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Comparison of electrochemical characteristics of NiCo₂O₄ and NiCo₂S₄ nanostructures for supercapacitors

This paper presents the results on the synthesis and study of the properties of NiCo₂O₄ and NiCo₂S₄ nanostructures obtained by hydrothermal synthesis for their use as supercapacitor electrodes. A method is developed for growing a nanostructure from a ternary metal oxide NiCo₂O₄ on a nickel substrate. The structural features of the synthesized NiCo₂O₄ and NiCo₂S₄ nanostructures are studied using X-ray phase analysis. The obtained samples have a cubic modification NiCo₂O₄ and NiCo₂S₄. The data on the morphology of the synthesized samples obtained by scanning electron microscopy are presented. The samples are in the form of nanoneedles and nanowires grown on a nickel substrate. Methods for the synthesis of NiCo₂O₄ nanostructures have been studied, optimal conditions for the growth of nanostructures from NiCo₂O₄ have been determined, and a NiCo₂O₄ sulfurization method has been developed to obtain a NiCo₂O₄ nanostructure. Comparative studies have been carried out on the effects of sulfurization on the electrochemical characteristics of the obtained electrodes. It is found that, despite the fact that NiCo₂O₄ oxide nanostructures have a high theoretical capacitance, the replacement of oxygen atoms by sulfur atoms increases the conductivity of the materials and leads to a further increase in the specific capacitance of the end electrodes. The maximum Cs obtained specific capacitance for NiCo₂S₄ is 1976 F g⁻¹ and while for NiCo₂O₄ it is 413 F g⁻¹ at a scan rate of 5 mV/s. The results of the dependence of the specific capacitance on the scanning speed during measurements are also presented.

Keywords: supercapacitors, energy storage, metal oxides, electrodes, nanomaterials, NiCo₂O₄, NiCo₂S₄ and nanostructures.

Introduction

With the growth in electricity consumption, the depletion of natural fossil fuel resources and pollution of the environment due to carbon dioxide emission, there is a growing global need to develop renewable energy sources. However, the production of electrical energy from renewable sources requires reliable and efficient storage systems to meet worldwide demand. In recent decades, there has been significant interest in the development of new technologies to solve energy problems. In this context, significant efforts have been put into the research and development of more efficient energy storage devices and systems. An example of such a device is electrochemical energy storage devices such as batteries and supercapacitors, which are promising due to their high energy density and power. An electrochemical capacitor is a device that stores electrical energy in an electrical double layer that forms at the interface between an electrolytic solution and an electronic conductor [1].

Supercapacitors (SCs), a new type of system for energy storage and conversion, are getting a lot of attention. SC can be divided into two categories: electrical double-layer capacitors and pseudocapacitors that store electrical energy through electrosorption, reduction and oxidation reactions. At present, owing to the high energy density (approaching 180 W·h·kg⁻¹), lithium-ion batteries are widely used in consumer domestic electronics. However, because of the slow transport of electrons and ions in these batteries, heat generation and dendrite formation are observed when operating at high power, which can lead to serious safety problems [2, 3].

Due to their high conductivity and capacitance, ternary metal sulfides are widely used for energy storage. Recently, great interest is being attracted by pseudocapacitors based on cobalt-nickel sulfide NiCo₂S₄, as they have low cost, high conductivity, good electrochemical activity, and also exhibit several oxide states that provide a high redox potential, originating simultaneously from Ni and Co ions in contrast to individual NiO and Co₃O₄ [4]. They also show an electronic conductivity about 100 times higher than that of NiCo₂O₄, although NiCo₂O₄ has a much better electronic conductivity than NiO and Co_xO_y [5]. Various nanostructures

based on NiCo_2S_4 , such as nanotubes, nanospheres, flower morphology, etc., have been synthesized for the production of supercapacitors.

Metal oxides represent an alternative as a promising material for manufacturing supercapacitor electrodes since they have a high specific capacitance and relatively low resistance, which simplifies the design of high energy and high-power supercapacitors [6]. In such materials, the mechanism of charge accumulation can occur both due to redox processes (Faraday reactions) and a double electric layer. Commonly used metal oxides are nickel oxide (NiO), ruthenium dioxide (RuO_2), manganese oxide (MnO_2), iridium oxide (IrO_2), tungsten oxide (WO_3), and cobalt oxide (Co_3O_4). Ternary metal oxides have advantages over single-component metal oxides because of the coexistence of a double metal cation, which allows for rich redox reactions.

In this study, our strategy is to improve electrochemical characteristics of electrodes based on cobalt-nickel oxide by sulfidization for supercapacitor devices. These electrodes demonstrated a high specific capacity for NiCo_2S_4 is 1976 F g^{-1} at a scan rate of 5 mV/s compared with NiCo_2O_4 (413 F g^{-1}). Characteristics such as the morphology and structure of the material are investigated, and the electrochemical characteristics of the electrodes are demonstrated.

Experimental

For hydrothermal synthesis, the precursors CoCl_2 (1.855 g), NiCl_2 (0.95 g) and urea (0.72 g) were dissolved in 60 ml of deionized water and stirred with a magnetic stirrer until a transparent homogeneous pink solution was formed. Then the solution was transferred to an autoclave, where a piece of nickel foam was also placed diagonally across the container. The autoclave was hermetically sealed and kept in a furnace at a temperature of 120°C for 6 hours. After cooling to room temperature, the precursor grown on nickel foam was washed with deionized water and dried at 50°C for 4 hours. The resulting NiCo_2O_4 product was sulfidized through hydrothermal treatment in an autoclave containing 1.8 g of Na_2S solution. The temperature of the furnace was 180°C , the treatment time lasted 8 hours. After cooling to room temperature, the resultant sample on a nickel substrate was processed in an ultrasonic bath to remove excess powders that did not adhere to the substrate. Then the samples were dried at a temperature of 50°C in air.

Results and Discussion

The phase composition in this work was determined using a MiniFlex Rigaku X-ray diffractometer. The XRD patterns were acquired by scanning in the range of 2θ from 5° to 90° and step size = 0.02° . The X-ray source was an X-ray tube with a copper anode, $\text{CuK}\alpha$ radiation at a wavelength of 1.5418 \AA , operating parameters of the tube: voltage 40 kV, current 44 mA. Figure 1 illustrates the XRD data of the synthesized NiCo_2O_4 and NiCo_2S_4 samples. The results show the formation of nickel-cobalt oxide, which is characterized by intense peaks at 2θ angles of 36.7° , 55.5° , 59.1° , and 65.1° , and these reflections can be well identified as (311), (422), (511), and (440) reflections from the NiCo_2O_4 phase [7]. In addition, two intense diffraction peaks at 44.7° and 52.1° are indexed by the (111) and (200) diffraction planes of nickel, which correspond to the substrate. Figure 1b shows that after sulfurization, the XRD pattern shows distinct peaks at 31.6° , 38.3° , 50.5° , and 55.3° , which correspond to diffraction on the (311), (400), (511), and (440) planes that can be attributed to a cubic phase of NiCo_2S_4 (Fig. 1b). However, individual peaks at 21.69° , 31.4° , 38.26° , 50.3° , and 55.4° correspond to the (101), (110), (003), (113), and (300) diffraction planes characteristic for the Ni_3S_2 phase (PDF no. 24–0334). This is because the replacement of Ni atoms by Co atoms does not change the crystal structure of Ni_3S_2 , except for changing the lattice parameters [8].

Figure 2 demonstrates SEM images of samples obtained using a Quanta 200i 3D scanning electron microscope (FEI Company, USA, 2008). Figure 2a shows typical morphology of three-dimensional (3D) nickel foam with as synthesized samples. It can be seen (Fig. 2b) that NiCo_2O_4 nanostructures in the form of nanoneedles uniformly grown on the substrate. Also, the nanoneedles grew at various angles relative to the substrate. This is caused by the high concentration of the precursor, which affected the growth direction of the nanoneedles. The diameter of nanoneedles can reach up to 200 nm (Fig. 2c).

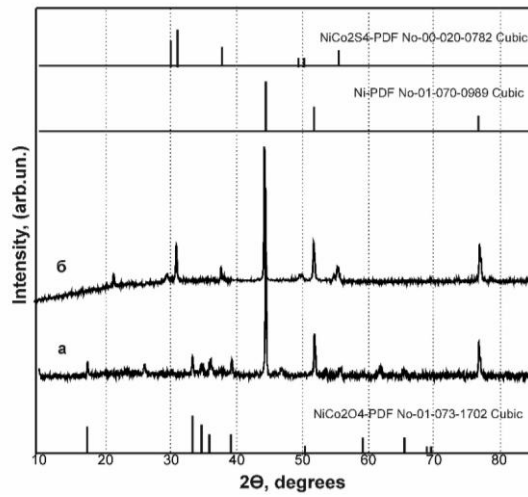


Figure 1. XRD pattern of synthesized samples NiCo₂O₄ (a) and NiCo₂S₄ (b)

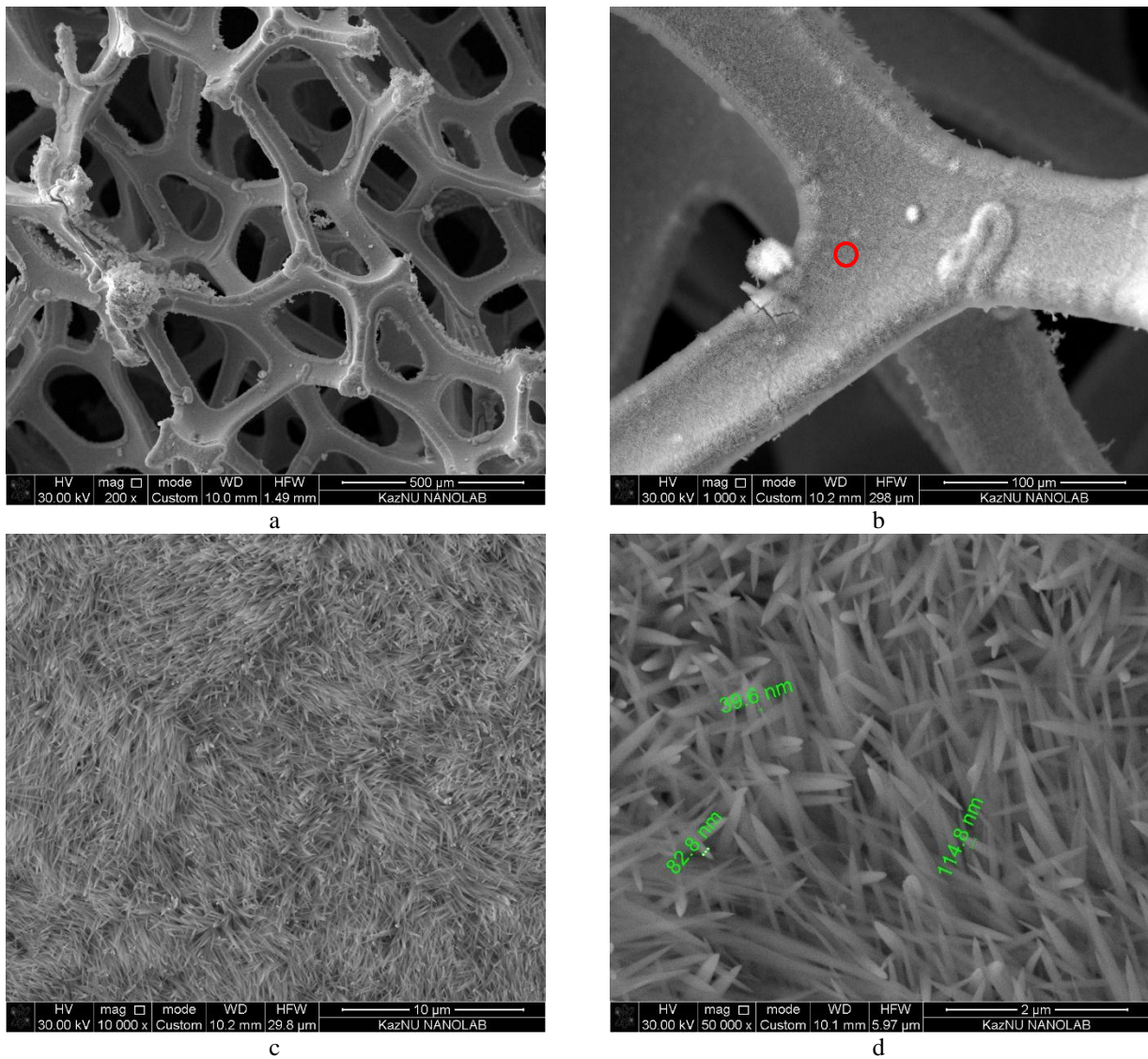


Figure 2. SEM images and morphology of NiCo₂O₄ at different magnifications

Figure 3 indicates the surface of the samples after sulfurization, exactly NiCo₂S₄ nanostructures. Figure 3a shows morphology with low magnification, so there are no changes compared to Figure 2a. Figure 3b also

has no distinguishing features compared to the samples before sulfurization. However, at high magnification (Figure 3c), there is no initially smooth surface of nanoneedles. Each needle has a nanosized branch, which increases the specific surface of the samples (Fig. 3d).

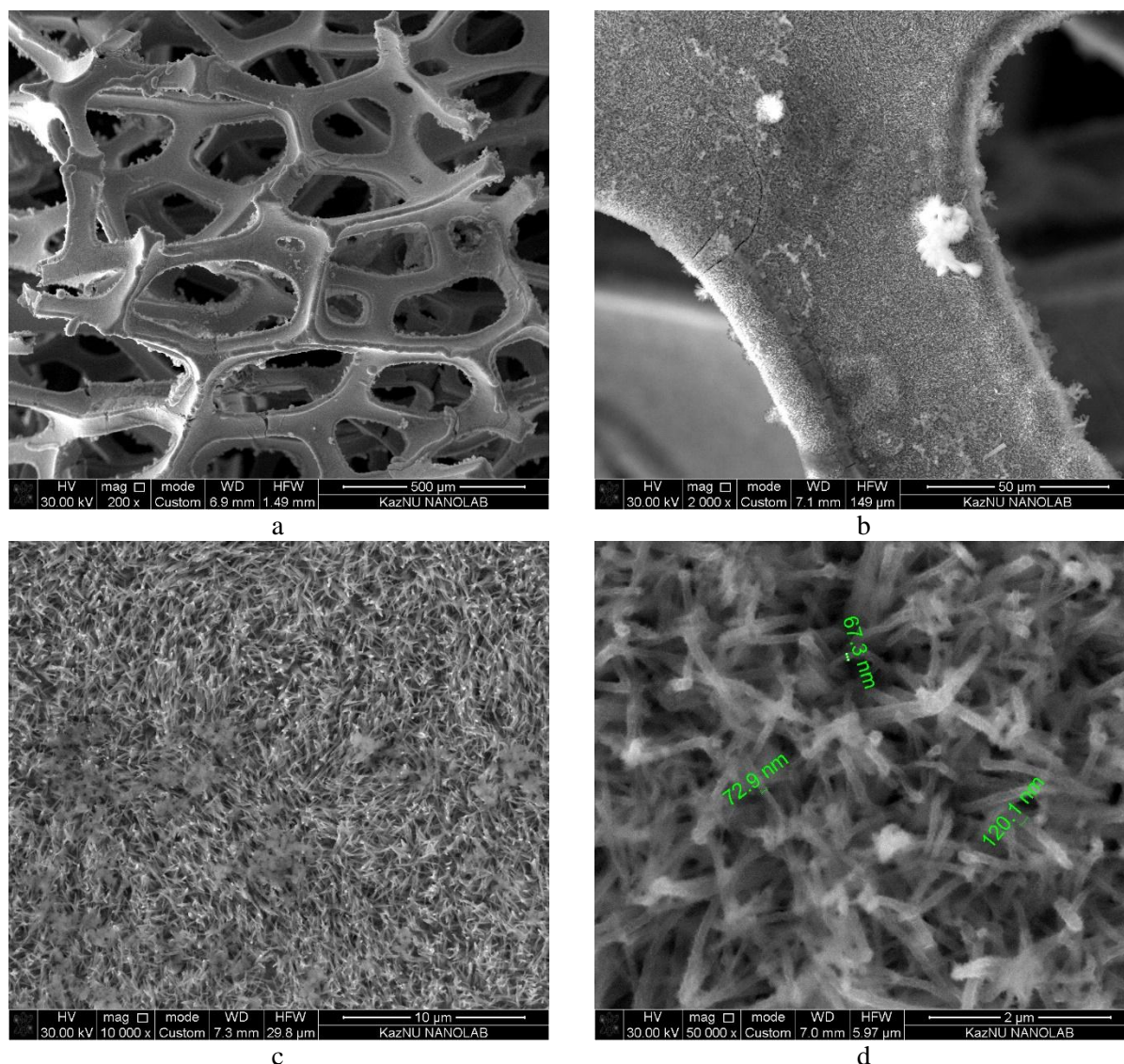
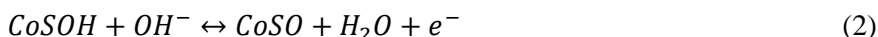


Figure 2. SEM images and morphology of NiCo_2S_4 at different magnifications

The electrochemical properties of the synthesized sample were tested by cyclic voltammetry (CV) and galvanostatic charge-discharge (GCD) measurements. All measurements of electrochemical characteristics were carried out using a 3M KOH aqueous electrolyte. In the three-electrode system, the active material in the form in which it was synthesized was used as the working electrode, while a platinum electrode was used as the counter electrode, and silver chloride (Ag/AgCl) electrode was used as the reference electrode. The area of the working electrode is $1 \times 1 \text{ cm}^2$. Before measurement, the samples were pressed under a pressure of 3 MPa.

Figure 4 shows the CV (current-voltage) characteristics of the obtained NiCo_2O_4 and NiCo_2S_4 samples, measured in a three-electrode system at scan rates of 5, 10, 20, and 50 mV/s and a potential range of -0.2 to 0.5 V. The shape of the CV curves indicates that the capacitive characteristics correspond to a material with a typical pseudocapacitance, the CV characteristic strongly differs from the electric capacitance of a double layer, which demonstrates a CV shape close to rectangular [9]. Two pairs of observed peaks mainly result from the Faraday redox reactions $\text{Co(II)} \leftrightarrow \text{Co(III)}$ and $\text{Ni(II)} \leftrightarrow \text{Ni(III)}$ [10]. The mechanism of charge accumulation by NiCo_2S_4 in an alkaline electrolyte can be explained by the following reactions [11–12]:



with an increase in the scan rate, the anodic and cathodic peaks shift towards more positive and negative potentials, respectively, due to redox reaction that is determined by dynamics of charge transfer in both samples (Fig. 4a, b) [13].

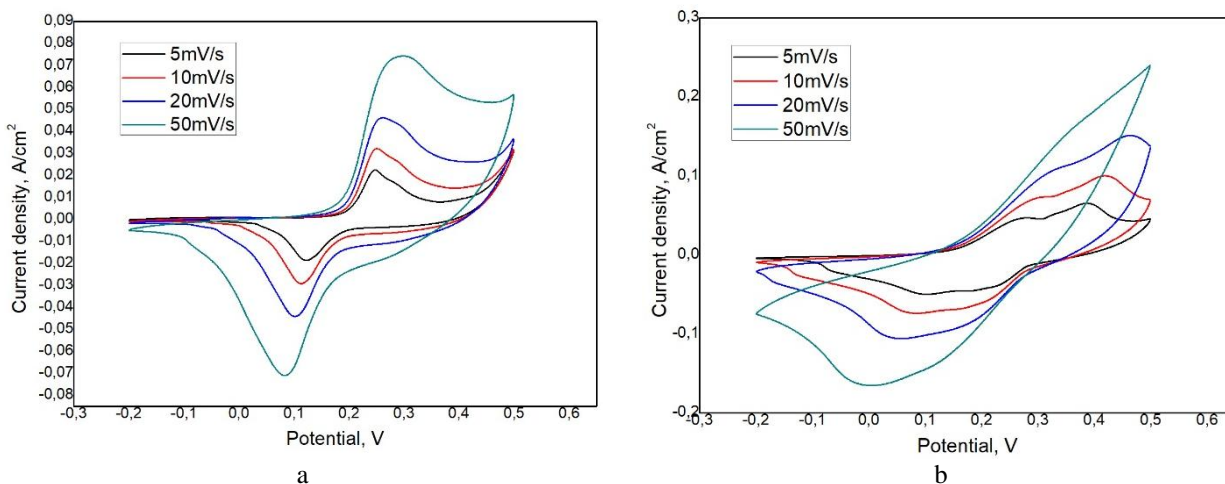


Figure 4. Cyclic voltammetry (CV) curves of NiCo₂O₄ (a) and NiCo₂S₄ (b) samples measured in a three-electrode system

It is seen from Figure 5a that NiCo₂S₄ sample has a large area under CV curves compared to that of NiCo₂O₄. Specific capacitance C_s depicted in Figure 5b was calculated from the CV curves at three-electrode measurements using the following equation (4):

$$C_s = \frac{1}{2mv(V_{max}-V_{min})} \oint I(V)dV \tag{4}$$

where C_s – specific capacitance, m – mass of deposited material, v – scan rate, $V_{max}-V_{min}$ – potential window, $I(V)$ – current, the integration is performed for 1 CV cycle. NiCo₂S₄ sample demonstrates high capacitance at all scan rates as opposed to NiCo₂O₄ sample. The C_s value considerably increases with decreasing scan rate since at a low scan rate H^+ ions diffuse deep inside the electrode. Maximal C_s value calculated from CV curves equals 1976 $\text{F}\cdot\text{g}^{-1}$ for NiCo₂S₄ and 413 $\text{F}\cdot\text{g}^{-1}$ for NiCo₂O₄.

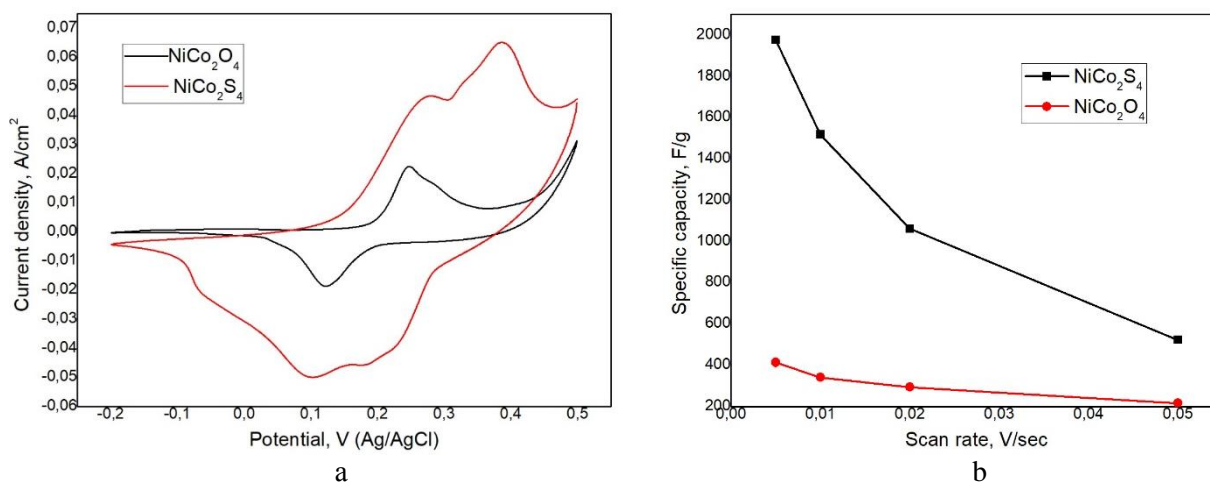


Figure 5. Comparative cyclic voltammetry curves of NiCo₂O₄ and NiCo₂S₄ samples measured at a scan rate of 5 mV/s (a) and dependence of specific capacitance on scan rate (b)

Conclusions

The paper presents the results of the synthesis of NiCoO_x nanostructures for the development of electrochemical energy storage systems. Methods for the synthesis of NiCo₂O₄ nanostructures by the hydrothermal method were worked out, followed by the production of NiCo₂S₄ nanostructures by sulfidization. The main characteristics, such as structure, phase composition and morphology were determined, and comparative studies of the electrochemical characteristics of the electrodes were carried out. It is shown that the sulfidization of oxides leads to an increase in the conductivity and specific capacitance of the samples. High capacitance values (1976 F·g⁻¹) were obtained, which is the main criterion in the development of energy storage systems. A comparison of the electrochemical properties showed that sulfidization of NiCo₂O₄ samples with the formation of the NiCo₂S₄ phase increases the electrical conductivity and increases capacitance by several times.

Acknowledgments

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Суперконденсаторларға арналған NiCo₂O₄ және NiCo₂S₄ нанокұрылымдардың электрохимиялық қасиеттерін салыстыру

Мақалада суперконденсаторларда электрод ретінде қолданылатын NiCo₂O₄ және NiCo₂S₄ нанокұрылымдарын гидротермалды әдіспен синтездеу және олардың қасиеттерін зерттеу нәтижелері көрсетілген. Үш оксиді металдан тұратын NiCo₂O₄ нанокұрылымдарын никель төсеніште өсіру әдісі оңтайланды. Алынған NiCo₂O₄ нанокұрылымдарының құрылымдық ерекшеліктері рентген фазалық

анализбен зерттелген. NiCo_2O_4 және NiCo_2S_4 нанокұрылымдарының үлгілері кубтық модификацияға ие екендігі анықталды. Алынған үлгілердің беттік морфологиясы сканерлеуші электрондық микроскопия арқылы зерттелінді. Үлгілер никель төсенішінде өскен наноине және нанотармақ пішіндес болып шықты. NiCo_2O_4 нанокұрылымдарын синтездеу әдісі және олардың өсуінің оңтайлы шарттары анықталды, сонымен қатар NiCo_2O_4 нанокұрылымдарынан күкірттеу әдісі арқылы NiCo_2S_4 нанокұрылымдарын алу әдісі тағайындалды. Күкірттеудің электрохимиялық сипаттамаларына әсерін байқау үшін салыстыру жұмыстары жүргізілді. Нәтижесінде, NiCo_2O_4 нанокұрылымдарының теориялық меншікті сыйымдылығы үлкен болғанына қарамастан, оттегі атомдарын күкірт атомдарына ауыстыру алынған NiCo_2S_4 үлгілердің меншікті сыйымдылығының жоғарлауына әкелетіндігі анықталды. NiCo_2S_4 электродтары үшін алынған ең үлкен меншікті сыйымдылық C_s 1976 Ф г^{-1} және NiCo_2O_4 электродтары үшін 413 Ф г^{-1} (5 мВ/сек сканерлеу жылдамдығында алынған) болды. Сонымен қатар, сканерлеу жылдамдығына меншікті сыйымдылықтың тәуелділігі берілген.

Кілт сөздер: суперконденсаторлар, энергияны сақтау, металл оксидтері, электродтар, наноматериалдар, NiCo_2O_4 , NiCo_2S_4 және нанокұрылымдар.

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Сравнение электрохимических характеристик наноструктуры из NiCo_2O_4 и NiCo_2S_4 для суперконденсаторов

В статье представлены результаты по синтезу и исследованию свойств наноструктур NiCo_2O_4 и NiCo_2S_4 , полученных методом гидротермального синтеза для применения их в качестве электродов суперконденсаторов. Отработан метод выращивания наноструктуры из тройного оксида металлов NiCo_2O_4 на никелевой подложке. Изучены структурные особенности синтезированных наноструктур NiCo_2O_4 и NiCo_2S_4 с помощью рентгенофазового анализа. Полученные образцы имеют кубическую модификацию NiCo_2O_4 и NiCo_2S_4 . Приведены данные по морфологии синтезированных образцов, полученных методом сканирующей электронной микроскопии. Образцы имеют форму наноиголки и нановетки, выращенные на никелевой подложке. Изучены методы синтеза наноструктур NiCo_2O_4 и определены оптимальные условия роста наноструктур из NiCo_2O_4 , а также отработан метод сульфидизации NiCo_2O_4 для получения NiCo_2S_4 наноструктуры. Проведены сравнительные исследования по влиянию сульфидизации на электрохимические характеристики полученных электродов. Обнаружено, что, несмотря на то, что оксидные наноструктуры из NiCo_2O_4 имеют высокую теоретическую емкость, замена атомов кислорода на атомы серы повышает проводимость материалов и приводит к дальнейшему росту удельной емкости конечных электродов NiCo_2S_4 . Максимальная C_s , полученная удельная емкость для NiCo_2S_4 , составляет 1976 Ф г^{-1} , и тогда как для NiCo_2O_4 она равна 413 Ф г^{-1} при скорости сканирования 5 мВ/с. Также представлены результаты зависимости удельной емкости от скорости сканирования при измерении.

Ключевые слова: суперконденсаторы, хранение энергии, оксиды металлов, электроды, наноматериалы, NiCo_2O_4 , NiCo_2S_4 и наноструктуры.