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Electrochemical Characteristics of Capacitor Systems Formed on Chemical Modified Carbon Basis

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Influence of chemical modification of an activated carbon (AC) material on its specific capacity is studied using methods of impedance spectroscopy, cyclic voltammetry and chronopotentiometry. As shown, the total capacity is the sum of two components—double electric layer (DEL) capacity and pseudocapacity; the contribution of the latter is insignificant (8–14%). The alloying with rare-earth metals and their compounds results in the rise of specific capacity of AC. Probably, the principal cause of such a growth is transformation of valence band of carbon material caused by introduction of additional electron states from the introduced metals. As a result, considerably greater number of ions (especially, positive ones) will take part in DEL forming and, consequently, predetermine growth of specific capacity.

З'ясовано вплив хемічної модифікації активованого вуглецевого (АВ) матеріялу на його питому місткість з використанням метод імпедансної спектроскопії, циклічної вольтамперометрії та хроноамперометрії. Показано, що загальна місткість є сумою двох складових — місткости подвійного електричного шару (ПЕШ) та псевдомісткости, причому, внесок останньої є незначним (8–14%). Леґування рідкісноземельними металами та їх сполуками призводить до підвищення питомої місткости АВ. Ймовірно, основною причиною такого зростання є трансформація валентної зони вуглецевого матеріялу за рахунок привнесення додаткових електронних станів від втілених матеріялів, в результаті чого значно більша кількість йонів (насамперед, позитивних) буде приймати участь у формуванні ПЕШ, а отже, й зумовлювати ріст питомої місткости.

Изучено влияние химической модификации активированного углеродного материала на его удельную ёмкость с использованием методов импедансной спектроскопии, циклической вольтамперометрии и хроноамперометрии. Показано, что общая ёмкость является суммой двух составляющих — ёмкости двойного электрического слоя (ДЭС) и псевдоёмкости, причем, вклад последней незначителен (8–14%). Легирование редкоземельными металлами и их соединениями улучшает удельную ёмкость активированного углерода. Вероятно, основной причиной такого роста является трансформация валентной зоны углеродного материала за счет добавления дополнительных электронных состояний от внедренных материалов, вследствие чего значительно большее количество ионов (в первую очередь, положительных) будет принимать участие в формировании ДЭС, а, следовательно, и обуславливать рост удельной ёмкости.

Key words: activated carbon material, double electric layer, specific capacity, Nyquist diagram, cyclic voltammogram.

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1. INTRODUCTION

The use of various methods of after-activation modification of an activated carbon (AC) is related to the necessity to improve its parameters as electrode material of electrochemical capacitors (EC) as it is not possible to attain necessary values of these parameters, in particular, specific resistance and specific capacity of a double electric layer (DEL) formed by the given material and electrolyte, during activation [1].

Coming from general principles of physics and topology of the developed surface, the principle decision of the indicated problem is possible by mean of the increase of electronic states density in AC matrix [2] and also participation of the most possible part of the developed surface in DEL forming, because, as known [3], as much as 50% of working pores do not wet by an electrolyte due to their chemical-structural features. One of possibilities of the indicated ideas realization is modification of AC by its alloying with rare-earth metals and their compounds, that would give possibility to multiply substantially the DEL capacity, and, consequently, capacity of capacitors formed on the basis of AC modified in such a manner. Erbium is used as rare-earth metal (its percentage in AC makes 0.1, 0.2, and 0.4 wt.%), Tm_2O_3, Eu_2O_3, Dy_2O_3, Ho_2O_3, Pr_2O_3, content of which in AC made 0.1 wt.% are used as rare-earth compounds. Copper additive in an amount of 0.1 wt.% was introduced into obtained alloyed materials to increase their electronic conductivity. The aim of this work was to study influence of introduction of the specified metals into AC on its physical and chemical properties and operating characteristics of capacitors with the DEL, formed on its basis [4].

2. EXPERIMENTAL

AC made of fruit stones by their carbonization with subsequent activation in a closed reactor at high pressure was used as research object [5].

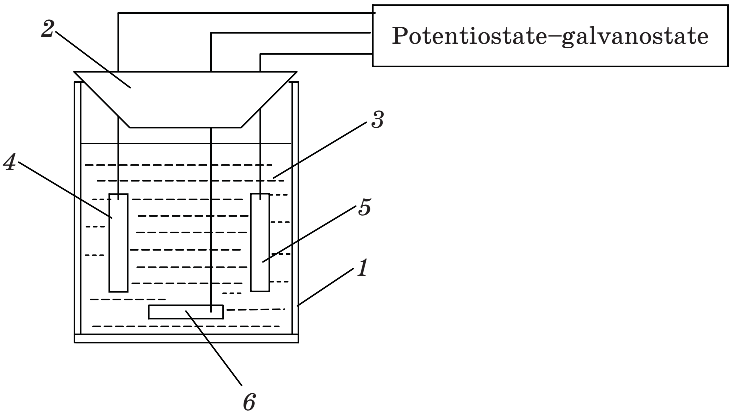


Fig. 1. Electrochemical cell: *1*—glass cell; *2*—pressurizing cover; *3*—electrolyte; *4*—working electrode; *5*—reference electrode; *6*—comparative electrode.

The alloying of AC with erbium was carried out using erbium nitrate. Research of alloying admixtures distribution in AC was conducted by the method of second ion mass spectrometry on MS-7201 mass-spectrometer.

A three-electrode electrochemical cell (Fig. 1) was used to obtain Nyquist diagrams. AC with a proper percentage of the alloyed material was used as working electrode; a comparative electrode was similar to the working one, a silver chloride electrode Ag/AgCl was used as a reference electrode. Potential of carbon material in relation to the reference electrode was –0.33––0.28 V. 30% KOH–water solution + 0.3% LiOH water solution was used as electrolyte. The impedance measuring was performed using Autolab PGSTAT/FRA-2 spectrometer (Holland) within the frequency range from 10^{-2} to 10^{5} Hz.

Registration of cyclic voltamperograms of carbon electrodes was performed within the potential range of –1–+0,2 V using the three-electrode cell described above with silver chloride reference electrode; scan rates were 5, 8, 10, 20, 30, 40, and 50 mV/s.

3. RESULTS AND DISCUSSION

Properties of rather wide rows of the systems, especially electrochemical ones, can be conveniently studied by the response of these systems to an external sinusoidal signal. The use of impedance spectroscopy method for solving of the problems indicated above is the most expedient for that, as it enables us to conduct research within the frequency range wide enough ($f = 10^{6}$–10^{-3} Hz) [6].

Nyquist diagram for Er-modified carbon materials (Fig. 2) consists

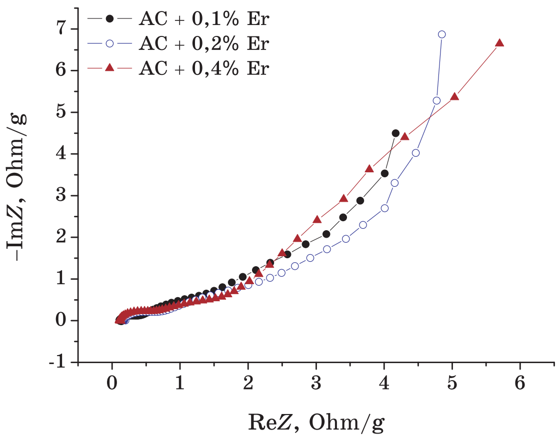


Fig. 2. Nyquist diagram of Er-modified AC.

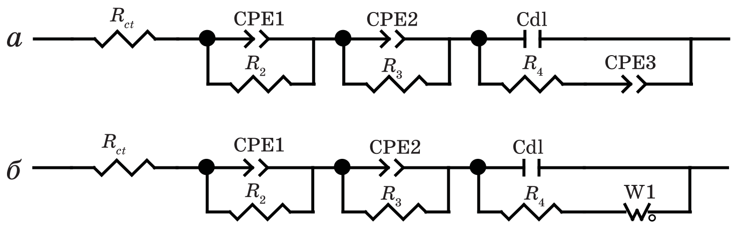


Fig. 3. Equivalent schemes for Nyquist diagrams for Er-modified AC: *a*—Er content is 0.1 and 0.2 wt.%; *б*—Er content is 0.4 wt.%.

in two asymmetric semicircles in the frequencies region of $1-10^5$ Hz. Low-frequency branch tends to infinity at $\omega \to 0$ for AC with Er content 0.1 and 0.2 wt.% that testifies to the typical behaviour of capacitor systems. It is inclined to the actual resistance axis for material with Er content of 0.4 wt.% by ~ 45° that can testify the presence of diffusive processes in the material under investigation, which are described by Warburg impedance.

Equivalent schemes, which simulate electrochemical processes, which take place on the electrode–electrolyte interface and in the material, favour the assumption described above (Fig. 3). Relative error for each parameter of the equivalent scheme does not exceed 5%; parameter $\chi^2 = 10^{-4}-10^{-5}$ that testifies to legitimacy of the offered choice.

Resistance R_{ct} corresponds to series equivalent resistance, which consists of the electrolyte resistance, resistance of lead and contacts. Two $R \parallel$ CPE-links can be linked to heterogeneity of DEL and fractal structure of electrode, resistance R_4 is polarization or electronic resistance of the material, C_{dl} is DEL capacity, constant phase element CPE_3 of capacity type corresponds to Faraday capac-

TABLE 1. Specific capacity of AC [F/g].

Material	Method		
	Impedance spectrometry	Voltamperometry	Chronopotentiometry
AC	56	64	69
AC + 0.1% Er	71	77	73
AC + 0.2% Er	75	83	72
AC + 0.4% Er	59	66	65
AC + 0.2% Er + 0.1% Cu	61	69	68
AC + 0.2% Er + 0.4% Cu	72	81	77
AC + 0.1% Tm_2O_3	—	68	63
AC + 0.1% Tm_2O_3 + 0.1% Cu	89	101	81
AC + 0.1% Eu_2O_3	80	86	67
AC + 0.1% Eu_2O_3 + 0.1% Cu	82	84	68
AC + 0.1% Dy_2O_3	78	83	65
AC + 0.1% Ho_2O_3	80	83	70
AC + 0.1% Pr_2O_3	54	59	58

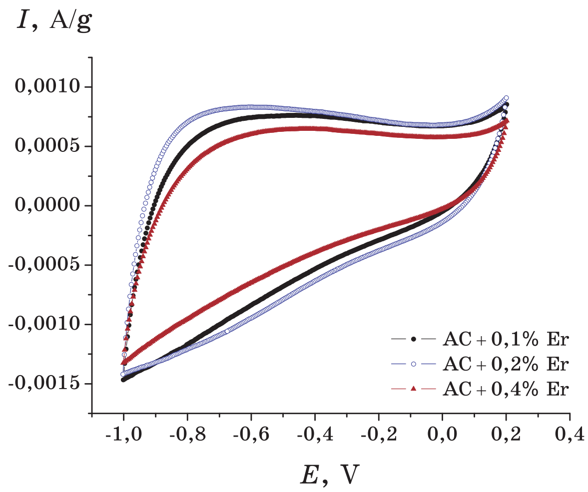


Fig. 4. Cyclic voltamperograms of Er-modified AC.

ity, W_o is diffusive Warburg impedance.

The increase of Er percentage results in the insignificant increase of total resistance $R_2 + R_3$ (from 16 to 25 Ohm). It testifies that Er introduction blocks C^+ ions transport through the electrode-electrolyte boundary and inhibits formation of DEL by them. Except for it, growth of Er content predetermines formation of heterogeneous DEL

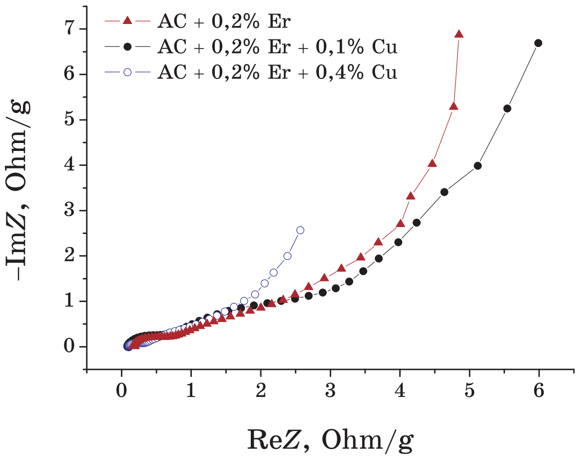


Fig. 5. Nyquist diagrams for Er- and Er + Cu-modified AC.

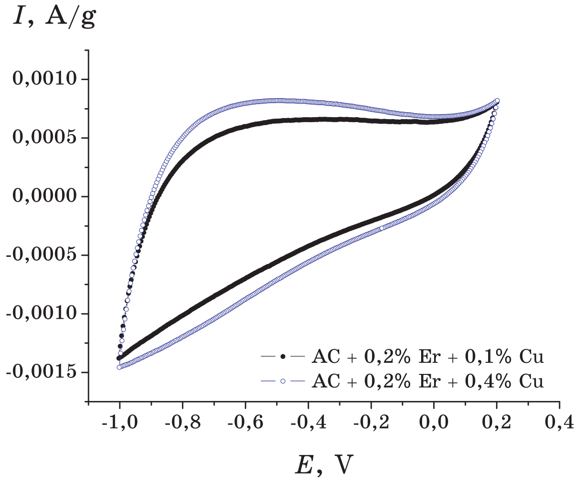


Fig. 6. Cyclic voltamperograms of Er + Cu-modified AC.

and intensification of diffusive processes in it (growth of CPE_1 and CPE_2 parameters confirms it). The first parameter is the constant phase element of capacity type ($n \sim 0.83$), the second one is of diffusive type ($n \sim 0.55$).

The n-parameter is present in a formula for determination of CPE element impedance $Z_{CPE} = A^{-1}(j\omega)^{-n}$ and characterizes a phase deviation. Growth of erbium concentration in AC results in the increase of CPE_3 parameter, which represents the constant phase element with the heterogeneously distributed capacity ($n = 0.82$–0.91). Owing to this fact, the total capacity of material is multiplied not only because of DEL ca-

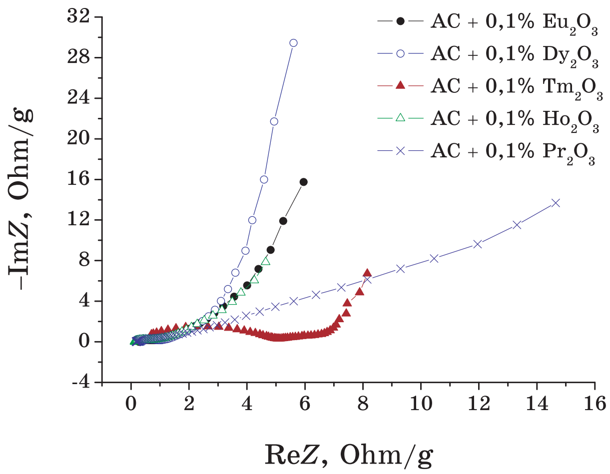


Fig. 7. Nyquist diagrams of AC doped by oxides of rare-earth metals.

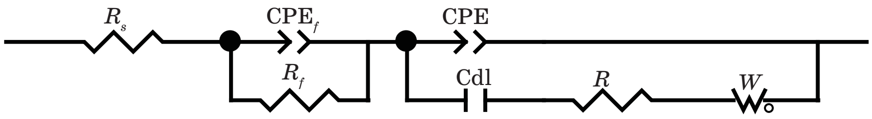


Fig. 8. Equivalent scheme for Nyquist diagram of chemically modified AC.

pacity, but also due to Faraday processes. Electronic resistance of material according to impedance spectroscopy data is 22.6, 22.7, and 24.3 Ohm, respectively. There is a maximum for DEL capacity at 0.2% Er content (Table 1). It is believed that the electronic state density is multiplied at Fermi level of carbon material owing to erbium presence and, as a result, higher number of C^+ ions takes part in DEL formation. Subsequent erbium introduction results in blocking of working pores of AC, as a result, reduction of DEL capacity takes place [7].

This assumption is confirmed by the results of potentiodynamic researches (Fig. 4). There is the difference in I–E curves, especially in the region of negative potentials, at which DEL capacity is provided by C^+ ions from the electrolyte side. Dissymmetry of these curves in relation to zero current line ($I = 0$) is the characteristic feature, which is evidence for the passing of processes unconnected with DEL forming (above all Faraday processes).

Introduction of copper in amounts of 0.1 and 0.4 wt.% into Er-modified material, which possesses maximal specific capacity, does not noticeably change the type of Nyquist diagram, predetermining the change of general impedance of the electrochemical system only (Fig. 5). Consequently, the equivalent scheme, which simulates motion of electrochemical processes in the system under investigation, is

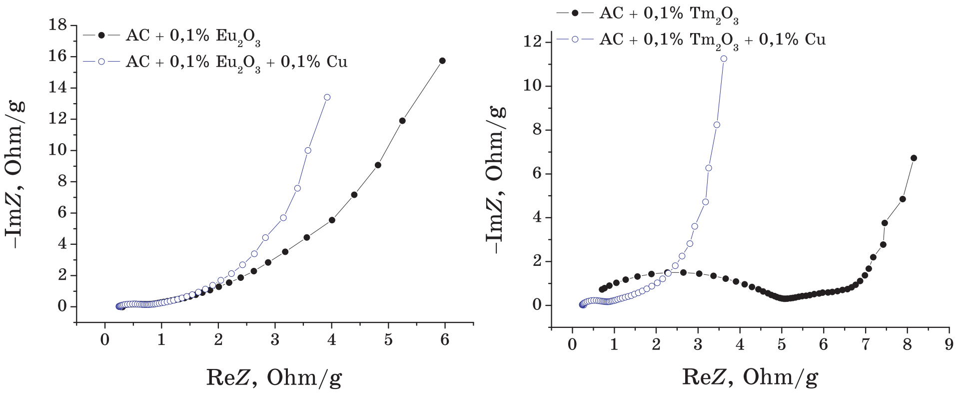
TABLE 2. Internal resistance [Ohm].

Material	Method	
	Impedance spectroscopy	Chronopotentiometry
AC + 0.1% Er	22.6	24.3
AC + 0.2% Er	22.7	23.2
AC + 0.4% Er	24.3	29.4
AC + 0.2% Er + 0.1% Cu	23.2	25.2
AC + 0.2% Er + 0.4% Cu	14.2	17.8
AC + 0.1% Tm_2O_3	39.5	47.3
AC + 0.1% Tm_2O_3 + 0.1% Cu	14.9	18.2
AC + 0.1% Eu_2O_3	9.2	11.3
AC + 0.1% Eu_2O_3 + 0.1% Cu	7.4	8.4
AC + 0.1% Dy_2O_3	11.9	13.3
AC + 0.1% Ho_2O_3	11.7	13.4
AC + 0.1% Pr_2O_3	30.9	32.8

of a similar form (see Fig. 3, *a*).

Electrochemical system based on the Er-modified material with 0.1 wt.% Cu content is characterized by slightly higher values of R_2 and R_3 parameters (2.8 and 3.7 Ohm, and 19.1 and 24.9 Ohm, respectively) and by practically unchanging electronic resistance R_4 (22.8 and 23.2 Ohm, respectively) in comparison with the material without copper. However, there is a reduction of all three resistances at 0.4 wt.% Cu concentrations in carbon material, especially electronic one (R_4, 14.2 Ohm). It is readily apparent on $-\mathrm{Im}Z = f(\mathrm{Re}Z)$ dependence. According to Table 1, such modification by copper does not lead to the increase of specific capacity of carbon material, and can be used to increase its electronic conductivity. Except for it, almost identical capacities of unalloyed and alloyed (0.4 wt.%) materials were achieved due to Faraday processes, which were caused by the run of mass-transfer processes (probably, redox reactions), rather than to DEL capacity. It was confirmed by the results of voltamperometric researches, according to which there is an 'influx' in the negative potential region for the material with 0.4 wt.% Cu content, which is attributed to Faraday processes (Fig. 6). A horizontal plateau on the anode branch of I–E-curve of other material points to the fact that the specific capacity of material is provided mainly by DEL capacity.

The use of rare-earth metals oxides as alloying material (Tm_2O_3, Dy_2O_3, Pr_2O_3, Eu_2O_3, Ho_2O_3) does not change cardinally the general type of impedance curve (Fig. 7) (except for AV alloyed with Tm_2O_3). However, equivalent schemes, which simulate electrochemical processes, slightly differ. In particular, for AC doped with Dy_2O_3 and Pr_2O_3 the



a *b*

Fig. 10. Nyquist diagrams of AC doped by oxides of rare-earth metals and copper.

schemes are similar to that in Fig. 3. There is also a difference: the constant phase element CPE$_3$ is the element of capacity type for the first material, while for the second material it is diffusive one. For Eu$_2$O$_3$- and Ho$_2$O$_3$-doped materials, a scheme is the same as well as for Cr- and Mn-doped AC (Fig. 8) [2]. For AC doped with Tm$_2$O$_3$, we could not find an equivalent scheme, which would describe satisfactory the behaviour of the electrochemical system.

As follows from Table 1, specific capacities for Eu$_2$O$_3$-, Ho$_2$O$_3$-, and Dy$_2$O$_3$-doped materials are practically identical. Taking into account the results of impedance spectroscopy and voltamperometry (Fig. 9), it is believed that the total specific capacities of the materials under investigation are provided by DEL capacity and pseudocapacity. For two other materials, in which Pr$_2$O$_3$ and Tm$_2$O$_3$ are used as alloying additions, the contribution of pseudocapacity is insignificant.

Additional alloying of these materials with copper in an amount of 0.1 wt.% results not only in growth of specific capacity, but also in reduction of total impedance of the system (Fig. 10).

Internal resistance, which characterizes electrophysical properties of electrode carbon material, is also parameter of significance. Its measurement was carried out by the methods of impedance spectroscopy and chronopotentiometry. In the first case, the value of internal resistance was obtained from the results of simulation, and in the second one, using formula $R = \dfrac{\Delta U}{2I}$, where ΔU is voltage drop on a discharge curve (Fig. 11), I—discharge current.

The values of internal resistance of the materials under study obtained by both methods are presented in Table 2.

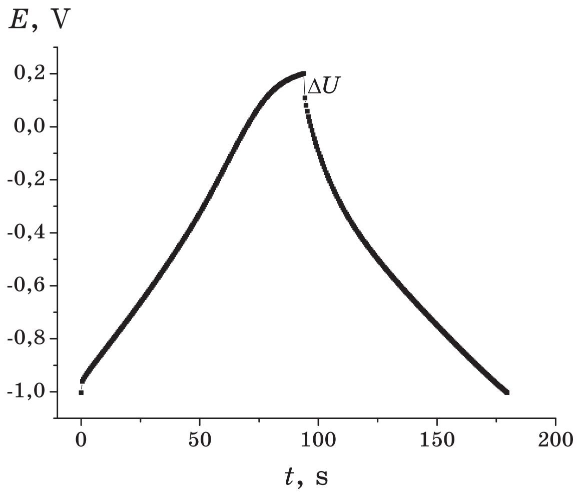


Fig. 11. A typical shape of charge–discharge curve.

It should be noted that a difference between these values is not very substantial (it does not exceed 7%). However, the chronopotentiometry method is more precise due to its simplicity.

Thus, chemical modification of AC by rare-earth metals and their compounds results in the increase of specific capacity of AC. The principal reason for such growth, according to previous researches, is transformation of valence area of carbon material caused by additional electronic states from the introduced metals, as a result considerably higher number of ions (first of all, positive ones) participates in DEL formation, and, consequently, predetermines the growth of specific capacity.

CONCLUSIONS

The equivalent schemes of capacitor system based on modified AC are proposed, which satisfactory describe electrochemical processes on electrode–electrolyte interface and in AC-matrix.

The total capacity of the system under investigation is the sum of two components—DEL capacity and pseudocapacity, and contribution of the latter is insignificant (8–14%).

The alloying with rare-earth metals and their compounds can result in the increase of specific capacity of AC up to 17%.

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