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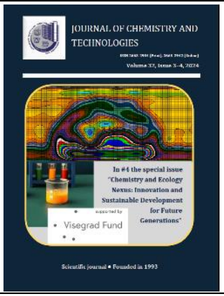

UDC 621.357

INCREASING THE ELECTROCHEMICAL ACTIVITY OF NICKEL-BASED ELECTRODE MATERIALS BY CORROSION TREATMENT

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Abstract

Recent studies have extensively explored the catalytic properties and synthesis of chalcogenide materials, with a particular focus on sulfides of iron-group metals. Of particular interest are nickel sulfides, in particular those that correspond in stoichiometry to natural millerite and hizlewudite. These chalcogenide compounds have garnered significant attention due to their high electrical conductivity, comparable to pure nickel, and their remarkable catalytic performance in oxygen electroreduction. Cyclic voltammetry measurements reveal that prolonging the corrosion treatment of bright sulfur-containing nickel coatings in concentrated acetic acid increases the sulfur content on the surface, leading to enhanced current densities in the cyclic voltammetry curves. Similarly, the elevated current densities observed for sulfur-free nickel coatings are linked to prolonged exposure in a saturated sodium sulfide solution. Regardless of the processing method, the presence of nickel sulfides or adsorbed sulfur enhances the electrochemical activity of the electrode material. Thus it has been shown, for the first time, that in both cases, during corrosion treatment of bright nickel deposits and during adsorption treatment of matte nickel in a sodium sulfide solution, stabilization of the cathodic current density value occurs after 24 hours of both types of treatment. Accordingly, the cathodic current density, in this case, is a parameter that determines the overall electrochemical activity of the studied materials. It has been shown that the formed during corrosion treatment nickel sulfides is the most stable and effective for the electroreduction of oxygen in a low alkaline medium.

Keywords: corrosion treatment; nickel foil; nickel sulfides; sodium sulfide; oxygen electroreduction.

ПІДВИЩЕННЯ ЕЛЕКТРОХІМІЧНОЇ АКТИВНОСТІ ЕЛЕКТРОДНИХ МАТЕРІАЛІВ НА ОСНОВІ НІКЕЛЮ ШЛЯХОМ КОРОЗІЙНОЇ ОБРОБКИ

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Анотація

Останнім часом значну увагу приділено вивченню каталітичних властивостей і хімічному синтезу халькогенідних матеріалів, зокрема сульфідів металів групи заліза. Особливий інтерес викликають сульфіди нікелю, зокрема такі, що за стехіометрією відповідають природнім мілериту та хізлевудиту. Ці халькогенідні сполуки характеризуються високою електропровідністю, порівнянною з провідністю чистого нікелю, а також значною каталітичною активністю в процесах електровідновлення кисню. На основі даних циклічної вольтамперометрії встановлено, що збільшення тривалості корозійної обробки блискучих нікелевих осадів, що містять сульфур, в концентрованій оцтовій кислоті сприяє підвищенню поверхневого вмісту сульфуру, що, у своєю чергою, призводить до зростання густини струму на циклічних вольтамперних кривих. Аналогічно, обробка безсульфурних нікелевих осадів у насиченому розчині сульфіду натрію також сприяє збільшенню катодної густини струму. Отже, незалежно від способу обробки, утворення сульфідів нікелю чи адсорбція сульфуру на поверхні електродного матеріалу забезпечує підвищення його електрохімічної активності. Таким чином, вперше показано, що в обох випадках, як після корозійної обробки блискучих сульфоровмісних нікелевих осадів в оцтовій кислоті, так і під час адсорбційної обробки безсульфоровмісних нікелевих осадів в насиченому розчині сульфіду натрію відбувається стабілізація величини катодної густини струму після 24 годин проведення обох видів обробки. Відповідно катодна густина струму в даному випадку є параметром, що визначає електрохімічну активність досліджуваних матеріалів. Показано, що сульфіди нікелю, які утворюються під час корозійної обробки, є найбільш стійкими та ефективними для електровідновлення кисню в помірнолужному середовищі.

Ключові слова: корозійна обробка; нікелева фольга; сульфіди нікелю; сульфід натрію; електровідновлення кисню.

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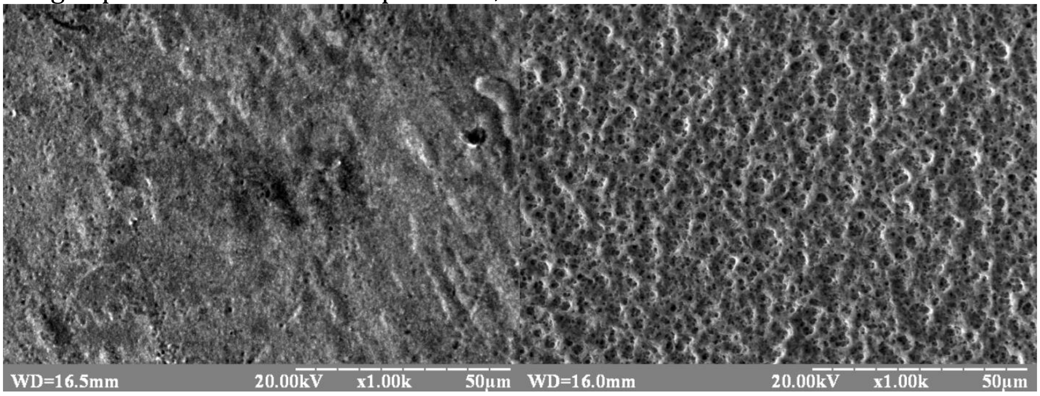
Introduction

Platinum-based materials are widely used as cathode materials in the electroreduction of oxygen in fuel cells [1]. To enhance electrochemical activity and achieve a highly developed surface, dispersed graphite as well as carbon nanostructured materials activated by platinum are utilized [2; 3]. The application of platinum group metals as electrode materials is due to their high catalytic activity as well as the lowest overpotential parameters on electrode processes. On the other hand, platinum group metals are noticebly expensive raw materials, finding cheaper yet equally effective alternatives are essential for production optimization. Recently, a significant volume of research has focused on the catalytic properties and synthesis of chalcogenide materials, particularly the sulfides of iron group metals [4–6]. Newly introduced materials have been used as catalysts for the electroreduction of oxygen and hydrogen, the anodic production of oxygen, as well as in their application in electrode materials, which are subsequently used as primary power sources and fuel cells [7; 8]. Nickel sulfides, in particular NiS and Ni_3S_2, are of special interest due to their high electrical conductivity comparable to that of a pure nickel [9; 10]. The high catalytic activity of these compounds, particularly in relation to the electroreduction of oxygen, according to [11; 12] is attributed to the effect of sulfur on the desorption of the product of oxygen electroreduction -hydroxyl ions (OH). The binding energy between nickel and sulfur exceeds that of nickel and oxygen, thus facilitating the desorption of hydroxyl ions. This acceleration of EC occurs in both neutral and alkaline environments. The high electrical conductivity, along with the potential for rapid redox processes on the surface of nickel sulfides in case of a high specific surface area is provided, contributes to significant pseudocapacitance, making these compounds suitable for use as electrode materials in supercapacitors [13; 14]. Chemical synthesis is often used to produce electrode materials based on nickel sulfides [4; 13–17]. Interestingly, studies investigating the corrosive behavior of nickel supplemented with sulfur indicate that a layer of Ni_3S_2 forms on the surface during anodic treatment in dilute sulfuric acid [18]. Previous studies demonstrated the formation of a Ni_3S_2 layer and sulfides with higher sulfur content when galvanic nickel coatings with elevated sulfur content are exposed to acetic acid vapors [19-21]. This work aims to explore how sulfur segregation in the form of sulfides and adsorbed sulfur affects the electrochemical properties of galvanic nickel coatings during corrosion treatments.

Experimental part

The study of electrochemical properties was conducted on electrodes made of electrodeposited nickel foil and titanium foil coated with nickel.

When creating titanium-based electrodes, three main stages can be distinguished: 1) preparation of the electrode surface; 2) electrodeposition of galvanic nickel coatings; and 3) corrosion treatment. The composition of the nickel plating electrolyte, the conditions of electrodeposition, and the features of corrosion treatment of electrodes with bright nickel coatings are described in detail in [19–21]. The duration of corrosion treatment in concentrated acetic acid varied between 2 and 240 hours. After corrosion testing, the soluble corrosion products were washed off with distilled water, and the resulting electrodes were gently dried with warm air. The initial state of the surface of nickel foil electrodes and its modification as a result of corrosion treatment are shown in Fig. 1.



a b

Fig. 1. SEM-images of the surface of nickel based electrode before treatment (a) and after corrosion treatment (b) in concentrated acetic acid for 72 h

Current work also investigated the electrochemical properties of electrodes obtained from electrochemically formed nickel foil with a thickness of 50 microns, created from a nickel plating electrolyte without the addition of a bright-forming saccharin additive. The temperature and current density were the same as those used for the electrodeposition of bright nickel coatings. The corresponding nickel foil was treated in a saturated solution of sodium sulfide for 2 to 72 hours.

Following this processing, the samples were thoroughly washed. According to the results of the EDX analysis [20; 21], conducted using the REM-106I with the Oxford INCA Energy 350 energy dispersion microanalysis system, the sulfur content in the galvanic nickel coatings derived from the nickel plating electrolyte without saccharin is approximately 10^{-2} wt.%, which is comparable to the determination error. From now on, such nickel coatings and foils will be referred to as "matte coatings". The introduction of saccharin to the nickel plating electrolyte leads to the inclusion of sulfur in the coatings structure at the level of 0.2–0.3 wt.%, influencing the production of bright coatings and foils. With partial and complete dissolution of the bright nickel coatings in acetic acid a slightly soluble layer of corrosion products is formed, which, as demonstrated in [20], may contain sulfides of various stoichiometric compositions, particularly Ni_3S_2. The study of the electrochemical properties of the developed electrode materials was based on polarization measurements conducted in a 0.1 M KOH solution, the measured alkalinity value corresponded to pH 11. The potentiodynamic cathode curves were recorded at a potential sweep rate of 1 mV/s using the digital potentiostat VersaStat 2000. The potential scan rate for cyclic voltammograms was 10 mV/s. For comparison, CV-curves were also obtained in sodium acetate solutions with a concentration of 30 g/dm^3 without (pH 8.4) and with the addition of concentrated acetic acid (pH 3.7) [20]. The studies were conducted at a temperature of 18 °C. A saturated chlorine-silver electrode served as the reference electrode, and a platinum electrode was used as the auxiliary electrode. On the polarization curves, the electrode potential values are given in the scale of a saturated silver-chloride reference electrode. The pH value of the tested solutions was measured using The Mettler Toledo SevenMulti mV/ORP ph Meter.

Results and Discussion

Polarization measurements were conducted in an alkaline medium using a 0.1 M KOH solution. This specific solution was chosen to shift the hydrogen release potential to more negative values. Under standard conditions, the potential of the hydrogen electrode in this solution is approximately −0.65 V, or about −0.85 V on the chlorine-saturated silver electrode scale. According to data [22; 23], the solubility of oxygen in such an electrolyte is considerably high, at $1.1 \cdot 10^{-6}$ mol·cm^{-3}, with a diffusion coefficient of $1.9 \cdot 10^{-5}$ cm^2·sec^{-1}. Given a diffusion layer thickness of around 10^{-3} cm, the maximum diffusion current for oxygen electroreduction can reach 0.1 mA/cm^2.

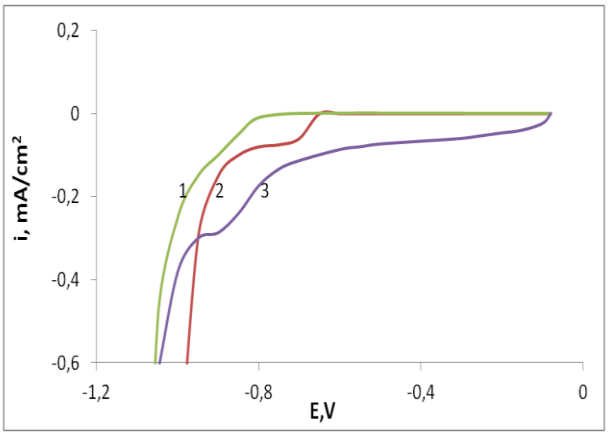


Fig. 2. Potentiodynamic polarization curves in 0.1 M KOH: 1 – matte nickel; 2 – bright nickel foil; 3 – bright nickel foil with a formed layer of sulfide corrosion products after 24 hours of exposure in acetic acid

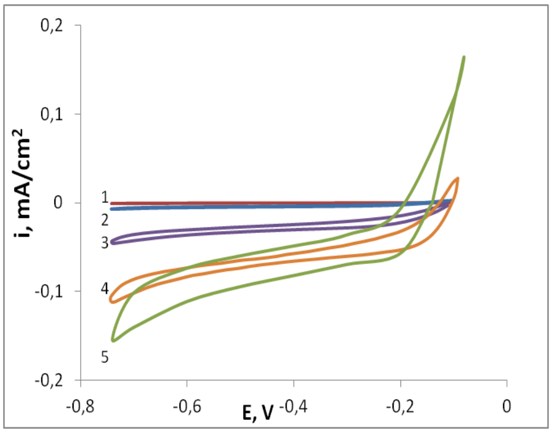


Fig. 3. CV-curves in 0.1 M KOH on electrodes made of bright galvanic nickel coatings with a formed layer of sulfide corrosion products, with different duration of exposure in acetic acid, in hours: 1 – 0; 2 – 2; 3 – 4; 4 – 24; 5 – 72.

As depicted in the potentiodynamic curves (Fig.2, curve 1,2), the introduction of sulfur into the nickel coatings results in a noticeable reduction of the overpotential for hydrogen release. On sulfur-supplemented nickel, in the potential range of −0.7 to −0.85 V, a wave is observed. According to the Pourbaix diagram for the Ni-S system [18], this wave likely corresponds to the electroreduction of the passive oxide layer on nickel disrupted by sulfur inclusions in the form of sulfide during oxygen electroreduction.

Two waves can be observed on the bright nickel electrode with the sulfide layer which has been formed during corrosion treatment in acetic acid (Fig. 2, curve 3). The first wave, occurring in the potential range of −0.1 to −0.8 V, has a limiting current of approximately 0.06 mA/cm², indicating the process of oxygen electroreduction. The second wave, occurring between −0.8 and −0.95 V, aligns with the Pourbaix diagram [18], suggesting that the reduction of sulfide compounds can occur concurrently with the electroreduction of oxygen and hydrogen.

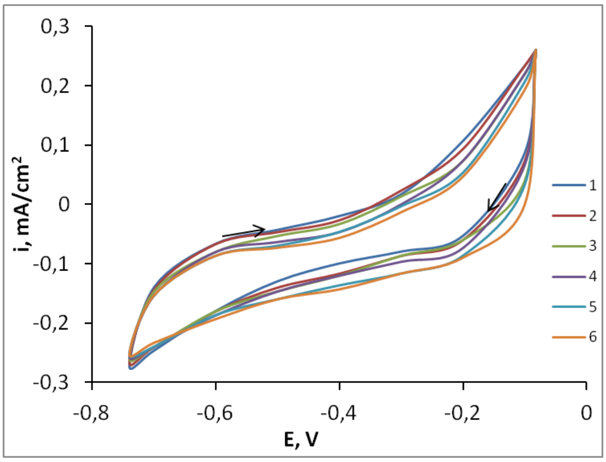


Fig. 4. CV-curves in 0.1 M KOH on a bright galvanic nickel electrode with a layer of sulfide corrosion products formed during 240 h of exposure in acetic acid

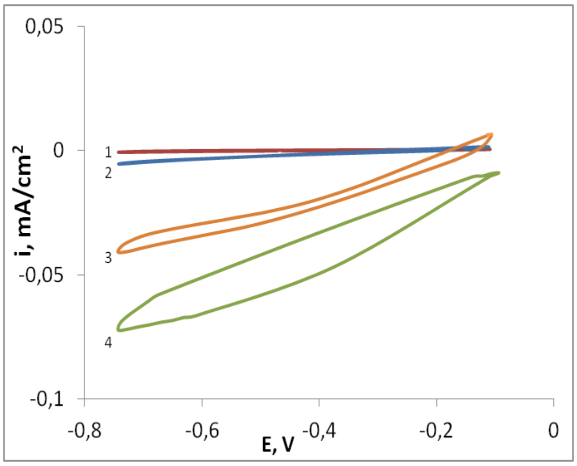


Fig. 5. CV-curves in 0.1 M KOH on electrodes made of matte galvanic nickel coatings, after exposure in a saturated solution of Na_2S for, in hours: 1 – 0; 2 – 2; 3 – 24; 4 – 72

Cyclic voltammetry (CV) curves were obtained in the potential range of −0.74 to −0.1 V. The maximum value within this range corresponds to the equilibrium potential of the nickel electrode in the test solution, while the minimum value delineates the stability limit of the sulfide layers, as established from the data in Fig. 1, which is also consistent with [18]. The reactions at the nickel cathode in the studied potential intervals reveal that an oxygen electroreduction reaction can occur.

From the CV measurements presented in Fig. 3, it is evident that increasing the exposure duration of bright nickel coatings in acetic acid enhances both the forward and reverse currents of the CV curve. This modification aligns with findings from [19], which indicate that the specific surface area of bright nickel coatings increases with prolonged exposure to concentrated acetic acid vapors. Additionally, references [19; 20] suggest that sulfur deposits segregate and grow on the surface, contributing to the formation of a sulfide layer.

It should be noted that with increasing in the duration of exposure, bright nickel in acetic acid leads to greater hysteresis in the cyclic voltammetry curve. The CV curves, obtained by forming a sulfide layer from bright nickel foil after 240 hours are shown in Fig. 4. This figure illustrates a significant increase in hysteresis, which may indicate enhanced capacitive properties of the current due to an increase in the specific surface area. After six cycles of the CV, the curve is slightly modified as a result of changes in stoichiometric composition due to rapid redox reactions and the reversible replacement of adsorbed sulfur with adsorbed oxygen [18]. Therefore, changes in the electrochemical properties of nickel coatings can be modified not only by the increase in specific surface area from corrosion fractures but also by the presence of adsorbed sulfur. To investigate that phenomena, samples of matte nickel foil obtained from an electrolyte without saccharin were exposed to a saturated solution of Na_2S for 2 to 72 hours and their CV curves were recorded, as shown in Fig. 5. During exposure in the saturated Na_2S solution, it was observed that the color of the matte nickel foil changed from silver to golden and dark brown with the increase in exposure time. Moreover, there were no visible changes in the coating surface structure. Since nickel is generally passive in an alkaline environment, the formation of a colored film suggests that its thickness is on the order of 10^{-1} microns.

As can be seen, from Fig. 4 with an increase in the duration of exposure of the foil in the Na_2S solution also leads to an increase in the current on the CV curves, but the values of the currents are slightly lower than for bright nickel which processed in acetic acid Fig. 3. In addition, the hysteresis of the CV curve is less pronounced. In fact, in this case, in a saturated solution of Na_2S, oxygen in the passive film is replaced by sulfur. The longer nickel is exposed to the sulfide solution, the darker the film becomes, indicating a higher surface concentration of sulfur. In fact, both bright nickel and matte nickel exhibit passive behavior within the studied potential range of −0.74 to −0.1 V in a 0.1 M KOH solution.

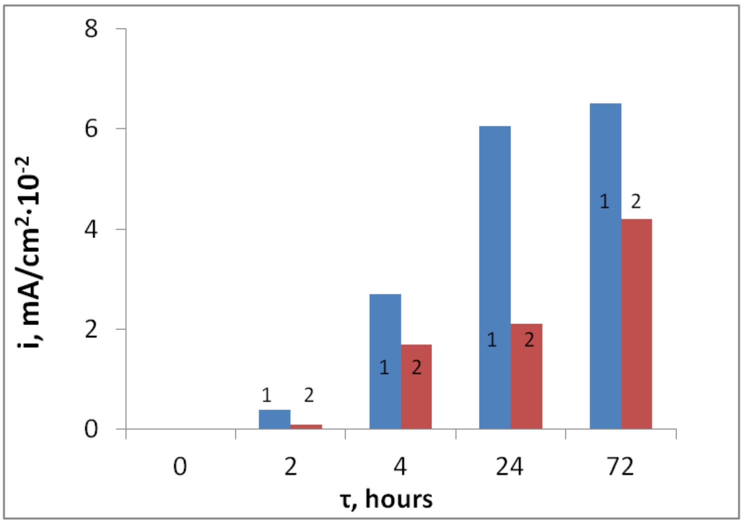
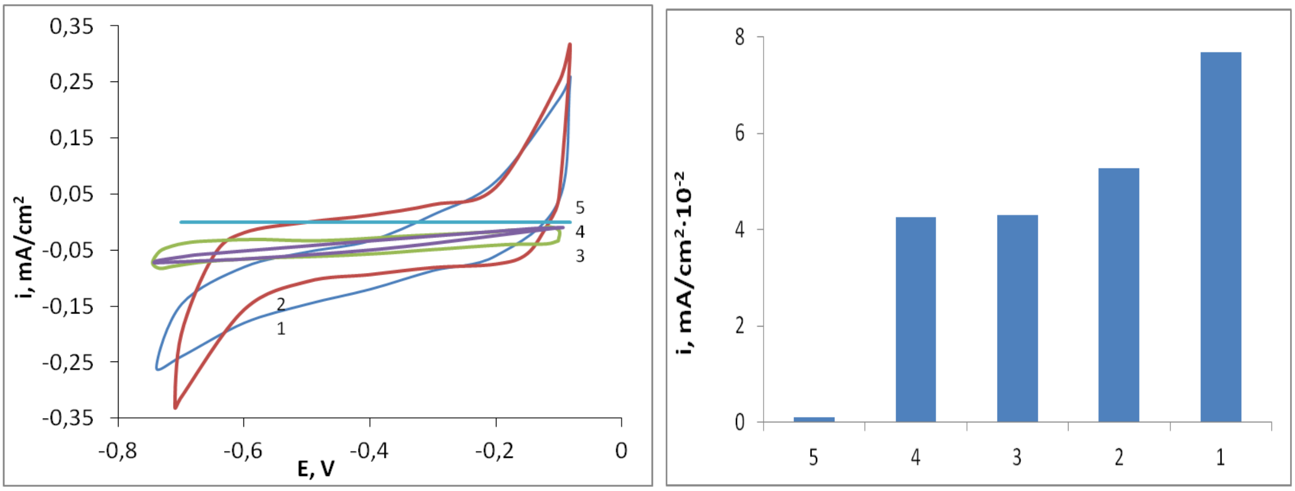


Fig. 6. Dependence of the average value of the cathode current at a potential of -0.4 V in 0.1 M KOH on the duration of pretreatment of nickel foil (hours): 1 - bright nickel foil in concentrated acetic acid; 2 - matte nickel foil in a saturated solution of Na_2S



a

b

Fig.7. CV-curves (a) and average values of cathode current density at a potential of -0.4 V of the corresponding curves (b) in 0.1 M KOH on: 1 – bright nickel foil with sulfide corrosion products formed within 240 h in concentrated acetic acid; 2 – on a titanium electrode with formed corrosion products due to complete dissolution of the electrodeposited bright nickel coating within 72 hours; 3 – on a platinum electrode; 4 – on a matte nickel electrode foil submerged for 72 hours in a saturated solution of Na_2S; 5 – untreated nickel foil

On this basis, the types of treatment studied for galvanic nickel deposits contribute to an increase in the surface concentration of sulfur. Sulfur replacing oxygen on the surface of nickel in a passive film [5; 18], facilitates the desorption of hydroxyl ions and catalyzes the overall process of oxygen electroreduction. Hence, with the amount of sulfur on the surface of nickel increases, the number of catalytically active centers also rises. As depicted, its electrochemical activity could be higher in relation to the electroreduction of oxygen, as evidenced by an increase in current on the CV curves (Fig. 3, Fig. 5). However, it is important to note that the maximum rate of oxygen electroreduction is limited by its solubility in water (the electrolyte) under these conditions. To illustrate this phenomenon, we constructed the dependencies of the average current density (calculated from the values of the forward and reverse current densities of the CV curve at a potential of −0.4 V) on the duration of nickel foil processing, as shown in Fig. 6. As indicated in Fig. 6, the main increase in current density occurs within the first 24 hours of processing. The slightly higher current values for bright nickel foil can be attributed to the increase in the actual surface area caused by corrosion fractures. After 72 hours of processing, the current on the treated matte foil is approximately 0.042 mA/cm^2, while the bright nickel foil, which has formed corrosion products, shows a current of 0.065 mA/cm^2. These current density values correspond to the order of the limiting diffusion current for oxygen electroreduction in a poorly mixed alkaline medium [22; 24]. For comparison, Fig. 7 shows average current density values at –0.4 V obtained on platinum and nickel electrodes processed in various ways. From Fig. 7b, it is evident that the average current density values on matte nickel foil treated in Na_2S solution are nearly equivalent to those on the platinum electrode, given that the surfaces of both materials exhibit similar microrelief and roughness. As expected, the cathode currents on electrodes with a sulfide layer, created by the corrosion treatment, are slighty higher. This is a cumulative result of the increase in electrochemical activity and specific surface area due to corrosion treatment.

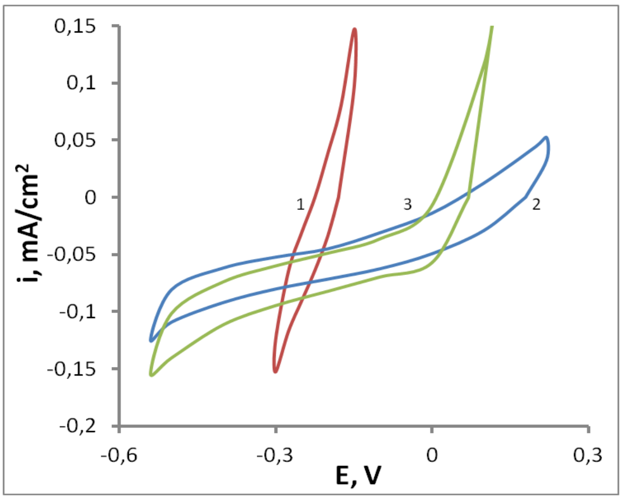


Fig. 8. CV-curves on a bright galvanic nickel electrode with a layer of sulfide corrosion products, at various pH of investigated medium: 1 – 3,7; 2 – 8,4; 3 – 11.

Summarizing the obtained results, it can be emphasized that this work first showed the following. The corrosion formation of sulfides on the surface of bright high-sulfur nickel foil is the most promising way to obtain catalysts for the process of oxygen electroreduction from the point of view of the possibility of practical application. A comparison of the CV-curves obtained in solutions with different pH values on nickel electrodes with a layer of sulfide corrosion products formed within 24 h was also carried out (Fig. 8). Given the shape of the obtained CV-curves (the presence of a rapid increase or decrease in current), the corresponding electrode material is the most stable and effective for the electroreduction of oxygen [25–27] in a low alkaline medium of acetate buffer. This is in good agreement with the data given for electrode materials based on artificial hyzlevudite obtained by a chemical method [12].

Conclusions

It has been established that the examined corrosion treatment methods for galvanic nickel coatings, which enriching surface of the coating with sulfur - either as adsorbed sulfur or through the formation of a sulfide layer - also significantly increase their electrochemical activity. When a solid sulfide layer is formed, or during the adsorption treatment of a nickel electrode in a saturated sodium sulfide solution, the cathodic current densities on the curves are comparable to those of platinum electrodes. On this basis, these treatments enable the production of innovative nickel-based electrode materials, particularly ones that are used for electroreduction of oxygen in fuel cells and other renewable energy sources.

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