxidation reaction. Previously, we demonstrated that the anodic treatment of Ni in electrolytes based on a new generation of ionic liquids, so-called deep eutectic solvents (DESs), under certain conditions significantly enhances the electrocatalytic activity in the hydrogen evolution reaction [9–11]. However, it remained unknown whether the anodic treatment of nickel in DESs also affects the kinetics of urea electrooxidation. This specific question became the subject of investigation in this study.

### **Experimental**

Two types of deep eutectic solvents were used for the anodic treatment: the so-called ethaline and reline, which are mixtures of choline chloride with ethylene glycol and urea, respectively, with a molar ratio of components of 1:2. They were prepared by mixing the components at a temperature of approximately 70–80°C. The residual water concentration in them, determined by the Fischer method, did not exceed 1 wt.%.

Samples of nickel foil (nickel content 99.9%) with a thickness of 1 mm and a visible surface area of 1 cm<sup>2</sup> were used. Before conducting the experiments, their surfaces were thoroughly degreased, etched in a hydrochloric acid solution (1:1 by volume), and dried. Electrochemical measurements were performed using the Potentiostat/Galvanostat/ZRA Reference 3000 (Gamry, USA). Standard glass cells with a volume of 100 cm<sup>3</sup>, thermostated at a temperature of 298 K, were employed. The anodic treatment of nickel in the selected DESs was carried out in potentiostatic mode at potentials of 0.1, 0.3, 0.5, 0.7, 1.0, 1.35, and 1.7 V for 2.5 hours. In these experiments, a silver wire served as the quasi-reference electrode, and a platinum mesh served as the auxiliary electrode [11].

The electrocatalytic activity of the nickel surface in reactions (1)–(3) was evaluated using linear voltammetry in deaerated aqueous solutions of 1 M NaOH and 1 M NaOH+0.33 M CO(NH<sub>2</sub>)<sub>2</sub> [4] at a temperature of 298 K. A saturated Ag/AgCl reference electrode<sup>1</sup> and a platinum auxiliary electrode were used in these experiments.

The surface morphology was studied using scanning electron microscopy (Zeiss EVO 40XVP).

### **Results and discussion**

Anodic treatment of the nickel surface in DESs

was carried out in potentiostatic mode at a series of selected electrode potential values. It is worth noting that the peculiarities of the kinetics of nickel anodic dissolution in deep eutectic solvents, their possible mechanism, and the justification for the choice of potential values for surface etching are extensively described in a previous publication [11]. Figures 1 and 2 demonstrate cyclic voltammograms of the Ni surface before and after treatment at selected potentials in ethaline and reline, respectively. The voltammetric curves were recorded both in «pure» 1 M NaOH solution and in a solution of 1 M NaOH additionally containing 0.33 M CO(NH<sub>2</sub>)<sub>2</sub>, allowing the evaluation of the surface electrocatalytic activity in reaction (3).

The *j* vs. *E* curves were recorded starting from the cathodic region corresponding to hydrogen evolution. Then, the electrode potential was scanned towards the anodic direction. It should be noted that the obtained *j* vs. *E* curves exhibit characteristic current fluctuations. These fluctuations are caused by the fact that the studied processes (primarily hydrogen and oxygen evolution) are accompanied by intense gas evolution in the near-electrode layer, which locally violates the uniform distribution of current across the electrode surface and partially blocks it. Since the current registration occurs not on an analog principle but on a digital one, and only at certain fixed time points during the potential scan, the obtained curves reflect local deviations in current from the «average» due to gas evolution on the electrode. In this study, unlike previous publications [9–11], algorithmic averaging («smoothing») of the obtained curves was not performed due to the complex geometric shape of the registered voltammograms.

It is evident that the regions of cathodic and anodic currents in all recorded voltammograms, which have an exponential-like shape, correspond to the hydrogen evolution reaction (1) and the oxygen evolution reaction (2), respectively. The waves of anodic current appearing on the voltammograms in solutions containing dissolved urea, at potentials close to 0.4–0.7 V, are attributed to the electrocatalytic oxidation of urea according to reaction (3) [4–6].

From the obtained data, it can be observed that the surface of the Ni electrode without anodic treatment exhibits some electrocatalytic activity towards the urea oxidation reaction: a current wave corresponding to process (3) appears on the voltammetric curve in the electrolyte with dissolved urea, but the height of this current plateau is relatively small. Furthermore, upon further polarization, the exponential region

<sup>1</sup> To prevent possible misunderstandings, it should be emphasized that the necessity of using two different reference electrodes (and thus two non-identical scales of electrode potentials) within one study is due to the fact that the «traditional» silver chloride electrode with a *water*-saturated solution of KCl cannot be used in *non-aqueous* environments of deep eutectic solvents.

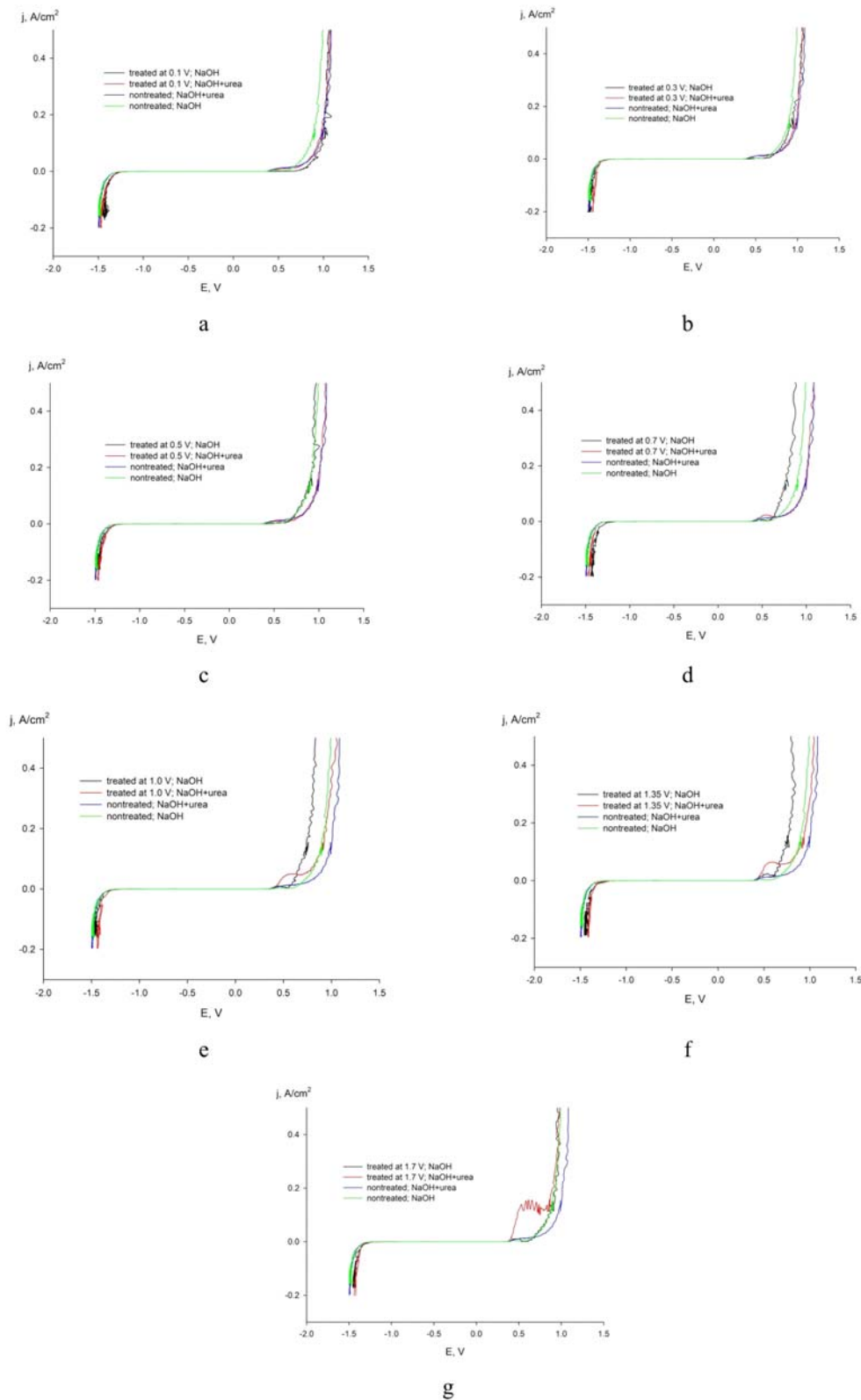


Fig. 1. Voltammograms of the nickel electrode, treated by anodic polarization in the *ethaline* solvent and untreated, recorded in 1 M NaOH solution (denoted as «NaOH») and 1 M NaOH+0.33 M CO(NH<sub>2</sub>)<sub>2</sub> solution (denoted as «NaOH+urea») at a scan rate of 50 mV/s and a temperature of 298 K. The potentials of anodic treatment in *ethaline* are indicated directly on the figure.

For comparison purposes, the corresponding curves for the untreated surface are provided on all constituents of the figure

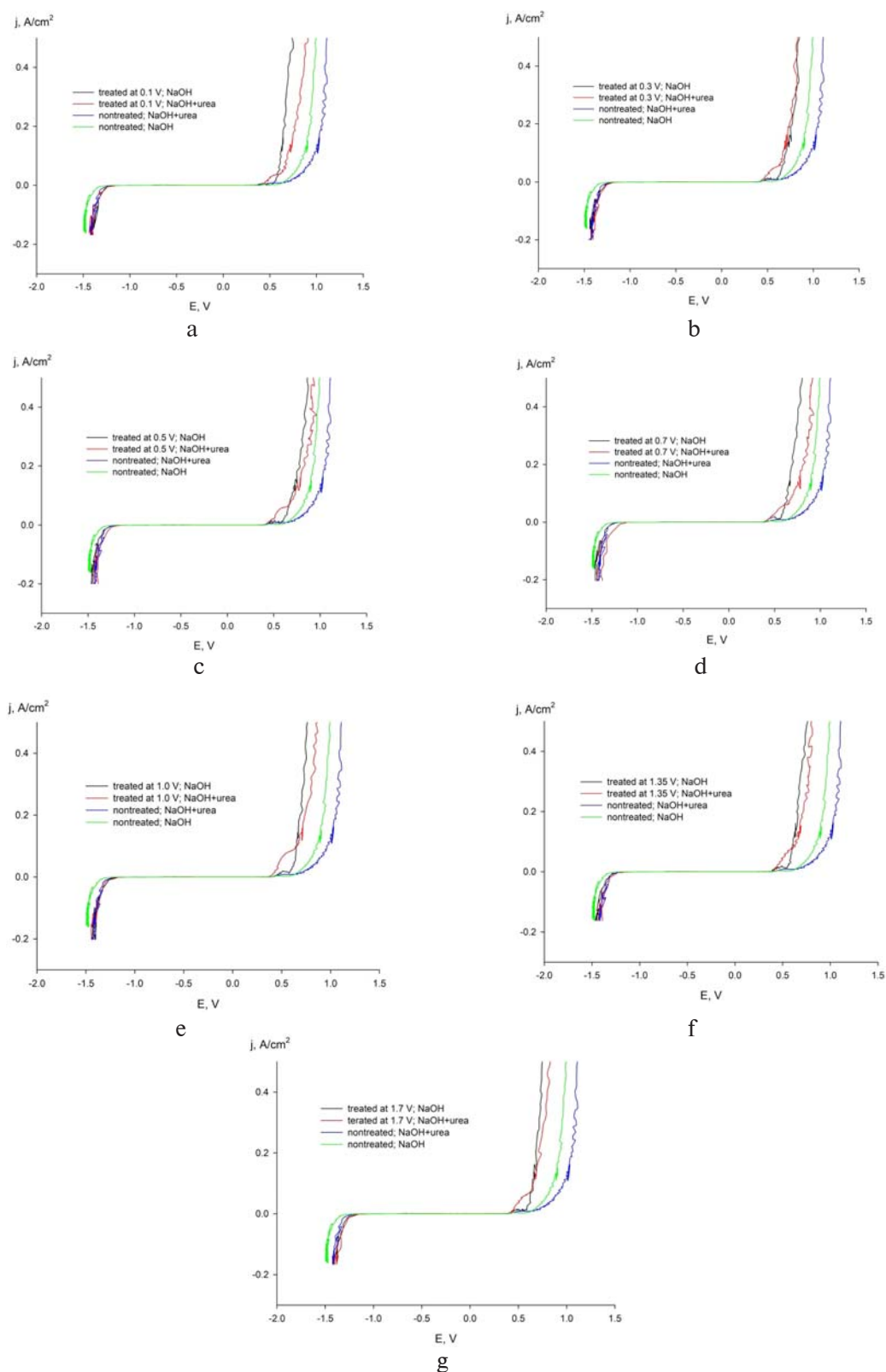


Fig. 2. Voltammograms of the nickel electrode, treated by anodic polarization in the *reline* solvent and untreated, recorded in 1 M NaOH solution (denoted as «NaOH») and 1 M NaOH+0.33 M CO(NH<sub>2</sub>)<sub>2</sub> solution (denoted as «NaOH+urea») at a scan rate of 50 mV/s and a temperature of 298 K. The potentials of anodic treatment in *reline* are indicated directly on the figure.

For comparison purposes, the corresponding curves for the untreated surface are provided on all constituents of the figure

corresponding to oxygen evolution in an alkaline medium shifts towards more positive potentials, indicating a process inhibition, possibly associated with the «poisoning» of the surface by adsorbed oxidation products of urea.

The anodic treatment of the nickel surface in a DES significantly influences its electrocatalytic activity concerning both the anodic oxygen evolution and urea oxidation. The nature of this influence depends on the magnitude of the potential of potentiostatic treatment and the nature of the deep eutectic solvent. Let us consider these patterns separately for the two DESs used (ethaline and reline).

The anodic treatment of nickel in ethaline solvent has a relatively weak effect on its electrocatalytic properties at two of the lowest applied potentials (0.1; 0.3, and 0.5 V). Presumably, this is because the lowest anodic dissolution potentials correspond to the lowest current densities, hence resulting in negligible surface alterations. Changes in electrocatalytic activity worthy of discussion are observed after anodic treatment at potentials of 0.7 V and higher. It is evident that the surface treated in ethaline at 0.7 V (Fig. 1, g) exhibits significantly higher activity in the oxygen evolution reaction, as the corresponding voltammetric curve in 1 M NaOH solution shifts towards more negative potentials, indicating reduced anodic polarization. Treatment of the nickel surface in ethaline at 0.7 V also contributes to an increase in current density corresponding to the wave of urea oxidation. Increasing the potential values of potentiostatic anodic treatment of Ni in ethaline (1.0; 1.35 and 1.7 V, Fig. 1, d, e, and f, respectively) leads to enhancement of these electrocatalytic effects. For instance, a well-defined wave of limiting current for urea electrooxidation, approximately 0.13 A/cm<sup>2</sup> (at 1.7 V, Fig. 1, f), is formed in the voltammogram. The diffusion-controlled nature of this limiting current is evidenced by its increase with the potential scan rate (Fig. 3), which is well-rectified in test coordinates  $j_{\max}$  vs.  $v^{1/2}$ , where  $v$  represents the potential scan rate.

However, it should be noted that nickel treatment in ethaline at the highest of the used potentials (1.7 V) practically does not affect the electrocatalytic activity in the oxygen evolution reaction (in 1 M NaOH solution without urea), as the corresponding voltammetric curves practically overlap each other.

To visualize and systematize the obtained results regarding the influence of nickel anode treatment on the electrocatalytic activity in reactions (2) and (3), they are summarized in Tables 1 and 2. In these

Tables, polarization values<sup>2</sup> at a current density of 0.1 A/cm<sup>2</sup> are selected as the quantitative criterion for electrocatalytic activity in the oxygen evolution reaction, while the current density at an electrode potential of 0.6 V, corresponding to the respective region of the voltammetric curve, is chosen for the urea oxidation reaction.

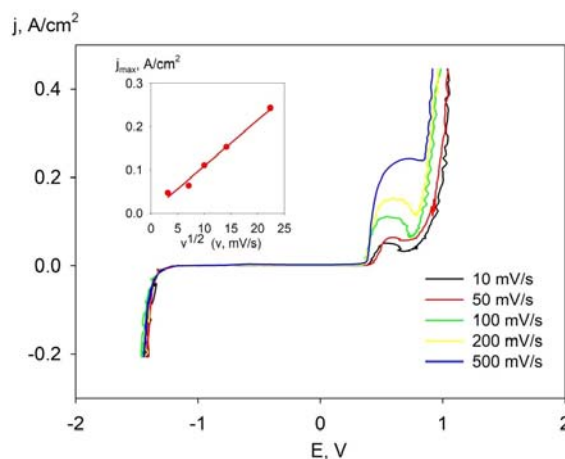


Fig. 3. Voltammograms of the nickel electrode treated by anodic polarization in *ethaline* solution, recorded in 1 M NaOH+0.33 M CO(NH<sub>2</sub>)<sub>2</sub> solution at various scan rates and a temperature of 298 K. Anodic treatment potential was 1.35 V. The inset illustrates the dependence of the maximum current density of urea oxidation on the square root of the scan rate

Analyzing the influence of anodic treatment of nickel surfaces in reline on their electrocatalytic characteristics (Fig. 2), it is noteworthy that, unlike the case with ethaline, anodic treatment at all used potentials, even relatively small ones, results in a significant shift of the voltammetric curve for oxygen evolution in the NaOH solution without urea, indicating an electrocatalytic effect. However, a monotonic dependence of electrocatalytic activity on the value of the anodic treatment potential in reline was not observed (Table 1). Regarding the reaction of urea oxidation, electrochemical anodic treatment of Ni in reline leads to increased electrocatalytic activity: the corresponding polarization curves shift towards more negative potentials, and waves corresponding to the reaction (3) are formed on the curves.

Presumably, the significant change in the electrocatalytic properties of nickel in the investigated anodic reactions is mainly due to alterations in surface morphology resulting from the anodic etching of the surface in the studied DESs. For illustration, SEM

<sup>2</sup> The equilibrium potential of the oxygen evolution reaction for polarization calculation was determined using the Nernst equation, taking into account the literature data on the pH of the solution used [12,13].

Table 1

Effect of nickel anodic treatment in DESs on the polarization of the oxygen evolution reaction in 1 M NaOH solution at a current density of 0.1 A/cm<sup>2</sup> ( $\eta_{0.1}$ )

DES used for the anodic treatment of the surface	Values of the electrode potential during potentiostatic anodic treatment, V	Polarization of the oxygen evolution reaction in a 1 M NaOH solution at a current density of 0.1 A/cm <sup>2</sup> , $\eta_{0.1}$ , V
without anodic treatment	–	0.66
ethaline	0.1	0.78
	0.3	0.68
	0.5	0.66
	0.7	0.53
	1.0	0.49
	1.35	0.51
	1.7	0.65
reline	0.1	0.40
	0.3	0.49
	0.5	0.49
	0.7	0.43
	1.0	0.44
	1.35	0.40
	1.7	0.44

Table 2

Effect of nickel anode treatment in DESs on the maximum value of the current for the electrooxidation of urea in a solution of 1 M NaOH+0.33 M CO(NH<sub>2</sub>)<sub>2</sub>

DES used for the anodic treatment of the surface	Values of the electrode potential during potentiostatic anodic treatment, V	Value of the current for the electrooxidation of urea at a potential of 0.6 V in a solution of 1 M NaOH+0.33 M CO(NH <sub>2</sub> ) <sub>2</sub> , A/cm <sup>2</sup>
without anodic treatment	–	0.012
ethaline	0.1	0.011
	0.3	0.011
	0.5	0.009
	0.7	0.020
	1.0	0.050
	1.35	0.064
	1.7	0.131
reline	0.1	0.036
	0.3	0.053
	0.5	0.061
	0.7	0.061
	1.0	0.085
	1.35	0.081
	1.7	0.067

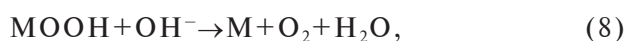
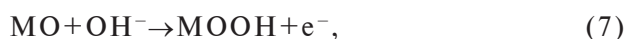
images of the Ni surface before and after anodic treatment in ethaline and reline at a potential of 1.7 V are provided in Fig. 4. It can be observed that the surface of the nickel foil before anodic treatment includes a certain amount of sporadic defects and heterogeneities (pores, cracks, depressions, etc.) (Fig. 4, a). Anodic treatment of Ni in the ethaline solution leads to the formation of a smooth and uniform surface with asymmetric star-like protrusions

(Fig. 4, b). Conversely, after anodic potentiostatic treatment in reline, a surface morphology having dimpled textures is formed (Fig. 4, c). A more detailed characterization of the influence of the anodic treatment potential of nickel in ethaline and reline on surface morphology and roughness is provided in a previous publication [11].

Thus, anodic treatment of nickel in DESs leads to changes in surface morphology patterns, and

consequently, to corresponding alterations in the concentration and nature of electroactive sites present on the electrode surface. Under conditions of sufficiently high anodic polarization, the nickel surface undergoes further changes associated with the formation of several molecular layers of oxide and hydroxide phases, in which nickel exists in various oxidation states (such as NiO<sub>2</sub>, NiO, NiOOH, NiO(OH)<sub>2</sub>, and NiOO<sub>2</sub>) [14].

In this context, it is important to note that according to modern understandings, the mechanism of the oxygen evolution reaction on oxidized metal surfaces in alkaline environments is described by the following *schematic* representation [15]:



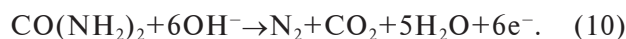
where M represents a metal atom on the surface.

Despite alternative reaction schemes for reaction (2) being presented in the literature [16], tailored to specific metal electrodes and detailing the mechanism of this electrochemical reaction, the general consensus is that the surface concentration of intermediates and the strength of M–O bonds in these intermediates (MOH, MO, and MOOH) are crucial for the electrocatalytic characteristics regarding the oxygen evolution reaction.

Previously, it has been shown that anodic treatment of the Ni surface, depending on the specific conditions of its implementation, significantly alters the distribution of surface concentrations of these

surface oxide-hydroxide compounds, which act as active catalytic centers, and therefore influences the electrocatalytic behavior of nickel in the oxygen evolution reaction [14]. It is evident that the surface prehistory of nickel, associated with its prior anodic treatment in DESs and the observed changes in surface morphology, should influence the characteristics of the electrocatalytic sites, explaining the phenomena of changes in electrocatalytic activity during O<sub>2</sub> evolution in an aqueous alkaline solution (Table 1).

The observed influence of nickel anodic treatment in DESs on its electrocatalytic activity regarding the oxidation of urea (Fig. 1 and 2, Table 2) should be considered in light of the two main proposed electrocatalytic mechanisms: direct (reactions (9) and (10)) and indirect (reactions (9) and (11)). In the first (direct) mechanism, the adsorption of urea molecules on active sites containing NiOOH formed during the anodic oxidation of Ni(OH)<sub>2</sub> (reaction (9)) is considered, where the direct electrochemical oxidation of CO(NH<sub>2</sub>)<sub>2</sub> occurs (reaction (10)):



Here, nickel hydroxide Ni(OH)<sub>2</sub> serves as a precursor to the electrocatalyst, and the electrocatalytic form NiOOH is not regenerated into the initial form Ni(OH)<sub>2</sub>.

In the indirect mechanism, similar to the direct one, the electrocatalytic form NiOOH is initially formed (according to reaction (9)), and then it chemically interacts with the adsorbed molecules of urea to produce the final decomposition products and regenerate Ni(OH)<sub>2</sub> (reaction (11)):

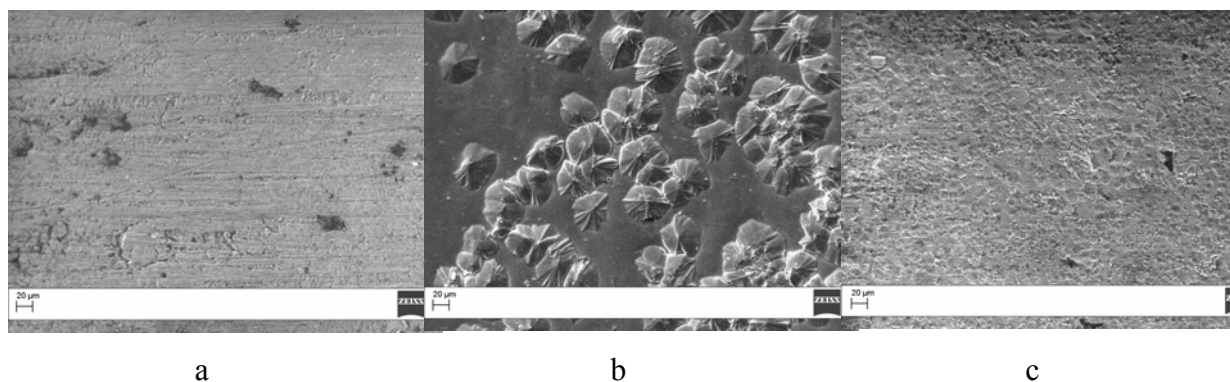
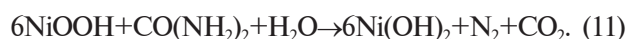


Fig. 4. SEM images of the nickel surface: a – before anodic treatment in DES; b – after anodic treatment in ethaline at 1.7 V; and c – after anodic treatment in reline at 1.7 V

Regardless of which mechanism predominates in a particular case under consideration (direct or indirect), the kinetics of the electrochemical oxidation of urea will be determined by the concentration and nature of nickel particles with variable oxidation states on the electrode surface. Obviously, anodic treatment of Ni in DESs allows influencing the physicochemical state of nickel surface compounds, thus determining the observed electrocatalytic effects (Table 2).

To conclude, as inferred from the comparison of the data in Tables 1 and 2, under all other equal conditions, anodic treatment of nickel in reline enhances electrocatalytic activity to a greater extent for the oxidation of urea and, especially, for the oxygen evolution reaction compared to anodic treatment in ethaline. In this context, it is interesting to note that the dimpled morphology of the nickel surface observed after anodic treatment in reline (Fig. 4, c) may, under certain conditions, contribute to the acceleration of oxygen evolution in an alkaline environment [17].

Differences in surface morphology and electrocatalytic activity of nickel surface after anodic etching in ethaline and reline may suggest that somewhat different intermediates containing nickel in variable oxidation states are involved in these studied anodic processes (2) and (3) in these eutectic solvents, and anodic treatment of Ni in the used DES affects the concentration of active catalytic sites and their properties somewhat differently. However, a detailed analysis of these differences requires further research and goes far beyond the scope of this work.

#### Conclusions

Analysis of experimental data demonstrates that anodic potentiostatic treatment of nickel in deep eutectic solvents, ethaline and reline, enhances the electrocatalytic activity in the anodic reactions of oxygen evolution and urea oxidation in alkaline media (1 M NaOH). The nature of the utilized deep eutectic solvents (DES) and the applied electrode potential for anodic treatment influence the electrocatalytic behavior of the Ni electrode. These observed effects are likely associated with changes in surface morphology and, consequently, the nature and concentration of electroactive sites. The obtained results could be utilized for the development of advanced electrode systems for hydrogen electrogeneration in green hydrogen energy applications.

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#### REFERENCES

1. Raveendran A., Chandran M., Dhanusuraman R. A comprehensive review on the electrochemical parameters and recent material development of electrochemical water splitting electrocatalysts // *RSC Adv.* – 2023. – Vol.13. – P.3843-3876.
2. A novel electrode for value-generating anode reactions in water electrolyzers at industrial current densities / Wang C., Wu Y., Bodach A., Krebs M.L., Schuhmann W., Schuth F. // *Angew. Chem. Int. Ed.* – 2023. – Art. No. e202215804.
3. Energy-saving cathodic H<sub>2</sub> production enabled by non-oxygen evolution anodic reactions: a critical review on fundamental principles and applications / Zhou W., Chen S., Meng X., Li J., Gao J. // *Int. J. Hydrogen Energy.* – 2023. – Vol.48. – P.15748-15770.
4. Boggs B.K., King R.L., Botte G.G. Urea electrolysis: direct hydrogen production from urine // *Chem. Commun.* – 2009. – P.4859-4861.
5. Recent progress in non-noble metal-based electrocatalysts for urea-assisted electrochemical hydrogen production / Paygozar S., Aghdam A.S.R., Hassanizadeh E., Andaveh R., Darband G.B. // *Int. J. Hydrogen Energy.* – 2023. – Vol.48. – P.7219-7259.
6. Recent development of nickel-based electrocatalysts for urea electrolysis in alkaline solution / Anuratha K.S., Rinawati M., Wu T.-H., Yeh M.-H., Lin J.-Y. // *Nanomaterials.* – 2022. – Vol.12. – Art. No. 2970.
7. Protsenko V.S. Thermodynamic aspects of urea oxidation reaction in the context of hydrogen production by electrolysis // *Int. J. Hydrogen Energy.* – 2023. – Vol.48. – No. 63. – P.24207-24211.
8. Thermodynamics of electrochemical urea oxidation reaction coupled with cathodic hydrogen evolution reaction in an alkaline solution: effect of carbonate formation / Protsenko V.S., Bobrova L.S., Butyrina T.E., Sukhatskiy O.D. // *Int. J. Hydrogen Energy.* – 2024. – Vol.59. – P.354-358.
9. Anodic treatment of Ni-Cu alloy in a deep eutectic solvent to improve electrocatalytic activity in the hydrogen evolution reaction / Protsenko V.S., Butyrina T.E., Makhota D.O., Korniy S.A., Danilov F.I. // *Port. Electrochim. Acta.* – 2023. – Vol.41. – P.29-45.
10. Modification of surface morphology and surface properties of copper-nickel alloy by anodic treatment in a deep eutectic solvent (ethaline) / Protsenko V., Butyrina T., Makhota D., Korniy S., Danilov F. // *Arch. Metall. Mater.* – 2023. – Vol.68. – No. 2. – P.477-482.
11. 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 / Protsenko V.S., Makhota D.O., Butyrina T.E., Korniy S.A., Danilov F.I. // *Voprosy Khimii i Khimicheskoi Tekhnologii.* – 2024. – No. 1. – P.89-98.



12. Protsenko V.S., Butyrina T.E., Danilov F.I. Kinetics and mechanism of electrochemical oxygen evolution in an alkaline solution on nickel coatings // *J. Chem. Technol.* – 2022. – Vol.30. – No. 1. – P.26-33.

13. *The pH* of aqueous NaOH/KOH solutions: a critical and non-trivial parameter for electrocatalysis / Hausmann J.N., Traynor B., Myers R.J., Driess M., Menezes P.W. // *ACS Energy Lett.* – 2021. – Vol.6. – P.3567-3571.

14. Nickel surface anodic oxidation and electrocatalysis of oxygen evolution / Juodkazis K., Juodkazyte J., Vilkauskaitė R., Jasulaitiene V. // *J. Solid State Electrochem.* – 2008. – Vol.12. – P.1469-1479.

15. *Electrocatalysis* for the oxygen evolution reaction: recent development and future perspectives / Suen N.T., Hung S.F., Quan Q., Zhang N., Xu Y.J., Chen H.M. // *Chem. Soc. Rev.* – 2017. – Vol.46. – P.337-365.

16. Lyons M.E.G., Brandon M.P. The oxygen evolution reaction on passive oxide covered transition metal electrodes in aqueous alkaline solution. Part 1 – nickel // *Int. J. Electrochem. Sci.* – 2008. – Vol.3. – P.1386-1424.

17. Taylor A.K., Andreu I., Gates B.D. Regular dimpled nickel surfaces for improved efficiency of the oxygen evolution reaction // *ACS Appl. Energy Mater.* – 2018. – Vol.1. – P.1771-1782.

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#### ВПЛИВ АНОДНОГО ОБРОБЛЕННЯ НІКЕЛЮ В НИЗЬКОТЕМПЕРАТУРНИХ ЕВТЕКТИЧНИХ РОЗЧИННИКАХ НА ЕЛЕКТРОКАТАЛІТИЧНУ АКТИВНІСТЬ У РЕАКЦІЯХ ВИДІЛЕННЯ КИСНЮ І ОКИСЛЕННЯ КАРБАМІДУ

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Вперше досліджено основні закономірності впливу анодного потенціостатичного оброблення поверхні нікелю в низькотемпературних евтектичних розчинниках, еталіне і реліне (евтектичні суміші холін хлориду з етиленгліколем і карбаміду, відповідно) на електрокаталітичну активність в електрохімічних реакціях виділення кисню і окислення карбаміду у водному лужному середовищі (1 М NaOH). Показано, що в залежності від обраного значення потенціалу оброблення та природи використаного евтектичного розчинника спостерігається суттєве зростання швидкості досліджених процесів. Так, після анодного оброблення нікелю за певних умов поляризація реакції виділення кисню при густині струму 0,1 А/см<sup>2</sup> може бути знижена на ≈150–200 мВ, а максимальний струм окислення карбаміду – збільшений на порядок (від 0,012 А/см<sup>2</sup> до 0,131 А/см<sup>2</sup> при концентрації CO(NH<sub>2</sub>)<sub>2</sub> у лужному розчині 0,33 моль/дм<sup>3</sup>). Спостережене зростання електрокаталітичної активності після анодного оброблення нікелю в низькотемпературних евтектичних розчинниках, напевне, пов'язані зі змінами паттернів поверхневої морфології та природи і концентрації відпо-відних електроактивних центрів на поверхні електрода. Результати, отримані в роботі, можуть бути використані для розроблення високо-ефективних електродних матеріалів для «зеленої» водневої енергетики.

**Ключові слова:** низькотемпературний евтектичний розчинник, нікель, потенціостатичне анодне оброблення, електрокаталітична поведінка, реакція виділення кисню, реакція електроокислення карбаміду, воднева енергетика.

#### INFLUENCE OF ANODIC TREATMENT OF NICKEL IN DEEP EUTECTIC SOLVENTS ON ELECTROCATALYTIC ACTIVITY IN OXYGEN EVOLUTION AND UREA OXIDATION REACTIONS

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The influence of anodic potentiostatic treatment of nickel surface in deep eutectic solvents, ethaline and reline (eutectic mixtures of choline chloride with ethylene glycol and urea, respectively), on the electrocatalytic activity in the electrochemical reactions of oxygen evolution and urea oxidation in an aqueous alkaline medium (1 M NaOH) was investigated for the first time. It was shown that, depending on the chosen treatment potential and the nature of the eutectic solvent used, a significant increase in the rate of the studied processes was observed. Specifically, after anodic treatment of nickel under certain conditions, the polarization of the oxygen evolution reaction at a current density of 0.1 A/cm<sup>2</sup> could be reduced by approximately 150–200 mV, and the maximum current density of urea oxidation could be increased by an order of magnitude (from 0.012 A/cm<sup>2</sup> to 0.131 A/cm<sup>2</sup> at a urea concentration of 0.33 mol/dm<sup>3</sup> in alkaline solution). The observed increase in electrocatalytic activity after anodic treatment of nickel in deep eutectic solvents is likely related to changes in surface morphology patterns and the nature and concentration of relevant electroactive sites on the electrode surface. The results obtained in this work can be used for the development of highly efficient electrode materials for green hydrogen energy.

**Keywords:** deep eutectic solvent; nickel; potentiostatic anodic treatment; electrocatalytic behavior; oxygen evolution reaction; urea oxidation reaction; hydrogen energy.

#### REFERENCES

1. Raveendran A, Chandran M, Dhanusuraman R. A comprehensive review on the electrochemical parameters and recent material development of electrochemical water splitting electrocatalysts. *RSC Adv.* 2023; 13: 3843-3876. doi: 10.1039/d2ra07642j.
2. Wang C, Wu Y, Bodach A, Krebs ML, Schuhmann W, Schuth F. A novel electrode for value-generating anode reactions in water electrolyzers at industrial current densities. *Angew Chem Int Ed.* 2023; e202215804. doi: 10.1002/anie.202215804.
3. Zhou W, Chen S, Meng X, Li J, Gao J. Energy-saving cathodic H<sub>2</sub> production enabled by non-oxygen evolution anodic reactions: a critical review on fundamental principles and applications. *Int J Hydrogen Energy.* 2023; 48: 15748-15770. doi: 10.1016/j.ijhydene.2023.01.063.

4. Boggs BK, King RL, Botte GG. Urea electrolysis: direct hydrogen production from urine. *Chem Commun.* 2009; 4859-4861. doi: 10.1039/b905974a.
5. Paygozar S, Aghdam ASR., Hassanizadeh E, Andaveh R, Darband GB. Recent progress in non-noble metal-based electrocatalysts for urea-assisted electrochemical hydrogen production. *Int J Hydrogen Energy.* 2023; 48: 7219-7259. doi: 10.1016/j.ijhydene.2022.11.087.
6. Anuratha KS, Rinawati M, Wu TH, Yeh MH, Lin JY. Recent development of nickel-based electrocatalysts for urea electrolysis in alkaline solution. *Nanomaterials.* 2022; 12: 2970. doi: 10.3390/nano12172970.
7. Protsenko VS. Thermodynamic aspects of urea oxidation reaction in the context of hydrogen production by electrolysis. *Int J Hydrogen Energy.* 2023; 48: 24207-24211. doi: 10.1016/j.ijhydene.2023.03.295.
8. Protsenko VS, Bobrova LS, Butyrina TE, Sukhatskyi OD. Thermodynamics of electrochemical urea oxidation reaction coupled with cathodic hydrogen evolution reaction in an alkaline solution: effect of carbonate formation. *Int J Hydrogen Energy.* 2024; 59: 354-358. doi: 10.1016/j.ijhydene.2024.02.006.
9. Protsenko VS, Butyrina TE, Makhota DO, Korniy SA, Danilov FI. Anodic treatment of Ni-Cu alloy in a deep eutectic solvent to improve electrocatalytic activity in the hydrogen evolution reaction. *Port Electrochim Acta.* 2023; 41; 29-45. doi: 10.4152/pea.2023410103.
10. Protsenko V, Butyrina T, Makhota D, Korniy S, Danilov F. Modification of surface morphology and surface properties of copper-nickel alloy by anodic treatment in a deep eutectic solvent (ethaline). *Arch Metall Mater.* 2023; 68(2): 477-482. doi: 10.24425/amm.2023.142425.
11. Protsenko VS, Makhota DO, Butyrina TE, Korniy SA, Danilov FI. 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. *Voprosy Khimii i Khimicheskoi Tekhnologii.* 2024; (1): 89-98. doi: 10.32434/0321-4095-2024-152-1-89-98.
12. Protsenko VS, Butyrina TE, Danilov FI. Kinetics and mechanism of electrochemical oxygen evolution in an alkaline solution on nickel coatings. *J Chem Technol.* 2022; 30(1): 26-33. doi: 10.15421/jchemtech.v30i1.245490.
13. Hausmann JN, Traynor B, Myers RJ, Driess M, Menezes PW. The pH of aqueous NaOH/KOH solutions: a critical and non-trivial parameter for electrocatalysis. *ACS Energy Lett.* 2021; 6: 3567-3571. doi: 10.1021/acsenergylett.1c01693.
14. 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. doi: 10.1007/s10008-007-0484-0.
15. Suen NT, Hung SF, Quan Q, Zhang N, Xu YJ, Chen HM. Electrocatalysis for the oxygen evolution reaction: recent development and future perspectives. *Chem Soc Rev.* 2017; 46: 337-365. doi: 10.1039/c6cs00328a.
16. Lyons MEG, Brandon MP. The oxygen evolution reaction on passive oxide covered transition metal electrodes in aqueous alkaline solution. Part 1 – Nickel. *Int J Electrochem Sci.* 2008; 3: 1386-1424.
17. Taylor AK, Andreu I, Gates BD. Regular dimpled nickel surfaces for improved efficiency of the oxygen evolution reaction. *ACS Appl Energy Mater.* 2018; 1: 1771-1782. doi: 10.1021/acsaem.8b00338.