Гідроксиди нікелю широко використовується як активна речовина суперконденсаторів. Для підвищення електрохімічної активності в структуру гідроксиду нікеля вводять активатори, наприклад сполуки Co та Al. Найбільш ефективним є введення активаторів безпосередньо в структуру гідроксиду нікелю. Вивчено характеристики подвійного Ni–Co (Ni:Co=8:1) та потрійного Ni–Co–Al (Ni:Co:Al=8:1:2) гідроксидів, отриманих одноступеневим зворотнім хімічним синтезом. Кристалічна структура зразків вивчена методом ренгенофазового аналізу, термогравіметрії та диференційної скануючої калориметрії, електрохімічні характеристики – методами циклічної вольтамперометрії та гальваностатичного зарядно-розрядного циклування в суперконденсаторному режимі. Проведено порівняльний аналіз характеристик зразків подвійного Ni–Co та потрійного Ni–Co–Al гідроксидів. Методами ренгенофазового аналізу, термогравіметрії і диференційної скануючої калориметрії показано, що Ni–Co–Al гідроксид є шаруватим потрійним гідроксидом зі структурою α-Ni(OH)₂ високої кристалічності. Ni–Co гідроксид є подвійним гідроксидом Ni–Co (Co²⁺ ізоморфно заміщує Ni²⁺) з решіткою β-Ni(OH)₂ низької кристалічності. Методом циклічної вольтамперометрії та гальваностатичного зарядно-розрядного циклування показано високу електрохімічну активність подвійного Ni–Co гідроксиду. Методом циклічної вольтамперометрії виявлено аномальна α-поведінку Ni–Co гідроксиду з решіткою β-Ni(OH)₂. Показано, що електрохімічна активність потрійного Ni-Co-Al гідроксиду суттєво нижча, ніж подвійного Ni–Co гідроксиду (максимальні питомі ємності 550,4 Ф/г та 741,5 Ф/г відповідно), незважаючи на структуру шаруватого гідроксиду та наявність двох активаторів. Висловлено обґрунтоване припущення щодо отруєння Ni–Co–Al потрійно-шарового гідроксиду сполуками алюмінію при зворотному хімічному синтезі

Ключові слова: подвійний Ni–Co гідроксид, потрійний Ni–Co–Al гідроксид, шаруватий потрійний гідроксид, питома ємність, суперконденсатор

INVESTIGATION OF CHARACTERISTICS OF DOUBLE Ni–Co AND TERNARY Ni–Co–Al LAYERED HYDROXIDES FOR SUPERCAPACITOR APPLICATION

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1. Introduction

Nickel hydroxide and its different modifications possess high electrochemical activity [1]. Therefore, $Ni(OH)_2$ is widely used in different electrochemical devices [2].

Monohydroxide and double hydroxides of nickel are used as the active material of nickel oxide electrode in alkaline Ni–Cd, Ni–Fe and Ni–MeH accumulators [3, 4]. Nickel hydroxide is also used as cathode material in lithium batteries [5]. Hydroxides of nickel are used as the active material of Faradic electrode of hybrid supercapacitors. $Ni(OH)_2$ is used on its own [6, 7] and in the form of a composite with nanocarbon materials [8]. For thin layer supercapacitors, a nickel film can be formed on the conductive substrate [10]. Due to transparency changes, nickel hydroxides are used as electrochromic material [11, 12]. $Ni(OH)_2$ has high electro-catalytic activity and is used for electrooxidation of various organic compounds [13], sensor applications [14].

Two forms of nickel hydroxide are known [15]: β-form (chemical formula $Ni(OH)_2$, brucite-like structure) and α-form (chemical formula $3Ni(OH)_2 \cdot 2H_2O$, hydrotalcite-like structure). However, the paper [16] describes the formation of nickel hydroxide structures that are intermediate 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-$Ni(OH)_2$ possesses high storage and cycling stability. Therefore, this form is widely used in alkaline accumulators [18] and hybrid supercapacitors [19]. β-$Ni(OH)_2$ can be synthesized chemically at low supersaturation, electrochemically in a slit diaphragm electrolyzer [5]. High-temperature synthesis [20] and ammine complex decomposition [18] methods are also used.

It is worth noting that α-Ni(OH)$_2$ possesses higher electrochemical activity than β-Ni(OH)$_2$. However, pure α-form is metastable and transforms into less active β-form in concentrated alkalis and at elevated temperatures [21, 22]. This results in a decrease of specific capacity. To stabilize α-form, stabilizing additives are introduced to nickel hydroxide [23], which results in the formation of layered double hydroxides (LDH) [24]. LDH has a crystal lattice of «host» hydroxide, with part of «host» cations (Ni^{2+}) substituted by «guest» cations, such as Al^{3+} [25]. The excessive positive charge results in the intercalation of various anions to preserve electroneutrality [28]. α-Ni(OH)$_2$ nickel-based LDH can be prepared by chemical synthesis [26], homogeneous precipitation [6], electrolysis in a slit-diaphragm electrolyzer [27].

It can be concluded, that a promising direction for improving specific characteristics of hybrid supercapacitors is synthesis and study of stabilized and activated forms of α-Ni(OH)$_2$, namely, layered double and triple hydroxides of nickel.

2. Literature review and problem statement

α-Ni(OH)$_2$ is most commonly stabilized by the introduction of Al^{3+} cation [29, 30]. An aluminum cation is electrochemically inert and its low atomic mass is a significant advantage. The lower molecular mass of inert activator results in a higher content of the electrochemically active component. It is worth to note, that Al^{3+} not only stabilizes α-form, but also improves the electrochemical activity, which means the higher specific capacity of nickel hydroxide [31, 32]. Introduction of aluminum cation results in activation of nickel hydroxide and this effect also manifests for β-Ni(OH)$_2$ [33]. Most likely this results from increased polarization of oxygen evolution, which is a side reaction during charge (electrochemical oxidation) of nickel hydroxide [34]. This enables the use of double Ni−Al hydroxides not only for supercapacitors [35, 36] but also for electrocatalysis [37]. High electrochemical characteristics are demonstrated specifically by monophase Ni-Al LDH, in which «guest» aluminum cation resides in the crystal lattice of «host» Ni(OH)$_2$. Thus, aluminum cation plays the role of structural activator. However, the disadvantage of aluminum activation is that upon degradation of LDH, aluminum cation dissolves in solution and is then absorbed onto the surface of hydroxide, poisoning Ni(OH)$_2$ and significantly lowering its electrochemical activity.

Another common additive to nickel hydroxides is cobalt compounds, which transform into Co(OH)$_2$ in alkaline medium. In addition, cobalt hydroxide has its own electrochemical activity [38]. Therefore, Ni−Co hydroxides possess the electrocatalytic activity and are used for oxygen evolution [39], isoniazid oxidation [40], in the electrolyte with potassium ferrocyanide [41]. Mixed cobalt and nickel hydroxides are used in electrochemical devices [59]. Cobalt, as an additive to nickel hydroxide, is widely used in alkaline accumulators [42] and supercapacitors [44].

The analysis shows that there are different opinions regarding the form of cobalt and nickel hydroxide that are to be used for the active material. The authors of [42] describe the formation of «core/shell» structure, i.e. nickel hydroxide core is coated with a shell of cobalt hydroxide. Other authors [43] describe cobalt-stabilized Ni(OH)$_2$. The paper [44] describes the synthesis of mixed Ni−Co hydroxide, and [45] – nanonetwork (nanomixture) of cobalt and nickel

hydroxides. A mixture of cobalt and nickel hydroxides was synthesized through delaminating of basic nickel and cobalt salts [46, 47]. An only the author of [42, 48] describes the synthesis of layered doubled hydroxides. It is worth to note that Ni-Co LDHs are the most promising.

Even greater effectiveness can be achieved for hydroxide activated with both additives (Al^{3+}, Co^{2+}). However, the combined effect of cobalt and aluminum on nickel hydroxide is not studied well. As in the case with double Ni−Co and Ni-Al hydroxides, the situation with the type of introduced additives for the ternary Ni-Co-Al system is ambiguous. The paper [49] describes the synthesis of Al, Co stabilized α-Ni(OH)$_2$ for use in nickel-metal hydride accumulators. At the same time, the authors of [50] describe the use of Co and Al-doped α-Ni(OH)$_2$ in hybrid supercapacitors. The paper [51] studies the influence of cobalt additive on Ni−Al LDH for use in alkaline accumulators. However, the term «doping» implies a small amount of introduced Co. It is described that doping with Co improves the specific capacity of Ni−Al LDH. Both Ni−Al layered double hydroxide (LDH) and Ni−Al−Co layered triple hydroxide (LTH) are proposed for use in supercapacitors [52]. However, the authors [52] call triple Ni−Al−Co hydroxide as layered double hydroxide. The authors either use an incorrect term, or the synthesized compound is indeed LDH and the third component is introduced additionally.

In summary, it can be noted that Ni−Al, Ni−Co LDH and Ni−Co−Al LTH, specially synthesized through the single-stage procedure, are promising materials for hybrid supercapacitors. Synthesis and properties of Ni-Al LDH are studied well, while electrochemical characteristics of Ni−Co LDH and Ni−Co−Al LTH are studied in significantly less detail.

3. The aim and objectives of the study

The aim of the work is to evaluate the effectiveness of Ni−Co layered double and Ni−Co−Al layered triple hydroxides as the active material of Faradic electrode of hybrid supercapacitors.

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

– to synthesize samples of Ni−Co layered double and Ni−Co−Al layered triple hydroxides using single-step chemical synthesis;

– to conduct a comparative analysis of structural properties of double and triple hydroxides;

– to conduct a comparative analysis of electrochemical characteristics of samples to evaluate their effectiveness for use in supercapacitors.

4. Materials and methods for synthesis of Ni−Co layered double and Ni−Co−Al layered triple hydroxide samples and study of their characteristics

4. 1. Synthesis of LDH and LTH samples

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

The following samples of layered hydroxides were synthesized: Ni$_8$Co LDH and Ni$_8$Al$_2$Co LTH.

Synthesis of layered double and layered triple hydroxides was conducted using reverse titration method: solution of nickel and cobalt nitrates with a ratio of Ni:Co=8:1 (for

LDH) or solution of nickel, cobalt and aluminum nitrates with a ratio of Ni:Al:Co=8:2:1 (for LTH) was added drop-wise into alkaline solution at 60 °C while continuous stirring. After addition of salt solution was complete, the obtained suspension was kept at reaction temperature while stirring for an hour for crystallization [53]. The sample of layered hydroxide was separated from the mother liquor by means of vacuum filtration. The formed hydroxide is similar to inorganic-organic [54], inorganic-inorganic [55, 56] and organic-inorganic [57] composites, in that it is also a composite material. In this case, nickel hydroxides play the role of a matrix with the mother liquor as a filler [58]. The composite is a closed-cell type. Because of such structure, it is rather difficult to wash wet precipitate of layered hydroxide from soluble salts. In this case, the two-stage method is used: drying at 70 °C for a day, grinding, second washing from soluble salts and repeated drying under the same conditions. Prior to the study, the samples were additionally ground in a mortar and sifted through a 71 μm mesh.

4. 2. Characterization of LDH and LTH samples

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) and differential scanning calorimetry (DSC). TG analysis was conducted using the Shimadzu DTG-60 thermal analyzer under air atmosphere and heating rate of 5 °C/min. DSC analysis was conducted using the DSC-60 differential scanning calorimeter under 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 cell SES-2 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.) on the nickel foam current collector. 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 supercapacitor regime. The study was conducted in a special cell YSE-2 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.) [50] on the nickel foam current collector [49]. Electrolyte – 6 M KOH. Counter-electrode – nickel mesh, Ag/AgCl(KCl sat.) reference electrode. Charge-discharge cycling was conducted in supercapacitor regime at current densities of 20, 40, 80 and 120 mA/cm^2 (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 layered double and Ni–Co–Al layered triple hydroxide

Results of XRD analysis.

Results of XRD analysis revealed that the Ni-Al–Co sample has a crystal lattice of α-Ni(OH)$_2$ (Fig. 1, *a*), with rather high crystallinity. At the same time, the Ni-Co sample only

has peaks of β-Ni(OH)$_2$ (Fig. 1, *b*). It should be noted that the crystallinity of Ni–Co is significantly lower than that of Ni–Al–Co hydroxide.
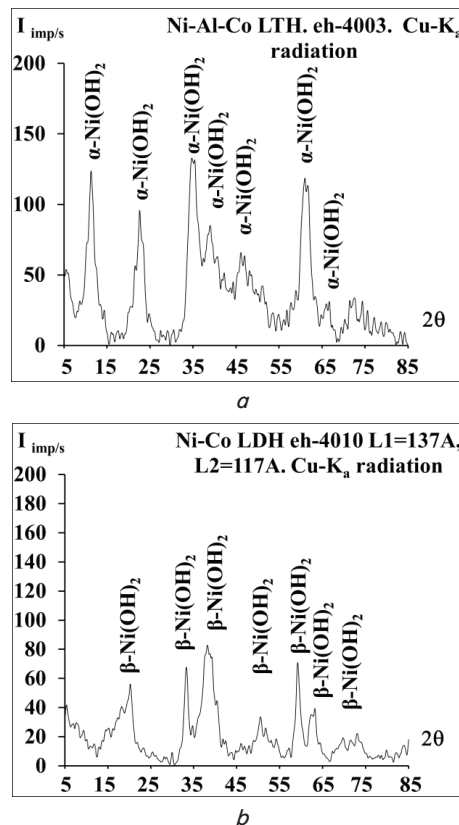

Fig. 1. XRD patterns of nickel hydroxide samples:
a – Ni–Al–Co LTH, *b* – Ni–Co LDH

Results of thermogravimetric analysis

TG curve of the Ni–Al–Co sample (Fig. 2, *a*) has two weight loss steps: the first step of 12.52 % and the second step of 22.72 %. These steps correspond to two endothermic peaks on the DTA curve. The first peak is at 156 °C. For the second peak, a split is observed, and it is possible that there are two overlapping endothermic peaks 331 °C and 363 °C.

TG curve of the Ni–Co sample (Fig. 2, *a*) has two weight loss steps: a rather weak step of 6.1 % and second, more pronounced of 18.18 %. These steps also have corresponding peaks on the DTA curve. First, weak and not well-defined is at 113 °C. The second peak is more intense and well-pronounced 270 °C.

Results of electrochemical studies

Cyclic voltammetry results for Ni–Co and Ni-Al–Co samples are shown in Fig. 3. Cyclic voltammogram of the Ni-Al–Co sample (Fig. 3, *a*) has a poorly-defined charge peak on the first cycle. Two charge peaks are observed in the second cycle. On the third-fifth cycles, one charge and one discharge peak are present. Charge peak is stabilized at 520–525 mV, discharge – at 400–405 mV. Specific charge peak current is 0.87 A/g of active material. Ni–Co sample (Fig. 3, *a*) demonstrates a different behavior. The first cycle on the voltammogram shows a poorly-defined charge peak of a different type. On the second – fifth cycles there is one discharge and charge peak. It should be noted that charge peak stabilizes at 470–475 mV, discharge – at 360–365 mV. Specific discharge peak current is significantly higher and is 4.46 A/g.

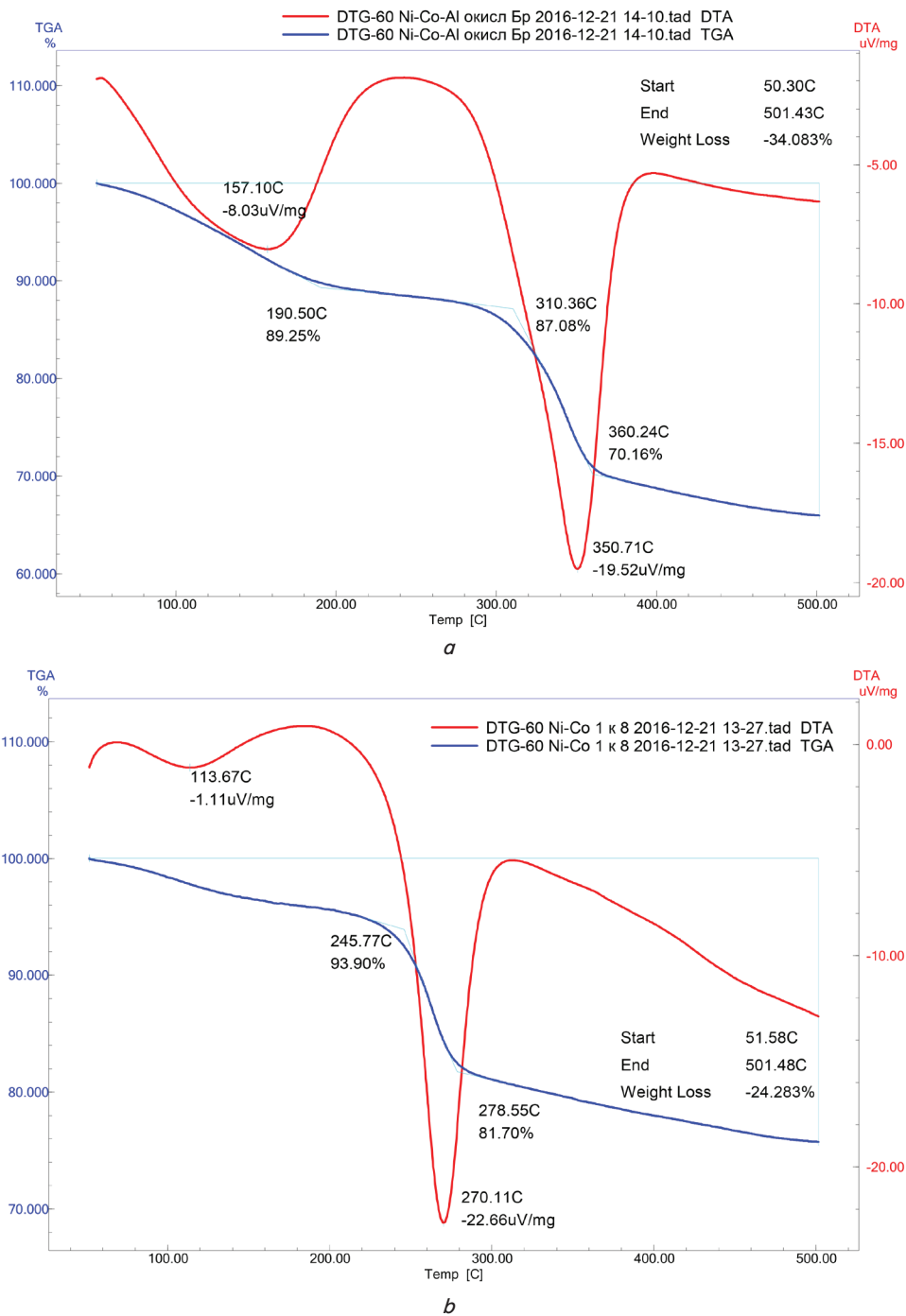Fig. 4 shows the specific capacities of synthesized samples.

Fig. 2. TG-DTA curves of nickel hydroxide samples: *a* — Ni-Al—Co LTH, *b* — Ni—Co LDH
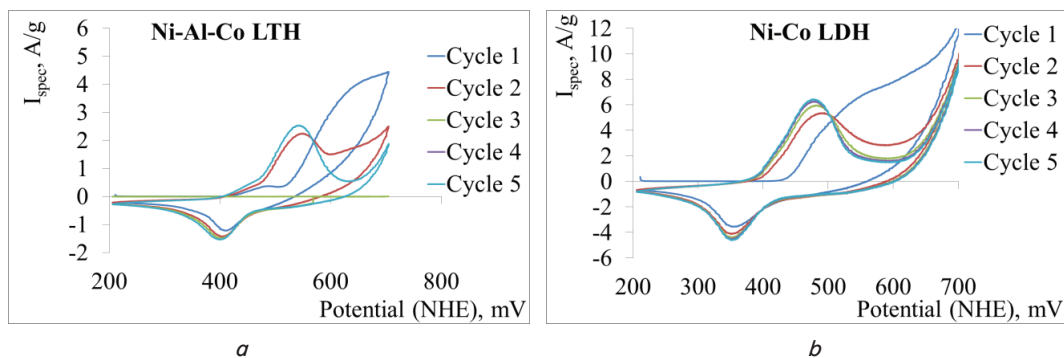

Fig. 3. Cyclic voltammograms of nickel hydroxide samples: *a* — Ni-Al—Co LTH, *b* — Ni—Co LDH

Full discharge

■ #5 Ni-Co
■ #3 Ni-Co-Al

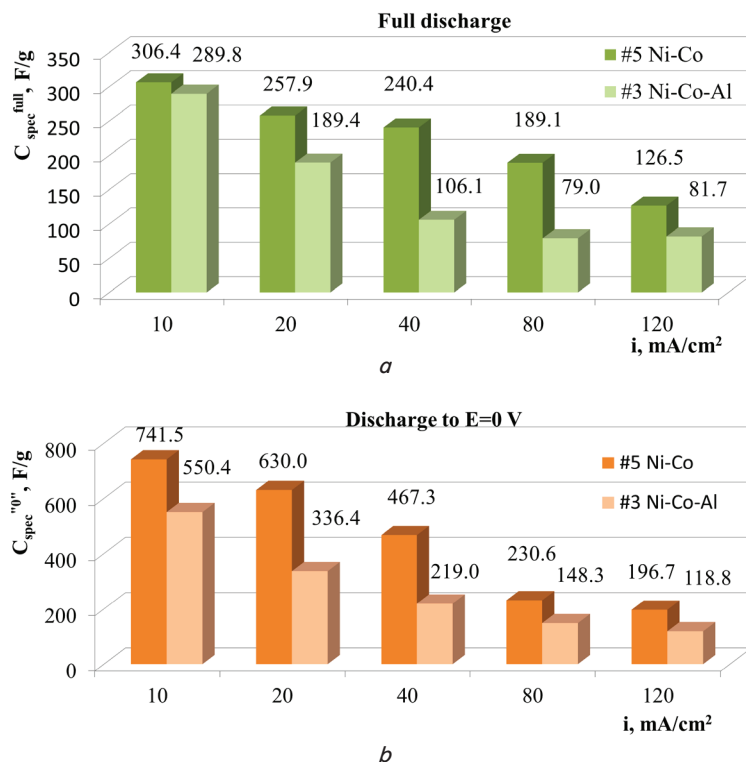**Discharge to E=0 V**

■ #5 Ni-Co
■ #3 Ni-Co-Al

Fig. 4. Specific capacities of different nickel hydroxide samples

It was found that the sample of triple Ni–Al–Co hydroxide possesses lower specific capacities than that of the Ni–Co sample obtained at full discharge. These dependencies are the same for all current densities. An exception is for a low current density of 10 mA/cm² at full discharge, where specific capacities of both samples are comparable.

6. Discussion of results obtained from studying characteristics of Ni–Co clayered double and Ni–Co–Al layered triple hydroxides

Crystal structure of nickel hydroxide samples. Results of XRD analysis (Fig. 1) revealed that Ni–Co layered double and Ni–Co–Al layered triple hydroxide have a different structure. Ni–Co–Al hydroxide has a crystal structure of α-Ni(OH)$_2$ with some amount of unidentified X-ray amorphous phase. In general, it can be concluded that the Ni–Co–Al sample is layered triple hydroxide. Large half-width at half-height for Ni–Co–Al hydroxide peaks indicates high crystallinity of the sample. At the same time, Ni–Co hydroxide on the XRD pattern shows peaks characteristic of β-Ni(OH)$_2$, which have a low height and large width, indicating low crystallinity. The presence of X-ray amorphous phase is also observed on the XRD pattern. However, layered double hydroxides of Ni have a lattice of α-Ni(OH)$_2$, therefore, Ni–Co hydroxide is not a classic layered double hydroxide. Most likely, this sample is co-precipitated double Ni–Co hydroxide, in which cobalt cations isostructurally substitute nickel cations in the β-Ni(OH)$_2$ crystal lattice. Results of thermogravimetric analysis support this conclusion. TG and DTA curves of the Ni–Co–Al sample are characteristic of α-form. TG curve has two weight loss steps, which correspond to a loss of crystal water (first step) and decomposition of hydroxide into oxide (second step). These

two steps correspond to two endothermic peaks on the DTA curve, which have comparable intensities. A more thorough analysis revealed that the second endothermic peak is split and is likely composed of two overlapping endothermic peaks (at 331 °C and 363 °C). Intensities of both peaks are equal. The nature of these two peaks is unclear and further study is required. However, a hypothesis can be made that these two peaks correspond to α-form and X-ray amorphous β-form, which has metastable lattice and contains additional water. TG and DTA curves of the Ni–Co sample are characteristic of β-Ni(OH)$_2$. TG curve has two weight loss steps. The first one is rather small and corresponds to a loss of bound water and decomposition of defective X-ray amorphous part. This is indicated by the peak temperature (113 °C), which is barely over the temperature of boiling water. The second peak corresponds to the decomposition of hydroxide into oxide. These steps correspond to two endothermic peaks on the DTA curve. However, the intensity of the second peak on the DTA curve (Fig. 2, *b*) is almost 20 times higher than that of the first peak. Comparison of the second endothermic peaks has revealed that for Ni–Co hydroxide (Fig. 2, *b*) the intensity of the second peak is 1.76 times higher than that of the Ni–Co–Al sample (Fig. 2, *a*).

This indicates that the crystal lattice of double Ni–Co hydroxide is significantly more stable than the lattice of triple Ni–Co–Al hydroxide.

Electrochemical characteristics of nickel hydroxide samples. Cyclic voltammograms of double Ni–Co and triple Ni–Co–Al hydroxides (Fig. 3) revealed fundamentally different electrochemical behavior. The Ni–Co sample shows abnormal behavior that is characteristic of α-Ni(OH)$_2$, despite XRD results stating that it is β-Ni(OH)$_2$. α-like behavior of this sample is further confirmed by peak potentials, which are 470–475 mV for the charge, and 360–365 mV for the discharge peak. At the same time, Ni–Co–Al hydroxide, which has α-form according to XRD results, has charge peak potentials of 520–525 mV, and 400–405 mV for discharge. It is known that charge and discharge peak potentials of β-Ni(OH)$_2$ are more positive than those for α-Ni(OH)$_2$. Possibly, the abnormal behavior of Ni–Co is related to activation with cobalt cations. Co^{2+} cation isostructurally substitutes Ni^{2+}, and can be oxidized to Co^{3+} in the cycling potential range, but cannot be reduced back. This results in the constant presence of Co^{3+} cations in the lattice of double Ni–Co hydroxide, which increase conductivity and possibly improve the electrochemical activity of the hydroxide. This is indicated by a high specific discharge peak current of 4.46 A/g. The cyclic voltammetry curve of triple Ni–Co–Al hydroxide has a poorly-defined charge peak on the first cycle, which is characteristic of α-Ni(OH)$_2$ and layered double hydroxides. However, on the second cycle two charge peaks are observed, which on the third – fifth cycle merge into a single peak with a potential value between the previous two peaks. It is possible, that the first charge peak (second cycle) characterizes X-ray amorphous or even nanosized part, which is observed on the XRD pattern. The second peak corresponds to a more crystalline α-phase. Two peaks of this phase are averaged on subsequent cycles. However,

the specific discharge peak current is rather low and is only 0.86 A/g, which is 5.18 times lower than that of Ni–Co hydroxide (4.46 A/g). Even though the second activator (Al^{3+}) was added to triple hydroxide during synthesis. It is possible that despite theoretical basis, the deviation in practice is likely because of hydroxide poisoning by surface-absorbed aluminum cations. It is possible, that during reverse titration synthesis (when there is a constant excess of base) in the presence of cobalt cations (practically the second «host»), processes that hinder the formation of layered hydroxide occur. This can result in the formation of a separate aluminum hydroxide phase. This phase is not observed on the XRD pattern of Ni–Co–Al hydroxide (Fig. 1, *a*). It should be notedt hat due to low content (below 5 %) and low crystallinity, such phase is difficult to identify.

Charge-discharge cycling in supercapacitor regime further support the results of cyclic voltammetry. It was found that specific capacity of double Ni–Co hydroxide is higher than that of triple Ni–Co–Al hydroxide. An exception is for a low current density of 10 mA/cm^2 at full discharge, where the capacities of both samples are comparable. It should be noted, that during charge-discharge cycling, the effect of aluminum poisoning is significantly lower. The maximum capacity obtained for Ni–Co hydroxide is 741.5 F/g, and for Ni–Co–Al hydroxide is 550.4 F/g. The decrease of capacity with increasing current density from 10 mA/cm^2 to 120 mA/cm^2 is similar for both samples: Ni–Co hydroxide – 72.5 %, Ni–Co–Al hydroxide – 78.4 %. This indicates similar electrochemical characteristics of both samples. It is worth to point out, that the activating effect of aluminum additive was negated by poisoning with aluminum compounds that were not incorporated into the structure of layered hydroxide. In order to avoid poisoning, further studies on the synthesis of Ni–Co–Al LTH at constant pH are required.

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7. Conclusions

1. Previously not synthesized samples of double Ni_8Co and triple Ni_8CoAl_2 hydroxides were prepared using single-stage reverse titration method.

2. By means of XRD analysis, thermogravimetry, and differential scanning calorimetry it was found that Ni–Co–Al is layered triple hydroxide with the structure of α-Ni(OH)$_2$ with high crystallinity. Ni-Co hydroxide is double Ni–Co hydroxide with the crystal lattice of β-Ni(OH)$_2$, in which part of Ni^{2+} is isostructurally substituted by Co^{2+}, and low crystallinity.

3. Comparative analysis of electrochemical characteristics of double Ni–Co and triple Ni–Co–Al hydroxide was conducted by means of cyclic voltammetry and galvanostatic charge-discharge cycling. The high electrochemical activity of Ni–Co hydroxide was found. By means of cyclic voltammetry, an abnormal, α-like behavior of Ni–Co with β-Ni (OH)$_2$ lattice was found. The electrochemical activity of triple Ni-Co-Al hydroxide was found to be significantly lower than that of double Ni–Co hydroxide, despite the structure of pure layered double hydroxide and presence of two activators. Maximum specific capacities are 741.5 F/g (Ni–Co hydroxide) and 550.4 F/g (Ni–Co–Al hydroxide). A hypothesis was proposed on the poisoning of Ni–Co–Al LTH with free aluminum compounds during reverse titration synthesis.

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