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SYNTHESIS OF NICKEL HYDROXIDE IN THE PRESENCE OF ACETATE ION AS A «SOFT» LIGAND FOR APPLICATION IN CHEMICAL POWER SOURCES

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Гідроксид нікелю широко використовується як активна речовина хімічних джерел струму. Механізм формування гідроксиду нікелю включає дуже швидку стадію утворення первинної аморфної частини та повільну стадію старіння (кристалізації). Поліпшення характеристик гідроксиду нікелю може бути досягнуто шляхом зниження швидкості першої стадії за рахунок взаємодії катіону нікелю з «м’яким» лігандом із утворенням слабкого комплексу. В якості «м’якого» ліганду запропоновано використати ацетат-аніон, який формує з Ni^{2+} комплекс без зовнішньої сфери. Вивчено вплив ацетат-аніона на кристалічну структуру, морфологію часток та електрохімічні властивості гідроксиду нікелю, отриманого шляхом хімічного синтезу при високому пересиченні. Кристалічна структура зразків вивчена методом ренгенофазового аналізу, морфологія часток – методом скануючої електронної мікроскопії, електрохімічні характеристики – методами циклічної вольтамперометрії. Проведено порівняльний аналіз характеристик зразків, синтезованих в присутності та у відсутності ацетату натрію. Для зразка, синтезованого в присутності ацетату натрію, методом ренгенофазового аналізу показано зниження кристалічності та формування біфазної системи, що складається з β-$Ni(OH)_2$ і α-$Ni(OH)_2$. При цьому в зразку зростає вміст часток малого розміру з підвищеною поверхнею. Порівняльне вивчення електрохімічних характеристик показало формування при синтезі в присутності ацетату більш активного зразку із електрохімічною поведінкою переважно α-модифікації. При циклюванні активність зразку зростає. Питомий струм зарядного піка зразку, синтезованого в присутності ацетат-іона, збільшується у 1,93 рази в порівнянні із зразком, синтезованим в тих же умовах, але у відсутності ацетату

***Ключові слова:** гідроксид нікелю, α-$Ni(OH)_2$, електрохімічна активність, лужний акумулятор, ацетат*

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1. Introduction

Owing to high electrochemical activity [1], nickel hydroxides are used in various electrochemical devices.

$Ni(OH)_2$, double nickel hydroxides are used as the active material of nickel oxide electrode for alkaline batteries [2, 3], and as oxide after sintering – in lithium batteries [4]. Various $Ni(OH)_2$ modifications are used as the active material of the Faradic electrode of hybrid supercapacitors. $Ni(OH)_2$ is used on its own [5] (in the form of nano-sized [6] or ultrafine particles [7]), and in the form of a composite with nanocarbon materials (graphene oxide [8], carbon nanotubes [9]). For thin layer supercapacitors, a nickel film can be formed on the conductive substrate [10].

Nickel hydroxide is used in electrochromic devices [11, 12] because thin layers of $Ni(OH)_2$ are almost transparent, while NiOOH has a dark-brown color. It is also used for the electrochemical oxidation of various organic compounds [13, 14] and in sensors [15, 16].

For a given application, there are optimal characteristics of nickel hydroxide. At the same time, the trend in chemical technology is directed synthesis of products with specific properties. Therefore, determining the influence of synthesis parameters on structural parameters and electrochemical properties of $Ni(OH)_2$ is a relevant problem.

2. Literature review and problem statement

The method and conditions of synthesis define the properties of nickel hydroxide, namely structural disorder [17], microstructure [18], crystallinity [19, 20]. These parameters have a major effect on electrochemical activity. The synthesis method determines the form of $Ni(OH)_2$ [21, 22]. There are two known stable allotropes of nickel hydroxide: 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 [23] describes the formation of nickel hydroxide structures that are in-between α-$Ni(OH)_2$ and β-$Ni(OH)_2$.

α-$Ni(OH)_2$ is more electrochemically active than β-$Ni(OH)_2$. It should be noted that the α-form is metastable, especially at high temperatures in concentrated alkali. Under these conditions, the α-form transforms into the β-form [24], which results in a decrease of specific capacity. To prevent this process, stabilizing additives are introduced to $Ni(OH)_2$ [25, 26], forming layered double hydroxides (LDH) [27, 28]. LDH consist of the host crystal lattice, in which part of host hydroxide cations (Ni^{2}) are substituted by guest cations such as Al^{3+} [29] or V^{4+} [30]. This results in the excess of positive charge, which is compensated by the intercalation of various anions [31]. Anions can be those of precursor metal salts (nitrate [32]) or those formed during synthesis (cyanate [33]), or intestinally introduced (carbonates [34, 35]). Both α-$Ni(OH)_2$, and nickel-based LDH can be prepared using chemical precipitation [35], homogeneous precipitation [36], electrolysis in the slit-diaphragm electrolyzer (SDE) [37, 38].

β-$Ni(OH)_2$ has significantly higher stability during storage and cycling. So, this form is widely used in alkaline batteries [39] and hybrid supercapacitors [40]. β-$Ni(OH)_2$ can be precipitated chemically at low supersaturation or electrochemically in the slit-diaphragm electrolyzer [41, 42]. High-temperature synthesis [43] and ammine complex decomposition [39] are also used.

Mixed (α/β) $Ni(OH)_2$ structure, described in [44, 45], combines advantages of both nickel hydroxide forms. The paper [46] described that synthesis in the slit-diaphragm electrolyzer (SDE) results in the formation of highly active nickel hydroxide with layered (α+β) structure. The sample demonstrated high electrochemical activity that exceeds that of β-$Ni(OH)_2$ and α-$Ni(OH)_2$. Electrochemical characteristics of (α+β) $Ni(OH)_2$ are also improved because of higher oxygen polarization during charge [47] and retarded aging [48].

It should be noted, that in the reaction of nickel cation with hydroxyl anions (formation of $Ni(OH)_2$), the rate of nucleation is significantly slower than the rate of crystal growth. As a result, the formation mechanism of nickel hydroxide consists of two stages: first (very fast) – formation of the initial amorphous particle; second (slow) – crystallization (aging) of the initial particle [49]. This results in the formation of hydrophilic precipitate with the matrix structure, similar to that of organic [50] and inorganic [51] composite materials. As described in [41], the matrix is formed by $Ni(OH)_2$, and the filler – mother liquor. Crystallinity and even allotrope type is significantly affected by ageing conditions (temperature, composition of mother liquor, etc.). In general, the crystallization stage plays a key role in the formation of $Ni(OH)_2$ properties. However, hydroxide properties can be altered by slowing down the stage of initial particle formation. On this stage, the reaction of nickel cation aqua complex with OH^- occurs, replacement of the aqua complex with a complex with higher stability constant will result in a lower reaction rate. However, if the complex is too stable, the hydroxide precipitate will not be formed as the solubility product will not be reached. Therefore, it is necessary to employ soft ligands that form rather weak complexes with nickel.

For this purpose, some authors use anions of mono-, di- and trivalent acids, such as citrate [53] and especially acetate ion [54, 55]. Acetate is most commonly used for nickel acetate. The synthesis of nickel hydroxide from nickel acetate precursor is achieved through various methods. The papers [55, 56] describe the use of dip method, [57] – mechanochemical method via grinding of nickel acetate with oxalic acid in a mortar, followed by treatment with alkali. Nickel acetate is also used for the synthesis of nickel hydroxide via homogeneous precipitation, and based on ammine compound, different types of hydroxide are formed: aqueous ammonia [58] leads to β-$Ni(OH)_2$, diethyleneglycol [59] – α-$Ni(OH)_2$, and the use of ethyleneglycol leads to the formation of (α/β) $Ni(OH)_2$ structure [60]. In [61], nickel acetate was also used in chemical synthesis. The authors proposed to dissolve nickel acetate (Ni^{2+} source) and KOH in glycerin and initiate the reaction by diluting the solution with water.

In general, nickel acetate is preferred. However, the use of this salt has a few significant disadvantages – low solubility in water, high cost. Nickel acetate is highly hygroscopic, and even at room temperature it undergoes hydrolysis with the release of acetic acid, which contaminates the air of the working area and causes corrosion of metal elements.

More promising and convenient is the synthesis method that utilizes more common and cheaper nickel salts (sulfate, chloride or nitrate) with the source of acetate ions being sodium acetate. However, the influence of acetate ion on the properties of forming nickel hydroxide has not been studied in detail.

3. The aim and objectives of the study

The aim of the work is to study the influence of acetate ion on the formation and properties of chemically precipitated nickel hydroxide, as the active material for chemical power sources.

To achieve this aim, the following objectives are set:

– to prepare nickel hydroxide samples in the presence and absence of acetate ions;

– to conduct a comparative analysis of structural and morphological characteristics of prepared samples and evaluate the effect of acetate ions;

– to conduct a comparative analysis of electrochemical characteristics of prepared samples and evaluate the role of acetate ions.

4. Materials and methods used for the preparation of nickel hydroxide samples and study of their characteristics

4. 1. Preparation method

Analytical grade reagents were used in this study with the exception of NaOH.

Nickel hydroxide powder was prepared using the reverse titration method (high supersaturation) [1, 22]. Nickel sulfate ($C(Ni^{2+})=0.2$ M) solution was dropwise added to the NaOH solution at 70 °C while continuous stirring. After the synthesis, the resulting solution was kept at the same temperature while stirring for 1 hour. To study the influence of acetate ions, 0.05 M sodium acetate (25 % molar relative to Ni^{2+}) was added to the nickel sulfate solution.

After aging, the hydroxide was vacuum filtered to separate it from the mother liquor. The samples were then dried at 90 °C overnight, ground, sifted through a 71 μm mesh, washed from soluble salts and dried again under the same conditions.

4. 2. Characterization of nickel hydroxide samples

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

The morphology and particle size were studied using the JEOL JSM-6510LV scanning electron microscope («JEOL», Japan).

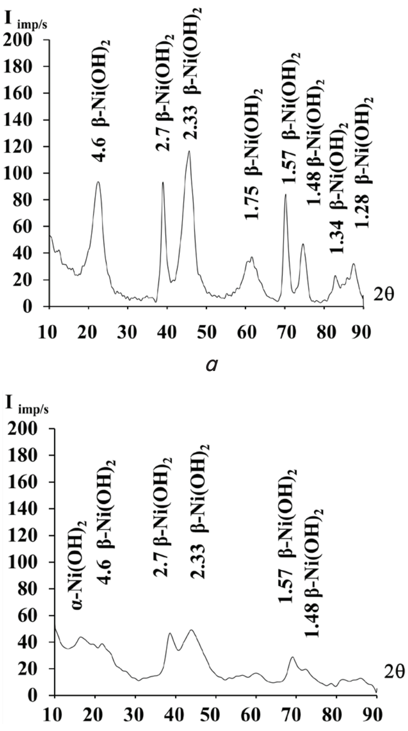
The electrochemical properties of the nickel hydroxide samples were studied by galvanostatic charge-discharge cycling in a special cell YSE-2 (USSR) using the digital potentiostat Ellins P-8 (Russia). The working electrode was prepared by pasting a mixture of the nickel hydroxide sample (82.5 % wt.), graphite (16 % wt.) and PTFE (3 % wt.) [62] on the nickel current collector [63]. Electrolyte – 6M KOH. Counter electrode – nickel mesh, reference electrode – Ag/AgCl (KCl sat.). The electrode was cycled between 200–700 mV (vs Ag/AgCl (KCl sat.)) at a scan rate of 1 mV/s.

5. Results of studying the influence of acetate ions on the characteristics of nickel hydroxide

5. 1. Influence of acetate ions on structure and morphology

The results of XRD analysis revealed that the sample prepared in the absence of acetate (Fig. 1, *a*) is β-$Ni(OH)_2$ with relatively high crystallinity. Synthesis in the presence of acetate results in the formation of $Ni(OH)_2$ with low crystallinity. The XRD pattern of the sample (Fig. 1, *b*) shows poorly defined reflexes of both β-$Ni(OH)_2$, and α-$Ni(OH)_2$.

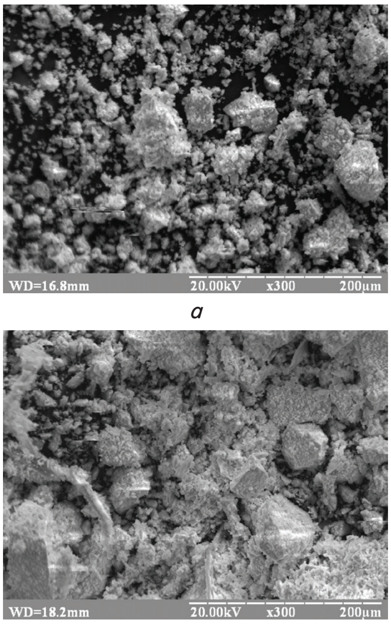
SEM images (Fig. 2) revealed that synthesis in the presence of sodium acetate results in the decrease of particle size (from 12–23 µm to 5–9 µm) and higher content of small particles. This also increases the size of larger particles (from 38–45 µm to 49–73 µm), with smaller particles forming on their surface, which increases their surface area.



a

b

Fig. 1. XRD patterns of nickel hydroxide samples: *a* — synthesized in the absence of acetate, *b* — synthesized in the presence of acetate



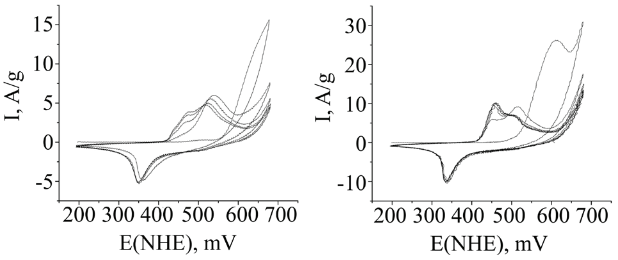
a

b

Fig. 2. SEM images of nickel hydroxide samples: *a* — synthesized in the absence of acetate, *b* — synthesized in the presence of acetate

5. 2. Influence of acetate ions on electrochemical characteristics of samples

The results of cyclic voltammetry are shown in Fig. 3. Cyclic curves of the sample prepared in the absence of acetate (Fig. 3, *a*) have one charge peak on the first cycle and two charge peaks (at 480 mV and 540 mV) on cycles 2–5. The peak at E=580 mV is predominant. On the voltammogram of the sample synthesized in the presence of acetate, there is a well-defined first charge peak (Fig. 3, *b*). Two charge peaks (at 505 mV and 440 mV) on cycles 2–5 are detected. With each subsequent cycle, the current of the first peak (E=440 mV) increases, while that of the second decreases.



a *b*

Fig. 3. Cyclic voltammograms of nickel hydroxide samples: *a* — synthesized in the absence of acetate, *b* — synthesized in the presence of acetate

A comparison of specific currents on the 5th cycle revealed that for the sample synthesized in the absence of acetate, this value is 5.8 A/g, while for the sample synthesized in the presence of acetate – 11.2 A/g.

6. Discussion on the results of the influence of acetate anions on the characteristics of nickel hydroxide

Influence on crystal structure and particle morphology of nickel hydroxide samples. The results of XRD analysis (Fig. 1) revealed that the sample synthesized in the absence of acetate anions is well-crystalline β-$Ni(OH)_2$, which is in agreement with other authors [1, 2] for such synthesis conditions. However, the presence of halo at low 2Θ angles indicates the presence of amorphous or X-ray amorphous components. Synthesis in the presence of acetate ions results in a significant decrease of crystallinity (Fig. 1, *b*). The XRD pattern of this sample has peaks of both β-$Ni(OH)_2$, and α-$Ni(OH)_2$. That is, either a bi-phase or layered (α+β) structure is formed. Thus, chemical synthesis in the presence of acetate ion results in the formation of the structure similar to electrochemically prepared $Ni(OH)_2$ in SDE [42, 46]. In both cases, the stage of formation of the initial amorphous particle is slowed down. In the case of SDE synthesis, the slowdown is due to the low rate of cathodic generation of OH^-. In the case of chemical synthesis in the presence of acetate, the slowdown is due to complex formation, as a result of the reaction between Ni^{2+} and acetate ion:

$$Ni^{2+}+CH_3COO^-\leftrightarrow[Ni(CH_3COO)_2].$$

The formed nickel acetate is a complex without the outer sphere. The instability constant $[Ni(CH_3COO)_2]$ is equal to $5.5\cdot10^{-2}$, meaning nickel acetate is a rather weak complex. However, complex formation decreased the formation rate of the initial amorphous particle. Additionally, due to the formation of coordination bonds, acetate ion can be incorporated into the initial amorphous particle, promoting the formation of α-$Ni(OH)_2$. However, the amount of introduced acetate is insufficient to bind all nickel cations. So, only part of nickel hydroxide is formed for the acetate complex. This results in the formation of a bi-phase system. This can also lead to different effects of acetate ions on morphology – particles formed from the acetate complex have a smaller size and more developed surface, while particles formed from the aqua complex at lower concentration – larger size. This assumption is supported by SEM results (Fig. 2, *b*).

Influence of acetate ions on electrochemical activity of nickel hydroxide samples. Cyclic voltammogram of the sample synthesized in the absence of acetate (Fig. 3, *a*) has shape characteristics of highly crystalline β-$Ni(OH)_2$. This is evidenced by the absence of the charge peak on the first cycle. Additionally, two anodic peaks are observed in cycles 2–5. The peak at 540 mV is characteristic of the β-form. The second peak at 480 mV corresponds to β_{bc}-$Ni(OH)_2$ (*bc* – badly crystalline) [19]. Cyclic curves of the sample synthesized in the presence of acetate ion (Fig. 3, *b*), have a completely different character. During the first cycle, there is a pronounced charge peak, which indicates the α-like behavior of the sample. With subsequent cycling, two anodic peaks are observed, which indicates the presence of two phases. The peak at 505 mV characterizes β-$Ni(OH)_2$. Peak shift by 35 mV into negative potentials indicates the improvement in electrochemical activity and decrease of crystallinity. This is further supported by the results of XRD analysis. The second peak at 440 mV is characteristic of α-$Ni(OH)_2$ with low crystallinity. During cycling (from 2 to 5 cycle), the material develops with an increase in the charge peak current of α-$Ni(OH)_2$. Thus, it can be said, that cycling results in the formation of a more active form of the sample, which contains large amounts of the α-form. In fact, it can be said that the activation of nickel hydroxide with acetate ions occurs similar to the carbonate activation described in [64].

It should be noted, that the conducted study demonstrated the possibility of forming electrochemically active nickel hydroxide via synthesis in the presence of ligand that forms a weak complex. Acetate ion was used as such ion in the study. However, acetate ion has a number of limitations, among which low solubility of nickel acetate, which limits acetate concentrations for a more complete binding of nickel to the complex. Further development of this study is the search for other ligands that form complexes with nickel cation with the corresponding instability constant.

7. Conclusions

1. Samples of nickel hydroxide were chemically precipitated at high supersaturation using nickel sulfate in the presence and absence of sodium acetate (25 % molar relative to Ni^{2+}).
2. The results of XRD analysis revealed that synthesis in the presence of acetate ion leads to the formation of a biphase system that contains low crystallinity β-$Ni(OH)_2$ and α-$Ni(OH)_2$. SEM results revealed that synthesis in the presence of acetate ion leads to a higher number of smaller particles with a large surface area. This is due to the formation of nickel acetate, which affects the kinetics of nickel hydroxide formation. The insufficient amounts of acetate ion for the complete binding of Ni^{2+} to the complex led to the formation of different nickel hydroxide particles in different conditions – from the acetate complex and from the aqua complex.
3. The comparative analysis of electrochemical characteristics of $Ni(OH)_2$ samples prepared in the presence and absence of acetate ion was conducted. It was found that formation in the presence of acetate results in the formation of more electrochemically active nickel hydroxide. Cyclic voltammetry results revealed the formation of a bi-phase system that is composed of α-$Ni(OH)_2$ and β-$Ni(OH)_2$ with low crystallinity, which predominantly behaves like the α-form, which is evidenced by the presence of the first charge peak. During cycling, the activity of the sample increases due to the formation of a higher content of the α-form. It was found that synthesis in the presence of acetate ion results in the increase of specific discharge peak current (equivalent to electrochemical activity) by 1.93 times.

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