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IMPROVEMENT OF CONTINUOUS TECHNOLOGY OF ELECTROCHEMICAL SYNTHESIS OF NICKEL HYDROXIDE BY IMPLEMENTATION OF SOLUTION RECYCLING

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Nickel hydroxide is widely used in supercapacitors, alkaline batteries, for the electrocatalytic oxidation of organic contaminants, etc. Due to their electrochemical activity, $Ni(OH)_2$ (α+β) samples with a layer structure synthesized in a slit diaphragm electrolyzer are the most promising. To improve the continuous technology of electrochemical synthesis of nickel hydroxide, the possibility of recycling the spent catholyte containing sodium sulfate was determined. For this, samples of nickel hydroxide were synthesized from a solution of nickel sulfate in the presence of sodium sulfate with concentrations of 40, 60, 80, 100, and 120 g/L. The crystal structure of the samples was studied by X-ray phase analysis; the electrochemical properties were studied by the method of cyclic voltammetry. It was shown that the base sample obtained without the presence of sodium sulfate was a monophase layered (α+β) structure with a high content of α-modification. The crystallinity of the sample was not high. It was revealed that the presence of sodium sulfate led to a decrease in the crystallinity of nickel hydroxide due to an increase in the electrical conductivity of the solution and a decrease in the voltage in the electrolyzer. Cyclic voltramperometry showed that synthesis in a slit diaphragm electrolyzer in the presence of Na_2SO_4 (40–80 g/L) did not lead to a significant change in the electrochemical activity of nickel hydroxide samples. An increase in the concentration of sodium sulfate in the catholyte to 100–120 g/L led to an increase in electrochemical activity – the specific current of the discharge peak was 3.7–3.9 A/g (compared to 2.1 A/g for the reference sample).

A comprehensive analysis of the characteristics of nickel hydroxide samples synthesized in the presence of sodium sulfate revealed the possibility and prospects of recycling the spent catholyte in a continuous technology for producing $Ni(OH)_2$ in a slit diaphragm electrolyzer. It was revealed that when introducing recycling, it was recommended to maintain a high concentration of sodium sulfate (80–100 g/L)

Keywords: nickel hydroxide, recycling, sodium sulfate, synthesis technology, electrochemical activity, slit diaphragm electrolyzer

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1. Introduction

Nickel hydroxides have a fairly high electrochemical activity [1]. Therefore, these substances are widely used in various electrochemical devices. Mono, double and ternary nickel hydroxides are used in the nickel oxide electrode of alkaline nickel-cadmium, nickel-iron, nickel-metal hydride batteries [2, 3]. Nickel hydroxide is also used in lithium batteries [4].

Various types of nickel hydroxides are used as the active substance of the Faraday electrode in hybrid supercapacitors. In this case, $Ni(OH)_2$ is used both individually [5] (in the form of nanoparticles [6] or ultrafine particles [7]), and as composite materials with nanocarbon structures (graphene oxide [8], carbon nanotubes [9]). For thin-layer supercapacitors, in the manufacture of electrodes on a conductive basis, a $Ni(OH)_2$ film is formed [10].

$Ni(OH)_2$ is practically transparent in thin layers, while NiOOH is brown-black. As a result, nickel hydroxide is used as an electrochromic substance [11, 12]. Nickel hydroxide is used for the electrocatalytic oxidation of organic compounds [13, 14], as well as in sensors [15, 16].

Nickel hydroxides can be obtained by various methods. It should be noted that all methods can be divided into batch and continuous ones. The main disadvantage of batch methods is the fluctuation of the hydroxide characteristics from batch to batch. Continuous methods are free of this drawback and are more promising for transformation into technology. And accordingly, the improvement of continuous methods for the synthesis of $Ni(OH)_2$ is relevant.

2. Literature review and problem statement

One of the main characteristics of $Ni(OH)_2$, which determine the electrochemical activity, are the parameters of the crystal lattice [17], in particular, heterogeneity [18], microstructure [19], crystallinity [20, 21]. These parameters are determined by the synthesis method and by the conditions of carrying out [22].

First of all, the synthesis method determines the type of $Ni(OH)_2$ [23]. Nickel hydroxide exists in two modifications [24]: β-form (formula $Ni(OH)_2$, brucite structure) and α-form (formula $3Ni(OH)_2 \cdot 2H_2O$, hydrotalcite-like structure). The paper [25] describes the existence of a form of nickel hydroxide intermediate between α-$Ni(OH)_2$ and β-$Ni(OH)_2$.

α-$Ni(OH)_2$ has a higher electrochemical activity than β-$Ni(OH)_2$. However, pure α-form has low stability, especially in concentrated alkalis at high temperatures. Under these conditions, the metastable α-modification transforms into a low-active type of β-modification, which the authors call β_{bc} (*bc* stands for badly crystalline) [26]. To stabilize the α-form, additives are introduced [27, 28]; in this case, layered double hydroxides (LDH) are formed [29, 30]. LDHs have a "host" hydroxide crystal lattice, in which part of the "host" cations (Ni^{2+}) are replaced by the "guest" cations, for example, Al^{3+} [31] or V^{4+} [32]. To compensate for the resulting excess charge, various anions are intercalated into the interlayer space of the crystal lattice [33]. These anions can be both anions of precursor salts (nitrates [34]) or anions formed during synthesis (cyanates [35]), or specially introduced anions (carbonates [35, 36]). α-$Ni(OH)_2$ (both mono α-$Ni(OH)_2$ and LDH) can be obtained by chemical synthesis [37], homogeneous deposition [38], electrochemically in a slit diaphragm electrolyzer [39].

β-$Ni(OH)_2$ has significantly higher stability, both electrochemical and thermal. That is why the β-form is widely used as an active substance in alkaline batteries [40] and hybrid supercapacitors [41]. The production of β-$Ni(OH)_2$ can be carried out by chemical deposition at low supersaturation, by electrolysis in a slit diaphragm electrolyzer [42]. High-temperature two-stage synthesis [43, 44] and decomposition method [40] are also used.

The mixed (α+β) structure of $Ni(OH)_2$ possesses the advantages of the α- and β- modifications of nickel hydroxide [45, 46]. The paper [47] has proved that during synthesis in a slit diaphragm electrolyzer (SDE), a highly active nickel hydroxide with a layer (α+β) structure is formed. The high electrochemical activity of the layered sample has been revealed, exceeding the activity of both β-$Ni(OH)_2$ and α-$Ni(OH)_2$. The electrochemical characteristics of (α+β) $Ni(OH)_2$ are also improved due to an increase in oxygen polarization upon charge [48] and slight aging [49]. The high activity of the obtained layered (α+β) nickel hydroxide makes electrochemical synthesis in SDE promising for industrial use.

It should be noted that the synthesis in SDE has another very significant advantage – the method is continuous. In chemical technology, it is known that continuous methods have an advantage over batch methods due to the stability of the characteristics of the resulting product. In addition, chemical technology differs from the chemical method in optimality from a technological and economic point of view. When obtaining nickel hydroxide, a solution of nickel sulfate is fed into the cathodic chamber of the SDE. As a result of electrolysis, hydrogen is released at the cathode and OH^- is formed, which reacts with nickel cations to liberate hydroxide. Under optimal synthesis conditions, after $Ni(OH)_2$ separation, the spent solution contains sodium sulfate and a residual amount of nickel sulfate. Once used, this solution must be purified. Since the synthesis in SDE is carried out at not very high nickel concentrations, the process consumes large amounts of water, which increases the cost of nickel hydroxide. To create an electrochemical technology for obtaining nickel hydroxide in SDE, it is promising to reuse spent catholyte. However, in this case, an excess amount of sodium sulfate will be present in the solution supplied to the cathodic chamber. There are two possible effects of increased sulfate concentration on the electrochemical activity of $Ni(OH)_2$. Firstly, with the increased content of sulfates, these anions can be incorporated into the crystal lattice of the hydroxide [50, 51]. Secondly, the addition of sodium sulfate to the solution will increase the electrical conductivity. This will decrease the voltage across the electrolyzer, which will lead to a decrease in temperature.

It should be noted that, upon preparation in SDE, $Ni(OH)_2$ has a matrix structure similar to organic composites [52]. Nickel hydroxide is the matrix former, and the mother liquor is the filler [45]. Upon receipt, the primary particles of nickel hydroxide move in the slotted gap of the SDE and undergo aging in the Lenz-Joule heat field, which is formed due to the passage of an electric current between the anode and cathode. It is the simultaneous growth of particles and partial crystallization due to aging that is the reason for the formation of a unique (α+β) layered structure. Anions play a significant role in the formation of such a structure and its stabilization. Both sulfates and carbonates can participate in the formation of the (α+β) layered structure of $Ni(OH)_2$. When using an anion exchange membrane, the key role of carbonate anions in the formation of a unique layered (α+β) structure of $Ni(OH)_2$ during synthesis in SDE has been proved in [53]. In [54], electrochemical synthesis of carbonate-activated $Ni(OH)_2$ (α+β) layered structure has been carried out in SDE.

The thermal field plays an essential role in the formation of the nickel hydroxide structure. When nickel hydroxide is formed, the rate of nucleation (formation of crystal nuclei) is significantly higher than the rate of crystal growth. As a result, nickel hydroxide particles are formed according to a complex two-stage mechanism [55]:

– 1st stage (high-speed) – formation of nuclei, their adhesion, and formation of a primary amorphous particle;

– 2nd stage (slow) – crystallization (aging) of the primary amorphous particle. The crystallization process is determined by the composition of the mother liquor, by the duration, and especially by the temperature.

Based on this, the temperature should be a key parameter for controlling the crystal structure of the resulting nickel hydroxide. In general, a high temperature during aging leads to a more preferable production of β-$Ni(OH)_2$ and an increase in crystallinity, while a low temperature leads to the formation of low-crystalline α-$Ni(OH)_2$. Heat treatment after preparation at high temperatures (104–120 °C) leads to the formation of nano-sized particles β-$Ni(OH)_2$ [56–58]. To obtain amorphous α- $Ni(OH)_2$, a cryosynthesis method using microemulsions is used [59].

The effect of temperature at the moment of preparation strongly depends on the method of synthesis and the form of the resulting nickel hydroxide. During the electrochemical template synthesis of thin films of nickel hydroxide, a double effect of temperature has been revealed. At low temperatures, more amorphous nickel hydroxide is formed with low adhesion to the substrate surface. Raising the temperature initially improves the characteristics of the α-$Ni(OH)_2$ film. However, a further increase in temperature leads to a significant deterioration in the electrochemical and electrochromic characteristics of the film, probably as a result of an increase in crystallinity [60]. For the chemical synthesis method, the temperature is also the main factor in controlling the type and crystallinity of the product [61]. It has been shown that at low temperatures (0–10 °C) α-$Ni(OH)_2$ is formed [62]. At a temperature of 15–30 °C, β_{bc}-$Ni(OH)_2$ is formed [61], and at a temperature of 40–60°C, highly crystalline β-$Ni(OH)_2$ is formed [62]. It has been shown that the electrochemical activity increases in the series "β-$Ni(OH)_2$ – β_{bc}-$Ni(OH)_2$ – α-$Ni(OH)_2$", i. e., with an increase in the synthesis temperature, the electrochemical activity of nickel hydroxide decreases. In this case, synthesis at elevated temperatures or heat treatment is often used in research [63–65]. A decrease in temperature during electrochemical synthesis in SDE also leads to a decrease in crystallinity [66]. It should be noted that the effect of temperature on the crystal structure of $Ni(OH)_2$ strongly depends on the type of hydroxide and the method of synthesis.

The characteristics of nickel hydroxide obtained electrochemically from solutions of nickel sulfate and sodium sulfate have not been studied. This fact does not allow improving the method of electrochemical production of $Ni(OH)_2$ in SDE for the creation of industrial technology.

3. The aim and objectives of the study

The study aims to assess the possibility of recycling the spent catholyte by studying the effect of sodium sulfate in a solution of nickel sulfate on the structural and electrochemical characteristics of $Ni(OH)_2$ obtained in a slit diaphragm electrolyzer.

To achieve the aim, the following objectives were set:

– to obtain samples of nickel hydroxide in a slit diaphragm electrolyzer with different content of sodium sulfate in a solution of nickel sulfate;

– to study the structural and electrochemical properties of the samples in order to determine the effect of sodium sulfate content;

– to conduct a comprehensive analysis of the characteristics with an assessment of the possibility of recyclings the spent catholyte.

4. Materials and methods for obtaining nickel hydroxide samples under conditions of changing thermal field and studying their characteristics

Method for obtaining nickel hydroxide samples. The basic synthesis method [53, 54] is based on electrolysis carried out in a flow-type slit diaphragm electrolyzer (SDE). A solution of nickel sulfate (concentration of Ni^{2+} 12.7 g/L) was fed into the cathodic chamber using a peristaltic pump, and a solution of NaOH (concentration of 100 g/L) was fed into the anodic chamber with the same flow rate of 0.2 l/h. The cathode was titanium, to prevent the accumulation of precipitate in the slits of the cathodic chamber; the anode was insoluble, nickel. The cathodic chamber was separated from the anodic one by a low-flow filter diaphragm. The preparation was carried out at an optimal current density of 12 A/dm^2 [53, 54]. As the current flowed, hydrogen was released at the cathode, and hydroxyl ions were generated, which reacted in bulk with the nickel cations to form a precipitate of nickel hydroxide. The precipitate was removed from the apparatus with a stream of catholyte. The hydroxide was separated from the catholyte by means of a vacuum pump, a Bunsen flask, and a Buchner funnel. Then, the samples were dried at 90 °C for 24 hours, ground, sieved through a 71 μm sieve, rinsed from soluble salts, and re-dried under the same conditions.

To study the effect of sodium sulfate, nickel hydroxide was prepared in the presence of nickel sulfate at concentrations of 40, 60, 80, 100 and 120 g/L.

Study of the characteristics of nickel hydroxide samples.

The crystal structure of the samples was studied by X-ray phase analysis (XRD) using a DRON-3 diffractometer (Russia) (Co-Kα radiation, angle range 10–90°2θ, scan rate 0.1°/s).

The electrochemical properties of nickel hydroxides were studied by cyclic voltammetry in a special NEC-2 cell using an Ellins P-8 electronic potentiostat (Russia). The working electrode was formed by putting a mixture of nickel hydroxide (81 % wt.), graphite (16 % wt.), and polytetrafluoroethylene (PTFE) (3 % wt.) on the foam nickel base [67]. Electrolyte – 6M KOH. The counter electrode was a nickel grid; the reference electrode was saturated silver chloride. The study was performed in the potential range of 200–700 mV (NHE) at a scan rate of 1 mV/s.

5. Results of studying the effect of sodium sulfate in catholyte on the characteristics of nickel hydroxide samples

The following labeling of nickel hydroxide samples was used in the study: S0.2-12SF120, where 120 – the concentration of Na_2SO_4 in g/L. Sample S0.2-12SF0 synthesized without the presence of sodium sulfate was used as a reference.

Effect of sodium sulfate on the structure of the samples. The diffraction pattern of the control sample S0.2-12SF0 (Fig. 1, *a*), synthesized without the presence of sodium sulfate, showed peaks of the low-crystalline β-phase. The α-$Ni(OH)_2$ peak was also identified at 2Θ=13–14°. The diffraction pattern also revealed peaks of two additional phases of nickel hydroxide at 2Θ=17.7° (this phase was indicated on the diffraction patterns by the sign *) and at 2Θ=10.5° (this phase was indicated on the diffraction patterns by the sign °). The diffraction patterns of samples S0.2-12SF100 and S0.2-12SF120 showed a peak in the small-angle region (at angles of 2Θ less than 10°). This indicated the formation of either an amorphous hydroxide phase or a phase with a large interplanar distance in the plane direction (001). In general, it should be noted that the introduction of sodium sulfate and increasing its concentration reduced the crystallinity of the samples (α+β) $Ni(OH)_2$.

Effect of sodium sulfate on the electrochemical properties of the samples.

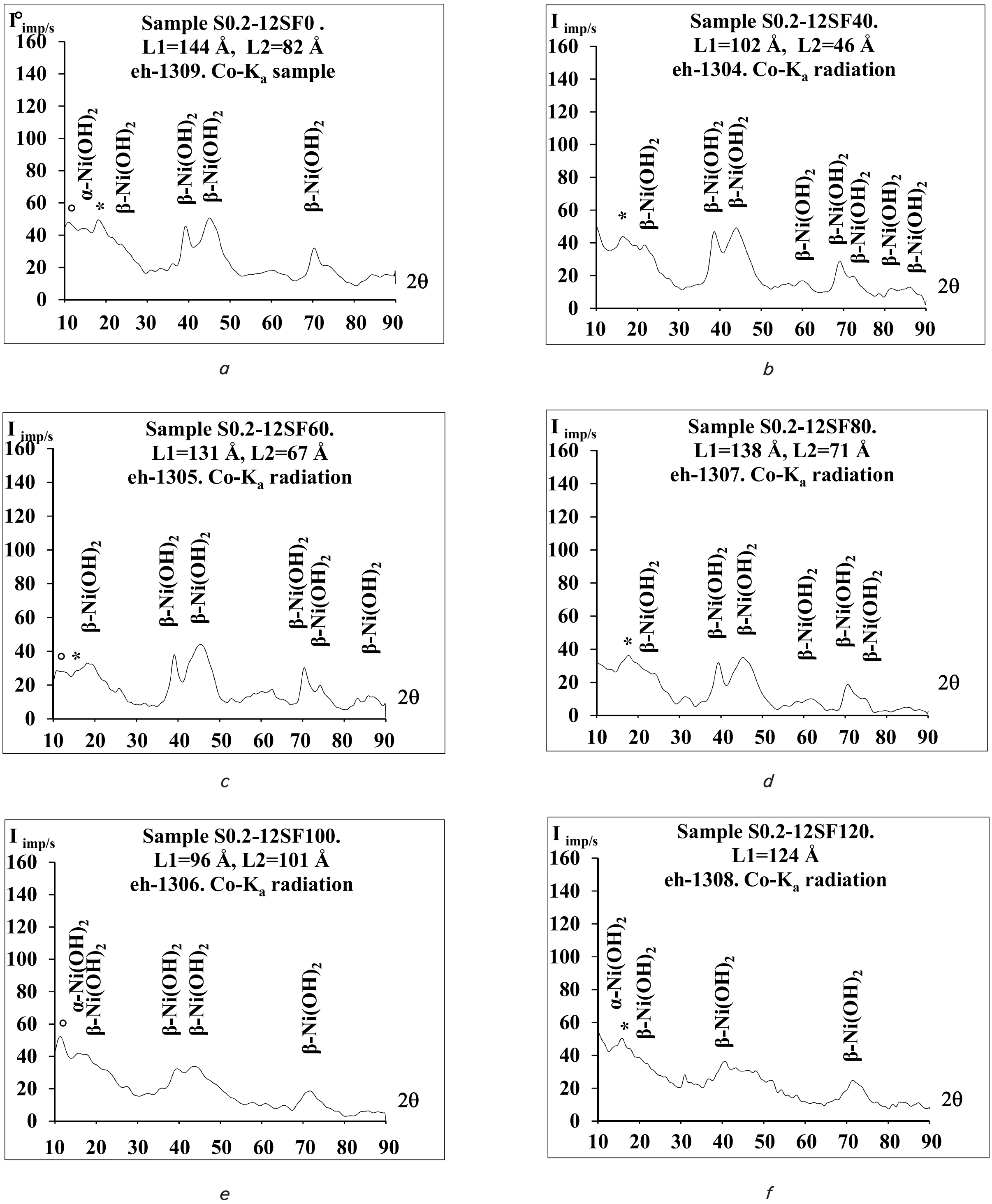

Fig. 1. Diffraction patterns of nickel hydroxide samples obtained in the presence of various amounts of Na_2SO_4:
a — S0.2-12SF0; *b* — S0.2-12SF40; *c* — S0.2-12SF60;
d — S0.2-12SF80; *e* — S0.2-12SF100; *f* — S0.2-12SF120

The cyclic voltammograms of the nickel hydroxide samples are shown in Fig. 2. The cyclic curve of sample S0.2-12SF0, synthesized in the absence of sodium sulfate, was characteristic of the (α+β) structure of $Ni(OH)_2$ [53, 54]: there was a pronounced peak on the first charging cycle, reversibility of the charge-discharge process was high.

The samples synthesized in the presence of low amounts of sodium sulfate (S0.2-12SF40, S0.2-12SF60, S0.2-12SF80) were characterized by the absence of a clear first charging peak, and the specific current of the discharge peak did not change. An increase in the sodium sulfate concentration to 100–120 g/L (samples S0.2-12SF100 and S0.2-12SF120) led to the appearance of a clear first charging peak and an increase in the specific current of the discharge peak.

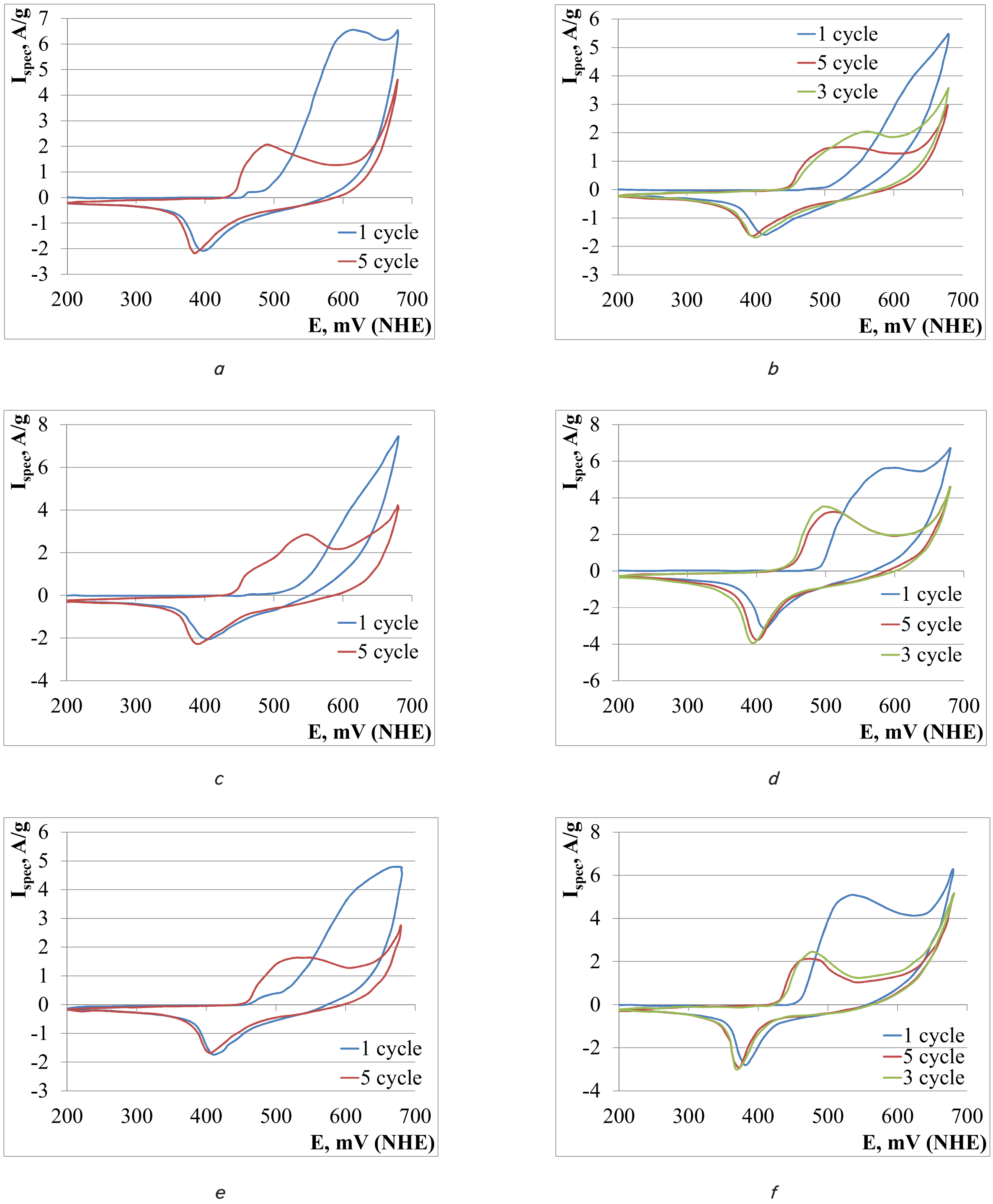

Fig. 2. Cyclic voltammograms of nickel hydroxide samples obtained in the presence of different amounts of Na_2SO_4: *a* – S0.2-12SF0; *b* – S0.2-12SF40; *c* – S0.2-12SF60; *d* – S0.2-12SF80; *e* – S0.2-12SF100; *f* – S0.2-12SF120

6. Discussion of the results of the sodium sulfate effect on the characteristics of nickel hydroxide samples

During recycling, a solution that already contained sodium sulfate was sent to the beginning of the process. From cycle to cycle, the concentration of Na_2SO_4 increased. The retention or increase in the electrochemical activity of nickel hydroxide synthesized in the presence of sodium sulfate would clearly indicate the possibility of recycling in technology.

Effect of sodium sulfate on the crystal structure of nickel hydroxide samples. The results of X-ray phase analysis (Fig. 1, *a*) showed that the control sample S0.2-12SF0 had an ($\alpha+\beta$) layered structure of $Ni(OH)_2$. The crystallinity of the sample was low. The peaks of two other structures of nickel hydroxide were also revealed. The peak at $2\Theta=17.7°$ corresponded to the phase intermediate between β-$Ni(OH)_2$ and α-$Ni(OH)_2$ along the interplanar distance of the (001) plane. This phase was indicated on the diffraction patterns by *. The peak at $2\Theta=10.5°$ corresponded to a phase with a larger interplanar spacing of the (001) plane than α-$Ni(OH)_2$. On the diffraction patterns, this phase was denoted by °. The introduction of sodium sulfate and an increase in its concentration led to a decrease in the crystallinity of the samples. This can be the result of two effects. The presence of an excess of sulfate ion in the solution led to defecting of the crystal lattice, and as a result, to amorphization. On the other hand, the introduction of sodium sulfate led to a decrease in the solution resistance, a decrease in the voltage on the cell and, as a result, a decrease in the catholyte temperature. And this, as shown in [66], led to a decrease in the crystallinity of nickel hydroxide.

Effect of sodium sulfate on the electrochemical properties of nickel hydroxide samples. The analysis of diffraction patterns was carried out according to the presence of a clearly defined first charging peak, and to the value and stability of the specific currents of the discharge peak and reversibility (the potential difference between the anodic and cathodic peaks) (Table 1).

Table 1

Parameters of cyclic voltammograms of various nickel hydroxide samples

Labeling	E_a^1, mV	E_a^5, mV	E_k, mV	ΔE, mV	I_{spec}, A/g
S0.2–12SF0	610	490	400	90	2.1
S0.2–12SF40	–	555	400	155	1.8
S0.2–12SF60	–	555	390	165	2.2
S0.2–12SF80	–	525	410	115	1.9
S0.2–12SF100	590	495	395	100	3.9
S0.2–12SF120	515	470	370	100	3.7

Designations: E_a^1, *– potential of the anodic peak of the 1st cycle;* E_a^5, *– potential of the anodic peak of the 5th cycle;* E_k *– potential of the cathodic peak,* ΔE *– potential difference between the anodic and cathodic peaks at the 5th cycle;* I_{sp} *– specific current of the cathodic peak of the 5th cycle*

The control sample of nickel hydroxide S0.2-12SF0 exhibited the properties of (α+β) $Ni(OH)_2$. The synthesis of hydroxide at low concentrations of Na_2SO_4 (40, 60, and 80 g/L) led to the disappearance of the first charge peak. The reversibility of the oxidation-reduction process also deteriorated. In this case, the specific current of the discharge peak remained practically unchanged. This indicated a slight deterioration in the charging properties of nickel hydroxide while maintaining the discharge characteristics. At low concentrations of sodium sulfate, the increase in electrical conductivity, and, accordingly, the decrease in temperature, was insignificant, and as a result, the decrease in the crystallinity of the sample was small, which was confirmed by the data of the X-ray phase analysis. This should have led to a slight increase in electrochemical activity. It was shown in [54] that sulfate ions during synthesis in SDE promoted the formation of the β-component of the layered (α+β) structure of $Ni(OH)_2$. As a result, synthesis in the presence of an additional amount of sulfate ions gave hydroxide samples with an increased proportion of the β-form. It should be noted that a clearly pronounced first charging (anodic) peak, indicating a high electrochemical activity, was characteristic of samples S0.2-12SF100 and S0.2-12SF120 synthesized in the presence of high concentrations of sodium sulfate. The same samples were characterized by the highest specific currents of the discharge peak and the best reversibility. All this indicated a high electrochemical activity exceeding the electrochemical activity of the reference sample S0.2-12SF0. At high concentrations of sodium sulfate, the main role was played by a decrease in crystallinity due to a decrease in solution resistance and, accordingly, a decrease in temperature during synthesis. In general, it should be noted that the presence of sodium sulfate in the catholyte led to the synthesis of highly active $Ni(OH)_2$ in SDE. In this case, obtaining at high concentrations of sodium sulfate made it possible to increase the electrochemical characteristics of the samples. Therefore, a conclusion can be drawn about the possibility and advisability of recycling the spent solution with sodium sulfate in the continuous technology of electrochemical synthesis of $Ni(OH)_2$ in SDE. It should be noted that the electrochemical activity of hydroxide samples was studied by the method of cyclic voltammetry. To clarify the optimal range of sodium sulfate concentrations, it is necessary to study the electrochemical characteristics by the method of galvanostatic charge-discharge cycling.

7. Conclusions

1. To identify the possibility of catholyte recycling, samples of nickel hydroxide have been synthesized in a slit diaphragm electrolyzer from a solution of nickel sulfate in the presence of sodium sulfate with concentrations of 40, 60, 80, 100 and 120 g/L.

2. X-ray phase analysis has shown that the control sample obtained without the presence of sodium sulfate has a unique (α+β) layered structure with a high content of α-like structures. It has been revealed that synthesis in the presence of sodium sulfate leads to a decrease in crystallinity due to an increase in the electrical conductivity of the solution and a decrease in the voltage in the electrolyzer. Cyclic voltamperometry has shown that the synthesis in SDE in the presence of Na_2SO_4 (40–80 g/L) does not lead to a significant change in the electrochemical activity of nickel hydroxide samples. An increase in the concentration of sodium sulfate in the catholyte to 100–120 g/L leads to an increase in electrochemical activity – the specific current of the discharge peak is 3.7–3.9 A/g (compared to 2.1 A/g for the control sample).

3. A comprehensive analysis of the characteristics of nickel hydroxide samples synthesized in the presence of sodium sulfate has revealed the possibility and prospects of recycling the spent catholyte in the continuous technology of obtaining $Ni(OH)_2$ in a slit diaphragm electrolyzer. It has been revealed that when introducing recycling, it is recommended to maintain a high concentration of sodium sulfate (80–100 g/L).

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