Розроблено новий безперервний метод електрохімічного отримання Ni–Al подвійно-шарового гідроксиду як активної речовини лужних Ni–Cd, Ni–Fe та Ni–MeH акумуляторів. ПШГ структура отриманих зразків була доведена методом РФА. Показано утворення електрохімічного активного Ni–Al ПШГ з високою питомою ємністю (237 мА·час/г). Оптимальні умови отримання: густина струму 18 А/дм²; використання розчину лугу в якості аноліту

Ключові слова: Ni–Al подвійно-шаровий гідроксид, електрохімічний синтез, щілинний діафрагмовий електролізер

Разработан новый непрерывный метод электрохимического получения Ni–Al слоистого двойного гидроксида как активного вещества щелочных Ni–Cd, Ni–Fe и Ni–MeH аккумуляторов. СДГ структура полученных образцов доказана РФА. Показано образование электрохимически активного Ni–Al СДГ с высокой удельной емкостью (237 мА·час/г). Оптимальные условия получения: плотность тока 18 А/дм²; использование раствора щелочи в качестве анолита

Ключевые слова: Ni–Al слоистый двойной гидроксид, электрохимический синтез, щелевой диафрагменный электролизер

OBTAINING OF Ni–Al LAYERED DOUBLE HYDROXIDE BY SLIT DIAPHRAGM ELECTROLYZER

V. Kovalenko**
PhD, Associate Professor
Department of Analytical Chemistry and
Food Additives and Cosmetics*
E-mail: vadimchem@gmail.com

V. Kotok**
PhD, Associate Professor
Department of Processes, Apparatus and
General Chemical Technology*
E-mail: valeriykotok@gmail.com
*Ukrainian State University of Chemical Technology
Gagarina ave., 8, Dnipro, Ukraine, 49005
**Department of Technologies of
Inorganic Substances and Electrochemical Manufacturing
Federal State Educational Institution of
Higher Education "Vyatka State University"
Moskovskaya str., 36, Kirov, Russian Federation, 610000

1. Introduction

The alkaline Ni–Cd, Ni–Fe and Ni–MeH accumulators are widely used as chemical power sources for transport, railroad and mining industry to power electrical motors of various capacities. The application of alkaline accumulators is very relevant for renewable energy devices [1]. It is known that the capacity of alkaline accumulators is defined by the capacity of nickel hydroxide electrode, with the cost of nickel hydroxide being 65–70 % of the total accumulator cost. Thus, the obtaining of $Ni(OH)_2$ is the main direction in the development of alkaline accumulators.

The polymorphism is characteristic for nickel hydroxide and two of its modifications are described [2]. β-form (chemical formula $Ni(OH)_2$, brucite structure) and α-form (chemical formula $3Ni(OH)_2·2H_2O$, hydrotalcite structure). β-$Ni(OH)_2$ possesses high cycling stability and is widely used as an active material in accumulators [3] and supercapacitors [4, 5]. α-$Ni(OH)_2$ possesses significantly better electrochemical properties than β-$Ni(OH)_2$. However, its stability in concentrated alkali is significantly lower, especially at elevated temperature, the α-$Ni(OH)_2$ transforms into β-$Ni(OH)_2$ [6], which is accompanied by loss of capacity. The stabilization of α-form is achieved by transforming pure α-$Ni(OH)_2$ into layered double hydroxide (LDH) $Ni_xMe^{+n}_{1-x}(OH)_2A^{-m}_{(n-2)/m}·0.66H_2O$. Cu^{+2} [7], Ti^{4+} [8], Mn^{3+} [9] can be used as stabilizing metal cation. The most promising is a formation of Ni–Al LDH [10, 11] because Al^{3+} has low atomic weight and is effective at stabilizing α-structure.

Thus, the development of highly active Ni–Al LDH samples is a relevant problem.

2. Literature review and problem statement

LDHs can be obtained using various methods that differ in a source of OH⁻ ions and order of mixing metal cations and hydroxyl ions.

The most common are chemical methods in which the source of hydroxyl ions is an alkaline solution. A titration method is used in which an alkaline solution is added to a solution of metal cations (Ni^{2+} and Al^{3+}). However, it has been demonstrated in the paper [8] that such method can lead to the formation of hydroxysalts that can have a significantly lower electrochemical activity. Thus, it is more feasible to employ precipitation at high supersaturation in which metal cation solution (Ni^{2+} and Al^{3+}) is slowly added to the alkaline solution [12], resulting in a formation of a single layered double hydroxide phase. The disadvantage of such method is that the formation of LDH at the start and the end of the process occurs at different pH, which affects the properties of the product. To overcome this disadvantage, a precipitation at constant pH is employed [13].

For the synthesis of highly disperse Ni–Al LDH, a homogeneous precipitation is used, in which precipitant-ions (OH⁻ anions) are formed as a result of thermal hydrolysis of amine compounds. Unlike alkali-induced precipitation, the OH⁻ are formed homogeneously in the volume of reacting

solution. During the synthesis procedure, the solution of nickel and aluminum nitrates with urea (hexamethylenetetramine or another water-soluble amine) is subjected to heating and ageing at 80–90 °C [14]. In the paper [15], the water-alcohol solution is used for synthesis. Microwave radiation was employed to heat the solution, in the paper [16]. A general disadvantage of the homogeneous precipitation method is energy consumption.

The majority of chemical methods for preparation of nickel hydroxide are batch processes. This is a significant disadvantage because batch production leads to a product with its properties varying from batch to batch. For industrial application, the continuous production should be preferred.

OH^- anions as precipitant-ions can be synthesized as a result of an electrochemical reaction. The hydroxylions formed react with metal cations to produce hydroxide. However, such method is generally used for the preparation of nickel hydroxide films [17]. It should be noted that electrochemical synthesis has a number of advantages: the reaction rate can be controlled by current density, ease of process automation. Thusly, the electrochemical synthesis is a promising method for obtaining nickel hydroxide.

In previously mentioned papers [5, 18], a method for continuous electrochemical obtaining of β-Ni(OH)$_2$ in a slit diaphragm electrolyzer (SDE) with the supply of nickel sulfate into the cathodic chamber has been developed. Such method is continuous and is very promising for the synthesis of nickel layered double hydroxides.

3. The aim and objectives

The aim of the work was the development of a continuous electrochemical method for obtaining of Ni-Al LDH in a slit diaphragm electrolyzer.

In order to achieve this aim, the following objectives must be fulfilled:

– to study the sample structure and prove the formation of Ni–Al during synthesis in SDE;

– to study the influence of synthesis current density and anolyte composition on the electrochemical properties of synthesized samples;

– to determine the optimal parameters of Ni–Al LDH electrochemical synthesis in SDE.

4. Methods employed for the development of a method of continuous electrochemical preparation of Ni–Al LDH

4. 1. Synthesis methods in slit diaphragm electrolyzer

The base synthesis method [5] is based on electrolysis conducted in a flowing slit diaphragm electrolyzer (SDE). The cathodic chamber is fed with a nickel sulfate solution using a peristaltic pump, the anodic chamber is fed with NaOH solution, with the same feed rate of 0.2 L/h.

Under supplied current, hydrogen evolution and generation of hydroxylanions occur at the cathode leading to the formation of nickel hydroxide. The precipitate was removed from apparatus by the catholyte flow. After leaving SDE, the precipitate was filtered immediately, using a vacuum pump, vacuum flask and Büchner funnel. Nickel hydroxide samples have been dried at 70 °C for one day, ground, sifted through a 71 µm sieve, washed from soluble salts and dried again under the same conditions.

For the synthesis of Ni-Al LDH, it was necessary to feed the solution of nickel and aluminum salts into the cathodic chamber. Chemically Ni-Al LDH is obtained from solutions of nitrate salts. However, the paper [19] has demonstrated the complications that arise from using nitrate solution for synthesis of nickel hydroxide in SDE. Because of that, the sulfate solution $C(Ni^{2+})=0.2$ mol/l has been used [18]. The molar ratio of Ni:Al=4:1 [20]. A NaOH solution has been proposed as an anolyte, similar to [18]. It is likely that sulfate Ni-Al LDH would form. However, in the paper [12], it is described that CO_3^{2-} demonstrates a significantly greater stabilizing effect for Ni-Al LDH. For the synthesis of carbonate Ni-Al LDH, Na_2CO_3 has been introduced into the anolyte in different ratios to alkali. Three series of experiments have been conducted:

1. Series 1. Study on the influence of synthesis current density (using pure alkali as an anolyte). The synthesis has been conducted at i=8, 10, 12, 14, 15,7 and 18 A/dm^2 during 4–8 hours. **Example of sample nomenclature – NiAl-A-0,2-8** (A – alkali as an anolyte, 8 – synthesis current density A/dm^2, varies depending on the real value).

2. Series 2. Study on the influence of synthesis current density (using a mixture of alkali and sodium carbonate NaOH: Na_2CO_3=40:60 as an anolyte). The synthesis has been conducted at i=8, 10, 12, 14, 15,7 and 18 A/dm^2 during 4–8 hours. **Example of sample nomenclature – NiAl-AC-0,2-8-40/60** (AC – alkali+carbonate as an anolyte, 8 – synthesis current density A/dm^2, varies depending on the real value, 40/60 – molar ratio of NaOH:Na$_2$CO$_3$).

3. Series 3. Study on the influence of carbonate to alkali ratio as an anolyte at constant current density. The synthesis has been conducted at current density, at which a samples with the highest specific capacity is obtained (based on results of series 1 and 2), during 4–8 hours. Increase or decrease of carbonate and specific ratios have been determined based on results of series 2. **Example of sample nomenclature – NiAl-AC-0,2-18-40/60** (AC – alkali+carbonate as an anolyte, 8 – synthesis current density A/dm^2, 40/60 – molar ratio of NaOH:Na$_2$CO$_3$, varies depending on the real value).

4. 2. Reference samples

The following samples have been used as reference:

a) an industrial sample produced by "Bochemie" (Czech Republic), used in the manufacturing of accumulators. The sample is denoted as **Bochemie**;

b) carbonate Ni-Al LDH prepared by precipitation at high supersaturation: a solution of nickel and aluminum nitrates (ratio 4:1) has been slowly added to a solution containing NaOH and Na_2CO_3 under continuous stirring and constant temperature of 65 °C. The sample is denoted as **NiAl–AC-chemical**.

4. 3. Study of the characteristics of Ni-Al LDH samples prepared in SDE under different conditions.

Crystal structure of samples has been studied by means of X-Ray diffraction (XRD) method using DRON-3 diffractometer (Russian Federation) (Co-Kα radiation, in the range of 10–90° 2θ, scan rate 0.1 °/s).

Electrochemical properties of nickel hydroxide samples have been evaluated using:

a) cyclic voltamperometry in a special cell YaSE-2 using digital potentiostat Ellins P-8 (Russian Federation). The working electrode has been prepared by pasting a mixture of nickel hydroxide (81 % wt.), graphite (16 % wt.) and

PTFE (3 % wt.) [21] on the current collector. The current collector has been prepared by welding a Ni mesh onto a Ni plate. Electrolyte – 6M KOH. Counter electrode – nickel mesh, reference electrode – saturated silver chloride. The study has been conducted in the potential range 0–500 mV at the scan rate of 1 mV/s;

b) galvanostatic charge-discharge cycling in accumulator regime. The study has been conducted using a custom-built model of the accumulator (Fig. 1). The working electrode has been prepared by pasting a mixture of nickel hydroxide sample (81 % wt.), graphite (16 % wt.) and PTFE (3 % wt.) [21] onto a special current collector (Ni mesh welded onto Ni foil). Electrolyte – 6M KOH. Counter electrode – cadmium (mass CdO+graphite+diesel oil was pasted onto a special current collector). After preparation, the cadmium electrode has been specifically charged. The capacity of the counter electrode was 2 times higher than of the working electrode. Reference electrode – silver chloride.
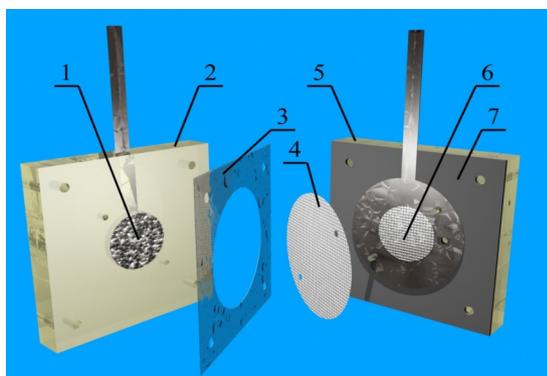

Fig. 1. A model of accumulator for electrochemical tests:
1 — counter electrode; 2, 5 — PMMA half-elements;
3 — gasket; 4 — separator; 6 — working electrode;
7 — rubber gasket. Charge — 18-h with 20 % overcharge, discharge at 0.2 C.

5. The analysis results of Ni–Al LDH samples prepared in SDE under different current densities and anolyte compositions

5. 1. The XRD analysis results of Ni-Al LDH samples

The XRD patterns of Ni–Al hydroxide samples prepared under different synthesis conditions are presented on Fig. 2. All patterns are characteristic for α-modification (peak at $2\Theta=13°$).

It should be noted that α-structure is the most pronounced at high current densities (15.7–18 A/dm²). Upon the decrease of current density, the crystallinity decreases and a small peak of β-modification appears (at $2\Theta=21°$) (Fig. 2, a). Significant introduction of alkali into the anolyte leads to the formation of a more pronounced α-structure, the crystallinity, however, decreases (Fig. 2, b). The decrease of carbonate content leads to the increase of crystallinity (Fig. 2, c).

5. 2. Cycling voltamperometry results of Ni–Al LDH samples

Fig. 3 shows cyclic voltamperograms obtained for Ni-Al LDH samples of series 1, and Fig. 4 – for series 2.

With the increase of synthesis current density (anolyte – pure alkali solution), the electrochemical activity of samples increases (Fig. 3), which is indicated by the increase of specific current from 0.2 A/g (NiAl-A-0,2-8) to 2.25 A/g (NiAl-A-0,2-18).
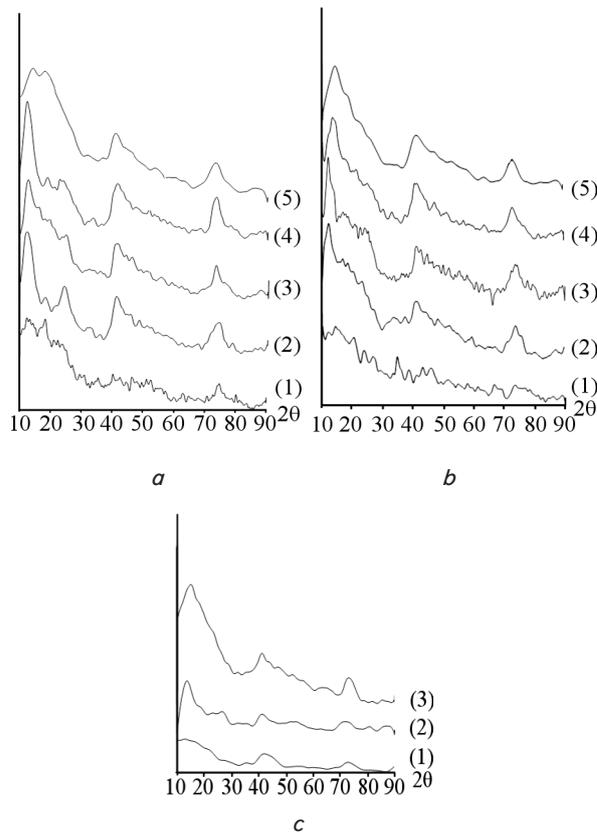

Fig. 2. XRD patterns of Ni-Al LDH samples: a — Series 1,
1 — NiAl-A-0,2-8, 2 — NiAl-A-0,2-12, 3 — NiAl-A-0,2-14,
4 — NiAl-A-0,2-15,7, 5 — NiAl-A-0,2-18; b — Series 2,
1 — NiAl-AC-0,2-8-40-60, 2 — NiAl-AC-0,2-12-40-60,
3 — NiAl-AC-0,2-14-40-60, 4 — NiAl-AC-0,2-15,7-40-60,
5 — NiAl-AC-0,2-18-40-60; c — Series 3,
1 — NiAl-AC-0,2-18-60-40, 2 — NiAl-AC-0,2-18-70-30,
3 — NiAl-AC-0,2-18-80-20

Samples prepared at 15.7–18 A/dm² are assumed to have even higher specific capacities. Upon introduction of carbonate into the anolyte (at ratio NaOH:Na₂CO₃ of 40:60), the electrochemical activity of samples decreases (Fig. 4), approaching to parameters of samples obtained with pure alkali as an anolyte only at high current densities – 2.05 A/g (NiAl-AC-0,2-18-40/60).

Based on the results presented in Fig. 3, 4, it has been discovered that the most active samples are formed at high synthesis current density with pure alkali as an anolyte. Because of that, it has been decided to conduct the synthesis of series 3 samples at a current density of 18 A/dm² and decreasing carbonate content (ratios NaOH:Na₂CO₃ 60:40, 70:30 and 80:20). Fig. 5 shows cyclic voltamperograms of Ni-Al LDHs obtained under these conditions.

From Fig. 5 it can be seen that the decrease of carbonate content leads to improvement of electrochemical activity, but it is still lower when compared to samples prepared with pure alkali as an anolyte.
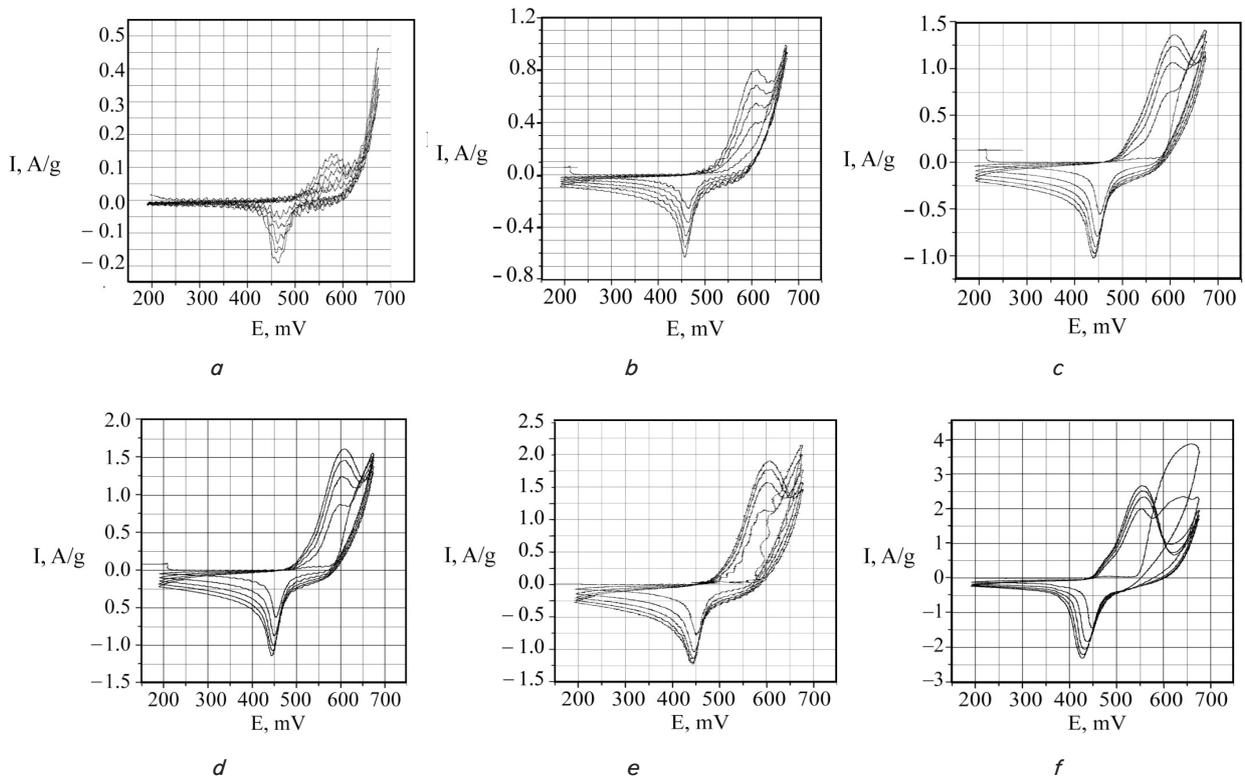
Fig. 3. Cyclic voltamperograms of Ni-Al LDH samples. Series 1: *a* — NiAl-A-0,2-8; *b* — NiAl-A-0,2-10; *c* — NiAl-A-0,2-12; *d* — NiAl-A-0,2-14; *e* — NiAl-A-0,2-15,7; *f* — NiAl-A-0,2-18
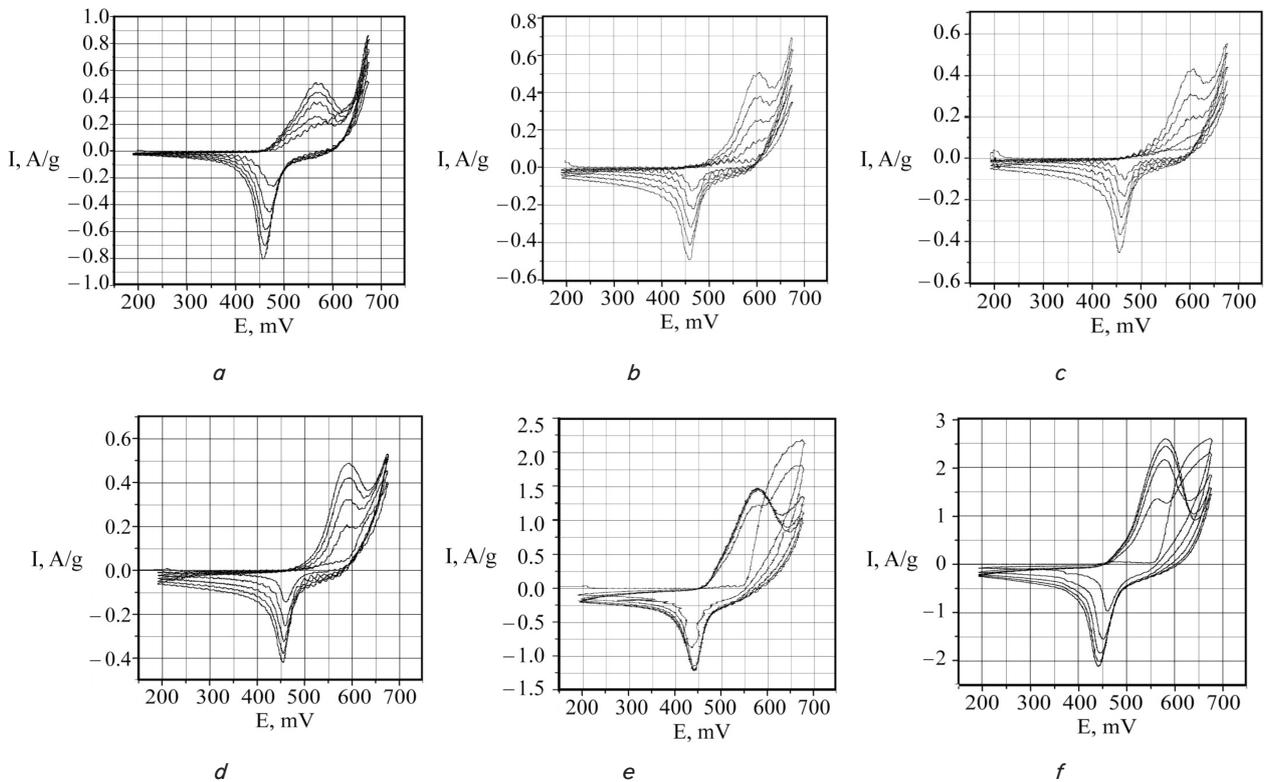

Fig. 4. Cyclic voltamperograms of Ni-Al LDH samples. Series 2: *a* — NiAl-AC-0,2-8-40/60; *b* — NiAl-AC-0,2-10-40/60; *c* — NiAl-AC-0,2-12-40/60; *d* — NiAl-AC-0,2-14-40/60; *e* — NiAl-AC-0,2-15,7-40/60; *f* — NiAl-AC-0,2-18-40/60
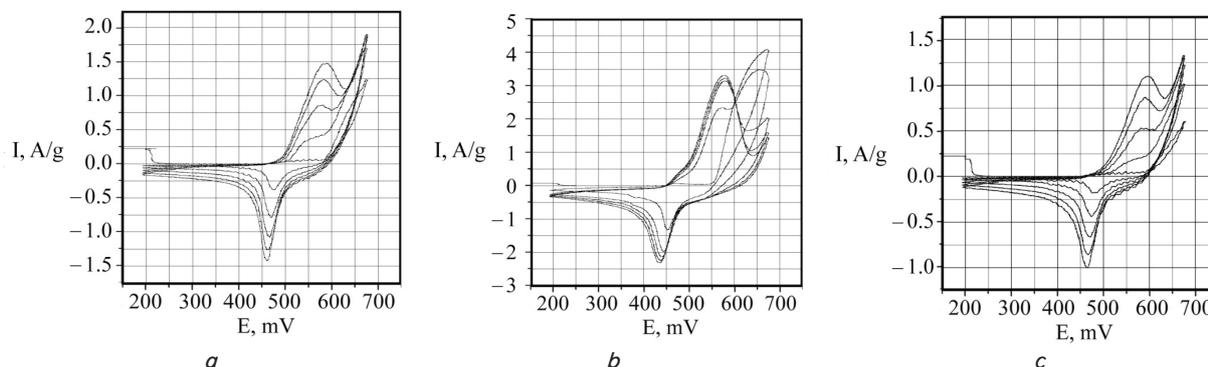
Fig. 5. Cyclic voltamperograms of Ni-Al LDH samples Ni−Al LDH. Series 3: *a* − NiAl-AC-0,2-18-60/40; *b* − NiAl-AC-0,2-18-70/30; *c* − NiAl-AC-0,2-18-80/20

5. 3. Results of charge-discharge studies of Ni-Al LDH samples in accumulator regime

Fig. 6 shows the histogram of specific capacities for Ni-Al LDH samples synthesized in SDE under different conditions, and reference samples – chemically synthesized Ni-Al LDH and the industrial sample.
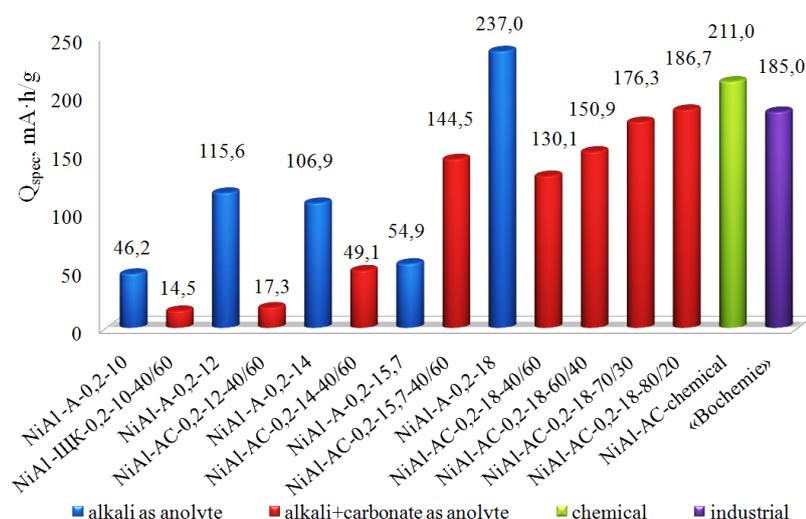

Fig. 6. Specific capacities of synthesized Ni-Al LDHs and reference samples

Higher synthesis current densities lead to the increase of specific capacity. This is characteristic for samples synthesized with alkali as an anolyte and for samples synthesized with analyte composed of alkali and sodium carbonate mixture. However, the introduction of carbonate into the anolyte significantly decreases the specific capacity of samples. The decrease of carbonate content in the anolyte leads to the increase of specific capacity, however, it is still lower than for a sample obtained with pure alkali as an anolyte. It should also be noted that the capacity of the sample prepared at 18 A/dm² with pure alkali as an anolyte is 237 mA·h/g. This exceeds specific capacities of both reference samples: "Bochemie" (185 mA·h/g) and NiAl-chemical (211 mA·h/g).

6. Discussion of the characteristics of Ni-Al LDH samples prepared in SDE under different synthesis parameters

XRD analysis. In general case, by means of XRD (Fig. 3) it has been proven that all synthesized samples have α-structure, i. e. are layered double hydroxides. It has been demon-strated that under low current density (8−10 A/dm²) samples contain some a small amount of β-modification. With the increase of current density, the β-modification peaks disappear and crystallinity increases. This can be explained by specifics of synthesis in SDE. During electrolysis OH⁻ is formed at the cathode and basifies the cathodic layer of electrolyte. The calculation of material balance has shown that at a current density below 14 A/dm², the number of formed hydroxyl ions is insufficient for complete precipitation of supplied amount of Ni^{2+} and Al^{3+}. On the other hand, at low current densities, the thickness of the basified electrolyte layer is smaller than the thickness of "cathode – diaphragm" slit. As a result, the condition for the formation of α and β-modification can be formed. The crystallinity increase is explained by the fact that the higher current density increases the amount of Joule heat in the cathodic chamber. The higher amount of heat leads to more rapid ageing of formed hydroxide and increase of crystallinity.

Electrochemical properties. Influence of current density (anolyte – alkali). Under low current densities, in accordance with the previously described mechanism, there is a layer with free Al^{3+} ions. It is known that Al^{3+} has a two-side effect on electrochemical properties of nickel hydroxide. By incorporating into the structure the aluminum becomes an activator and increases the specific capacity (by forming LDH), but when adsorbed onto the surface it becomes poison and decreases the electrochemical activity. This thesis is supported by the comparison of specific capacities of synthesized samples with specific capacities of reference samples – chemically synthesized Ni−Al LDH and industrial nickel hydroxide sample. The specific capacity of Ni−Al LDH synthesized in SDE exceeds capacities of reference samples only at i=18 A/dm².

Electrochemical properties. Influence of current density (anolyte – alkali with sodium). In this case, the tendency is analogous to the one observed for samples synthesized with alkali as an anolyte. It should be mentioned that the introduction of carbonate greatly reduces specific capacity, especially at low current densities. This can be related to the fact that OH⁻ is formed at the cathode and diffuses out from it into solution. At the same time, the carbonate anions are transferred through the diaphragm and end up in catholyte from another side of the slit. Under low current density, a

layer near the diaphragm contains free Al^{3+}; that react with carbonate. However, aluminum carbonate is completely hydrolyzed by water to $Al(OH)_3$, which is incorporated into the sample as a separate phase. In the accumulator, $Al(OH)_3$ dissolves in alkali and poisons nickel hydroxide electrode. With the increase of current density, the number of free Al^{3+} decreases and this effect is partially negated.

Electrochemical properties. Influence of carbonate content in the anolyte (at i=const). Based on previous speculations, the content of carbonate in this series has been reduced in the array "60–40–30–20". The specific capacity in this array increases, which supports previously stated mechanism. Even at the ratio of $NaOH:Na_2CO_3=80:20$, the specific capacity was still lower than for chemically prepared Ni-Al LDH and sample prepared with alkali as an anolyte. This indicated that introduction of carbonate into the anolyte during electrochemical synthesis of Ni-Al LDH in SDE is not feasible.

7. Conclusions

1. By means of XRD, it has been proven that hydroxide samples synthesized in slit diaphragm electrolyzer are Ni-Al LDH. The increase of crystallinity with the increase of current density because of heating has been demonstrated.

2. The influence of current density and anolyte composition on the electrochemical properties of Ni-Al LDH samples synthesized in SDE has been studied. It has been demonstrated that with decreasing current density the capacity of samples decreases because of the presence of free aluminum cations that poison hydroxide samples. It has been demonstrated that introduction of carbonate into the anolyte has a negative impact, especially at low current densities. An assumption has been made that this occurs as a result of formation of a separate aluminum hydroxide phase near the diaphragm due to complete hydrolysis in the presence of carbonate anion. The decrease in the content of carbonate in the anolyte reduces the poisoning effect and increases the specific capacity of samples. Thus, it has been demonstrated that the use of alkali-carbonate anolyte for synthesis is not feasible.

3. A continuous method of electrochemical synthesis of Ni-Al LDH in a slit diaphragm electrolyzer has been proposed. Optimal synthesis parameters have been established: current density 18 A/dm², anolyte – NaOH solution. The sample obtained at optimal conditions demonstrated the specific capacity of 237 mA·h/g, which exceeds capacities of chemically synthesized Ni–Al LDH (201 mA·h/g) and industrial sample (185 mA·h/g).

References

1. Posada, J. O. G. Aqueous batteries as grid scale energy storage solutions [Text] / J. O. G. Posada, A. J. R. Rennie, S. P. Villar, V. L. Martins, J. Marinaccio, A. Barnes et. al. // Renewable and Sustainable Energy Reviews. – 2017. – P. 1174–1182. doi: 10.1016/j.rser.2016.02.024

2. Hall, D. S. Raman and Infrared Spectroscopy of α and β Phases of Thin Nickel Hydroxide Films Electrochemically Formed on Nickel [Text] / D. S. Hall, D. J. Lockwood, S. Poirier, C. Bock, B. R. MacDougall // The Journal of Physical Chemistry A. – 2012. – Vol. 116, Issue 25. – P. 6771–6784. doi: 10.1021/jp303546r

3. Vidotti, M. Eletrodos modificados por hidroxido de niquel: um estudo de revisao sobre suas propriedades estruturais e eletroquimicas visando suas aplicacoes em eletrocatalise, eletrocromismo e baterias secundarias [Text] / M. Vidotti, R. Torresi, S. I. C. de Torresi // Quimica Nova. – 2010. – Vol. 33, Issue 10. – P. 2176–2186. doi: 10.1590/s0100-40422010001000030

4. Kovalenko, V. L. Nickel hydroxide obtained by high-temperature two-step synthesis as an effective material for supercapacitor applications [Text] / V. L. Kovalenko, V. A. Kotok, A. A. Sykchin, I. A. Mudryi, B. A. Ananchenko, A. A. Burkov et. al. // Journal of Solid State Electrochemistry. – 2016. – Vol. 21, Issue 3. – P. 683–691. doi: 10.1007/s10008-016-3405-2

5. Kovalenko, V. Definition of factors influencing on Ni(OH)₂ electrochemical characteristics for supercapacitors [Text] / V. Kovalenko, V. Kotok, O. Bolotin // Eastern-European Journal of Enterprise Technologies. – 2016. – Vol. 5, Issue 6 (83). – P. 17–22. doi: 10.15587/1729-4061.2016.79406

6. Hu, M. Structural transformation and its effects on the electrochemical performances of a layered double hydroxide [Text] / M. Hu, Z. Yang, L. Lei, Y. Sun // Journal of Power Sources. – 2011. – Vol. 196, Issue 3. – P. 1569–1577. . doi: 10.1016/j.jpowsour.2010.08.041

7. Bao, J. Structure and Electrochemical Performance of Cu and Al Codoped Nanometer α-Nickel Hydroxide [Text] / J. Bao, Y. J. Zhu, Q. S. Xu, Y. H. Zhuang, R. D. Zhao, Y. Y. Zeng, H. L. Zhong // Advanced Materials Research. – 2012. – Vol. 479-481. – P. 230–233. doi: 10.4028/www.scientific.net/amr.479-481.230

8. Solovov, V. Influence of temperature on the characteristics of Ni(II), Ti(IV) layered double hydroxides synthesised by different methods [Text] / V. Solovov, V. Kovalenko, N. Nikolenko, V. Kotok, E. Vlasova // Eastern-European Journal of Enterprise Technologies. – 2017. – Vol. 1, Issue 6 (85). – P. 16–22. doi: 10.15587/1729-4061.2017.90873

9. Zhou, F. Coprecipitation Synthesis of NixMn1-x(OH)2Mixed Hydroxides [Text] / F. Zhou, X. Zhao, A. van Bommel, A. W. Rowe, J. R. Dahn // Chemistry of Materials. – 2010. – Vol. 22, Issue 3. – P. 1015–1021. doi: 10.1021/cm9018309

10. Rocha, M. A. A New Insight on the Preparation of Stabilized Alpha-Nickel Hydroxide Nanoparticles [Text] / M. A. Rocha, H. Winnischofer, K. Araki, F. J. Anaissi, H. E. Toma // Journal of Nanoscience and Nanotechnology. – 2011. – Vol. 11, Issue 5. – P. 3985–3996. doi: 10.1166/jnn.2011.3872

11. Qi, J. Effect of crystallinity on the electrochemical performance of nanometer Al-stabilized -nickel hydroxide [Text] / J. Qi, P. Xu, Z. Lv, X. Liu, A. Wen // Journal of Alloys and Compounds. – 2008. – Vol. 462, Issue 1-2. – P. 164–169. doi: 10.1016/j.jallcom.2007.07.102

12. Li, Y. W. Effect of interlayer anions on the electrochemical performance of Al-substituted α-type nickel hydroxide electrodes [Text] / Y. W. Li, J. H. Yao, C. J. Liu, W. M. Zhao, W. X. Deng, S. K. Zhong // International Journal of Hydrogen Energy. – 2010. – Vol. 35, Issue 6. – P. 2539–2545. doi: 10.1016/j.ijhydene.2010.01.015

13. Hu, B. Controllable synthesis of zinc substituted α- and β-nickel hydroxide nanostructures and their collective intrinsic properties [Text] / B. Hu, S.-F. Chen, S.-J. Liu, Q.-S. Wu, W.-T. Yao, S.-H. Yu // Chemistry – A European Journal. – 2008. – Vol. 14, Issue 29. – P. 8928–8938. doi: 10.1002/chem.200800458

14. Gong, L. Facile solvothermal synthesis Ni(OH)2 nanostructure for electrochemical capacitors [Text] / L. Gong, X. Liu, L. Su // Journal of Inorganic and Organometallic Polymers and Materials. – 2011. – Vol. 21, Issue 4. – P. 866–870. doi: 10.1007/s10904-011-9519-1

15. Yang, L.-X. Hydrothermal synthesis of nickel hydroxide nanostructures in mixed solvents of water and alcohol [Text] / L.-X. Yang, Y.-J. Zhu, H. Tong, Z.-H. Liang, L. Li, L. Zhang // Journal of Solid State Chemistry. – 2007. – Vol. 180, Issue 7. – P. 2095–2101. doi: /10.1016/j.jssc.2007.05.009

16. Xu, L. 3D Flowerlike α-Nickel Hydroxide with Enhanced Electrochemical Activity Synthesized by Microwave-Assisted Hydrothermal Method [Text] / L. Xu, Y.-S. Ding, C.-H. Chen, L. Zhao, C. Rimkus, R. Joesten, S. L. Suib // Chemistry of Materials. – 2008. – Vol. 20, Issue 1. – P. 308–316. doi: 10.1021/cm702207w

17. Fomanyuk, S. S. Kinetics of electrochromic process in thin films of cathodically deposited nickel hydroxide [Text] / S. S. Fomanyuk, Y. S. Krasnov, G. Y. Kolbasov // Journal of Solid State Electrochemistry. – 2013. – Vol. 17, Issue 10. – P. 2643–2649. doi: 10.1007/s10008-013-2169-1

18. Kovalenko, V. L. Electrochemical obtaining of Ni(OH)$_2$ from sulphate solution by flowing slit diafragm electrolyzer [Text] / V. L. Kovalenko, V. A. Kotok, V. V. Malishev // RSE-SEE, 1st regional symposium on electrochemistry of South-East Europe. – Rovinj, Croatia, 2008. – P. 201–203.

19. Kovalenko, V. L. The synthesis of nickel hydroxide by electrolysis from nickel nitrate solution in the slit diaphragm electrolyzer. Electrochemical properties [Text] / V. L. Kovalenko, V. A. Kotok // Collection of research papers of National mining university. – 2015. – Issue 49. – P. 181–186.

20. Kotok, V. A. The stability of aluminium-substituted alpha-nickel hydroxide [Text] / V. A. Kotok, N. D. Koshel, V. L. Kovalenko, A. A. Grechanuk // First Regional Symposium on Electrochemistry of South-East Europe "RSE-SEE". – Croatia Rovinj, 2008. – P. 204–206.

21. Kotok, V. Optimization of nickel hydroxide electrode of the hybrid supercapacitor [Text] / V. Kotok, V. Kovalenko // Eastern-European Journal of Enterprise Technologies. – 2017. – Vol. 1, Issue 6 (85). – P. 4–9. doi: 10.15587/1729-4061.2017.90810