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DES-ASSISTED ELECTRODEPOSITION AND CHARACTERIZATION OF AN ELECTROCATALYST FOR ENHANCED UREA OXIDATION IN GREEN HYDROGEN PRODUCTION

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An important task of modern materials science is the development of highly efficient electrocatalysts for green hydrogen production. Specifically, this involves the urea oxidation reaction (UOR), which is an energetically advantageous and attractive alternative to the anodic oxygen evolution reaction, coupled with hydrogen evolution at the cathode. In this work, we present for the first time the use of systems based on a new generation of environmentally friendly room-temperature ionic liquids – deep eutectic solvents (DESs) – for the electrodeposition of electrocatalysts for UOR. The electrochemical performance of electrodeposited nanocomposite Ni–CeO_2 electrocatalysts was evaluated in alkaline solution, showing an appreciable reduction in the anodic potential of UOR compared to oxygen evolution, reaching up to approximately 0.2 V at a current density of 0.1 mA cm^{-2}. The obtained results are significant for the development of electrochemical synthesis methods for electrocatalysts used in green renewable energy.

Keywords: electrodeposition, deep eutectic solvents, composite coating, green hydrogen production, urea oxidation reaction, electrocatalysis.

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Introduction

The global transition to sustainable energy systems has highlighted the urgent need for efficient and cost-effective methods of hydrogen production. Green hydrogen, generated through electrochemical water splitting using renewable energy sources, represents a promising solution for achieving carbon-neutral energy cycles [1,2]. However, the high energy input required for conventional water electrolysis, particularly for the oxygen evolution reaction (OER), remains a significant challenge. In this context, the urea oxidation reaction (UOR) has garnered increasing attention as an alternative anodic process due to its lower thermodynamic standard potential and promising role in wastewater remediation, offering a dual benefit of hydrogen generation and environmental sustainability [3,4]. The electrochemical processes involved in this strategy are summarized as follows:

Cathodic reaction in an alkaline solution:

$$2H_2O + 2e^- \rightarrow H_2 + 2OH^-, \quad E^0 = -0.83\,V\ (vs.\ SHE).$$

Anodic reactions in an alkaline solution:

- conventional water electrolysis involves the oxygen evolution reaction:

$$4OH^- \rightarrow O_2 + 2H_2O + 4e^-, \quad E^0 = 0.40\,V\ (vs.\ SHE)$$

- in contrast, the urea oxidation reaction may occur at a sufficiently lower potential [5]:

$$CO(NH_2)_2 + 8OH^- \rightarrow N_2 + 6H_2O + CO_3^{2-} + 6e^-,$$
$$E^0 = -0.852\,V\ (vs.\ SHE)$$

By replacing OER with UOR, the energy consumption of the overall process can be significantly reduced. However, a major obstacle in this pathway is the slow electrode kinetics of UOR, which necessitates highly efficient catalysts [3]. Nickel-based electrocatalysts have emerged as leading candidates for promoting UOR, owing to their high catalytic activity, cost-effectiveness, and stability in alkaline media [3,4]. Nevertheless, optimizing the structure, morphology, and electronic properties of these electrocatalysts is crucial for enhancing their performance. Among the wide variety of synthesis methods for Ni-based electrocatalysts, electrodeposition from deep eutectic solvent (DES)-based solutions holds a special place [6,7].

Deep eutectic solvents (DESs) have recently gained traction as versatile and eco-friendly alternatives to conventional aqueous or organic electrolytes in electrodeposition processes [8]. DESs offer unique advantages, including tunable composition, low volatility, and the ability to control the growth and morphology of electrodeposited materials, making them ideal for designing advanced electrocatalysts [6].

In this study, we report, for the first time, the DES-assisted electrodeposition of Ni-based electrocatalysts specifically tailored for the urea oxidation reaction. This novel approach leverages the unique properties of DESs to synthesize electrocatalysts with enhanced activity and durability, contributing to the advancement of green hydrogen technologies.

Materials and methods

A typical representative of DES, *reline*, was used. Reline is a eutectic mixture of choline chloride and urea at a molar ratio of 1:2, respectively. In addition to nickel (II) salt, which serves as the precursor for electrodeposited nickel, the electrolyte also contained cerium (III) salt. The incorporation of this rare-earth element into the nickel coating is known to enhance electrocatalytic activity, particularly concerning the hydrogen evolution reaction [9,10]. The detailed procedure for electrolyte preparation and the deposition methodology has been published elsewhere [9,10]. The composition of the electrolyte and the electrodeposition conditions are presented in Table.

The electrocatalytic activity was assessed by recording cyclic voltammograms in aqueous solutions of 1 M NaOH and 1 M NaOH+0.33 M $CO(NH_2)_2$ at 298 K. A Reference 3000 potentiostat (Gamry, USA) was used for the measurements. In the three-electrode configuration, the working electrode was the coating deposited onto a platinum substrate, the counter electrode was a platinum disk, and the reference electrode was a saturated Ag/AgCl electrode.

To investigate the morphological characteristics of the electrocatalytic coatings, scanning electron microscopy (SEM) was used (Zeiss EVO 40XVP electron microscope). The chemical composition of the coatings was determined using energy-dispersive X-ray spectroscopy (EDS) with an Oxford INCA Energy 350 attachment integrated into the electron microscope. X-ray phase analysis was performed using a DRON-3.0 X-ray diffractometer with monochromatized CuK_α radiation.

Results and discussion

Figure 1a demonstrates the surface morphology and XRD patterns of coatings electrochemically deposited from reline containing dissolved nickel and cerium salts. It is evident that the surface of the sample is mosaic-island-like, highly heterogeneous and defective, which could *a priori* be a factor contributing to its high catalytic activity. The obtained coatings, according to EDX analysis, contain (wt.%) 13.59 Ni, 55.19 Ce, 22.79 O, and 5.93 C. X-ray phase analysis (Fig. 1b) showed that the coating includes a face-centered cubic phase of nanocrystalline nickel, as indicated by the corresponding broadened peaks that align with reference data for X-ray scattering from the crystallographic planes of nickel. The crystalline domain size, evaluated using the Scherrer equation, was found to be approximately 40–50 nm. In addition to the peaks from nanocrystalline nickel, the diffraction patterns also show peaks corresponding to the CeO_2 phase, as well as very small reflections, presumably from nickel-cerium intermetallics (not labeled in the figure) [9]. Thus, the formed coating is a thin film nanocomposite material that contains an electrodeposited metallic matrix with a dispersed CeO_2 phase inclusion. It is worth noting that cathodic electrodeposition of Ni–CeO_2 composite coatings from aqueous solutions has been previously described in the literature [11,12]. However, aqueous solutions allow the incorporation of no more than 10–25 wt.% Ce

Plating bath composition and electrolysis conditions used to prepare electrocatalytic coatings

Plating bath composition		Electrodepostion conditions	
solvent	reline	cathode current density	0.3 A dm^{-2}
$NiCl_2·6H_2O$	0.1 mol dm^{-3}	temperature	343 K
$CeCl_3·7H_2O$	0.4 mol dm^{-3}	electrodepostion duration	100 min
		stirring rate (by a magnetic stirrer)	500 rpm
		anode	Ni plate

into the coating [12].

It is interesting to observe that attempts to obtain a coating from an electrolyte containing 0.1 M Ni(II) ions without the addition of cerium(III) salt and test it for electrocatalytic behavior were unsuccessful. Under the electrodeposition conditions outlined in Table, the coatings formed on the cathode were loose and poorly adhered to the substrate, quickly exfoliating after being removed from the plating bath and attempted to be rinsed. Therefore, data on «pure» nickel deposits (without cerium) and their electrocatalytic performance are not presented in this work.

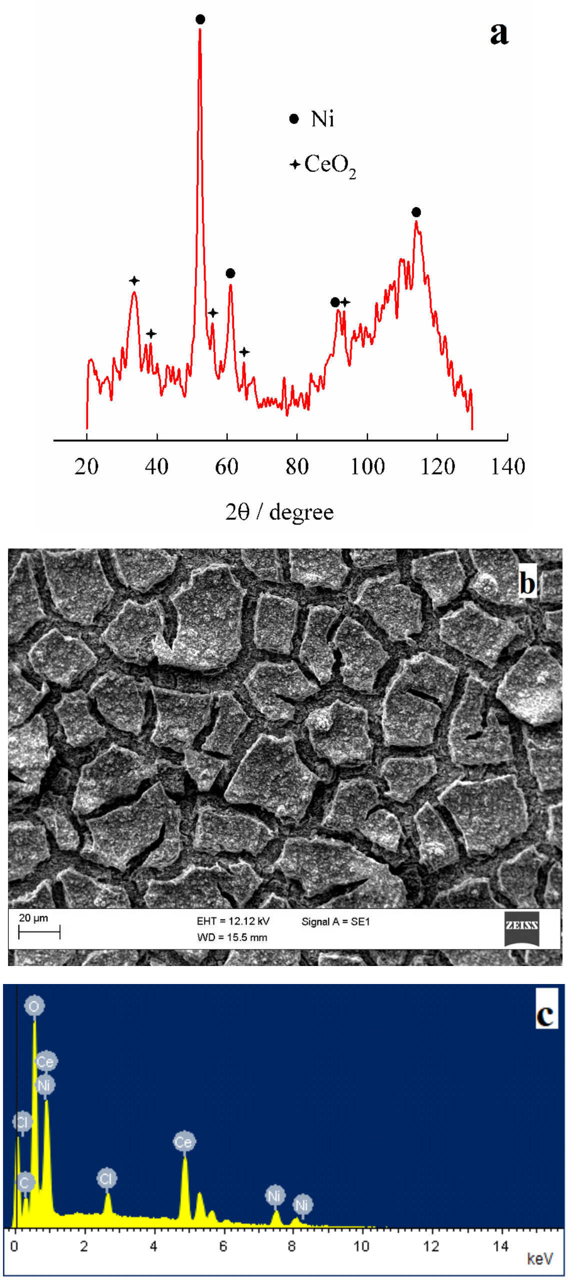

Fig. 1. (a) XRD pattern; (b) SEM image; and (c) EDX spectrum of deposited coating

Figure 2 shows the cyclic voltammetry curves recorded on the deposited coating in aqueous solutions of 1 M NaOH and 1 M NaOH+0.33 M $CO(NH_2)_2$. In the 1 M NaOH solution, the anodic-cathodic current wave in the potential range of approximately 0.2 to 0.5 V corresponds, as known [13], to the electrochemical redox conversion $Ni^{II}(OH)_2 \Leftrightarrow Ni^{III}OOH$. According to the proposed mechanisms for the UOR [3], this redox couple enables the electrocatalytic action. This can be realized, for example, through the interaction of nickel in the +3 oxidation state at active sites of NiOOH with urea molecules [14]:

$$6NiOOH + CO(NH_2)_2 + 2OH^- \rightarrow$$
$$\rightarrow 6Ni(OH)_2 + N_2 + CO_3^{2-} + H_2O$$

In this reaction, the final decomposition products of urea are formed, and the $Ni(OH)_2$ catalyst is regenerated.

The electrocatalytic mechanism results in the formation of a clearly defined urea oxidation current wave on the anodic branch of the voltammogram obtained in the 1 M NaOH+0.33 M $CO(NH_2)_2$ solution (Fig. 2).

It should be noted that the decrease in electrode potential for the deposited Ni–CeO_2 coating upon adding urea to the sodium hydroxide solution is significant: for example, at a current density of 0.1 mA cm^{-2}, the anodic potential shifts by approximately 200 mV. This effect rivals the best electrocatalysts for UOR currently reported in the literature [3]. Moreover, as shown in Figure 2, the

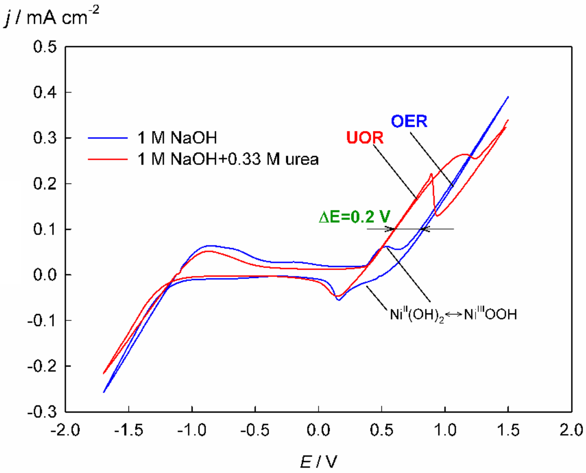

Fig. 2. Cyclic voltammograms of the coating deposited from a reline-based solution in aqueous solutions of 1 M NaOH and 1 M NaOH+0.33 M $CO(NH_2)_2$. Temperature: 298 K. Scan rate: 50 mV s^{-1}

anodic process operates effectively at relatively high current densities, reaching at least 0.2÷0.25 mA cm^{-2}.

Conclusions

This study demonstrates, for the first time, that the electrocatalytic performance of Ni–CeO_2 composite coatings electrochemically deposited from DES can be significantly enhanced for the urea oxidation reaction. This finding is crucial not only for advancing electrochemical synthesis methods for green energy electrocatalysts but also for developing new applications such as direct urea fuel cells, urea sensors, and urea removal processes from wastewater [15].

Further research should focus on a detailed investigation of the mechanisms underlying the formation of electrocatalytic coatings from DES-based electrolytes and the oxidation of urea on these coatings. In particular, it is important to understand the influence of the cerium-containing phase on electrocatalytic activity. Additionally, exploring the effects of electrolyte composition and deposition conditions on electrocatalytic performance could help optimize and enhance the observed effects.

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ЕЛЕКТРООСАДЖЕННЯ ТА ХАРАКТЕРИСТИКА ЕЛЕКТРОКАТАЛІЗАТОРА ДЛЯ ПОКРАЩЕНОГО ОКИСЛЕННЯ КАРБАМІДУ В ЗЕЛЕНІЙ ВОДНЕВІЙ ЕНЕРГЕТИЦІ ЗА УЧАСТЮ DES

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Важливим завданням сучасного матеріалознавства є розробка високоефективних електрокаталізаторів для виробництва «зеленого» водню. Особливої уваги заслуговує реакція окислення карбаміду, яка є енергетично вигідною та привабливою альтернативою анодному виділенню кисню, сполученому з виділенням водню на катоді. У цій роботі вперше показано використання систем, заснованих на новому поколінні екологічно безпечних іонних рідин, які працюють при кімнатній температурі, – низькотемпературних евтектичних розчинників (DES), для електроосадження електрокаталізаторів для реакції окислення карбаміду. Електрохімічні властивості електроосаджених нанокомпозиційних електрокаталізаторів $Ni-CeO_2$ були оцінені в лужному розчині, і продемонстроване суттєве зниження анодного потенціалу реакції окислення карбаміду порівняно з виділенням кисню, досягаючи приблизно 0,2 В при густині струму 0,1 мА/см^2. Отримані результати є значущими для розвитку методів електрохімічного синтезу електрокаталізаторів, які використовуються в зеленій відновлюваній енергетиці.

Ключові слова: електроосадження, низькотемпературні евтектичні розчинники, композиційне покриття, виробництво зеленого водню, реакція окислення карбаміду, електрокаталіз.

DES-ASSISTED ELECTRODEPOSITION AND CHARACTERIZATION OF AN ELECTROCATALYST FOR ENHANCED UREA OXIDATION IN GREEN HYDROGEN PRODUCTION

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Keywords: electrodeposition; deep eutectic solvents; composite coating; green hydrogen production; urea oxidation reaction; electrocatalysis.

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