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Electrochemical and electrical properties of nickel molybdate / carbon material composites

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The aim of this paper is to establish the optimal content of carbon material in composites with nanocrystal hydrate nickel molybdate. To achieve this, $NiMoO_4$ / C composites with a carbon material content of 1, 5 and 10% by weight (with and without ultrasonic irradiation) were obtained by hydrothermal method. As a result of electrochemical studies, it was found that the maximum specific capacitance of 628 F/g is reached by a composite with a carbon content of 1% after ultrasonic exposure, while this composite shows excellent electrical conductivity, which is 0.47 S/m.

Keywords: nickel molybdate, carbon material, composite, specific capacitance, electrical conductivity, hybrid capacitor.

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Introduction

Mixed oxides of transition metals such as metal molybdates $MMoO_4$ (M - Ni, Co, Mn) due to their multiple valence states and high electrical conductivity are considered the best materials for electrodes of electrical energy storage devices compared to single oxides of transition metals [1]. Nickel, cobalt and manganese molybdates are widely used in hybrid capacitors [2] however they have a number of disadvantages, which limits their ability to achieve theoretical capacitance (theoretical capacitance of $NiMoO_4$ is 735 F/g). Thus, the electrochemical charge/discharge testing the binary transition metal oxides are subjected to degradation, swelling of the material and the phase transition. One way to solve this problem is to form composites based on binary oxides of molybdates with carbon material, which allows us to increase the electrical conductivity of the material and the number of active centers for ion adsorption [3]. Another effective way to improve the specific energy characteristics of materials for the electrodes of hybrid capacitors is ultrasonic modification. Because ultrasonic dispersion of oxides, sulfides of transition metals and composites based on them leads to a decrease in the particle size of materials and the formation on their surface of uncompensated chemical bonds capable of interacting with electrolyte ions [4]. In addition, $NiMoO_4$ is an inexpensive, chemically stable and environmentally friendly material with good electron transport characteristics (electrical conductivity varies in the range from 10^{-13} to 10^{-6} S/m) combined with the electrochemical activity of nickel ions [5].

In this paper, hydrate nickel molybdate / carbon material composites ($NiMoO_4$/C) with a percentage of carbon material of 1, 5 and 10 % by weight (with and without ultrasonic irradiation) obtained by hydrothermal method [6]. We performed electrochemical studies and measured the specific conductivity of materials to determine the optimal content of carbon material in composites.

I. Materials and methods

Modification of the carbon material was carried out for 1 h in distilled water using an ultrasonic dispersant operating frequency range 20 - 25 kHz. Electrochemical studies were performed using an 8-channel charge / discharge stand "Tionid" in a three-electrode cell by cyclic voltammetry and galvanostatic charges / discharge testing. The working electrodes were formed from composites, the auxiliary was a platinum electrode, and the reference electrode was a chlorine-silver electrode. A 33 % aqueous solution of potassium hydroxide was used as the electrolyte. The working electrode was formed from a mixture of: 80% composite and 20 % conductive additive (acetylene carbon black), which was mixed with alcohol and pressed into a nickel mesh with an area of 25 мм^2. The mass of active material in each electrode was approximately 15 mg. Specific discharge capacitances of materials were calculated from cyclic voltammograms by the formula: $\mathrm{C} = \frac{Q}{m\Delta U}$, where Q – the charge is given (accumulated) by the electrochemical system during cathode (anode) scanning, m - mass of material, ΔU – potential range. Specific capacitances from discharge curves were calculated by the formula: $\mathrm{C} = \frac{I\Delta t}{m\Delta U}$, I – current, Δt – discharge time. Electrical conductivity at room temperature was studied using a measuring complex AUTOLAB PGSTAT12 in the frequency range 10^{-2} –10^5 Hz at a voltage of 0 V. The real part of conductivity defined by the formula: $\sigma = \frac{h}{Z'S}$, where h - the thickness of the sample, Z' - the real part of the resistivity, S - surface area of the test sample (diameter was 14 mm).

II. Results and discussions

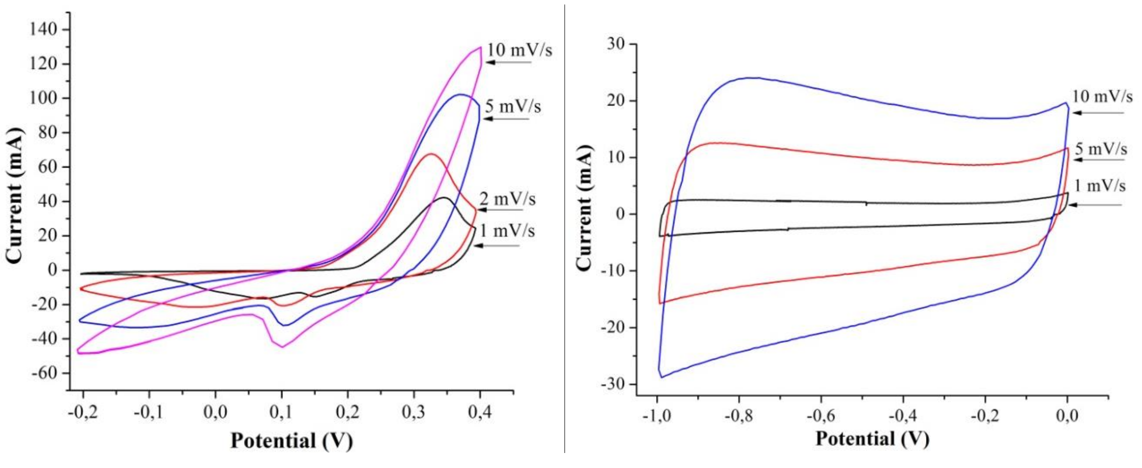
Cyclic voltammograms (CVs) of nanocrystal $NiMoO_4$ hydrate were taken in the potential range of -0.2 to 0.4 V at a scan rate of 1 - 10 mV / s are presented in Fig. 1a. During the anodic scanning of the electrode based on $NiMoO_4$ hydrate in the KOH electrolyte the reaction of splitting water molecules takes place, followed by the release of oxygen molecules: $2H_2O \rightarrow O_2 + 2H_2$ [7]. In our case, the reaction of oxygen evolution takes place at a potential of 0.4 V and leads to a significant increase in specific current and, accordingly, the destruction of the material. Therefore, we limited the potential scanning range to 0.4 V. The specific discharge capacitances of $NiMoO_4$ hydrate were 575, 486, 347 and 242 F/g at scan rates of 1, 2, 5 i 10 mV/s.

The carbon material has a specific capacitances of 90, 80 and 76 F/g at scan rates of 1, 5 and 10 mV/s, respectively, in the range of -1 to 0 V using a three-electrode cell (Fig. 1b). The specific capacitance of the carbon material is mainly provided by the charge / discharge of the electric double layer at the electrode / electrolyte interface, which is facilitated by the large specific surface area of the carbon material ~ 1200 m^2 / g with a large number of micro pores [8].

In $NiMoO_4$ / C composites, the content of carbon material was 1, 5 and 10 % by weight, as it was found [9] that in the mechano-chemical synthesis of materials, the highest specific capacitance is achieved by a composite based on nickel hydroxide with a carbon content of 10 %. Therefore, we formed four $NiMoO_4$ / C composites with carbon content: 1 and 10% (without ultrasonic exposure) and 1 and 5 % (carbon material was subjected to ultrasonic dispersion (denoted as C us)).

The monoclinic crystal structure of nickel molybdate hydrate is constructed of pairs of NiO_6 and $NiO_5(OH_2)$ octahedrons that share common edges connected by MoO_4 tetrahedrons, thus forming a network structure with open channels [10]. $NiMoO_4$ hydrate contains coordinated water bound by a hydrogen bond to the crystal lattice, as well as lattice water. Coordinated water molecules can be removed by thermal desorption of hydrate at a temperature of 280 - 400 ℃, , followed by the formation of a triclinic crystal structure α-$NiMoO_4$, while lattice water can be easily removed by heating to lower temperatures, namely 120 – 160 ℃ [11]. The migration of protons through the oxide lattices is significantly enhanced by the presence of molecules of coordinated water [12]. Solid-state diffusion of protons leads to increased electrochemical activity of nickel molybdate hydrate and therefore higher specific capacitance.

Redox peaks on the CVs of composites (Fig. 2 a, b)



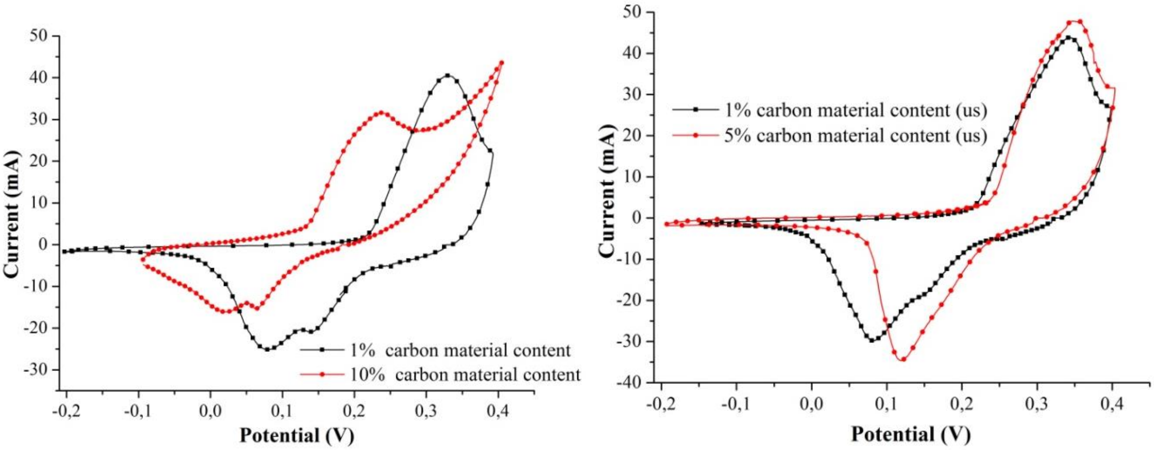
a) b)

Fig. 1. Cyclic voltammograms of the electrode based on nanocrystal $NiMoO_4$ hydrate (**a**) and the electrode based on carbon material (**b**) using three electrode cells.

are the result of the interaction of nickel ions from the structure of molybdate with OH^- ions from the electrolyte, followed by the formation of $Ni(OH)_2$. Oxidation of nickel hydroxide to nickel oxyhydroxide occurs under charge (positive current). During the discharge (negative current), nickel ions are reduced: $Ni^{3+} + e^- \rightarrow Ni^{2+}$. It should also be noted that along with the intercalation of protons in the crystal structure of nickel hydroxide, there is an intercalation of K^+ ions from the electrolyte into the layered structure of NiOOH, which explains the asymmetry of the redox peaks of the materials. Fig. 2a shows that the area of CV, and accordingly the charge accumulated / given at a scan rate of 1 mV/s, a composite with a carbon content of 1 % is much higher than a composite with a content of C – 10 %. For a 1 % C us composite, the area of the discharge curve is higher than for a 5 % C us composite.

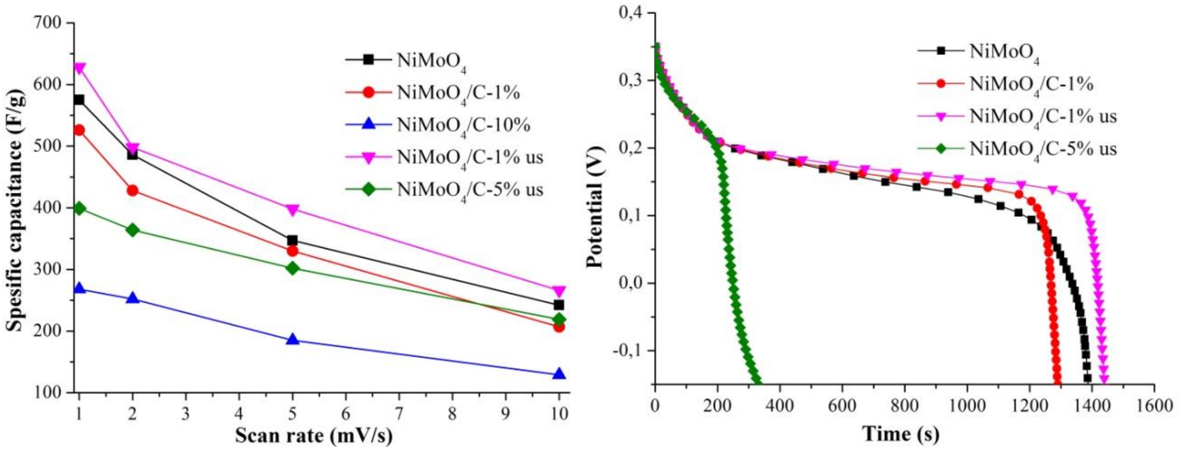
The dependences of the specific capacitances of composites with different content of carbon material on the scan rate are presented in Fig. 3. It is established that the maximum specific capacitance of 628 F/g at a scan rate of 1 mV/s in the potential range of -0.15 - 0.4 V reaches a composite with a carbon material content of 1 % pre-dispersed by ultrasound, whereas the specific capacitance of pure hydrate of nickel molybdate was 575 F/g. Ultrasonic treatment of carbon material increases the average range of diameters of micro- and mesopores and accordingly increases the capacitive characteristics of composites [8]. However, as the carbon content increases to 10 %, the specific capacitance decreases to 260 F/g, which is probably due to a decrease in the redox activity of nickel ions.

Charge / discharge tests were performed in the potential range of -0.15 to 0.35 V at specific currents of 0.2, 0.5 and 1 A/g. The nonlinear discharge curves are confirmed by the Faraday type of charge accumulation due to the intercalation of electrolyte ions into the material structure and redox reactions, and agree well with the available peaks on the CVs curves of these composites. The specific capacitance at a discharge current of 0.2 A/g was 558 F/g for the $NiMoO_4$ hydrate, 520 F/g - $NiMoO_4$/C (1 % C), 576 F/g – $NiMoO_4$/C (1 % C us), 133 F/g - $NiMoO_4$/C (5%C us) and 95 F/g – $NiMoO_4$/C (10 % C) composites.



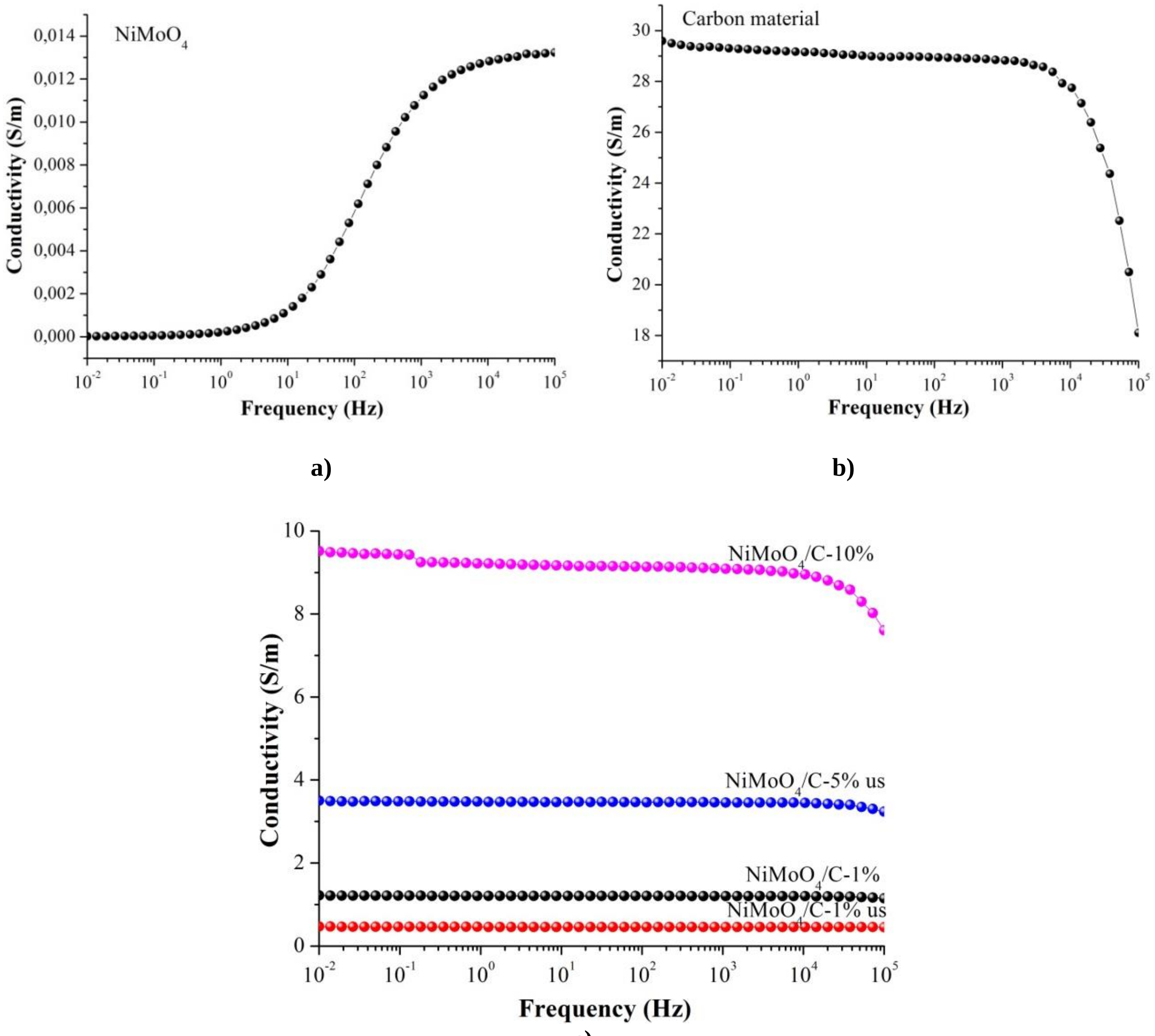
a) **b)**

Fig. 2. Cyclic voltammograms of $NiMoO_4$ / C composites at scan rate of 1 mV/s. The content of carbon material was by weight 1 and 10% (**a**) and 1 and 5% (carbon material was pre-dispersed by ultrasound (us) for 1 h) (**b**).



a) **b)**

Fig. 3. Dependence of the specific capacitance on the scan rate of $NiMoO_4$ hydrate and $NiMoO_4$ / C composites with 1 - 10 % carbon material content (**a**). Discharge curves at a current of 0.2 A/g of $NiMoO_4$ hydrate and composites with different carbon material content (**b**).



a) b)

c)

Fig. 4. Frequency dependences of electrical conductivity of nickel molybdate hydrate (**a**), carbon material (**b**) and composites with a carbon material content of 1 - 10 % (**c**).

To determine the optimal ratio between the content of carbon material in the composites and the electrical properties of the materials we measured the frequency dependence of the specific conductivity (Fig.4). It is established that the specific electrical conductivity of $NiMoO_4$ hydrate is $1.07 \cdot 10^{-4}$ S/m and is 100 times higher than the conductivity of pure nickel hydroxide determined in [4]. Such high electrical conductivity is mainly provided by molybdenum atoms, while nickel atoms are responsible for redox reactions. The higher electrical conductivity of molybdate can also be explained by the presence of oxygen vacancies in MoO_4 tetrahedrons, which act as active centers for redox reactions and provide dissociation of water molecules into OH^- groups. Oxygen vacancies contribute to better charge accumulation kinetics and, accordingly, increase the capacitive characteristics of molybdate [13]. Nanocrystal $NiMoO_4$ shows a plateau in the low-frequency region with a subsequent increase in conductivity with increasing frequency (Fig. 4a). The frequency independence of the conductivity is related to the orientation polarization of the induced dipoles along the direction of the applied electric field. With increasing frequency, the relaxation time for orientation polarization is significantly reduced, resulting in a sharp increase in conductivity on alternating current [14].

As a result of the formation of composites with carbon material, the electrical conductivity of materials increases significantly (Fig. 4c). Carbon material with an electrical conductivity of 29 S/m (Fig. 4b) and a large number of micro- and mesopores is an ideal matrix for the deposition of nanocrystal $NiMoO_4$, avoids agglomeration of nanoparticles and at the same time forms an interconnected conductive network that increases electron tunneling. At 1% carbon content, the specific electrical conductivity of composites is 1.22 S/m and 0.47 S/m with ultrasonic irradiation and increases with increasing carbon content.

From the results of electrochemical and electrical studies it was found that $NiMoO_4$ hydrate and composites based on it show the electrochemical behavior characteristic of battery-type materials and are promising materials as cathodes of hybrid capacitors. The optimal ratio between electrical conductivity and specific capacitance has a composite with a carbon material content of 1 % (Fig. 5), for which the specific

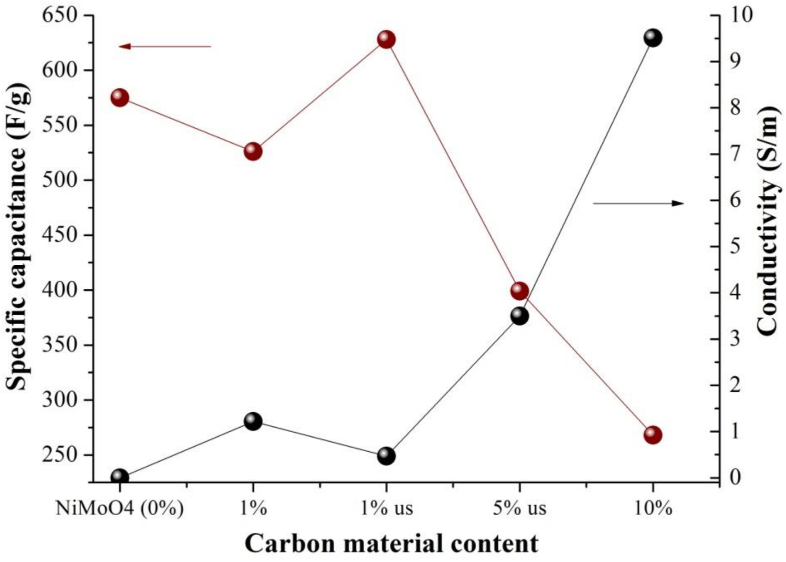


Fig. 5. Specific capacitance and electrical conductivity of hydrate $NiMoO_4$ and $NiMoO_4$ / C composites.

capacitance calculated from CV at a scan rate of 1mV/s reaches a maximum value of 628 F/g, while this composite has a conductivity of 0.47 S/m.

Conclusions

The results of electrochemical and electrical studies of nickel molybdate hydrate and composites based on it demonstrate that these materials are promising as cathodes of hybrid capacitors. Namely, the crystal structure of $NiMoO_4$ hydrate promotes the redox reactions and intercalation of electrolyte ions, while the formation of composites with carbon material provides active sites for the deposition of nanocrystal $NiMoO_4$ and increases electron tunneling. It was found that the specific capacitance of $NiMoO_4$ / C composites decreases with increasing carbon content. The composite with 1% carbon content after ultrasonication has an optimal ratio between capacitive and electrical characteristics, namely the specific capacitance is 628 F/g, while the specific conductivity is 0.47 S/m.

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[1] H. Chen, S. Chen, Y. Zhu, C. Li, M. Fan, D. Chen, G. Tian, K. Shu, Electrochimica Acta 190, 57 (2016); https://doi.org/10.1016/j.electacta.2015.12.212.
[2] D. Cai, D. Wang, B. Liu, Y. Wang, Y. Liu, L. Wang, H. Li, H. Huang, Q. Li, T. Wang, ACS applied materials & interfaces 5(24), 12905 (2013); https://doi.org/10.1021/am403444v.
[3] Y. Hao, H. Huang, Q. Wang, Q. Wang, G. Zhou, Chemical Physics Letters 728, 215 (2019); https://doi.org/10.1016/j.cplett.2019.05.010.
[4] O. Khemii, I. Budzulyak, L. Yablon, D. Popovych, O. Morushko, R. Lisovskiy, Materials Today: Proceedings 35, 595 (2019); https://doi.org/10.1016/j.matpr.2019.11.207.
[5] B. Moreno, E. Chinarro, M. T. Colomer, and J. R. Jurado, J. Phys. Chem. C 114 (10), 4251 (2010); https://doi.org/10.1021/jp907870a.
[6] O.M. Popovych, I.M. Budzulyak, V.O. Yukhymchuk, S.I. Budzulyak & D.I. Popovych, Fullerenes, Nanotubes and Carbon Nanostructures 1 (2021); https://doi.org/10.1080/1536383X.2021.1925253.
[7] O. Rabbani, S. Ghasemi, S.R. Hosseini, Journal of Alloys and Compounds 840, 155665 (2020); https://doi.org/10.1016/j.jallcom.2020.155665.
[8] B.I. Rachiy, M.O. Nykoliuk, I.M. Budzulyak, & A.I. Kachmar, Nanoscale Research Letters 12(1), 79 (2017); https://doi.org/10.1186/s11671-017-1842-1.

[9] O.M. Hemiy, L.S. Yablon, I.M. Budzulyak, S.I. Budzulyak, O.V. Morushko, A.I. Kachmar, J. Nano- Electron. Phys. 8 (4), 04074 (2016); https://doi.org/10.21272/jnep.8(4(2)).04074).

[10] K. Eda, Y. Kato, Y. Ohshiro, T. Sugitani, & M.S. Whittingham, Journal of Solid State Chemistry 183(6), 1334 (2010); https://doi.org/10.1016/j.jssc.2010.04.009.

[11] J.A. Rodriguez, S. Chaturvedi, J.C. Hanson, A. Albornoz, J.L. Brito, The Journal of Physical Chemistry B 102(8), 1347 (1998); https://doi.org/10.1021/jp972137q.

[12] S. Deabate, F. Henn, S. Devautour, J.C. Giuntini, Journal of the Electrochemical Society 150(6), J23 (2003); https://doi.org/10.1149/1.1573203.

[13] C. Qing, C. Yang, M. Chen, W. Li, S. Wang, Y. Tang, Chemical Engineering Journal 354, 182 (2018); https://doi.org/10.1016/j.cej.2018.08.005.

[14] S. Maiti, B.B. Khatua, RSC advances 3(31), 12874 (2013); https://doi.org/10.1039/C3RA41617H.

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Електрохімічні та електричні властивості композитів молібдат нікелю / вуглецевий матеріал

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Основною метою дослідження є встановлення оптимального вмісту вуглецевого матеріалу у композитах з нанокристалічним гідратом молібдату нікелю. Для цього гідротермальним методом отримали композити $NiMoO_4/C$ з відсотковим вмістом вуглецевого матеріалу 1, 5 та 10 % по масі (з та без ультразвукового опромінення). В результаті проведення електрохімічних дослідження встановлено, що максимальної питомої ємності 628 Ф/г досягає композит з вмістом вуглецевого матеріалу 1 % після ультразвукового диспергування, водночас даний композит демонструє чудову електропровідність, яка становить 0,47 См/м.

Ключові слова: молібдат нікелю, вуглецевий матеріал, композит, питома ємність, електропровідність, гібридний конденсатор.