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The influence of ultrasonic modification on structure of activated carbon and characteristics of supercapacitors on its basis

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Influence of ultrasonic radiation during cavitation regime on electrochemical properties of wood based activated carbon was studied. The optimal mode for ultrasonic treatment of activated carbon was determined, wherein the specific capacity of supercapacitors, produced on the basis of such carbon, increases from 52 F/g to 151 F/g. It was shown that ultrasonic treatment does not cause significant changes of the porous structure of the activated carbon but reduces the number of surface groups. The Nyquist plots for supercapacitors made of both original and modified carbon, were analyzed. Equivalent electrical circuits which model the impedance hodograph were constructed. For this purpose, de Levie model was used, modified by parallel $R_{SC}C_{SC}$ — link of chain. It was shown that ultrasonic radiation allows not only to change effectively the properties of a surface, but also shifts a position of the Fermi level to the energy region, which is characterized by a high density of delocalized electron states. Quantity reduction of surface groups and the change of an electronic structure of activated carbon is a reason for the increase of charge accumulation efficiency in an electric double layer at the boundary with electrolyte.

Keywords: activated carbon, ultrasonic, supercapacitor, Fermi level.

Исследовано влияние ультразвукового излучения в кавитационном режиме на электрохимические свойства древесного активированного угля. Установлен оптимальный режим ультразвуковой обработки активированного угля, при котором удельная емкость суперконденсаторов, изготовленных на основе такого угля, растет от 52 Ф/г до 151 Ф/г. Показано, что ультразвуковая обработка не вызывает значительных изменений пористой структуры активированного угля, но уменьшает количество поверхностных групп. Проанализированы диаграммы Найквиста для суперконденсаторов, изготовленных как из исходного, так и из модифицированного угля. Построено эквивалентные электрические схемы, моделирующие годографы импеданса. Для этого использована модель де Леви, модифицированная подключением $R_{SC}C_{SC}$ — звена. Показано, что ультразвуковое излучение позволяет не только эффективно изменять свойства поверхности, но и сдвигает положение уровня Ферми в энергетическую область, которая характеризуется повышенной плотностью состояний делокализованных электронов. Уменьшение количества поверхностных групп и изменение электронного строения активированного угля является причиной роста эффективности накопления заряда в двойном электрическом слое на границе его раздела с электролитом.

Вплив ультразвукової модифікації на структуру активованого вугілля і характеристики суперконденсаторів на його основі. *В.В.Пташник, І.М.Бордун, М.М.Садова.*

Досліджено вплив ультразвукового випромінювання у кавітаційному режимі на електрохімічні властивості деревного активованого вугілля. Встановлено оптимальний режим ультразвукової обробки активованого вугілля, при якому питома ємність суперконденсаторів, виготовлених на основі такого вугілля, зростає від 52 Ф/г до 151 Ф/г. Показано, що ультразвукова обробка не спричиняє значних змін пористої структури активованого вугілля, але зменшує кількість поверхневих груп. Проаналізовано діаграми Найквіста для суперконденсаторів, виготовлених як з вихідного, так і з модифікованого вугілля. Побудовано еквівалентні електричні схеми, що моделюють годографи імпедансу. Для цього використано модель де Леві, модифіковану підключенням паралельної $R_{SC}C_{SC}$ — ланки. Показано, що ультразвукове випромінювання дозволяє не лише ефективно змінювати властивості поверхні, але і зсуває положення рівня Фермі в енергетичну область, яка характеризується підвищеною густиною станів делокалізованих електронів. Зменшення кількості поверхневих груп і зміна електронної будови активованого вугілля є причиною зростання ефективності накопичення заряду у подвійному електричному шарі на межі його розділу з електролітом.

1. Introduction

Electrochemical capacitor with an electric double layer (EDL), or supercapacitor is a relatively new class of devices for the accumulation of electrical energy, which according to 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 by several orders of magnitude more capacity than usual capacitors of the same size and higher specific energy. Compared with traditional accumulators, supercapacitors have higher specific power although their specific energy is less [1]. Such features allow using supercapacitors at power units of hybrid transport, in the systems for improving the quality of electric energy, during combustion engine starting in all — weather conditions, in systems of volatile memory [2–4].

Activated carbon materials are the most common materials for supercapacitor electrode manufacture with both aqueous and non-aqueous electrolyte. This is due to the well-developed porous structure of activated carbon, its good electrical conductivity, environmental friendliness and low cost. However, conventional methods for production of activated carbon do not provide the electrode material of the right quality. Therefore, the modification methods of both raw materials [5, 6] and already obtained carbon materials [7] are moving up to the first place in technological processes. Various acids and heat treatment processes in inert atmospheres are most commonly used for carbon modification. Such treatment significantly alters, in the first place, the porous structure and the surface groups. However, such modification techniques are energy-consuming and environmentally hazardous. Therefore, the reagentless methods of influence on activated carbon are used as alternative ones, among which the leading place belongs to ultrasonic (US) technologies [7, 8].

Therefore, the aim of the paper was to study the influence of ultrasonic radiation during cavitation on the properties of activated carbon (the porous structure, the content of surface groups, electronic structure) and to analyse the work of supercapacitors made of modified coal by the method of impedance spectroscopy.

2. Experimental

Activated carbon obtained from the birch wood by means of water steam activation at temperature of 800–900°C was used as an original material. For the experimental studies the original carbon was crushed mechanically, sifted on sifting machine and the fractions with a particle size of 40–63 μm and 80–90 μm were selected. The sampled carbon fractions with the larger particles size were placed in reactor of ultrasonic unit BAKU 9050 with capacity of 0.5 L and were filled with carbon dioxide-free distilled water to study the effect of ultrasound during cavitation. In the reactor the studied carbon was in the form of 15–20 wt% of dispersion. The exposure time of ultrasound was 1–25 min with radiation power of 30 W. The ultrasonic exposure frequency was 42 kHz.

The parameters of the porous structure of activated carbon (specific surface area, total pore volume, micropore volume, average pore diameter) were determined by means of isothermal adsorption/desorption of nitrogen at boiling point (T = 77 K) using the automated analyzer Quantachrome Autosorb (Nova 2200e). Before measuring,

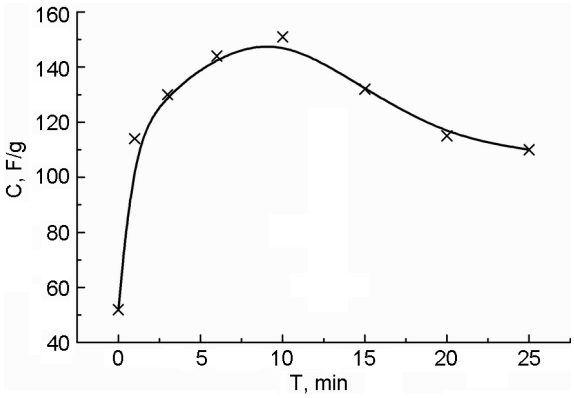

Fig. 1. The change of specific capacity of activated carbon depending on ultrasonic exposure.

the material samples underwent degassing in vacuum at 453 K for 20 h.

Surface properties of the studied activated carbon were determined by Boehm titration method; it is a method of acid-base titration used to determine the total amount of oxygen-containing surface groups (acidic or basic) on carbon surface [9].

To determine the granulometric composition of the carbon after modification a sifting machine was used, which had 4 sieves with holes of 90, 80, 63 and 40 μm for the corresponding fractionation. It was established that size reduction of activated carbon occurs regardless of the duration of ultrasonic exposure, where the following proportions being preserved — 35–37 % of the carbon are not reduced, 6–7 % are fractions of 63–80 μm and less than 40 μm in size, and the remaining is a fraction of 40–63 μm. That was the fraction of both original and dried activated carbon after modification which was used for the electrode manufacture for the electric double layer capacitors. In order to form the electrodes a PTFE (polytetrafluoroethylene) binding component was used, with a ratio of activated carbon to binder as 19:1. The 30 % aqueous solution of potassium hydroxide served as electrolyte for the electric double layer capacitors. Specific capacity was determined on the basis of galvanostatic charge/discharge measurements of the supercapacitors using the formula:

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

where I is the current intensity, t is the discharge time, U is the magnitude of the voltage drop during the discharge, m is the mass of a smaller supercapacitor electrode.

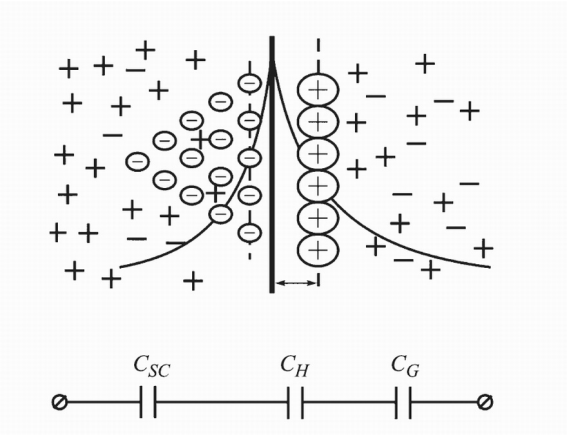

Fig. 2. A model of electrical double layer for non-metallic electrodes and corresponding electrical circuit [13].

When it was possible, the electrodes with the same mass were used.

Impedance studies of activated carbon were carried out in three-electrode cell with a silver-chloride reference electrode. The measurements were carried out in the frequency range of 10^{-3}–10^{6} Hz by means of spectrometer AUTOLAB ECOCHEMIE-100. The formation of the impedance models was performed using the software package ZView 2.3.

3. Results and discussion

The dependence of specific capacity of activated carbon on the time of ultrasonic exposure during cavitation is shown in Fig. 1. As shown in Fig. 1, specific capacity of the material depends on treatment time and reaches the maximum value of 151 F/g after 10 min of ultrasonic exposure, which is almost three times more than the value of specific capacity of the original material, which amounts to 52 F/g. The discovered increase of specific capacity of activated carbon can be caused by both a change in the porous structure and a change in the composition of the surface groups. However, further increase of the exposure time reduces specific capacity of activated carbon. Such kind of behavior requires further analysis to determine the causes of specific capacity changes.

The parameters of the porous structure of the original activated carbon and activated carbon after 10-min ultrasonic irradiation are shown in Table 1. As shown in Table 1, the porous structure does not undergo significant changes during ultrasonic treatment.

Table 1. Parameters of the porous structure of activated carbon

Activated carbon	S_{BET}, m^2g^{-1}	V_{total}, cm^3g^{-1}	V_{micro}, cm^3g^{-1}	Mean pore diameter, nm
Original carbon	799	0.449	0.214	2.63
Modified activated carbon (ultrasound by 10 min)	824	0.431	0.226	2.45

Table 2. Total number of surface groups of activated carbon

Activated carbon	Original carbon	After US influence, 1 min	After US influence, 3 min	After US influence, 10 min	After US influence, 15 min	After US influence, 20 min
Surface groups, mmol/g	1.36	1.26	1.2	1.12	1.14	1.13

It is known [10] that ultrasound exposure on aquatic environment is accompanied by the appearance of products of sonochemical reactions, where the formation of free radicals and hydrogen peroxide causes oxidizing effect on the modified surface. Therefore, the composition of the chemical surface groups of activated carbon, especially oxygen-containing, is changing. The composition of these groups determines not only the hydrophilic properties of the surface, but also affects specific capacity and internal resistance of activated carbon when it is used as the active material for the supercapacitor electrodes [11, 12]. The studies [8] demonstrate that the total amount of surface groups decreases during 10-min ultrasound exposure. The measurements of the total number of surface groups for the more prolonged ultrasonic exposure on activated carbon have shown that specific capacity and internal resistance attain saturation (Table 2). Thus, the change of the surface properties can not provide such effect on specific electrical capacity of activated carbon after ultrasonic exposure. Therefore, to determine other causes that can have effect on the capacitive characteristics of the supercapacitor, it is necessary to analyze the peculiarities of EDL at the boundary of electrolyte and nonmetallic solid phase of an electrode (Fig. 2).

As shown in Fig. 2, high capacitive characteristics of the supercapacitor during its work give the optimal combination of the porous structure with appropriate electronic structure. The latter must provide unblocking of Helmholtz capacitance C_H with the capacity of space charge region in a solid C_{SC}. These two capacities determine the total capacity of the electric double layer since the Gouy-Chapman capacity C_G in the

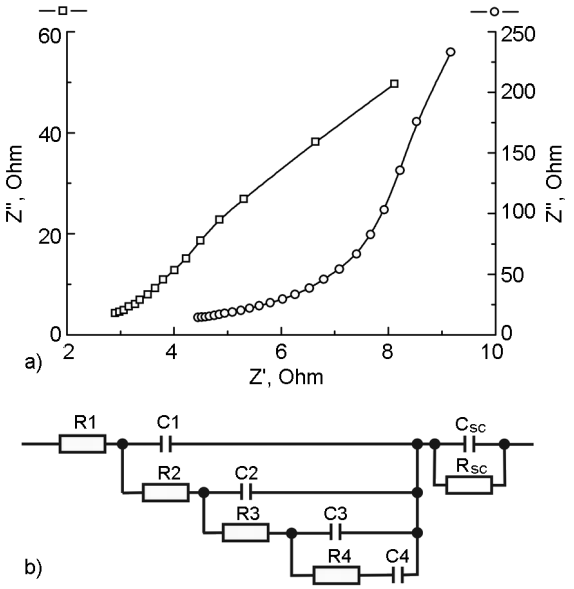

Fig. 3. A typical Nyquist plot (a) for original (-o-) and modified (-□-) activated carbon and the equivalent electrical scheme (b), which models the relevant impedance hodographs.

electrolyte is much higher than capacity of the dense part of the EDL — the Helmholtz layer. Taking this fact into account, according to the scheme in Fig. 2, the total capacity of the EDL can be determined according to the formula:

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

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

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

Table 3. The results of parametric identification of the elements of the equivalent electric circuit

Material	$R1$, Ohm	$\sum_{i>1} R_i$ $(i \neq 1)$, Ohm	$\sum_i C_i$, F	C_{SC}, F	R_{SC}, Ohm
Original activated carbon	4.36	534.61	0.83	0.48	2.29
Modified activated carbon (ultrasound 10 min)	2.52	93.55	8.46	1.24	1.65

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

The problem of unblocking is practically non-existent for metal electrodes however, it is important for carbon electrodes. This is due to the fact that the Debye length in carbon materials is large enough.

Therefore, during the production of activated carbon, which would be used as material for supercapacitor electrodes, it is necessary to provide conditions for the increase of states density of delocalized charge carriers at the Fermi level. In this case capacity C_H would be unblocked to the maximum by the limiting effect of the capacity of the depletion region of a space charge of activated carbon according to the equations (2) and (3). Specifically supplying the great value of C_{SC} in many cases becomes determinative in comparison with obtaining the large surface area not only from the perspective of capacitive characteristics of activated carbon, but also its powered parameters [15]. The value of C_{SC} can be established by means of modeling the impedance dependences.

Figure 3a shows a typical Nyquist plot for both original activated carbon and irradiated by ultrasound. The absence of a semicircle in high-frequency range indicates that the pseudo-capacity input to the total capacity is negligibly small. This demonstrates good reversibility of charge-discharge processes of the supercapacitor with electrodes based on activated carbon under examination.

As far as the Nyquist plots are similar, it means that they will differ by the value of the relevant components of the EDL capacities. This allows to use a modified by parallel $R_{SC}C_{SC}$ — link of chain during de Levi impedance hodograph construction [16], as it is shown in Fig. 3b.

The results of computer parametric identification for the bias $U = 0$ V for two supercapacitors with electrodes which have equivalent mass are shown in Table 3. A significant increase of specific capacity of

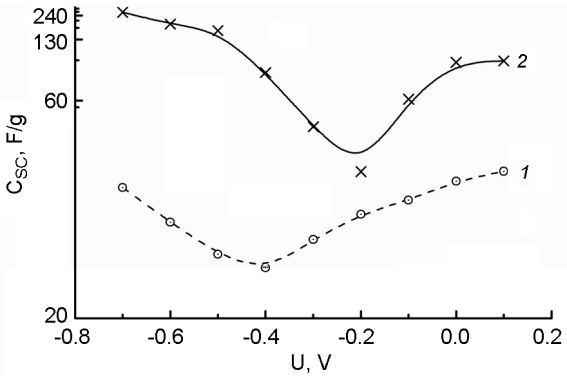

Fig. 4. Dependences of specific value C_{SC} on the constant bias voltage value for original activated carbon (*1*) and activated carbon after a 10-min ultrasonic exposure (*2*).

the Helmholtz layer $\sum_i C_i$, as well as nearly a twofold decrease in material resistance $R1$ by the increasing concentration of free charge carriers and capacity increase in the space charge region is shown.

Applying the constant bias voltage when measuring impedance dependences will cause the value change of C_{SC}. Fig. 4 shows the dependence of specific value C_{SC} on the magnitude of the applied constant bias voltage. Minimum of capacity value of the space charge region C_{SC} for original carbon is at $U = -0.4$ V, and for treated carbon is at $U = -0.2$ V.

Therefore, the minimum in volt-farad dependences during ultrasonic exposure is shifting to the positive region. It defines a chemical potential μ_E of each material in the electrolyte [14]:

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

where F is corresponding position of the Fermi level, φ_S is potential value, that corresponds to the minimum of $C(U)$ dependence.

Since the electrolyte remains unchanged, then

$$\mu_{E1} = \mu_{E2}. \tag{5}$$

Hereof, the shift of the Fermi level can be estimate as:

$$F_2 - F_1 = e(\varphi_{S2} - \varphi_{S1}), \quad (6)$$
$$F_2 - F_1 = e(-0.2 - (-0.4)) = 6.2\ eV,$$

where the indices 1 and 2 indicate original and modified activated carbon, respectively.

So then, we receive a positive value of the minimum shift on $C(U)$ dependence and a significant increase of the capacity C_{SC} after ultrasonic irradiation of activated carbon (Fig. 4). It may be concluded that ultrasound leads to the shift of the Fermi level at 0.2 eV in to energy region with higher density of electronic states, which determines the capacity value of space charge region C_{SC} according to the formula (3). The consequence of this process will be both increase of specific capacity of the material and decrease of its internal resistance.

4. Conclusions

Thus, based on the conducted studies the following conclusions can be drawn:

The studied influence of ultrasonic irradiation in cavitation regimes on carbon materials using the sample of wood activated carbon has shown an increase in specific capacity of supercapacitors from 52 F/g for original carbon to 151 F/g for the carbon, treated with ultrasound in optimal regime.

The change of the porous structure and the composition of surface groups have been considered among possible reasons for the capacity increase. It was found that ultrasonic treatment does not cause significant changes of the porous structure of carbon material, and the total amount of surface groups in the course of treatment gradually decreases and attains the saturation, resulting in increased hydrophilic properties of carbon, and, consequently, in better adsorption of the aqueous electrolyte by the supercapacitor electrodes. However, it is impossible to explain the change of specific capacity of carbon for this reason alone, because the value of content of surface groups does not correlate with specific capacity value after treatment time.

The analysis of volt-farad dependences, obtained on the basis of the Nyquist plot modeling, has shown that the shift of the Fermi level to the energy region, which is characterized by high density of delocalized electrons states occurs as a result of ultrasonic exposure. This is the reason for unblocking of the Helmholtz layer capacity due to the increase in the capacity of the space charge region layer in carbon material. Such redistribution of the values of capacitiy of which form the electrical double layer, after ultrasonic exposure improves the supercapacitors properties, namely increases their specific capacity.

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