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SYNTHESIS OF Ni(OH)$_2$ BY TEMPLATE HOMOGENEOUS PRECIPITATION FOR APPLICATION IN THE BINDER-FREE ELECTRODE OF SUPERCAPACITOR.

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
*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
**Ukrainian State University of
Chemical Technology
Gagarina ave., 8, Dnipro, Ukraine, 49005

Гідроксид нікелю широко використовується як активна речовина гібридних суперконденсаторів. Найбільш електрохімічно активним є α-Ni(OH)$_2$, синтезований темплатним гомогеним осажденням. Недоліком об'ємного темплатного синтезу є включення темплату в склад гідроксиду та необхідність його видалення. Для перетворення недоліку в перевагу було запропоновано визначити можливість використання залишкової кількості темплату в якості внутрішнього зв'язуючого для виготовлення високоефективного намазного електроду суперконденсатора без введення зовнішнього зв'язуючого. Для цього були отримані зразки Ni(OH)$_2$ методом темплатного гомогенного осадження при використанні в якості темплата полівінилового спирту та естеру целюлози Culminal C8465 з концентраціями 0,05 % і 0,5 %.

Структурні властивості зразків були вивчені методом рентгенофазового аналіза, розміри та морфологію частинок – методом скануючої електронної мікроскопії. Електрохімічні характеристики вивчались гальваностатичним зарядно-разрядним циклюванням намазного електрода, виготовленого без введения зв'язуючого, в режимі суперконденсатора.

Виявлено, что при використанні ПВС кристалічність суттєво вища, а частинки не утворюють крупних агрегатів. Збільшення концентрації ПВС в 10 разів не вплинуло на дані характеристики. При використанні Culminal C8465 кристалічність зразків нижча, при підвищенні концентрації вона збільшується. Збільшення концентрації Culminal C8465 також призводить до значної агрегації частинок. Показано різну поведінку ПВС та Culminal C8465. ПВС має слабку дію як зв'язуюча речовина, а Culminal C8465 має високі зв'язуючі характеристики. Комплексним анализом електрохімічних характеристик намазних електродів, виготовлених без введения зовнішього зв'язуючого, доведена можливість використання залишкових кількостей темплата в якості внутрішнього зв'язуючого. Максимально отримана питома ємність для електрода без зовнішнього зв'язуючого склала 197 Ф/г при використанні в якості темплата Culminal C8465. Рекомендовано провести вибір для синтезу гідроксиду нікелю водорозчинного ВМС, здатного бути темплатом при синтезі та зв'язуючим при виготовленні намазного електроду

Ключові слова: гідроксид нікелю, темплатний синтез, гомогенне осадження, суперконденсатор, зв'язуюче

1. Introduction

In the modern world, supercapacitors (SC) are a new type of chemical power sources (CPS). They are used for starting of electrical motors in various devices: pump stations, electromobiles, electric locomotives, tools, etc. SC are also used as starting CPS for ignition of gas and diesel engines, as back-up power supplies for computer, medical equipment and various devices. Hybrid supercapacitors possess the best characteristics. Because of high charge and discharge rates of the hybrid supercapacitor electrode, the electrochemical reaction occurs on the surface and in a thin layer of particles of active material. Thus, there are special requirements to active material of Faradic electrode, regarding specific surface area, crystal structure and electrochemical activity [1, 2]. In particular, the active material should be mainly composed of nano- and submicron-sized particles with a high specific surface area. Ni(OH)$_2$ is widely used as the active material of Faradic electrode of supercapacitors. Nickel hydroxide is employed on its own [3], as nanosized [4] or ultrafine powder [5], and as a composite with nanocarbon material, (graphene oxide [6], carbon nanotubes [7]).

Many methods have been proposed for synthesis of nickel hydroxide and nickel-based layered double hydroxides [8]. Obtaining is possible by direct chemical precipitation (slow addition of basic solution to a solution of nickel salt) [9] or reversed synthesis (slow addition of nickel salt solution to a solution of a base) [10, 11], and also two-step high-temperature synthesis [12] or sol-gel method [13]. Electrochemical methods are also used for the synthesis of nickel hydroxide [14, 15], including synthesis in the slit diaphragm electrolyzer [16, 17].

Polymorphism is characteristic of nickel hydroxide and two structural modifications have been described [18]. β-form (formula $Ni(OH)_2$, brucite-like crystal structure) and α-form (formula $3Ni(OH)_2 \cdot 2H_2O$, hydrotalcite-like crystal structure). β-$Ni(OH)_2$ has high cycling stability and is widely used as the active material of accumulators and supercapacitors. α-$Ni(OH)_2$ has significantly higher electrochemical characteristics in comparison to β-$Ni(OH)_2$, and can be used in supercapacitors more effectively. Thus, development and optimization of synthesis methods for preparation of highly active α-$Ni(OH)_2$ are relevant problems.

2. Literature review and problem statement

Synthesis method and its conditions directly define the micro- and macrostructure of particles, which determines the electrochemical activity of nickel hydroxide. For effective application in supercapacitors, nickel hydroxide should have specific properties [19], particularly, it should be α-$Ni(OH)_2$ with optimal crystallinity and submicron- [5] and nano-sized [4, 20] particles.

The nickel hydroxide synthesis reaction can be summarized by the equation:

$$Ni^{2+}+2OH^{-}\rightarrow Ni(OH)_2. \quad (1)$$

For this reaction, the nucleation rate significantly exceeds the rate of crystal growth. Formation mechanism for nickel hydroxide consists of two stages [21]: the first stage (very fast) – formation of the initial amorphous particle; the second stage (slow) – crystallization (ageing) of the initial particle. This results in the formation of a hydrophilic precipitate that contains a large amount of mother liquor. During filtering (especially under vacuum), the precipitate particles are pressed and are caked during subsequent drying, which leads to a significant increase in particle size and a decrease in specific surface area. Two approaches can be used to prevent that:

1) use of a synthesis method with low nucleation rate and a very high rate of crystal growth;

2) addition of special compounds that would prevent merging of initial particles.

The first approach can be realized by means of homogeneous precipitation [22]. The basis is the formation of OH^- ions in the solution volume as a result of thermal hydrolysis of ammine compounds (urea [23, 24], hexamethylenetetramine [25]). Homogeneous precipitation can be conducted in aqueous solutions and mixed solvents [26] or non-aqueous solvents like ionic liquids [27]. For the preparation of ultrafine or nano-sized hydroxide, homogeneous precipitation should be conducted at elevated temperatures up to 150–180 °C. Microwave heating is employed for the same reason [28].

The second approach is realized by the application of surfactants [28] or templates. This is a so-called template synthesis, i. e. synthesis of the compound inside the matrix (template). This method is usually applied for the formation of coats such as electrochromic $Ni(OH)_2$ films [29, 35], tripolyphosphate coats [30] or direct formation of Faradic electrode on the surface of the nickel foam [36]. This results in the formation of composite materials similar to polymer composites [31]. The paper [37] describes the application of water-soluble templates for synthesis of nickel hydroxide.

The most promising approach is a combination of homogeneous precipitation and template synthesis. PEG6000 [33] and Culminal C8465 [38] have been proposed as water-soluble templates.

However, template synthesis has a significant disadvantage. After synthesis, it is of importance to remove the template. Difficulties with template removal led to the whole template-free direction for the preparation of ultrafine systems. For supercapacitor applications, the presence of a template in the active material can lead to partial blocking of the material surface, template oxidation and other side-effects. From this point of view, it is of most importance to remove as much template as possible from the active material, particularly from nickel hydroxide. However, when preparing a pasted supercapacitor electrode, a binder is added to the active mass [34], to prevent it from falling off from the current collector. However, the binder is an inert component of the active mass, which lowers its specific characteristics. The binder is also introduced in the form of a suspension or emulsion and requires special conditions for storage and application.

Because of this, there is also a possibility of using the remaining template as a binder for the preparation of the pasted electrode. It should be noted that there are almost no papers regarding this problem, which is relevant for the synthesis of active materials for supercapacitors and other applications.

3. The aim and objectives of the study

The aim of the work is to evaluate the possibility of using nickel hydroxide synthesized by template homogeneous precipitation for the preparation of a highly effective pasted supercapacitor electrode without an additional binder.

For achieving the set aim, the following objectives were formulated:

– to prepare nickel hydroxide samples with different water-soluble templates in different concentrations for homogeneous precipitation;

– to study the influence of templates on the crystal structure, morphology and particle size of prepared samples at the synthesis stage;

– using the synthesized samples, to prepare pasted supercapacitor electrodes without the addition of a binder and to study their electrochemical characteristics;

– to conduct a comparative analysis in order to evaluate the possibility of using template remains as the inner binder for the preparation of a highly active pasted Faradic electrode for the hybrid supercapacitor.

4. Materials and methods for synthesis and analysis of nickel hydroxide samples

4. 1. Templates used for homogeneous precipitation of $Ni(OH)_2$

The template for the synthesis of nickel hydroxide from aqueous solution must meet a few requirements. It must be a water-soluble high-molecular compound and have a chemical affinity towards nickel compounds. Two water-soluble templates for the formation of a 3D matrix were proposed. Based on [38], cellulose ester Culminal C8564, which forms a 3D matrix when dissolved in water, was chosen as the first template. As the second template, it was proposed to use polyvinyl alcohol (PVA). The prospect of using PVA is supported by its wide application as a porosity-controlling agent in the synthesis of mesoporous alumina [39], hydroxyapatite crystals (in combination with sodium dodecylsulfate) [40].

PVA is also used:

– for the synthesis of mesoporous MFI zeolite [41];

– MgO for dye removal from wastewater [42];

– formation of mono- [43, 44] and multilayer [45] films based on nickel and cobalt hydroxide;

– 3D-structured macroporous oxides and hierarchic zeolites used in catalysis [46];

– for improving the adhesion of films on the surface of ITO [47].

Both compounds have hydroxyl groups in their structure, which can interact with nickel hydroxide because of weak coordination interactions.

4. 2. Preparation of nickel hydroxide samples

For the synthesis of the reference $Ni(OH)_2$ sample, homogeneous precipitation by urea hydrolysis was employed. The synthesis procedure is described in the literature [18]: the solution containing 60.9 g/L $Ni(NO_3)_2{\cdot}6H_2O$ and 229.3 g/L urea was heated in a water bath for 3 hours. The temperature of the solution was kept at 85 °C. After the synthesis procedure was finished, the solution was poured into a large volume of distilled water to quench the reaction. For template homogeneous precipitation, the Culminal C8465 and PVA templates were added to the synthesis solution with the concentration of 0.05 % and 0.5 % (wt). Sample labels are listed in Table 1.

Table 1

Labels of nickel hydroxide samples and template concentrations

Label	0*	1–0.05	1–0.5	2–0.05	2–0.5
Template	–	PVA	PVA	Culminal C8465	Culminal C8465
Template concentration, wt. %	0	0.05	0.5	0.05	0.5

*Note: * – reference sample prepared without the template*

After synthesis, the prepared samples were filtered, dried at 60 °C, ground, sifted through a nickel mesh, washed with distilled water from soluble salts and dried again.

4. 3. Characterization of nickel hydroxide samples

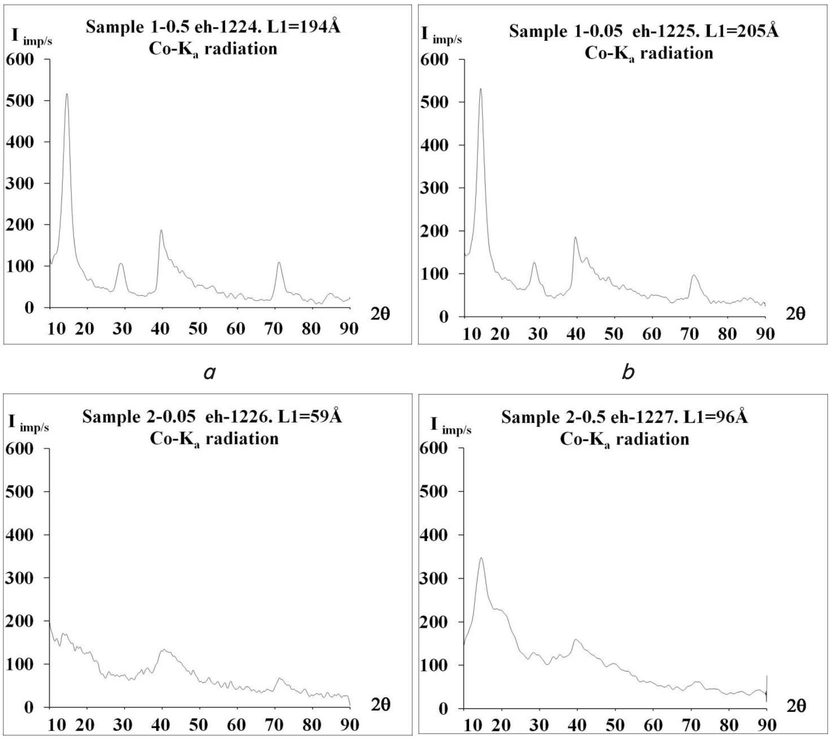
The crystal structure of the samples was studied by means of X-ray diffraction analysis (XRD) using the DRON-3 diffractometer (Russia) (Co-Kα, radiation, scan range 10–90° 2θ, scan rate 0.1°/s).

The shape and size of the particles were studied using the scanning electron microscope 106 – I (SELMI, Ukraine).

Electrochemical properties of nickel hydroxide were evaluated by means of galvanostatic charge-discharge cycling in a special cell YSE (USSR) using the digital potentiostat Ellins P-8 (Russia). The working electrode was prepared by pasting a mixture of nickel hydroxide (84 % wt,) and graphite (16 % wt.) onto the nickel foam matrix. The binder was not introduced to the active mass. For sample 0, 3 % of PTFE was used as a binder [34]. 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 (15 cycles at each current density). Discharge curves were used to calculate specific capacities C_{sp} (F/g) for discharge to 0 V and full discharge.

5. Results of studying the characteristics of nickel hydroxide samples synthesized with templates with different concentrations

The results of XRD analysis (Fig. 1) show that the samples prepared with PVA (1-0.5 and 1-0.05) have higher crystallinity than those synthesized in the presence of Culminal C8465 (2-0.5 and 2-0.05). It should also be noted that in case of PVA increasing template concentration by 10 times (from 0.05 % to 0.5 %) has almost no effect on crystallinity, but in case of Culminal C8465, this leads to a notable increase.

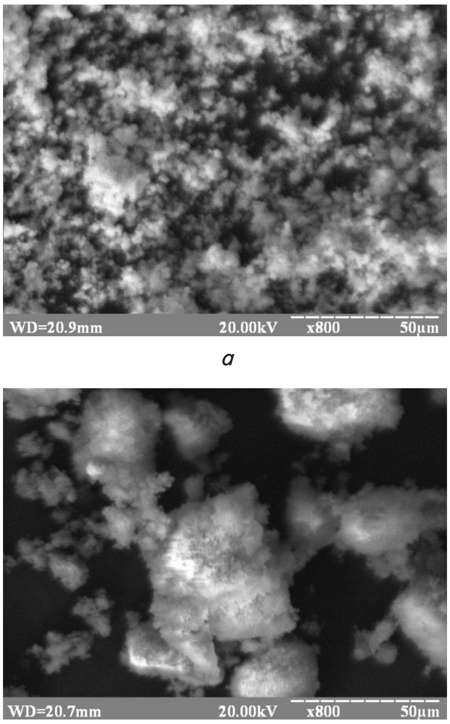


a *b*

c *d*

Fig. 1. XRD samples of nickel hydroxide samples: *a* – 1–0.5; *b* – 1–0.05; *c* – 2–0.05; *d* – 2–0.5

Fig. 2 shows SEM images of the samples prepared in the presence of 0.5 % PVA (sample 1–0.5) and 0.5 % Culminal C8465 (sample 2–0.5). It is noted that the Culminal C8465 template leads to a smaller size of the initial particles, but it also intensifies agglomeration. With PVA, agglomeration almost does not occur. At low template concentrations, the particles of samples 2–0.05 and 1–0.05 are almost identical.



a

b

Fig. 2. SEM images of nickel hydroxide samples: *a* – 1–0.5; *b* – 2–0.5

Fig. 3 shows specific capacities of different nickel hydroxide samples at different current densities of charge-discharge cycling in the supercapacitor regime.

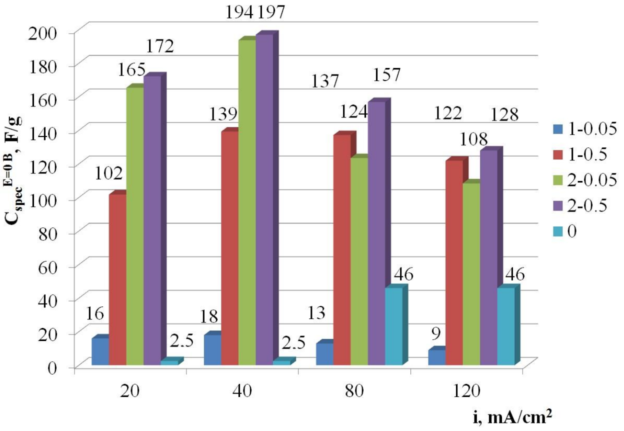


Fig. 3. Specific capacity of nickel hydroxide samples at different current densities of galvanostatic charge-discharge, F/g

It should be noted that the reference sample 0, which was prepared without the template, showed a very low specific capacity of 2.5 F/g at current densities of 20 and 40 mA/cm^2, and only after increasing the current density to 80 and 120 mA/cm^2 the specific capacity increased to 46 F/g. Sample 1–0.05 showed a very low specific capacity of 13–18 F/g, which at i=120 mA/cm^2 dropped to 9 F/g. Sample 1–0.5, synthesized with 0.5 % PVA, shows an increase in the specific capacity with an increase of the cycling current density from 20 to 40 mA/cm^2, however, with a further increase of the current density to 120 mA/cm^2, the capacity decreases. Similar dependency is also characteristic for samples 2–0.05 and 2–0.5, synthesized with Culminal C8465. The maximum capacity is also observed at 40 mA/cm^2 and drops at higher current densities. It should be noted; that the samples synthesized in the presence of Culminal C8465 have significantly higher capacities than the samples synthesized in the presence of PVA (at the same concentrations). The specific capacities of samples 1–0.05, 2–0.05 and 2–0.5, used in the pasted electrode without binder, significantly exceed specific capacities of the reference sample 0, pasted into the electrode with 3 % PTFE as a binder. The obtained specific capacity values are comparable to the world's best samples [4, 5, 24].

6. Discussion of the study results of nickel hydroxide samples synthesized with different template concentrations

Influence of the template and its concentration on crystallinity of samples. The XRD patterns presented in Fig. 1 revealed that all samples are α-$Ni(OH)_2$. The influence of PVA and Culminal C8465 on crystallinity is fundamentally different. The use of PVA (samples 1–0.5 and 1–0.05) resulted in significantly higher crystallinity than with Culminal C8465 (samples 2–0.5 and 2–0.05). In addition, an increase in the PVA concentration by 10 times almost has not affected the crystallinity. PVA probably forms a 3D matrix with a larger cell size than Culminal C8465. In case of Culminal C8465, an increase in concentration by 10 leads to higher crystallinity. This is in agreement with the literature [38], in which it is described that an increase in the Culminal C8465 concentration leads to a higher temperature in the reaction solution, resulting in a higher thermal effect on nickel hydroxide particles.

Influence of the template and its concentration on morphology and particle size. For template homogeneous precipitation, it was discovered that a significant part of the precipitate passes through a paper filter with the pore diameter of 70 μm. Therefore, for all further experiments, filtering was carried out using microfiltration membranes "Vladipore". It was observed that the samples prepared in the presence of PVA (1–0.5 and 1–0.05) were more difficult to filter than the samples prepared in the presence of Culminal C8465 (2–0.5 and 2–0.05). Additionally, high template concentrations lead to longer filtering time, which indicates a smaller particle size. This conclusion is supported by the results of scanning electron microscopy (Fig. 2), which reveals higher particle aggregation at the Culminal C8465 concentration of 0.5 % (sample 2–0.5). At the same time, for sample 1–0.5, prepared in the presence of PVA with the same concentration, the formation of large aggregates is not observed. Visual observation and SEM results allow concluding that PVA and Culminal C8465 behave fundamentally differently as templates for homogeneous precipitation of nickel hydroxide. PVA most likely plays the role of a physical template, which almost doesn't react with the forming nickel hydroxide and does not show binder properties as it does not cause particle aggregation. At the same time, Culminal C8465, in addition to the formation of a 3D matrix, probably also reacts with the forming hydroxide and beehives like a binder resulting in particle aggregation, especially at a high concentration.

Influence of the template and its concentration on specific capacity of samples. The aim of the research was to evaluate the possibility of using the remaining template as an inner binder for the preparation of a highly effective pasted supercapacitor electrode, without an additional binder. When analyzing such pasted electrode, it should be taken into account that the charge of nickel hydroxide is accompanied by oxygen evolution. This reaction is significantly accelerated in the supercapacitor regime. The evolving oxygen can separate the active material from the current collector, thus lowering specific capacity because of lower mass and not because of its degradation. The following analysis is conducted with consideration of these facts.

Reference sample 0 showed low capacities of 2.5 F/g at 20 and 40 mA/cm^2. This is explained by the blocking effect of the active surface of the submicron hydroxide particle by a large content (3 %) of the binder. This conclusion is supported by an increase in specific capacity to 46 F/g with the increased current density and the results of the paper [38], where similar hydroxide, synthesized using homogeneous precipitation without a template, showed the specific capacity of 120 F/g when 1.5 % of the binder was used.

Samples prepared with PVA as a template. Specific capacities of samples 1–0.5 and 1–0.05 support the previous conclusion about weak binding properties of PVA. Sample 1–0.05 showed very low capacity, which dropped to 9 F/g at 120 mA/cm^2. This indicated an insufficient binding effect of the remaining PVA and removal of the active material with evolving oxygen. This is also confirmed by visual observation, as a large amount of active material was found at the bottom of the cell after cycling. Increasing PVA concentration during synthesis to 0.5 % leads to the higher content of PVA in hydroxide. As a result, the electrode prepared with sample 1–0.5 without a binder proved to be rather effective with the maximum specific capacity of 139 F/g at 40 mA/cm^2, but it decreased at higher current densities.

Samples prepared with Culminal C8465 as a template. Samples (2–0.5 and 2–0.05) showed significantly higher specific capacities than samples (1–0.5 and 1–0.05) for all current densities. Even at the concentration of 0.05 % Culminal C8465, the remaining template showed the binding effect. The maximum specific capacities were 194 and 197 F/g for sample 2–0.05 and 2–0.5 respectively (at i=40 mA/cm^2). At higher current densities, capacity drops, which is not characteristic for hydroxides prepared by homogeneous precipitation. The decrease is related to insufficient binding or binder content, which leads to mechanical separation of the active material from the current collector upon oxygen evolution.

It can be summarized, that template remains can indeed be utilized as an internal binder, making the use of an additional binder for the preparation of highly effective pasted supercapacitor electrodes unnecessary. However, the method of using the remaining template as a binder has a limitation. The limitation is related to the choice of such template that would act as a template during synthesis and as a binder for electrode preparation. Additional research is necessary to determine the optimal template concentration.

7. Conclusions

1. The influence of PVA and Culminal C8465 (at concentrations of 0.05 % and 0.5 % each), as templates for homogeneous synthesis, on the crystal structure, morphology and particle size of nickel hydroxide has been studied. It was discovered, that the use of PVA results in significantly higher crystallinity and lower agglomerate formation. Increasing PVA concentration by 10 times had no effect on these characteristics. For Culminal C8465, the crystallinity is significantly lower, but it increases with template concentration. Higher concentration of Culminal C8465 also leads to significant particle aggregation. It was discovered that on the synthesis stage, PVA behaves like a weak binder and Culminal C8465 shows strong binding properties.

2. Complex analysis of electrochemical characteristics of pasted electrodes prepared without a binder confirmed the possibility of using the remaining template as an inner binder. The highest specific capacity for the electrode without an external binder was 197 F/g when Culminal C8465 was used as a template. It was discovered that PVA is a significantly weaker binder than Culminal C8465 when nickel hydroxide samples were used without an additional binder for electrode preparation. It was revealed that it is of importance to choose a water-soluble template, that would play the role of a template during the synthesis of nickel hydroxide and would also serve as a binder for the preparation of pasted electrode. The optimization of template concentration is also necessary.

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