

Бінарні сполуки Ni-Co, такі як оксид-гідроксиди та кобальтат нікелю, є перспективними активними речовинами суперконденсаторів. Вивчено характеристики бінарних Ni-Co оксид-гідроксидів, отриманих високотемпературним двохступневим синтезом при використанні гарячого та холодного гідролізу. Кристалічна структура зразків вивчена методом рентгенофазового аналізу та термогравіметрії, морфологія часток – методом скануючої електронної мікроскопії, електрохімічні характеристики – методами циклічної вольтамперометрії та гальваностатичного зарядно-розрядного циклювання в суперконденсаторному режимі.

Методом скануючої електронної мікроскопії показано, що зразки холодного і гарячого гідролізу складаються із наноструктурованих часток типу «бутон квітки», сформованих пластинчастими первинними частками товщиною 70–90 нм. Методами рентгенофазового аналізу та термогравіметрії показано, що обидва зразки є гідратованими кобальтатами нікелю з різним ступенем гідратації, при наявності чистого кобальтату нікелю. Циклічною вольтамперометрією та гальваностатичним зарядно-розрядним циклюванням показано, що в зразку Ni-Co оксид-гідроксида холодного гідролізу електрохімічно активною є тільки нікелева складова. Максимальна ємність зразку холодного гідролізу – 185,7 Ф/г (при 10 мА/см²). З підвищенням густини струму циклювання до 120 мА/см² питома ємність падає в 4,47 рази. Для зразка гарячого гідролізу виявлена активність як нікелевої, так і кобальтової складової: при зростанні густини струму циклювання з 10 мА/см² до 120 мА/см² питома ємність збільшується в 1,25 рази до 192,5 Ф/г. Для зразку гарячого гідролізу показана дуже висока оберненість та висока ефективність з 1 циклу роботи

Ключові слова: бінарний Ni-Co оксид-гідроксид, кобальтат нікелю, високотемпературний двохступневий синтез, питома ємність, суперконденсатор

INVESTIGATION OF CHARACTERISTICS OF BINARY NI–CO OXY-HYDROXIDES FOR SUPERCAPACITOR APPLICATION

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1. Introduction

Different types of nickel hydroxides possess high electrochemical activity [1]. Therefore, Ni(OH)₂ is widely used in different electrochemical devices [2].

Nickel hydroxide along with double nickel hydroxides is used as an active material of nickel oxide electrode in alkaline Ni-Cd, Ni-Fe and Ni-MeH batteries [3, 4]. Nickel hydroxide is also used in cathodes for lithium batteries [5, 6]. Nickel hydroxides are used as an active material of the Far-

adic electrode of hybrid supercapacitors. Ni(OH)₂ is used on its own [7, 8], and in the form of composite with nanocarbon materials [9]. For thin layer supercapacitors, a nickel film can be formed on the conductive substrate [10]. Due to the ability to undergo a colour change, nickel hydroxide is used as electrochromic material [11, 12]. Ni(OH)₂ has high electrocatalytic activity and is used for electrooxidation of various organic compounds [13], it is also used in sensors [14].

Two polymorphs of nickel hydroxides are known [15]: β hydroxide (chemical formula Ni(OH)₂, brucite-like structure) and α-hydroxide (chemical formula 3Ni(OH)₂·2H₂O, hydrotaalcite-like structure). However, the paper [16] describes the formation of nickel hydroxide structure that is in-between α-Ni(OH)₂ and β-Ni(OH)₂. The paper [17] describes the formation of nickel hydroxide with layered (α+β) structure.

β-Ni(OH)₂ has high storage and cycling stability. Therefore, it is widely used in alkaline batteries [18] and hybrid supercapacitors [19]. β-Ni(OH)₂ can be precipitated chemically at low supersaturation or electrochemically in the slit diaphragm electrolyzer [5]. High-temperature synthesis [20] and ammine complex decomposition [18] are also used.

It should be noted that α-Ni(OH)₂ has higher electrochemical activity than β-Ni(OH)₂. However, α-form is metastable, and in alkaline media and at high temperatures, it transforms into less active β-form [21, 22], resulting in loss of capacity. To stabilize α-form, stabilizing additives are introduced to nickel hydroxide forming layered double hydroxides (LDH) [23, 24]. LDH consist of a host crystal lattice, in which part of host hydroxide cations (Ni²⁺) are substituted by guest cations such as Al³⁺ [25]. α-Ni(OH)₂ and nickel-based LDH can be prepared using chemical precipitation [26], homogeneous precipitation [6], electrolysis in the slit-diaphragm electrolyzer [27]. The excess of positive charge in the LDH lattice is compensated by the intercalation of various anions [28].

However, Al³⁺ is an inert cation that does not take part in the electrode reaction. The introduction of significant amounts of electrochemically active additive should also lead to improved characteristics of nickel hydroxide. Co²⁺ can be used as such additive, as it decreases polarization of oxygen evolution [29], which improves the characteristics of Ni(OH)₂. To improve the capacity of active material, it would seem larger cobalt content is required. This would result in the formation of binary hydroxide compounds [30], oxyhydroxides [31]. And even more active material is mixed Ni-Co, nickel-cobaltate NiCo₂O₄ with spinel structure [32, 33].

It can be concluded that a promising direction for improving the characteristics of hybrid supercapacitors would be the synthesis and study of binary oxide, hydroxide, and oxyhydroxide Ni-Co compounds.

2. Literature review and problem statement

It is known that cobalt compounds are high-performance additives to nickel hydroxide, which transform into Co(OH)₂ in alkaline media. In addition, cobalt hydroxide has its own electrochemical activity [34]. So, Ni-Co hydroxides possess the electrocatalytic activity and are used for oxygen evolution [35], oxidation of isoniazid [36], in the electrolyte with potassium ferrocyanide [37]. Mixed cobalt and nickel hydroxides are used in electrochemical devices [57]. Cobalt, as an additive to nickel hydroxide, is widely used in alkaline batteries [38] and supercapacitors [39, 40].

The conducted analysis shows that there are different opinions regarding the form of cobalt and nickel hydroxides that are to be used for the active material. The author of the paper [38] describes the formation of a “core/shell” structure, i. e. nickel hydroxide core is coated with a shell of cobalt hydroxide. Other authors [39] describe cobalt-stabilized Ni(OH)₂. The paper [40] describes the synthesis of mixed Ni-Co hydroxide, and [41] – nanonetwork (nanomixture) of cobalt and nickel hydroxides. A mixture of cobalt and nickel hydroxides was synthesized through the delamination of basic nickel and cobalt salts [42, 43]. The authors of the papers [38, 44] describe the synthesis of layered double hydroxides.

An even greater activity can be expressed by nickel cobaltate NiCo₂O₄, due to the high content of electrochemically active components (Ni²⁺, Co³⁺). The electrochemical activity mechanism is based on protonation-deprotonation of nickel and cobalt ions. However, the proton diffusion rate in the spinel crystal lattice of nickel cobaltate is slow. To improve the electrochemical activity, it is required to synthesize nano-sized [45], submicron [46] or mesoporous [47] nickel cobaltate particles. Template synthesis was used to prepare submicron porous microspheres [46]. Different synthesis methods result in nanoparticles with different morphology. The hydrothermal method was used to prepare chain-like nanowires [48] and urchin-like particles [49]. Chemical precipitation from the water-alcohol mixture was used to prepared dandelion-like particles [50]. Polymers were used to prepare 3d-hierarchical nickel cobaltate nanostructure networks [51], and sol-gel – aerogel [52, 53]. All prepared structures possess high electrochemical characteristics. However, all the described synthesis methods utilized complex techniques and high-cost components.

To synthesize nano-structured nickel hydroxide particles, the author proposes high-temperature two-stage synthesis [20]. When using nickel and cobalt perchlorates as starting reagents in a 1:2 molar ratio, nano-sized nickel cobaltate or nickel-cobalt oxyhydroxide can be prepared. This method has not been previously used for the synthesis of these compounds, which requires a complex study of their properties for future use in supercapacitors.

3. The aim and objectives of the study

The aim of the work is to determine the effectiveness of binary Ni-Co oxyhydroxide compounds prepared using high-temperature two-stage synthesis, as an active material of Faradic electrode of a hybrid supercapacitor.

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

- to conduct the synthesis of Ni-Co oxyhydroxide compounds, using a two-stage high-temperature method, using hot and cold hydrolysis;
- to conduct an analysis of structural properties and morphology of prepared samples;
- to study electrochemical characteristics of prepared samples to evaluate their effectiveness for use in supercapacitors.

4. Materials and methods used for synthesis and study of binary Ni-Co oxyhydroxide compounds

4. 1. Synthesis of Ni-Co oxyhydroxides

Analytical grade reagents were used in the study with the exception of NaOH (granulated, chemically pure grade).

For the possible synthesis of nickel cobaltate, it was proposed to use the molar ratio Ni:Co=1:2. High-temperature two-stage synthesis [20] was used, which consists of the following stages:

Preparation of nickel and cobalt perchlorates. Preparation of nickel perchlorate solution:

a) basic nickel carbonate was synthesized by adding sodium carbonate to nickel sulfate solution under stirring. The basic nickel carbonate precipitate was filtered off of mother liquor and washed to a negative reaction to sulfate ions;

b) excess of basic nickel carbonate was treated with a calculated volume of 45 % perchloric until pH=6;

c) the obtained solution was filtered off from the excess of basic carbonate.

The cobalt perchlorate solution was prepared following the same procedure. Both solutions were mixed and evaporated to the previously calculated mass (salt to water ratio 1:1).

High-temperature two-stage synthesis. Precursor synthesis stage. The necessary amount of NaOH and water was put into a 500 ml Teflon beaker. The beaker was sealed with a lid installed with the condenser and heated with constant stirring. Upon reaching 170 °C, the solution of nickel and cobalt perchlorates was drop-wise added to the beaker. The temperature was then lowered to 140 °C and the reaction mixture was kept under these conditions for 24 h.

High-temperature two-stage synthesis. Precursor hydrolysis stage. Synthesis stage results in the formation of precursors – sodium nickelate and cobaltate. Precursor hydrolysis would then result in the desired product. Two types of hydrolysis were used:

– hot hydrolysis. 150 ml of mother liquor from the reaction vessel was replaced with 150 ml of distilled water. The resulting mixture was kept at 170 °C with stirring for 18 h (**NiCo₂ Oxy-Hydr Hot** sample);

– cold hydrolysis. The entire reaction mixture was dumped into 5 l of distilled water and stirred at room temperature for 18 h (**NiCo₂ Oxy-Hydr Cold** sample).

The samples were then vacuum filtered to remove the mother liquor. The formed oxyhydroxide is similar to organic-organic [54], inorganic-inorganic [55, 56] organic-inorganic [57] composites, is a composite material. In this case, a matrix is formed by the hydroxide itself with the mother liquor acting as a filler [58]. The composite has a closed-cell structure. Because of such structure, the precipitate is difficult to wash off from soluble salts. This requires the use of a two-stage method: drying at 90 °C for a day, grinding, washing with distilled water and additional drying under the same conditions. Before analysis, the samples were additionally ground using a mortar and sifter through a 71 μm mesh.

4. 2. Characterization of Ni-Co oxyhydroxides

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

Thermal properties, type of crystal lattice and water content were determined by means

of thermogravimetric analysis (TG). TG analysis was conducted using the Shimadzu DTG-60 thermal analyzer under the air atmosphere and heating rate of 5 °C/min.

Electrochemical properties of nickel hydroxides were studied using the following methods:

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 (3 % wt.) [59] on nickel foam current collector [60]. Electrolyte – 6 M KOH. Counter-electrode – nickel mesh, reference electrode – Ag/AgCl(KCl sat.). The analysis was conducted in the potential window of 200–700 mV (Ag/AgCl) at a scan rate of 1 mV/s;

b) galvanostatic charge-discharge cycling in the supercapacitor regime. The cell, working, counter-electrode, reference electrode, and electrolyte were the same as for cyclic voltammetry. Charge-discharge cycling was conducted in the supercapacitor regime at current densities of 20, 40, 80 and 120 mA/cm² (10 cycles at each current density). Discharge curves were used to calculate specific capacity C_{sp} (F/g) for full discharge (till constant negative potential) and discharge to 0 mV.

5. Characterization results for Ni-Co oxyhydroxides

Visual observation revealed that both cold and hot hydrolysis methods lead to very fine black powders.

Results of scanning electron microscopy.

Fig. 1 shows SEM images of the **NiCo₂ Oxy-Hydr Cold** and **NiCo₂ Oxy-Hydr Hot** samples.

It was found that both samples consist of nano-structured flower-like particles that are composed of 70–90 nm thick plates. No significant differences are observed between cold and hot hydrolysis samples.

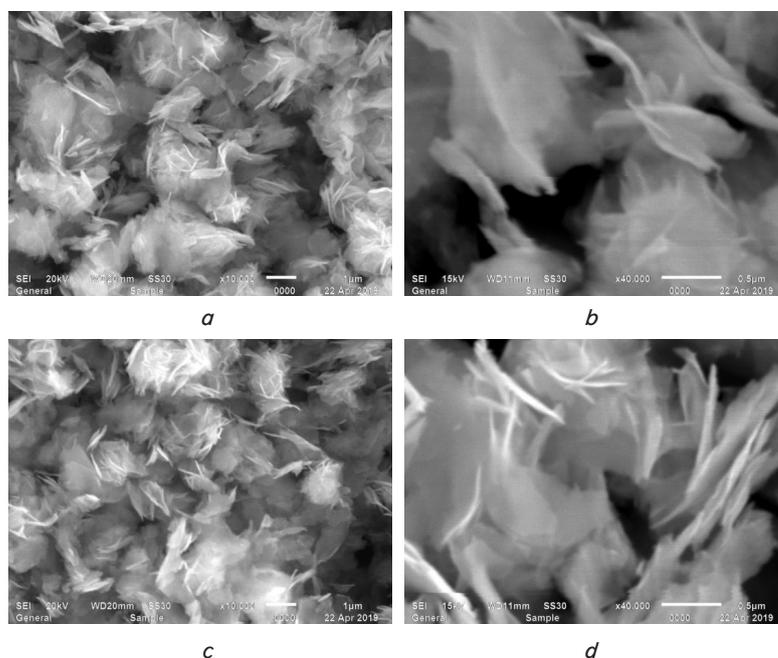


Fig. 1. SEM images of the samples: *a, b* – NiCo₂ Oxy-Hydr Cold, *c, d* – NiCo₂ Oxy-Hydr Hot

XRD results.

XRD patterns of both samples (Fig. 2) are almost identical, however, the crystallinity of the **NiCo2 Oxy-Hydr Hot** sample is somewhat higher. A strong peak is observed at $2\theta=17^\circ$, which corresponds to monohydroxides Ni(OH)_2 , Co(OH)_2 , and nickel cobaltate NiCo_2O_4 . A weaker peak at $2\theta=40^\circ$ is observed, which corresponds to Ni(OH)_2 and Co(OH)_2 , near at $2\theta=40^\circ$ there is a weak peak corresponding to NiCo_2O_4 . It should be noted that for the **NiCo2 Oxy-Hydr Cold** sample (Fig. 1, a), the peak of nickel cobaltate is almost unidentifiable. It is possible that the samples have a bi-phase structure.

Thermogravimetry results

The TG curve of the **NiCo2 Oxy-Hydr Cold** sample (Fig. 3, a) shows a weight loss plateau and two mass loss steps. The first plateau of gradual mass loss is observed up to 247°C (6.88%). The first step of 3.85% is observed within $247\text{--}271^\circ\text{C}$, the second step of 5.88% is within $271\text{--}344^\circ\text{C}$.

The TG curve of the **NiCo2 Oxy-Hydr Hot** sample (Fig. 3, b) has the same characteristics with rather insignificant differences in mass loss and temperatures.

Results of electrochemical characterization

The results of cyclic voltammetry of the **NiCo2 Oxy-Hydr Cold** and **NiCo2 Oxy-Hydr Hot** samples are shown in Fig. 4. The voltammogram of the **NiCo2 Oxy-Hydr Cold** sample (Fig. 4, a) has a poorly-defined charge peak on the first cycle at $490\text{--}510\text{ mV}$. For subsequent cycles, the potential shifts to $580\text{--}600\text{ mV}$. The specific current of the charge peak also rises on the fifth cycle 0.95 A/g . The **NiCo2 Oxy-Hydr Hot** sample (Fig. 4, b) demonstrates a different behaviour. On the voltammogram, the charge and discharge curves of all six cycles are the same. It should be noted that instead of the charge peak, there is a plateau of $420\text{--}630\text{ mV}$. The charge peak is found at $380\text{--}385\text{ mV}$. The specific peak current is lower and is 0.65 A/g .

Fig. 5 shows the specific capacities of the synthesized samples.

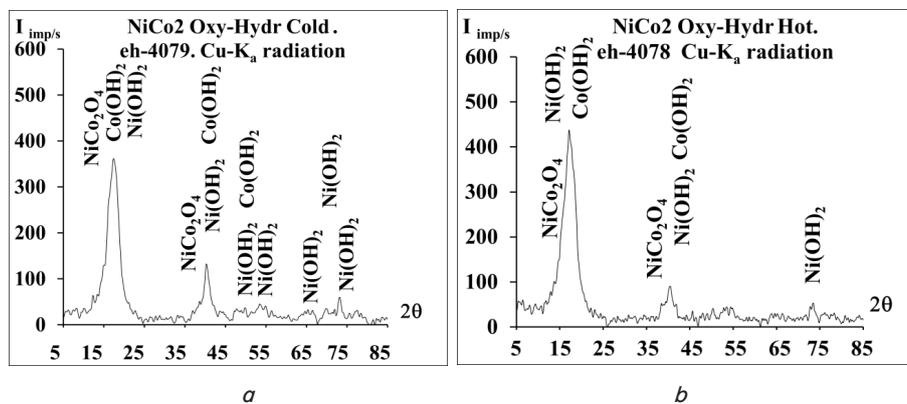


Fig. 2. XRD patterns of the samples: a – NiCo2 Oxy-Hydr Cold, b – NiCo2 Oxy-Hydr Hot

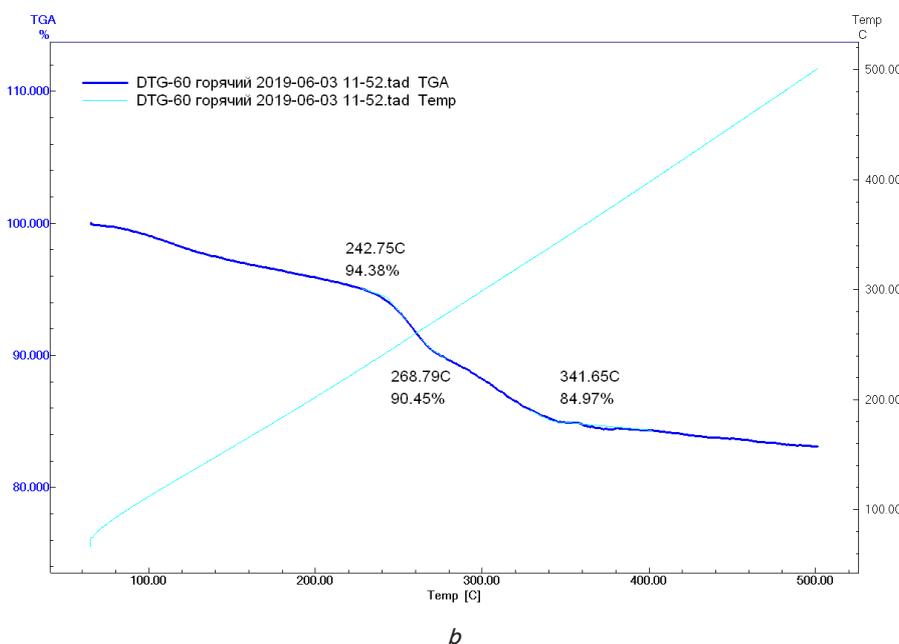
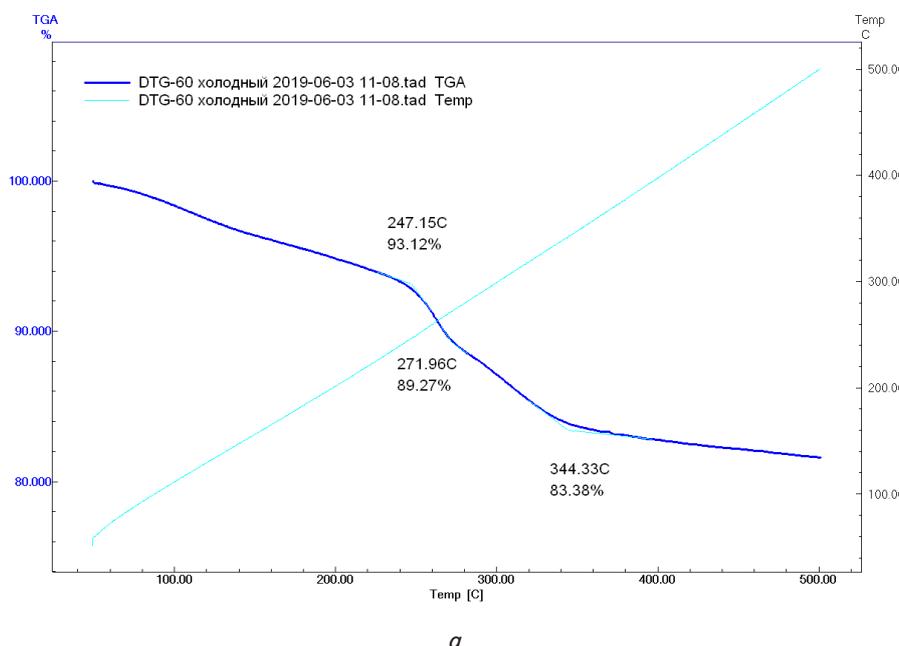


Fig. 3. TG curves of the samples: a – NiCo2 Oxy-Hydr Cold, b – NiCo2 Oxy-Hydr Hot; холодный – cold; горячий – hot

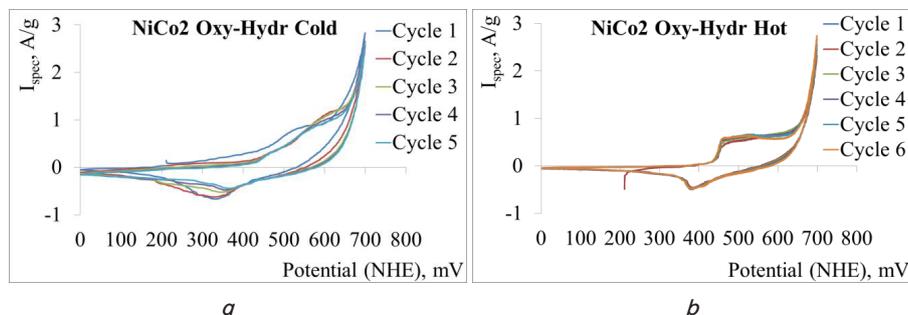


Fig. 4. Cyclic voltammograms of the samples:
a – NiCo2 Oxy-Hydr Cold, b – NiCo2 Oxy-Hydr Hot

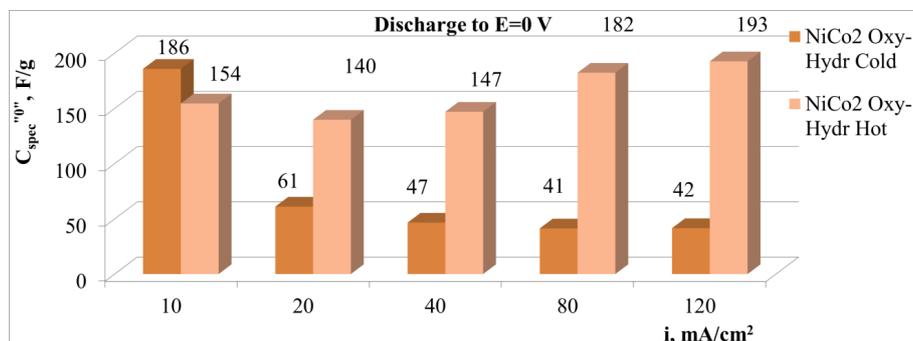


Fig. 5. Specific capacities of the synthesized samples

It was found that the dependency of the capacity on current density is significantly different for the **NiCo2 Oxy-Hydr Cold** and **NiCo2 Oxy-Hydr Hot** samples. The **NiCo2 Oxy-Hydr Cold** sample shows the maximum capacity at 10 mA/cm², which drops significantly with increasing current density. For the **NiCo2 Oxy-Hydr Hot** sample, in the current density series “10 mA/cm² – 20 mA/cm² – 40 mA/cm² – 80 mA/cm² – 120 mA/cm²”, specific capacity drops somewhat initially, but then increases reaching the maximum at 120 mA/cm².

6. Discussion of results of characterisation of Ni-Co binary oxy-hydroxides

Particle morphology.

It was found that the particles of both samples are nano-structured and have flower-like forms. The flowers are composed of 70–90 nm thick plates. The morphology of both samples appears to be identical.

Crystal structure. The results of XRD analysis (Fig. 2) revealed that both samples (**NiCo2 Oxy-Hydr Cold** and **NiCo2 Oxy-Hydr Hot**) have a very similar crystal structure. However, there are some minor contradictions. On the one hand, there are peaks corresponding to β -Ni(OH)₂ at 2θ 17° and 40°. But there are also no peaks for it at 34°, shown in Fig. 1 in [53]. At the same time, the peak at $2\theta=17^\circ$ can correspond to nickel cobaltate NiCo₂O₄ (Fig. 1 [47] and Fig. 2 [53]). The XRD pattern of NiCo₂O₄ (Fig. 1 [47]) shows that the peak with the highest intensity is located at $2\theta=36^\circ$. Rather strong peaks must also be at $2\theta=58^\circ$ and $2\theta=65^\circ$. However, the low-intensity peak of nickel cobaltate at $2\theta=36^\circ$ was found on the XRD pattern of the **NiCo2 Oxy-Hydr Hot** sample. Peaks at $2\theta=58^\circ$ and $2\theta=65^\circ$ are also not observed, or rather cannot be differentiated from the background. In

summary, it can be concluded that the prepared samples are likely to be Ni-Co oxyhydroxide as a hydrated form of nickel cobaltate NiCo₂O₄·xH₂O, partially transformed to NiCo₂O₄. The water content (x) for the hot hydrolysis sample **NiCo2 Oxy-Hydr Hot** is lower, which corresponds to a high hydrolysis temperature – 170 °C.

The results of the thermogravimetric analysis support this conclusion. The total water loss is 17–18 %, which is significantly lower than for nickel hydroxide (21 % and 24 % for Ni(OH)₂ samples prepared using high-temperature two-stage synthesis with hot and cold hydrolysis [20]). It should be noted that in the case of synthesis of pure NiCo₂O₄, the mass loss would be absent or minimal due to dehydration. Fig. 6 of the paper [43] shows the TG curves of cobalt oxyhydroxide, with the total mass loss of 13–17 %, which corresponds to the mass loss of experimental samples (Fig. 3).

The shapes of the TG curves in Fig. 3 correspond to the TG curves of the paper [43] (Fig. 6). The first mass loss plateau (prior to 247 °C) corresponds to the loss of structural water and water within the lattice defects. Lower water content in the **NiCo2 Oxy-Hydr Hot** sample is supported by small mass loss. The first mass loss step is observed at 247–271 °C, which likely corresponds to the decomposition of double cobalt(II)-nickel hydroxide lattice. The second step at 271–344 °C likely characterizes the decomposition of a more stable double cobalt(III)-nickel hydroxide lattice. The mass loss due to water removal likely overlaps with the mass gain from the oxidation of Co(II) to Co(III).

Electrochemical characterization. Cyclic voltammetry of the **NiCo2 Oxy-Hydr Cold** and **NiCo2 Oxy-Hydr Hot** samples (Fig. 4) revealed fundamental differences in electrochemical behavior. The voltammogram of the **NiCo2 Oxy-Hydr Cold** sample (Fig. 4, a) has a shape resembling β -Ni(OH)₂, prepared using high-temperature two-stage synthesis with cold hydrolysis [20]. This indicates that this sample has Ni²⁺ as an electrochemically active cation, while cobalt cation is not involved in electrochemical reactions. The **NiCo2 Oxy-Hydr Hot** sample demonstrated different electrochemical properties. During the anodic scan, the charge plateau at 420–630 mV is observed instead of the charge peak. This indicates the presence of a number of similar structures with different hydration degrees, likely sodium nickelate, and electrochemical activity of cobalt. There is one cathodic peak, but it is broad, which indicates the discharge of different nickel cobaltates with different hydration levels and involvement of cobalt in the electrochemical process. It's worth mentioning that all cycles are the same, meaning the entire active part of the compounds is involved in the electrochemical process from the first cycle. Additionally, the reversibility (the difference between charge and discharge peak potentials) for the **NiCo2 Oxy-Hydr Hot**

sample is only 40 mV, while for the **NiCo2 Oxy-Hydr Cold** sample it is 240 mV. Reversibility value is the characteristic of internal supercapacitor resistance and energy loss during the “charge-discharge” cycle. However, the specific current of the discharge peak for the **NiCo2 Oxy-Hydr Hot** sample is 0.65 A/g, which is lower than that of the **NiCo2 Oxy-Hydr Cold** sample (0.95 A/g). Because the cyclic voltammogram was recorded at a low scan rate (1 mV/s), this indicates the lower activity of the hot hydrolysis sample at low cycling currents.

Charge-discharge cycling in the supercapacitor regime supports the conclusions of cyclic voltammetry results. At low current densities (10 mA/cm²), the specific capacity of the **NiCo2 Oxy-Hydr Cold** sample (185.7 F/g) is higher by 16.9 % than that of the **NiCo2 Oxy-Hydr Hot** sample (154.4 F/g). At higher current densities, the specific capacity of the **NiCo2 Oxy-Hydr Cold** sample decreases sharply by 77.6 % (to 41.3–41.5 F/g at 80–120 mA/cm²). Such behavior is characteristic of nickel monohydroxide prepared under the same conditions (cold hydrolysis) and is due to a lower depth of the electrochemical process within the hydroxide particle. Such dependency and low specific capacity confirm the lack of cobalt cation involvement in the reaction. With an increase in the cycling current density to 120 mA/cm², the hot hydrolysis sample **NiCo2 Oxy-Hydr Hot** not only doesn't show a decrease of capacity but instead an increase by 24.7 % (to 192 F/g). It should be noted that at the maximum cycling current density (120 mA/cm²), the capacity of the hot hydrolysis sample **NiCo2 Oxy-Hydr Hot** is 363.9 % of the specific capacity of the cold hydrolysis sample **NiCo2 Oxy-Hydr Cold**. The capacity increase could occur due to the increase of the available reactive surface area, due to the breakdown of particle agglomerates. However, the contribution of this mechanism is rather small, as according to the SEM data, the particle does not appear to be aggregated, and the breakdown of nano-structured particles is unlikely. Therefore, an increase in the specific capacity at higher current densities

indicated an increase in the electrochemical activity due to the cobalt component.

7. Conclusions

1. Ni-Co oxyhydroxides were synthesized using the previously unused method of high-temperature two-stage synthesis with hot (170 °C) and cold (20 °C) hydrolysis.

2. By means of scanning electron microscopy, it was found that the samples of cold and hot hydrolysis are nano-structured powders composed of flower-like particles, composed of 70–90 nm thick plates. The results of XRD and thermogravimetric analyses revealed that both samples are binary Ni-Co oxyhydroxides (hydrated nickel cobaltates with different hydration levels) with the presence of pure nickel cobaltate. The hot hydrolysis samples contain less water and more nickel cobaltate.

3. Cyclic voltammetry and galvanostatic charge-discharge cycling were used to conduct a comparative study of binary Ni-Co oxyhydroxides prepared by hot and cold hydrolysis. It was found that in the cold hydrolysis Ni-Co sample, only the nickel component is electrochemically active. The maximum capacity of the cold hydrolysis sample is achieved at low cycling current density (10 mA/cm²) – 185.7 F/g. With the increase of current density to 120 mA/cm², the specific capacity drops by 4.47 times. The hot hydrolysis sample was found to have both nickel and cobalt components active. This leads to this sample having increased capacity with increasing current density from 10 mA/cm² to 120 mA/cm² by 1.25 times, up to 192.5 F/g. Additionally, the hot hydrolysis sample possesses high reversibility and high effectiveness of the electrochemical component from cycle 1. Thus, it can be concluded that the sample of hydrated nickel cobaltate, prepared using high-temperature two-stage synthesis with hot hydrolysis is a promising material for the Faradic electrode for high hybrid supercapacitors.

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