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Doping of porous activated carbon with Er, a metal with a high electronic states density

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The effect of doping porous carbon material (PCM) with erbium, as a metal with a high density of electronic states, on the electrochemical properties of PCM was investigated. It was established that the optimal concentration of introduced erbium 0.2% leads to a significant increase in specific capacity for the devices formed on the basis of erbium-doped carbon material. And the doping of PCM with both erbium (0.2 wt.%) and copper (0.1 wt.%) results not only in the specific capacity increase but also lowers total system impedance.

Keywords: porous carbon material, erbium, copper, high density of electronic states, specific capacity.

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Introduction

The main factors influencing the increase in specific characteristics of the electric double layer, EDL (that is formed at the interface between the electrode and the electrolyte) are an increase in the density of electronic states due to a change in the Fermi level of the activated carbon surface layers and the involvement of max possible developed surface amount in charge/discharge processes [1]. One of the ways to influence the PCM properties for these purposes is to introduce metals with a high electronic states' density into its matrix. It is known that the EDL capacitance determines electric double-layer capacitor (EDLC) capacitance. Therefore, considering the fact that the electrolyte concentration choice is determined by electrolyte's maximum conductivity, it is possible to increase the accumulated EDL charge amount by increasing the density of electronic states near the Fermi level in the electrode material. Thus, the idea arose to purposefully increase the filling of electronic states of the activated carbon valence band by doping. It has been shown that 3d transition metals and rare-earth elements (Er in particular) have the highest density of electronic states near the Fermi level.

I. Main part

We investigated the effect of erbium injection into PCM, on its physical and chemical properties [2], and on the specific capacitance and energy values of capacitors with EDL formed on its basis.

Er injection was carried out by displacing its salts with zinc in an acidic medium. The amount of introduced Er was 0.1–0.4 wt.%. Fig. 1 shows the dependence of the specific capacity on the introduced Er amount.

The injected erbium effect on the behaviour of electrochemical capacitor systems formed on the basis of PCM+Er was studied using the impedance spectroscopy method.

A three-electrode electrochemical cell (Fig. 2) was used for research, having PCM (with the appropriate percentage of Er) as the working electrode. Impedance measurements were performed using an Autolab PGSTAT/FRA-2 spectrometer (Netherlands) in the frequency range of 10^{-2}–10^{5}Hz.

Obtaining cyclic voltammograms of carbon electrodes was carried out in the range of potentials -1÷0.2V using the above three-electrode cell with a chlorine-silver reference electrode; the scanning speeds were 5, 8, 10, 20, 30, 40 and 50 mV/s, respectively.

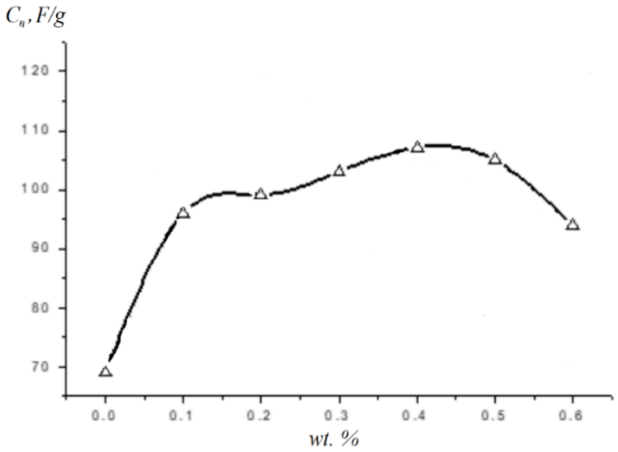


Fig. 1. Dependence of the PCM specific capacity on the erbium percentage content.

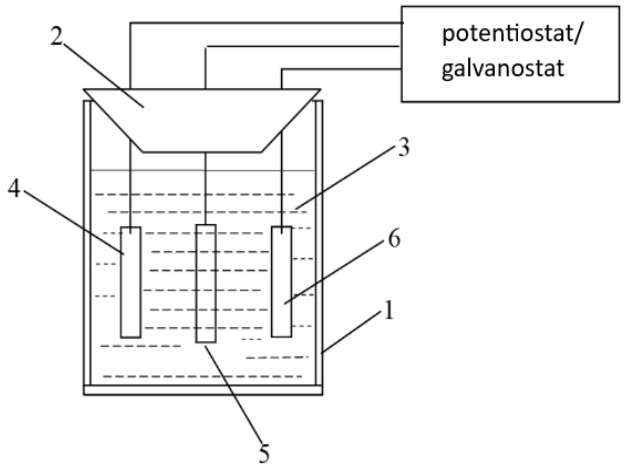
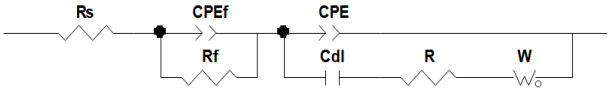


Fig. 2. Electrochemical cell: 1 – glass cell; 2 – hermetic cover; 3 – electrolyte; 4 – working electrode; 5 – comparison electrode; 6 – auxiliary electrode.

As a rule, impedance dependences for activated carbon materials are modelled by an RC-equivalent circuit. However, in this case, there are difficulties with the parameters' selection for the equivalent circuit, since most carbon materials have a rather complex distribution of pores by size. As a result, the experimental diagrams differ significantly from both ideal hodograph (straight line with a phase angle φ=45°) and the porous electrode impedance hodograph.

One of the possible ways to overcome such an obstacle is to use the equivalent circuit shown in Fig. 3. In this scheme, R_s is the series equivalent resistance that includes the electrolyte resistance, wires and contacts resistance, CPE_f is the constant phase element of the capacitive type which takes into account the capacity inhomogeneity caused by Faraday processes, R_f is the Faraday resistance, CPE is the element of constant phase, which takes into account the electrode's porous structure with signs of fractality, R is the polarization resistance, C_{dl} is the capacity of the electric double layer, W is the Warburg diffusion impedance.



Element	Freedom	Value	Error	Error %
Rs	Free(+)	0.98468	N/A	N/A

Fig. 3. Equivalent diagram for Nyquist diagrams obtained for chemically modified PCM.

The calculation of the equivalent circuit elements' parameters was carried out in automatic mode using the installed computer program FRA-2.

Another way to find the capacity of the material is to use calculation formulae:

$$C_p(\omega) = \frac{-(\mathrm{Im}Z - \omega L)}{\omega\,[(\mathrm{Re}Z - R_s)^2 + (\mathrm{Im}Z - \omega L)^2]}, \quad (1)$$

where C_p is the storage capacity, L is the inductance, ω is the cycle frequency ($\omega = 2\pi f$, where f – frequency of the applied signal), R_s – series equivalent resistance, which includes the electrolyte resistance, wires and contacts resistance. For supercapacitors with low resistance and low capacity, the capacity can be calculated using the formula:

$$C = \frac{-1}{2\pi f \cdot \mathrm{Im}Z}. \quad (2)$$

For supercapacitors with high capacity and low internal resistance the storage capacity is calculated according to:

$$C_p(\omega) = \frac{-\mathrm{Im}Z}{\omega\,[(\mathrm{Re}Z)^2 + (\mathrm{Im}Z)^2]}. \quad (3)$$

Equation (3) follows from (1) at $R_s \to 0$, $L \to 0$.

Taking into account the studied material high capacity and the absence of inductance L (according to impedance studies) as well as taking into account the resistance R_s, which cannot be neglected here (R_s~0.7...1.3Ω according to impedance studies; the measurement error did not exceed 5%) it is advisable to use formula (1) to calculate the carbon material capacity using the value of R_s:

$$C_p(\omega) = \frac{-\mathrm{Im}Z}{\omega\,[(\mathrm{Re}Z - R_s)^2 + (\mathrm{Im}Z)^2]}. \quad (4)$$

The results of calculating the capacity according to formulae (2)–(4) are illustrated in Fig. 4.

It should be noted that the capacitance C_p is determined as the point of intersection between the ordinate axis (axis C) and the horizontal line extrapolated to the curve $C=f(\mathrm{Re}Z)$ in the low-frequency range.

The percentage content of Er in PCM is 0.1, 0.2 and 0.4 wt.% respectively. In order to increase the electronic conductivity of the obtained doped material, copper was additionally introduced into it in the amount of 0.1 wt.% along with Er.

For PCMs doped with Er the Nyquist diagram (Fig. 5) is a combination of two asymmetric semicircles in the frequency range of 1...10^5Hz. Low-frequency branch for PCM with 0.1 and 0.2 wt.% by the content of Er at $\omega \to 0$

goes to infinity that is characteristic of the capacitor systems behaviour. For material with 0.4 wt.% content of Er it is inclined at ~45° angle to the real resistance axis which may indicate the diffusion processes' presence (described by the Warburg impedance) in the studied material.

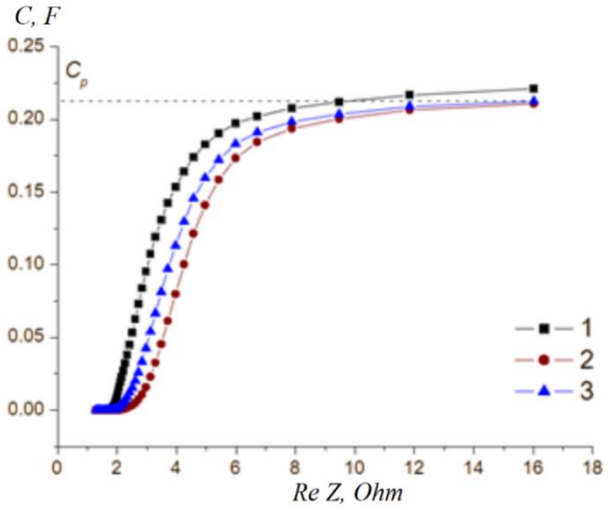


Fig. 4. Estimated capacity of PCM with 0.2 wt.% erbium content: 1 – according to equation (2); 2 – according to equation (3); 3 - according to equation (4).

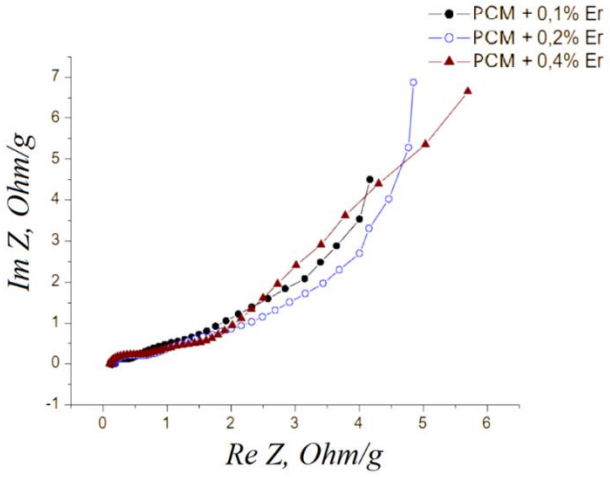


Fig. 5. Nyquist diagrams for Er.

Indicated assumptions can be confirmed by equivalent circuits (Fig. 6) that simulate electrochemical processes at the electrode-electrolyte contact boundary and in the material itself. The relative error for each equivalent circuit parameter does not exceed 5%, the parameter χ^2 is in range of $10^{-4}...10^{-5}$ that confirms the proposed choice.

The resistance R_{ct} corresponds to the series equivalent resistance, which includes the electrolyte resistance, wires and contacts resistance, two R||CPE - links are related to the EDL heterogeneity and the electrode fractal structure, R_4 is the polarization (or electronic) resistance of the material, C_{dl} is the EDL capacity, CPE_3 – the capacitive type and constant phase element that corresponds to the Faraday capacitance, W_1 is the Warburg diffusion impedance.

Er percentage increase raises total resistance of R_2+R_3 (from 16 to 25Ω) which shows that the Er introduction complicates the transport of K^+ ions across the electrode-electrolyte interface and prevents them from EDL formation. In addition, an Er content growth exhibits formation of a non-homogeneous EDL and diffusion processes intensification in it, that indicated by CPE_1 and CPE_2 parameters increase. CPE_1 is a constant phase element of the capacitive type (n~0.83), and the CPE_2 is of a diffusion type (n~0.55). Parameter n is included in the formula for the CPE $Z_{\mathrm{CPE}} = A^{-1}(j\omega)^{-n}$ element impedance and characterizes the phase deviation. An increase in the concentration of erbium in PCM leads to an increase in the CPE_3 parameter, which is a constant phase element with a non-uniformly distributed capacity (n=0.82...0.91). Thanks to this, the total capacity increases not only due to the EDL capacity but also due to Faraday processes. For the EDL capacity, a maximum is observed when the Er content is at the level of 0.2 wt.% (Table 1).

Most likely, the introduction of erbium increases the density of electronic states [3] near the Fermi level of the carbon material, resulting in larger K^+ ions amount that form EDL. Further introduction of erbium blocks PCM working pores that lessens capacity of EDL.

Introduction of copper amount of 0.1 and 0.4 wt.% into the PCM doped with erbium (which has the maximum specific capacity) does not noticeably change the the Nyquist diagram, causing only a change in the electrochemical system overall impedance (Fig. 7). Accordingly, the equivalent circuit that models the course of electrochemical processes in the studied system will have a similar appearance (Fig. 6a).

Electrochemical system made on the basis of Er-modified material with 0.1 wt.% copper content is characterized by larger values of R_2 and R_3 parameters (2.8Ω and 3.7Ω, 19.1Ω and 24.9Ω, respectively) and practically unchanged electronic resistance R_4 (22.8Ω and 23.2Ω, respectively) in comparison with material not doped with copper. However, there is a decrease in all

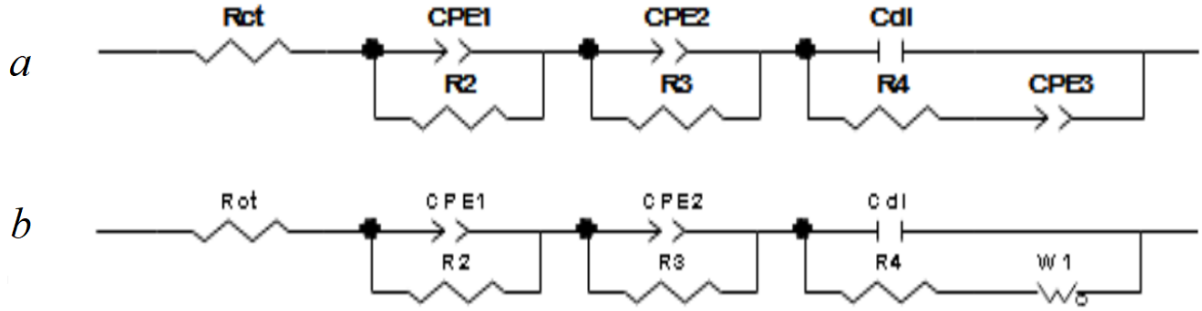


Fig. 6. Equivalent schemes for Nyquist diagrams obtained for Er-modified PCM: a – 0.1 and 0.2 wt.% of Er content; b – 0.4 wt.% of Er content.

Table1.

Specific capacity of PCM, F/g

Material	Research method		
	Impedance spectroscopy	Volt-amperometry	Chrono-amperometry
PCM	56	64	69
PCM + 0.1 % Er	71	77	73
PCM + 0.2 % Er	75	83	72
PCM + 0.4 % Er	59	66	65
PCM + 0.2 % Er + 0.1 % Cu	61	69	68
PCM + 0.2 % Er + 0.4 % Cu	72	81	77

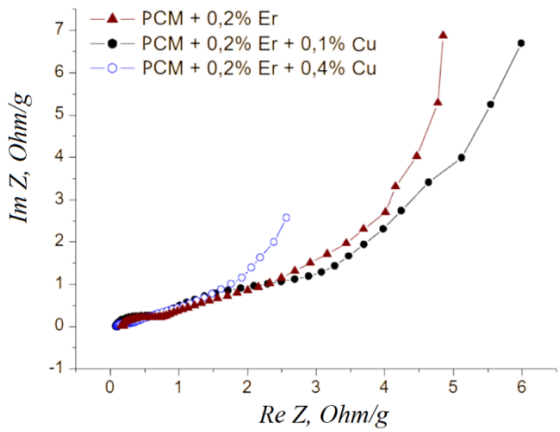


Fig. 7. Nyquist diagrams for Er and Er+Cu -modified PCMs.

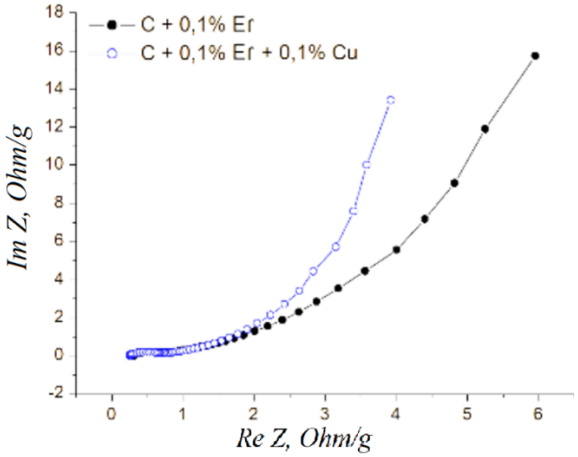


Fig. 8. Nyquist diagrams of PCM doped with erbium and copper.

three resistances at 0.4 wt.% concentration of copper in the carbon material, especially electronic R_4 (14.2Ω), which is clearly described in the dependence – ImZ=f(ReZ). According to the Table 1, the introduction of copper does not increase specific capacitance of EC based on PCM but increases its electronic conductivity. In addition, almost the same capacities of undoped and doped (0.4 wt.% Cu) samples are based not on the EDL capacity but Faraday one, caused by mass transfer processes (probably redox reactions). This is confirmed by the voltammetric studies results, that exhibit an "inflow" (usually attributed to Faraday processes) in the negative region of potentials for a 0.4 wt.% copper content sample (Fig. 8). The anodic branch horizontal plateau of the I-U curve of another sample indicates that the material's specific capacity is provided mainly by the EDL capacity.

Thus, additional doping of these materials with copper in the amount of 0.1 wt.% leads not only to a specific capacitance increase, but also decreases total system impedance (Fig. 8).

The obtained results indicate that PCM doping with Er has the most significant effect on the spectra intensity of its valence band at the Fermi level, and accordingly on the electronic density which is reflected in the specific capacity value. In particular, the specific capacity of ECs formed on the basis of Er-doped PCM is ~65% higher than the similar capacity of ECs formed on the basis of undoped PCM.

Conclusions

It was established that the erbium optimal concentration in the porous carbon material is 0.2 wt.%, which is evidenced by the maximum possible specific capacity of the corresponding storage devices formed on its basis. Erbium percentage content increase leads to heightened total resistance due to the K^+ ions transport difficulty.

The joint introduction of erbium and copper into the porous carbon material increases its electronic conductivity and its specific capacitance is determined by both contributions of the electric double layer capacitance and the Faraday capacitance.

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Легування пористого активованого вуглецю Er, металом з високою густиною електронних станів

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Досліджено вплив легування пористого вуглецевого матеріалу (ПВМ) ербієм, як металом з високою густиною електронних станів, на електрохімічні властивості ПВМ. Встановлено, що оптимальною концентрацією впровадженого ербію є 0.2 %, при якій досягається істотне збільшення питомої ємності пристроїв, сформованих на основі легованого ербієм вуглецевого матеріалу. А сумісне легування ПВМ ербієм (0.2 мас. %) та міддю (0.1 мас. %) призводить не тільки до зростання питомої ємності, але й до зменшення загального імпедансу системи.

Ключові слова: пористий вуглецевий матеріал, ербій, мідь, висока шустина електронних станів, питома ємність.