

Було синтезовано подвійні шаруваті гідроксиди з різним співвідношенням нікелю та алюмінію у присутності іонів Ag^+ та без срібла: Ni:Al – 80:20 %, Ni:Al:Ag – 80:15:5 % та 75:15:5 %. Отримані порошки гідроксидів нікелю мали структуру подібну до α -модифікації $Ni(OH)_2$ з великою кількістю дефектів кристалічної решітки. У результаті проведених експериментів з гальваностатичного зарядно-розрядного циклування було показано, що додавання срібла при хімічному синтезі збільшує коефіцієнт використання гідроксиду при швидких зарядах, але зменшує його при повільних. Також було запропоновано можливий механізм, що пояснює вплив додавання іонів срібла при синтезі на розрядні характеристики порошоків гідроксидів. Механізм полягає у тому, що оксид срібла, який є напівпровідником, розпорошений у гідроксиді та збільшує питому електропровідність порошку. Збільшення електропровідності при швидких зарядах позитивно впливає на ефективність заряду оскільки початкова фаза має меншу електропровідність, ніж окиснена форма – $NiOOH$. Оскільки під час заряду йде паралельно два процеси – основний процес зарядження активної речовини та побічний виділення молекулярного кисню, електропровідність буде грати вирішальну роль при заряді електроду. При малій електропровідності активної речовини та швидкому режимі заряду, струм буде йти здебільше на побічний процес виділення кисню. У випадку повільних зарядів наявність додаткової електропровідності за рахунок присутності оксиду срібла не так сильно впливає на ефективність заряду, оскільки в таких умовах розряду достатньо власної електропровідності гідроксиду. При цьому наявність оксиду срібла буде зменшувати кількість гідроксиду, що в свою чергу буде зменшувати коефіцієнт використання, який розраховується на загальну масу порошку

Ключові слова: гідроксид нікелю, лужний акумулятор, $Ni(OH)_2$, шаруватий подвійний гідроксид, оксид срібла

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INVESTIGATION OF Ni-AL HYDROXIDE WITH SILVER ADDITION AS AN ACTIVE SUBSTANCE OF ALKALINE BATTERIES

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1. Introduction

The market of secondary chemical power sources (CPS) is growing every year. Thus, the growth of production volume of CPS from 2006 to 2016 is on average 8 % each year [1]. Alkaline secondary batteries are one of three most produced CPS types in the world. In 2016, their total output amounted to 3 billion dollars USA (Ni-Cd and Ni-MH), with their total capacity being slightly less than 3 GW-h. These data indicated that alkaline CPS are in demand, which means that research aimed at their improvement is of relevance.

Secondary alkaline CPS have a number of advantages that secure their usage in modern technology. The main advantages of alkaline CPS are: long cycle life, wider range of working temperatures, operation at very low temperatures (up to $-50\text{ }^{\circ}\text{C}$) [2]. Also, secondary alkaline power sources can be discharged at high currents, have a long shelf life, do not require special conditions for storage and transportation. The combination of the aforementioned advantages forms a basis for application of alkaline CPS in transport, aviation, space industry. Also, these power sources are not flammable, do not contain volatile components, which makes

them such CPS that are not subject to regulation by fire and aviation safety authorities.

For all alkaline CPS systems Ni–Cd, Ni–MH, Ni–Fe, Ni–Zn and Ni–H₂, the common component is a positive electrode, the main component of which is nickel (II) hydroxide [3]. This compound defines the characteristics of the battery. It is also used in electrodes of asymmetric supercapacitors (SC) [4]. However, requirements to Ni(OH)₂ for application in SC electrodes are fundamentally different [5, 6]. This creates a demand for the development of fundamentally different synthesis and treatment methods of materials based on nickel hydroxide.

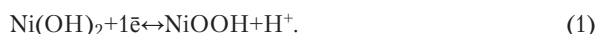
In addition to being used in CPS, Ni(OH)₂, as a component of nickel oxide, has a wide range of application, which includes: electrochromic films on transparent [7, 8] and reflective [9] substrates, wastewater treatment from organic compounds and synthesis of new organic compounds [10, 11]. It also finds application in devices for water decomposition [12, 13], in sensors [14, 15], as an element in fuel cells [16, 17], and as a component of anti-corrosion coatings [18].

The listed applications of active materials based on Ni(OH)₂ require the development of approaches for directed synthesis. The principle of this approach is a conscious choice of synthesis method and conditions and also initial compounds to obtain the optimal properties for the target application.

It should be said that a complex approach regarding the choice of synthesis method and conditions depending on the target application of the material is yet to be developed. That latter is true for the synthesis of compounds for chemical power sources. The research on the influence of synthesis conditions on the resulting properties of compounds, and also new synthesis methods would allow accumulating experimental data for the development of a complex approach to the synthesis of active materials. In particular, the development of new synthesis methods would allow preparing new materials with higher specific characteristics.

2. Literature review and problem statement

One of the most important characteristics of active material effectiveness is utilization coefficient. This characteristic shows to what extent the active material works in the CPS electrode. The utilization coefficient is calculated as the ratio of the discharge capacity to the theoretical capacity of the material. For nickel hydroxide in commercial CPS, the average utilization coefficient reaches 70–90 % [2, 3, 19]. The theoretic capacity of nickel hydroxide for one electron transfer reaction is 289 mA·h/g (1):



Thus, the capacities achieved upon discharge of the positive electrode of the commercial battery reach 260 mA·h/g.

It is known that part of nickel atoms in the charged state can be in the +4 oxidation state. Thus, the maximum theoretical capacity, assuming the transition of all atoms from Ni²⁺ to Ni⁴⁺ can be twice as high, i. e. 578 mA·h/g. Achievement of such specific capacity is impossible because the oxidized form should be NiO₂. However, the latter was no isolated in pure form, indicating its thermodynamic instability. Nevertheless, this calculation illustrated that maximum possible

capacities are yet to be achieved and there is potential for their further improvement through the synthesis of more active forms of nickel hydroxide.

Thus, the published papers show examples of nickel hydroxide coprecipitation in the form of layered double hydroxide (LDH) with aluminum [20], zinc [21], cobalt [22], chromium and manganese [23], titanium [24]. When such LDH are used as active materials of CPS, the latter demonstrate high specific characteristics. In addition, the Ni–Fe LDH has proven to be an effective catalyst for water decomposition [25, 26]. However, these compounds had not found wide application on an industrial scale possibly because of the variability of their characteristics. Nevertheless, the attempts to increase specific characteristic of such compounds through the formation of triple layered hydroxides are continued [27, 28]:



where X1, Y1, Y2, L, Z, n – indices which can be fractional values; Me², Me³ – metal cations; A – acid anions.

Improvement of specific characteristics is likely related to the increased proton diffusion coefficient in the crystal lattice of nickel hydroxide. It should be noted that the stage of proton diffusion through the crystal lattice is limiting [29]. On the other hand, during the discharge of NiOOH, which is a semiconductor with good electric conductivity, it transforms to dielectric Ni(OH)₂. Thus, the introduction of conductive additives on the microlevel can increase discharge time and, as a result, the utilization coefficient.

In the present work, it is proposed to introduce silver in the form of Ag₂O, which is a p-type semiconductor by coprecipitating it with Ni–Al layered double hydroxide. It is also assumed that silver oxide would contribute to capacity because of involvement in the electrochemical reaction in the way as this occurs on the positive electrode of zinc–silver secondary batteries with an alkaline electrolyte:



Thus, a positive effect of silver additive on the electrode characteristics is expected.

It should be noted that literature research did not yield any references regarding the effect of silver added on the synthesis stage of active materials for the positive electrode of alkaline CPS. Based on this, synthesis and research of active materials with silver additive can be an interesting scientific problem.

3. The aim and objectives of the study

The aim of the study was to prepare and test new material for alkaline secondary batteries based on Ni–Al layered double hydroxide with the addition of Ag₂O.

In order to achieve the set aim, the following objectives were formulated:

- to synthesize double hydroxides of Ni–Al with and without silver additive;
- to evaluate the influence of silver additive on the structure of prepared samples and specific characteristics of the electrode.

4. Materials and methods used for the study of LDH powders based on nickel and aluminum with and without silver additive

Materials used in the research.

All nickel hydroxide powders were prepared according to the procedure described below.

A 1M solution of metal salts (nickel, aluminum, silver) was fed into a solution of 2M sodium hydroxide containing the necessary amount of Na₂CO₃ at 35 °C, at a feed rate of 2 drops per second. The ratio of metal cations was varied depending on the target composition of the powder. It was assumed that the resulting powders would correspond to the following formulas Ni_{1-x}Al_x(OH)₂(CO₃)_{x/2}·0.66H₂O or Ni_{1-x-y}Al_x(OH)₂(CO₃)_{x/2}·Ag₂O·0.66H₂O [30].

The precipitated powders were washed off from alkali to pH=7–8, vacuum filtered, and dried at 45–55 °C, ground and sifted through a 71 μm mesh. The sifted powder was then soaked in distilled water for a day, vacuum filtered and dried again. The operation was conducted in order to remove soluble salts.

As a result, three LDH powders with molar ratios of cations in the initial solution: Ni:Al – 80:20 %, Ni:Al:Ag – 80:15:5 %, Ni:Al:Ag – 75:20:5 % were prepared. For simplicity, all sample labels are summarized in Table 1.

Table 1

Sample labels

Sample	Ni:Al – 80:20 %	Ni:Al:Ag – 80:15:5 %	Ni:Al:Ag – 75: 20:5 %
Label	N80:A20	N80:A15:S5	N75:A20:S5

Structural analysis of prepared double hydroxide powders with and without silver additive

XRD patterns of the samples were recorded on the DRON-3 diffractometer (Russia), with monochromated Co-Kα radiation.

Evaluation of electrochemical characteristics of nickel hydroxide powders.

For the recording of potentiodynamic curves, a mesh electrode with the pasted active mass on it and a cell, shown in Fig. 1 were used [5].

The composition of the active mass is listed in Table 2 [3].

All potentiodynamic curves were recorded in the potential window 200 – 700 mV vs NHE, scan rate 1 mV/s, number of cycles – 5. Ag/AgCl (KCl sat.) was used as a reference electrode.

Utilization coefficient was calculated from the results of charge-discharge cycling, which was conducted in the cell shown in Fig. 4 [3].

The composition of the active mass was the same as listed in Table 2, [3]. The counter electrode of greater capacity was used a counter-electrode and Ag/AgCl (KCl sat.) was used as a reference electrode. The capillary that was connecting the reference electrode with the cell was a thin tube with a nylon fiber soaked in the electrolyte solution – 4.5 M KOH solution.

The capacity of the working electrode was calculated from the mass of active material pasted on the electrode, assuming one electron reaction:

$$Q_t = \frac{\Delta m_{w.e.} \cdot \omega \cdot \alpha}{K} \tag{4}$$

where Δ*m*_{w.e.} – mass increase after pasting, g; ω – content of Ni(OH)₂ in the active mass; α – coefficient for calculating the

mass of Ni(OH)₂ from the formulas Ni_{1-x}Al_x(OH)₂(CO₃)_{x/2} × 0.66H₂O or Ni_{1-x-y}Al_x(OH)₂(CO₃)_{x/2}·Ag₂O·0.66H₂O through the nickel content (was calculated for each powder separately).

K – electrochemical equivalent of hydroxide, assuming one electrode reaction for the charge of Ni(OH)₂, 3.46 g/a.h.

Charge current in the cell was equal to:

$$I_c = Q_c \cdot k, \tag{5}$$

where *k* – coefficient, which was equal to 0.1 for 18-hour charge, and 1.8 for 1-hour (fast) charge.

Discharge current was calculated from the following formula:

$$I_d = \frac{Q}{T_d}, \tag{6}$$

where *T*_d – discharge time, 5 hours.

Discharge characteristics were recorded onto a personal computer using the high resistance (20 MOhm) multi-meter UNI-T UT-70B (China). Discharge characteristics are represented as a dependency of the potential on the utilization coefficient (*K*_u). The X-axis values were calculated as time divided by the theoretic discharge time, which was 5 hours. Discharge was conducted in a five-hour regime (*T*_D=5 hours).

5.1. Structural analysis of Ni–Al double hydroxide powders with and without silver

The XRD patterns of all samples are shown in Fig 1.

Analysis of the obtained XRD patterns allows us to say that all powders have similar in structure: low intensity and definition of peaks, high level of the signal between peaks. It should also be noted that the first peak for all samples lies at 12–14° 2θ, which indicates that all samples have the same polymorphic form. The position of the first peak also corresponds to α-form.

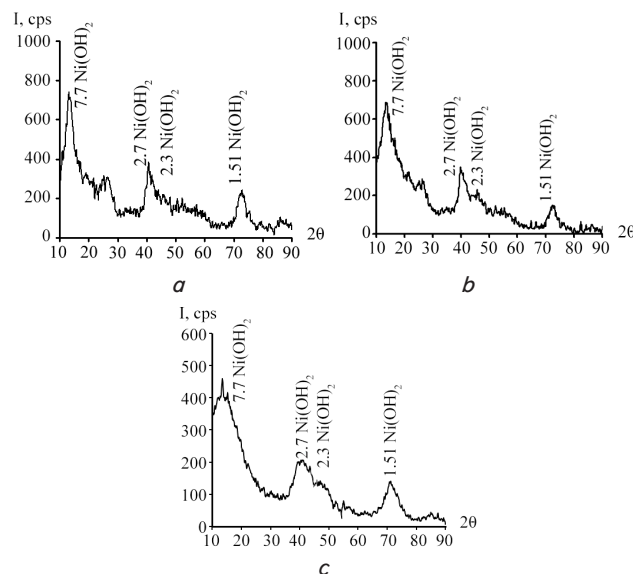


Fig. 1. XRD patterns of nickel hydroxide samples: a – N80:A20; b – N80:A15:S5; c – N75:A20:S5

Poor definition of the first peak can indicate the presence of crystals with different sizes in the (001) plane. In

addition, no peaks corresponding to silver or silver compounds are observed, which is supposedly because of low silver content.

5.2. Experimental results of evaluating electrochemical characteristics of prepared powders

In order to evaluate electrochemical characteristics of Ni-Al hydroxide with and without silver additive, cyclic voltamperograms (Fig. 2) were recorded. It should be mentioned that the characteristics are similar in shape and peak positions. Thus, the oxidation (charge) potential lies in the range of +600 to +610 mV. Reduction peak potentials of all powders lie in the range from +430 to +460 mV vs NHE [31, 32]. It can be observed that there is a notable difference in the position of reduction peak potentials. Also, only two peaks are observed for all samples – one for oxidation and one reduction, with the oxidation peak current being higher than that of the reduction peak. This also means a larger surface under the curve, meaning higher capacity of this process. This is because of process irreversibility and oxygen evolution during charge. Both reasons lead to an increase of the total current of the curve (Fig. 2), which leads to an increase of the anodic peak. Pure oxygen evolution can be observed at a potential above 650 mV, and is expressed as a rising curve. Stationary process parameters are achieved closer to the end of cycling, because closer to the fourth-fifth cycle peak positions and values become closer to those of the previous cycle.

A typical discharge curve of Ni-Al hydroxide with silver additive is shown in Fig. 3, *a* (sample N80:A15:S5). It can be seen that the average discharge potential is about +490 mV, there is also only one discharge plateau, which indicates a single-phase sample. Fig. 3, *b* shows the dependency of the utilization coefficient on the number of the charge-discharge cycle.

Fig. 2 shows the utilization coefficient that is higher than 1 (i. e. more than 100 %), however, this does not contradict the logic. As previously mentioned, the utilization coefficient was calculated as the quantity of electricity obtained from discharge, divided by its theoretical value. Theoretical capacity was calculated assuming one electron reaction, but because part of nickel atoms can react with the release of 2 electrons, this value becomes reasonable. It should also be considered that the electrodes were charged to 180 % of the theoretical capacity (assuming one electron electrochemical reaction).

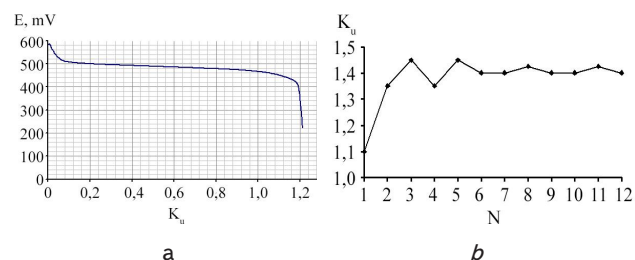


Fig. 3. Electrochemical characteristics of synthesized powders: *a* – discharge curve for powder N80:A15:S5 (18-hour charge, 5-hour discharge); *b* – dependency of the utilization coefficient on the number of the charge-discharge cycle for sample N80:A20 (18-hour charge, 5-hour discharge)

For each hydroxide sample, 2 dependencies of the utilization coefficient on the number of the charge-discharge cycle were obtained: slow (18 hours) and fast (1 hour) charge. An averaged value was also calculated, which did not include utilization coefficients of the first two charge-discharge cycles. This is because during the first two cycles the active material is still formed, resulting in lower utilization coefficient than during the main operation – Fig. 3, *b*. Averaged values of the utilization coefficient obtained for different charge regimes are shown in Fig. 4.

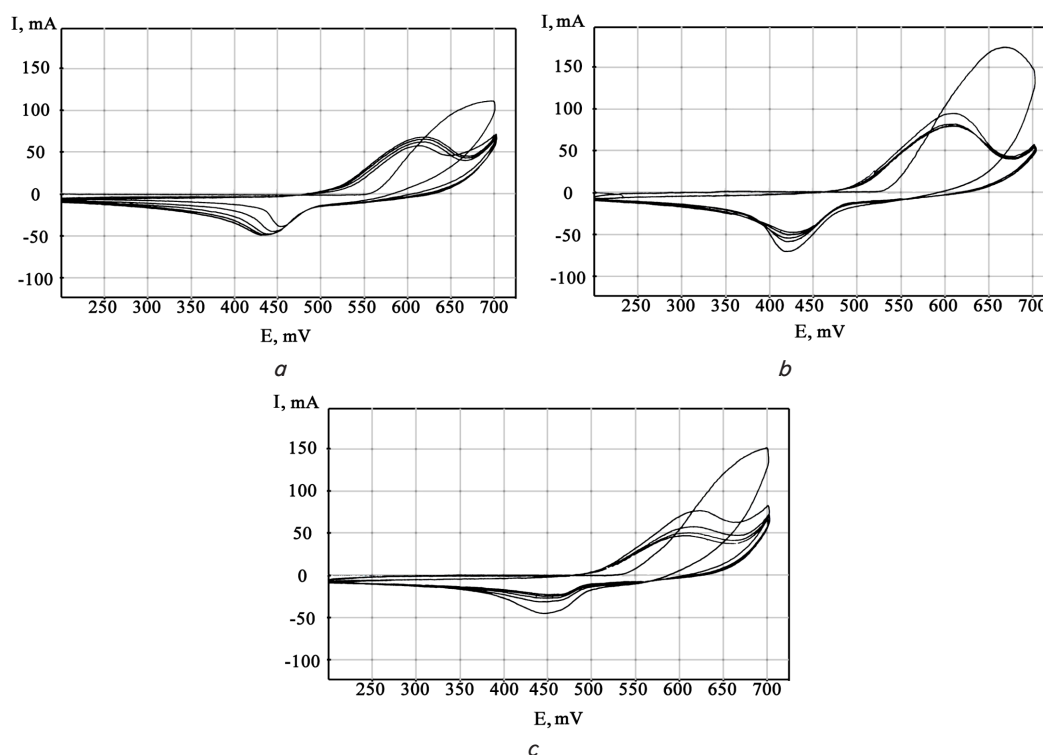


Fig. 2. Cyclic voltamperograms of nickel hydroxide samples: *a* – N80:A20; *b* – N80:A15:S5; *c* – N75:A20:S5

From the presented histogram, it can be concluded that in case of slow charges, the addition of silver has a negative impact – Ni-Al hydroxide without silver shows higher capacities. However, for the fast charge, the capacities of powders with silver are higher.

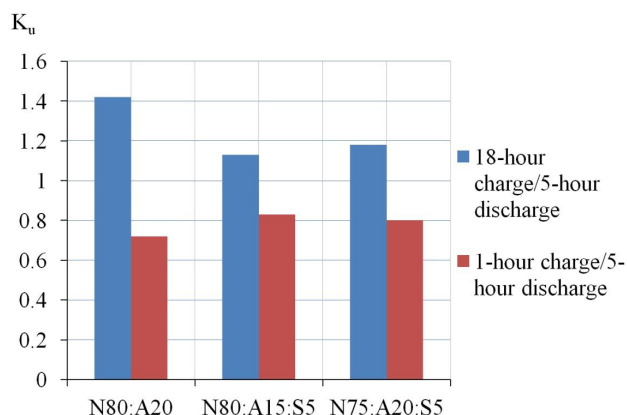


Fig. 4. Average utilization coefficients of nickel hydroxide powder obtained for fast and slow charges

It is notable that the higher utilization coefficient for the fast charge is demonstrated by the powder with higher nickel content – sample N80:A15:S5, with K_u of 0.83. For the slow charge regime, the higher utilization coefficient is observed for the sample without silver additive (N80:A20), with the utilization coefficient of 1.42.

6. Discussion of results of structural and electrochemical activity studies

Hydroxides based on nickel and aluminum with and without silver additive have been chemically prepared. In all cases, the powders can be characterized as α -like LDH.

In addition, for hydroxides synthesized with the addition of silver, no silver in the form of Ag_2O , AgO or Ag was observed on the XRD patterns, which is likely related to its low content in the hydroxide.

In addition, no additional peaks were observed, but only those that correspond to oxidation or reduction of nickel hydroxide. This and the absence of additional plateaus on the discharge curve indicate that powders consist of a single phase. Low content of silver has no noticeable effect on XRD patterns or cyclic voltamperograms.

Nevertheless the effect of silver on charge effectiveness was observed. For samples containing silver, the utilization coefficient was higher in case of charging at high currents $K_u=0.83$ (N80:A15:S5). This supports the previous assumption that silver compounds formed during precipitation would act as a conductive additive. In case of the fast regime, they can also improve charge efficiency, especially at the initial stages when electrical conductivity of the hydroxide is low.

However, the highest utilization coefficient for slow discharges was observed for the sample without silver $K_u=1.42$. This is likely because the presence of silver results in the lower relative content of nickel in the powders.

7. Conclusions

1. Nickel-aluminum layered double hydroxide powders with silver additive and different metal cation ratios have been prepared: Ni:Al:Ag – 80:15:5 % and 75:20:5 %. For comparison, Ni-Al LDH powder without silver was also prepared, with the cation ratio: Ni:Al 80:20 %. All powders were composed of a single phase, corresponding to α -form.

2. The samples prepared in the presence of silver have demonstrated better utilization coefficient when cycled at fast one-hour charging regimes $K_u=0.8-0.83$. The sample synthesized without silver showed better characteristics at a slow discharge rate $K_u=1.42$.

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