Гідроксид нікелю широко використовується як активна речовина суперконденсаторів. Найбільш активними є зразки Ni(OH)₂ (α+β) шарової структури, синтезовані в щілинному діафрагмовому електролізері (ЩДЕ). Вивчена можливість карбонатної активації шаруватого (α+β) Ni(OH)₂ шляхом синтезу зразків в щілинному діафрагмовому електролізері при використанні в якості аноліту суміші натрій гідроксиду з натрій карбонатом. Мольну частку карбонату натрію в суміші NaOH+Na₂CO₃ контролювали ацидіметричним титруванням в присутності двох індикаторів. Синтез зразків гідроксиду нікелю проводили при мольній долі карбонату натрію від 0,16 (NaOH без додаткового введення карбонату) до 0,83. Кристалічна структура зразків вивчена методом ренгенофазового аналізу, електрохімічні характеристики – методами циклічної вольтамперометрії та гальваностатичного зарядно-розрядного циклування в акумуляторному режимі. Методом ренгенофазового аналізу показано, що при збільшенні мольної частки карбонату в аноліті до 0,49 кристалічність монофазної шаруватої (α+β) модифікації збільшується. Виявлено, що при подальшому підвищені частки карбонату відбувається різка аморфізація структури зразків в результаті часткового розпаду решітки гідроксиду з утворенням основних солей та формуванням біфазної системи. Цей висновок підтверджується даними циклічної вольтамперометрії та розрядними кривими. Вивчення електрохімічних характеристик показало, що до мольної частки карбонату 0,39 відбувається карбонатна активація гідроксиду зі збільшенням питомої ємності. Збільшення частки карбонату до 0,49 призводить до зниження питомої ємності, а подальше підвищення вмісту карбонату призводить до розпаду гідроксиду до основних солей і суттєвому зниженню електрохімічної активності. Для досягнення максимального активуючого ефекту оптимальна мольна частка карбонату натрію повинна становити 40 %. Зразок гідроксиду нікелю, синтезованого в даних оптимальних умовах, має питому ємність 234 мА·год/г та високу активуємість сполуками кобальту, питома ємність зростає до 254 мА·год/г

Ключові слова: карбонат, активація, гідроксид нікелю, шарова (α+β) структура, лужний акумулятор, щілинний діафрагмовий електролізер

ANIONIC CARBONATE ACTIVATION OF LAYERED (α+β) NICKEL HYDROXIDE

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1. Introduction

Different types of nickel hydroxides posses rather high electrochemical activity [1]. Therefore, these compounds are widely used in different electrochemical devices.

$Ni(OH)_2$, along with double and triple nickel hydroxides, is a core component of nickel oxide electrode in alkaline Ni-Cd, Ni-Fe and Ni-MeH accumulators [2, 3]. $Ni(OH)_2$ is also used in lithium batteries [4].

Nickel hydroxides are used as the active material of the Faradic electrode of hybrid supercapacitors. $Ni(OH)_2$ is used on its own [5] (nano-sized [6] or ultrafine [7]), and in the form of composite with nanocarbon materials (graphene oxide [8], carbon nanotubes [9]). For thin layer supercapacitors, a film of $Ni(OH)_2$ can be formed on the conductive substrate [10].

Because thin films of $Ni(OH)_2$ are transparent, and NiOOH has dark-brown color, nickel hydroxide is used as electrochromic material [11, 12].

Nickel hydroxide has high electrocatalytic activity and is used for electrooxidation of various organic compounds [13, 14], and in the sensors [15, 16].

Each use case requires a specific set of nickel hydroxide parameters. Directed synthesis of the product with desired characteristics has become a trend in the modern chemical industry. Activation is one of the relevant methods for improving structural properties and electrochemical activity of nickel hydroxide.

2. Literature review and problem statement

Synthesis method and parameters determine characteristics of nickel hydroxide, namely irregularity of crystal lattice [17], microstructure [18], crystallinity [19, 20]. In turn, these parameters affect electrochemical activity.

Synthesis method primarily influences the type of $Ni(OH)_2$ [21]. Two polymorphs of nickel hydroxides are known: β-hydroxide (chemical formula $Ni(OH)_2$, brucite-like structure) and α-hydroxide (chemical formula $3Ni(OH)_2·2H_2O$, hydrotalcite-like structure). However, the paper [22] describes the formation of nickel hydroxide structure that is in-between $α-Ni(OH)_2$ and $β-Ni(OH)_2$.

α-Ni(OH)$_2$ has higher electrochemical activity than β-Ni(OH)$_2$. However, it has low stability, especially in concentrated alkali and at elevated temperatures. Under these conditions, the metastable α-form transforms into β-form with low activity, called β$_{bc}$ (bc – badly crystalline) by the authors [23]. This transformation results in a decrease of specific capacity. To stabilize the α-form, stabilizing additives are introduced to nickel hydroxide [24, 25], forming layered double hydroxides (LDH) [26, 27]. LDH consist of the host crystal lattice, in which part of host hydroxide cations (Ni^2) are substituted by guest cations such as Al^{3+} [28] or V^{4+} [29]. The excess of positive charge is compensated by intercalation of various anions [30]. Anions can be those of precursor metal salts (nitrate [31]) or those formed during synthesis (cyanate [32]) or specially introduced (carbonates [33, 34]). α-Ni(OH)$_2$ and nickel-based LDH can be prepared using chemical precipitation [34], homogeneous precipitation [35], electrolysis in the slit-diaphragm electrolyzer [36].

β-Ni(OH)$_2$ has significantly higher stability. That is why, this form is widely used in alkaline batteries [37] and hybrid supercapacitors [38]. β-Ni(OH)$_2$ can be precipitated chemically at low supersaturation or electrochemically in the slit-diaphragm electrolyzer [39]. High-temperature synthesis [40] and ammine complex decomposition [37] are also used.

Mixed (α/β) Ni(OH)$_2$ structure combines the advantages of both nickel hydroxide forms [41, 42]. The paper [43] described that synthesis in the slit-diaphragm electrolyzer (SDE) results in the formation of highly active nickel hydroxide with the layered (α+β) structure. The sample demonstrated high electrochemical activity that exceeds that of β-Ni(OH)$_2$ and α-Ni(OH)$_2$. Electrochemical characteristics of (α+β) Ni(OH)$_2$ are also improved because of higher oxygen polarization during charge [44] and insignificant aging [45]. High activity of such layered (α+β) nickel hydroxide makes electrochemical SDE synthesis promising for industrial applications.

It should be noted, that nickel hydroxide synthesized in the SDE has a matrix structure that is similar to organic [46] and inorganic [47] composite materials. The matrix is formed by nickel hydroxide with the mother liquor being the filler [39]. During synthesis, initially formed particles pass along the slit of the SDE, their aging is induced by the field of Joule heat, which results from electric current passing between the anode and cathode. Such a combination of growth with partial crystallization results in the formation of the unique (α+β) layered structure. Formation and stabilization of such structure are heavy influenced by anions. The influence of anions on LDH properties is studied rather well [1, 30]. In [33], it is noted that carbonate ions possess greate stabilizing properties. The feature of (α+β) Ni(OH)$_2$ synthesis in the SDE [43] lies in that the cathodic chamber is fed with a nickel sulfate solution with the precipitant (hydroxyl ions) formed due to electrolysis. Thus, only sulfate ions are present in the cathodic chamber. However, the anodic chamber of the SDE is fed with NaOH, which can contain some amount of carbonates. If the diaphragm is used, the pressure difference between the anodic and cathodic chamber can lead to the transfer of carbonate-containing anolyte into the catholyte as a result of diffusion and filtration. There is also a diffusion mechanism for the transfer of carbonates into the cathodic chamber. Both sulfate and carbonate can play a role in the formation of the (α+β) layered structure Ni(OH)$_2$. By using the anion-exchange membrane [48], it was found that carbonate ions play a key role in the formation of the unique layered (α+β) Ni(OH)$_2$ structure during SDE synthesis. Intercalation of additional ions can occur due to their inclusion into the initial matrix. During crystallization, additional ions can stabilize the metastable α-form. However, the synthesis of the layered (α+β) structure in the SDE [48] was conducted at low carbonate concentrations in the anolyte.

Activating additives are introduced to nickel hydroxide in order to improve its electrochemical activity. The activator can be added to existing nickel hydroxide or during Ni(OH)$_2$ synthesis. Activators can be split into 2 groups: a) surface activators; b) structural activators. Cobalt compounds, which increase the polarization of oxygen evolution, are commonly used as a surface activator. Cobalt compounds in the form salts, oxides or hydroxide are added to the active mass. As structural activators, soluble salts of zinc or aluminum are added during the synthesis stage of hydroxide [49, 50]. This leads to coprecipitation with the formation of double hydroxides and LDH.

One type of structural activation is anionic activation of nickel hydroxide, namely with carbonates. The effect of carbonates on the β- and α-form is fundamentally different. During the formation of the α-form or LDH, carbonate ions are intercalated into the disordered interlayer space [1]. Carbonate ions, as part of the α-phase structure, play two roles – stabilizer [1, 30] and activator [1]. Carbonate ions have an especially strong effect on layered double hydroxides of nickel. Additionally, some authors point out the stabilizing effect [24, 29], while others note the activating effect [32, 33]. It should be noted that carbonate stabilization and activation of LDH are widely studied. Carbonate activation of β-form is rather rare. The authors of [51, 52] indicate that the possible activation mechanism is the formation of defects in the crystal lattice of hydroxide due to partial substitutions of hydroxyl ions with carbonates, which lowers stability and increases electrochemical activity. It should be noted, that activation was conducted for highly-crystalline β-Ni(OH)$_2$. In this case, unlike for LDH, carbonate ions are impurities and this can be considered as doping. Despite a small number of papers on carbonate activation of β-Ni(OH)$_2$, compared to LDH, it is used on an industrial scale by the "APS Plant" (Saratov, Russia).

The promising (α+β) Ni(OH)$_2$ contains intertwined layers of β- and α-forms. Presented data on carbonate activation of β-hydroxide along with the proven key role of carbonates in the formation of (α+β) structure [49] allows assuming that carbonate activation can be a promising method for improving the electrochemical activity of (α+β) Ni(OH)$_2$. In the case of carbonate activation, activation of both α- and β-components can occur.

3. The aim and objectives of the study

The aim of the study is to determine the possibility for carbonate activation of nickel hydroxide synthesized in the slit-diaphragm electrolyzer.

To achieve the set aim, the following objectives were formulated:

– to prepare samples of nickel hydroxide in the slit-diaphragm electrolyzers with NaOH and Na$_2$CO$_3$ in different ratios as the anolyte;

– to conduct a comparative analysis of structural properties and evaluate the effect of carbonate ions as an activator;

– to conduct a comparative analysis of electrochemical characteristics of the samples to determine the possibility of

carbonate activation and optimal carbonate content in the anolyte.

4. Materials and methods for the preparation of activated nickel hydroxide samples and study of their characteristics

4. 1. Method for the preparation of activated nickel hydroxide samples

Analytical grade reagent was used in the research.

Synthesis method [36, 39] is based on electrolysis in the flowthrough slit-diaphragm electrolyzer (SDE). The cathodic chamber was fed with a nickel sulfate solution (concentration Ni^{2+} 12.7 g/L), anodic chamber – NaOH solution (concentration 50 g/L), at a feed rate of 0.2 L/h, using the peristaltic pump. Cathode – titanium, to prevent precipitation of hydroxide onto the electrode surface, anode – insoluble nickel. The synthesis was conducted at an optimal current density of 10 A/dm^2 [36, 39].

Current flow through the cathode results in hydrogen evolution and formation of hydroxyl ions, which react with nickel cations forming nickel hydroxide. Formed hydroxide particles flow across the cathode in the slit of the electrolyzer and are subjected to the Joule heat. The precipitate is removed from the electrolyzer with the catholyte flow. After leaving the SDE, the hydroxide was immediately separated from the catholyte by means of vacuum filtration. The samples were then dried at 90 °C overnight, ground, sifted through a 71 µm mesh, washed from soluble salts and dried again in the same conditions.

For activation, a series of nickel hydroxide samples were prepared using a mixture of NaOH:Na$_2$CO$_3$ in different rations as an anolyte. The molar part of sodium carbonate in the anolyte was 0; 0.1; 0.2; 0.3; 0.4; 0.5; 0.6; 0.7. The real molar parts of sodium carbonate and hydroxide were determined by titration with 0.1N HCl in the presence of phenolphthalein and methyl orange.

4. 2. Characterization of nickel hydroxide samples

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

Electrochemical properties of nickel hydroxide were studied by means of:

a) cyclic voltammetry in a special YSE-2 cell using the Ellins P-8 digital potentiostat (Russia). The working electrode was prepared by pasting a mixture of nickel hydroxide (81 % wt.), graphite (16 % wt.) and polytetrafluoroethylene (PTFE) (3 % wt.) [54] onto the nickel foam current collector [53]. Electrolyte – 6M KOH. Counter-electrode – nickel mesh, reference electrode –

Ag/AgCl (KCl sat.). The electrode was cycled between 200–700 mV (vs Ag/AgCl (KCl sat.)) at a scan rate of 1 mV/s;

b) galvanostatic charge-discharge cycling in the accumulator mode. The study was conducted using a custom-made accumulator mode. The working electrode was made by pasting a mixture of nickel hydroxide (81 % wt.), graphite (16 % wt.) and PTFE (3 % wt.) [54] on the special current collector (Ni mesh welded onto the Ni foil). Electrolyte – 6M KOH. Counter-electrode – cadmium (CdO+graphite+oil, pasted onto the special current collector). Cadmium electrode was specifically charged after preparation. The capacity of the counter-electrode was 2 times higher than that of the working electrode, thus the capacity of the accumulator model is determined by the capacity of the nickel-oxide electrode. Reference electrode – Ag/AgCl (KCl sat.). Charge – 18 hours with 20 % overcharge. The accumulator was charged by 120 % of the theoretical capacity of nickel hydroxide mass on the electrode. This was done to achieve full charge of hydroxide considering oxygen evolution that occurs simultaneously. The discharge was conducted at a 0.2 C rate (discharge current was 0.2 of the theoretic capacity of the working electrode) to 0 V. Charge and discharge were conducted on the custom-built stand, current density and potential were measured using the UT-70 digital multimeter (China). Specific capacity was calculated based on the set current, discharge time and mass of hydroxide on the electrode.

The promising samples were tested for cobalt activation. A solution of cobalt sulfate (5 % Co^{2+} relative to Ni^{2+}) was added to the active mass. The obtained active mass was used to prepare the working electrode for galvanostatic charge-discharge cycling as described above. The label of the samples activated with cobalt was changed to reflect the presence of cobalt, for instance, Sample 4 with Co.

5. Results of studying the influence of carbonate activation on characteristics of nickel hydroxide samples

5. 1. Results of determining the anolyte composition and labeling of nickel hydroxide samples

Table 1 lists sample labels, along with theoretical and experimentally determined molar parts of alkali and sodium carbonate.

Other samples were also used for control:

– the commercial sample of analytical grade basic nickel carbonate (NiOH)$_2$CO$_3$, labeled as Basic carbonate;

– the industrial sample of nickel carbonate prepared at the "APS Plant" (Saratov, Russia). This sample is carbonate-activated, by continuous precipitation with a solution of sodium hydroxide with the addition of sodium carbonate. Labeled as Sample APS.

Table 1

Labeling of nickel hydroxide samples

Molar part	Component	Sample 0-ref*	Sample 0	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5	Sample 6	Sample 7
Theoretical	NaOH	1.0	1.0	0.9	0.8	0.7	0.6	0.5	0.4	0.3
	Na$_2$CO$_3$	0	0	0.1	0.2	0.3	0.4	0.5	0.6	0.7
Experimental	NaOH	0.965	0.84	0.76	0.72	0.68	0.61	0.41	0.29	0.17
	Na$_2$CO$_3$	0.035	0.16	0.24	0.28	0.32	0.39	0.49	0.71	0.83

Note: * – reference sample, synthesized using analytical grade granulated alkali with minimum storage time as an anolyte

5. 2. Influence of carbonate activation on the sample structure

The results of XRD revealed that with increasing the carbonate content in the anolyte, crystallinity increases in the series "Sample 0 – Sample 1 – Sample 2 – Sample 3 – Sample 4 – Sample 5" (Fig. 1, *a–f*), and these samples have the layered (α+β) structure. Increasing the molar part of carbonate to 0.7 and above (Sample 6 and Sample 7) (Fig. 1, *g, h*) results in a significant drop in crystallinity.

Control sample Sample 0-ref has low crystallinity. Sample APS is highly crystalline β-Ni(OH)$_2$.
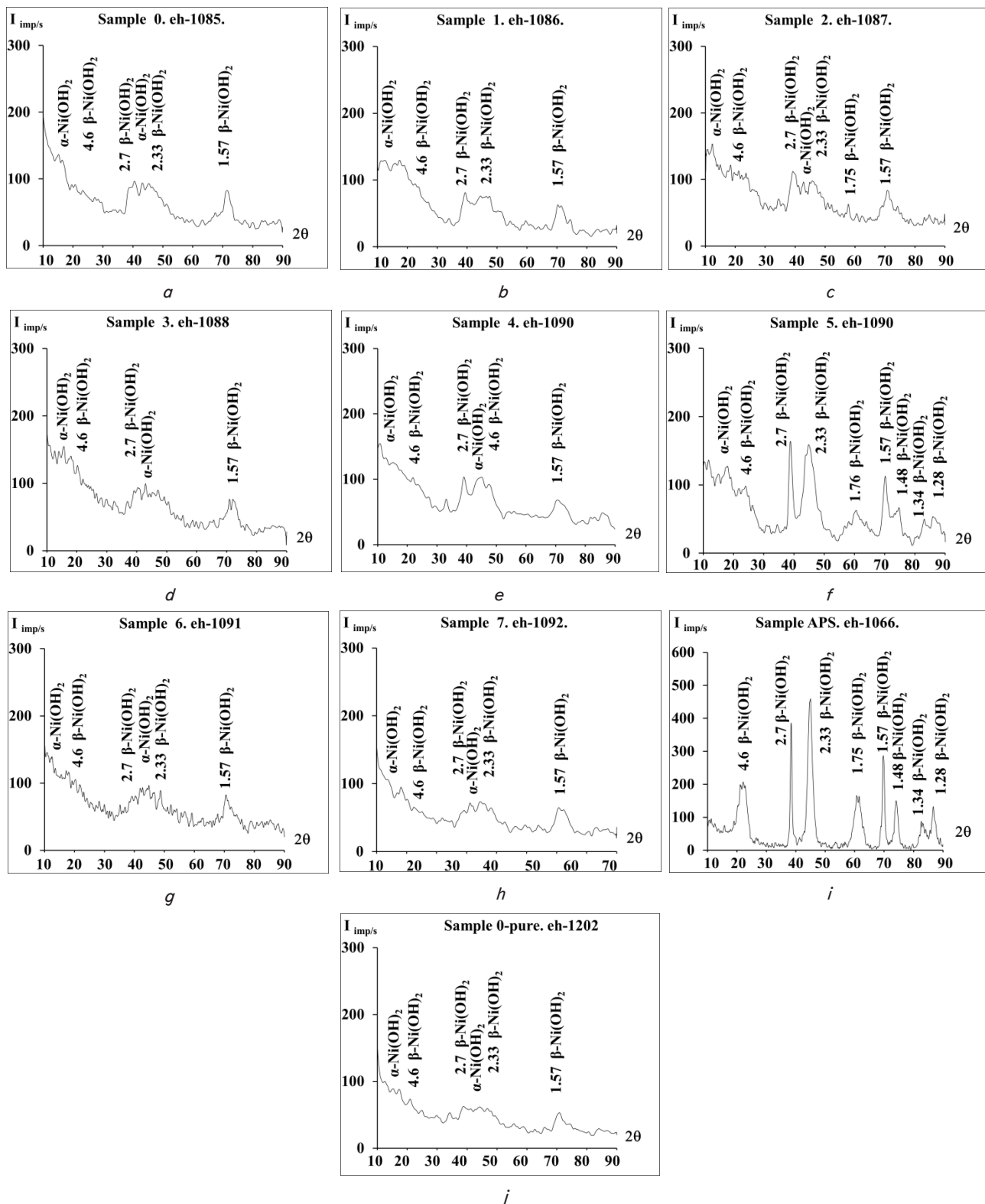

Fig. 1. XRD patterns of nickel hydroxide samples: *a* – Sample 0, *b* – Sample 1; *c* – Sample 2; *d* – Sample 3; *e* – Sample 4; *f* – Sample 5; *g* – Sample 6; *h* – Sample 7; *i* – Sample APS; *j* – Sample 0-ref

5. 3. Influence of carbonate activation on electrochemical characteristics of the samples

Cyclic voltammetry results of carbonate-activated and control samples are shown in Fig. 2. The cyclic curve of Sample APS (Fig. 2, i) has no pronounced peak on the first cycle, charge and discharge peak currents increase with each cycle. For sample Basic carbonate ((Fig. 2, j), change and discharge peaks are poorly defined, peak currents increase with each cycle. Cyclic curves of the carbonate-activated samples at the molar parts of carbonate below 0.49 (Fig. 2, $a-f$) have a well-defined first charge peak, with only one charge and dis-

charge peak for all cycles. The values of charge and discharge peaks remain almost constant from 2 to 5 cycle. The maximum values of the charge and discharge peaks are shown by Sample 4 (Fig. 2, e) – 2.9 and 2.5 A/g, respectively. Further increase of the carbonate content in the anolyte (Sample 6 – Fig. 2, g, Sample 7 – Fig. 2, i) leads to a significant change in the curve's character. The charge curve of Sample 6 has two poorly defined peaks, and the current of the charge peak decreased to 0.3 A/g, the discharge peaks are almost undefined. Sample 7 has a similar character of the cyclic curve with even lower currents.
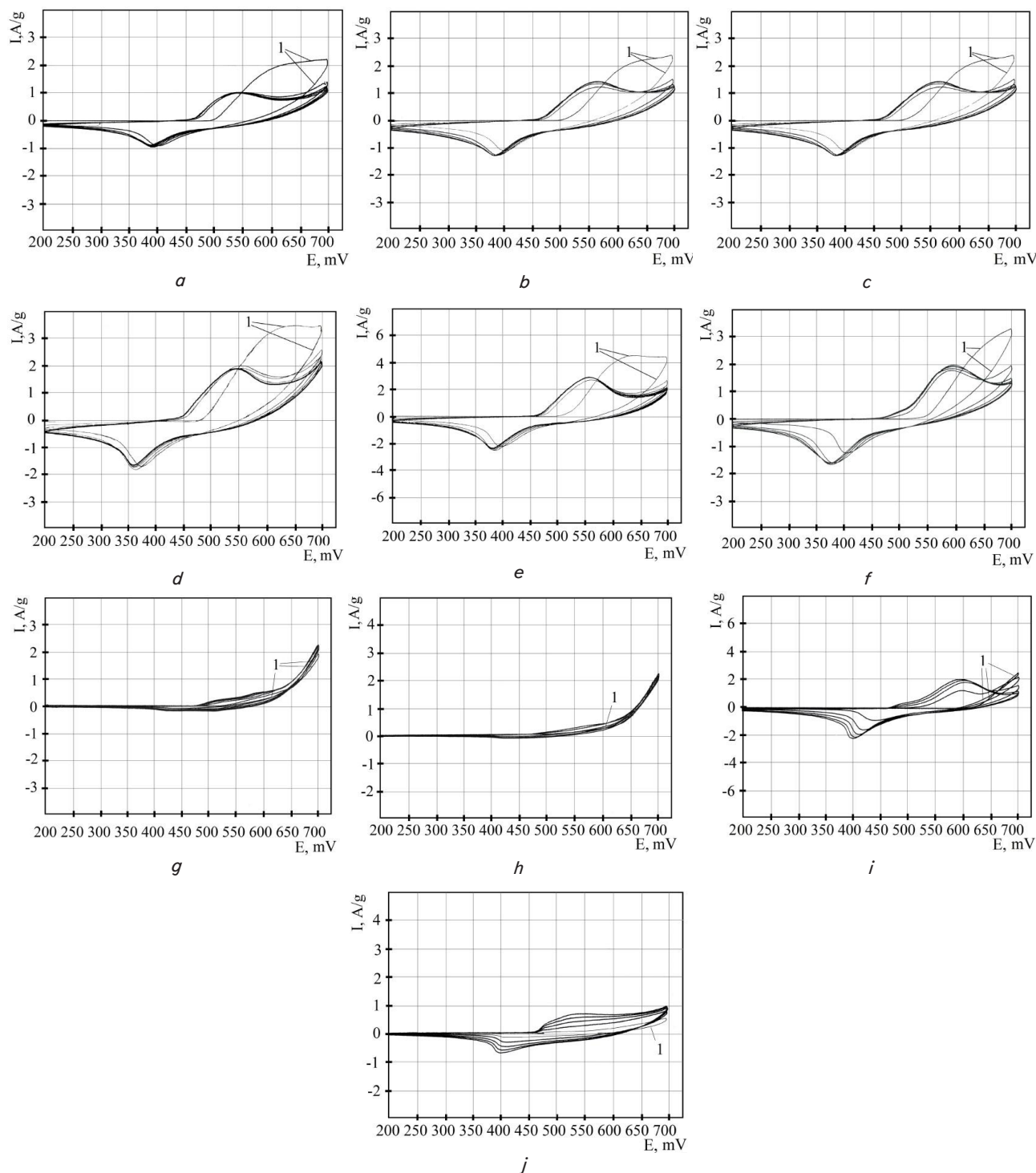

Fig. 2. Cyclic voltamperometry curves of Ni(OH)$_2$ samples: a — Sample 0, b — Sample 1; c — Sample 2; d — Sample 3; e — Sample 4; f — Sample 5; g — Sample 6; h — Sample 7; i — Sample APS; j — Basic carbonate

Fig. 3 shows the discharge curves of galvanostatic charge-discharge cycling of carbonate-activated samples. It should be noted; that the curves of Sample 0-ref and Sample 6 have kinks, and utilization coefficients for these samples are minimal.
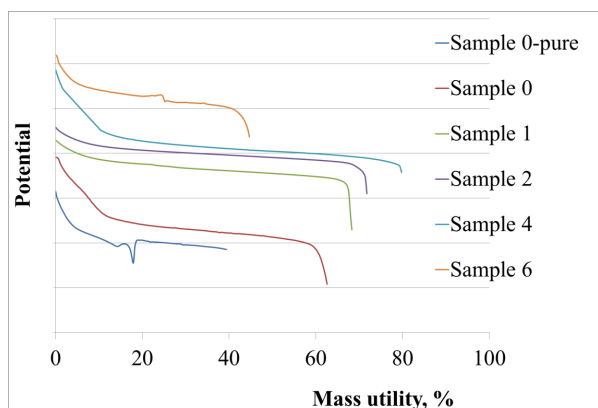

Fig. 3. Discharge curves of carbonate-activated samples

Fig. 4 shows the specific capacities of the samples during galvanostatic discharge in the accumulator regime.
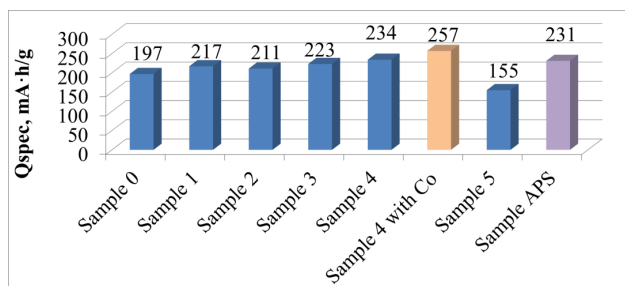

Fig. 4. Specific capacities of nickel hydroxide samples, mA·h/g

Increasing the sodium carbonate concentration in the anolyte in the series "Sample 0 – Sample 1 – Sample 2 – Sample 3 – Sample 4" increases specific capacity. While the specific capacity of Sample 5 dropped significantly.

6. Discussion of the results of studying the influence of carbonate on characteristics of nickel hydroxide samples

Influence on the crystal structure of nickel hydroxide samples. The results of XRD analysis (Fig. 1) revealed that control Sample APS, despite carbonate activation, is β-Ni(OH)$_2$ with high crystallinity. However, the peak at $2\Theta=21°$ has a lower intensity and higher width. This indicates the presence of defects in the crystal lattice in the (001) plane. Carbonate-activated samples synthesized in the SDE at the molar part of sodium carbonate below 0.49 have the monophase layered (α+β) structure, which contains α- and β-forms. With the increase of the molar part of carbonate in the series "Sample 0 – Sample 1 – Sample 2 – Sample 3 – Sample 4 – Sample 5", crystallinity increases. This indicates that with increasing the carbonate content, these anions are incorporated into the structure stabilizing the α-component and introducing defects within the β-component. It is possible; that by intercalation into the initial amorphous hydrox-

ide particle, they become formation centers for metastable α-form and stabilize it. Increasing the carbonate content in the anolyte (Sample 6 and Sample 7) results in a significantly more amorphous structure. It is possible that an excessive amount of carbonate resulted in the partial breakdown of the crystal lattice of nickel hydroxide and formation of basic salt with low electrochemical activity. The bi-phase nature of Sample 6 is supported by the discharge curve (Fig. 3), which shows a pronounced step, characteristic of consecutive discharge of two phases. Sample 0-ref, prepared with the lowest carbonate content in the anolyte, also has low crystallinity. The discharge curve of this sample also has a step, which confirms its bi-phase nature. This can be explained by an insufficient supply of carbonate ions from the catholyte for the formation of monophase (α+β) Ni(OH)$_2$, which is in agreement with the data on the key role of carbonate ions [48].

Influence on electrochemical characteristics of nickel hydroxide samples. The cyclic curve of Sample APS (Fig. 2, *i*) is characteristic of highly crystalline β-Ni(OH)$_2$, the specific currents of the charge and discharge peaks increase with each cycle, which indicates working through of the sample. However, the specific currents of the charge and discharge peaks have rather high values (2.0 and 2.1 A/g, respectively), because this sample is carbon-activated. Sample Basic carbonate (Fig. 2, *j*) has low electrochemical activity, and is also worked through during cycling, the charge and discharge peaks are poorly defined. The cyclic curves of carbonate-activated samples can be split into two groups. In the first group, the samples synthesized at the molar part of carbonate below 0.49 (Fig. 2, *a–f*), the cyclic curves are characteristics of (α+β) layered Ni(OH)$_2$. Judging by the specific currents of the charge and discharge peaks, electrochemical activity increases in the series "Sample 0 – Sample 1 – Sample 2 – Sample 3 – Sample 4", and only for Sample 5 electrochemical activity decreases. This conclusion is supported by the discharge curves in Fig. 3. These data clearly show the activating effect of carbonate ions. However, at a higher molar part of carbonate in the anolyte (the second group, which includes Sample 6 and Sample 7), a significant drop in electrochemical activity occurs (Fig. 2, *g, i*): peaks on the discharge curve are almost absent. This can be explained by the breakdown of the nickel hydroxide crystal lattice and formation of a low-active basic salt. The discharge curve of Sample 6 (Fig. 3) shows that the breakdown occurred partially with the formation of the bi-phase structure.

Charge-discharge cycling in the accumulator regime supports the cyclic voltammetry data and confirms activation with carbonate ion. At the molar part of carbonate below 0.34, specific capacity increases from 217 mA·h/g to 234 mA·h/g. It should be noted that the listed the specific capacities of carbonate-activated samples are comparable to the data presented by other researchers. In [3] for samples β-Ni(OH)$_2$ activated with Zn^{2+}, Co^{2+}, and Ca^{2+}, specific capacities are cited as 242–260 mA·h/g. The authors of [17] obtained specific capacities from 231 mA·h/g to 255 A·h/g, for nickel hydroxide samples with different crystallinity. The specific capacity is comparable to the specific capacity of carbonate-activated Sample APS. However, with increasing the carbonate content in the anolyte, the specific capacity decreases significantly: the capacity of Sample 5 is only 155 mA·h/g. This can be explained by the higher crystallinity of the sample. Because of discovered loss in electrochemical activity during the cyclic voltammetry test, Sample 6 and Sample 7 were not subjected to galvanostatic

charge-discharge cycling. Therefore, it can be concluded that for the synthesis of carbonate-activate nickel hydroxide in the SDE, the molar part of sodium carbonate in the anolyte should not exceed 0.4.

It should be noted; that cobalt activation of the nickel oxide electrode is used in the production of the alkaline accumulator. When a new type of nickel hydroxide is introduced into the technological process, it is tested for cobalt activation. A similar test was conducted for Sample 4, which demonstrated the highest specific capacity among the carbonate-activated samples, by introducing the surface activator to the active mass in the form of cobalt sulfate. From Fig. 4 it can be seen; that with Co-activation, specific capacity increases from 234 mA·h/g to 257 mA·h/g, which indicates good activation with cobalt.

The conducted study allows recommending electrochemical synthesis of carbonate-activated nickel hydroxide in the SDE with sodium hydroxide and sodium carbonate with the molar part of carbonate within 0.35–0.4 as the anolyte for industrial applications.

7. Conclusions

1. Carbonate-activated nickel hydroxide samples were synthesized in the slit-diaphragm electrolyzer by introducing carbonate as an activator into the alkaline anolyte with different molar parts of sodium carbonate in the mixture with sodium hydroxide.

2. By means of XRD analysis, it was found that carbonate ions incorporated into the crystal lattice of nickel hydroxide. Upon increasing the molar part of carbonate in the anolyte to 0.49, the crystallinity of the layered ($\alpha+\beta$) structure increases. It was found that a further increase of the carbonate part results in a more amorphous structure due to a partial breakdown of the hydroxide lattice with the formation of basic salts and formation of the bi-phase system. This conclusion is supported by cyclic voltammetry and discharge curves.

3. Comparative analysis of electrochemical characteristics of $Ni(OH)_2$ samples synthesized in the SDE with a mixture of sodium hydroxide and carbonate confirmed the influence of carbonate ions. It was found that for the molar part of carbonate below 0.39, carbonate activation of hydroxide occurs resulting in an improved specific capacity. Increasing the carbonate part to 0.49 results in lower specific capacity, and even further increase results in the breakdown of hydroxide into basic salts and a significant drop in electrochemical activity. Thus, it was found; that to achieve the maximum activating effect, the optimal molar part of sodium carbonate (in a mixture with sodium hydroxide) should be about 40 %. The specific capacity of nickel hydroxide under this optimal condition is 234 mA·h/g. It was found; that this sample is susceptible to activation with cobalt compounds, which further improved capacity to 254 mA·h/g.

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