1. Introduction

Chemical sources of current (CSC) are the only type of autonomous energy sources, which enable operation of multitude of technical devices with electrical circuit of functioning. Achievements in the field of CSC are so important that they often determine the feasibility of developing a technical device. There are several types of electrochemical systems that can be employed to create CSC, however, practically applied are only a few of them [1]. One of the leading places in terms of industrial production is taken by nickel-iron and nickel-cadmium alkaline batteries [2]. The alkali CSC possess the following advantages:

1) capability to withstand deep recharge and recharging;
2) considerable operational life cycle;
3) capability to preserve during periods of inaction;
4) ease of service and large mechanical strength.

Alkali CSC are used as sources of power supply in the systems for electrochemical treatment of water, which is a promising technique to prepare water for reuse. The method makes it possible to perform water purification from technogenic and natural contaminants. Electrochemical treatment of water is reagent free, which allows bringing down the cost of the process. The possibility to control electrical conductivity and water salinity enables reusing it for commercial purposes, thus reducing the load on the environment.
The electrolysis leads to the formation of low-soluble compounds of metal cations and helps reduce electrical conductivity of water. Technical implementation of the method is impossible without using a power source with stable voltage.

Nickel-cadmium and nickel-iron batteries are mainly manufactured with lamellar electrodes in which active masses are enclosed in lamellas – flat steel boxes with perforated walls. A positive electrode of such CSC is a mixture of nickel hydroxide Ni(OH)$_2$ and electro-conductive additive – graphite or metallic nickel. A shortcoming of the oxide-nickel electrode (ONE) is a low coefficient of the utilization of active mass, which does not exceed 80%.

Improving specific electrical characteristics of ONE of alkali CSC is directly linked to the operation resource of water treatment plants. Therefore, development of the new type of a modified electrode is an important scientific and technical task.

2. Literature review and problem statement

A decrease in the coefficient of utilization of oxide-nickel electrode is related to the high electric resistance of nickel hydroxide. During charging, Ni(OH)$_2$ converts into NiOOH – a compound, enriched with oxygen. The transformation is accompanied by a change in the structure of active mass, which acquires greater electric conductivity as a result. Limited capacity of ONE is the result of characteristics of the electrode discharge. Studies on the improvement of electrical parameters of ONE are aimed at changing its structure by the introduction to composition of electrode or to electrolyte of substances-activators. Most designs are based on the application of various nanostructured materials in order to modify the electrode. Authors of paper [3] report the development of a new type of electrodes for the alkaline battery, based on using multilayer carbon nanotubes and nanocomposites “nickel oxide – multilayered carbon nanotubes”. Electrodes have a great discharge capacity, but the large surface of nanoparticles predetermines the course of numerous side reactions, in particular nickel deposition, which blocks the flow of OH$^-$ ions to the electrode.

In paper [4], ONE with a developed surface was received by the deposition of Ni-Zn alloy with subsequent etching of zinc. A disadvantage of the proposed technology is the difficulty of maintaining a constant composition of the alloy during electrochemical deposition, as well as its uniform distribution in the deposit building on a mesh cathode.

Hybrid electrodes in the form of composite materials composed of carbon nanotubes or graphene with nickel hydroxide deposited on the surface were studied in [5]. Electrodes possess high specific capacity and are capable of enabling fast charge and discharge. The disadvantages of electrodes are the complexity and cost of obtaining carbon materials with preset properties.

A method for the electrodeposition of graphene from suspension for obtaining composite electrodes was applied in paper [6]. The samples obtained were characterized by enhanced capacity and capacity yield. Graphene oxide, obtained by the Hammers method, does not have a permanent composition and, therefore, cannot ensure reproducible properties of the samples of electrodes.

Research into composite electrodes, obtained by applying the suspension of powders of Ni(OH)$_2$ and SnO$_2$ on graphite, was undertaken in [7]. Compared to conventional ONE, experimental samples had greater capacity, but the complexity of the process of obtaining electrodes is a serious shortcoming of the work.

The influence of CuO additive on the electrical properties of ONE was examined in [8]. The given additive causes a decrease in the resistance of active mass, which contributes to a more complete course of electrochemical reactions of the oxidation and reduction of electrodes. However, the paper failed to describe issues related to the possibility of the course of corrosion processes in the systems that contain compounds of copper and metallic nickel.

Modification of ONE by adding hydroxides of cobalt and lithium was studied in paper [9]. By suppressing the process of oxygen release and increasing the dispersion of active mass, the modified electrode can be exposed to a deeper charge, which improves its capacity. Using a process of chemical deposition of zinc to increase the surface of the electrode may cause a fall of the active mass during electrode operation.

A known additive, which makes it possible to improve capacity and capacity output of ONE is lithium hydroxide, which is introduced to the electrolyte of an alkaline battery. According to data in article [10], the introduction of LiOH to the alkaline electrolyte enhanced the capacity and capacity output of the sintered ONE. The authors used the electrolyte containing 35 g·l$^{-1}$ of the additive during research. The paper lacks any substantiation for such a content of the additive, which makes it impossible to establish the influence of its concentration on the properties of ONE.

Thus, an analysis of the scientific literature reveals that there are two approaches in order to enhance the capacity of ONE. The first one is to change the electrode properties by employing nanostructured materials. This approach is still not applicable for industrial production because of the difficulty of obtaining nanostructured materials with reproducible properties.

The essence of the second approach is the introduction of additives of activators to the composition of electrolyte. It is more advantageous in practical terms as it makes it possible not to change the existing battery fabrication technology. An unresolved problem in this area is the substantiation of selecting the optimal concentration of an additive. For example, the concentration of LiOH, which is recommended to maintain in the electrolyte, varies from 1 to 50 g·l$^{-1}$. Although the introduction of lithium hydroxide can significantly improve the performance of ONE, there are no data in the literature to explain the choice of such a concentration of the additive. Thus, the research that aims to establish effect of the content of LiOH in the electrolyte on the properties of ONE is a significant technical task.

3. The aim and objectives of the study

The aim of present study was to determine effect of the concentration of lithium hydroxide in the electrolyte of alkali battery accumulator on the electrical characteristics of oxide-nickel electrode.

To achieve the set aim, the following tasks have been formulated:

– to study effect of the additive of lithium hydroxide on the features of charging and discharging characteristics of the oxide-nickel electrode in a solution of potassium hydroxide;
– to examine effect of the additive of lithium hydroxide on electrical capacitance and capacity output of the oxide-nickel electrode.
4. Procedure for research into electrical characteristics of the oxide-nickel electrode

The study was conducted in a three-electrode electrochemical cell. A beaker made of chemically resistant glass with a volume of 250 cm$^3$ served as the cell. We used a sample of sintered ONE as a working electrode in the form of a nickel grid-current collector with the pressed mixture of Ni(OH)$_2$ and graphite. We employed a nickel foil with a thickness of 0.1 mm as an auxiliary electrode. Electrode potentials were measured relative to the saturated chloride-silver reference electrode of brand EVL-1M1. The reference electrode was placed in a separate beaker and was connected to the cell by a salt key filled with the solution of KCl thickened by agar agar.

Preparation of the working electrode to operation implied its washing with distilled water and activation - charging and discharging in the aqueous solution containing 300 g·l$^{-1}$ KOH. Charging the electrode was conducted by its anodic polarization at $j_a = 2$ A·dm$^{-2}$. Cathode current density $j_c$ was 0.2 A·dm$^{-2}$. The activated electrodes were stored in the KOH solution. The end of charging or discharging process was determined by the electrode’s chronopotentiogram.

At the end of charging, a dramatic shift in the potential of ONE was observed towards a region of positive values, which corresponded to the process of oxygen release. The end of discharging was accompanied by a shift in the potential of ONE to the region of negative values, which corresponded to the process of hydrogen release.

The auxiliary electrode was washed with tap water before the experiment, degreased by a sodium carbonate aqueous suspension, washed with tap water and distilled water and dried.

Electrolytes for the experiments were prepared on distilled water using KOH and KCl of qualification “ch.d.a.”, and LiOH with qualification “ch.”

Polarization of the electrodes was carried out under galvanostatic mode using the power source PINTEK PW-3032R (Pintek, Taiwan). The magnitude of current was registered by the multimeter Keithley-2000 (Keithley, USA). The multimeters Keithley 2000 (Keithley, USA) were applied to register values of the potentials of ONE; their readouts were recorded to a personal computer.

5. Results of study into effect of lithium ions on electrical characteristics of the oxide-nickel electrode

Determining a capacity of ONE was conducted based on an analysis of chronopotentiograms (charge-discharge curves) of the working electrode, obtained at its polarization under galvanostatic mode. Experiments were performed in the solutions containing KOH and LiOH.

A typical charge curve of ONE obtained in the KOH solution without additives is shown in Fig. 1, a. The dependence derived can be conditionally divided into three sections. The first section corresponds to the moment of circuit closing (Fig. 1, a, section 1). In this case, there is a sharp surge in the potential of ONE, corresponding in absolute magnitude to the value of electrode polarization at current passage. The magnitude of the jump is due to the nature of this electrochemical system and it characterizes the magnitude of full impedance along a part of the chain “ONE-electrolyte”. Temporal dependence of the potential of ONE along section 2 of the chronopotentiogram is linear, which indicates stationarity of the oxidation process of nickel hydroxide. After a certain amount of electricity passes through the electrode, with this amount of electricity corresponding to the end of the oxidation process of the bulk of hydroxide, the curve exhibits a smooth bend. In this case, the rate of the electrode potential’s shift towards the region of positive values increases (Fig. 1, a, section 3). An increase in the rate of potential shift along section 3 testifies to that the surface of ONE experiences the occurrence of a new electrode process. In this case, that process is the oxidation of hydroxyl ions, which is accompanied by the release of oxygen:

$$2\text{OH}^- \rightarrow \text{O}_2 + 2\text{H}_2\text{O}.$$  \hspace{1cm} (1)

The emergence of a smooth inflection on the chronopotentiogram is the moment when the charging of ONE is completed. The basic electrochemical reaction along sections 1 and 2 is the oxidation of nickel hydroxide to metahydroxide, which is accompanied by a drop in the concentration of alkali in the electrolyte. Output by the current of hydroxide oxidation does not reach 100 %. This is indicated by the appearance of oxygen bubbles at the surface of the samples at charging.

![Fig. 1. Charge curves of ONE obtained in the solution of KOH: a – charging curve of ONE obtained in the solution containing 300 g·l$^{-1}$ of KOH; b – charging curves of ONE obtained in the solution containing 300 g·l$^{-1}$ of KOH and LiOH. $c_{\text{LiOH}}$ g·l$^{-1}$: 1 – 50; 2 – 1; 3 – 10. $j_a$=2 A·dm$^{-2}$](image)
cathodic polarization is the process of hydrogen reduction whose rate along sections 1 and 2 is low and gradually increases in line with the reduction of NiOOH.

\[ 2\text{H}_2\text{O} - 2\text{e}^- \rightarrow \text{H}_2 + 2\text{OH}^- \]  

(2)

The concentration of alkali in the electrolyte, according to (2), increases during charging. Adding LiOH to the electrolyte does not cause a change in the shape of charging characteristics of the electrode (Fig. 2, b). We can also distinguish three sections on them that correspond to the course of the above processes.

Research results show that adding LiOH predetermines an increase in the capacity of ONE (Fig. 3, a). A change in the concentration of LiOH in the electrolyte from 1 to 100 g·l\(^{-1}\) causes an increase in specific density of the electrode from 0.89 (A·h)·cm\(^{-2}\) to 1.84 (A·h)·cm\(^{-2}\). A corresponding increase in the capacity output is from 79 to 89 % (Fig. 3, b). Cation Li\(^+\), having an insignificant ionic radius (0.68 Å), rapidly diffuses to the electrode matrix and is easily absorbed by the active mass. This prevents the diffusion of OH\(^-\) ions into the crystal lattice of NiOOH. In addition, the ion of Li\(^+\) reduces agglomeration of grains of nickel metal-hydroxide with the formation of structure with less activity. This process has a positive effect on the penetration depth of reaction's front into the grain of the active mass. As a consequence, there is an increase in the charging capacity of the electrode due to the elimination if diffusion inhibition. In parallel, the adsorption of the Li\(^+\) ions leads to an increase in the electrical conductivity of Ni(OH)\(_2\) and a rise in the polarization of reactions of oxygen release. This leads to an increase in the current output of the basic reaction and also increases the working capacity of the electrode.

In the course of the study we determined effect of adding LiOH on specific, rather than the absolute value of the capacitance of the electrode. Using the samples of sintered ONE does not make it possible to calculate the absolute value of the capacitance of electrodes. This is due to the existence of advanced porous structure of active mass, which is in contact with the electrolyte. That is why we studied influence of the additive on specific capacitance, which was calculated as the ratio of actual capacity to the surface area of the sample of ONE.

![Fig. 2. Discharge curves of ONE obtained in the solution of KOH: a – discharging curves of ONE obtained in the solution containing 300 g·l\(^{-1}\) of KOH; b – discharging curves of ONE obtained in the solution containing 300 g·l\(^{-1}\) of KOH and LiOH, \(c_{\text{LiOH}}\) g·l\(^{-1}\): 1 – 100; 2 – 1; 3 – 50. \(j_e=0.2\) A·dm\(^{-2}\)](image)

An analysis of Fig. 3 shows that the presence of the LiOH additive in the electrolyte leads to an increase in specific capacity (Fig. 3, a) and increases capacity output (Fig. 3, b) of ONE. The largest effectiveness of the additive’s action is observed at its introduction to the electrolyte in the amount of 1–10 g·l\(^{-1}\). A further increase in the concentrations of lithium hydroxide is less effective, although specific capacity and capacity output of ONE in the electrolyte, which contains 100 g·l\(^{-1}\) of LiOH, are higher in absolute values. The electrolyte containing >70–100 g·l\(^{-1}\) of LiOH is saturated relative to this compound under the given circumstances. A further increase in its concentration is impossible. The introduction of LiOH to electrolyte in amounts larger than 50 g·l\(^{-1}\) is impractical due to the achievement of limiting concentration of the additive. Another constraint is a rather high cost of LiOH.

Conducting a repeated charge and discharge of the electrode leads to an increase in its specific capacity (Fig. 3, a; the difference between 1 and 2). Experiments that were carried out in the solution of KOH without adding LiOH demonstrate its considerable gain in the process of cycling (Fig. 4).

![Fig. 3. Dependence of specific capacity and capacity output of ONE on the concentration of LiOH: a – dependence of specific capacity of ONE on the concentration of LiOH; b – dependence of capacity output of ONE on the concentration of LiOH. \(c_{\text{LiOH}}=300\) g·l\(^{-1}\), \(j_e=0.2\) A·dm\(^{-2}\), 1, 2 – data for the first and second cycles of charge-discharge](image)

Since an increase in the number of charge-discharge cycles does not affect the character of charging-discharg-
ing dependences, then an increase in the specific capacity of ONE is caused by a gradual impregnation of electrode with the electrolyte solution. The process of impregnation is accompanied by an increase in the working area of the electrode. In the case of electrochemical reaction, which occurs at the interphase boundary, an increase in the area corresponds to the removal of diffusion constraints and an increase in the amount of a substance of active mass that can enter the reaction.

6. Discussion of results of studying electrical characteristics of the oxide-nickel electrode

An increase in the electrical capacitance and capacity output of ONE in solutions with the addition of LiOH is typically associated with an increase in the number of defects in the active mass of the electrode. The influence of the additive is also demonstrated by increasing dispersion of the active mass [11].

A reason for the low utilization rate of the active mass of ONE is the high specific electrical resistance of Ni(OH)\(_2\) (\(\approx 10^9\) Ohms·m). Ni(OH)\(_2\) is a p-type semiconductor. Its electrical conductivity is predetermined by the presence of stoichiometric excess of oxygen in the lattice. A certain number of OH– ions in the lattice of Ni(OH)\(_2\), is substituted with oxygen ions O\(^2–\) and a similar quantity of Ni\(^2+\) ions is replaced with Ni\(^3+\) ions. Places in the lattice with a lack of electrons (Ni\(^3+\) ion) are the electron defects, the places with a lack of protons – the proton defects [12].

A charging process of ONE is accompanied by increased electrical conductivity of the active mass and proceeds without difficulty. The electrode charging starts in a place of dense contact between a grain of Ni(OH)\(_2\), and an electro conductive additive. During anodic polarization, ions of OH\(^–\) approach the surface of the grain and detach a proton off Ni(OH)\(_2\), turning into a water molecule:

\[
\text{Ni(OH)}_2 + \text{OH}^- + e^- \rightarrow \text{NiOOH} + \text{H}_2\text{O},
\]

As a result of reaction (3), Ni(OH)\(_2\), is enriched with oxygen and becomes more electroconductive. The formed metalhydroxide NiOOH is a compound of the \(\text{Ni}_x\text{O}_y\cdot\text{H}_2\text{O}\) type. Nickel hydroxide is capable of enriching with oxygen continuously; in its crystal lattice the ions of OH\(^–\) gradually transform into the O\(^2–\) ions; ions of Ni\(^2+\) – into the Ni\(^3+\) ions. The oxides that form during charging have high electrical conductivity, which is why the process easily moves into the volume of grain.

Since the initial phase is a modification of \(\beta\)-Ni(OH)\(_2\), \(\beta\)-NiOOH predominantly forms during charging. At the same time there occurs the formation of modification \(\gamma\)-NiOOH. An increase in the proportion of \(\gamma\)-phase is contributed by factors impeding the course of an orderly process: high speed of charging, elevated temperature and concentration of the electrolyte. Both metalhydroxides in the charged state are characterized by oxidation that exceeds the stoichiometric: \(\beta\)-phase is matched by the oxidation degree NiO\(_{1.4}\), \(\gamma\)-phase – NiO\(_{1.8}\). Electrochemical reversibility of \(\beta\)-NiOOH is higher while the self-discharge is larger. The density of \(\gamma\)-NiOOH (3.85 g·cm\(^–3\)) is significantly lower than that of \(\beta\)-NiOOH (4.15 g·cm\(^–3\)), which is why an increase in the proportion of \(\gamma\)-phase enhances a growth of the volume of active mass of ONE and causes deformation of the electrodes.

Charge and discharge of ONE depend on the ratio of speed of detachment or delivery of protons to the grain surface and the diffusion rate inside the grain. When charging, if the surface is quickly enriched with oxygen while new protons fail to approach the boundary of interface from the volume of the grain, the potential of the electrode will shift towards a region of even more positive values (Fig. 2, a, b). Such a shift would cause the course of electrochemical process of the OH– ions discharge with a release of gaseous oxygen.

Discharge of the electrode is the process inverse to reaction (3). During discharging, the surface of the electrode’s grain is depleted of oxygen. If the rate of diffusion of protons into the volume of grain is lower than the diffusion rate from the solution, there will occur a surge of potential and the discharge will stop. In any case, depletion of the outer layer with oxygen reduces its electrical conductivity. Therefore, even if the rates of diffusion of protons are equal, the discharge may cease because of the loss of contact between electrically conductive additive and the underlying layers of grains, rich with oxygen as yet. Under operation conditions of ONE, its capacity is always limited by the conditions of discharge and the active mass is not utilized in the process to the full.

ONE is characterized by the effect of “aging”, which leads to a gradual decline in the capacity of electrode [13]. The reason causing aging of the electrode is the gradual enlargement of grains of the active mass. This leads to additional diffusion inhibition of discharge, which proceeds in line with a solid-phase mechanism. The diffusion coefficient of a proton in ONE has an order of \(10^{11}–10^{13}\) cm\(^2\)·s\(^–1\). To ensure high charging current density, active mass must possess high dispersion, and graphite particle size must be smaller than that of grains of Ni(OH)\(_2\). Reduced potential of ONE during discharge is due to diffusional limitations for protons and ohmic losses in the points of contact between grains of the mass and graphite (Fig. 3, a, b). Such a decrease causes the course of new electrochemical process – hydrogen evolution.

A significant increase in the capacity of electrode in the presence of Li\(^+\) ions is explained as follows [11–13]. The ions of Li\(^+\) are adsorbed at the electrode surface and increase the overvoltage of oxygen release, which positively influences the depth of electrode charge. In addition, due to the small ionic radius (0.68 Å), Li\(^+\) enters the lattice of Ni(OH)\(_2\), replacing the proton. This leads to the stabilization of dispersed structure of active mass, preventing agglomeration of the grains. As a result, the aging process of ONE slows down while service life of the electrode increases.

7. Conclusions

1. We examined the influence of lithium hydroxide on the charge and discharge process of sintered ONE. It is shown that the introduction of LiOH in the amount of 1–100 g·l\(^–1\) to the solution of KOH does not cause a change in the characteristics of charge-discharge electrode curves. The charge curve of ONE in the KOH solution with the addition of LiOH consists of three sections. The sections correspond to the formation of double electric layer (1), to the stationary charge mode (2), and to the process of oxygen release at the surface of the electrode (3). The discharge curve of ONE also consists of three sections. They correspond to the formation of double electric layer (1), to the course of reduction
in the content of LiOH in the electrolyte from 1 to 100 g·l⁻¹ leads to a growth of the electrode’s specific capacity from 0.79 (А·h)·cm⁻² to 1.84 (А·h)·cm⁻². Due to an increase in the dispersion degree of active mass and increased depth of the electrode’s charge, the addition of LiOH contributes to an increase in the electrode’s capacity output.

References