APPLICATION OF DEEP EUTECTIC SOLVENTS TO PREPARE ELECTROCATALYSTS FOR GREEN HYDROGEN PRODUCTION

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We investigated the electrochemical modification of metal surfaces by using electrolytes based on a novel type of ionic liquids known as deep eutectic solvents (DESs). The anodic treatment of the Cu–Ni alloy in DESs significantly improves its electrocatalytic properties towards the hydrogen evolution reaction (HER). Modification of the chemical composition of nickel coatings via codeposition from DES-based electrolytes containing Fe(II), Mo(VI), Ce(III), and La(III) salts leads to a significant increase in electrocatalytic activity towards the HER, which can be used in development of hydrogen energy.

Keywords: electrochemical surface treatment, electrodeposition, deep eutectic solvent, electrocatalysis, hydrogen production, alloy, surface modification

Introduction. The creation of novel and efficient electrocatalysts is a crucial objective not only in modern electrochemical science but also in the field of chemical materials science as a whole. This issue gains particular significance due to the urgent need for electrocatalysts in generating "green" hydrogen through water electrolysis [1]. An appealing approach to developing highly effective electrocatalysts involves their electrochemical synthesis using systems based on deep eutectic solvents (DESs), which belong to a new generation of room-temperature ionic liquids [2]. DESs offer promising alternatives to both conventional aqueous electrolytes and non-aqueous systems, presenting numerous advantages in terms of physicochemical properties, operational characteristics, environmental impact, and economic viability [3]. In this study, we explored the potential and prospects of utilizing DES-assisted electrolytes for producing electrocatalytic materials for the hydrogen evolution reaction (HER) through anodic and cathodic modification of metal surfaces.

Experimental, results and discussion. Two representatives of DESs were used: ethaline and reline (eutectic mixtures of choline chloride with ethylene glycol and urea, respectively). The methods for the ethaline and reline preparation have been described in numerous literature sources, including our previous publications [4–10].

A copper-nickel alloy (45 wt.% Cu) was used as an object for anodic treatment in DESs [4–6]. To perform cathodic modification of the nickel-based electrocatalyst surfaces, their chemical composition was modified (micromodified) through the incorporation of alloying components during

electrodeposition. Salts of nickel (II), iron (II), molybdenum (VI), cerium (III), and lanthanum (III) were dissolved in either ethaline or reline to fabricate the plating electrolytes. Detailed information regarding the preparation of electrolytes and the electrochemical deposition procedures can be found in publications [4–10]. The electrocatalytic activity of the resulting catalysts was assessed for the HER in an alkaline aqueous solution of 1 M NaOH at a temperature of 298 K. The evaluation was performed using techniques such as linear/cyclic voltammetry and electrochemical impedance spectroscopy.

This study aimed to investigate the anodic surface modification of a copper-nickel alloy through potentiostatic treatment in ethaline or reline, with a particular focus on understanding the underlying patterns. Notably, this research represents the first exploration of such modification methods. The experimental results revealed that the anodic treatment of the Cu–Ni alloy occurred under conditions promoting the passivation of the anode through the formation of poorly soluble compounds on the electrode surface and in the near-electrode layer. These compounds were identified as the products of the anodic dissolution of the alloy components. It was observed that the anodic modification of the copper-nickel alloy did not induce the formation of oxide layers on the surface or selective etching of individual components within the binary alloy.

The experimental results demonstrated that the anodic modification of the Cu–Ni alloy surface in DESs induces notable alterations in its electrocatalytic behaviour towards the HER in an aqueous alkaline solution [4–6]. As is known, the exchange current density of an electrochemical reaction is a measure of electrocatalytic activity. We have determined, for the first time, that the anodic modification of the copper-nickel alloy surface in ethaline or reline leads to a significant enhancement in electrocatalytic activity towards the HER (Table 1). Specifically, the exchange current density can increase by more than two orders of magnitude. These observed effects can be attributed to the changes in the surface morphology of the alloy induced by the anodic treatment in DESs-based electrolytes.

In addition, we explored the potential for cathodic surface modification in DESs through the electrochemical deposition of nickel alloys containing various transition metals and lanthanides, including iron, molybdenum, cerium, and lanthanum. Utilizing DESs in this context offers advantages over conventional aqueous electrolytes for electrodeposition processes. DESs provide greater flexibility in manipulating the electrocatalytic characteristics of the resulting electrocatalysts by adjusting parameters such as the concentration of metal salts in the electrolyte, temperature, and current density within broad ranges. The summarized results regarding the electrocatalytic activity of the formed surface films are presented in Table 2.

Table 1. Effect of anodic modification of the Cu–Ni alloy at different electrode potentials on the exchange current density of the HER in 1 M NaOH solution

Type of DES	Electrode potential of anodic treatment, V	Exchange current density, j_0, A/cm^2
without treatment	–	$1.09 \cdot 10^{-5}$
ethaline	0.5	$2.30 \cdot 10^{-5}$
ethaline	1.35	$5.07 \cdot 10^{-3}$
ethaline	1.7	$2.24 \cdot 10^{-5}$

Table 2. Exchange current density of hydrogen evolution reactions in 1 M NaOH solution on electrocatalysts electrodeposited from DES-based electrolytes

Type of plating bath	Composition of deposit	Exchange current density, j_0, A/cm^2	Ref.
ethaline-based, only Ni(II) salt in the bath + 15 wt% H_2O	Ni without other metal alloying component	$3.63 \cdot 10^{-5}$	[7]
ethaline-based, Ni(II) and Fe(II) salts in the bath + 15 wt% H_2O	Ni + 7.3 wt.% Fe	$1.65 \cdot 10^{-4}$	[7]
reline-based, Ni(II) salt in the bath + $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ + $C_6H_8O_7 \cdot H_2O$	Ni + 5.28 wt.% Mo	$1.11 \cdot 10^{-3}$	[8]
ethaline-based, Ni(II) and Ce(III) salts in the bath	Ni + 2.65 wt.% Ce	$5.99 \cdot 10^{-3}$	[9]
reline-based, Ni(II) and Ce(III) salts in the bath	Ni + 59 wt.% Ce	$1.02 \cdot 10^{-2}$	[9]
ethaline-based, Ni(II) and La(III) salts in the bath	Ni + 1.75 wt.% La	$3.70 \cdot 10^{-3}$	[10]

The results clearly indicate that the formation of alloys during cathodic deposition from DES-based electrolytes significantly enhances the electrocatalytic activity. Among the alloying components, molybdenum, cerium, and lanthanum demonstrate particularly remarkable effects. Even at relatively low contents (up to 1–3 wt.%), which correspond to micromodification of the chemical composition, the presence of cerium and lanthanum in the coating leads to a substantial increase in the exchange current density of the HER by several orders of magnitude.

The increased electrocatalytic activity observed during the introduction of metals into the nickel matrix can be related to both the synergistic interaction of the alloy components (as a result of the hypo-hyper-d-electronic interaction of transition metals) and the presence of active sites on the surface, where the modifying metal exists in different oxidation states, that can perform the function of electron carriers.

Conclusions. In summary, we have investigated the impact of anodic and cathodic treatment in DESs on the electrocatalytic characteristics of metal surfaces. The observed significant enhancement in electrocatalytic activity makes the synthesized electrode materials highly promising for applications in the electrolytic production of "green" hydrogen. These findings highlight the potential of utilizing DESs for the development of efficient and sustainable electrocatalysts.

1. *Osman A.I., Mehta N., Elgarahy A.M., Hefny M., Al-Hinai A., Al-Muhtaseb A.H. and Rooney D.W*. Hydrogen production, storage, utilisation and environmental impacts: a review // Environ. Chem. Lett. – 2022. – 20. – P. 153–188.
2. *Zhang C., Fu Y., Gao W., Bai T., Cao T., Jin J. and Xin B.* Deep eutectic solvent-mediated electrocatalysts for water splitting // Molecules. – 2022. – 27. – No. 8098.
3. *Smith E.L., Abbott A.P. and Ryder K.S*. Deep eutectic solvents (DESs) and their applications // Chem. Rev. – 2014. – 114. – P. 11060–11082.
4. *Protsenko V.S., Butyrina T.E., Makhota D.O., Korniy S.A. and Danilov F.I.* Anodic treatment of Ni-Cu alloy in a deep eutectic solvent to improve electrocatalytic activity in the hydrogen evolution reaction // Portugal. Electrochim. Acta. – 2023. – 41. – P. 29–45.
5. *Protsenko V., Butyrina T., Makhota D., Korniy S. and 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. – P. 477–482.
6. *Protsenko V.S., Butyrina T.E., Makhota D.O., Korniy S.A. and Danilov F.I.* Electrochemical treatment of nickel-copper alloy in ionic liquid based on eutectic mixture of choline chloride and ethylene glycol as a way to increase electrocatalytic activity towards hydrogen evolution reaction // Funct. Mater. – 2022. – 29. – – P. 93–99.
7. *Danilov F.I., Bogdanov D.A., Smyrnova O.V., Korniy S.A. and Protsenko V.S*. Electrodeposition of Ni–Fe alloy from a choline chloride-containing ionic liquid // J. Solid State Electrochem. – 2022. – 26. – P. 939–957.
8. *Protsenko V.S., Bobrova L.S., Butyrina T.E., Baskevich A.S., Korniy S.A. and Danilov F.I.* Electrodeposited Ni–Mo coatings as electrocatalytic materials for green hydrogen production // Heliyon. – 2023. – 9. – Art. No. e15230.
9. *Protsenko V.S., Pavlenko L.M., Bobrova L.S., Korniy·S.A. and Danilov F.I*. Electrodeposition of coatings from urea–choline chloride-based plating baths containing Ni(II) and Ce(III) chloride salts and electrocatalytic activity of electrodeposits towards the hydrogen evolution reaction // J. Solid State Electrochem. – 2022. – in press. – https://doi.org/10.1007/s10008-023-05499-6.
10. *Protsenko V.S., Pavlenko L.M., Bobrova L.S., Korniy S.A., Butyrina T.E. and Danilov F.I*. Ni–La coatings as electrocatalysts for hydrogen evolution reaction deposited from electrolytes based on a deep eutectic solvent // Voprosy Khimii i Khimicheskoi Tekhnologii. – 2023. – № 3. – P. 103-109. (in Ukrainian).