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*В сучасному світі одним із перспективних напрямів є отримання і використання багатофункціональних речовин. Ni-Al подвійно-шаровий гідроксид широко використовується як активна речовина суперконденсаторів. При цьому сполуки нікелю забарвлені і можуть бути використані як пігменти. Вивчені характеристики зразків біфункціональних індигокармін-інтеркальованих Ni-Al (Ni:Al=4:1) гідроксидів, отриманих синтезом при рівноважному рН та рН=14. Кристалічна структура зразків вивчена методом рентгенофазового аналізу та термогравіметрії, пігментні властивості – методом вимірювання і розрахунку характеристик кольору в системах CIE Lab і XYZ, електрохімічні характеристики – методами циклічної вольтамперометрії та гальваностатичного зарядно-розрядного циклування в суперконденсаторному режимі. Проведено порівняльний аналіз електрохімічних характеристик зразків Ni-Al-індигокармін і Ni-Al-карбонат гідроксидів. Методами рентгенофазового аналізу та термогравіметрії показано, що Ni-Al-індигокармін гідроксид є подвійно-шаровим гідроксидом зі структурою  $\alpha$ -Ni(OH)<sub>2</sub> середньої (синтез при рН=13) та низької (синтез при рівноважному рН) кристалічності. Показано, що синтезовані Ni-Al-індигокармін ПШГ мають колір на межі синього та голубого (тон кольору 483–485 нм) середньої світлоти. Методом гальваностатичного зарядно-розрядного циклування показано високу електрохімічну активність Ni-Al-індигокармін подвійно-шарового гідроксиду (синтезованого при рН=14), що перевищує електрохімічну активність карбонат-інтеркальованого гідроксиду: максимальна питома ємність при повному розряді складала 1007 Ф/г гідроксиду і 2996 Ф/г Ni, при розряді до 0 В – 946 Ф/г гідроксиду. Вперше для Ni-Al-індигокармін ПШГ виявлено наявність на розрядній кривій двох площадок, які відповідають розряду Ni<sup>3+</sup> та індигокармін-аніону*

*Ключові слова: Ni-Al подвійно-шаровий гідроксид, пігмент, питома ємність, суперконденсатор, розрядна площа*

# BIFUNCTIONAL INDIGOCARMIN-INTERCALATED Ni-AL LAYERED DOUBLE HYDROXIDE: INVESTIGATION OF CHARACTERISTICS FOR PIGMENT AND SUPERCAPACITOR APPLICATION

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## 1. Introduction

Nickel compounds are widely used for different purposes. As a 3d element, nickel and its compounds are used as catalysts. Owing to the formation of stable compounds in different oxidation states and the ability to transition between them, nickel compounds (hydroxides and oxides) are used in electrochemical devices. Additionally, compounds are colored and are used as pigments.

Different types of nickel hydroxides possess rather high electrochemical activity [1]. So, these compounds are widely used in different electrochemical devices [2, 3]. Nickel hydroxide along with double nickel hydroxides is used as

the active material of nickel oxide electrode in alkaline accumulators [4, 5]. Nickel hydroxide is also used in cathodes for lithium batteries [6]. Ni(OH)<sub>2</sub> is used as an active material of the Faradaic electrode of hybrid supercapacitors (SC). Nickel hydroxide is used on its own [7, 8], and in the form of composite with nanocarbon materials [9]. Due to reversible electrochemical color change, Ni(OH)<sub>2</sub> is used as an electrochromic material [10]. Nickel hydroxide and Ni-LDH are used in electrocatalysis [11, 12], namely for electrochemical oxidation of organic compounds [13], and sensors [14].

There are two known stable allotropes of nickel hydroxide [15]:  $\beta$ -form (chemical formula Ni(OH)<sub>2</sub>, brucite-like

structure) and  $\alpha$ -form (chemical formula  $3\text{Ni}(\text{OH})_2 \cdot 2\text{H}_2\text{O}$ , hydrocalcite-like structure). However, the paper [16] describes the formation of nickel hydroxide structures that are in-between  $\alpha$ - $\text{Ni}(\text{OH})_2$  and  $\beta$ - $\text{Ni}(\text{OH})_2$ . The paper [17] describes the formation of nickel hydroxide with layered ( $\alpha+\beta$ )-structure.

$\beta$ - $\text{Ni}(\text{OH})_2$  has high storage and cycling stability. Thus, it is widely used in alkaline batteries [18] and hybrid supercapacitors with the alkaline electrolyte [19]. It can be precipitated chemically at low supersaturation or electrochemically in the slit-diaphragm electrolyzer [17]. High-temperature synthesis [20] and ammine complex decomposition [18] are also used.

It should be noted that  $\alpha$ - $\text{Ni}(\text{OH})_2$  has higher electrochemical activity than  $\beta$ - $\text{Ni}(\text{OH})_2$ . However,  $\alpha$ -form is metastable, and in alkaline media and high temperatures, it transforms into less active  $\beta$ -form [21, 22] resulting in loss of capacity. To stabilize  $\alpha$ -form, stabilizing additives [23] are introduced to nickel hydroxide forming layered double hydroxides (LDH) [24]. LDH consist of the host crystal lattice, in which part of host hydroxide cations ( $\text{Ni}^{2+}$ ) are substituted by guest cations such as  $\text{Al}^{3+}$  [25]. The excess of positive charge is compensated by the intercalation of various anions [26].  $\alpha$ - $\text{Ni}(\text{OH})_2$  and nickel-based LDH can be prepared using chemical precipitation [27], homogeneous precipitation [6], electrolysis in slit-diaphragm electrolyzer [28]. It should be noted that nickel LDH is one of the most promising hydroxide forms for use in supercapacitors.

On the other hand,  $\text{Ni}^{2+}$  compounds are colored and can be used as pigments. Pure  $\text{Ni}(\text{OH})_2$  has a light-green color of rather low intensity and has rather low pigment characteristics. However, the synthesis of Ni-LDH intercalated with anionic dyes can yield promising pigments with various colors used in different fields, such as cosmetics for making nail polish [29].

It should be noted that rather promising would be the synthesis and study of layered double hydroxides of nickel that could fit two functional roles and possess high electrochemical activity and pigment characteristics.

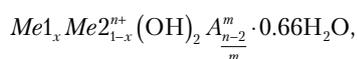
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## 2. Literature review and problem statement

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To evaluate the possibility of synthesizing bi-functional Ni-LDH that would possess electrochemical activity and intense coloration, it is necessary to analyze what is a layered double hydroxide.

Layered double hydroxide (LDH) is an  $\alpha$ -form of "host" metal hydroxide with part of ions in the crystal lattice substituted with the ions of "guest" metal. For instance, the  $\text{Ni}^{2+}$  cation is substituted with the  $\text{Al}^{3+}$  cation. This leads to the formation of an excess positive charge in the crystal lattice which can be compensated by the inclusion of additional anions. A general formula for divalent metal-based LDH is



where  $\text{Me}_1 = \text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Zn}^{2+}$  etc.,  $\text{Me}_2 = \text{Al}^{3+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Cr}^{3+}$ ,  $\text{Ti}^{4+}$  etc. A – various-purpose anions. Under normal conditions, these can be anions of precursor salts. But more commonly intercalated anions have special functional prop-

erties. For instance, stabilizing [30] or activating [12, 31] anions can be introduced into the LDH structure. A promising application for LDH is as nano-containers for special anions, such as drugs [32, 33], dyes [29], sensors [34], corrosion inhibitors [35], etc.

In practical terms, LDH are ionic constructors with three main components [24]: "host" metal cation, "guest" metal cation, and intercalated anion. Directed choice of these components allows for the construction of LDH with required properties [35].

Thus, to obtain electrochemically active pigment LDH, it is necessary to use  $\text{Ni}(\text{OH})_2$  as the "host" hydroxide.

The "guest" cation should stabilize LDH and ideally activate the electrochemical properties of LDH.  $\text{Al}^{3+}$  is commonly used to stabilize LDH [36, 37]. Aluminum is electrochemically inert, so its low atomic mass is a significant advantage. The lower molecular mass of the inert activator means higher content of the electrochemically active component. It should be mentioned that  $\text{Al}^{3+}$  not only stabilizes LDH but also increases the specific capacity of nickel hydroxide [38, 39]. Introduction of aluminum cation results in the activation of nickel hydroxide, which is also observed for  $\beta$ - $\text{Ni}(\text{OH})_2$  [40]. This is likely due to the increased polarization of oxygen evolution, which is a side-reaction of the nickel hydroxide charge (electrochemical oxidation) process [41]. This allowed for using Ni-Al LDH not only in supercapacitors [42, 43] but also in electrocatalysis [44].

Carbonate is commonly intercalated into electrochemically active Ni-Al LDH, and not only stabilizes LDH but also plays the role of activator [31, 45]. However, carbonate has two disadvantages for the formation of bi-functional (pigment and electrochemically active) Ni-Al LDH. Firstly, it is not electrochemically active and is effectively ballast, which lowers the specific capacity of LDH. Secondly, the intercalation of carbonate into LDH does not affect color, resulting in the formation of light-green compounds without significant pigment properties.

Various anionic dyes can be used to prepare LDH based pigments, which allows broadening the color pallet significantly: Acid Yellow 17 in Zn-Al LDH [46], o-Methyl Red in Mg-Al LDH [47], and o-Methyl Red in Ni-Fe LDH [48], Mordant Yellow 3 in Zn-Al [49, 50], Acid Yellow 3 in Zn-Al LDH [51], bi-anion Acid Green 28 in Zn-Al LDH [52]. Some authors used LDH to remove dyes from wastewater, thus forming dye-intercalated LDH. Namely, it is proposed to use Zn-Al LDH for the removal of Evans Blue [53], Orange type dyes – with Zn-Al LDH [54]. Various dyes [54], including Remazol Brilliant Violet [55], were removed using Ni-Al LDH, blue dyes (including Maya Blue) [56] – using Zn-Al LDH, Methyl Orange [57] – using Zn-Al LDH, Amaranth [58] – using Mg-Al LDH, Acid Yellow 42 [59] – using Mg-Al LDH, Kongo Red [60] – using Ni-Al LDH, and Indigo carmine [61] – using Mg-Fe LDH.

The most promising and expensive are blue palette pigment, so a blue water-soluble dye should be used for intercalation into Ni-Al LDH. Intercalated organic dye anions have large molecular mass, which in case of inertness would lead to a significant drop in electrochemical characteristics of Ni-Al LDH. Therefore, to prepare blue Ni-Al LDH pigment with high electrochemical activity, electrochemically active blue anionic dye should be used. Among all described dyes, only Indigo carmine fits such requirements, which is used

in analytical chemistry as a redox indicator, and is able to undergo reversible oxidation and reduction.

Thus, the assumed bi-functional (pigment and electrochemically active) material could be Ni-Al-Indigo carmine LDH. And while color characteristics of such LDH, synthesized in different ways, have been studied in [62], the electrochemical properties of indigo carmine intercalated Ni-Al LDH have not been studied at all, even though the material is rather promising for use in supercapacitors.

### 3. The aim and objectives of the study

The aim of the work is to determine if Indigo carmine intercalated Ni-Al layered double hydroxide can be used as both active materials of the Faradic supercapacitor electrode and effective nail polish pigment.

To achieve the aim, the following objectives were formulated:

- to prepare Indigo carmine intercalated Ni-Al layered double hydroxide samples, using the single-stage chemical synthesis method under different conditions;
- to conduct an analysis and compare the structural properties of the prepared LDH samples;
- to study the pigment characteristics of the prepared samples;
- to compare the electrochemical characteristics of Indigo carmine intercalated Ni-Al LDH and carbonate intercalated Ni-Al LDH and evaluate the effectiveness of use in supercapacitors.

## 4. Materials and method used in the synthesis and study of Na-Al layered double hydroxide samples

### 4.1. Synthesis of LDH samples

Analytical grade reagents were used in the study except for NaOH (granulated, Chemically pure grade).

Analytical grade Indigo carmine, 5,5'-indigodisulfonic acid disodium salt ( $C_{16}H_8N_2Na_2O_8S_2$ ) was used as a dye.

To improve stability, it was proposed to conduct the synthesis of the following samples of layered double hydroxides with the general formula  $Ni_4AlA_{0.5}$ , where A – Indigo carmine. For a comparative study of electrochemical characteristics, the sample of Ni-Al LDH with the same formula was synthesized, with anion changed to carbonate.

Ni-Al LDH samples were synthesized using chemical precipitation at a constant pH. LDH was precipitated by feeding three solutions (nickel and aluminum nitrates, alkali, and indigo carmine; 0.5 L each) at the same rate into the reaction beaker containing 100 ml of the initial solution. Two types of synthesis were conducted: at an equilibrium pH (labeled as **Ni4Al-Ind pH=equil**) and at pH=14 (labeled **Ni4Al-Ind pH=14**). In case of equilibrium pH synthesis, the stoichiometric amount of each reagent was used with distilled water as the initial solution. For synthesis at pH=14, an excess of alkali was used to sustain pH=14. Initial solution – 0.1 M NaOH. The synthesis was conducted at 60 °C and continuous stirring. After solutions were added, the reaction mixture was kept under the same conditions for an hour to undergo crystallization [63]. The formed precipitate was then vacuum filtered to remove the mother liquor. The formed hydroxide

is a composite material, similar to polymer composites [64]. In this case, the matrix is formed by the hydroxide itself with the mother liquor acting as a filler [65]. 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 (70 °C, 24 h), grinding, rinsing 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 LDH samples

The crystal structure of the samples was studied by means of X-ray diffraction analysis (XRD) using the DRON-3 diffractometer (Russia) (Cu-K $\alpha$  radiation, scan range 10–90° 2 $\theta$ , 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.

Color characteristics of Indigo carmine intercalated Ni-Al LDH samples were measured using a spectrophotometer. A thin layer of the pigment sample was placed into a polyethylene ZIP-bag, which was placed onto a flat solid base. As a result of measurements, chromaticity ( $x, y, z$ ) and color ( $X, Y$ ) coordinates were recorded. Color tone value (predominant wavelength –  $\lambda$ ) and color purity ( $P, \%$ ) were determined from the color graph in  $X, Y$  coordinates. Color coordinates were also recalculated into CIE 1976  $L^*a^*b^*$ . Lightness ( $L$ ) and color saturation ( $S$ ) were calculated. The diffuse reflection coefficient was also measured.

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.) [66] on the nickel foam current collector [67]. 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 supercapacitor regime. The cell, working, counter-electrode, reference electrode, and electrolyte were the same as for cyclic voltammetry. Charge-discharge cycling was conducted in a supercapacitor regime at current densities of 20, 40, 80, and 120 mA/cm<sup>2</sup> (10 cycles at each current density). Discharge curves were used to calculate the specific capacity  $C_{sp}$  (F/g) at full discharge (till constant negative potential) and discharge to 0 mV.

## 5. Characterization results of bi-functional Ni-Al layered double hydroxide

### XRD analysis results.

XRD analysis results reveal that both samples have a crystal lattice that of  $\alpha$ -Ni(OH)<sub>2</sub>. It should be noted that the **Ni4Al-Ind pH=equil** sample (Fig. 1, b), synthesized at an equilibrium pH, has a significantly lower crystallinity.

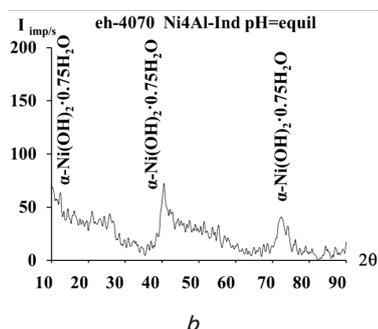
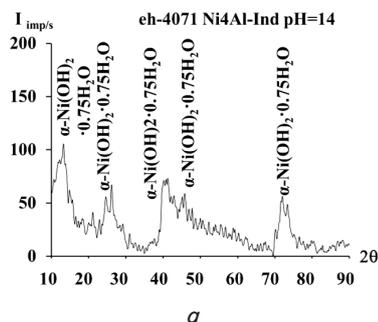


Fig. 1. XRD patterns of LDH samples: *a* – Ni4Al-Ind pH=14, *b* – Ni4Al-Ind pH=equil

#### Results of thermogravimetric analysis

The TG curve of the Ni4Al-Ind pH=14 sample (Fig. 2, *a*) has two mass loss steps: the first step of 10.85 % and the second step of 23.21 %. The first step corresponds to the endothermic peak on the DTA curve (215 °C), and the second – sharp exothermic peak (400 °C).

The TG curve of the Ni4Al-Ind pH=equil sample (Fig. 2, *b*) shows a similar picture, except, the temperature of the first peak (167 °C) is shifted towards lower temperatures and the temperature of the second peak (465 °C) – towards higher temperatures.

#### Results of color characterization.

Color characteristics of Ni-Al-Indigo carmine LDH are listed in Table 1. It should be noted that both pigments have color bordering between blue and light blue (483–485 nm), and low color purity. Both pigments are characterized by average lightness and low color saturation. It should be noted that the Ni4Al-Ind pH=equil sample, synthesized at an equilibrium pH, has a darker color (lower lightness) and higher color saturation.

#### Results of electrochemical characterization

The cyclic curves of Indigo carmine intercalated samples are shown in Fig. 3.

Table 1

Color characteristics of Ni-Al LDH samples

Sample	Diffuse reflectance coefficient, %			Color tone $\lambda$ , nm	Color purity P, %
	1	2	Average		
Ni4Al-Ind pH=14	15.47	15.37	15.42	483	4
Ni4Al-Ind pH=equil	9.12	9.14	9.13	486	5
Sample	CIE Lab			Saturation	
	a	B	L (Lightness)	S	
Ni4Al-Ind pH=14	-2.81	-9.51	50.33	9.92	
Ni4Al-Ind pH=equil	-3.31	-10.80	40.35	11.30	

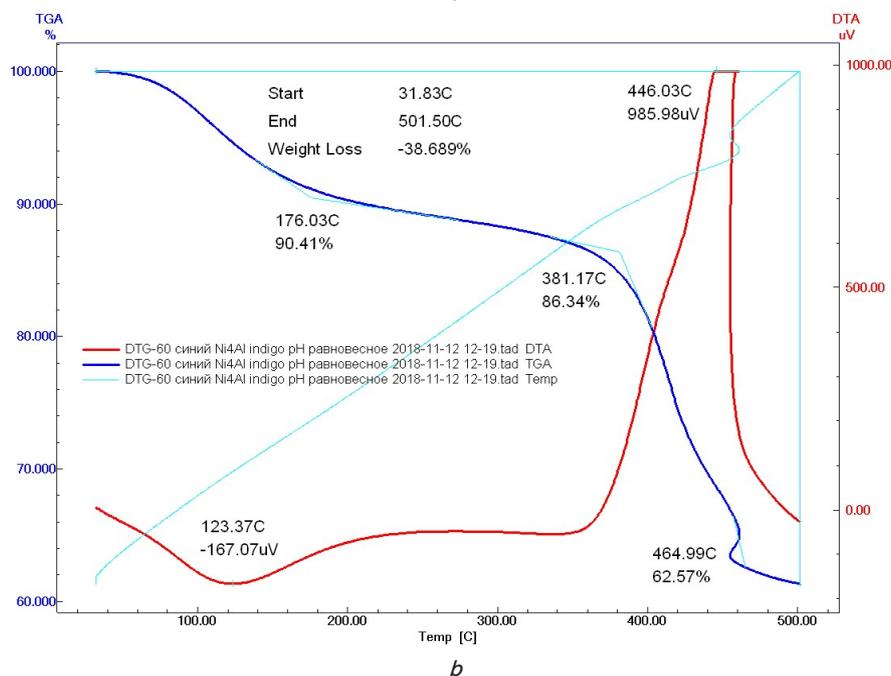
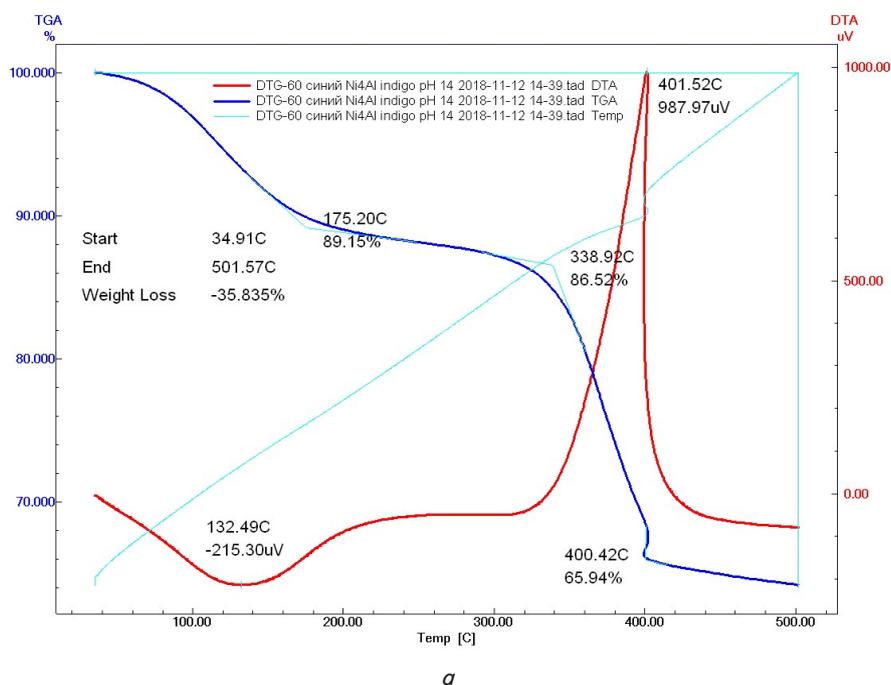


Fig. 2. TG-DTA curves of LDH samples: *a* – Ni4Al-Ind pH=14, *b* – Ni4Al-Ind pH=equil; синий – blue; равновесное – equilibrium

The voltammogram of the **Ni4Al-IndpH=14** sample (Fig. 3, *a*) shows a poorly defined charge peak on the first cycle. Starting from cycle two, only one charge and discharge peak are observed. It should be noted that the charge peak of cycles 3–5 is wide. The charge peak is stabilized at 615–618 mV (specific current 2.84 A/g), discharge – 385–395 mV, with a specific current of 1.73 A/g. The characteristics of both curves are similar. The voltammogram of the **Ni4Al-IndpH=equil** sample (Fig. 3, *b*) shows a poorly defined charge peak on the first cycle. The second and third cycles also have one charge and discharge peak. However, the charge peak of **Ni4Al-IndpH=equil** is narrower and more defined. The charge peak is stabilized at 623–626 mV (specific current 2.54 A/g), discharge – at 420–425 mV with the specific current of 1.72 A/g.

During charge-discharge cycling, a new occurrence was discovered – the presence of two potential plateaux for indigo carmine intercalated Ni-Al LDH samples (Fig. 4). The first plateau is situated at +305–(+205) mV, the second – –510–(–720) mV.

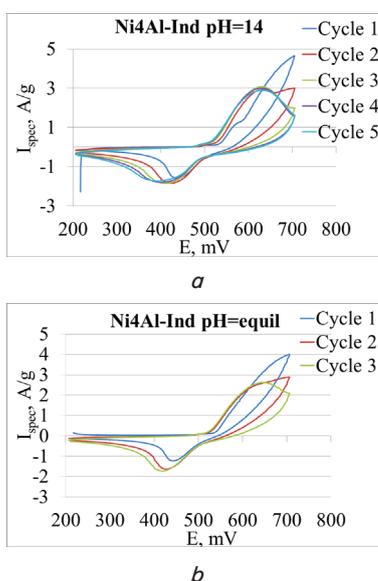


Fig. 3. Cyclic voltammograms of LDH samples *a* – **Ni4Al-Ind pH=14**, *b* – **Ni4Al-Ind pH=equil**

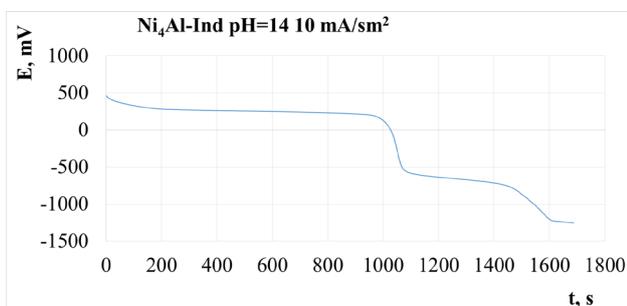


Fig. 4. Discharge curve of the **Ni4Al-Ind pH=14** sample

Fig. 5 shows the specific capacities of synthesized Ni-Al LDH intercalated with indigo carmine and carbonate.

It was found that the samples synthesized at pH=14 (**Ni4Al-Ind pH=14** and **Ni4Al-CO3 pH=14**) have higher specific capacities than those synthesized at an equilibrium pH (**Ni4Al-Ind pH=equil** and **Ni4Al-CO3 pH=equil**). It was also found that indigo carmine intercalated samples

(**Ni4Al-IndpH=14** and **Ni4Al-IndpH=equil**) have higher specific capacities than those intercalated with carbonate (**Ni4Al-CO3 pH=14** and **Ni4Al-CO3 pH=equil**).

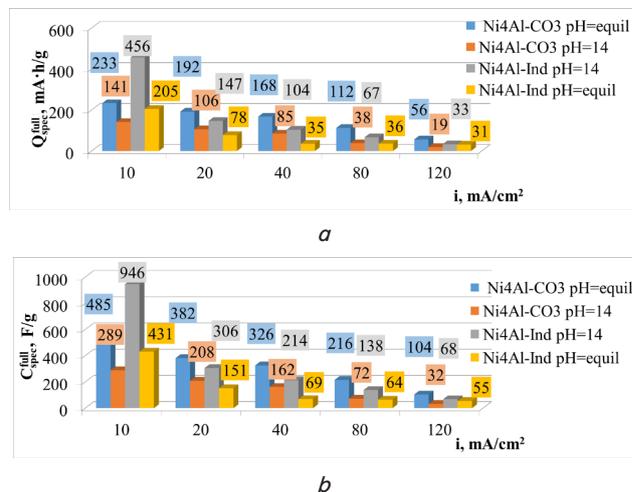


Fig. 5. Specific capacities of carbonate and indigo carmine intercalated Ni-AL LDH: *a* – full discharge; *b* – discharge 0 V

This tendency is characteristic for all current densities, except for a low current density of 10 mA/cm<sup>2</sup> at discharge to 0 V, where the specific capacities of both samples are comparable.

### 6. Discussion of the results of characterization of Ni-Al layered double hydroxides

**Crystal structure.** The results of XRD analysis (Fig. 1) revealed that both indigo carmine intercalated Ni-Al samples have a crystal lattice that of  $\alpha$ -Ni(OH)<sub>2</sub> with some amount of X-ray amorphous phase. A separate Al-containing phase is not observed. It can be concluded that both samples are layered double hydroxides. Larger half-width at half-height of the **Ni4Al-Ind pH=14** sample indicated higher crystallinity. At the same time, the **Ni4Al-Ind pH=equil** sample, at lower, equilibrium pH, has very low crystallinity. The results of the thermogravimetric analysis support this conclusion. The TG and DTA curves of both **Ni4Al-Ind pH=equil** and **Ni4Al-Ind pH=14** are characteristic of that of  $\alpha$ -form. The TG curve has two mass loss steps which correspond to the loss of structural water (first step) and breakdown of hydroxide into oxide (second step). The first step corresponds to a poorly defined endothermic peak. For carbonate LDH or LTH [45], the second mass loss peak should coincide with the endothermic peak, which should be more intense than the first endothermic peak. At the same time, for both indigo carmine intercalated samples, there is a strong exothermic peak on the DTA curve, instead of the expected endothermic peak corresponding to the breakdown of the hydroxide structure. This peak is most likely due to the combustion of organic indigo carmine. The first endothermic peak characterizes the stability of  $\alpha$ -Ni(OH)<sub>2</sub>, and the second – thermal stability of indigo carmine in the hydroxide crystal lattice. So it can be concluded that the synthesis at an equilibrium pH leads to the formation of LDH with a less stable structure, in comparison to LDH prepared at pH=14 (temperatures of the first endothermic peak are 167 °C and 215 °C, respectively). For indigo carmine, the situation is

reversed – synthesis at an equilibrium pH has a stronger stabilized effect on the intercalated organic anion (temperatures of the second exothermic peak are 465 °C and 402 °C, respectively). Considering that lower stability indicates higher electrochemical activity, it should be concluded that increasing synthesis pH lowers the activity of the hydroxide component of LDH while increasing the electrochemical activity of intercalated indigo carmine.

**Color characteristics of samples.** Visually, both samples of indigo carmine intercalated Ni-Al LDH have a light-blue color. Measurement of color characteristics in CIELab and XYZ systems confirms visual observation. The color tone of both samples is the same 483 nm and 485 nm. The prepared samples have an average lightness: **Ni4Al-Ind pH=equil**  $L=40.35\%$ , **Ni4Al-Ind pH=14**  $L=50.33\%$ . The blue color of the **Ni4Al-Ind pH=equil** sample is easily explained by the blue color of indigo carmine and light-green of hydroxide. However, during synthesis at pH=14 m, it is important to consider that indigo carmine is an acid-base indicator, with transition pH of 11.6–14. And just after pH=13 indigo carmine turns yellow. However, synthesis at pH=14 produces compounds of blue color. It is possible that the pH near the precipitation zone doesn't exceed 13, and the dye is absorbed in its blue form. Precipitation at the pH near the color transition results in higher lightness for the **Ni4Al-Ind pH=14** sample. In general, it can be said that both samples of indigo carmine intercalated Ni-Al LDH can be used as blue pigments.

**Electrochemical characteristics of nickel hydroxide samples.** Cyclic voltammetry of Ni-Al indigo carmine layered hydroxides, prepared at different pH (Fig. 3), revealed that they have fundamentally the same electrochemical behavior. Cyclic voltammograms of both samples have a poorly defined charge peak on the first cycle, which is characteristic of  $\alpha$ -Ni(OH)<sub>2</sub> and LDH. However, for the sample synthesized at pH=14 (**Ni4Al-Ind pH=14**), two peaks are observed on the first cycle, with the first peak situated at 565 mV, which is rather small, with a current density of 1.05 A/g. On the second and subsequent cycles, only one peak at 625–630 mV is observed. The discharge curves reveal gradual working through the material and shift of the peak potential towards negative values (from 430 mV on the first charge cycle to 405–410 mV on the fifth cycle). Reversibility (potential difference between the charge and discharge peak) is about 210–230 mV, which exceeds the reversibility values of  $\alpha$ -Ni(OH)<sub>2</sub> [45] (120–150 mV). This can be explained by the intercalation of electrochemically active, but rather large anion, which leads to higher polarization of both charge and discharge process. Specific discharge current is stabilized at 1.7–1.72 A/g for both samples, which indicates high electrochemical activity.

The following was found during galvanostatic charge-discharge cycling. The discharge curve (Fig. 4 shows the discharge curve as an example) shows two discharge plateaus. For the **Ni4Al-Ind pH=14** sample, the first plateau is realized in the +300–(+180) mV range, with the discharge duration of 1050 s, the second plateau – in the –680–(–850) mV range, with the discharge duration of 480 s. It should be noted that in the analyzed literature, no mention of two discharge plateaus for Ni-Al LDH has been found. The presence of two discharge plateaus indicated the occurrence of two discharge processes. This means either two-stage discharge of the electrochemically active component or the presence of two electrochemically active components. Some sources mention that as part of Ni-Al LDH, Ni<sup>2+</sup> can be cy-

clered on only up to Ni<sup>3+</sup>, but also up to Ni<sup>4+</sup>. Thus, Ni<sup>2+</sup> can partake in a 2-electron reaction. However, the potential of the first plateau strictly coincides with the discharge of Ni<sup>3+</sup> into Ni<sup>2+</sup>. The potential of Ni<sup>4+</sup>+1e<sup>-</sup>→Ni<sup>3+</sup> should be significantly more positive. Thus, the second discharge plateau does not correspond to the two-electrode discharge of the nickel cation. However, the LDH structure contains the second electrochemically active component – intercalated indigo carmine. So it is reasonable to assume that the second plateaus corresponds to the discharge of the oxidized form of indigo carmine. However, the exact nature of this plateau requires additional study.

Using the results of galvanostatic charge-discharge cycling, specific capacities were calculated for indigo carmine intercalated Ni-Al LDH at discharge to 0 V (Fig. 5, b) and full discharge (Fig. 5, a). Comparative analysis reveals the difference in the effect of carbonate and indigo carmine. Carbonate intercalated LDH had notably higher capacities when the synthesis was conducted at an equilibrium pH, while for indigo carmine samples, synthesis at an equilibrium pH results into LDH with a lower specific capacity. The maximum specific capacity is observed for indigo carmine intercalated LDH synthesized at pH=14. This is likely related to the different influence of carbonate and indigo carmine on the stabilization of the LDH structure. Comparative analysis of the most active **Ni4Al-IndpH=14** and **Ni4Al-CO3 pH=equil** samples, discharged to 0 V, shows that in indigo carmine intercalated LDH only Ni participates in the electrochemical reaction and carbonate in carbonate intercalated LDH is electrochemically inert. At a low current density (10 mA/cm<sup>2</sup>), the specific capacities of the **Ni4Al-IndpH=14** and **Ni4Al-CO3 pH=equil** samples are comparable – 1,007 F/g and 1,040 F/g. However, with increasing current density, the specific capacity of indigo carmine intercalated LDH exceeds that of carbonate intercalated. Thus, it can be concluded that indigo carmine has a greater activating effect on Ni-Al LDH than carbonate. It should also be mentioned that these values were calculated per 1g of compounds, while the Ni content in indigo carmine and carbonate intercalated samples differs (33.6% and 45.1%, respectively). When converting the values to Ni, we get 2,997 F/g (Ni-Al-indigo carmine LDH) and 2,306 F/g (Ni-Al-carbonate LDH). These data prove a higher electrochemical activity of nickel in Ni-Al-indigo carmine LDH. At full discharge (Fig. 5, a), even at a low current density (10 mA/cm<sup>2</sup>), the specific capacity of the **Ni4Al-Ind pH=14** sample significantly exceeds that of **Ni4Al-CO3 pH=equil** (946 F/h and 485 F/g, respectively). These data further support the involvement of indigo carmine in the electrochemical process, contributing to effective capacity.

In general, it should be mentioned that indigo carmine intercalated Ni-Al LDH possesses high electrochemical activity and good pigment properties. That said, the applicability of these results is limited due to the synthesis of Ni-Al LDH was only conducted at two pH values. To further improve characteristics, optimization of the LDH composition and synthesis method should be conducted.

## 7. Conclusions

1. Preparation of previously not synthesized indigo carmine intercalated Ni<sub>4</sub>Al layered double hydroxide was conducted at an equilibrium pH and pH=14.

2. Using XRD and thermogravimetry analysis methods, it was found that Ni–Al–indigo carmine hydroxide is a layered double hydroxide with the structure of  $\alpha$ -Ni(OH)<sub>2</sub>. The sample synthesized at pH=14 has average crystallinity, while the crystallinity of the sample synthesized at an equilibrium pH is low.

3. High pigment properties of the synthesized samples were discovered. The sample had a light-blue color (color tone 483–485 nm) with the lightness of 40–50 % and average color purity.

4. Comparative analysis of the electrochemical characteristics of indigo carmine and carbonate intercalated Ni–Al LDH samples was conducted using cyclic voltammetry and galvanostatic charge-discharge cycling. The high

electrochemical activity of Ni–Al–indigo carmine LDH was found. For indigo carmine intercalated LDH, a previously not described phenomenon was observed during charge-cycling – the presence of two discharge plateaus, the first in the +300–(+180) mV range, corresponding to the discharge of nickel cations, the second – in the –680–(–850) mV range, likely corresponding to the cycling of indigo carmines. It was found that the specific capacity of indigo carmine intercalated Ni–Al LDH exceeds that of carbonate intercalated. In the case of indigo carmine intercalate hydroxide, synthesis at pH=14 results in the highest activity. The highest specific capacity at full discharge was 1,007 F/g hydroxide and 2996 F/h Ni, at discharge to 0 V –946 F/g.

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