

Electrochemical Properties of the Nanoporous Carbon/Aprotic Electrolyte System

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(Received 23 July 2017; published online 16 October 2017)

The paper describes researches of the behaviour of capacitor systems based on the nanoporous carbon in aprotic electrolytes. Carbon material have been obtained by carbonization of fruit seeds and used for the formation of electrodes of electrical storage devices. Much attention is paid to research of the structural characteristics of carbon using the isothermal nitrogen adsorption method. The purpose of the research is establishing of regularities of electrochemical processes at the electrode/electrolyte interface versus high surface area of carbon material, which formed by choice of technological parameters of obtaining and modification, as well as the type of aprotic electrolyte used.

Keywords: Nanoporous carbon, Specific capacity, Electrochemical capacitor.

DOI: [10.21272/jnep.9\(5\).05001](https://doi.org/10.21272/jnep.9(5).05001)

PACS numbers: 61.43.Gt, 81.05.Uw, 82.47.Uv

1. INTRODUCTION

The activity of electrical energy accumulating devices, which are constructed on the principle of charge/discharge of electric double layer (EDL), depends on the kinetics of processes at electrode/electrolyte interface. Such devices have been estimated by means of value current density through the active electrode area and EDL capacity as a function of potential. In this context the mechanism for energy storage is based on non-faradic processes, i.e. a current is used to charge of EDL. Therefore as the task need to obtain surface state with no-redox reactions at the electrode/electrolyte interface during the synthesis and modification of electrode materials. Nanoporous carbon (NC) often used as such electrode material due to chemically stability to different electrolytes and high specific surface area (~ 2000 m²/g) [1]. The key factors determining the performances of electrochemical capacitors are properties of electrolyte [2, 3]. In theory the high value of specific capacity depends on the high values of specific surface area. However, the practical situation is more complicated and usually there is no linear relationship between measured capacity and specific surface area of electrode material. The main reason for this phenomenon is that ions in the solution of the aprotic electrolytes do not penetrate the small diameter nanopores of carbon based electrodes. EDL capacitors (EDLCs) store the electric charge directly across the double layer of the electrode, since the carbon form has a nanoporous structure allowing the electrolyte ions to pass through and develop a double layer at exposed surface in electrolyte. As a result the surface area of the nanopores has no influence on the general capacity of EDLC electrode material.

The purpose of the work is to establish the regularities of electrochemical processes at NC/electrolyte in-

terface depending on the state of the developed surface, which was formed by selecting the technological parameters for its obtaining and modification, as well as the type of aprotic electrolyte used.

2. OBJECTS AND METHODS

As the object of study we used NC obtained by carbonization of fruit pits and as a comparison carbon materials derived from natural Anthracitic Donetsk (Ukraine) by steam activation method in a boiling layer at a temperature of ~ 900 °C with different parameters of porous space. The synthesis of NC passes in two stages. In advance for remove the volatile components of the material and the formation of primary porosity the feedstock is heat treated without air access. The fruit seeds were crushed mechanically to fractions ~ 5 mm after that placed in an autoclave. The process of material carbonization passes under pressure of water vapor (6-8)·10⁵ Pa and thermal activation at temperature of 900 °C. Carbon material obtained in such way was washing chemically in concentrated hydrochloric acid from the mineral additives. Neutral pH ensured by washing in 30% nitric acid and distilled water. At the second stage, obtained carbon was dried and activated in a boiling layer. Moreover, for the disclosure of internal porosity and the formation of new pores the material was subjected the gas stream (a mixture of hot air and argon) at 400 °C.

The determination of structural and adsorption characteristics of the material was carried out use nitrogen adsorption at temperature (-196 °C) by surface area analyzer Quantachrome Autosorb (Nova 2200e). The samples were previously degassed in a vacuum at 180 °C during 20 h. The calculation of adsorption isotherms allowed to obtain pore size distribution, specific surface area and specific pore volume. The specific sur-

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face area was calculated by the multipoint BET method in the adsorption isotherm P/P_0 range from 0.05 to 0.35. The total volume of pores was determined under pressure of saturation $P/P_0 \sim 1.0$. The average pore diameter was calculated according to the Horvath-Kawazoe method. The micropore volume V_{micro} (cm^3/g) and its specific surface S_{micro} (m^2/g) were determined by t -method.

Electrochemical studies were conducted in a two-electrode electrochemical cell (EC) using Autolab PGSTAT/FRA-2 spectrometer. The electrodes were prepared from carbon material of 0.005 g in mass and 0.25 cm^2 in surface. Then, electrodes were placed in glass cell with electrolyte solution and hermetic sealing of the cell was carried out. All steps of EC preparing were carried out in a dry box, drained by P_2O_5 , in an argon atmosphere. The solution of 1M tetrabutylammonium tetrafluoroborate in acetonitrile ($\text{TEABF}_4/\text{ACN}$) and solution of 1M lithium tetrafluoroborate in γ -butyrolactone (LiBF_4/GBL) were used as organic electrolytes.

The study of electrochemical properties of carbon materials were performed by galvanostatic and potentiodynamic cycling, as well as electrochemical impedance spectroscopy (EIS) method in the frequency of range of 10^{-2} - 10^5 Hz. The data of EIS were modeled to typical equivalent electrical circuit using ZView2 computer program.

3. RESULTS AND DISCUSSION

For research we selected materials, which were thermally modified at temperature 400°C during: 90 min. – NC1, 120 min. – NC2, 150 min. – NC3, 180 min. – NC4. Six carbon materials derived from natural anthracite with different parameters of porous structure were explored for a comparison (Table 1).

Table 1 – The structure and adsorption characteristics of carbon derived from anthracite

Sample	S_{BET} , m^2/g	V_{total} , cm^3/g	V_{micro} , cm^3/g
A1	450	0.26	0.20
A2	680	0.34	0.18
A3	880	0.49	0.23
A4	940	0.50	0.25
A5	980	0.55	0.17
A6	990	0.59	0.17

Isotherms of nitrogen adsorption/desorption for NC explored (Fig. 1) are characteristic for polymolecular adsorption in micro- and mesoporous of organic origin materials [4]. For all samples, there is a H4-type hysteresis loop classified by IUPAC [5], which is associated with capillary condensation in mesoporous regions. The growth of the adsorption branch of the isotherm near $P/P_0 = 1$ due to multiple processes of condensation and evaporation of nitrogen in meso- and macropores.

Galvanostatic measuring of the cells, whose electrodes were formed based on NC with the different time of thermal modification, showed almost linear behavior of the discharge processes (Fig. 2). The discharge curves characterize the capacitive behavior of EC. The sharp decline in voltage during discharge indicates the presence of internal resistance of EC. The

internal resistance of systems based on LiBF_4/GBL electrolyte (Fig. 2, b) is 30-50% higher than one for systems based on $\text{TEABF}_4/\text{ACN}$ electrolyte (Fig. 2, a). The main reason for high internal resistance of EC is small number of mesopores and large number of micropores with small diameters that are not available to electrolyte ions. The ions of organic electrolyte are too large to penetrate into micropores of NC. The existence of a large number of micropores in size range of 0.8-1.2 nm is confirmed by low temperature porosimetry method.

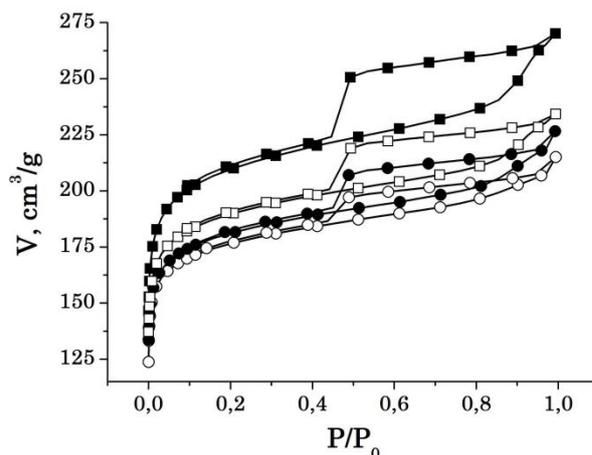


Fig. 1 – Isotherms of nitrogen adsorption/desorption of carbon samples: NC1 – \circ –, NC2 – \bullet –, NC3 – \square –, NC4 – \blacksquare –

The determination of specific surface area, total pore volume and pore size distribution for the NC were carried out using the analysis of adsorption isotherms (Table 2).

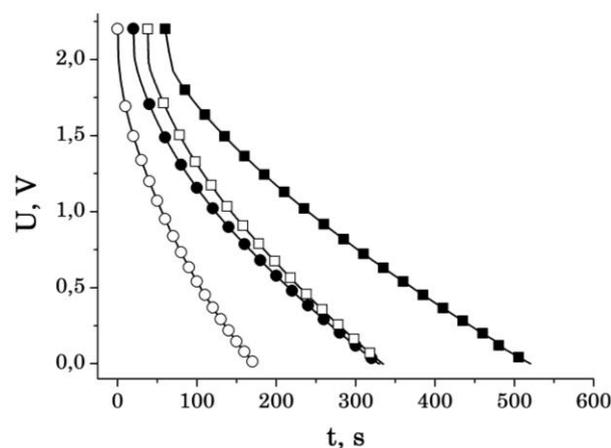
Table 2 – Structural and adsorption characteristics of NC

Sample	t , min	S_{BET} , m^2/g	S_{micro} , m^2/g	V_{total} , cm^3/g	V_{micro} , cm^3/g
NC1	90	681	616	0.332	0.247
NC2	120	696	619	0.351	0.252
NC3	150	725	655	0.362	0.266
NC4	180	799	722	0.418	0.297

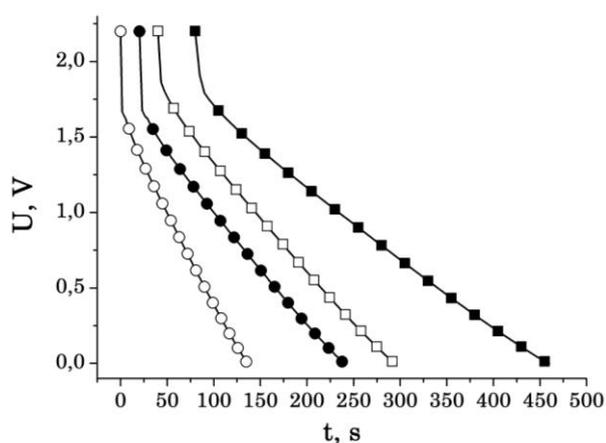
The specific capacity of carbon materials depending on the type of electrolyte is found from discharge curves (Table 3).

As a result the value of specific capacity of EC increases due to the increasing available micropores when comparing structural and adsorption properties of NC and data of Table 3. Carbon materials (A2, A3 and NC1, NC2) characterized by increasing of internal resistance and lower specific capacity due to the unavailable electrolytically micropores. Anthracite derived porous carbon materials A1-A3 have a low quantity of transport pores and micropore volume is (50-80)% of the total pore volume. The main reason is that electrode material NC1 and NC2 have low specific capacity and high internal resistance due to low quantity of opened micropores and low specific surface area.

Typical cyclic voltammograms of EC based on aprotic electrolytes are shown in Fig. 3. At low scan rates ($< 10 \text{ mV/s}$) all samples showing perfect polarization. Cyclic voltammograms have a symmetric form, which



a



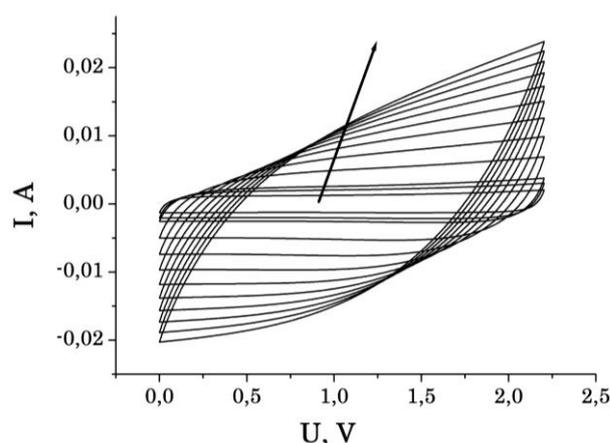
b

Fig. 2 – Discharge curves of EC based on thermally modified carbon material: NC1 —○—, NC2 —●—, NC3—□—, NC4 —■— in different electrolytes: TEABF₄/ACN (a) and LiBF₄/GBL (b)

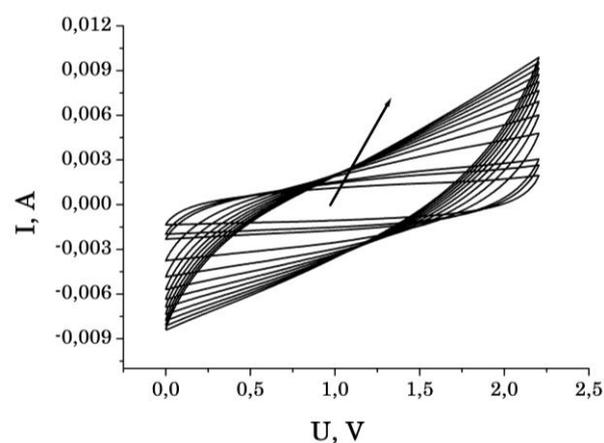
Table 3 – Dependence of NC specific capacity in electrolyte solutions

Sample	C_{sp} , F/g	
	TEABF ₄ /ACN	LiBF ₄ /GBL
NC1	22.6	20.3
NC2	37.4	36.8
NC3	40.2	32.1
NC4	53.8	48.6
A1	16.4	22.6
A2	24.9	48.3
A3	47.3	76.2
A4	45.7	75.8
A5	57.6	79.8
A6	59.3	81.5

indicates the quasi-turnover of the charge/discharge of the EDLC. On cyclic voltammograms, in the voltage range (0-2.2 V) there is no redox peaks, indicating the absence of pseudocapacitive charge storage [6]. The general character of the voltammograms is typical for EC working on the charge/discharge principle of EDLCs.



a



b

Fig. 3 – Cyclic voltammograms of EC based on carbon material: A5 (a) and NC4 (b) in TEABF₄/ACN electrolyte

When the scan rates increase to 40 mV/s the anthracite derived carbon materials in the TEABF₄/ACN electrolyte are still stable. In case of higher scan rates there are warping effects of voltammograms and deviate from the ideal rectangular shape due to increasing internal resistance of EC, so-called "starvation of electrolyte" effect. This effect is associated with removal of electrolyte ions during charging and their adsorption on border of EDL. Therefore, a high scan rate increases a number of micropores which are available to the electrolyte. However, its main reason produces of large internal resistance. The fact is the result of diffusion which prevents or sometimes restricts movement of electrolyte in these pores. Consequently, increasing of discharge time due to reduced of ion mobility in the pores during charge/discharge rates. As a result, the capacity at high speeds charge/discharge rates, does not depend on these pores [7].

As it can be seen in Fig. 3, the value of currents, as should be expected, increases with increasing of scan rate. However, the current values for A5 and A6 samples, based on TEABF₄/ACN electrolyte, are higher in 2 times than for other carbon samples.

EC, formed on the basis of anthracite derived carbon, are treated as ideal EDLCs at a scan rate 10 mV/s (Fig. 4). The similar properties of other carbon materi-

als and deviations from the ideal rectangular shape are evident. This may be due to the fact insufficient number of mesopores in the samples, which serve as transport pores for the electrolyte.

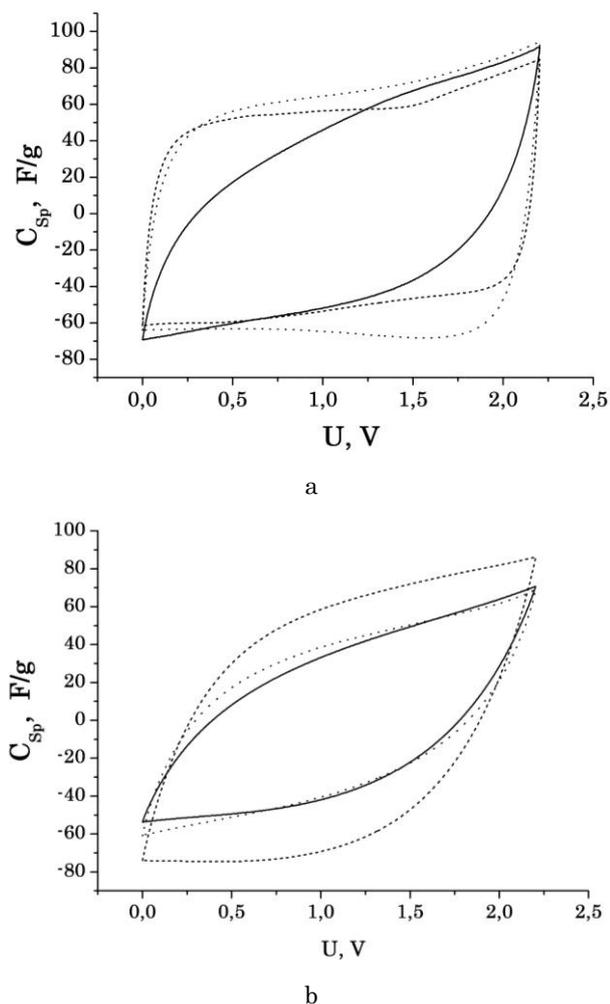


Fig. 4 – Dependence of specific capacitance of EC from voltage at scan rates 10 mV/s for samples: A6, ----- A5, — NC4 in TEABF₄/ACN a) and LiBF₄/GBL b) electrolyte

To study the capacitive behavior of NC, and the dependence of the specific capacity on the potential change rate of the cell was investigated using cyclic voltammograms. Table 4 shows that there is a decrease of specific capacity with the increase of the scan rates for all samples. However, this decrease is insignificant for carbon, obtained from anthracite (A5, A6) in the TEABF₄/ACN electrolyte solution (specific capacity is changed to 10 % in all scan rates), which allows the use of these materials at high discharge currents.

To study the electrochemical processes of NC in these electrolytes impedance spectroscopic method was used. Nyquist diagrams, that describing the behavior of carbon materials in organic electrolytes, shown on Fig. 5.

The Nyquist diagrams for EC (Fig. 5) are typical for capacitive accumulation of electric charge at the NC/electrolyte boundary. The semicircle region is observed in high frequency range for all materials in these diagrams, indicating the presence of electrochemical reaction on the electrodes: the electric current

Table 4 – Dependence of NC specific capacity from scan rates in different electrolytes

Electro-lyte	TEABF ₄ /ACN				LiBF ₄ /GBL			
	s, mV/s	5	10	20	40	5	10	20
	<i>C_{sp}</i> , F/g							
NC1	32.2	21.7	15.3	9.2	29.3	19.3	10.1	4.2
NC2	44.5	31.5	22.1	11.3	35.5	23.4	12.2	5.1
NC3	54.3	35.2	24.6	12.3	42.8	28.2	14.7	6.2
NC4	64.4	44.2	27.3	14.5	58.6	38.6	20.1	8.5
A3	19.4	11.5	7.1	4.2	26.2	12.3	6.1	2.9
A4	29.2	27.3	23.8	17.8	24.3	19.3	12.8	6.9
A5	65.3	64.5	63.1	55.2	28.5	18.8	9.5	4.3
A6	56.2	55.1	53.5	48.6	35.1	29.3	17.1	6.9

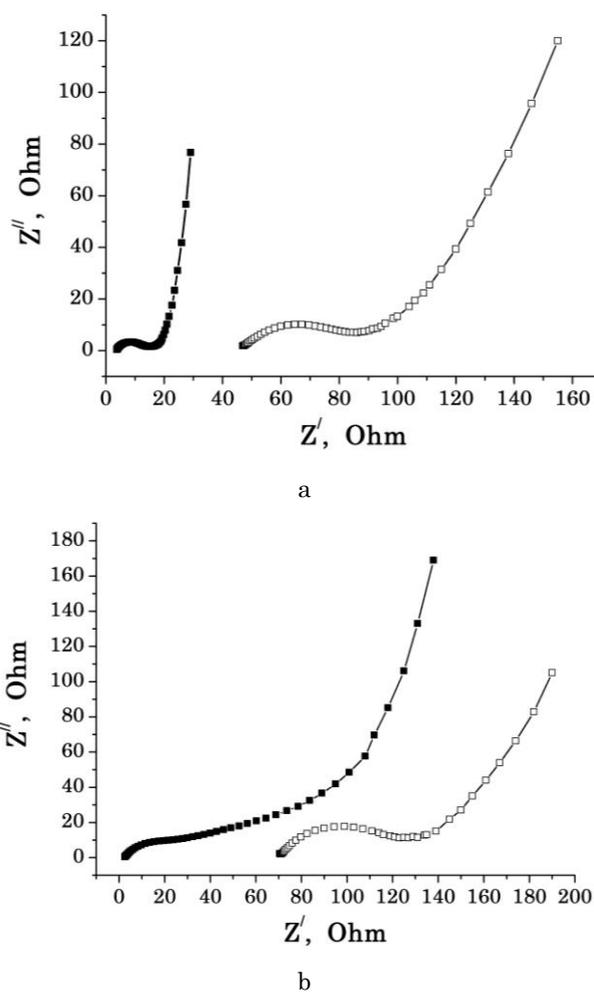


Fig. 5 – Nyquist diagrams of EC based on carbon material: A6 a) and NC4 b) in TEABF₄/ACN —□— and LiBF₄/GBL —■— electrolytes

flows through the electrode/electrolyte boundary. Additional resistance is appeared characterizing the redox-reaction on the interphase boundary. At medium frequencies, the semicircle transforms into a sloping straight line, which is responsible for the diffusion processes in the pores of the carbon material. In the low frequency range, the imaginary part of the impedance increases, indicating the capacitive behavior of the system in this range. As follows from diagrams obtained, the internal resistance of systems based on the

LiBF₄/GBL electrolyte is an order of magnitude higher than the corresponding one for systems with TEABF₄/ACN electrolyte.

The equivalent circuit (Fig. 6) was used for fitting the Nyquist diagrams. It consists of ohmic resistance (R_s) in high frequency ranges, which is the resistance of the electrolyte, contacts and connections. Constant phase element (CPE_1) associated with diffusive ion transportation (a value of exponential multiplier n , included in the formula for calculating of the impedance element $Z_{CPE}(j\omega) = A^{-1}(j\omega)^{-n}$, equal to 0.48) which corresponds diffusion of ion electrolyte to the electrode/electrolyte interface.

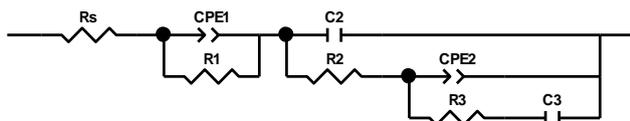


Fig. 6 – Equivalent electric circuit for modeling Nyquist diagrams obtained for the electrode/electrolyte system

The element R_1 is the resistance of the diffusion process. $C_2 || R_2$ -chain represent the process of EDL formation in transport pores: C_2 is homogeneous distributed capacity of EDL and R_2 – the resistance of this process. CPE_2 corresponds, according to the data obtained, to the diffusion process of ions in the micro

pores of the carbon material (values of $n = 0.58$). R_3 and C_3 are the resistance of penetration and accumulated capacity of EDL in these pores, respectively.

4. CONCLUSION

The effect of thermal modification on the parameters of the porous structure of carbon materials is considered. It is set, that nanoporous carbon material has a different morphology and pore size distribution depending on the technological regimes. Due to the optimization of the thermal modification parameters, samples of practically homogeneous mono-porous carbon with a specific surface area up to 800 m²/g, pore of 1-2 nm in size and mesoporous content up to 10% can be obtained.

It is find out, that the values of the energy parameters of the EC correlate with the specific surface magnitude of the materials and the size of the electrolyte ions. The maximum specific capacity of 60-70 F/g is obtained for carbonaceous materials with specific surface area more than 700 m²/g using TEABF₄/AC as an electrolyte.

The kinetic features of the passing of electrochemical processes in the carbon/non-aqueous electrolyte system are considered using impedance spectroscopy method. An equivalent scheme has been selected that allows a satisfactory modeling of the impedance spectrum over the entire range of frequencies studied. Physical interpretation is proposed for each element of the scheme.

Електрохімічні властивості системи нанопористий вуглець/апротонний електроліт

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У роботі описуються дослідження поведінки конденсаторних систем на основі нанопористого вуглецю в апротонних електролітах. Для формування електродів накопичувачів електричної енергії використано вуглецевий матеріал, отриманий карбонізацією фруктових кісточок. Велика увага приділяється дослідженню структурних характеристик вуглецю методом ізотермічної адсорбції азоту. Робота переслідує мету встановлення закономірностей перебігу електрохімічних процесів на межі розділу електрод/електроліт в залежності від стану розвинутої поверхні вуглецевого матеріалу, яка формується шляхом підбору технологічних параметрів отримання і модифікації, та виду застосовуваного електроліту.

Ключові слова: Нанопористий вуглець, Питома ємність, Електрохімічний конденсатор.

Электрoхимические свойства системы нанопористый углерод/апротонный электролит

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В работе описываются исследования поведения конденсаторных систем на основе нанопористого углерода в апротонных электролитах. Для формирования электродов накопителей электрической энергии использован углеродный материал, полученный карбонизацией фруктовых косточек. Большое внимание уделяется исследованию структурных характеристик углерода методом изотермической адсорбции азота. Работа преследует цель установления закономерностей протекания электрохимических процессов на границе раздела электрод / электролит в зависимости от состояния развитой поверхности углеродного материала, которая формируется путем подбора технологических параметров получения и модификации, и вида применяемого электролита.

Ключевые слова: Нанопористый углерод, Удельная емкость, Электрохимический конденсатор.

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