Гідроксид нікелю широко використовується як активна речовина суперконденсаторів. Наибільш активними є зразки $Ni(OH)_2$ (α+β) шарової структури, синтезовані в щілинному діафрагмовому електролізері (ЩДЕ). Проведено вивчення впливу темплатного синтезу та ультразвуку на властивості зразків. Проведено синтез зразків гідроксиду нікелю при введенні полівінілового спирту в якості темплату та використанні ультразвукової обробки суспензії $Ni(OH)_2$ безпосередньо після формування. Синтезовані зразки гідроксиду нікеля вивчені методами рентгенофазового аналіза, скануючої электроної мікроскопії і адсорбції – десорбції азоту по методу БЕТ. Електрохімічні характеристики визначені гальваностатическим зарядно-разрядним циклюванням в режимі суперконденсатора. Порівняльний аналіз характеристик зразків $Ni(OH)_2$ показав как позитивний, так і негативний вплив темплату та ультразвука. Використання ПВС як темплата та ультразвукової обробки веде до різкого зниження питомої поверхні (до 6 $м^2/г$) та збільшенню середнього діаметра пор (до 1181 Å). Використання темплатного синтезу та ультразвуку знижує кристалличность та збільшує долю α-модифікації, що дозволяє збільшити питому ємність. Максимальне значення 233 Ф/г отримано при густині струму 40 $мА/см^2$ для зразка, що отриманий при спільній дії ультразвуку і темплату. В цих умовах питома ємність зразка, синтезованого без темплату та ультразвуку, складає 76 Ф/г. Однак при підвищенні густини струму до 120 $мА/см^2$ ємність даного зразка збільшується до 303 Ф/г. В той же час для зразків, синтезированих з темплатом та ультразвуком, при підвищенні густини струму спостерігається зниження ємності, що пов'язано з ускладненням розпаду агломератів частинок. У випадку використання темплату це може бути пояснено зв'язуючим ефектом залишків ПВС, що не були видалені, у випадку використання ультразвуку – ущільненням та спресовуванням частинок. По результатам порівняльного аналізу рекомендовано вибрати темплат, що легше видаляється та провести отримання $Ni(OH)_2$ в ЩДЕ безпосередньо в ультразвуковому полі та збільшити потужність випромінювача

Ключові слова: гідроксид нікелю, питома ємність, суперконденсатор, ультразвукова обробка, темплатний синтез, полівініловий спирт

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INFLUENCE OF ULTRASOUND AND TEMPLATE ON THE PROPERTIES OF NICKEL HYDROXIDE AS AN ACTIVE SUBSTANCE OF SUPER-CAPACITORS

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1. Introduction

Operation of electrical devices, especially with electric motors, without connection to electric grids (electric automobiles, hand-held electric tools, pumps stations, etc.) requires the use of accumulators. However, the starter current of the electric motor is 5–50 times higher than its working current, which lowers the effectiveness of accumulators. For starting electric motors, modern chemical power sources (CPS) – supercapacitors (SC) are used. SC are also used as starter CPS for ignition of gas and diesel engines, as uninterruptible power supplies for computers, medical equipment and even buildings and premises. Hybrid supercapacitors possess the best characteristics. A characteristic feature of supercapacitors is the high charge-discharge rate. As a result, the electrochemical process occurs on the surface and within a thin layer of active material particles at the Faradic electrode. Therefore, there are special requirements [1, 2] to the specific surface area, crystal structure and electrochemical activity of the active material of such electrode. $Ni(OH)_2$ as an active material is widely used as a Faradic electrode of hybrid supercapacitors. Nickel hydroxide is used on its own [3] as a nanosized [4] or ultradisperse powder [5], and as composites with nanocarbon materials [6, 7].

Supercapacitors should employ highly effective nickel hydroxide. The electrochemical activity of $Ni(OH)_2$ is

determined by the type of nickel hydroxide, particle size and aggregate breakdown ability during cycling [8]. These parameters depend on the synthesis method and conditions. However, the influence of synthesis parameters on structure, morphology and particle size is not sufficiently studied, which complicated the synthesis of highly active $Ni(OH)_2$. Studying the influence of synthesis conductions on the characteristics of nickel hydroxide is a relevant problem, as it would allow developing a directed method for the synthesis of highly effective $Ni(OH)_2$ designed for specific application.

2. Literature review and problem statement

Micro- and macrostructure of nickel hydroxide particles, which significantly affect electrochemical properties, are directly affected by the synthesis method and conditions. Synthesis conditions influence the inhomogeneity of the crystal lattice [9], microstructure [10], crystallinity [11, 12].

The synthesis method primarily determines the type of $Ni(OH)_2$ [13]. Nickel hydroxide has two allotropes: β-hydroxide (chemical formula $Ni(OH)_2$, brucite structure) and α-hydroxide (chemical formula $3Ni(OH)_2{\cdot}2H_2O$, hydrotalcite-like structure). At the same time, the paper [14] states that there is a range of intermediate structures of nickel hydroxide in-between α-$Ni(OH)_2$ and β-$Ni(OH)_2$.

α-$Ni(OH)_2$ possesses better electrochemical characteristics than β-$Ni(OH)_2$. However, its stability is significantly lower: in concentrated solutions of the base, and especially at high temperature, the metastable α-form transforms into the β-form [15], which leads to the loss of capacity. α-$Ni(OH)_2$ and nickel-based layered double hydroxides (LDH) can be prepared using various methods: direct and reverse chemical synthesis (titration method) [16], homogeneous precipitation [16, 17], electrochemically in a slit-diaphragm electrolyzer [18] and catholically directly onto a substrate [19, 20].

β-$Ni(OH)_2$ possesses high cycling stability and is widely used as an active material in accumulators [21] and supercapacitors [21, 22]. β-$Ni(OH)_2$ can be prepared chemically [21, 24], electrochemically in a slit-diaphragm electrolyzer and directly on the substrate surface [23]. High-temperature synthesis is also used [25, 26].

The modern trend is the application of $Ni(OH)_2$ with mixed α/β form, which has the advantages of both phases [27, 28]. Paper [29] describes the formation of highly effective nickel hydroxide, which has a layered structure of (α+β) phases but is not a mixture of these two forms. The hydroxide sample was synthesized electrochemically in a slit-diaphragm electrolyzer (SDE) from a nickel sulfate solution. The high electrochemical activity of this nickel hydroxide sample, which exceeds the activity of β-$Ni(OH)_2$ and α- $Ni(OH)_2$, has been discovered. The use of this layered (α+β) nickel hydroxide is rather promising, especially if its electrochemical characteristics are to be improved.

It should be noted that main parameters of high electrochemical activity of nickel hydroxide for use in supercapacitors are α or (α+β) phase, optimal not high crystallinity, small particle size and ability of its agglomerates to be broken into smaller components [8]. These parameters can be achieved in various ways. Paper [29] describes that during synthesis in SDE, nickel hydroxide has a matrix structure similar to organic [30] or inorganic [31] composite materials. Nickel hydroxide acts as a micelle-forming agent with the filler being the mother liquor. A promising approach to influence the forming hydroxide is the use of templates and ultrasound irradiation.

The template compounds are used to decrease particle size and for the creation of micro- and mesopores. The mechanism of template synthesis is that the template forms a 3-D matrix with nickel hydroxide forming inside of its cells. The template can be employed in any synthesis method, including homogeneous precipitation [17] and cathodic deposition [32, 33].

The ultrasound treatment prevents the aggregation of $Ni(OH)_2$ particles and alters their structure. Ultrasound can be applied during the synthesis of α-$Ni(OH)_2$ [34, 35], and also for β-$Ni(OH)_2$ [36, 37]. This allows for the controlled synthesis with the selection of α or β form [38]. When synthesizing β-$Ni(OH)_2$ using ultrasound, the formation of the hydroxide with nanosized [39] or microsized particles [40] or mesoporous hydroxide [41] is possible.

Thus, the positive influence of ultrasound treatment and use of template synthesis on the electrochemical properties of the synthesized hydroxide has been described. It should be noted that the influence of these factors had been studied only for the chemical synthesis method. It is known that nickel hydroxide formation is complex and consists of two stages [42]: fast formation of the primal amorphous particle and slow ageing (crystallization). As a result, even a slight change in synthesis conditions can lead to radical changes in the characteristics of $Ni(OH)_2$. Because of that, a large number of synthesis methods have been proposed and many nickel hydroxide samples with different characteristics have been prepared [43]. The synthesis method in a slit diaphragm electrolyzer described in the papers [8, 45] is unique and has no analogues in the world. During synthesis in SDE, nickel hydroxide is formed while moving through a cathodic slit. At the same time, the particle moving through the SDE also goes through the heat field, which causes partial crystallization. This results in the formation of a unique (α+β) layered structure with high electrochemical activity, which was described in the paper [29]. It should be noted that the synthesis in SDE is continuous, which allows for the synthesis of nickel hydroxide with constant characteristics. The increase in the electrochemical activity of $Ni(OH)_2$, prepared in SDE using template synthesis and ultrasound treatment is a promising approach. However, the influence of the template and ultrasound on the characteristics of nickel hydroxide prepared under unique conditions in SDE has not been studied.

3. The aim and objectives of the study

The aim of the work is to study the influence of the template and ultrasound treatment on physico-chemical and electrochemical characteristics of nickel hydroxide electrochemically synthesized in SDE.

To achieve the set aim, the following objectives were stated:

– to conduct the synthesis of nickel hydroxide samples in SDE in the presence of the template, with ultrasound treatment and combined influence of the template and ultrasound, and also without them;

– to study structural, surface and electrochemical characteristics of the prepared samples and evaluate the influence of the added template and ultrasound treatment;

– to conduct a comparative analysis of the sample characteristics and evaluate the effectiveness of the template

additive and ultrasound treatment for the preparation of $Ni(OH)_2$ with high electrochemical activity.

4. Materials and methods employed for the synthesis of samples and study of their characteristics

4. 1. Choice of a template for nickel hydroxide synthesis

Template synthesis of compounds from aqueous solutions requires the use of water-soluble polymers. For this research, it was proposed to use polyvinyl alcohol (PVA) as a template. The prospect of using PVA as a template is supported by its broad application as an agent for controlling porosity for the synthesis of mesoporous alumina [45], hydroxyapatite crystals (in combination with sodium dodecylsulfate) [46]. PVA is also used for the synthesis of mesoporous MFI zeolite (as a secondary template) [47], multilayer coating based on nickel and cobalt hydroxide [48], 3D-structured macroporous oxide and hierarchic zeolite for catalysis [49].

4. 2. Nickel hydroxide synthesis

Labeling of nickel hydroxide samples prepared under different conditions is presented in Table 1. A detailed description of synthesis conditions is given below.

Table 1

Labeling of nickel hydroxide samples

Sample	Lable
$Ni(OH)_2$, without PVA and ultrasound treatment	S0.2-12
$Ni(OH)_2$ with ultrasound treatment	S0.2-12 US
$Ni(OH)_2$ in the presence of PVA	S0.2-12 PVA
$Ni(OH)_2$ in the presence of PVA and ultrasound treatment	S0.2-12 US+PVA

Base synthesis method. The base synthesis method [8] is based on electrolysis conducted in a flow-through slit-diaphragm electrolyzer (SDE). The cathodic chamber was fed with a nickel sulfate solution (Ni^{2+} concentration of 12.7 g/L) using a peristaltic pump, anodic chamber – NaOH solution (concentration of 50 g/L), with an equal feed rate of 0.2 l/h. Cathode – titanium, anode – nickel (insoluble). The synthesis was carried out at a current density of 12 A/dm^2.

When current passes through the cathode, hydrogen evolution occurred, resulting in the formation of hydroxyl anions, which reacted with nickel cations in the volume, resulting in the formation of nickel hydroxide precipitate. The precipitate was removed from the electrolyzer with the catholyte flow. The hydroxide was separated from the catholyte immediately after leaving the electrolyzer by vacuum filtration. The hydroxide samples were dried at 90 °C for a day, ground, sifted through a 71 μm sieve, washed from soluble salts and dried again under the same conditions.

Synthesis method with the template. For the synthesis of nickel hydroxide sample in the presence of the template, 1 % (wt.) of PVA was added to the catholyte (nickel sulfate). Nickel hydroxide synthesis and treatment were the same as for the base method.

Synthesis method with ultrasound treatment. For the preparation of the nickel hydroxide sample, it was proposed to conduct ultrasound treatment of $Ni(OH)_2$ suspension in the mother liquor immediately after it left the SDE. The outlet was connected to a special cell (Fig. 1).

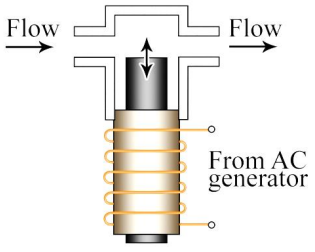

Fig. 1. Schematic of the cell for ultrasound treatment of nickel hydroxide

A magnetostriction ultrasound emitter was placed perpendicular to the flow of suspension. The treatment was conducted across the channel at 21.5 kHz and power density of 4 W/cm^3, the average time for which hydroxide particles were subjected to ultrasound treatment was 35 s.

4. 3. Study of characteristics of nickel hydroxide samples

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

The surface morphology of nickel hydroxide samples was studied using the scanning electron microscope REMMA 120-02 (Ukraine).

The specific surface area was determined using the BET method by means of low-temperature nitrogen adsorption using the high-speed gas sorption analyzer Quantochrome Corp., NOVA 2200 E.

Electrochemical properties of nickel hydroxide samples were studied by means of galvanostatic charge-discharge cycling in a special cell YSE-2 (USSRA) using the digital potentiostat Ellins P-8 (Russia). The working electrode was prepared by pasting a mixture of a nickel hydroxide sample (82.5 % wt.), graphite (16 % wt.) and PTFE (1.5 % wt.) [50] onto the nickel foam current collector. Electrolyte – 6M KOH. Counter-electrode – nickel mesh, reference electrode – Ag/AgCl (KCL sat.). Charge-discharge cycling was conducted in the supercapacitor regime at current densities of 20, 40, 80 and 120 mA/cm^2 (10 cycles at each current density). The specific capacity C_{sp} (F/g) was calculated from discharge curves.

5. Results of studying the influence of the template and ultrasound treatment on the characteristics of nickel hydroxide samples

Fig. 2 shows XRD patterns of different nickel hydroxide samples prepared by the base synthesis method, in the presence of PVA as a template and with ultrasound treatment. Sample S0.2-12 is a layered (α+β) $Ni(OH)_2$ with low crystallinity. The presence of PVA as a template leads to a significant decrease of crystallinity, resulting in an almost X-ray amorphous sample. Ultrasound treatment (sample S0.2-12 US) also lowers crystallinity, but to a lower extent. Additionally, an increase of the α-phase content is observed in the layered (α+β) structure, which is indicated by the increased intensity of peaks at 12–13° angles. At combined

influence of PVA and ultrasound (sample S0.2-12 US+PVA), the hydroxide type and crystallinity are similar to sample S0.2-12 PVA.

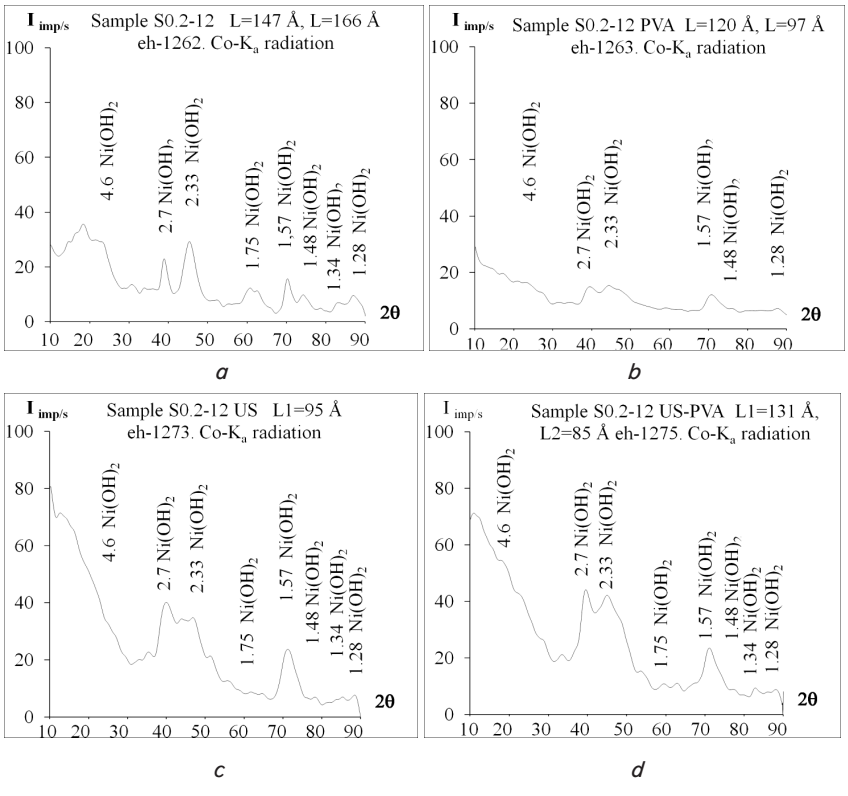

Fig. 2. XRD patterns of nickel hydroxide samples:
a – S0.2-12, *b* – S0.2-12 PVA; *c* – S0.2-12 US; *d* – S0.2-12 US+PVA

Fig. 3 shows SEM images of different $Ni(OH)_2$ samples. It should be noted that sample S0.2-12 is composed of agglomerated particles covered with smaller sharp hydroxide particles.

The introduction of the template and the use of ultrasound don't have a major effect on surface morphology. Ultrasound treatment (sample S0.2-12 US) led to a decreased number of smaller particles on the surface of larger particles and exposure of angles and edges of large particles.

Table 2 shows specific surface area, volume and pore radius for different samples of nickel hydroxide. It should be noted that the synthesis of nickel hydroxide in the presence of PVA as a template (sample S0.2-12 PVA) resulted in a lower specific surface area of 13 m^2/g (in comparison to 81 m^2/g for sample S0.2-12) and some reduction of the average pore diameter.

Ultrasound treatment results in a more significant decrease in S_{sp} – to 6 m^2/g for samples S0.2-12 US and S0.2-12 US+PVA. A significant increase of the average pore diameter is observed after ultrasound treatment: 1180 Å for sample S0.2-12 US+PVA and 562 Å for sample S0.2-12 US (in comparison to 36 Å for sample S0.2-12).

Table 2
Results of studying the porous structure of samples using the BET method

Sample	S_{sp}, m^2/g	Pore volume, cm^3/g	Average pore radius, Å
S0.2-12	81	0.15	36
S0.2-12 US	6	0.17	562
S0.2-12 PVA	13	0.16	24
S0.2-12 US+PVA	6	0.36	1,180

Fig. 4 shows specific capacities of different $Ni(OH)_2$ samples. It should be noted that sample S0.2-12, prepared electrochemically without the introduction of PVA and use of ultrasound treatment, shows a sharp increase in specific capacity with an increase of current density from 33 F/g at 20 mA/cm^2 to 307 F/g at 120 mA/cm^2. For samples prepared with the addition of PVA as a template and with the use of ultrasound treatment (S0.2-12 US, S0.2-12 PVA and S0.2-12 US+PVA), the nature of the dependency of specific capacity on current density changes.

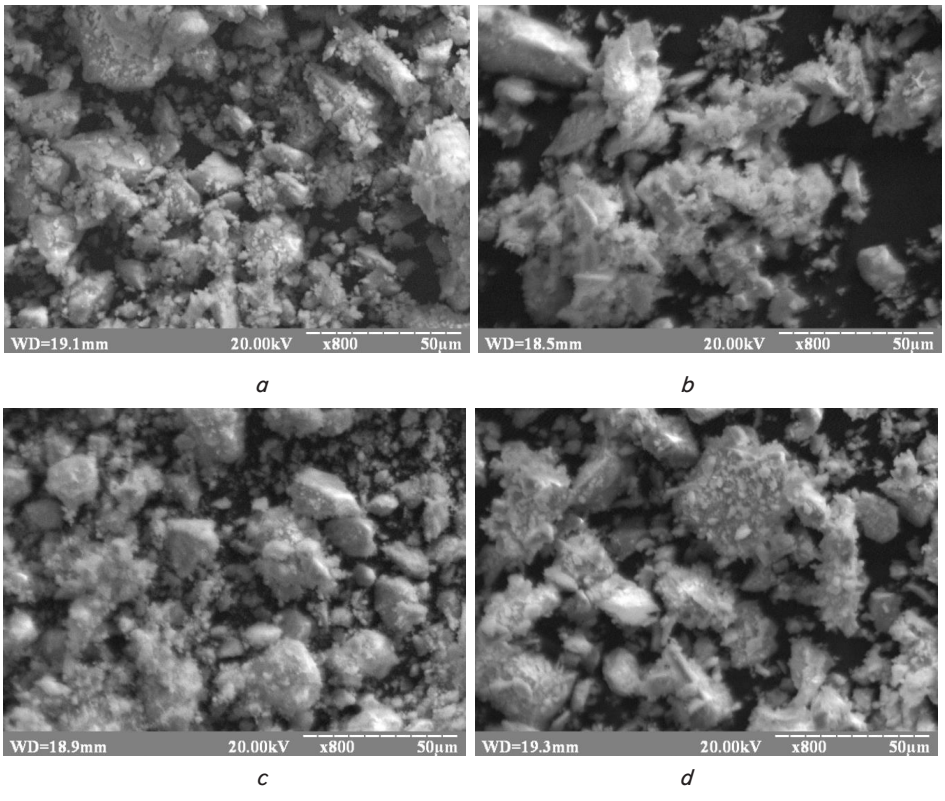

Fig. 3. SEM images of different nickel hydroxide samples:
a – S0.2-12, *b* – S0.2-12 PVA; *c* – S0.2-12 US; *d* – S0.2-12 US+PVA

The specific capacity increases at first, reaching its maximum, and decreases with further increase of current density. The maximum values of specific capacity for all samples are observed at i=40 mA/cm^2 and are 119 F/g (sample S0.2-12 US), 196 F/g (sample S0.2-12 PVA) and 243 F/g (sample S0.2-12 US+PVA).

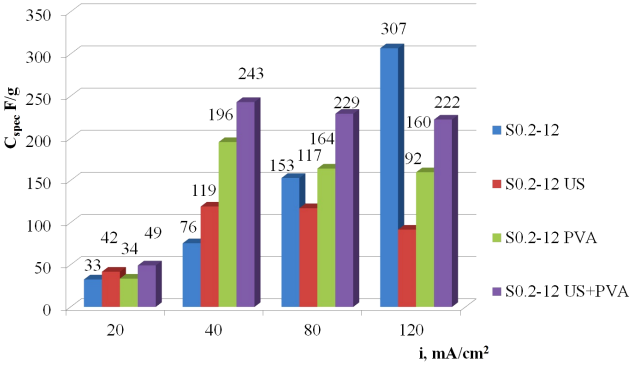

Fig. 4. Specific capacities of different nickel hydroxide samples, F/g

In the sample series "S0.2-12 US – S0.2-12 PVA – S0.2-12 US+PVA", the specific capacity increases at any current density. At i=120 mA/cm^2, the specific capacity of sample S0.2-12, prepared without the template and ultrasound exceeds specific capacities of the samples prepared in the presence of PVA as a template and with ultrasound treatment.

6. Discussion of the results of studying the influence of the template and ultrasound treatment on the characteristics of nickel hydroxide samples

Influence of the template and ultrasound treatment on the crystal structure of nickel hydroxide samples. The results of XRD analysis (Fig. 2) have revealed that the introduction of PVA as a template to the catholyte results in a significant decrease of crystallinity of nickel hydroxide samples. This is because the template prevents aggregation of primary hydroxide particles. The ultrasound treatment also results in a decrease of crystallinity, but to a lesser extent than the template. This results in the formation of (α+β) structure with the increased content of α-form. This is probably explained by the fact that ultrasound treatment allows adding energy to the primal amorphous particles of $Ni(OH)_2$, which stabilizes metastable α-forms.

Influence of the template and ultrasound treatment on the surface morphology of nickel hydroxide particles and their porous structure. SEM images have revealed, that sample S0.2-12, prepared without ultrasound and template consists of shards 20–40 μm in size, covered with small needle-like particles. They also revealed that ultrasound treatment significantly decreases the number of small needle-like particles on the surface of bigger ones. This can lead to a decrease of specific surface area of the samples during ultrasound treatment. This conclusion is supported by the results of studying the porous structure using the BET method. The application of ultrasound decreases specific surface area 13.5 times. However, the average pore radius increases 15.6 times (sample S0.2-12 US) and 32.8 times (for sample S0.2-12 US+PVA). When using ultrasound treatment, it was assumed that possible dispersion of nickel hydroxide would occur. However, the cavitation phenomena most likely knocked-off small needle-like particles from the surface and lead to partial condensation of primal amorphous particles. Possibly, the power of ultrasound treatment was insufficient to pulverize the particles. The decrease of the specific surface area and average pore radius during synthesis in the presence of the template (sample S0.2-12 PVA) can indicate that PVA as a template is not washed out from the prepared sample and blocks the part of the active surface, which can result in a decrease of the specific surface area.

Influence of the template and ultrasound treatment on electrochemical characteristics of nickel hydroxide samples. Analysis of the data presented in Fig.4, shows that specific capacity of sample S0.2-12, prepared electrochemically without the introduction of PVA and application of ultrasound treatment shows a significant increase of capacity by 9.2 times (from 33 F/g to 307 F/g) with an increase of current density from 20 mA/cm^2 to 120 mA/cm^2. This is explained by the breakdown of particle agglomerates of nickel hydroxide with an increase of the active surface. The results of XRD analysis have revealed a decrease in crystallinity and an increase of the α-form content when PVA was introduced as a template and when ultrasound treatment was employed, which should have led to an increase of electrochemical activity of samples S0.2-12 US, S0.2-12 PVA and S0.2-12 US+PVA. However, this is only observed at low current densities (20–40 mA/cm^2). When cycling current density is increased, the specific capacity of sample S0.2-12 increases more rapidly, and at i=120 mA/cm^2 exceeds specific capacities of samples prepared with the template and ultrasound. For samples S0.2-12 US, S0.2-12 PVA and S0.2-12 US+PVA, the nature of the dependency of specific capacity on current density changes. The specific capacity increases at first, reaching its maximum, and decreases with further increase of current density. This indicates difficulties in the breakdown of agglomerated particles into smaller ones. In case when PVA was introduced as a template, this difficulty can be explained by the binding effect of the remaining template, which was not removed during washing. In order to avoid this negative effect, a choice of a more easily removable template is suggested. The difficulty in the particle breakdown in case of ultrasound treatment is explained by condensation of the formed particles. This is likely a result of employing ultrasound treatment on already formed particles of nickel hydroxide. For further research, in order to avoid this effect it is suggested to conduct an electrochemical synthesis of $Ni(OH)_2$ in SDE directly in the ultrasound field of higher power and select a different template.

7. Conclusions

1. The structure, surface morphology, porosity and electrochemical properties of samples synthesized in a slit-diaphragm electrolyzer with the introduction of PVA as a template and ultrasound treatment, and also without them, were studied. It was revealed that the sample synthesized without ultrasound and template has a layered (α+β)-structure of low crystallinity. The particles of this sample are of shard type, with their surface covered with significantly smaller needle-like particles. It has been revealed that the introduction of polyvinyl alcohol as a template leads to an significant decrease of crystallinity. The ultrasound treatment of the nickel hydroxide suspension directly after it

was removed from the slit-diaphragm electrolyzer leads to a insignificant decrease of crystallinity, increased content of α-form, and significant decrease of the specific surface area and increase in the pore diameter. The combined influence of PVA as a template and ultrasound treatment is similar to the influence of ultrasound alone, but with an even further increase in the average pore radius. The high electrochemical activity of samples synthesized with PVA and ultrasound has been discovered. The maximum specific capacity of 243 F/g was obtained for samples synthesized with the template and ultrasound treatment at a current density of 40 mA/cm^2.

2. A comparative analysis of characteristics of $Ni(OH)_2$ samples, synthesized with the addition of the template (PVA) and the use of ultrasound treatment has been conducted. Both positive and negative influence of these factors on the electrochemical activity of the samples has been discovered. Application of the template and ultrasound decreases crystallinity and increases the content of α-form, which results in the increased capacity of the samples. However, this effect is observed at low current densities. At higher current densities, a decrease of capacity is observed, which is because of difficulties in the breakdown of agglomerated particles into smaller components. In case of the introduced template, this is explained by the binding effect of the remaining PVA, and in case of ultrasound treatment – particle condensation resulted from cavitation phenomena.

3. In order to avoid negative effects on electrochemical activity, it is recommended to replace the template with a more easily removable one and also conduct an electrochemical synthesis of $Ni(OH)_2$ in SDE directly in the ultrasound field of higher power.

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