

Проведено вивчення характеристик зразків $\text{Ni}(\text{OH})_2$, синтезованих в щільному діафрагмовому електролізері (ЩДЕ), та модельних механічних сумішей з різним вмістом $\alpha\text{-Ni}(\text{OH})_2$ та $\beta\text{-Ni}(\text{OH})_2$. Методом рентгенофазового аналізу показано наявність в зразках $\text{Ni}(\text{OH})_2$, синтезованих в ЩДЕ, α і β структур. Методом циклічної вольтамперометрії виявлено активуючий ефект добавки $\alpha\text{-Ni}(\text{OH})_2$ до $\beta\text{-Ni}(\text{OH})_2$. Порівняльним аналізом показана принципова відмінність зразків, одержаних в ЩДЕ, від зразків, що є механічною сумішшю, що доводить шарувату ($\alpha+\beta$) структуру

Ключові слова: ($\alpha+\beta$) шарувата структура, гідроксид нікелю, щільний діафрагмовий електролізер, суміш α і β гідроксидів нікелю

Проведено изучение характеристик образцов $\text{Ni}(\text{OH})_2$, синтезированных в щелевом диафрагменном электролизере (ЩДЭ), и модельных механических смесей с различным содержанием $\alpha\text{-Ni}(\text{OH})_2$ и $\beta\text{-Ni}(\text{OH})_2$. Методом рентгенофазового аналізу показано наличие в образцах $\text{Ni}(\text{OH})_2$, синтезированных в ЩДЭ, α и β структур. Методом циклической вольтамперометрии выявлен активирующий эффект добавки $\alpha\text{-Ni}(\text{OH})_2$ к $\beta\text{-Ni}(\text{OH})_2$. Сравнительный анализ показывает принципиальное отличие образцов, полученных в ЩДЭ, от образцов, являющийся механической смесью, что доказывает слоистую ($\alpha+\beta$) структуру

Ключевые слова: ($\alpha+\beta$) слоистая структура, гидроксид никеля, щелевой диафрагменный электролизер, смесь α и β гидроксидов никеля

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COMPARATIVE INVESTIGATION OF ELECTROCHEMICALLY SYNTHESIZED ($\alpha+\beta$) LAYERED NICKEL HYDROXIDE WITH MIXTURE OF $\alpha\text{-Ni}(\text{OH})_2$ AND $\beta\text{-Ni}(\text{OH})_2$

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1. Introduction

Nickel hydroxides are electrochemically active materials, capable of reversible oxidation and reduction [1], which lead to their wide application in various electrochemical devices.

$\text{Ni}(\text{OH})_2$ and layered double hydroxides are active materials of nickel oxide electrode of Ni-Cd, Ni-Fe and Ni-MeH accumulators [2, 3]. Nickel hydroxide is also used at the positive electrode in lithium accumulators [4].

Nickel oxide electrode with $\text{Ni}(\text{OH})_2$ as an active material is actively used as the Faradaic electrode in hybrid supercapacitors. Nickel hydroxide is used on its own [5], as nano-sized [6] or ultradisperse powder [7], and as a composite with nanocarbon materials (graphene oxide [8], carbon nanotubes [9]). For thin-layer supercapacitors, a thin film of nickel hydroxide is formed on a conductive substrate [10].

Because thin films of $\text{Ni}(\text{OH})_2$ are transparent and NiOOH has a black-brown color, nickel hydroxide is used in electrochromic devices [11, 12].

Owing to its catalytic activity, nickel hydroxide is also used for the electrochemical oxidation of various organic compounds [13, 14] and in sensors [15, 16]. For each field of application, there are optimal parameters of nickel hydroxide. One of the main characteristics is electrochemical activity, and establishing the dependence of electrochemical activity on structural, morphological and other properties is a relevant problem.

2. Literature review and problem statement

Polymorphism is characteristic for nickel hydroxide and two of its polymorphs are described [17]. β -form (chemical formula $\text{Ni}(\text{OH})_2$, brucite structure) and α -form (chemical formula $3\text{Ni}(\text{OH})_2 \cdot 2\text{H}_2\text{O}$, hydrotalcite structure). At the same time, the paper [18] indicates a whole range of intermediate nickel hydroxide structures. $\beta\text{-Ni}(\text{OH})_2$ possesses high stability and can be prepared by chemical precipitation at high supersaturation [19], decomposition of ammine complex [20]

or high-temperature two-stage synthesis [21]. α -Ni(OH)₂ can be synthesized using various methods, for instance, homogeneous precipitation [22], including in a solvent mixture [23] or under vacuum [24], and also using microwave synthesis [25]. As a film, α -Ni(OH)₂ can be prepared using cathodic deposition, including cathodic template synthesis [26]. This form is more electrochemically active but is less stable than β -Ni(OH)₂. In order to stabilize the α -structure, various additives, such as cations of other metals [27], are introduced into nickel hydroxide during synthesis [27]. Another effective method is the formation of layered double hydroxides (LDH), in which part of nickel cations are substituted with tri- or tetravalent cations, and the excessive positive charge is compensated with anions: Al³⁺ and CO₃²⁻ [28, 29], Ti⁴⁺ and CO₃²⁻ [30].

α -Ni(OH)₂ possesses significantly higher electrochemical characteristics than β -Ni(OH)₂, however, its stability is significantly lower. Thus, the most promising material for various applications is a material containing both α -Ni(OH)₂ and β -Ni(OH)₂. The paper [31] describes the synthesis of pure β -Ni(OH)₂, coated with Al-stabilized α -Ni(OH)₂. This allowed to significantly improve the capacity of the material. Even more promising can be the synthesis of mixed α/β -phase, which should possess even higher electrochemical activity. Similar mixed phases have been synthesized using Al³⁺ [32], Ca²⁺ and PO₄³⁻ [33] additives, but these phases contain additional inert ions. Previously [31], nickel hydroxide samples with high electrochemical activity have been synthesized using a slit diaphragm electrolyzer (SDE). Results of XRD analysis have revealed the presence of α -Ni(OH)₂ and β -Ni(OH)₂ and the hypothesis about the layered structure has been proposed. The proposed hypothesis can be proven by contradiction. By assuming that synthesized samples are a mixture of α -Ni(OH)₂ and β -Ni(OH)₂, physical modeling can be conducted by preparing physical mixtures with various ratios. Study of these mixtures would allow establishing the validity of this hypothesis about the layered structure of nickel hydroxide samples prepared using the SDE. This also allows studying the electrochemical properties of such mechanical mixtures.

3. The aim and objectives of the study

The aim of the study is to prove the hypothesis of the layered structure of nickel hydroxide samples synthesized in the SDE and determine the properties of the mechanical mixture of α -Ni(OH)₂ and β -Ni(OH)₂ by means of comparative study.

To achieve the aim, the following objectives must be accomplished:

- to synthesize nickel hydroxide samples in the SDE and study their structural and electrochemical characteristics;
- to prepare model mechanical mixtures with various ratios between α -Ni(OH)₂ and β -Ni(OH)₂ and study their structural and electrochemical properties;
- to conduct a comparative analysis of electrochemically synthesized samples and model mixtures.

4. Methods employed in comparative study of nickel hydroxide samples

4.1. Synthesis of nickel hydroxide samples in slit diaphragm electrolyzer

Synthesis procedure [34] is based on electrolysis conducted in the flow-through SDE. A solution of nickel sulfate

was fed into the cathodic chamber, using a peristaltic pump, and the NaOH solution was fed into the anodic chamber, at a feed rate of 0.2 L/h.

The applied current leads to hydrogen evolution at the cathode and formation of hydroxyl ions, which react with nickel cations causing precipitation of nickel hydroxide. The precipitate was removed from the electrolyzer by the flow of catholyte. After leaving the SDE, the hydroxide precipitate was immediately vacuum filtered. Hydroxide samples were dried at 70 °C during a day, ground, sifted through a 71 μ m nickel mesh, washed from soluble salts and dried again.

A few nickel hydroxide samples were synthesized at different current densities; and were labeled as follows: S0.2-10 – 10 A/dm², S0.2-15.7 – 15.7 A/dm².

4.2. Preparation of model mixtures

Initial materials.

A commercial nickel hydroxide powder «Bochemie» (Czech Republic) was used as crystalline β -Ni(OH)₂.

As α -Ni(OH)₂, the Ni-Al carbonate layered double hydroxide (LDH) with the formula Ni_{0.8}Al_{0.2}(OH)₂(CO₃)_{0.1}·0.66H₂O was used. The sample was prepared by precipitation at high supersaturation, by slowly adding a solution containing salts of nickel and aluminum nitrates (total metal concentration was 1M) into the alkali solution with sodium carbonate at $t = 60$ °C and continuous stirring.

Preparation of model mixtures.

Model mixtures were obtained by thorough mechanical mixing (without grinding) of α -Ni(OH)₂ and β -Ni(OH)₂ powders in various ratios. In order to negate the influence of particle size [35], all samples were sifted through the 71 μ m mesh. The following mixture samples were prepared: 100 % β -Ni(OH)₂ (label B100A0), 80 % β -Ni(OH)₂ and 20 % α -Ni(OH)₂ (label B80A20), 70 % β -Ni(OH)₂ and 30 % α -Ni(OH)₂ (label B70A30), 50 % β -Ni(OH)₂ and 50 % α -Ni(OH)₂ (label B50A50) and 100 % α -Ni(OH)₂ (label B0A100).

4.3. Methods employed for studying characteristics of samples prepared in SDE and mixture samples

Crystal structure of the samples has been studied by means of X-ray diffraction (XRD) analysis, using a DRON-3 diffractometer (Russia) (Co-K α radiation, range 10–90° 2 θ , scan rate 0.1 /s).

Electrochemical properties of nickel hydroxides were studied by means of cyclic voltamperometry in a special cell YSE-2 using a digital potentiostat Ellins P-8 (Ellins, Russia). The working electrode was prepared by pasting a mixture of nickel hydroxide sample (81 % wt.), graphite (16 % wt.) and PTFE (polytetrafluoroethylene) (3 % wt.) [36] onto a current collector. The current collector was made by welding the Ni mesh onto the Ni plate. Electrolyte – 6M KOH. Counter-electrode – nickel mesh, reference electrode – Ag/AgCl (KCl sat.). The samples were cycled in the potential range of 0–500 mV at a scan rate of 1 mV/c.

5. Results of studying nickel hydroxide samples prepared in SDE and model mixtures of nickel hydroxide samples

XRD analysis results. The XRD patterns of mixture and electrochemically prepared nickel hydroxide samples are presented in Fig. 1.

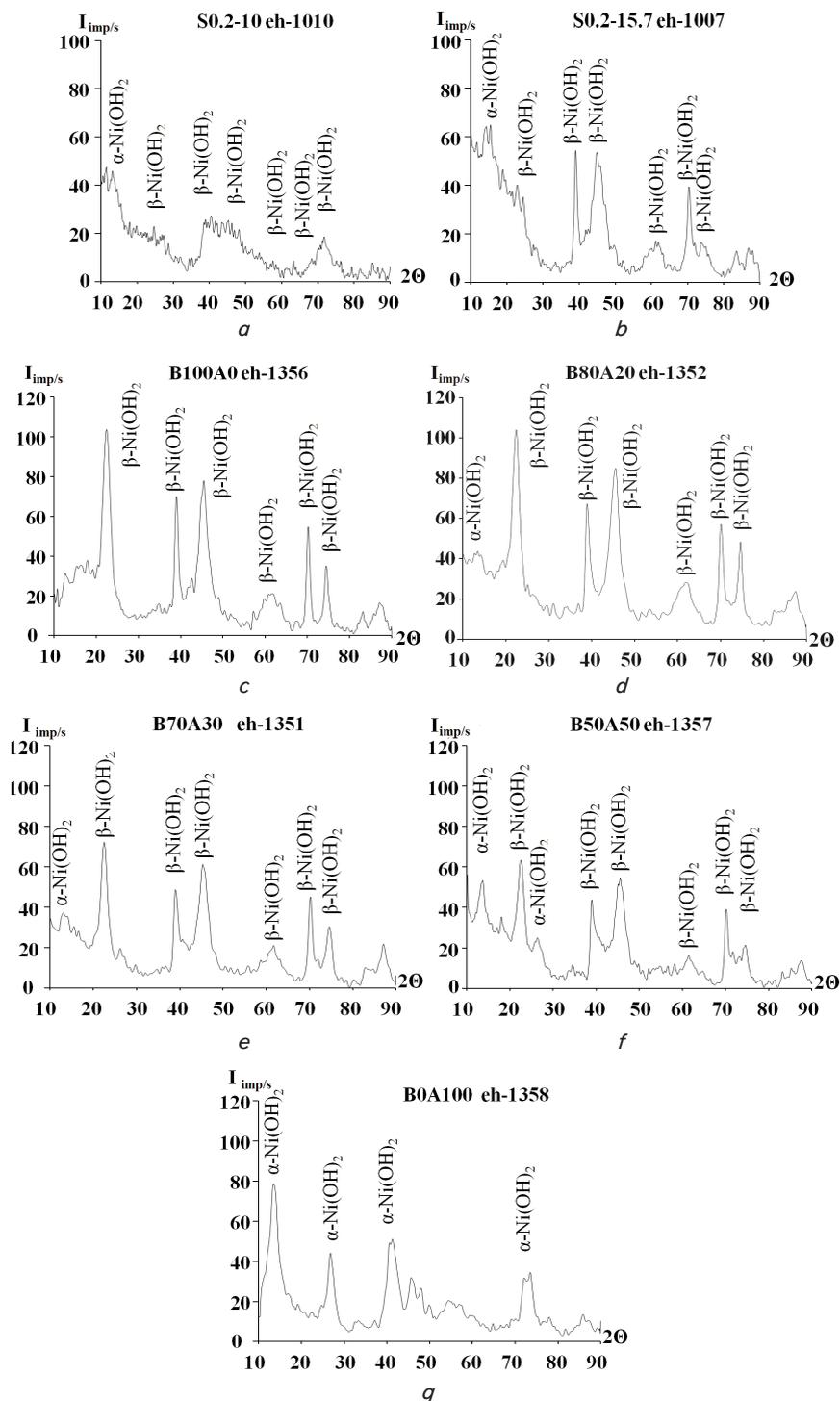


Fig. 1. XRD patterns of nickel hydroxide samples: *a* – S0.2-10, *b* – S0.2-15.7, *c* – B100A0, *d* – B80A20, *e* – B70A30, *f* – B50A50, *g* – B0A100

XRD patterns of mixture samples show the presence of α -Ni(OH)₂ as a small peak at $2\Theta=13^\circ$ for samples with the α -Ni(OH)₂ content of 20 % and 30 % (Fig. 1, *d*, *e*), while sample B50A50 shows comparable intensities of peaks corresponding to α and β forms. Electrochemically prepared sample S0.2-10 (Fig. 1, *a*) has a low crystallinity, however, weak peaks corresponding to α -Ni(OH)₂ and β -Ni(OH)₂ are observed. Sample S0.2–15.7 (Fig. 1, *b*) shows relatively high crystallinity and pronounced peaks that correspond to α ($2\Theta=13^\circ$) and β ($2\Theta=21^\circ$) forms.

Results of cyclic voltammetry analysis. Fig. 2 shows cyclic voltamperograms of samples prepared in the SDE and mixture model samples of nickel hydroxide.

Mixture samples B80A20 (Fig. 2, *d*), B70A30 (Fig. 2, *e*) and B50A50 (Fig. 2, *f*) don't show an oxidation peak during the first cycle.

Such electrochemical behavior is characteristic of β -Ni(OH)₂. This is supported by the absence of the first oxidation peak on the voltamperogram of sample B100A0, which is composed of β -Ni(OH)₂ only.

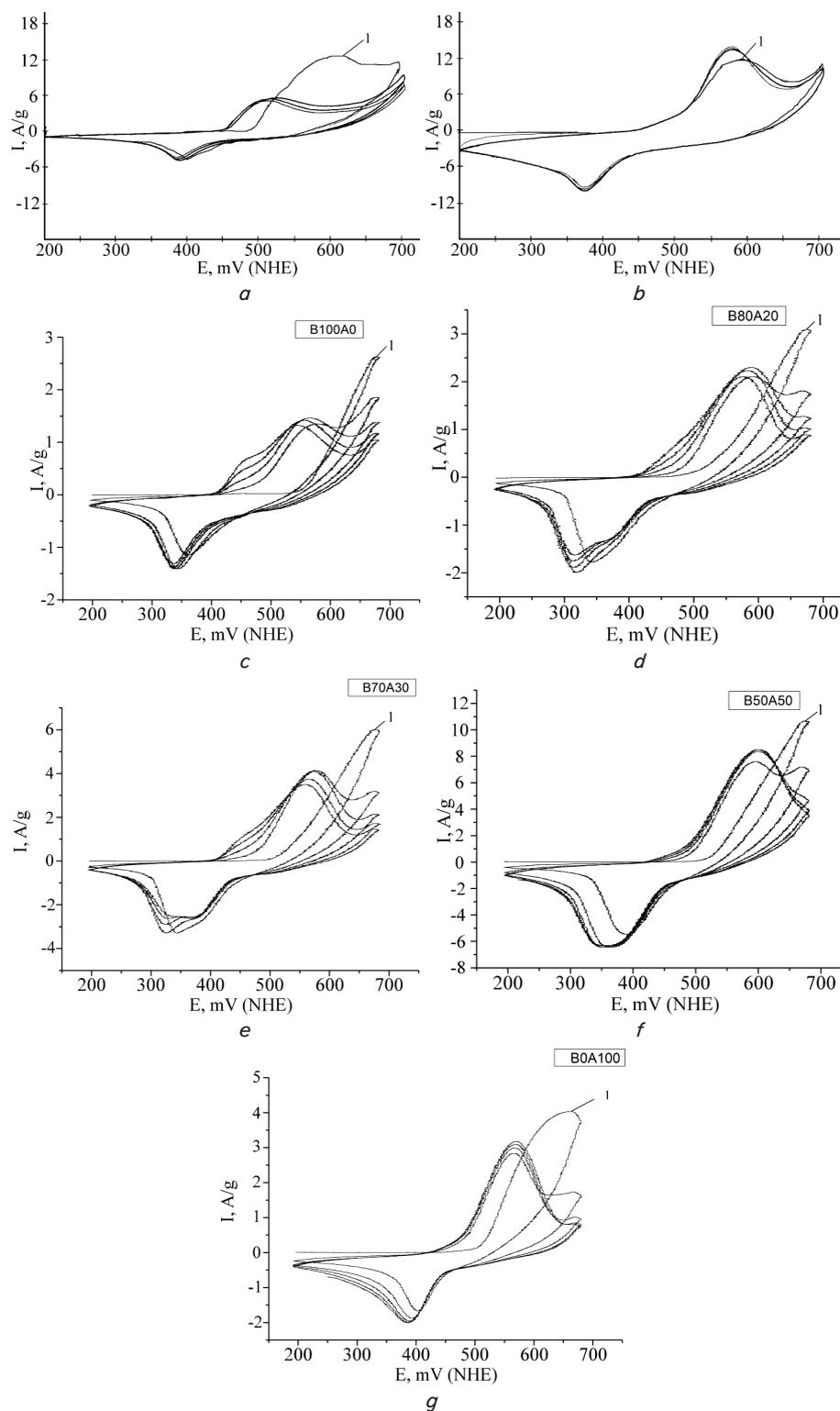


Fig. 2. CVA of samples (1 – first cycle): *a* – S0.2-10, *b* – S0.2-15.7, *c* – B100A0, *d* – B80A20, *e* – B70A30, *f* – B50A50, *g* – B0A100

At the same time, sample B0A100 (Fig. 2, *f*) is composed of α -Ni(OH)₂ only and shows a pronounced oxidation peak during the first cycle. It should be noted that two reduction peaks can be observed on the curves of samples B80A20 (Fig. 2, *d*), B70A30 (Fig. 2, *e*). Sample B50A50 (Fig. 2, *g*) shows a wide reduction peak, which is likely a combination of two neighboring peaks. It should also be noted that specific reduction peak currents for samples B80A20, B70A30

and B50A50 are higher than those of samples B0A100 and B100A0, from which mixture samples have been prepared. At the same time, electrochemically prepared in the SDE samples S0.2-10 and S0.2-15.7 have a fundamentally different behavior. Cyclic voltammograms show a well-defined oxidation peak at the first cycle, while only one reduction peak is observed. The specific current of the reduction peak is high, indicating a high electrochemical activity of the samples.

6. Discussion of results of studying nickel hydroxide powder prepared in SDE and mixture model hydroxide samples

XRD analysis. By means of XRD analysis (Fig. 2), it was discovered that samples synthesized in the SDE are indeed composed of α - and β -forms, with the crystallinity of sample S0.2-10 lower than that of S0.2-15.7. A hypothesis was proposed that samples prepared in the SDE have a layered structure, i.e. the particles are composed of alternating layers of α -Ni(OH)₂ and β -Ni(OH)₂. The α - and β -forms will also constitute a single phase without phase boundary between them. XRD patterns of mixture samples B80A20, B70A30 and B50A50 also shows peaks of α -Ni(OH)₂ and β -Ni(OH)₂. The relatively high intensity of the peak corresponding to α -Ni(OH)₂ ($2\theta=13^\circ$), comparable to the intensity of the peak corresponding to β -Ni(OH)₂ ($2\theta=21^\circ$), is characteristic for sample B50A50, which contains 50 % α -Ni(OH)₂ (Fig. 2, *f*). In addition, the peaks corresponding to α - and β -forms are well-defined. XRD pattern of sample S0.2-10 shows the peak corresponding to α -Ni(OH)₂, while the peak corresponding to β -form is almost not pronounced. XRD pattern of sample S0.2-15.7 shows no separation of α - and β -phases (as in Fig. 2, *f*), which results in one wide peak. It is possible that in addition to α -Ni(OH)₂ and β -Ni(OH)₂, the sample also contains a series of intermediate forms, in which interlaced distance *c* varies between 4.6 Å (β -Ni(OH)₂) and 7.6 Å (α -Ni(OH)₂). It can also be assumed that samples electrochemically synthesized in the SDE likely contain more than 50 % α -nickel hydroxide. This data supports the hypothesis of the layered structure of electrochemically prepared samples. The formation of such layered structure can be explained by unique synthesis conditions in the SDE. During electrolysis, the OH⁻ ions are formed at the cathode, which results in the basification of the cathode layer with the formation of nickel hydroxide. The hydroxide particle moves across the slit in mother liquor while also being in the field of Joule heat. This can result in conditions suitable for formation of α - and β -forms [39, 40]. Increase in crystallinity with an increase in current density from A/dm² to 15.7 A/dm² is because the amount of Joule heat at the cathode increases with increasing current density. Increased heat leads to a higher ageing rate of forming hydroxide and increased crystallinity [38].

Cyclic voltammetry. The comparative analysis of cyclic voltammograms has revealed fundamental differences in electrochemical behavior between mixture and electrochemically synthesized samples.

Cyclic voltamperogram of pure β -Ni(OH)₂ (sample B100A0) shows no oxidation peak at the first cycle. Such behavior is characteristic of highly crystalline β -Ni(OH)₂, which has very low conductivity. During the first cycle, the oxidation (formation of NiOOH) occurs not as a result of the electrochemical process but because of Ni(OH)₂ being oxidized by oxygen ad atoms formed during evolution at the anode. The potential of reduction peaks is $E=340$ mV. At the same time, the curve of pure α -Ni(OH)₂ (sample B0A100) shows the oxidation peak at $E=660$ mV during the first cycle, which is characteristic of α -form. The reduction peak potential is $E=370$ mV. Upon addition of α -Ni(OH)₂ to β -Ni(OH)₂ (model samples B80A20, B70A30 and B50A50), anodic behavior during the first cycle is almost unchanged, but the first oxidation peak is absent. The cathodic curve of mixture samples B80A20 and B70A30 shows two reduction

peaks at different potentials 330 mV and 380 mV that correspond to reduction of α -Ni(OH)₂ and β -Ni(OH)₂, respectively. Sample B50A50 shows a wide reduction peak, which is likely composed of overlapping peaks corresponding to reduction of α -Ni(OH)₂ and β -Ni(OH)₂. As such, it can be concluded; that in model samples composed of a mixture of α -Ni(OH)₂ and β -Ni(OH)₂, each of the phases is reduced on its own.

This is caused by the existence of phase boundary between two phases, the transition through which requires additional energy during the reduction process. However, in a series of samples «B100A0 (100 % β -Ni(OH)₂) – B80A20 (20 % α -Ni(OH)₂) – B70A30 (30 % α -Ni(OH)₂) – B50A50 (50 % α -Ni(OH)₂) – B0A100 (100 % α -Ni(OH)₂)», the specific current values are «1.5 A/g – 2.3 A/g – 3.5 A/g – 6.9 A/g – 2.0 A/g». A few conclusions can be drawn from this. First, the addition of α -Ni(OH)₂ increases the electrochemical activity of the mixture in comparison to pure β -Ni(OH)₂. Second, the addition of 30 % α -Ni(OH)₂ and more; results in significant improvement of electrochemical activity. In addition, specific currents of samples B70A30 and B50A50 exceed those not only of β -Ni(OH)₂ (sample B100A0), but also α -Ni(OH)₂ (sample B0A100), which were the initial materials for the preparation of mixtures. Thus, it can be concluded that there is a significant synergy between α -Ni(OH)₂ and β -Ni(OH)₂ in mixture sample. The reason for such synergy is currently unclear and requires additional investigation.

The samples electrochemically prepared in the SDE show different electrochemical behavior. Cyclic voltamperograms of samples S0.2-10 and S0.2-15.7 show defined oxidation peaks during the first cycle. There are single reduction peaks at potentials characteristic of α -Ni(OH)₂. The first oxidation peak of electrochemically synthesized samples is more defined than that of pure α -Ni(OH)₂. XRD patterns of these samples (Fig. 1, *a, b*) demonstrate peaks of both α and β phases. Specific peak reduction currents are rather high 6.5 A/g (S0.2-10) and 11.7 A/g (S0.2-15.7) and exceed those of mixture samples, including pure α -Ni(OH)₂ (B0A100) – 2 A/g. This indicated a significantly higher electrochemical activity of electrochemically prepared samples. This can be described with the proposed hypothesis of the layered structure α -Ni(OH)₂ – β -Ni(OH)₂ – α -Ni(OH)₂ – β -Ni(OH)₂ of the samples. α -phase is engaged first as more active one, which is expressed by reduction peak potentials of samples S0.2-10 and S0.2-15.7 that correspond to potentials of α -Ni(OH)₂. α -phase serves as a conductor of the electrochemical process inside the hydroxide particle, initiating β -Ni(OH)₂. Because there is no distinct phase boundary between two phases, the whole structure works as a single system.

In summary, it can be said that samples S0.2-10 and S0.2-15.7 that were synthesized in the SDE are composed of both α -Ni(OH)₂ and β -Ni(OH)₂, however, they are not a simple mixture of separate phases; and show electrochemical behavior that is different from the mixture samples. Thus, this proves the hypothesis about the layered structure ($\alpha+\beta$) of samples electrochemically synthesized in the SDE by contradiction.

7. Conclusions

1. Hydroxide samples synthesized in the slit diaphragm electrolyzer have been studied. By means of XRD analysis, it was revealed that the samples contain both α -Ni(OH)₂ and

β -Ni(OH)₂, and a series of intermediate phases. Synthesized samples show high electrochemical activity: presence of the oxidation peak during the first cycle, and single reduction peaks with high specific currents of 6.5–11.7 A/g.

2. Model mixtures containing 0 % α -Ni(OH)₂ (pure β -Ni(OH)₂); 20 % α -Ni(OH)₂; 30 % α -Ni(OH)₂; 50 % β -Ni(OH)₂ α -Ni(OH)₂; 100 % α -Ni(OH)₂ have been prepared from commercial β -Ni(OH)₂ and chemically synthesized Ni-Al LDH (as α -Ni(OH)₂ sample) by means of mechanical mixing. By means of XRD analysis, it was revealed that samples composed of α -Ni(OH)₂ and β -Ni(OH)₂ mixture show peaks of separate phases. By means of cyclic voltamperometry, it has been established that mixture samples don't show an oxidation peak during the first cycle, while the cathodic curves show two separate peaks, corresponding to reduction of α and β components. A synergetic effect re-

sulting in increased electrochemical activity of α -Ni(OH)₂ and β -Ni(OH)₂ mixture had been discovered – specific currents of reduction peaks were 2.3 A/g (20 % α -phase), 3.5 A/g (30 % α -phase), 6.9 A/g (50 % α -phase), which exceed the characteristics of initial β -Ni(OH)₂ (1.5 A/g) and α -Ni(OH)₂ (2.0 A/g).

3. Characteristics of nickel hydroxide samples synthesized in the SDE and model samples that are mechanical mixtures of α -Ni(OH)₂ and β -Ni(OH)₂ have been analyzed. It was discovered that electrochemically synthesized samples are composed of α -Ni(OH)₂ and β -Ni(OH)₂, however, they are not a mixture of separate phases, as they significantly differ in their electrochemical behavior from mixture samples. Thus, using mechanical modeling, the layered (α + β) structure of samples electrochemically synthesized in the slit diaphragm electrolyzer has been proved by contradiction.

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