Vadym PTASHNYK[1], Igor BORDUN[2], Volodymyr POHREBENNYK[2,4], Jakub TAKOSOGLU[3], Maria SADOVA[2]

Lviv National Agrarian University (1), Lviv Polytechnic National University (2), Ukraine
Kielce University of Technology (3), State Higher Vocational School (4), Poland

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Impedance investigation of activated carbon material modified by ultrasound treatment

Abstract. *The influence of ultrasonic radiation in the cavitation regime on the properties of wood activated carbon has been studied. The optimum mode of ultrasound treatment that leads to increase of specific capacity of supercapacitors from 52 F/g to 151 F/g was determined. It was shown that ultrasound treatment does not cause significant changes in porous structure of activated carbon, but reduces the amount of surface groups. The impedance dependencies for the supercapacitors made both of the original and modified carbon have been analyzed. The equivalent electrical circuits modelling the impedance hodographs have been constructed. De Levie impedance model, modified by series connection of parallel $R_{SC}C_{SC}$-links, was used. It has been shown that ultrasonic radiation changes the properties of the surface and the Fermi level position shifts to the energy region with high states density of delocalised electrons.*

Streszczenie. *Badano wpływ promieniowania ultradźwiękowego w reżimie kawitacyjnym na właściwości węgla aktywnego drzewnego. Określono optymalny tryb leczenia ultrasonograficznego, który prowadzi do zwiększenia zdolności produkcyjnych superkondensatorów od 52 F / g do 151 F / g. Wykazano, że leczenie ultrasonograficzne nie powoduje istotnych zmian porowatej struktury węgla aktywnego, ale zmniejsza ilość grup powierzchniowych. Zależności impedancyjne dla superkondensatorów dokonano zarówno w oryginalnym, jak i modyfikowanym węglu. Zostały skonstruowane równoważne obwody elektryczne modelujące hodografy impedancji. Stosowano model impedancji De Levie, zmodyfikowany przez szeregowe połączenie równoległych łączników RSCCSC. Wykazano, że promieniowanie ultradźwiękowe zmienia właściwość powierzchni, a położenie poziomu Fermi przesuwa się do obszaru energetycznego z gęstą gęstością delokalizowanych elektronów.*
Badanie impedancji materiału z węgla aktywowanego zmodyfikowanego metodą ultradźwięków

Keywords: activated carbon; ultrasound; supercapacitor; Fermi level.
Słowa kluczowe: węgiel aktywowany; ultradźwięk; superkondensator; Poziom Fermi.

Introduction

The electrochemical capacitor with an electric double layer (EDL), or supercapacitor is a relatively new class of devices to store the electrical energy, which by its parameters and functional capabilities is between the traditional primary and secondary power sources and electrostatic capacitors. The prefix “super” indicates that these devices have higher capacitance by several orders than conventional capacitors of the same dimensions and larger specific energy. Compared with traditional batteries, supercapacitors have higher power density, although they lose them in energy density [1]. Such features allow using the supercapacitors in engines of hybrid vehicle, into the systems of improving the quality of electrical energy, when starting the internal combustion engines in all weather conditions, in the systems of volatile memory, etc [2–4].

Activated carbon materials are the most common materials for the supercapacitor electrodes manufacturing both with aqueous and non-aqueous electrolyte. This is due to well-developed porous structure of activated carbon, good electrical conductivity, environmental friendliness and low cost. However, traditional methods of activated carbon production do not supply the high quality electrode material. Therefore, the methods of modification of the raw materials [5, 6] or as produced carbon materials become of great importance in technological processes [7]. Various acids and heat treatments in inert atmospheres are often used for modifications. This processing substantially changes the porous structure and surface groups. However, such modification techniques are energy-intensive and environmentally hazardous. As an alternative to them the nonchemical methods of influence on the activated carbon can be used, among which an important place belongs to ultrasonic technologies [8]. The results given in [8], are related to the research of changes in the composition of the activated carbon surface groups owing to ultrasonic treatment.

The purpose of the work is in studying the influence of ultrasound radiation in the cavitation regime on the electronic structure of activated carbon and analyzing functioning the supercapacitors of modified carbon by the method of impedance spectroscopy.

Experimental

Activated carbon produced of birch wood by activation with steam at temperature 800–900 ºC has been used as the initial material. For experimental studies the initial carbon has been mechanically crushed, sieved at the sifting machine and fractions of the particles with size of 80–90 μm have been selected. The prepared carbon has been placed into the bath of ultrasonic device BAKU-9050 and filled with degassed distilled water to study the influence of ultrasound in the cavitation mode. The investigated carbon was in the bath of ultrasonic unit in the form of 15–20 weight % dispersion. The duration of ultrasonic influence was 1–25 min at the radiation power of 30 W. The frequency of ultrasonic influence was 42 kHz.

The porous structure parameters of activated carbon (specific surface area, total pore volume, volume of micropores, mean diameter of pores) were determined by isothermal adsorption/desorption of nitrogen at the boiling point (T = 77 K) in an automatic gas sorption analyzer Quantachrome Autosorb (Nova 2200e). Samples previously were degassed in vacuum at 453 K for 20 hours.

The surface properties of prepared carbons were evaluated by Boehm titration method which is an acid-base titration method for determination the amount of surface oxygen groups (acidic or basic) at carbon surfaces [9].
Electrodes for electric double layer capacitors were produced from the fraction of 40–63 μm both of initial and dried after modification and sifted activated carbon. The Teflon binding component in a weight ratio of activated carbon to binder as 19:1 has been used to form the electrodes. 30 % aqueous solution of potassium hydroxide served as electric double layer capacitor electrolyte. Galvanostatic charge/discharge measurements supply specific capacitance, determined by the formula:

(1) $$C = \frac{2I \cdot t}{U \cdot m},$$

where I is current, t is discharge time, U is voltage range used for capacitor operation, m is smaller mass of capacitor electrode. However, we tried to select identical mass for both electrodes.

Impedance studies of activated carbon were conducted in the three-electrode cell with silver chloride electrode of comparison. The measurements were performed in a frequency range of 10^{-3}–10^{6} Hz using the spectrometer Autolab PGSTAT-100. Impedance models were build by ZView 2.3 software package.

Results and discussion

The dependence of the specific capacitance of activated carbon on the ultrasonic treatment time in the cavitation mode is shown in Figure 1. As seen from the figure, the specific capacitance with increasing influence time up to 10 min significantly increases that may be caused both by the change in the porous structure and the change of surface groups composition. However, further increasing the treatment time reduces the specific capacitance of activated carbon. And this behaviour requires further analysis to establish the reason of changing the specific capacitance.

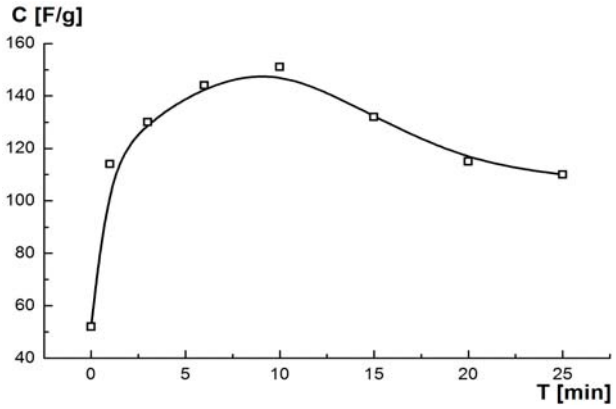

Fig. 1. Dependence of specific capacitance of activated carbon from the time of ultrasonic treatment

The porous structure parameters of initial activated carbon and ultrasound treated for 10 min activated carbon are given in table 1. As can be seen, porous texture has little change after the treatment.

Table 1. Porous structure parameters of activated carbons.

Activated carbon	S_{BET}, (m^2g^{-1})	V_{total}, (cm^3g^{-1})	V_{micro}, (cm^3g^{-1})	Mean pore diameter, (nm)
Initial carbon	799	0,449	0,214	2,63
Modified activated carbon (ultrasound by 10 min)	824	0,431	0,226	2,45

It is known [10] that ultrasonic influence on the aqueous environment is accompanied by appearance of products of sonochemical reactions and the formation of free radicals and hydrogen peroxide causes the oxidative effect on the modified surface. Consequently, the composition of the surface chemical groups of activated carbon is modified especially ones containing oxygen. The composition of the groups not only determines the hydrophilicity of the surface, but also affects the specific capacitance and internal resistance of activated carbon during its use as an active electrode material of the supercapacitors [11, 12]. In the work [8] it is shown that the total number of surface groups decreases at ultrasonic treatment up to 10 min. The measurement of the total number of surface groups for longer influence of ultrasound on activated carbon has revealed that this parameter reaches saturation (tabl. 2). Thus, the only change in surface properties can not influence in such a way the specific electrical capacitance of activated carbon after ultrasonic treatment.

Table 2. The total number of surface groups in activated carbon.

Activated carbon	Initial carbon	After ultrasound influence				
		1 min	3 min	10 min	15 min	20 min
Surface groups, (mmol/g)	1,36	1,26	1,2	1,12	1,14	1,13

To understand the reasons affecting the supercapacitor capacitance characteristics, it is necessary to analyse the features of EDL at the interface of the electrolyte and the electrode non-metallic solid phase (Figure 2).

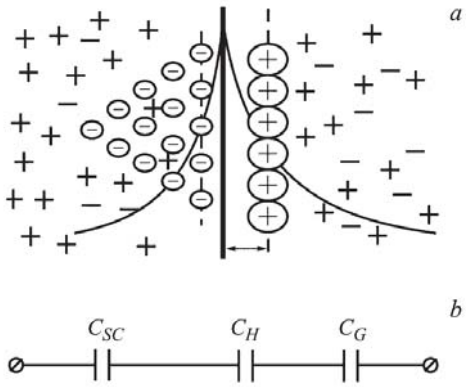

Fig. 2. Model of electric double layer for non-metallic electrodes (a) and the equivalent electrical circuit (b) [13]

As we can see in Figure 2, high capacitance characteristics of the supercapacitor during functioning are supplied by the optimal combination of the porous structure with an appropriate electronic structure. The latter must provide the unblocking of Helmholtz capacitance C_H by the capacitance of the region of space charge in a solid body C_{SC}. These two capacities determine the total capacitance of EDL, as in the electrolyte the capacitance of the Gouy-Chapman C_G is much higher than the capacitance of the dense part of EDL – Helmholtz layer. Taking into account this fact, in accordance with the scheme in Fig. 2, b, the total capacitance C of EDL can be determined by the formula:

(2) $$C = \frac{C_H \cdot C_{CS}}{C_H + C_{CS}}.$$

The unblocking of the capacitance C_H contributes to increasing the capacitance C_{SC}, which is related to the density of electronic states at the Fermi level [14]:

(3) $$C_{SC} = e\sqrt{\varepsilon\varepsilon_0 D(F)},$$

where e is elementary charge, ε is permittivity, ε_0 is vacuum permittivity, $D(F)$ is the density of electronic states at the Fermi level.

The problem of unblocking is practically absent for metal electrodes, however, it is important for carbon ones. This is due to the fact that in the carbon materials, the radius of Debye shielding is large enough.

So, while obtaining carbon materials for electrodes of the supercapacitors it is necessary to provide conditions for increasing the states density of delocalized charge carriers at the Fermi level. This will contribute to the maximum unblocking of the capacitance of C_H from the limiting effect of the capacitance of the depletion region of the space charge of activated carbon in accordance with relations (2) and (3). It should be added that providing high value C_{SC} is in many cases decisive in comparison with obtaining a large surface area not only from the point of view of capacitive characteristics of activated carbon, but power parameters [15]. Also is possible to set the parameter value C_{SC} by simulation results of obtained impedance dependencies.

Nyquist typical diagrams are presented in Figure 3 both for the initial activated carbon, and for the ultrasound irradiated one. The absence of a semicircle in the area of high frequencies shows slightly small contribution of pseudo-capacitance to the total capacitance. This indicates a good reversibility of the processes of charge-discharge of the supercapacitor with electrodes based on the studied activated carbon.

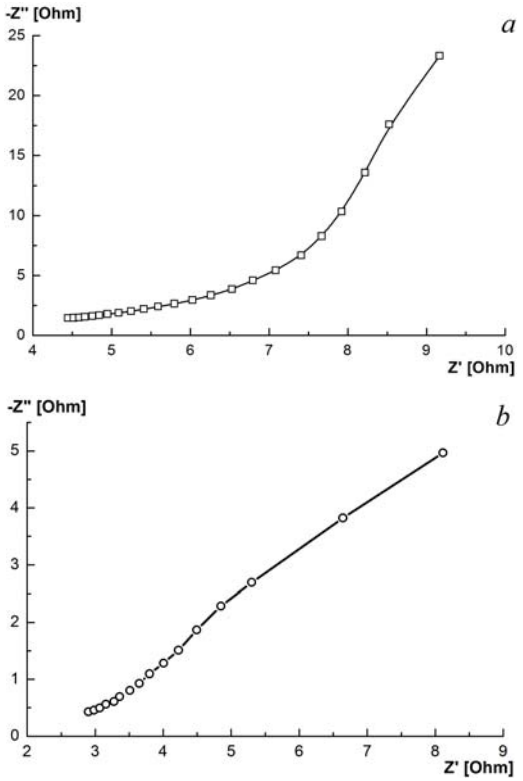

Fig. 3. Typical Nyquist diagrams for the initial (a) and modified (b) activated carbon

As Nyquist diagrams (Fig. 3, a; and Fig. 3, b) are similar, it means that they will differ by the value of the relative component capacities of EDL. This gives opportunity to use De Levie impedance model [16], modified by series connection of parallel $R_{SC}C_{SC}$-link, as shown in Figure 4.

The results of computer simulation of the model parameters for the case of bias voltage U=0 V for two supercapacitors with the same mass of electrodes are shown in Table 1.

From the data of Table 3 we see a significant increase of the specific capacitance of Helmholtz layer $\sum_i C_i$, as well as nearly a twofold decrease in the resistance of material *R1* due to the increase of the free charge carriers concentration and increase the capacitance of the space charge region.

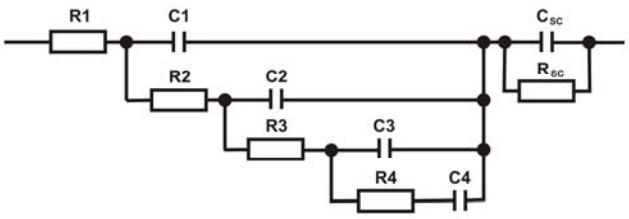

Fig. 4. Equivalent electrical circuit modelling the impedance hodographs for the initial and modified activated carbon

Table 3. Results of parametric identification of the elements of the equivalent electrical circuit

Material	*R1*, [Ohm]	$\sum_{i>1} R_i$, [Ohm]	$\sum_i C_i$, [F]	C_{SC}, [F]	R_{SC}, [Ohm]
Initial activated carbon	4,36	534,61	0,83	0,48	2,29
Modified activated carbon (ultra-sound 10 min)	2,52	93,55	8,46	1,24	1,65

The supply of potential bias at the measurement of impedance dependencies causes change in the capacitance value C_{SC}. Figure 5 represent the dependence of the specific value C_{SC} on the applied potential bias. A minimum capacitance value of the space charge region C_{SC} for initial carbon is at U = –0,4 V, and for 10 min ultrasonic irradiated at U = –0,2 V.

So, minimum at capacitance-voltage dependence as a result of ultrasonic influence shifts in a positive region. And its position determines the chemical potential of each of the materials in the electrolyte μ_E [14]:

$$\mu_E = F - e\varphi_S, \tag{4}$$

where e is elementary charge, F is position of Fermi level, φ_S is potential which corresponds to minimum on the graph $C(U)$.

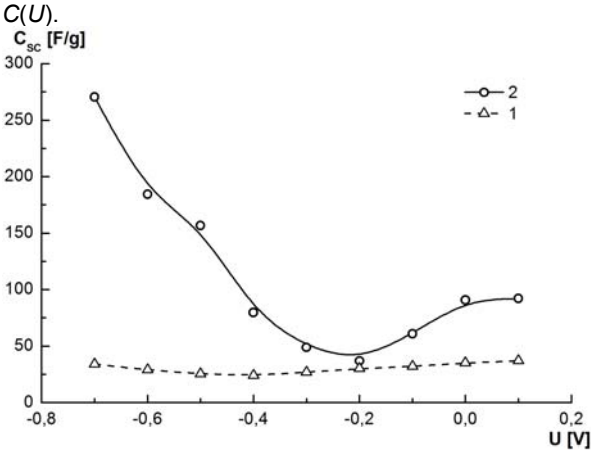

Fig. 5. Dependence of capacitance specific value C_{SC} on the constant bias voltage for the initial activated carbon (1) and for activated carbon after 10 min ultrasonic influence (2)

Since the electrolyte remains constant, then

$$\mu_{E1} = \mu_{E2}, \qquad F_1 - e\varphi_{S1} = F_2 - e\varphi_{S2} \tag{5}$$

Based on this the shift of the Fermi level may be calculated as,

$$F_2 - F_1 = e(\varphi_{S2} - \varphi_{S1}), \quad (6)$$

where indexes 1 and 2 indicate the initial and modified material accordingly.

Thus, due to the positive value of minimum displacement at $C(U)$ dependence we can conclude that ultrasonic influence on activated carbon caused to the shift of the Fermi level to the energy region with greater density of states. As a result both an increase in specific capacitance of the material and reducing of its internal resistance occur.

Conclusions

Ultrasonic irradiation of activated carbon materials in cavitation mode not only grinds carbon particles, but also effectively changes the surface properties of carbon. The total number of surface groups in the process of treatment gradually decreases and saturates. Also it was found that ultrasound treatment does not cause significant changes in the porous structure.

Analysis of impedance data showed that this is accompanied by the Fermi level shifts to the energy region, characterized by high density of delocalized electron states. This fact is important for reducing the resistivity of carbon material and deblocking of Helmholtz layer capacitance by increasing the capacitance of layer of space charge region in the carbon material. This improves the characteristics of supercapacitors manufactured from activated carbon modified by ultrasound.

For wood activated carbon the increase of specific capacitance of supercapacitors from 52 F/g for initial carbon to 151 F/g for carbon after ultrasound treatment in the optimum mode was shown.

***Authors**: dr. Eng. Wadym Ptashnyk, Lviv National Agricultural University, Department of Electrotechnical Systems, ul. V. Velykogo, 1, 80381, Dubliany, Lviv, Ukraine, E-mail: ptashnykproject@gmail.com; doc. dr inż. Igor Bordun, Lwow National University of Technology, Department of Applied Physics and Nanofed Science, ul. Kn. Romana str., 5, 79005, Lviv, Ukraine, Email: bordun.igor@gmail.com; prof. dr. Eng. Volodymyr Pohrebennyk, Lviv National Technical University, Institute for Sustainable Development, im. V. Chornovila, ul. Gen. Chyprunki, 130, 790057, Lviv, Ukraine, Email: vpohreb@gmail.com; State Higher Vocational School, Staszica Str. 1, Nowy Sacz, 33-300, Poland; dr. Eng. Jakub Takosoglu, Swietokrzyska University of Technology, Faculty of Mechatronics and Machine Building, al. Tysiąclecia Państwa Polskiego 7, 25-314, Kielce, Poland, E-mail: gba@tu.kielce.pl; postgraduate Maria Sadova, Lviv National University of Technology, Department of Applied Physics and Nanofed Science, ul. Kn. Romana str., 5, 79005 Lviv, Ukraine, E-mail: mariiasadova@gmail.com*

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