Nickel hydroxide is widely used in supercapacitors, alkaline batteries, for the electrocatalytic oxidation of organic contaminants, etc. Due to their electrochemical activity, $Ni(OH)_2$ ($\alpha+\beta$) samples of a layer structure synthesized in a slit diaphragm electrolyzer are the most promising. The effect of the thermal field on the structural characteristics of layered $(\alpha + \beta)$ Ni(OH)₂ was studied. The effect was assessed in two ways: 1) internal (in situ) cooling directly in the electrolyzer by cooling the cathode from the rear side; 2) external (ex situ) heating directly after the electrolyzer when passing through a spiral heat exchanger heated to 90 °C. The crystal structure of the samples was studied by X-ray phase analysis. It was shown that the base sample obtained without changing the thermal field was a monophase layered $(\alpha+\beta)$ structure with a high content of a-modification and a gradient transition from a to β through a number of intermediate structures. The crystallinity of the sample was not high. During the internal cooling of the cathode, the crystallinity decreased and the fraction of the a-modification increased. External heating of the nickel hydroxide suspension immediately after leaving the electrolyzer led to the recrystallization of the samples with the decomposition of the $(\alpha+\beta)$ layered structure and formation of β -Ni(OH)₂ with high crystallinity. It was found that external 6-minute heating did not change the crystal structure. This is explained by the fact that the aging process of nickel hydroxide at an elevated temperature is a crystal-chemical transformation, which is characterized by an induction period, during which the rate of the process is minimal.

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As a result, the study has shown the possibility of controlling the type of forming crystalline modification of nickel hydroxide and its crystallinity by changing the internal (in situ) or external (ex situ) thermal field

Keywords: nickel hydroxide, layered $(a+\beta)$ structure, internal cooling, external heating, aging, induction period, slit diaphragm electrolyzer

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1. Introduction.

Based on a fairly high electrochemical activity, various nickel hydroxides are widely used in electrochemical devices [1].

Mono, double and triple nickel hydroxides are used in the nickel oxide electrode of alkaline nickel-cadmium, nickel-iron, nickel-metal hydride batteries [2, 3]. Nickel hydroxide is also used in lithium batteries [4].

Various types of nickel hydroxides are used as the active ingredient in the Faraday electrode of hybrid supercapacitors. $Ni(OH)_2$ is used both individually [5] (in the form of nanoparticles [6] or ultrafine particles [7]) and in the form of composite materials with nanocarbon materials (graphene ox-

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CHANGES IN THE NICKEL HYDROXIDE PROPERTIES UNDER THE INFLUENCE OF THERMAL FIELD IN SITU AND EX SITU DURING ELECTROCHEMICAL SYNTHESIS

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ide [8], carbon nanotubes [9]). A Ni(OH)₂ film is also formed for thin-layer supercapacitors on a conductive basis [10].

Based on the color change in the redox couple Ni(OH)₂ (almost transparent in thin layers)/NiOOH (brown-black), nickel hydroxide is used as an electrochromic material [11, 12].

Nickel hydroxide is used for the electrocatalytic oxidation of organic compounds [13, 14], as well as in sensors [15, 16].

For each specific application, there are special requirements for the optimal parameters of nickel hydroxide. The trend in modern chemical technology is the targeted formation of the required product characteristics. However, this requires precise information on how the characteristics of nickel hydroxide depend on the production conditions. One of the key characteristics of nickel hydroxide is the crystal lattice parameters.

2. Literature review and problem statement

The main parameters of Ni(OH)₂ that determine the electrochemical activity are the characteristics of the crystal lattice [17], in particular, the inhomogeneity of the crystal lattice [18], microstructure [19], crystallinity [20, 21]. And these parameters are determined by the method and conditions of synthesis [22].

First of all, the synthesis method determines the type of Ni(OH)₂ [23]. Nickel hydroxide is in the form of two modifications [24]: a β -form (chemical formula Ni(OH)₂, brucite structure) and an α -form (chemical formula 3Ni(OH)₂·2H₂O, hydrotalcite-like structure). However, the paper [25] describes the existence of nickel hydroxide with a structure intermediate between α -Ni(OH)₂ and β -Ni(OH)₂.

 α -Ni(OH)₂ has a higher electrochemical activity than β -Ni(OH)₂. However, a pure α -form has low stability, especially in concentrated alkalis at high temperatures. Under these conditions, the metastable α -modification turns into a low-active type of β -modification, which the authors call β bc (bc is badly crystalline) [26]. Additives are introduced to stabilize the α -form [27, 28]. In this case, layered double hydroxides (LDH) are formed [29, 30]. LDHs have a "host" hydroxide crystal lattice, in which a part of the "host" cations (Ni^{2+}) is replaced by "guest" cations, for example, Al^{3+} [31] or V^{4+} [32]. Various anions are intercalated into the interlayer space of the crystal lattice to compensate for the formed excess charge [33]. These anions can be either anions of precursor salts (nitrates [34]) or anions formed during synthesis (cyanates [35]), or specially introduced anions (carbonates [35, 36]). α-Ni(OH)₂ (both mono α -Ni(OH)₂ and LDH) can be obtained by chemical synthesis [37], homogeneous deposition [38], and electrolysis in a slit diaphragm electrolyzer [39].

 β -Ni(OH)₂ has significantly higher stability, both electrochemical and thermal. That is why the β -form is widely used as an active substance in alkaline batteries [40] and hybrid supercapacitors [41]. The preparation of β -Ni(OH)₂ is possible chemically at low supersaturation, electrochemically in a slit diaphragm electrolyzer [42]. High-temperature two-step synthesis [43, 44] and the method of the amino complex decomposition [40] can also be used.

The mixed (α/β) structure of Ni(OH)₂ possesses the advantages of the α - and β -modifications of nickel hydroxide [45, 46]. In [47], it has been proved that during the synthesis in a slit diaphragm electrolyzer (SDE), a highly active nickel hydroxide with a layered $(\alpha+\beta)$ structure is formed. The high electrochemical activity of the layered sample has been revealed, exceeding the activity of both β -Ni(OH)₂ and α -Ni(OH)₂. The electrochemical characteristics of $(\alpha+\beta)$ Ni(OH)₂ are also improved due to the increase in oxygen polarization during charging and slight aging [48]. The high activity of the obtained layered $(\alpha+\beta)$ nickel hydroxide makes electrochemical synthesis in SDE promising for industrial use.

It should be pointed out that when Ni(OH)₂ is obtained in SDE, it has a matrix structure similar to organic composites [49]. Nickel hydroxide is the matrix former, and the mother liquor is the filler [45]. In the synthesis, the primary particles of nickel hydroxide move in the SDE slit and undergo aging in the Lenz-Joule heat field, which is formed due to the passage of an electric current between the anode and the cathode. It is the simultaneous growth of the particles and partial crystallization due to aging that is the reason for a unique (α + β) layered structure formation. Anions play a significant role in the formation of such a structure and its stabilization. Both sulfates and carbonates can participate in the formation of $(\alpha+\beta)$ layered structure of Ni(OH)₂. Using an anion-exchange membrane, the key role of carbonate anions in the formation of a unique $(\alpha+\beta)$ layered structure of Ni(OH)₂ during the synthesis in SDE was proved in [50]. In [51], electrochemical synthesis of carbonate-activated Ni(OH)₂ $(\alpha+\beta)$ layered structure was carried out in SDE.

The thermal field plays an essential role in the formation of the structure of nickel hydroxide. When nickel hydroxide is formed, the rate of nucleation (formation of crystal nuclei) is significantly higher than the rate of crystal growth. As a result, nickel hydroxide particles are formed by a complex two-stage mechanism [52]:

 - 1st stage (high-speed) – formation of nuclei, their adhesion and formation of a primary amorphous particle;

- 2nd stage (slow) - crystallization (aging) of the primary amorphous particle. The crystallization process is determined by the composition of the mother liquor, duration and, especially, temperature.

Based on this, the temperature should be a key parameter for controlling the crystal structure of the resulting nickel hydroxide. In general, high temperature during aging leads to a more preferable production of β -Ni(OH)₂ and an increase in crystallinity, while a low temperature leads to the formation of low crystalline α -Ni(OH)₂. It should be noted that crystallization under the action of the thermal field can occur both during the synthesis (in situ) and after it (ex situ) during special heat treatment.

Heat treatment after preparation at high temperatures (104-120 °C) leads to the formation of nano-sized β -Ni(OH)₂ particles [53-55]. The cryosynthesis method using microemulsions is applied to obtain amorphous α -Ni(OH)₂ [56].

The effect of temperature at the moment of preparation strongly depends on the method of synthesis and the form of the resulting nickel hydroxide. A double effect of temperature was revealed during the electrochemical template synthesis of thin films of nickel hydroxide. At low temperatures, more amorphous nickel hydroxide is formed with low adhesion to the substrate surface. An increase in temperature first improves the characteristics of the α -Ni(OH)₂ film [57]. However, a further increase in temperature leads to a significant deterioration in the electrochemical and electrochromic characteristics of the film, probably, as a result of an increase in crystallinity [58]. For the chemical synthesis method, the temperature is also the main factor in controlling the type and crystallinity of the product [59]. α -Ni(OH)₂ is shown to be formed at low temperatures (0-10 °C) [60]. βbc-Ni(OH)₂ is formed at a temperature of 15-30 °C [59], and highly crystalline β -Ni(OH)₂ is formed at a temperature of 40-60 °C [60]. The electrochemical activity is shown to increase in the series " β -Ni(OH)₂ – β bc-Ni(OH)₂ – α -Ni(OH)₂", i. e. the electrochemical activity of nickel hydroxide decreases with an increase in the synthesis temperature. Moreover, synthesis at elevated temperatures or heat treatment are often used in research [61-63]. A decrease in the synthesis temperature during chemical synthesis and homogeneous deposition of Ni-Ti LDH also leads to a decrease in crystallinity [64]. It should be noted that the temperature effect on the crystal structure of Ni(OH)₂ strongly depends on the type of hydroxide and the method of synthesis.

A promising and highly active layered $(\alpha+\beta)$ Ni(OH)₂ contains alternating layers of β - and α -structures. At the same time, the effect of heat treatment during electrochemical synthesis in SDE and heat post-treatment on the crystal structure of nickel hydroxide has not been studied. This does not allow optimizing the method of electrochemical production in SDE for the targeted production of Ni(OH)₂ for various applications.

3. The aim and objectives of the study

The aim of the study is to determine the effect of the thermal field at the time of production (in situ) or during post-treatment (ex situ) on the structural characteristics of $(\alpha+\beta)$ layered Ni(OH)₂ electrochemically synthesized in a slit diaphragm electrolyzer.

To achieve the aim, the following objectives were set:

 to obtain samples of nickel hydroxide in a slit diaphragm electrolyzer while cooling the cathode during synthesis;

- to obtain samples of nickel hydroxide in a slit diaphragm electrolyzer during heat treatment of various duration immediately after leaving the apparatus;

- to carry out a comparative analysis of the structural properties of the samples with an assessment of the thermal field effect in situ and ex situ.

4. Materials and methods for obtaining nickel hydroxide samples under conditions of changing the thermal field and study of their characteristics

Method for obtaining nickel hydroxide samples. The synthesis method [51, 52] is based on electrolysis carried out in a flow-through slit diaphragm electrolyzer (SDE). A solution of nickel sulfate (concentration of Ni²⁺ - 12.7 g/l) was fed into the cathode space using a peristaltic pump, and a solution of NaOH (concentration -50 g/l) was fed into the anode space with the same flow rate of 0.2 l/h. The cathode was titanium, to prevent sediment adhesion in the slit of the cathode space, and the anode was insoluble nickel. The cathode space was separated from the anode space using a lowflow filtering diaphragm. The production was carried out at an optimal current density of 10 A/dm^2 [51, 52]. When the current flowed at the cathode, hydrogen was evolved, and hydroxyl ions were generated, which reacted in the volume with nickel cations to form a nickel hydroxide precipitate. The precipitate was removed from the apparatus with a stream of catholyte. The hydroxide was separated from the catholyte using a vacuum pump, a Bunsen flask, and a Buchner funnel. After that, the samples were dried at 90 °C for a day, ground, sieved through a 71 µm sieve, washed to remove soluble salts and dried again under the same conditions.

To study the thermal field effect at different stages of obtaining nickel hydroxide, two series of experiments were carried out.

In the first series of the experiments, the thermal field effect in situ was determined, i.e. inside the SDE, at the moment of Ni(OH)₂ formation. During the synthesis, while passing through the slit cathode space, the particles of nickel hydroxide were in the Lenz-Joule field of heat released during the passage of the electric current. Therefore, it was decided to study the effect of the thermal field by cooling the catholyte. Because it was structurally impossible to place the refrigerator in the "cathode - diaphragm" slotted gap, the cathode was cooled from its rear side. SDE consisted of two thick-walled polymeric half-cells with fixed electrodes. For cooling, a rectangular recess was made in the cathode half-cell with inlet and outlet fittings for passing water as a coolant from the rear side of the cathode. The increase of the cooling water flow rate reduced the temperature of the catholyte. In this series, the temperature of the suspension was continuously measured at the outlet from the SDE.

In the second series of the experiments, the thermal field effect ex situ was determined, i. e. outside the SDE, immediately after Ni(OH)₂ synthesis. Since the particles of nickel hydroxide were already partially heated under the action of the Lenz-Joule heat inside the SDE, the influence of the external thermal field was determined by heat treatment of the suspension of nickel hydroxide in the mother liquor at the outlet of the electrolyzer. Spiral heat exchangers made of thin-walled glass tubes were used for the heat treatment. The nickel hydroxide suspension was passed inside through the tubes of the heat exchanger placed in a glass with hot water (the water temperature was maintained at 90 °C). The study of the heat treatment effect was carried out by changing the treatment time. For this, heat exchangers with different numbers of spiral turns (2, 4 and 6) were made.

Study of the characteristics of nickel hydroxide samples. The crystal structure of the samples was studied by X-ray phase analysis (XPA) using a DRON-3 diffractometer (Russia) (Co-K α radiation, angles range 10–90° 2 θ , scanning rate 0.1°/s).

5. Results of studying the thermal field effect on the characteristics of nickel hydroxide samples

Nickel hydroxide samples labeling

Table 1 shows the labeling of nickel hydroxide samples for both series of determining the thermal field effect, indicating the key parameters.

Nickel hydroxide sample labeling

Table 1

Series 1. Internal cooling effect (thermal field in situ)						
Sample labeling	IC-1*	IC-2	2 IC-3	IC-4	IC-5	
Cooling water flow rate, l/h	_	0	0.05	0.1	0.2	
Catholyte temperature,°C	39	37	32	28	26	
Series 2. External heating effect (thermal field ex situ)						
Sample labeling	EH-N2		EH-N4	EI	I-N6	
Number of spiral heat exchanger turns	2		4		6	
Treatment time, min	6.00		12.62	17	17.33	

Note: * – *control sample synthesized without additional ther*mal field effect

The effect of internal cooling (thermal field in situ) on the structure of the samples. The peaks of the low-crystalline β -phase are observed on the diffractogram of the control sample IC-1 (Fig. 1, *a*) synthesized without additional heat influence. The α -Ni(OH)₂ peak is also identified at $2\Theta{=}13{-}14^\circ{}.$ When the cathode is cooled, the temperature of the catholyte decreases. In this case, the total crystallinity decreases, and the α -Ni(OH)₂ peak becomes more and more pronounced. The diffractograms of samples IC-3, IC-4, and IC-5 show a peak in the low-angle region (at angles 2Θ less than 10°). This indicates the formation of either an amorphous hydroxide phase or a phase with a large interplanar spacing in the direction of the (001) plane. In general, it should be noted that internal cooling insignificantly affects the crystal structure of the $(\alpha+\beta)$ Ni(OH)₂ samples.



Fig. 1. Diffractograms of nickel hydroxide samples under internal cooling (thermal field in situ): *a* – Sample IC-1, *b* – Sample IC-2; *c* – Sample IC-3; *d* – Sample IC-4; *e* – Sample IC-5

The effect of external heating (thermal field ex situ) on the structure of the samples.

The diffractogram of the EH-N2 sample (Fig. 2, *a*), obtained during external heating in a two-turn heat exchanger, has a very low crystallinity. It is possible to distinguish peaks of both α -Ni(OH)₂ and β -Ni(OH)₂, with a high con-

tent of the α -phase. It should be noted that there is a peak at $2\Theta=11^{\circ}$, corresponding to a phase with a higher water content than α -Ni(OH)₂. Longer heating in a four-turn heat exchanger (sample EH-N4, Fig. 2, *b*) leads to the formation of a pronounced phase of the β -modification of Ni(OH)₂. This increases the crystallinity sharply.



Fig. 2. Diffractograms of nickel hydroxide samples under external heating (thermal field ex situ): *a* – Sample EH-N2, *b* – Sample EH-N4; *c* – Sample EH-N6

An increase in the heat treatment time in a six-turn heat exchanger (sample EH-N6) leads to an even greater increase in the crystallinity of the β -modification of Ni(OH)₂. Clear peaks of α -Ni(OH)₂ are not observed. However, a plateau is observed in the angle range 2Θ =10-17°, indicating the presence of a certain amount of X-ray amorphous α -like phase.

6. Discussion of the results of the thermal field effect on the characteristics of nickel hydroxide samples

In the case of a two-stage mechanism of formation of nickel hydroxide, the temperature should primarily affect the stage of crystallization of the primary amorphous particle [53]. An increase in temperature, both in situ (at the time of the synthesis) and ex situ (after the synthesis), should lead to an increase in crystallinity (an increase in the crystallite size). In this case, due to the greater stability, β -Ni(OH)₂ will be formed predominantly.

The effect of internal (in situ) cooling on the crystal structure of nickel hydroxide samples. The results of X-ray phase analysis (Fig. 1, a) show that the control sample IC-1 has an $(\alpha+\beta)$ layered structure of Ni(OH)₂. The crystallinity of the sample is low. It should be noted that in the interval of Bragg angles 20 10-22 °C there is a plateau, on which the α -Ni(OH)₂ and β -Ni(OH)₂ peaks are weakly distinguished. It should be noted that in this region of the Bragg angles there are phase peaks corresponding to the (001) plane: 13° for α -Ni(OH)₂ and 22° for β -Ni(OH)₂. The presence of a plateau indicates the existence not only of α and β structures in the sample but also of a number of structures with a distance for the (001) plane intermediate between 4.6 Å (β -Ni(OH)₂) and 7.6 Å (α -Ni(OH)₂). In addition, there are structures with an interplanar spacing greater than 7.6 Å. An increase in the interplanar distance of more than 4.6 Å indicates the presence of water molecules in the interplanar space. Such forms can generally be called α -like structures. Most likely, α -like structures are not in the form of separate phases but are intermediate, transitional structures between the α -Ni(OH)₂ and β -Ni(OH)₂ layers. This also indicates that in the (α + β) layered structure of sample IC-1, the layers of the α and β structures do not have an interface plane, but smoothly merge into one another. This means that actually the IC-1 sample is monophasic. The absence of the β -Ni(OH)₂ peak (at 2 Θ =21) with an intensity significantly exceeding the plateau level indicates a high proportion of α -like structures. Internal cooling of the cathode by a water flow from the rear side of the cathode leads to a decrease in the catholyte temperature. It should be noted that this type of cooling was not effective due to the very low thermal conductivity of titanium and the difficulty in organizing a high flow rate of the cooling water. As a result, the temperature dropped from 39 °C to 26 °C at the maximum flow of cooling water. Internal cooling leads to a decrease in the crystallinity of the sample, which is reflected in the broadening of the peaks and a decrease in their intensity. It should be noted that the proportion of meta-stable α -like Ni(OH)₂ increases, which is indicated by a clearer definition of the peak at 13° and an increase in intensity at a given angle. In this case, the intensity at 22°, corresponding to β -Ni(OH)₂, significantly decreases. α -Ni(OH)₂, as well as α -like Ni(OH)₂, have a higher chemical and electrochemical activity. Thus, upon internal cooling, more active nickel hydroxide samples are formed. It should also be noted that the effect of internal cooling of this type does not have a very dramatic effect on the crystal structure of nickel hydroxide samples. When using internal cooling of another type, for example, using Peltier elements, it is possible to obtain more amorphous samples of nickel hydroxide, consisting mainly of α -Ni(OH)₂.

The effect of external (in situ) heating on the crystal structure of nickel hydroxide samples.

It should be noted that external heating is actually postheat treatment. This heat treatment receives a triple suspension containing a mother liquor, nickel hydroxide particles, partially crystallized in the Lenz-Joule heat field inside the electrolyzer, and hydrogen gas bubbles. In this way, heating should lead to recrystallization (Ostwald aging) by transition to β -Ni(OH)₂ with an increase in crystallinity [59, 60]. X-ray phase analysis confirms this assumption. After treatment for 12.62 minutes, the diffractogram of the EH-N4 sample (Fig. 2, b) shows clearly pronounced peaks of β -Ni(OH)₂. The crystallinity of the sample is significantly higher than that of the control IC-1 sample (Fig. 1, a). The α -Ni(OH)₂ peaks were not detected. However, the presence of a low-intensity plateau at Bregg angles of 11-19° indicates the existence of an X-ray amorphous component. Therefore, we can conclude that metastable α -like structures transform into stable β -Ni(OH)₂ upon external heating. This leads to an ordering and an increase in the crystallinity of the β -structure. Thus, it should be concluded that the unique $(\alpha+\beta)$ layered structure decomposes upon post-heat treatment with the formation of β -Ni(OH)₂. An increase in the treatment time to 17.33 minutes leads to the further increase in crystallinity and the formation of a highly crystalline β -Ni(OH)₂ sample (Fig. 2, *c*). Based on the published data, this can lead to a decrease in the electrochemical activity of the sample [58-60]. However, this increases stability. The above tendency of the external heating effect does not fit the characteristic of the crystal lattice of the EH-N2 sample, i. e. with external heat treatment for 6 minutes. The diffractogram of the EH-N2 sample (Fig. 2, a) indicates that, after a brief heat treatment, the sample still has an $(\alpha+\beta)$ layered structure of low crystallinity, which is practically the same as the structure of the IC-1 control sample obtained in SDE without additional thermal field effect. This fact can be explained by two reasons. Firstly, the triple suspension contains two components with high heat capacity - an aqueous mother liquor (4.19 kJ/kg K)) and hydrogen gas (14 kJ/(kg K)). Due to this, the temperature of the triple suspension does not have time to rise significantly during the short treatment. Secondly, Ostwald aging (recrystallization) is a crystal-chemical transformation, which is characterized by an induction period, during which no changes in the crystal lattice occur. Most likely, the induction period is comparable to the duration of sample treatment. It should be noted that X-ray phase analysis characterizes the crystal structure of the sample in general. However, short-term external heat treatment can lead to recrystallization on the particle surface, which can lead to an increase in the stability of the Ni(OH)₂ particles. Anyway, this hypothesis requires experimental verification.

7. Conclusions

1. Samples of nickel hydroxide have been synthesized in a slit diaphragm electrolyzer with internal (in situ) cooling of the cathode from the rear side with a different flow of cooling water. 2. Samples of nickel hydroxide have been synthesized in a slit diaphragm electrolyzer with external (ex situ) heating. The heating has been carried out by passing a triple suspension with Ni(OH)₂ after leaving the electrolyzer through a spiral glass heat exchanger placed in a container with hot water. The syntheses have been carried out at different treatment times - 6, 12.62 and 17.33 minutes.

3. The method of X-ray phase analysis has shown that the control sample obtained without heating or cooling has a unique $(\alpha+\beta)$ layered structure with a high content of α -like structures. It is shown that the α -like and β -like structures of Ni(OH)₂ in the particles gradually transform into one another with the help of intermediate structures and there is no phase interface. It has been found that during the internal cooling of the cathode with an increase in the flow of cooling water, the crystallinity of the sample decreases with an increase in the proportion of α -like structures. It has been determined that during the external heating of sufficient duration, the transformation of meta-stable α -like structures occurs, with the formation and ordering of β -Ni(OH)₂ leading to a sharp increase in crystallinity. The process of Ostwald aging of electrochemically synthesized (α + β) Ni(OH)₂ has been revealed to have an induction period, during which no changes in the crystal lattice occurred during heating. The duration of the induction is determined to be in the range of 6–13 minutes.

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36

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