

Для визначення впливу кількості зв'язуючої речовини на значення питомих ємностей були проведені зарядно-розрядні дослідження з різним вмістом політетраетилену в складі оксиднонікелевого електрода. Було показано, що додавання політетрафторетилену покращує адгезію активної маси до електрода, що збільшує значення питомої ємності. З іншого боку, велика кількість політетрафторетилену веде до прояву екрануючого ефекту, що зменшує питому ємність

Ключові слова: гідроксид нікелю, оксиднонікелевий електрод, питома ємність, суперконденсатор, розряд, політетрафторетилен, адгезія

Для определения влияния количества связующего на значение удельных емкостей были проведены зарядно-разрядные исследования с различным содержанием политетрафторэтилена в составе оксидноникелевого электрода. Было показано, что добавление политетрафторэтилена улучшает адгезию активной массы к электроду, что увеличивает значение удельной емкости. С другой стороны, большое количество политетрафторэтилена ведет к появлению экранирующего эффекта, что уменьшает удельную емкость

Ключевые слова: гидроксид никеля, оксидноникелевый электрод, удельная емкость, суперконденсатор, разряд, политетрафторэтилен, адгезия

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OPTIMIZATION OF NICKEL HYDROXIDE ELECTRODE OF THE HYBRID SUPERCAPACITOR

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1. Introduction

Supercapacitors are electrochemical power cells (EPC), which recently have found wide application in many fields of engineering. They are capable of producing high values of charge and discharge currents. These power cells are used in systems where high efficiency of power storage and power discharge in short time are required. Supercapacitors are in demand for systems in which current consumption is not linear and rises sharply at some moments in time: starting of electric motors, devices with high-rate energy accumulation, high charge rate electronic devices. Operation specifics of supercapacitors (high charge-discharge currents) significantly influence the design and properties of utilized compounds.

Hybrid supercapacitors possess the best properties among other types of supercapacitors. One of their electrodes is operated based on charge-discharge principle of EDL, and the second electrode (so-called Faradic) is based on rapid occurrence of electrochemical reactions.

The electrochemical process at Faradic electrode mostly occurs on the surface and in a thin layer of active material particles. Under such conditions, the active material is required to possess specific physico-chemical characteristics [1, 2]. The ma-

terial is required to have a high specific surface area and a specific structure that guarantees high electrochemical activity.

Nickel(II) hydroxide is used as an active material for supercapacitors [3, 4]. An electrode prepared from $\text{Ni}(\text{OH})_2$, is called nickel oxide electrode and is widely used as a Faradic electrode [5, 6] for hybrid supercapacitors [7].

Despite many works dedicated to design and other problems related to operation of supercapacitors, there are still many questions that are not sufficiently disclosed in the literature. One these questions, which is relevant is a composition of electrode active mass.

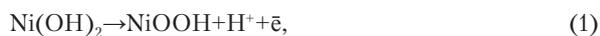
Generally, in addition to active material ($\text{Ni}(\text{OH})_2$), an electroconductive additive (graphite or other carbon-containing materials), activator (cobalt or zinc compounds) and binder are introduced into active mass. The binder ensures contact of active mass components with the current collector and each other, and prevents components from falling off upon gas evolution during charge. However, all mentioned additives, including a binder, are the ballast that doesn't partake in current-generating reaction. Introduction of additives reduces the content of active material which reduces resulting capacity of the electrode. Thus, the proper ratio of these components is important for characteristics of the chemical power cell.

The present work is dedicated to the choice of the binder content and its influence on charge-discharge characteristics of nickel oxide electrode.

2. Literature review and problem statement

As a binder for various types of electrodes, a polytetrafluoroethylene suspension (PTFE) [8] is commonly used, the main component of which is polytetrafluoroethylene $[-CF_2-CF_2-]_n$.

PTFE suspension is also widely used as a binder for fuel cells [9, 10]. Application of this compound for binding of active mass components with the current collector is tied with its two advantages: high adhesion to active mass components and low reactivity. It should be noted that during charging, according to solid-state (1) and summarized (2) reaction, nickel hydroxide transforms into nickel oxyhydroxide:



NiOOH possesses high oxidative power, which makes use of sufficiently inert fluorine-containing organic compounds justified. On the other hand, PTFE usage as an active mass component, poses two negative factors: first, PTFE reduces the content of active material in active mass, reducing the specific capacity of the electrode, second PTFE (as a dielectric) can partially screen active material, which also leads to decrease of specific capacity. Upon addition of PTFE and other types of binders into active mass, the latter effect is more pronounced than the first one. Usually, upon introduction of excessive amounts of binder the specific capacity decreases sharply. It should be noted that screening effect is more pronounced for nano-sized particles with the high specific surface area.

Sadly, the amount of binder introduced into active mass is not specified in a majority of scientific papers. The composition of active mass is not specified in studies of nano-sized nickel hydroxide particles [3], Al-stabilized α -Ni(OH)₂ [4, 5], ultrathin nickel oxide and nickel hydroxide powders [11], Ni(OH)₂/reduced graphene oxide [6], Ni-Al LDH/multi-walled carbon nanotubes [7], Ni(OH)₂ of various sizes [12]. It should be noted that in the majority of listed articles the nano-sized materials have been studied, for which screening effect should be strongly pronounced. In order to avoid this effect, nanostructures, in particular, nanocomposites with Ni(OH)₂ are grown directly on the nickel foam surface [13].

Usually, the binder content is no more than 10 % (wt.). In previously conducted studies the following contents of PTFE have been used: 5 % – for accumulator regime [14, 15], 3 % – for supercapacitor regime [16, 17] and 1.5 % – for nano-sized nickel hydroxide sample prepared by high-temperature two-stage synthesis [18]. However, these values were chosen based on general assumptions and no optimization has been conducted.

Thusly, no rationale behind choosing the binder content has been found in the literature. In rare cases the binder content is taken from previous reports or chosen at random, based on general assumptions. However, the binder content can significantly impact the resulting capacity, especially for high rate charge-discharge regimes which are typical for su-

percapacitors. Thus, the optimization of the binder content in active mass of supercapacitor can significantly improve its characteristics.

3. The aim and objectives of the study

The aim of the work was to determine the influence and find the optimal concentration of PTFE in active mass of nickel oxide electrode at fast (supercapacitor) charge-discharge regimes.

Two objectives have been set:

- to prepare electrode samples with various content of PTFE binder in active mass, using industrial materials;
- to conduct a charge-discharge test under different current densities and to evaluate the influence of the PTFE content on the electrode capacity under different current densities.

4. Research methods and materials used in nickel oxide electrode active mass optimization experiments

Materials used. An industrial sample of nickel hydroxide supplied by “Bochemie” (Czech Republic) has been used in all experiments. Before the investigation, the sample has been ground and sifted through 70 μ m nickel grate.

PTFE suspension F-4d has been used as a binder. Accumulator-grade graphite GAK-1 has been used as an electroconductive additive.

A nickel foam matrix with a porosity of 100–250 ppi welded to a nickel strip has been used as a current collector (Fig. 1).

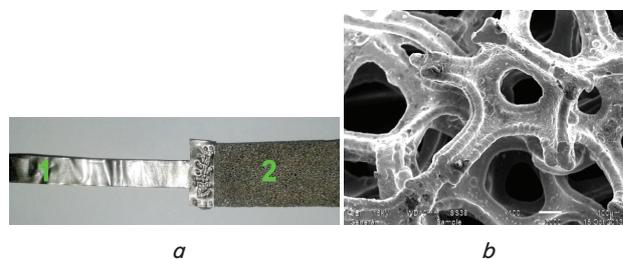


Fig. 1. Current collector for electrochemical studies; *a* – general look: 1 – Ni strip, 2 – nickel foam matrix; *b* – microphotography of nickel foam ($\times 100$ magnification)

Electrode preparation and composition of active masses. In order to assess the electrochemical characteristics as series of active masses composed of Ni(OH)₂, graphite and PTFE has been prepared. Compositions of masses are listed in Table 1.

Table 1

Compositions of active masses used in experiments

№	1	2	3
Composition	1 % PTFE 16 % Graphite 83 % Ni(OH) ₂	2 % PTFE 16 % Graphite 82 % Ni(OH) ₂	3 % PTFE 16 % Graphite 81 % Ni(OH) ₂

Electrode preparation. Pasted electrodes have been used in experiments. First, the required amount of Ni(OH)₂ and graphite have been weighted and mixed evenly. Next,

60 % PTFE suspension has been weighted and added to a dry mixture with a small amount of distilled water. The mass has been mixed to obtain a homogeneous paste. The obtained mass has been pasted on previously weighted nickel foam matrix. The obtained electrode has been dried at 90 °C for 15 min. After removing excessive active mass using a soft brush and weighting the electrode was ready for investigations.

Research methods. In order to study surface morphology of the nickel foam and nickel hydroxide particles, the scanning electron microscope JEOL JSM-6510LV (Japan) has been used. Investigation of the crystal structure of an industrial Ni(OH)₂ sample has been conducted using Dron-3 diffractometer (Russian Federation) in Co-K α monochromatic radiation.

Charge-discharge characteristics have been recorded on electron potentiostat-galvanostat Ellins P-8 (Russian Federation) using a YaSE-2 three-electrode electrochemical cell (USSR) (Fig. 2). The working electrode has been prepared as previously described, counter electrode – Ni mesh, reference electrode – Ag/AgCl (KCl sat.). 6 M KOH solution has been used as an electrolyte.

Each electrode has been studied by means of galvanostatic charge-discharge cycling at current densities of 10, 20, 40, 80 and 100 mA/cm² consecutively, 10 cycles for each current density (charge and discharge currents were the same). The specific electrode characteristics have been calculated based on the electrode mass, discharge time and potentials.

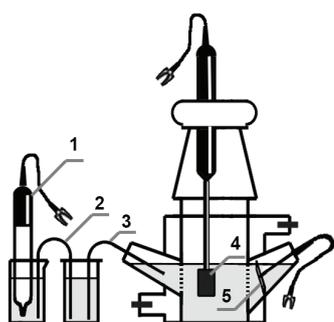


Fig. 2. YaSE-2 schematic: 1 – reference electrode; 2, 3 – capillaries; 4 – working electrode; 5 – auxiliary electrode

5. The research results for nickel oxide electrodes with various compositions

5.1. The results of the structural and morphological analysis of industrial Ni(OH)₂

The results of XRD analysis of industrial sample “Bochemie” (Fig. 3) showed that it is highly crystalline Ni(OH)₂ with a low number of structural defects [13, 19].

The particle surface morphology has been studied using scanning electron microscope (Fig. 4).

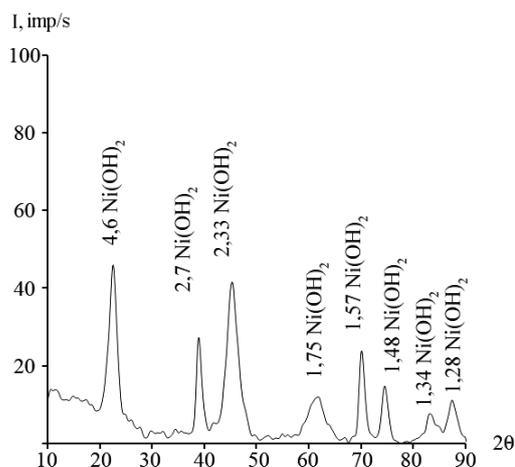


Fig. 3. XRD pattern of industrial nickel hydroxide sample “Bochemie”

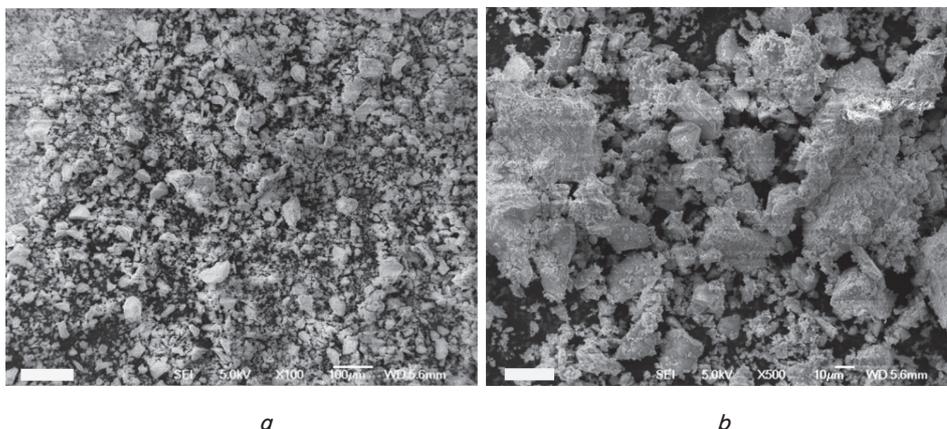


Fig. 4. Microphotographs of industrial nickel hydroxide sample “Bochemie”: a – $\times 100$ magnification; b – $\times 500$ magnification

Presented SEM images of surface morphology of Ni(OH)₂ sample “Bochemie” allows to speak of shard-like structure. Agglomerates consist of various-sized particles and have no typical shape.

5.2. Galvanostatic charge-discharge cycling results of pasted electrodes with various PTFE content

Fig. 4–6 show histograms obtained after galvanostatic charge-discharge cycling of electrodes with different binder content.

On a specific capacity histogram for active mass with 1 % PTFE two processes can be observed (Fig. 5). Under minimum current density the specific capacity gradually increases. The average specific capacity is 2 F/g. Under high current density a reversed behavior is observed. Specific capacity gradually decreases from 12 F/g to 2 F/g, i. e. 6 times.

For active mass with 2 % of the binder, the picture is completely different (Fig. 6). Under low current density there is also a small increase of specific capacity, similar to mass with 1 % PTFE. For maximum current density drop in specific capacity is less pronounced. It should also be noted that capacity values for different current densities at 2 % PTFE are closer to each other than at lower concentration.

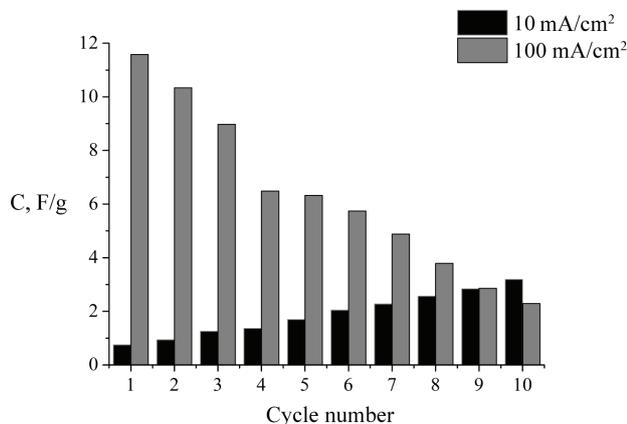


Fig. 5. Specific capacity of electrode with 1% PTFE during cycling

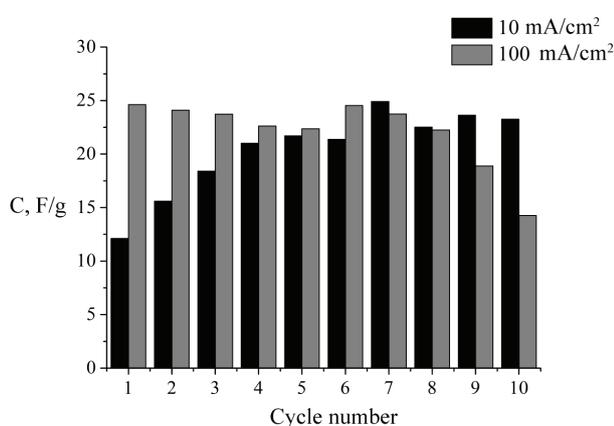


Fig. 6. Specific capacity of electrode with 2% PTFE during cycling

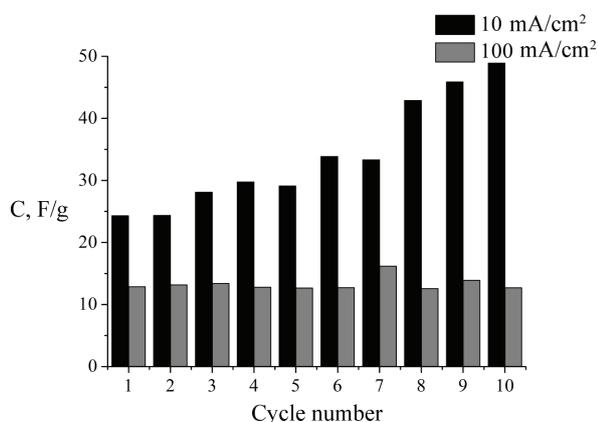


Fig. 7. Specific capacity histogram for electrode with 3% PTFE during cycling

For electrode containing 3% PTFE (Fig. 7) the observed picture significantly differs from previous cases. It can be said that the average capacity at a minimal current density is higher than at maximum. This behavior is significantly different from previous electrodes. Additionally, high stability of specific capacity under maximum current density could be noticed, which has not been observed in cases of 1 and 2% PTFE.

In order to see the general picture of specific capacity dependence on the binder concentration under different current densities, the generalized histograms have been built (Fig. 8).

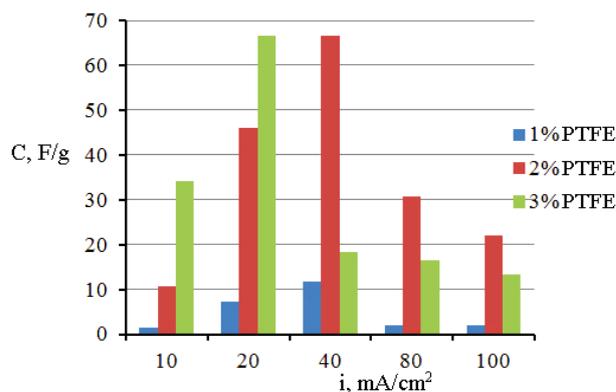


Fig. 8. Dependency of specific capacity for electrodes with different PTFE content on charge-discharge current density

For 1% PTFE the specific capacity has been increasing initially and reached a maximum value at 40 mA/cm² and then decreased abruptly. At 2% binder concentration the specific capacity has been increasing gradually and after 40 mA/cm² has not changed significantly and then somewhat dropped. The 3% PTFE content initially leads to an increase of specific capacity and then to a significant decrease, followed by a stabilization of specific capacity value.

6. Discussion of the results obtained after charge-discharge studies of nickel oxide electrode with different composition

In case of low PTFE content (1%, Fig. 5), two effects can be observed. Under low current density the specific capacity value is low and gradually increasing per cycle. This indicated gradual work-trough inside of hydroxide particles, which is characteristic of highly crystalline hydroxides with a low number of crystal lattice defects [15]. The average specific capacity under low current density is 2–3 F/g, which is rather low [17, 18]. Such low specific capacity is likely related to two factors: low electrochemical activity of the hydroxide itself, especially under high current densities, and insufficient contact with the current collector. The latter is due to insufficient PTFE content. Insufficient binder content explains the dependence of specific capacity on the cycle number under maximum current density for this electrode (Fig. 5). By analyzing this dependency, it can be concluded that under high current densities, a decrease of specific capacity during cycling is tied with the evolution of large volumes of oxygen which causes active mass to fall off. The oxygen evolution during charge is a side reaction, the rate of which is proportional to charge current density [20, 21]. When 2% PTFE have been used in active mass composition the electrode specific capacity has been greatly increased (Fig. 6). As in the previous case, the specific capacities acquired at low current densities, have been increasing with each cycle, which is related to work-trough inside hydroxide particles. However, in comparison to the histogram for 1% PTFE, the initial capacity values have been improved by an order, with an average capacity of 15 F/g. Obviously, such change can be related to the improved contact of hydroxide particles with the current collector metal, and, as a result, to improved current density distribution. It is notable that specific capacity values obtained under minimum and maximum current densities are similar. Additionally, capacity decrease with

the cycle number is lower than in case with 1 % PTFE. It can be related to that such PTFE content is sufficient for secure contact and holding of particles upon oxygen evolution during charge under high current densities.

For the electrode containing 3 % PTFE, the obtained dependencies are significantly different from previous ones. Fig. 7 shows a gradual capacity increase with each cycle number during charge-discharge cycling under minimum current density. In this case the same effect described above takes place i.e. work-trough of the particle inside. In addition, there are significant differences from previous graphs. One of which is the lower electrode capacity under high current density (about 13 F/g). Additionally, at 100 mA/cm² high stability of specific capacity during cycling is observed.

Thus, on one hand, high binder content improves the stability of specific capacity under high current density, by preventing fall off of active mass upon oxygen evolution during charging. On the other hand, this data shows that under high current density the screening effect starts to manifest because of the high amount of dielectric binder – PTFE.

Thus, it can be concluded that when using PTFE for this type of hydroxide the optimal concentration is 2 %.

In order to compare the capacities of electrodes with different PTFE content under different current densities, generalized histograms (Fig. 8) showing dependencies of average capacities on charge-discharge current densities have been built. Analysis of these histograms has revealed a few facts. Maximum capacity value for 1 % PTFE is observed at 80 mA/cm². In this case increase of specific capacity is tied with work-trough inside the hydroxide particles as a result of the topochemical discharge reaction. The decrease of specific capacity above 80 mA/cm² is tied to insufficient PTFE content. The latter leads to fall off of active mass and (or) loss of electric contact with the current collector. The reason behind the contact loss is a side reaction of oxygen evolution during charging.

For PTFE content of 2 % a somewhat different picture is observed. The specific capacity increases initially, but drops afterwards, though the drop is lower in comparison to other PTFE concentrations. The increase of specific capacity is tied to activation of nickel hydroxide, and

stabilization indicated that at such PTFE content, the active mass has secure contact with the current collector at 40–100 mA/cm².

For PTFE content of 3 %, specific capacity is significantly reduced after reaching the maximum value at 20 mA/cm² (C=67 F/g). The increase is related to the activation of particles of active mass, the following sharp drop is related to the screening effect, which is manifested at higher current densities. The mechanism of such screening lies in that upon increasing current density to specific values, the real current density on particles rises significantly, because of a higher amount of PTFE spread across particles of active material. As previously said the PTFE is dielectric and so it screens the part of the surface that is discharging. Thusly, the working surface of particles is reduced, causes an increase of real current density. Such high real current density causes rapid exhaustion of electroconductive NiOOH on the particle surface. This results in particle being covered with a layer of dielectric – Ni(OH)₂, leading to loss of contact with electrode i. e. the ability to further discharge.

7. Conclusions

1. The effect of the PTFE binder content on specific capacity of electrodes prepared from highly crystalline industrial nickel hydroxide manufactured by “Bochemie” at different charge-discharge current densities has been studied. It has been shown that two key parameters essential when choosing the binder content:

- adhesion of active mass to the electrode, which is defined by the binder content and the presence of side reactions with gas evolution;
- screening of active material’s surface by a dielectric binder, high content of which in active mass reduces electrode capacity at high current densities.

2. It has been demonstrated that the optimal PTFE content in active mass for nickel hydroxide supplied by “Bochemie” is 2 %. It also has been shown; that optimal value is dependent on various factors, with the main being morphology, size and structure of each given hydroxide.

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