

B.I. Rachiy¹, N.Ya. Ivanichok², V.V. Moklyak^{2,3}, P.I. Kolkovskiy⁴, O.I. Bulbuk⁵,
A.M. Soltys¹, D.S. Borchuk¹, L.Z. Khrushch¹

Effect of thermochemical activation temperature on electrical conductivity and concentration of charge carriers in the obtained porous carbon materials

¹Vasyl Stefanyk Precarpathian National University, Ivano-Frankivsk, Ukraine, bogdan.rachiy@pnu.edu.ua

²G.V. Kurdyumov Institute for Metal Physics, N.A.S. of Ukraine, Ukraine, natalia.ivanichok@pnu.edu.ua

³Ivano-Frankivsk National Technical University of Oil and Gas, Ukraine, mvymcv@gmail.com

⁴Vernadsky Institute General and Inorganic Chemistry, Ukraine, pkolkovskyy@gmail.com

⁵Ivano-Frankivsk National Medical University, Ukraine, obulbuk@ifnmu.edu.ua

By changing the temperature of chemical activation of plant biomass, nanoporous carbon materials with a specific surface area of up to 1050 m²/g were obtained. The obtained carbon materials were used to form composites with different percentages of conductive additive. Electrochemical impedance spectroscopy was used to investigate the physicochemical processes occurring at the carbon electrode/electrolyte interface in a 30% aqueous KOH solution.

The concentration of charge carriers in the obtained carbon materials was determined, the values of which are in the range of $6 \cdot 10^{18} - 35 \cdot 10^{18} \text{ cm}^{-3}$, and its dependence on the temperature of thermochemical activation was established. It was established that an increase in the temperature of thermochemical activation from 600°C to 900°C leads to an increase in the capacity of the space charge region by almost 10 times. The formation of nanoporous carbon material/conductive additive composites contributes to the correlation between the values of specific capacitance and electrical resistance for the studied materials.

Keywords: nanoporous carbon material, low-temperature porometry, electrical conductivity, impedance spectroscopy, Mott-Schottky models, space charge capacity.

Received 08 August 2024; Accepted 10 December 2024.

Introduction

Nanoporous carbon material (NCM) is characterized by excellent structural properties (i.e., surface area, porosity, and pore size distribution) and surface chemical composition, which largely depend on the method of its preparation, including the activator and modes of activation, and the raw materials [1-3].

For the industrial production of NCM, substances with high carbon content and a small content of inorganic compounds are usually used as raw materials. Such substances include wood, coconut or walnut shells, fruit stones, brown coal, coffee grounds, peat, polymers, etc. [2,4-8]. Currently, the production of NCM from food

waste, agricultural, and industrial waste is the subject of active research aimed at their controlled disposal and obtaining cheap and environmentally friendly raw materials for active carbon materials.

Coffee grounds are waste products produced as a byproduct of coffee brewing. Although coffee waste is not very harmful to the environment, it does create some environmental problems, primarily when disposed of in landfills. The consumption of coffee in all its types on the planet is growing by at least 1% per year for the last 20 years [9]. If we compare the years 2021 and 2022, then in January 2022, the import of coffee in Ukraine increased by 37.1%, approximately 97 thousand tons [10]. World exports of green coffee in August 2022 amounted to

529.8 thousand tons [11]. At first glance, the disposal of coffee grounds may not seem like a pressing issue; however, statistical data on coffee imports clearly demonstrate the scale of this problem in today's world. Most waste coffee grounds have a similar chemical composition. They are rich in cellulose, which makes up about half of their mass; 20% are proteins, and another 20% are lignins [12, 13]. Dry coffee grounds contain a significant amount of nitrogen (27.9 g/kg), potassium (11.7 g/kg), magnesium (1.9 g/kg) and phosphorus (1.8 g/kg) [14]. Organic compounds, such as cellulose, lignin, and others, which are part of the coffee grounds, decompose at high temperatures with the formation of carbon. This carbon has a porous structure, which gives the material valuable properties. Nanoporous carbon material based on waste coffee grounds has a high specific surface, which allows it to be used as an adsorbent for water and air purification, as a catalyst in chemical processes, as well as in energy, as an electrode material for constructing supercapacitors [4]. Waste coffee grounds are a relatively cheap and widely available raw material. This makes the production process of porous carbon material cost-effective and contributes to waste coffee grounds reductions and recycling of organic materials. This corresponds to modern trends towards environmentally friendly production.

The temperature of thermochemical activation is one of the main factors affecting the electrophysical properties of nanoporous carbon materials, especially in the context of their thermochemical activation. The process for changing the structure and properties of the carbon material under the influence of temperature and chemical reactions is thermochemical activation. Thermochemical reactions between the activator and the carbonized material occur to obtain NCM. The electrophysical properties of nanoporous carbon materials, such as conductivity and capacitance, change depending on the obtaining temperature. An increase in the obtaining temperature leads to an increase in the content of graphitized inclusions, which increases the conductivity of the obtained NCM. An increase in porosity leads to a decrease in the current-conducting channels and a decrease in the conductivity of the NCM, as well as the appearance of additional resistance at the border of contact of carbon particles. The condition of the surface and the presence of functional groups on it affect the surface properties of the NCM, which, in turn, can affect its electrophysical characteristics. Considering these factors, NCM obtaining temperature is important in the research and use of nanoporous carbon materials for electrophysical applications such as supercapacitors, batteries, sensors, and other electronic devices.

This paper investigates the regularities of the effect of the thermochemical activation temperature on the electrical conductivity, charge carrier concentration, and space charge capacity in NCM obtained from raw materials of plant origin (coffee grounds) and composites based on them.

I. Materials and methods of research

A series of nanoporous carbon materials were

obtained by thermochemical activation of waste coffee grounds, as a raw material, using potassium hydroxide. The obtaining process included several stages: drying of raw materials, mixing with an activator, carbonization at different temperatures, and further processing. By varying the carbonization temperature from 400 °C to 900 °C (in steps of 100 °C), NCM with different porosity were obtained. NCM were labeled as S400 – S900 according to the activation temperature, for example, S900 is NCM obtained at 900 °C. The method of thermochemical activation is described in more detail in the previous article [15].

The porous structure of the obtained NCM was studied using a method of low-temperature (-196°C) adsorption/desorption of nitrogen using the Quantachrome Autosorb automatic analysis system (version 2200e). The specific surface area (S_{BET}) was estimated by applying the equation of Brunauer, Emmett, and Teller [16] to experimental N_2 isotherms. The method proposed by de Boer and Lippens [17] was used to estimate the specific surface area and volume of micropores.

Impedance studies of the NCM/electrolyte and the composites (NCM/conductive additive)/electrolyte system were carried out in three-electrode electrochemical cells on an Autolab PGSTAT/FRA-2 spectrometer. In the three-electrode cell, a chlorine-silver electrode (Ag/AgCl) was used as a reference electrode, it was filled with a saturated aqueous solution of potassium chloride. A platinum electrode was used as an auxiliary electrode. For all studies, a 30% aqueous solution of potassium hydroxide was used as an electrolyte. The frequency range from 10 mHz to 100 kHz and the potential range from -1 V to 0.4 V in steps of 0.2 V were selected for research.

II. Results and discussion

The electrochemical characteristics of NCM largely depend on the porous structure of the using raw materials or precursors. One of the important factors that significantly affects the structure and morphology of the obtained NCM is the temperature of thermochemical activation.

NCM with different porous structures was studied with adsorption/desorption of nitrogen. Nitrogen adsorption/desorption isotherms for carbon materials S400-S700 (Fig. 1a, b) have a similar appearance. They show hysteresis in the region of low relative pressures, which manifests itself as a divergence of the adsorption and desorption branches at low pressures and is probably due to the irreversible retention of nitrogen molecules in the pores of the carbon material, the size of which is close to the size of the adsorbate molecules. The obtained isotherms (Fig. 1a, b) can be attributed to type II isotherms according to the IUPAC classification [18]. These isotherms are characteristic of non-porous or macroporous adsorbents and are determined by the physical sorption of the adsorbate on the surface of the material. The difference between these materials lies in the volume of sorbed nitrogen required to fill the monolayer, which is manifested in the increase in the specific surface area of the NCM with increasing activation temperature (Table 1). On the isotherms (Fig. 1 c) obtained for the

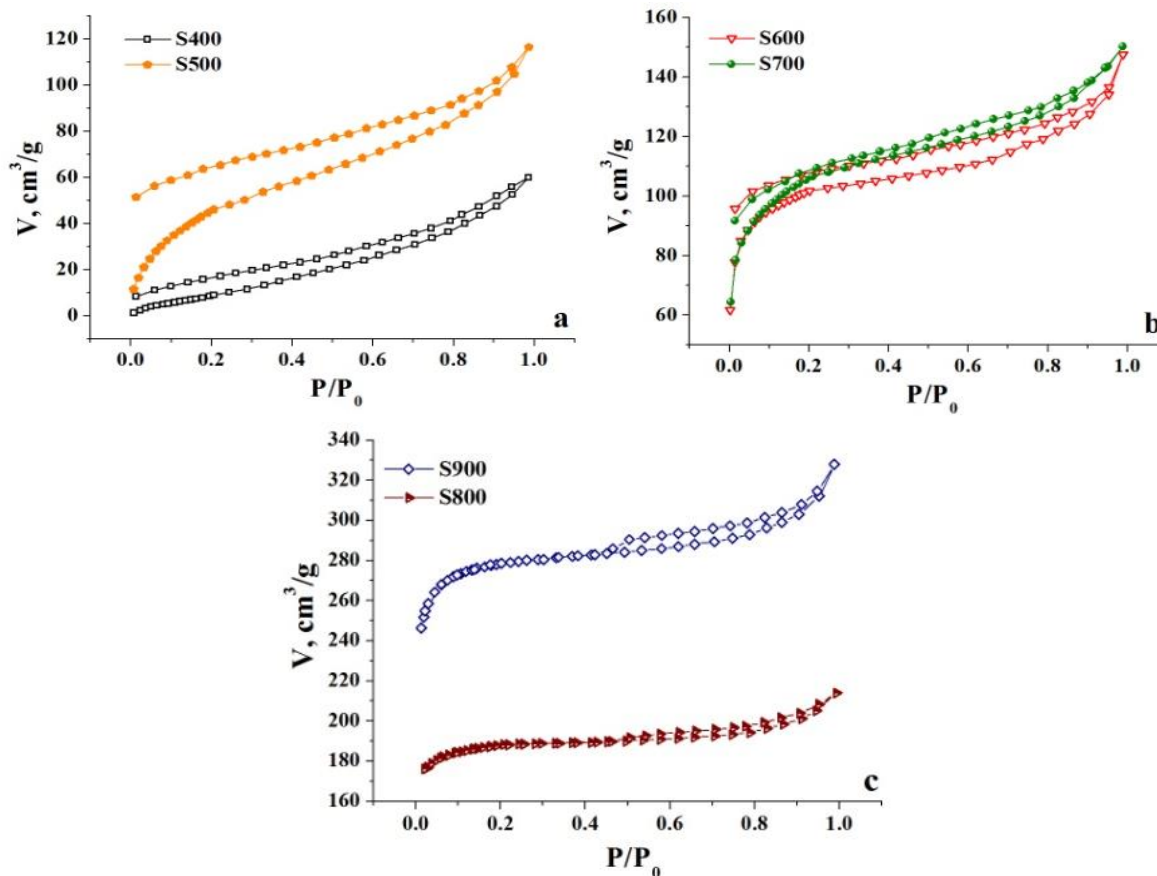


Fig. 1. Nitrogen adsorption/desorption isotherms for thermochemically activated NCM.

S800 and S900 materials, there is a high-pressure hysteresis of the H4 type [18], which is associated with capillary condensation of the adsorbate in the mesopores of the carbon material.

From the obtained experimental nitrogen sorption isotherms, the parameters of the porous structure of carbon materials were calculated. In particular, the specific surface area (S_{BET}), the specific surface area of micropores (S_{micro}), the total pore volume (V_{total}), and the micropore volume (V_{micro}) were determined, which are given in Table 1.

The table shows that the activation temperature within 800-900 °C is optimal for obtaining NCM with a highly developed surface area, which makes them promising for use as porous electrodes of electrochemical power sources.

Table 1.

Parameters of the porous structure of NCM

Sample	S_{BET} , m^2/g	S_{micro} , m^2/g	V_{total} , cm^3/g	V_{micro} , cm^3/g
S400	31	-	0.092	-
S500	172	80	0.161	0.038
S600	374	319	0.228	0.132
S700	446	402	0.237	0.162
S800	703	671	0.331	0.272
S900	1056	996	0.507	0.398

When using NCM as an electrode material in electrochemical systems, it is necessary to take into account the electrophysical parameters of the carbon

material/electrolyte system. The specific surface area of the electrode material and the ionic conductivity of the electrolyte are the main parameters that should be paid attention to when designing charge storage systems since it is the electrolyte that determines the operating voltage range of the unit cell and the electrical conductivity of the formed system. It is advisable to study the electrochemical interaction at the electrode/electrolyte interface by impedance spectroscopy using the Mott-Schottky model. The Mott-Schottky model is used to determine the density of charge carriers in bulk semiconductors when they are in contact with the electrolyte, as well as to determine the potential of the flat zone of the semiconductor material [18]. In electrochemistry, the application of impedance spectroscopy and the Mott-Schottky model allows us to determine the potentials associated with Faradaic reversible redox reactions, calculate the accumulated charge in the system under study, and investigate the range of working potentials of the electrode material [19, 20].

To construct the Mott-Schottky curves, data obtained by impedance spectroscopy were used (Fig. 2 and Fig. 3). Electrodes weighing 16.5 mg and measuring 5 mm × 5 mm were made from the materials under study and placed in a nickel grid. The electrodes of the composite material, NCM/conductive additive, also weighed 16.5 mg, and the percentage of the conductive additive was within 5÷25% (Fig. 3).

The formed electrodes were placed in a drying cabinet heated to a temperature of 80-95 °C, and after complete drying, three-electrode electrochemical cells were formed. From the Nyquist diagrams, using the Mott-Schottky

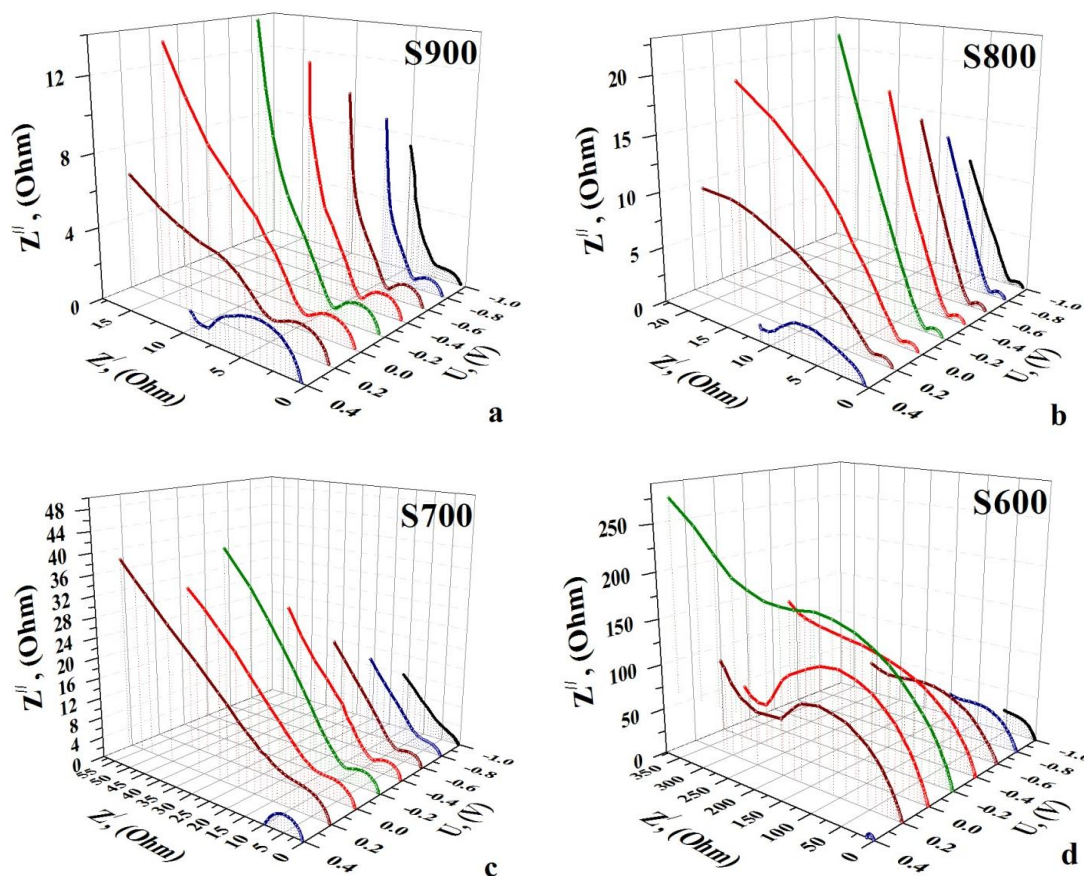


Fig. 2. Nyquist diagrams of the NCM/electrolyte system for materials obtained at temperatures of 600-900°C.

model, the concentration of charge carriers in the studied materials and the flat zone potential were determined.

The Nyquist diagrams presented in Fig. 2 show an increase in the resistance of the NCM/electrolyte system by more than 20 times when the thermochemical activation temperature is reduced to 600 °C. For materials activated at 900 °C and 800 °C (Fig. 2 a, b), the impedance spectra obtained in the potential window from -0.2 to -1.0 V have a typical appearance for materials with a capacitive electric charge accumulation at the electrode/electrolyte interface. High impedance values at low frequencies indicate the capacitive behavior of the system, in this case, the slope of the impedance diagram approaches 90°.

In the potential window of -0.2 ÷ 0.4 V for low frequencies, the angle of inclination of the diagram decreases with a partial transition of the straight line into a semicircle, which is probably the beginning of diffusion processes on the electrodes that occur at low and medium frequencies and positive potentials with the participation of OH⁻ groups.

For materials activated at 700 °C and 600 °C (Fig. 2c, d), there is no vertical section of the impedance curve in the range of negative potentials and low frequencies. This is probably due to the sample's high internal resistance, the complicated process of DEL formation at the electrode/electrolyte interface, and the increase in charge transfer resistance in this system, which reduces the slope of the curve to 45°. The electrochemical behavior of the S700 material (Fig. 2 c) is practically the same in the entire range of applied potentials, only at a potential of 0.4 V, the

Nyquist diagram takes the shape of a semicircle. For the S600 material (Fig. 2 d), which is characterized by a significant internal resistance compared to the previous samples, the Nyquist diagrams for the entire range of applied potentials are a semicircle with a slight increase in impedance at low frequencies.

A semicircle is observed in all Nyquist diagrams (Fig. 2 and Fig. 3) in the high-frequency range. The dimensions of the semicircle vary somewhat depending on the material (Fig. 2) and the content of the conductive additive (Fig. 3). However, the nature of the occurrence of this semicircle is practically the same for all materials and is associated with an increase in resistance due to the transfer of electrolyte ions in the solution. This resistance is caused by diffusion processes that are dominant at high potential change frequencies. At high frequencies, the formation of DEL at the electrode/electrolyte interface or the redox reaction at the electrode occurs so rapidly that the rate of ion transport in the solution becomes the limiting factor. This means that ions do not have enough time to diffuse to the electrode and participate in the previously described processes. As a result, resistance arises, and a semicircle appears on the Nyquist diagram, indicating that the impedance consists of a combination of active and reactive components (inductance or capacitance), which may be inherent in the mass transport of ions [22, 23].

The Nyquist diagrams (Fig. 3) of the (NCM/ conductive additive)/electrolyte system characterize the capacitive behavior of these materials. The numerical value of the impedance varies depending on the content of

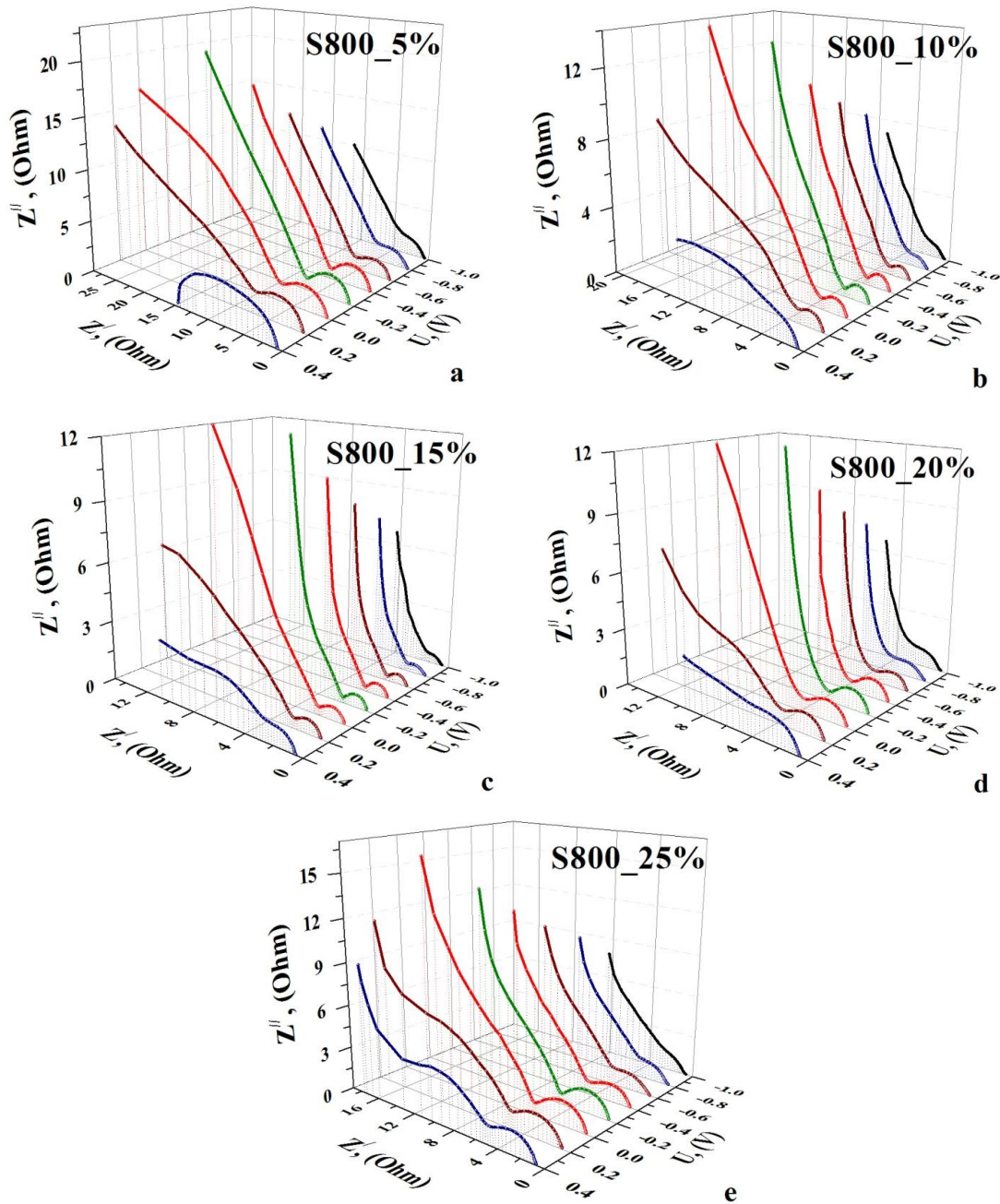


Fig. 3. Nyquist diagrams of the system (NCM/conductive additive)/electrolyte of the material obtained at 800°C.

the conductive additive. For all materials, the imaginary component of the impedance increases at low frequencies (Fig. 3), which indicates the dominance of the capacitive behavior of the composite/electrolyte system. Another semicircle is formed in the range of medium frequencies and the region of positive potentials. The formation of two semicircles on the Nyquist diagrams is probably due to the presence of two processes that occur simultaneously. Each of these processes occurs in its frequency range and has corresponding characteristics [22, 23]. Therefore, the semicircle in the mid-frequency range can be associated with the difficult diffusion of OH⁻ groups into the pores of the NCM to form the DEL, which leads to the formation of additional electrical resistance.

Using data from the Nyquist diagrams, the specific capacitance of the NCM/electrolyte system (Fig. 4 a) and

the composite (NCM / conductive additive) / electrolyte (Fig. 4 b) was determined. The specific capacitance was determined at a frequency of 10 MHz from the formula:

$$C = \frac{1}{2\pi \cdot f \cdot Z''} ,$$

where Z'' – is the apparent resistance, and f – is the frequency.

On all volt-farad curves (Fig. 4) there is a decrease in specific capacitance with increasing potential from -1 V to 0 and there is a region of minimum capacitance, which corresponds to the potential of zero charge. At an open circuit voltage (-0.2 V), charge accumulation occurs spontaneously due to the electrostatic mechanism [24].

Carbon materials S600 and S700 have a low specific

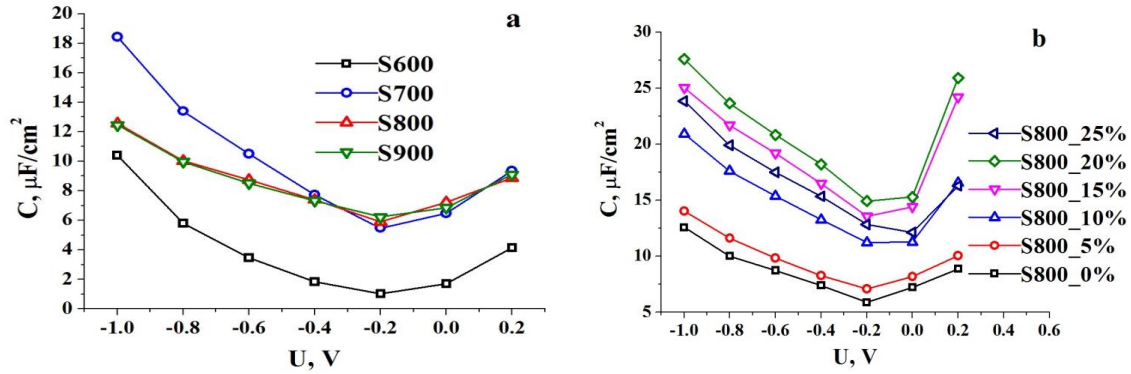


Fig. 4. Dependence of the specific capacitance of the NCM/electrolyte system (a) and the composite (NCM/conductive additive) / electrolyte (b) on the applied potential.

surface area (Table 1), however, in terms of the material capacity per area (Fig. 4), the maximum specific capacity is observed for the S700 material. The specific capacity of the S800 and S900 materials, despite the significant difference in the specific surface area, is practically the same (Fig. 4 a). The specific capacitance of the S800 material depends on the content of the conductive additive (Fig. 4 b), in particular, the increase in capacity to 50% occurs at the limit of 15-20% carbon black.

Considering the similarity of the behavior of the studied carbon systems with the behavior of semiconductors, the Mott-Schottky model can describe the boundary between the carbon electrode and the electrolyte. Using the dependence of the specific capacitance of the space charge on the applied potential from the equation:

$$C_{sc} = \left(\frac{2\epsilon\epsilon_0 e^2 N}{kT} \right)^{1/2} \cosh \left[\frac{(U - U_{fb})e}{2kT} \right]$$

it is possible to determine the potential of the flat band and the concentration of charge carriers. In this formula, U_{fb} is the potential of the flat band, U is the electrode potential, N is the concentration of charge carriers, T is the absolute temperature and k is the Boltzmann constant.

In the negative potential region, electrons accumulate on the surface of n-type semiconductors, which leads to an exponential increase in capacitance, and this statement is confirmed by the equation above. A similar charge accumulation process due to K^+ ions occurs at the interface between the carbon material and the electrolyte in the negative potential region. Increasing the potential from -1 V to 0 decreases the number of electrons in the near-surface region, which reduces the accumulated charge. In the zero potential range, the specific capacitance of the system practically does not change. The next increase in potential into the positive region leads to a predominance of holes in the semiconductor and, according to the equation, the specific capacitance increases exponentially. In the studied system, the capacitance increases due to the electric double layer (DEL) of OH^- ions, and at high positive potentials, reactions with oxygen evolution occur. To establish the type of conductivity of the studied system from the volt-farad curves (Fig. 4), the dependence of the inverse square of the specific capacitance of the NCM/electrolyte system

on the applied potential was obtained (Fig. 5).

The Mott-Schottky dependences in the negative potential range are practically linear (Fig. 5), which is typical for n-type semiconductors and also has a positive slope. This dependence for carbon material/electrolyte systems indicates its similar properties to semiconductors. In this case, according to the Mott-Schottky theory, the electrode potential and capacitance are related by the equation:

$$\frac{1}{C^2} = \left(\frac{2}{\epsilon\epsilon_0 A^2 e N_D} \right) \left[U - \left(U_{fb} + \frac{kT}{e} \right) \right]$$

In this formula, A – is the surface area of the composite under study, U_{fb} is the flat band potential, and N_D is the charge carrier concentration.

The concentration of charge carriers and the potential of the flat band of NCM and their composites with a conductive additive were calculated from the slope of the Mott-Schottky graphs and the intersection of the approximation line with the potential axis was found (Fig. 5, Table 2).

Following changes in the concentration of charge carriers of NCM depending on the temperature of production, it was found that these values are within the range of $6 \cdot 10^{18}$ - $35 \cdot 10^{18} \text{ cm}^{-3}$. The maximum value of $N_D = 3.53 \cdot 10^{19} \text{ cm}^{-3}$ was determined for the N700 material. It was found that the carrier concentration decreases to $6 \cdot 10^{18} \text{ cm}^{-3}$ with an increase in the preparation temperature to 900°C (Table 2), probably due to the development of the NCM's porous structure from 450 to $1050 \text{ m}^2/\text{g}$.

A higher concentration of charge carriers characterizes composite materials of NCM/conductive additive; already at 5% carbon black, the concentration of charge carriers increases by 30%. An increase in the percentage content of carbon black from 5 to 25% leads to a growth in the concentration of charge carriers almost 10 times, to $2.25 \cdot 10^{20} \text{ cm}^{-3}$. Increasing carbon black content decreases the potential of the flat band from -1.27 V to -1.51 V.

The Stern model was used to determine the capacitance of the space charge region, which describes the formation scheme of the DEL at the NCM/electrolyte interface. The Stern model includes the Helmholtz and Guy-Chapman theories [25]. According to the Helmholtz model, negative and positive charges are placed in fixed positions on both sides of the phase interface, and the

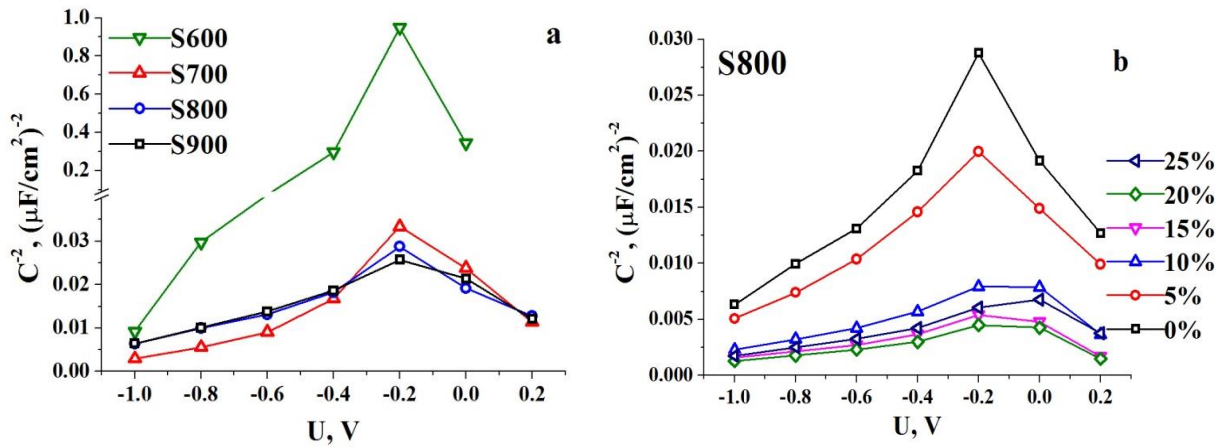


Fig. 5. Mott-Schottky plots of the NCM/electrolyte system (a) and composite (NCM/conductive additive)/electrolyte (b).

Table 2.

Charge carrier concentration and potential of a flat band of NCM and the composite NCM/conductive additive

Sample	S600	S700	S800	S900	S800 5%	S800 10%	S800 15%	S800 20%	S800 25%
$N_D \cdot 10^{18}, \text{cm}^{-3}$	6.07	35.3	16.3	6.00	21.5	67.2	136	202	225
U_{fb}, V	-1.00	-1.06	-1.28	-1.21	-1.27	-1.35	-1.42	-1.44	-1.51

electric double layer formed by them appears like a flat capacitor. A layer of ions is formed on the surface of the carbon material, which has a thickness δ equal to the ion diameter [25]. The change in potential in the formed DEL is linear (Fig. 6).

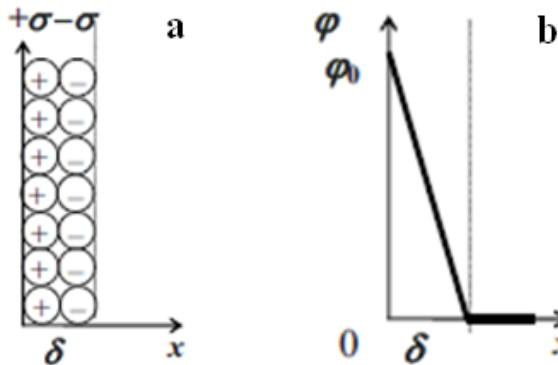


Fig. 6. Schematic presentation of the model of the formation of DEL according to the Helmholtz theory: a) distribution of charges, b) distribution of potentials [25].

This model's disadvantage is that it does not take into account the interactions between ions in the electrolyte at a distance greater than the thickness of the formed DEL and does not establish the properties of the DEL depending on the electrolyte concentration.

The shortcomings of the Helmholtz theory are considered in the Guy-Chapman model, in which the magnitude of the accumulated charge in the DEL depends on the electrolyte concentration, and the magnitude of the applied potential is considered. However, this theory does not consider the real sizes of ions, and this model is not suitable for concentrated solutions; it is used only for dilute solutions. Considering the shortcomings of the theories described

above, the proposed Stern model suggests that the DEL comprises internal and external parts (Fig. 7).

The inner (compact) layer contains charges of the opposite sign from the charges on the electrode surface. The outer (diffuse) layer is a region where the charge concentration decreases, and the potential decreases from the potential on the electrode surface to zero with increasing distance (Fig. 7). The charges within the inner layer generate a Helmholtz potential, defined by the potential difference between the solid electrode's surface and the electrolyte. Using the Stern model, the capacitance of the DEL can be represented by an equivalent electrical circuit (EEC), which consists of a series and parallel capacitance connection (Fig. 8).

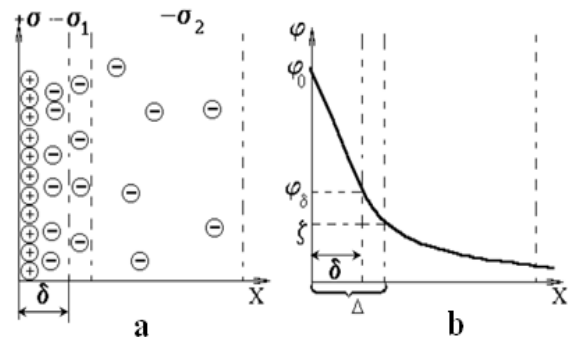


Fig. 7. Schematic representation of the model of the formation of the DEL according to Stern's theory (a) and the potential distribution in it (b) [25].

In the EEC presented in Figure 8, the capacitance of volume charge (C_{SC}) and the capacitance of surface state charge (C_{SS}) are connected in parallel. They are components of the capacitance of space charge in a solid (C_{Ch}). The following series-connected Helmholtz layer capacitance (C_H) is the capacitance of the dense part of the DEL and the Gui-Chapman layer capacitance (C_G) is

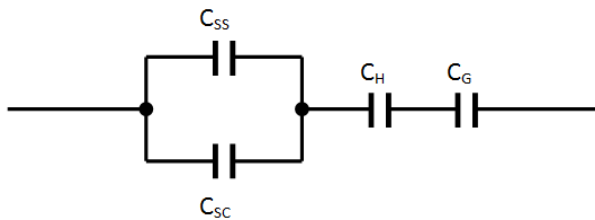


Fig. 8. The simplest equivalent scheme of DEL [25].

contact resistance between NCM particles, which increases the composites' specific capacitance. The maximum value of specific capacity is determined for a percentage of soot content of 20%.

Conclusions

By thermochemical activation of waste coffee

Table 3.

Space charge region capacitance of NVM and NVM/conductive additive composite

Sample	S600	S700	S800	S900	S800 5%	S800 10%	S800 15%	S800 20%	S800 25%
$C_{Ch}, \mu\text{F}/\text{cm}^2$	1.09	7.55	8.35	9.05	10.94	25.61	42.31	58.89	35.87

the capacitance of the diffusion part of the DEL [25]. The total capacity of the system can be determined from the expression:

$$\frac{1}{c} = \frac{1}{c_{SC+C_{SS}}} + \frac{1}{C_H} + \frac{1}{C_G}.$$

To determine the capacitance of the space charge region of the NCM/electrolyte electrochemical system, the specific capacitance determined at the open circuit potential is represented by the following expression:

$$\frac{1}{c} = \frac{1}{C_{Ch}} + \frac{1}{C_H} + \frac{1}{C_G}.$$

The thickness of the diffusion part of the double electric layer varies from 1 to 10 nm, depending on the electrolyte concentration. At an electrolyte concentration greater than 10^{20} cm^{-3} , it practically disappears [26]. In this experiment, a 6 M aqueous solution of KOH was used as the electrolyte. In concentrated electrolyte solutions, the capacitance of the diffusion part of the DEL is much greater than the capacitance of the dense part of the DEL. Therefore, the capacitance of the Guy-Chapman layer can be neglected. Based on these considerations, the total capacity of the system can be written as the following expression: $\frac{1}{c} = \frac{1}{C_{Ch}} + \frac{1}{C_H}$. Thus, the Helmholtz capacitance can be shunted by the space charge capacitance, which depends on the properties of the nanoporous carbon material, the structure of the electrode, and its potential [27]. The Helmholtz capacitance is $20 \mu\text{F}/\text{cm}^2$ in the NCM/electrolyte electrochemical system when using a 6 M aqueous KOH solution as the electrolyte and considering that the size of hydrated K^+ ions is 0.53 nm [25]. The value of the space charge capacitance, calculated considering the above assumptions, is presented in Table 3.

By tracing the dependence of the capacitance of the space charge region of NCM on the temperature of thermochemical activation, it was found that the capacitance increases with the temperature of obtaining NCM. This is probably due to the development of the porous structure and ordering of graphite crystallites during heat treatment at high temperatures, as well as an increase in the content of sp^3 carbon. The formation of NCM composites with a conductive additive reduces the

grounds with potassium hydroxide, nanoporous carbon materials with a specific surface area ranging from $400 \text{ m}^2/\text{g}$ to $1050 \text{ m}^2/\text{g}$, depending on the activation temperature, were obtained. NCM/conductive additive composites were formed based on the obtained carbon materials and their conductive properties were investigated.

It has been shown that these materials can be used to manufacture both positive and negative electrodes of supercapacitors. For pure NCM, the specific capacitance in the negative region is 1.5 times greater than the corresponding capacitance value in the positive region. For composites of NCM/conductive additives, the maximum values of the material's specific capacitance are practically identical in both the negative and positive potential regions. The obtained NCM charge carrier concentration was determined to be between $6 \cdot 10^{18}$ and $35 \cdot 10^{18} \text{ cm}^{-3}$, and its dependence on the temperature of thermochemical activation was established. It was shown that the maximum value of $N_D = 3.53 \cdot 10^{19} \text{ cm}^{-3}$ was obtained for the material thermochemically activated at $700 \text{ }^\circ\text{C}$. The formed NCM composites with 5% conductive additives are characterized by a 30% higher concentration of charge carriers than pure NCM. It has been shown that increasing the percentage content of the conductive additive from 5% to 25% leads to an increase in the concentration of charge carriers from $2.15 \cdot 10^{19}$ to $2.25 \cdot 10^{20} \text{ cm}^{-3}$. It has been established that increasing the temperature of thermochemical activation from 600 to $900 \text{ }^\circ\text{C}$ leads to an almost tenfold increase in the capacitance of the space charge region. The formation of composites based on NCM with the addition of conductive additives promotes a correlation between the specific capacitance values and the electrical resistance for the studied materials.

Rachiy B.I. – Doctor of Sciences, Professor;
Ivanichok N.Ya. – PhD, Researcher;
Moklyak V.V. – Doctor of Sciences, Senior Scientist;
Kolkovskiy P.I. – PhD, Researcher;
Bulbuk O.I. – PhD;
Soltys A.M. – PhD student;
Borchuk D.S. – PhD student;
Khrushch L.Z. – PhD.

- [1] A. Barroso-Bogeat, M. Alexandre-Franco, C. Fernández-González, A. Macías-García, V. Gómez-Serrano, *Temperature dependence of the electrical conductivity of activated carbons prepared from vine shoots by physical and chemical activation methods*, Microporous and Mesoporous Materials, 209, 90 (2015); <https://doi.org/10.1016/j.micromeso.2014.07.023>.
- [2] H. Marsh, F. Rodriguez-Reinoso, Activated Carbon (Elsevier Science & Technology Books, 2006)
- [3] M. Olivares-Marín, J.A. Fernández, M.J. Lázaro, C. Fernández-González, A. Macías-García, V. Gómez-Serrano, F. Stoeckli, T.A. Centeno, *Cherry stones as precursor of activated carbons for supercapacitors*, Materials Chemistry and Physics, 114, 323 (2009); <https://doi.org/10.1016/j.matchemphys.2008.09.010>.
- [4] S.-V. Sklepova, N. Ivanichok, P. Kolkovskiy, ... M. Bembenek, L. Ropyak, *Porous Structure and Fractal Dimensions of Activated Carbon Prepared from Waste Coffee Grounds*, Materials, 16, 6127 (2023); <https://doi.org/10.3390/ma16186127>.
- [5] J.M. Dias, M.C.M. Alvim-Ferraz, M.F. Almeida, J. Rivera-Utrilla, M. Sánchez-Polo, *Waste materials for activated carbon preparation and its use in aqueous-phase treatment: A review*, Journal of Environmental Management, 85, 833 (2007); <https://doi.org/10.1016/j.jenvman.2007.07.0>.
- [6] S.K. Sriramoju, P.S. Dash, S. Majumdar, *Meso-porous Activated Carbon from Lignite Waste and its Application in Methylene Blue Adsorption and Coke Plant Effluent Treatment*, Journal of Environmental Chemical Engineering, 9, 104784 (2020); <https://doi.org/10.1016/j.jece.2020.104784>.
- [7] N.Ya. Ivanichok, O.M. Ivanichok, B.I. Rachiy, P.I. Kolkovskiy, I.M. Budzulyak, V.O. Kotsyubynsky, V.M. Boychuk, L.Z. Khrushch, *Effect of the carbonization temperature of plant biomass on the structure, surface condition and electrical conductive properties of carbon nanoporous material*, Journal of physical studies, 25, 3801 (2021); <https://doi.org/10.30970/jps.25.3801>.
- [8] B.K. Ostafiychuk, N.Y. Ivanichok, S.-V. Sklepova, O.M. Ivanichok, V.O. Kotsyubynsky, P.I. Kolkovskiy, I.M. Budzulyak, R.P. Lisovskiy, *Influence of plant biomass activation conditions on the structure and electrochemical properties of nanoporous carbon material*, Materials Today: Proceedings, 62, 5712 (2022); <https://doi.org/10.1016/j.matpr.2022.01.486>.
- [9] Global coffee market trends – 2024: consumers choose quality. – Electron. text. data.: access mode.: <https://gemini.ua/trendi-globalnogo-kavovogo-rinku-2024-spozhyvachi-obirayut-yakist/>.
- [10] Ukraine buys coffee: TOP–5 countries from which it is brought. – Electron. text. data.: access mode.: <https://economics.segodnya.ua/ua/economics/enews.html>.
- [11] A. Vitiuk, A. Zalievska, *Analysis of the development of the coffee beverages market in Ukraine*, Innovation and Sustainability, 4, 72 (2023); <https://doi.org/10.31649/ins.2023.4.72.80>.
- [12] Mussatto, Solange I.; Carneiro, Livia M.; Silva, João P.A.; Roberto, Inês C.; Teixeira, José A. (January 2011). *A study on chemical constituents and sugars extraction from spent coffee grounds*. Carbohydrate Polymers. 83 (2): 368 (2011); <https://doi.org/10.1016/j.carbpol.2010.07.063>.
- [13] Josiah McNutt, Quan (Sophia) He, *Spent coffee grounds: A review on current utilization*, Journal of Industrial and Engineering Chemistry, 71, 78 (2019); <https://doi.org/10.1016/j.jiec.2018.11.054>.
- [14] Lina F. Ballesteros, José A. Teixeira, Solange I. Mussatto, *Chemical, Functional, and Structural Properties of Spent Coffee Grounds and Coffee Silverskin*, Food and Bioprocess Technology, 7, 3493 (2014); <https://doi.org/10.1007/s11947-014-1349-z>.
- [15] S.-V.S. Sklepova, I.M. Gasyuk, N.Ya. Ivanichok, P.I. Kolkovskiy, V.O. Kotsyubynsky, B.I. Rachiy, *The porous structure of activated carbon-based on waste coffee grounds*, Physics and Chemistry of Solid State, 23, 484 (2022); <https://doi.org/10.15330/pcss.23.3.484-490>.
- [16] S. Brunauer, P.H. Emmett, E. Teller, *Adsorption of Gases in Multimolecular Layers*. Journal of the American Chemical Society, 60, 309 (1938); <http://dx.doi.org/10.1021/ja01269a023>.
- [17] B. Lippens, J.H. de Boer, *Studies on pore systems in catalysts V. The t method*, Journal of Catalysis, 4, 319 (1965); [https://doi.org/10.1016/0021-9517\(65\)90307-6](https://doi.org/10.1016/0021-9517(65)90307-6).
- [18] M. Thommes, K. Kaneko, A.V. Neimark, J.P. Olivier, R. Francisco, J. Rouquerol, K.S.W. Sing, *Physisorption of gases, with special reference to the evaluation of surface area and pore size distribution (IUPAC Technical Report)*, Pure and Applied Chemistry, 87, 1051 (2015); <https://doi.org/10.1515/pac-2014-1117>.
- [19] Jaclyn D. Wiggins-Camacho, Keith J. Stevenson, *Effect of nitrogen concentration on capacitance, density of states, electronic conductivity, and morphology of N-doped carbon nanotube electrodes*, The Journal of Physical Chemistry C, 113, 19082 (2009); <https://doi.org/10.1021/jp907160v>.
- [20] Alberto Adán-Más, Teresa M. Silva, Liliane Guerlou-Demourgues, Maria Fátima Montemor, *Application of the Mott-Schottky model to select potentials for EIS studies on electrodes for electrochemical charge storage*, Electrochimica Acta, 289, 47 (2018); <https://doi.org/10.1016/j.electacta.2018.08.077>.
- [21] A.I. Kachmar, V.M. Boichuk, I.M. Budzulyak, V.O. Kotsyubynsky, B.I. Rachiy, R.P. Lisovskiy, *Effect of synthesis conditions on the morphological and electrochemical properties of nitrogen-doped porous carbon materials, Fullerenes Nanotubes and Carbon Nanostructures*, 27, 669 (2019); <https://doi.org/10.1080/1536383X.2019.1618840>.
- [22] John O'M. Bockris, Amulya K. N. Reddy, Maria Gamboa-Aldeco, Modern Electrochemistry 2A. Fundamentals of Electrochemistry (Springer New York, NY. Springer-Verlag US, 2000); <https://doi.org/10.1007/b113922>.

- [23] Allen J. Bard, Larry R. Faulkner, *Electrochemical Methods: Fundamentals and Applications*, 2nd Edition (Wiley & Sons, 2000).
- [24] B.P. Bahmatyuk, A.S. Kurepa, I.I. Grygorchak, *Impedance Spectroscopy Of Supercapacitors Based On Nanoporous Activated Carbon Material*, Journal of National University "Lvivska Politechnika", 687, 188 (2010); <https://ena.lpnu.ua:8443/server/api/core/bitstreams/16a0e7cd-47e7-4821-a434-bb517987d1c4/content>.
- [25] B.E. Conway, *Electrochemical supercapacitors. Scientific fundamentals and technological applications* (New York: Kluwer Academic Plenum Publishers, 1999).
- [26] M. Itagaki, S. Suzuki, I. Shitanda, K. Watanabe, H. Nakazawa, *Impedance analysis on electric double layer capacitor with transmission line model*, Journal of Power Sources, 161, 415 (2007); <https://doi.org/10.1016/j.jpowsour.2006.09.07>.
- [27] I.I. Hryhorchak, *Molecular energy storage: basic principles and new directions of technologies*, Herald of the Carpathian University, Mathematics. Physics, 1, 170 (2000).

Б.І. Рачій¹, Н.Я. Іванічок², В.В. Мокляк^{2,3}, П.І. Кольковський⁴, О.І. Бульбук⁵,
А.М. Солтис¹, Д.С. Борчук¹, Л.З. Хрущ¹

Вплив температури термохімічної активації на електропровідність та концентрацію носіїв заряду в отриманих пористих вуглецевих матеріалах

¹Прикарпатський національний університет імені Василя Стефаника, Україна, bogdan.rachiy@pnu.edu.ua

²Інститут металофізики ім. Г.В. Курдюмова НАН України, Україна, natalia.ivanichok@pnu.edu.ua

³Івано-Франківський національний технічний університет нафти і газу, Україна, mvmcv@gmail.com

⁴Інститут загальної та неорганічної хімії ім. Вернадського, Україна, pkolkovskyy@gmail.com

⁵Івано-Франківський національний медичний університет, Україна, obulbuk@ifnmu.edu.ua

Шляхом зміни температури хімічної активації рослинної біомаси отримані нанопористі вуглецеві матеріали з значенням питомої поверхні до 1050 м²/г. На основі отриманих вуглецевих матеріалів сформовані композити з різним процентним вмістом струмопровідної добавки. Методом електрохімічної імпедансної спектроскопії досліджено фізико-хімічні процеси, що відбуваються на межі розділу вуглецевий електрод/електроліт у 30% водному розчині КОН.

Визначено концентрацію носіїв заряду в отриманих вуглецевих матеріалах, значення якої знаходяться в межах $6 \cdot 10^{18} - 35 \cdot 10^{18}$ см⁻³, та встановлено її залежність від температури термохімічної активації. Встановлено, що зростання температури термохімічної активації від 600 °С до 900 °С призводить до збільшення ємності області просторового заряду практично в 10 раз. Формування композитів нанопористий вуглецевий матеріал/струмопровідна добавка сприяє кореляції між значеннями питомої ємності і електроопору для досліджуваних матеріалів.

Ключові слова: нанопористий вуглецевий матеріал, низькотемпературна порометрія, електропровідність, спектроскопія імпедансу, моделі Мотта-Шотткі, ємність просторового заряду.