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Electrochemical Properties of Hybrid Supercapacitors Formed Based on Nanoporous Carbon and Nickel Tungstate

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In this work, the morphology of carbon material (CM) has been researched by the nitrogen adsorption/desorption method. Furthermore, it was determined that the specific surface area is about 1200-1300 m^2/g. $NiWO_4$ was synthesized by co-precipitation method, and its structure was investigated by XRD. Additionally, the electrochemical properties of CM and $NiWO_4$ were studied by the methods of chronoamperometry and voltammetry, and the use of these materials as electrodes of hybrid supercapacitors (HSC) – anode and cathode, respectively, was tested. A hybrid electrochemical system of the CM/KOH/$NiWO_4$ type was formed. The use of this system makes it possible to increase the operating voltage range of HSC based on aqueous electrolytes from 0-1 V to 0.6-1.6 V, and, consequently, to increase the energy characteristics of a unit cell by more than 2 times. It is shown that at operating currents of 1 mA, the specific capacity of the HSC is 57.1 F/g, while the specific energy density and power are 7.09 Wh/kg and 1.39 W/kg, respectively.

Keywords: Electrochemical energy storage devices, Nickel tungstate, Porous carbon material, Aqueous electrolyte.

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1. INTRODUCTION

One of the most common devices for the accumulation and storage of electrical energy is an electrochemical capacitor (EC), which is due to the fact that ECs have a high specific power, long cycle life and short charge/discharge time [1, 2].

The most common material for the production of EC electrodes is carbon material (CM) [3]. The advantages of CMs are low cost, ease of manufacture and versatility of existing forms (foam, powders, composites, monoliths, foils). CM-based ECs operate on the charge/discharge principle of an electric double layer (EDL). Therefore, for effective recharging of EDL, materials with a large specific surface area and pore size adapted to the size of ions are needed, which is decisive for the performance of ECs [4, 5]. The porosity of CM and the pore size distribution were controlled depending on the chemical or physical activation performed. The most important parameters of the activation process are time, temperature and type of activating agent [6, 7].

Despite the large specific surface area of CMs, the amount of charge accumulated in the EDL is not large enough, which in turn limits the specific capacity and energy density of the device. Therefore, one of the ways to increase the energy density of EC is the formation of hybrid ECs, in which positive and negative electrodes are made of materials with different mechanisms of accumulation of electric charge due to an expansion of the operating voltage range [8, 9]. An increase in the voltage of a unit cell leads to a significant increase in the specific energy, and the use of CMs leads to an increase in the specific power of the device.

In this work, we study the effect of the porous structure of CMs on the electrochemical characteristics of HSCs formed based on CM and nickel tungstate.

2. SYNTHESIS AND RESEARCH OF MATERIALS AND METHODS

Nickel tungstate powdered material was obtained by co-precipitation method by mixing $Na_2WO_4 \cdot 2H_2O$ and $NiCl_2 \cdot 6H_2O$. Thus, $NiCl_2 \cdot 6H_2O$ (8 mmol) was dissolved in 50 ml of distilled water and stirred at 70 °C for 10 min during the synthesis procedure. At the next stage, 40 ml of $Na_2WO_4 \cdot 2H_2O$ (8 mmol) dissolved in distilled water was added dropwise. The addition process was carried out for 1 h, then the resulting suspension was further stirred at 70 °C for 3 h. Finally, the light green precipitate was repeatedly washed with deionized water several times and dried at 80 °C for 8 h in air.

CMs were derived from plant raw materials by carbonization and activation with potassium hydroxide. Moreover, dried apricot seeds as a feedstock were crushed to fractions from 0.25 to 1 mm and carbonized in a closed furnace at 330 to 350 °C with a heating rate of 10 °C/min. Thus, the resulting carbon was mechanically crushed to fractions from 200 to 250 μm and mixed with potassium hydroxide and water in a weight ratio: $m(C) : m(KOH) : m(H_2O) = 1 : 1 : 2$. The resulting mixture was thoroughly stirred for 1 to 2 h, after which it was dried in a thermostat to constant weight. Then, the dry material was placed in a furnace and heated in an argon atmosphere from 900 to 920 °C at a heating rate of 10 °C/min and kept at this temperature for 20 min. Finally, after cooling, the resulting material was washed with 5 % aqueous HCl and distilled water to neutral pH and again dried at 90 °C to constant weight [10].

The characteristics of the porous structure (surface area and total pore volume) of CM were determined by analyzing sorption isotherms of nitrogen at its boiling point (77 K), obtained using a Quantachrome Autosorb Nova2200e (Quantachrome Instruments, Boynton Beach, FL, USA).

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Electrochemical investigation of the electrode material/electrolyte system was carried out in a three-electrode cell. The working electrode was made of a mechanical mixture of the material under study and acetylene black in a ratio of 80 : 20. A platinum electrode was used as an auxiliary electrode, and a silver chloride (Ag/AgCl) reference electrode was placed in a 3.5 M aqueous solution of KCl and combined with the working chamber through an agar-agar salt bridge. A 30 % aqueous solution of KOH was used as the electrolyte. Electrochemical study was carried out using an Autolab PGSTAT/FRA-2 spectrometer in galvanostatic and potentiodynamic modes. Galvanostatic research was carried out at currents in a range of 1 to 100 mA. The cyclic voltammetry (CVA) investigation was performed at a scan rate of 1 to 50 mV/s. The specific capacitance of EC and hybrid supercapacitor (HSC) was calculated according to the procedure described in [11].

The performance characteristics of laboratory samples of HSC were determined in a two-electrode cell. In HSC, the cathode was made from a mechanical mixture of $NiWO_4$ and acetylene black in a ratio of 80 : 20. Another electrode (anode) was made by mixing CM with acetylene black, also in a ratio of 80 : 20. Finally, the resulting electrode materials were pressed into a nickel mesh. Afterwards, the electrodes were leaked by the electrolyte, separated by a separator and placed in a two-electrode cell of 25×25 size. After that, they were sealed.

3. RESULTS AND DISCUSSION

The crystal structure of $NiWO_4$ was investigated using X-ray diffraction analysis (CuKα radiation) in an angle range of $10° < 2\theta < 90°$. The obtained material is amorphous and/or nanoscale in accordance with low intensity of diffraction peaks. Also, $NiWO_4$ was kept in air at 600 °C for 1 h. Nevertheless, diffraction peaks corresponding to nickel tungstate from the database of inorganic crystal structure (ICSD No. 15852) were established in the obtained X-ray diffraction pattern.

The morphology of the obtained CM was investigated by the method of low-temperature adsorption/desorption of nitrogen, the quantitative characteristics of its porous structure are presented in Table 1.

Table 1 – Sorption properties of CM

S_{BET}, m^2/g	S_L, m^2/g	S_{DFT}, m^2/g	$S_{t\text{-}micro}$, m^2/g
1236	1405	1085	1040
$S_{BJH\text{-}meso}$, m^2/g	S_{micro}, %	V_{total}, cm^3/g	V_{micro}, cm^3/g
160	84	0.69	0.41

In particular, the specific surface area was determined by the BET (S_{BET}) method with a linear dependence of $1/[W(p_0/p)^{-1}]$ on p_0/p in the adsorption isotherm range for the p_0/p ratio in the range from 0.05 to 0.35 [12]. In addition, Langmuir (S_L) and DFT (S_{DFT}) methods were used to determine the total surface area of microporous CMs. The area of micropores was determined by the *t*-method ($S_{t\text{-}micro}$), and mesopores – by the BJH method ($S_{BJH\text{-}meso}$). The total pore volume (V_{total}) was calculated from the amount of adsorbed nitrogen at $P/P_0 \sim 1.0$, the volume of micropores (V_{micro}) was determined using the *t*-method. In the obtained CM, the specific area of mesopores is up to 15 % of the total surface area, which is 1200-1300 m^2/g. It is determined by the above three methods and correlates within an error of 10 %. The micropore volume determined by the *t*-method is 0.41 cm^3/g, which is about 60 % of the total pore volume determined at maximum pressure. Mesopores play the role of transport channels for adsorbate or electrolyte to enter micropores.

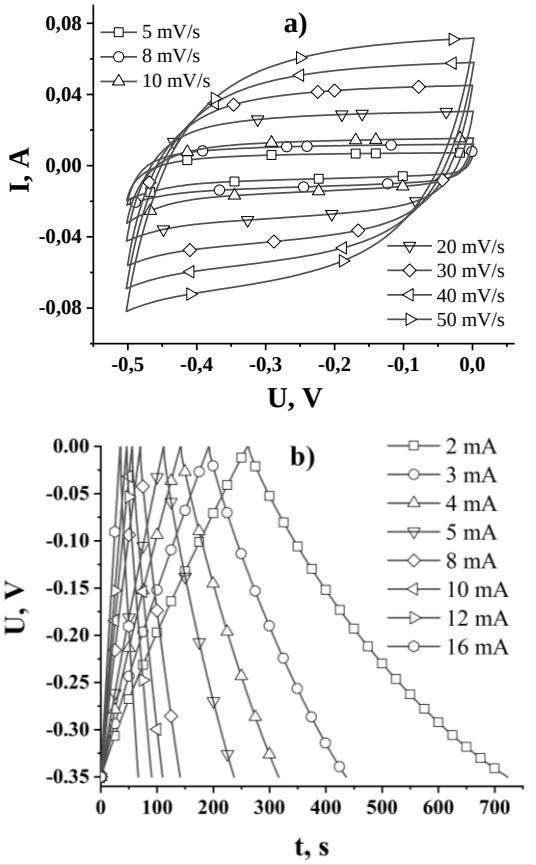

Fig. 1 – CVA curves (a) and galvanostatic charge-discharge curves (b) of the CM

Electrochemical studies of the obtained CM were carried out using a three-electrode cell. Cyclic voltammograms of the material under research are typical for EC with EDL (Fig. 1a). On the one hand, with increasing scan rate, the CVA curves deviate from a rectangular shape due to an increase in the internal resistance of the electrochemical system. On the other hand, with increasing scan rate, small diameter pores are available for electrolyte ions, they cause internal resistance, which is the result of diffusion, which restricts the movement of electrolyte ions in these pores [13].

The value of the specific capacity of the carbon electrode was determined from area *A* of the CVA curves by integrating the cathodic current $I(U)$ to the potential *U*, in the range from the anode limiting voltage U_a to the cathode limiting voltage U_c and dividing by the scan rate *s*, mass of the nanocomposite and voltage rate $(U_a - U_k)$ by the formula: $C = A/(2ms(U_a - U_k))$. At a scan rate of 5 mV/s, the specific capacity is 110 F/g and decreases to 79 F/g at a scan rate of 50 mV/s.

Fig. 1b shows the charge/discharge curves obtained for the carbon electrode. The investigated CM is electrochemically stable in this electrolyte, as evidenced by the linear dependence of the voltage on the discharge current, varying within 2-16 mA. Moreover, based on the obtained discharge curves, the specific capacities of the CM were determined. At a discharge current of 2 mA, the specific capacity is 212 F/g.

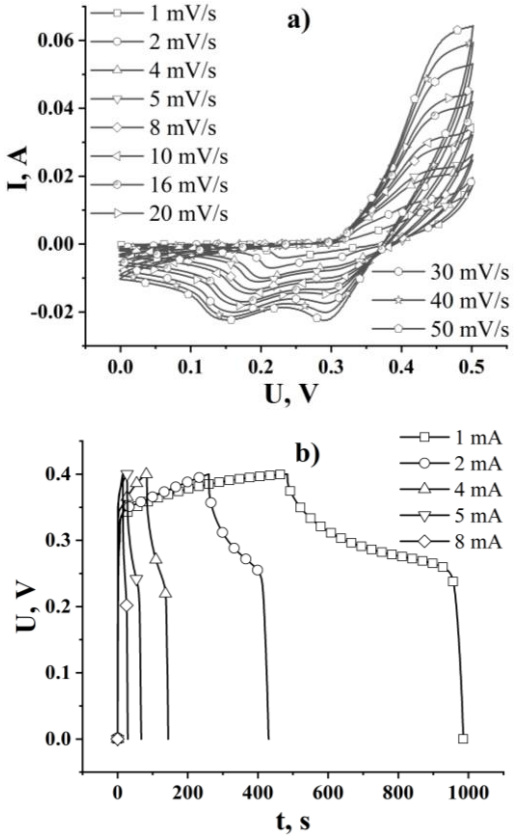

Fig. 2 – CVA curves (a) and galvanostatic charge-discharge curves (b) of the $NiWO_4$/electrolyte system

The CVA curves of the nickel tungstate/electrolyte electrochemical system are shown in Fig. 2a. All CVA curves have redox peaks, one anodic and cathodic peaks ($U = 0.23$ V) at low scan rates (1-5 mV/s), which shift towards a lower potential ($U = 0.15$ V) at a scan rate of 50 mV/s, and with an increase in the scan rate ($s > 10$ mV), a second cathode peak begins to appear ($U = 0.3$ V). The presence of peaks indicates the passage of electrochemical reactions, due to which the charge is accumulated. An increase in the scan rate by an order of magnitude (from 1 to 10 mV/s) leads to a twofold decrease in the specific capacity of the system, which indicates the prospect of using these materials at low scan rates.

Fig. 2b illustrates the discharge curves for the $NiWO_4$/electrolyte system obtained by the galvanostatic method. A linear section is observed in the voltage range 0.2-0 V, which is related to the capacity of the EDL formed at the electrode/electrolyte interface, and a plateau in the range 0.25-0.35 V, which is associated with pseudo-minus charge storage. Based on the experimentally obtained discharge curves (Fig. 2b), the dependence of the specific capacity of the system on the value of the discharge current was calculated. The specific capacity value at a discharge current of 1 mA is 105 F/g and gradually decreases with an increase in the discharge current.

Therefore, based on research of the electrochemical behavior of a CM in the negative potential range and nickel tungstate in the positive one, a hybrid electrochemical system of the CM/KOH/$NiWO_4$ type was formed. The use of materials with different nature of charge accumulation in an electrochemical system allows it to operate at higher voltages and, accordingly, increases the energy characteristics of a unit cell. The study of the joint functioning of electrode materials in a hybrid electrochemical system was carried out by the potentiodynamic method. To determine the optimal operating voltage of a single element, potentiodynamic investigations were carried out in a voltage range of 0-1.6 V. The operating potential window was 1 V. Fig. 3 illustrates the CVA curves obtained for HSC of the CM/KOH/$NiWO_4$ type at various operating potentials and a scan rate of 1 mV/s. In the entire voltage range, the operation of the electrochemical system is stable.

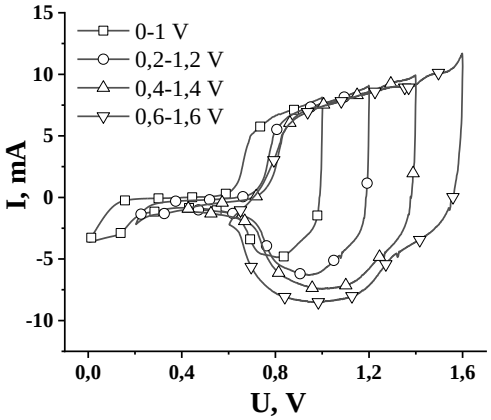

Fig. 3 – CVA curves for HSC at different working potentials

Based on the experimentally obtained CVA curves (Fig. 3), the values of the specific capacity of HSC were determined, which are 27.3, 32.9, 47.1, and 62.4 F/g in accordance with the values of the working potential 0-1, 0.2-1.2, 0.4-1.4, and 0.6-1.6 V. The HSC showed stability in the voltage range 0.6-1.6 V; therefore, further electrochemical research was carried out in that potential range.

Fig. 4 shows the dependence of the specific capacity on the scan rate for the CM/KOH/$NiWO_4$ system. It can be seen that the specific characteristics of the device decrease. In addition, depending on the scan rate, the redox reactions responsible for the amount of charge accumulation must be fast and vice versa, otherwise the charge accumulation decreases sharply.

The dependence of the specific capacity on the scan rate was calculated based on the obtained potentiodynamic curves for CM (Fig. 1a) and $NiWO_4$ (Fig. 2a). For CM at a scan rate of 5 mV/s, the capacity is 110 F/g and decreases linearly to 79 F/g with increasing scan rate to 50 mV/s. For $NiWO_4$ at a scan rate of 1 mV/s, the capacity is 98 F/g and decreases faster than for CM to 15 F/g at 50 mV/s, which is associated with the low rate of adsorption/desorption of ions.

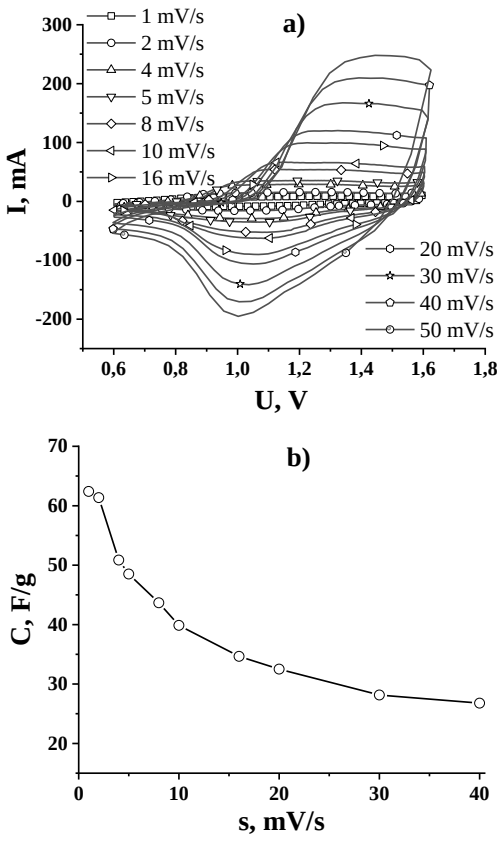

Fig. 4 – CVA curves of the CM/KOH/$NiWO_4$ system at a scan rate of 1-50 mV/s (a), dependence of the specific capacity on the scan rate (b)

The value of the specific capacity was calculated at various charge-discharge currents based on the charge-discharge curves for CM (Fig. 1b) and $NiWO_4$. It was determined that for CM with a discharge current of 2 mA, the capacity is 212 F/g, while for $NiWO_4$, the capacity is 104 F/g at a discharge current of 1 mA. It was determined that the capacity in this case for $NiWO_4$ decreases much faster than for CM based on the calculated capacity from the charge-discharge curves for $NiWO_4$ and CM.

HSC differs from classical EC by the presence of an unpolarized electrode, in this case of $NiWO_4$, on which Faraday reactions can be seen. Although the capacitance for potentiodynamic or galvanostatic curves drops faster for $NiWO_4$ than for CM with increasing scan rate or discharge current, using an unpolarized electrode in the HSC we managed to raise the operating voltage to 1.6 V. The capacity of this HSC is 62.4 F/g at a scan rate of 1 mV/s and reaches 26.8 F/g at a scan rate of 40 mV/s. In this case, the specific energy and specific power are 7.09 W·h/kg and 1.39 W/kg, respectively.

The pseudocapacitive behavior of HSC is additionally confirmed by galvanostatic curves (Fig. 5) of a non-linear nature. The voltage plateaus formed are in good agreement with peaks observed on the corresponding CVA. The specific capacity for CM/KOH/$NiWO_4$ HSC is 57.1 F/g, which corresponds to a discharge current of 1 mA. These values are higher than the value for a symmetric supercapacitor under the same conditions.

Therefore, based on the data obtained from Fig. 4b, the total capacity of materials can be divided into EDL capacity (C_{EDL}) and diffusion-controlled redox capacity due to fast Faraday reverse reactions (C_F) [14]. In the kinetic model [15], it is assumed that the scan rate affects the total specific electrochemical capacity of the system, since the diffuse component of the capacitance (C_V) is a function of the reaction time. As a result, the scan rate can be considered inverse to the diffusion time. Thus, in the case of semi-infinite linear diffusion, the total capacity is related to the scan rate by the following equation: $C = C_{s=\infty} + a/s^{-1}$, where a is a constant value and $C_{EDL} = C_{s=\infty}$.

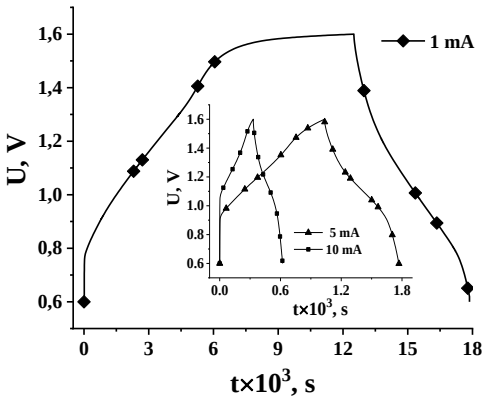

Fig. 5 – Galvanostatic curves for CM/KOH/$NiWO_4$ HSC at charge/discharge currents of 1, 5 and 10 mA

Table 2 – Specific capacitive characteristics of the CM/KOH/$NiWO_4$ system

Capacitor type	CM/$NiWO_4$
C_{EDL}, F/g	32.8
C_{max}, F/g	90.9

Extrapolation of the dependences of C on $s^{-1/2}$ to the Y-axis made it possible to determine the specific capacity of the EDL of the materials under research (Table 2). A decrease in the scan rate leads to an increase in the specific capacity. Thus, the dependence of the specific capacity on the scan rate can be extrapolated in the other direction to $s = 0$, using the functional dependence on s [14]. Since C increases linearly with $s^{1/2}$, then $1/C$ should decrease linearly with $s^{1/2}$. Then, $1/C = 1/C_{s=\infty} + bs^{-1}$, where $C_{s=\infty}$ is the maximum specific capacity that can be obtained, and b is a constant. The inverse value of the specific capacity linearly depends on $s^{1/2}$. Extrapolation of the dependences of C^{-1} on $s^{1/2}$ to the Y-axis allowed us to determine the maximum specific capacity of the studied materials (Table 2).

4. CONCLUSIONS

It was found that in HSCs based on CM and $NiWO_4$ it is possible to increase the operating voltage to the limits of 0.6-1.6 V, which provides their high specific capacity, in particular, at a discharge current of 1 mA. Moreover, it was determined that the specific capacity is 57.1 F/g, and the specific energy density and power are 7.09 W·h/kg and 1.39 W/kg, respectively.

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REFERENCES

1. B.E. Conway, *Electrochemical Supercapacitors – Scientific Fundamentals and Technological Applications* (Kluwer Academic/Plenum: New York: 1999).
2. C. Largeot, C. Portet, J. Chmiola, P. Taberna, Y. Gogotsi, P. Simon, *J. Am. Chem. Soc.* **130**, 2730 (2008).
3. R.Y. Shvets, I.I. Grygorchak, A.K. Borysyuk, S.G. Shvach-ko, A.I. Kondyr, V.I. Baluk, A.S. Kurepa, B.I. Rachiy, *Phys. Solid State* **56** No 10, 2021 (2014).
4. S. Kandalkar, D. Dhawale, C. Kim, C. Lokhande, *Synth. Met.* **160**, 1299 (2010).
5. E. Frackowiak, F. Beguin, *Carbon* **39**, 937 (2001).
6. M. Inagaki, *New Carbons; Control of Structure and Functions* (Elsevier: Amsterdam: 2000).
7. R.C. Bansal, J. Donnet, F. Stoeckli, *Active Carbon* (Marcel Dekker: New York: 1988).
8. V. Khomenko, E. Raymundo-Pin˜ero, E. Frackowiak, F. Beguin, *Appl. Phys. A* **82**, 567 (2005).
9. J.P. Zheng, *J. Electrochem. Soc.* **150**, A484 (2003).
10. B.K. Ostafiychuk, I.M. Budzulyak, M.M. Kuzyshyn, B.I. Rachiy, R.A. Zatorskiy, R.P. Lisovskiy, V.I. Mandzyuk, *J. Nano-Electron. Phys.* **5** No 3, 03049 (2013).
11. B.I. Rachiy, I.M. Budzulyak, E.A. Ivanenko, S.L. Revo, *Surf. Eng. Appl. Electrochem.* **51** No 5, 501 (2015).
12. A.P. Karnaukhov, Novosibirsk: Science. Sib. enterprise of the Russian Academy of Sciences, 470 (1999).
13. B.I. Rachiy, Yu.Yu. Starchuk, P.I. Kolkovskyy, I.M. Bud-zulyak, L.S. Yablon, V.O. Kotsyubynsky, O.V. Morushko, O.M. Khemiy, *Surf. Eng. Appl. Electrochem.* **56** No 6, 697 (2015).
14. H. Wang, L. Pilon, *Electrochimica Acta* **64**, 130 (2012).
15. S. Ardizzone, G. Fregonara, S. Trasatti, *Electrochimica Acta* **35**, 263 (1990).

Електрохімічні властивості гібридних суперконденсаторів, сформованих на основі нанопористого вуглецю та вольфрамату нікелю

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В роботі проведено дослідження морфології поверхні вуглецевого матеріалу (ВМ) методом адсорбції/десорбції азоту та визначено питому площі поверхні, яка становить 1200-1300 м²/г. Методом співосадження синтезовано $NiWO_4$ та досліджено його структуру. Досліджено електрохімічні властивості ВМ та $NiWO_4$ методами хроноамперометрії та вольтамперометрії, а також апробовано використання даних матеріалів як електродів гібридних суперконденсаторів (ГК) – анода та катода відповідно. Сформовано гібридну електрохімічну систему типу ВМ/KOH/$NiWO_4$. Використання такої системи дозволяє підвищити робочий діапазон напруги ГК на основі водних електролітів з 0-1 В до 0,6-1,6 В, а отже, і підвищити енергетичні характеристики одиничної комірки більше, ніж у 2 рази. Показано, що при робочих струмах 1 мА питома ємність ГК становить 57,1 Ф/г, при цьому питома густина енергії та потужність становлять 7,09 Вт·год/кг та 1,39 Вт/кг відповідно.

Ключові слова: Електрохімічні накопичувачі енергії, Вольфрамат нікелю, Пористий вуглецевий матеріал, Водний електроліт.