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ACTIVATION OF THE NICKEL FOAM AS A CURRENT COLLECTOR FOR APPLICATION IN SUPER-CAPACITORS

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Пінонікель широко використовується як струмовідвод та основа гідроксиднонікелевого фарадеєвського електроду гібридних суперконденсаторів. Активація пінонікелю дозволить збільшити ємність гідроксиднонікелевого електроду або сформувати високошвидкісні електроди без нанесення додаткової активної маси. Для активації пінонікелю запропонована багаторазова (1–20 раз) короткотривала (5 хв) обробка в 0,1 М розчині HCl, H_3BO_3 або $H_2C_2O_4$. Вивчена можливість активації комерційних зразків пінонікелю виробництва «Новомет-Пермь» (Російська Федерація) та «Linyi Gelon LIB Co Ltd» (Китай). Активовані та неактивовані зразки пінонікеля вивчені методами ренгенофазового аналізу та скануючої електронної мікроскопії, електрохімічні характеристики визначені циклічною вольтамперометрією та гальваностатичним зарядно-розрядним циклування в режимі суперконденсатора. Порівняльний аналіз зразків пінонікелю китайського та російського виробництва виявив суттєву пасивність та складність активації пінонікелю китайського виробництва. Висловлено припущення, що висока пасивність визначається тим, що зразок складається із сплаву Ni-P або Ni-B. Максимальна питома ємність 0,084 Ф/см^2 отримана при 20-ти кратній обробці в розчині HCl. Механізм активації – збільшення питомої активної поверхні нікелю. Однак це значення менше питомої ємності неактивованого пінонікелю російського виробництва (0,333 Ф/см^2). Показано, що пінонікель російського виробництва легко активується. Максимальний активаційний ефект проявляється при обробці в розчині щавлевої кислоти: питомі ємності склали 1,213 Ф/см^2 (при 1-но кратній обробці), 6,578 Ф/см^2 (при 5-ти кратній обробці) та 20,003 Ф/см^2 (при 20-ти кратній обробці). Механізм активації – утворення на поверхні пінонікеля шару оксалату нікелю. За результатами порівняльного аналізу показано ефективність активації пінонікелю російського зразка шляхом багаторазової короткотермінової обробки в розчині щавлевої кислоти. Зроблено висновок щодо неефективності активації зразка пінонікелю китайського виробництва шляхом багаторазової короткотермінової обробки в розчині щавлевої, соляної та борної кислоти. Для активації пінонікелю китайського виробництва необхідна розробка іншого методу

Ключові слова: пінонікель, питома ємність, суперконденсатор, травління, щавлева кислота, соляна кислота, струмовідвод

1. Introduction

Supercapacitors (SC) are modern chemical power sources (CPS). SC are widely used for starting various electric motors in electric automobiles, pump stations, electric tools and other devices. 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. A characteristic feature of supercapacitors is 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 specific surface area, crystal structure and electrochemical activity of the active material of such electrode. Nickel oxide electrode with $Ni(OH)_2$ as an active material is widely used as a Faradic electrode in hybrid supercapacitors. Nickel hydroxide is used on its own [3], as a nanosized [4] or ultradisperse powder [5], and as a composite with nanocarbon materials (graphene oxide [6], carbon nanotubes [7]).

Supercapacitors require highly effective current collectors, which must provide good electrical contact with the active material. There are two strategies for electrode preparation: pasting of the active material onto the current collector [8, 9] and formation of the active material directly on the surface of the current collector [10, 11]. Formation of the active material on the current collector is used for the preparation of catalysts, for instance, for oxygen evolution [12] or methanol electrolysis [13], and for electrochromic devices [14, 15].

When using the basic solution as an electrolyte, the nickel foam is highly effective current collector [8]. Nickel foam is manufactured by depositing nickel (chemically or electrochemically) onto graphite foam, which then gets burnt out. This results in the formation of the highly porous open-cell structure of nickel tubes.

The nickel foam is a perspective current collector for the nickel oxide electrode. This is because the surface of nickel is covered with a thin layer of nickel oxide, which in the basic medium transforms into electrochemically active nickel hydroxide, which would contribute to the capacity of the electrode.

However, the natural oxide layer of nickel is very thin and dense, with insignificant capacity. Thus, activation of the nickel foam surface with the formation of the highly active nickel oxide layer and increase of its capacity is a relevant problem.

2. Literature review and problem statement

Synthesis method and conditions directly define electrochemical properties of nickel hydroxide. There are various synthesis methods for the preparation of nickel hydroxide and nickel-based layered double hydroxides. Preparation of hydroxides can be achieved chemically via direct titration precipitation (addition of the basic solution to a solution of nickel salt) [16] and reverse titration (addition of nickel salt solution to a solution of base) [17, 18]. Other methods such as two-stage high-temperature synthesis [19], sol-gel [20] and homogeneous precipitation [21] are also employed.

Preparation can be achieved with electrochemical methods [22, 23] including synthesis in a slit-diaphragm electrolyzer [24, 25]. These methods allow for the synthesis of electrochemically active nickel hydroxide samples, however, they are not suited for the activation of the nickel foam surface because $Ni(OH)_2$ is formed as a separate phase. At the same time, the activation requires the formation of nickel hydroxide or oxide layer directly on the surface of nickel foam.

Thin films of nickel oxide or hydroxide can be formed chemically [26], and electrochemically [27, 28]. Nickel hydroxide can be prepared electrochemically by cathodic deposition as a result of basification of the cathodic space [29, 30]. The major disadvantage of this method is insufficient adhesion to the surface of nickel foam. Nickel hydroxide film can also be prepared via anodic formation [31, 32]. During anodic polarization, the oxidation of nickel occurs, resulting in the formation of an oxide/hydroxide film [33, 34]. It should be noted that films prepared by anodic oxidation have an insufficient thickness and low porosity.

Nickel oxide film on the surface of Ni has been prepared chemically using the solvothermal method [35], head deposition [36, 37], including induction [38], and also thermal oxidation in air [39]. In this case, the nickel hydroxide film is a conversion coating (i. e. formed by conversion of the substrate material [40]) and possesses high electrochemical activity. However, the disadvantages of these methods are high power consumption and complexity.

It should be noted, that the deposition of the oxide/hydroxide layer is only a part of the activation process. In order to improve adhesion and increase capacity, the process of surface development by etching can be employed. The etching processes are well-studied, however the combination of etching and formation of the oxide-hydroxide layer has almost not been studied, despite their prospects.

3. The aim and objectives of the study

The aim of the work is to evaluate the effectiveness of activation of commercial nickel foam samples of various manufacturers by combining the processes of etching and formation of the active layer of nickel hydroxide.

To achieve this aim, the following objectives were set:

– to conduct activation of nickel foam samples from different manufacturers by etching multiple times in solutions of different acids;

– to study the physical and electrochemical characteristics of activated and non-activated samples;

– to conduct a comparative analysis of the sample characteristics and evaluate the possibility for activation of different nickel foam samples.

4. Materials and activation methods for nickel foam samples and study of their characteristics

4. 1. Nickel foam samples for activation

For activation, two commercial nickel foam samples were used:

1) Nickel foam manufactured by "Novomet-Perm" (Russian Federation). The sample has a thickness of 2 mm and high stiffness. The nickel foam was manufactured by chemical formation of a thin layer of nickel, followed by electrochemical deposition of a thicker layer of nickel. Sample label – R.

2) Nickel foam manufactured by "Linyi Gelon LIB Co Ltd" (China). Sample thickness is 0.3 mm and the sample has high flexibility. The sample was manufactured by chemical formation of a thin layer of nickel. Sample label – Ch.

4. 2. Activation of nickel foam samples

Activation of nickel foam samples was conducted by treating them in 1M solutions of HCl, H_3BO_3 and $H_2C_2O_4$ for a short period multiple times. The samples were treated for 5 min, 1, 5, 10 and 20 times. After each etching, the samples were placed into a 1M Na_2CO_3 solution to neutralize the remaining acid. After the last cycle of etching-neutralization, the nickel foam sample was washed with distilled water and dried at 20 °C for 24 hours.

The labeling of treated samples is composed of initial labeling (R – Russian sample, Ch – Chinese sample) with the addition of acid label (Cl – HCl, Bo – H_3BO_3 and Ox – $H_2C_2O_4$) and number of treatment times. For instance: RCl5 – Russian nickel foam activated in hydrochloric acid 5 times; ChOx20 – Chinese nickel foam activated in oxalic acid 20 times.

4. 3. Study of characteristics of nickel foam samples

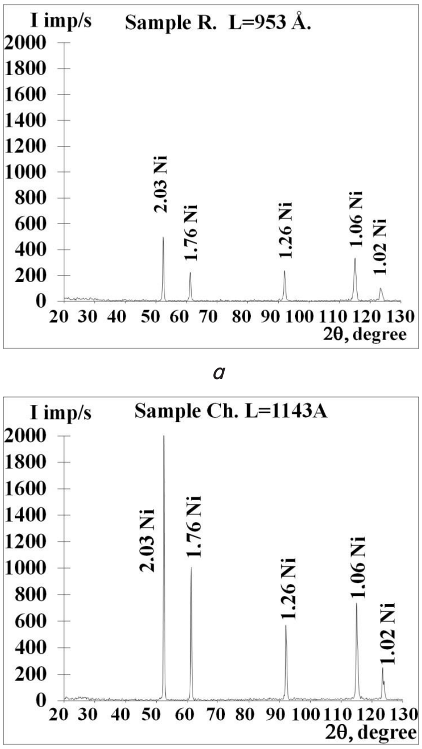
Crystal structure and crystallinity of the samples were studied by means of X-ray diffraction analysis (XRD) using the diffractometer DRON-3 (USSR) (Co-Kα scan range 10–90° 2θ, scan rate 0.1°/s).

Morphology of nickel foam samples was studied using the scanning electron microscope 106 – I (SELMI, Ukraine).

Electrochemical characteristics of activated and non-activated nickel foam samples were studied by means of cyclic voltamperometry and galvanostatic charge-discharge cycling. The measurements were conducted in a special cell YSE-2 (USSR), using the digital potentiostat Ellins P-8 (Russian Federation). Nickel foam samples were used as a working electrode. Electrolyte – 6M KOH. Counter-electrode – nickel mesh, reference electrode – Ag/AgCl (KCl sat.). Cyclic voltamperogram was recorded in the potential range of 0–500 mV, scan rate 1 mV/S. 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). Specific capacity C_{sp} (F/cm^2) was calculated from discharge curves.

5. Results of studying the influence of activation on characteristics of nickel foam samples

Fig. 1 shows XRD patterns of Ch and R samples prior to activation. The results reveal that both samples are primarily pure nickel, however, it should be noted that the crystallinity of the Chinese sample (sample Ch) is higher than that of the Russian sample (sample R): the crystallite size, calculated from the first peak, is 1143 Å and 953 Å, respectively. The XRD patterns of activated samples do not differ from the ones of initial samples.

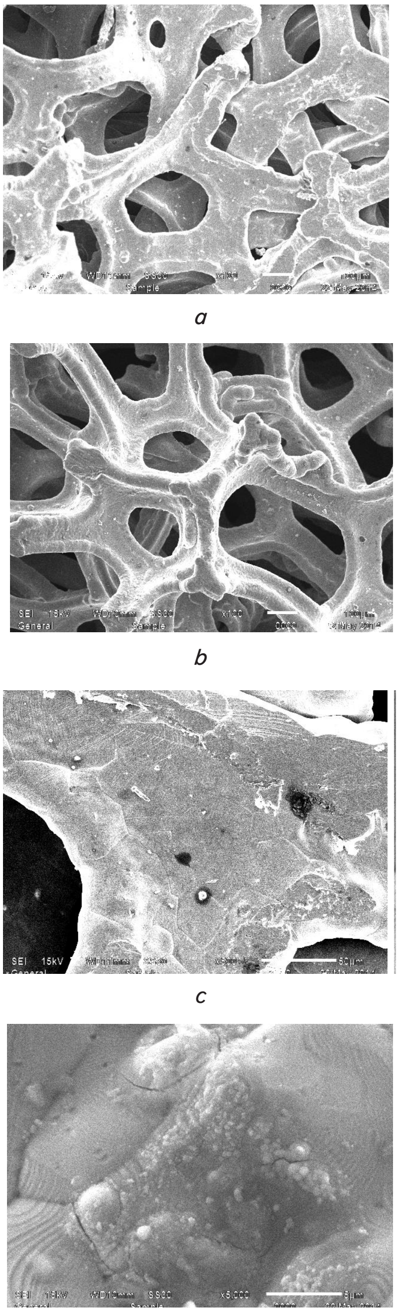


a

b

Fig. 1. XRD patterns of nickel foam samples prior to activation: *a* – sample R, *b* – sample Ch

Fig. 2 shows SEM images of different samples. It should be noted that the wire diameter of Ch sample is smaller than that of R. 20-times treatment in hydrochloric acid (sample RC20) resulted in the partial dissolution of the nickel foam surface. The SEM images of ROx20 sample revealed that 20-times resulted in the formation of nickel oxalate on the surface of nickel foam.



a

b

c

d

Fig. 2. SEM images of nickel foam samples: *a* – Ch; *b* – R; *c* – RC20; *d* – ROx20

Fig. 3 shows cyclic voltamperometry curves and Fig. 4 shows specific capacities of different nickel foam samples. It should be noted that treatment of Chinese nickel foam in oxalic, boric and hydrochloric acid (for a small number of times) results in almost no activating effect. Potentials and specific currents of discharge peaks (Fig. 3) show almost no difference from initial samples. Only 20-times etching in hydrochloric acid results in activation.

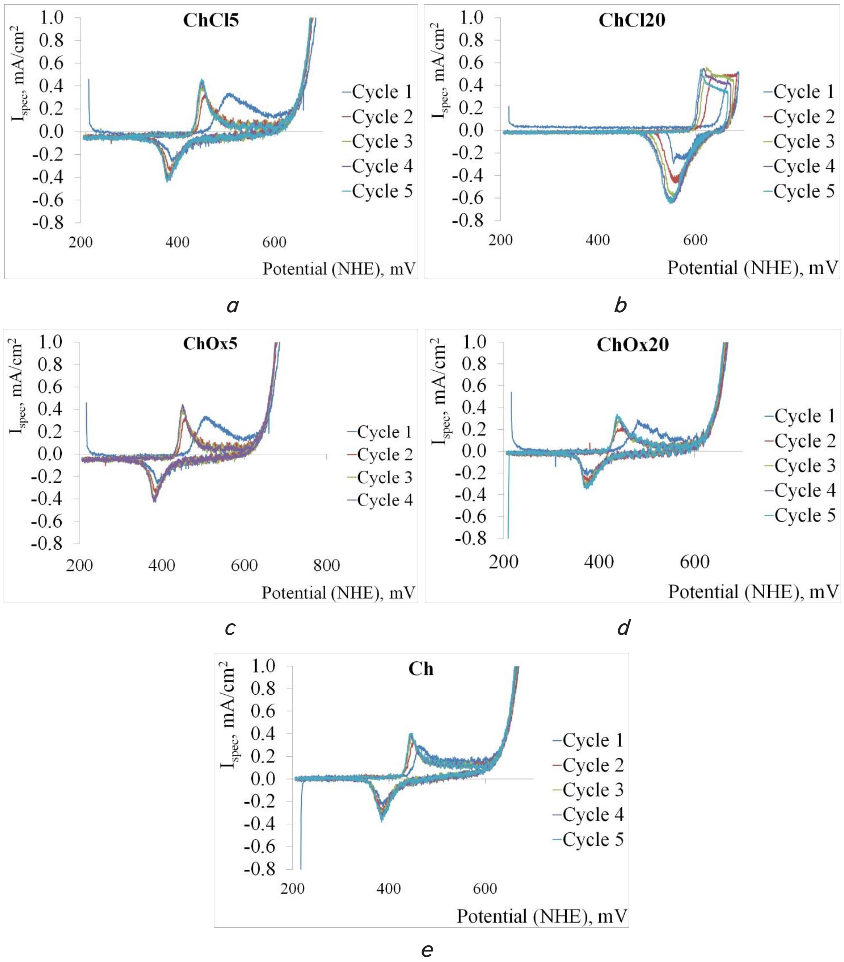


Fig. 3. Cyclic voltamperograms of nickel foam samples: *a* — ChC5; *b* — ChC20; *c* — ChOx5; *d* — ChOx20; *e* — Ch

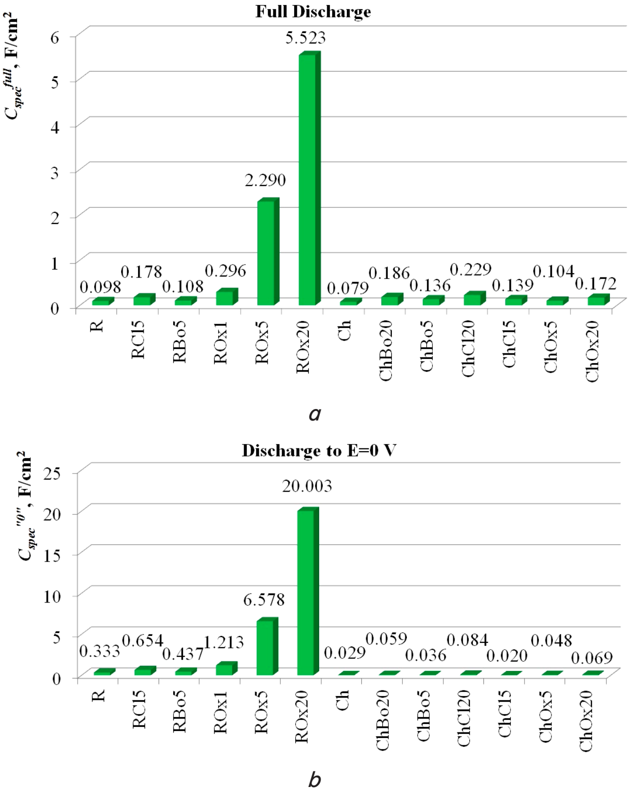


Fig. 4. Specific capacities of different nickel foam samples, F/g: *a* — full discharge; *b* — discharge to 0V potential

It should be noted that non-activated Russian and Chinese nickel foam samples show fundamentally different electrochemical properties: specific capacities at a discharge to E=0 V are 0.029 F/cm^2 and 0.333 F/cm^2 for samples Ch and R, respectively. Treatment of Chinese nickel foam samples only marginally increased specific capacity. The strongest effect was observed from etching in hydrochloric acid. The Russian nickel foam sample was more susceptible to activation. The strongest effect was observed from activation in oxalic acid. With 1-time (sample ROx1), 5-times (sample ROx5) and 20-times etching in oxalic acid (sample ROx20), the specific capacities are 1.213 F/cm^2, 6.578 F/cm^2 and 20.003 F/cm^2, respectively. These data indicated a significant activation of Russian nickel foam after multiple times treatment in oxalic acid solution.

6. Discussion of results of studying the influence of activation on characteristics of nickel foam samples

A hypothesis was proposed regarding possible activation mechanisms for treatment in solutions of hydrochloric, boric and oxalic acids. Etching in hydrochloric acid can result in an increase of specific surface area, which should result in the increased specific capacity. During treatment in solutions of weak acids (boric and oxalic), there is a possibility for weakly-soluble nickel borate and nickel oxalate to form. With further submersion of nickel sample into the basic solution, the conversion of borate (oxalate) to electrochemically active nickel hydroxide would occur. The following discussion is based on this hypothesis.

Feature study of nickel foam samples from different manufacturers. The results of X-ray diffraction analysis (Fig. 1) have revealed that nickel foam from Russian manufacturer (sample P) has lower crystallinity than nickel foam from Chinese manufacturer (sample Ch). The nickel foam from Chinese manufacturer is produced by chemical deposition by reduction with sodium hypophosphite or sodium borohydride. As a result, not pure Ni but Ni-P or Ni-B alloy is formed. The reflexes of Ni-P and Ni-B alloys are not observed on the XRD pattern (Fig. 1, b), because of a small content of the dopant, making it indistinguishable from the crystal lattice of pure nickel.

Influence of activation on the surface of nickel foam. The XRD analysis for activated samples had been conducted, however, no differences from initial samples were observed. This is explained by a small thickness of the formed layers. The SEM images support the proposed hypothesis about activation mechanisms of nickel foam. The surface of sample RC20, treated in hydrochloric acid shows partial dissolution (Fig. 2, *c*). The insignificant dissolution is explained by the chemical stability of nickel towards acids. Formation of nickel oxalate has been observed on the surface of sample ROx20 (Fig. 2, *d*). This layer is a conversion layer, which resulted in the reaction between nickel oxide and oxalic acid.

Influence of activation on electrochemical characteristics of nickel foam samples.

Activation of nickel foam samples from Chinese manufacturer. The obtained data during the study of electrochemical characteristics indicate low reactivity of Chinese nickel foam. The specific capacity of initial Ch samples is 11.4 times lower than that of the sample R. This is explained by a thin and dense nickel oxide layer, on the surface of Ni-P and Ni-B alloys (which constitute Chinese nickel foam). Activation of Chinese nickel foam in solutions of hydrochloric, boric and oxalic acids further confirms its low reactivity. Increasing the number of treating times leads to an increase in capacity for all samples. The biggest effect resulted from multiple treatments in hydrochloric acid. Thus, for Chinese nickel foam, the activation factor was the increase of specific surface area resulted in surface etching. The higher capacity was obtained for the sample ChC20 – 0.084 F/cm^2 (discharge to E=0 B) and 0.229 F/cm^2 (full discharge). However, these values are comparable to the non-activated sample from Russian manufacturer. It should be noted that maximum specific capacities for activated Chinese nickel foam samples are more than 25 times lower than capacities cited in the literature [31]. In general, it can be said that activation of Chinese nickel foam by multiple short-term treatment in solutions of hydrochloric, boric and oxalic acids proved to be ineffective.

Activation of nickel foam samples from Russian manufacturer. Nickel foam from Russian manufacturer was more susceptible to activation. The comparative analysis (Fig. 4, *b*) has revealed that the activation effect of acids increases in the series "boric – hydrochloric – oxalic". It should be noted, that one-time treatment in oxalic acid resulted in higher capacity (sample ROx1 – 1.213 F/cm^2) than 5-times treatment in hydrochloric acid (sample RC5 – 0.2654 F/cm^2). The highest activation effect was achieved after 20-times treatment in a solution of oxalic acid: the specific capacity has increased more than 60 times, from 0.333 F/cm^2 (sample R) to 20.003 (sample ROx20). Comparison of the obtained data with other published papers is complicated, because other papers cite specific capacities of nickel hydroxide or films in Farads per gram [32, 35-37]. However, when conducting this research, the change in the mass of nickel foam samples was lower than the sensitivity of analytical scales (0.0001 g), which did not allow for the calculation of such value. However, some papers present spatial specific capacities. The papers [31, 38] state that after anodic treatment of nickel foil, a layer of nickel hydroxide with a specific surface capacity of 3.2–4.5 F/cm^2 was formed. It was also stated that this value is high and allows this coating to be used in supercapacitors. It should be noted, that the nickel foam sample from Russian manufacturer treated 20 times in oxalic acid demonstrated the specific surface capacity of 20.003 F/cm^2. This is 4.44 higher than the value presented in the literature [31, 38]. It should be noted that for nickel foam from Russian manufacturer, the activation mechanism is the formation of a weakly-soluble salt, when it is treated multiple times for short duration. For oxalic acid treatment, the nickel oxalate is formed, which transforms into electrochemically active nickel hydroxide in the working electrolyte.

7. Conclusions

1. Nickel foam samples from "Novomet-Perm" (Russian Federation) and "Linyi Gelon LIB Co Ltd" (China) have been activated by multiple treatments (1, 2, 5, 10 and 20 times) for short time (5 min) in 1M solutions of hydrochloric, oxalic and boric acids. Physical and electrochemical characteristics of activated and non-activated samples have been studied.

2. The comparative analysis has revealed low reactivity of nickel foam from Chinese manufacturer, owing to its manufacturing method and composition (Ni-P or Ni-B alloy). The specific capacity of non-activated nickel foam sample was 0.029 F/cm^2, which is 11.5 times lower than the specific capacity of non-activated nickel foam samples from Russian manufacturer (0.333 F/cm^2). The low effectiveness of multiple short-term treatment of nickel foam from Chinese manufacturer in solutions of hydrochloric, boric and oxalic acids has been discovered. The maximum specific capacity of Chinese nickel foam has been achieved after treatment in hydrochloric acid for 20 times and is 0.084 F/cm^2. The main activation mechanism is the increase in the specific surface area of nickel foam. It is concluded, that activation of nickel foam from Chinese manufacturer requires the development of a different activation method.

3. The results of the comparative analysis have revealed the effectiveness of activation by multiple short-term treatment in a solution of oxalic acid for the nickel foam sample from Russian manufacturer. The maximum specific capacities are 1.213 F/cm^2 (one treatment), 6.578 F/cm^2 (treated 5 times) and 20.003 F/cm^2 (treated 20 times). The activation mechanism has been determined, which is the formation of the nickel oxalate layer of the surface of nickel foam.

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