Energy Characteristics of Hybrid Electrochemical Systems of the $C/Li_2SO_4/Li_{1.2}Mn_{1.8}O_4$ Type

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Potentiodynamic and galvanostatic investigations of hybrid electrochemical capacitor (HEC) models formed on the base of nanoporous carbon material (NCM) are performed. NCM is obtained from raw materials of plant origin (hemp fire) and modified lithium–manganese spinel $Li_{1.2}Mn_{1.8}O_4$. The influence of the surface morphology of carbon material on the electric capacity of the HEC is revealed. The total electric capacitance of the HEC models is determined, and its distribution is carried out on the capacitance, which is ensured by the formation of a double electric layer (DEL), and the redox capacitance due to the passage of Faraday reverse reactions.

Проведено потенціодинамічні та ґальваностатичні дослідження макетів гібридних електрохемічних конденсаторів (ГЕК), сформованих на основі нанопористого вуглецевого матеріялу (НВМ), одержаного із сировини рослинного походження (костри коноплі), та модифікованої літій-манґанової шпінелі $Li_{1.2}Mn_{1.8}O_4$. Встановлено вплив морфології поверхні НВМ на величину електромісткости ГЕК. Визначено загальну електричну місткість макетів ГЕК і проведено розподіл її на місткість, яка забезпечується формуванням подвійного електричного шару, і окиснювально-відновну місткість за рахунок проходження Фарадейових зворотніх реакцій.

Key words: nanoporous carbon, hybrid electrochemical capacitor, aqueous electrolyte, capacity, electrochemical properties.

Ключові слова: нанопористий вуглець, гібридний електрохемічний конденсатор, водний електроліт, місткість, електрохемічні властивості.

(Received 5 March, 2020)

1. INTRODUCTION

Modern batteries provide high specific energy, which makes them ideally suited for wide practical application, but their low specific power is their disadvantage. Nevertheless, electrochemical capacitors (supercapacitors) have significantly higher values of specific power, which is several times higher than the specific power of batteries, but do not have sufficient specific energy. The specific capacity of such devices is mainly determined by the electrolytically accessible surface area of the electrode material. Supercapacitors content is based on high-porosity materials such as nanoporous carbon, carbon nanotubes or graphene. Moreover, the HECs concept is aimed at filling the energy range formed between batteries and electrochemical capacitors. Thus, in HEC research, the design of a single cell is asymmetric, in which both the capacitance of the DEL in the carbon electrode and the pseudocapacitance of the electrode material of the supercapacitors and battery respectively are used [1]. HEC have a higher specific energy compare to symmetric capacitors, due to the higher operating voltage of the cell. The operating voltage of such capacitors is in the range of 1.8–2 V of aqueous electrolytes, which can significantly increase their specific energy [2]. In this work, we conducted a research of the relationship between the energy parameters of hybrid electrochemical systems in a 1 M aqueous solution of Li_2SO_4 salt and the parameters of the porous structure of carbon materials.

2. OBJECTS AND METHODS

NCM was obtained by the method of thermochemical activation of plant biomass with orthophosphoric acid hemp fires in an argon atmosphere at a temperature of 550°C. The ratio between the amount of acid and the precursor was 0.25:1–2.00:1 in increments of 0.25 [3]. The obtained activated carbon was used as the cathode material for the HECs. The synthesis of modified lithium–manganese spinel with the composition $Li_{1.2}Mn_{1.8}O_4$ was carried out using ceramic technology, which was tested and research. A heterogeneous single-phase system was obtained in the process of solid-phase sintering with a predictable composition, morphology, and structure for use in HEC as anode material [4]. The specific energy characteristics of the $NCM/Li_2SO_4/Li_{1.2}Mn_{1.8}O_4$ hybrid electrochemical capacitor were carrying out by the potentiodynamic and galvanostatic methods using a two-electrode cell. The preparations of electrodes were based on a mixture of the active material, the conductive additive SUP T-50 (China) and the polyvinylidene fluoride material (F-42L) at a ratio of 75:20:5, respectively. $Li_{1.2}Mn_{1.8}O_4$ and NCM were used as positive and negative electrodes, respectively, and 10 mg of

each were pressed into a 5 mm×5 mm nickel wire mesh and placed in an electrochemical cell. The unipolar aqueous solution of lithium sulphate was used as an electrolyte. Electrochemical research were performed an Autolab PGSTAT/FRA-2 spectrometer in galvanostatic and potentiodynamic modes. The charge−discharge measurements were done at current value at 1 mA. Cyclic voltammetry measurements were performed at scan rates from 1 to 16 mV/s.

3. RESULTS AND DISCUSSION

The energy characteristics of electrochemical systems largely depend on the characteristics of the polarized electrode. Theoretically, high values of material capacitance are provided by a large surface area of NCM. However, the practical situation is more complicated, and usually, the measured capacitance does not have a linear relationship with the specific surface area of the electrode material. The main reason for this is that nanopores with a small diameter are inaccessible to the electrolyte solution due to the fact that the ions, together with their solvations, are shells too large to enter the nanopores. Therefore, the surface area of these inaccessible nanopores will not contribute to the total capacity of the DEL of the electrode material. In order to improve the specific energy characteristics of the HEC, it is necessary to research the relationship between the structural characteristics (specific surface area, pore size distribution and pore volume) of the carbon material and redox reactions on the Faraday electrode. Thus, potentiodynamic investigations with a scan rate from 1 to 16 mV/s within the operating potentials of 0−1 V (Fig. 1) were performed in order to obtain information on the boundaries potentials, turnover reactions, kinetics and the capacity of the electrochemical cell.

The shape of voltammograms (Fig. 1) is typical and almost the same for all systems. It is characteristic of electrochemical systems, with polarized and non-polarized Faraday electrodes, on which redox reactions occur (the process of intercalation−deintercalation of lithium ions into a spinel structure). The specific capacity of the HEC based on carbon material was determined (Fig. 2) due to obtained potentiodynamic curves (Fig. 1).

The determination of the maximum working voltage of the research electrochemical system was carried out by voltammetry. The cycling procedure of sample was carried out by increasing the maximum working potential from 1 V to 1.8 V with 0.2 V steps. The CVA voltamperograms for HEC based on cathode of C075 is shown in Fig 3. More than 50 charge−discharge cycles were conducted for each potential window to detect gas evolution and degradation of the electrodes. In the entire potential window, the electrochemical behaviour of the HEC is stable.
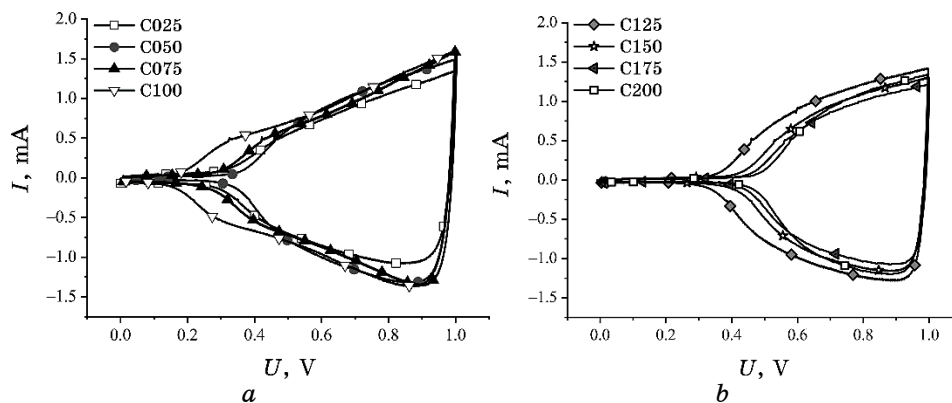
Fig. 1. Cyclic voltammograms of HEC based on materials: *a*) C025-C100; *b*) C125-C200.
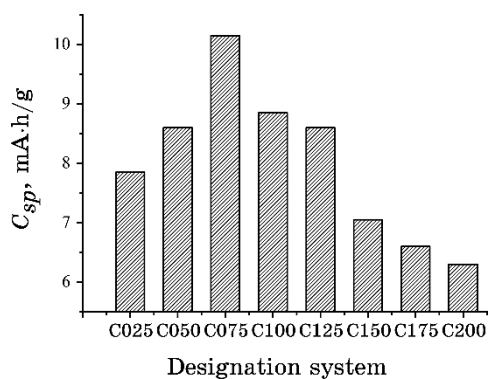

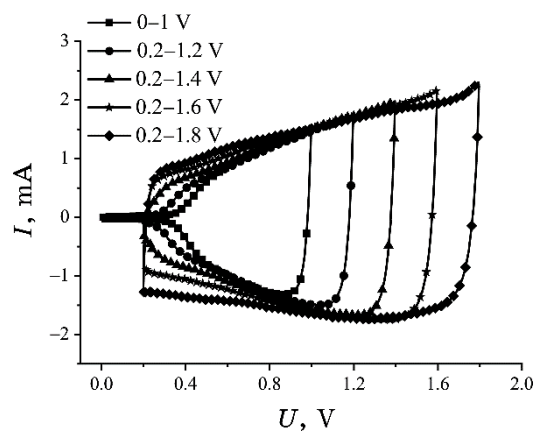**Fig. 2.** The specific capacity of HEC based on the obtained NCM.

Fig. 3. Cyclic voltammograms of HEC based on material C075.

However, with a potential increase of more than 1.8 V, gas evolution processes occur, which lead to the destruction of the electrochemical system. At potentials of 0−0.2 V, the capacity of the electrochemical system is provided solely by the capacity of the polarized electron based on the NCM (Fig. 3). At potentials of 0−0.2 V, the capacity of the electrochemical system is provided by the capacity of the polarized electrode based on the NCM (Fig. 3). The voltammograms for other systems are almost identical in shape, but the values of charge−discharge are current differ.

The dependence of the specific capacity of the HEC on the used carbon material and the working voltage window was determined based on the voltammograms data (Fig. 4). Moreover, it was determined that the HEC based on the cathode material of carbon C075, has a maximum specific capacity of 35 mA·h/g with a maximum cell voltage of 1.8 V. Thus, the obtained result is explained by the properties of NCM material (C075) has the highest specific surface area ($S_{BET} = 1990$ m^2/g) and the optimal pore distribution for access of the electrolyte solution into the volume of material, which has one of the highest surface areas among the obtained (investigated) samples [3].

The kinetics of charge accumulation in the HEC was research with increasing scan rate from 1 to 16 mV/s in a potential window of 0.2−1.8 V. The dependence of the specific capacitance on the scan rate for HEC is presented in Fig. 5.

The dependence of the specific capacitance on the scan rate for HEC is presented in Fig. 5. There is a monotonous decrease in the specific capacitance with increasing of scan rates for all electrochemical systems. Thus, at relatively high scan rate, the intercalation−deintercalation process of Li$^+$ ions into the spinel structure on a non-polarized electrode does not have time to fully occur, as well as insufficient mobility of electrolyte ions within the certain pores on the carbon electrode (especially, submicropores whose surface only partially available for electrolyte).

The total capacity of the HEC can be divided into the capacity, of a double electric layer (C_{DEL}) on the polarized electrode and diffusion-controlled redox capacity due to the Faraday reverse redox reactions (C$_F$) of the non-polarized electrode [5], which can be calculated based on obtained curves Fig. 5. In the kinetic model [5], it is assumed that the scan rate affects the total specific capacity of the electrochemical system, since the diffuse component of the capacitance (C_F) is a function of the reaction time. Therefore, the scan rate can be considered inverse to the time of diffusion $C = C_{s=\infty} + as^{-1/2}$ where a is a constant, $C_{sp} = C_{s=\infty}$. The specific capacity of electrochemical systems linearly depends on $s^{-1/2}$, as follows from Fig. 6.

The decrease of the scan rate leads to an increase in the specific capacity of the electrochemical system.
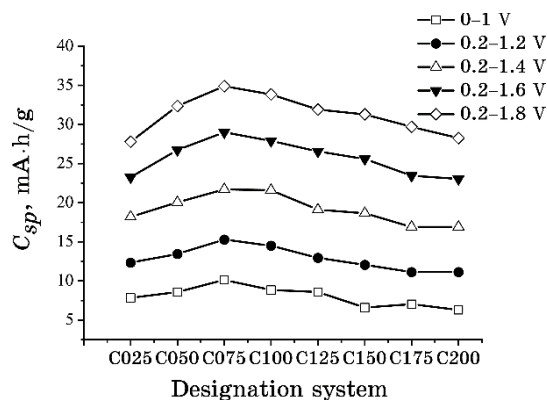
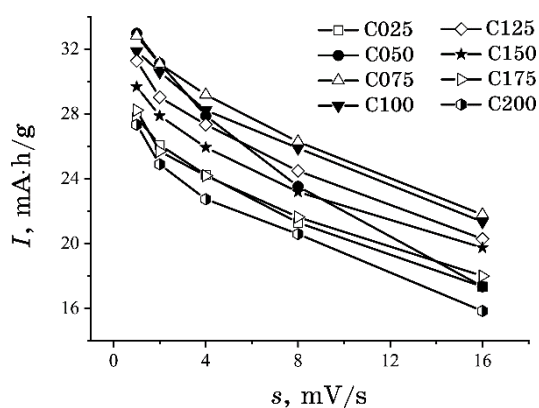**Fig. 4.** Specific capacity of HEC based on materials of C025–C200.

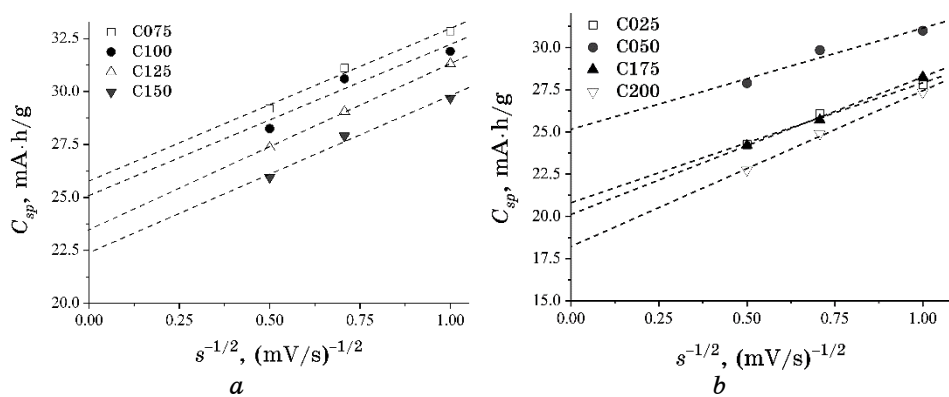**Fig. 5.** The dependence of the specific capacitance on the scan rate for HEC.

Fig. 6. The dependence of the specific capacitance on $s^{-1/2}$: *a*) C075, C100, C125, C150; *b*) C025, C050, C175, C200.

Thus, the dependence of the specific capacity on the scan rate can be extrapolated to the other side to $s = 0$ using the functional dependence on s [5]. Since the C increases linearly with $s^{-1/2}$, then, $1/C$ should decrease linearly with $s^{1/2}$. Then, $1/C = 1/C_{s=0} + bs^{1/2}$ where $C_{s=0}$ is the maximum specific capacity available, b is a constant value (Fig. 7).

The determination of the capacitance, which is ensured by the formation of DEL (C_{DEL}) and the maximum specific capacity (C_{max}) of the studied electrochemical systems (Table), is possible based on of extrapolation of the dependences of C on $s^{1/2}$ and C^{-1} on $s^{1/2}$ of the Y-axis (Fig. 7). It can be concluded that the specific capacity provided by the formation of DEL is within $60-70\%$ of the total specific capacity for all hybrid electrochemical systems under research, and the maximum capacity that can be provided by HEC formed on the base of the obtained materials is $\cong 39$ mA·h/g, when analysing the data in the Table.

A chronopotentiometric research method was used to evaluate the electrode stability and to determine the specific capacitance and energy and the internal resistance of the HEC. Typical charge−discharge curve for HEC based on $NCM/Li_2SO_4/Li_{1.2}Mn_{1.8}O_4$, which were obtained at 1 mA charge−discharge process (Fig. 8).

The electrochemical cell shows an oblique voltage profile that is characteristic of the capacitive behaviour of supercapacitors formed based on of carbon materials.

Considering the aqueous electrolyte solution, oxygen is simultaneously released on the positive electrode when lithium ions deintercalation from the $Li_{1.2}Mn_{1.8}O_4$ spinel (charging process) and hydrogen is released on the carbon negative electrode during the adsorption of lithium ions (charging process). However, the voltage of the galvanostatic charge−discharge process of the electrochemical system was controlled in the range from 0.2 to 1.8 V (safe voltage window without O_2 and H_2 emission).

The specific energy characteristics of the HEC were calculated based on the obtained discharge curves (Fig. 8). The highest specific capacity is demonstrated by the $C075/Li_2SO_4/Li_{1.2}Mn_{1.8}O_4$ electrochemical cell, about 38.6 mA·h/g at a charge−discharge current of 1 mA, which is correlated with the corresponding values obtained using the potentiodynamic method.

4. CONCLUSIONS

Hybrid electrochemical cells were formed based on of synthesized electrode materials, namely NCM. Thus, NCM was obtained by thermochemical activation of hemp fire with orthophosphoric acid and lithium−manganese spinel of the composition $Li_{1.2}Mn_{1.8}O_4$, synthesized according to ceramic technology. The maximum specific capacitance of the HEC was calculated from the data of potentiodynamic and gal-
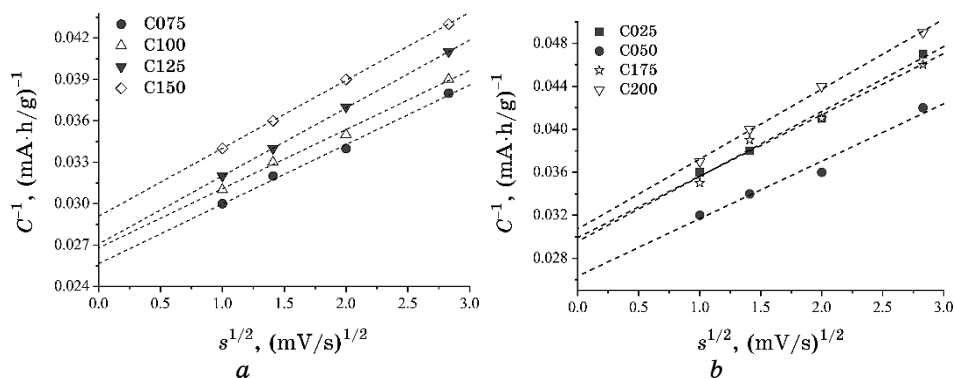
Fig. 7. The dependence of C^{-1} on $s^{1/2}$: *a*) C075, C100, C125, C150; *b*) C025, C050, C175, C200.

TABLE. The capacity of the DEL and the maximum specific capacity of the HEC.

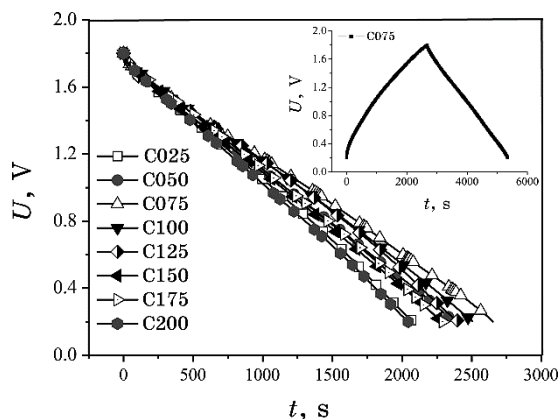| HEC	C025	C050	C075	C100	C125	C150	C175	C200
C_{DEL}, mA·h/g	20.89	25.13	26.05	25.02	23.43	22.40	20.06	18.27
C_{max}, mA·h/g	34.28	37.74	39.06	37.45	37.04	34.48	33.33	32.26
$C_{\text{DEL}}/C_{\text{max}}$	0.61	0.67	0.67	0.67	0.63	0.65	0.60	0.57

Fig. 8. Charge−discharge curves of HEC.

vanostatic investigation. It was determined that the highest value of specific capacity is about 35 mA·h/g at a cell voltage of 1.8 V and is possessed by an electrochemical system, for which the cathode was made of carbon material C075.

Thus, the specific capacity of the investigated HEC is dependent on the electrochemically accessible surface area of the carbon electrode that is involved in the formation of the DEL. The separation of the total specific capacity of the HEC by the capacity, which is ensured by the formation of a DEL and diffusion-controlled redox capacity due to faraday reverse redox reactions on polarized and non-polarized electrodes, respectively. It was determined that the specific capacity provided by the formation of DEL is in the range of $60-70\%$ of the total specific capacity for all the research hybrid electrochemical systems, and the maximum capacity of the HEC based on of the obtained materials is $\cong 39$ mA·h/g.

ACKNOWLEDGEMENT

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