Fe²⁺- and Er²⁺-intercalative modification of porous and electron structure of activated carbon and its influence on supercapacitor parameters*

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An influence of both porous and electron structure on the processes in an electric double layer (EDL) determining the main working parameters of carbon-based supercapacitors has been studied in order to improve them. The investigations involved impedance spectroscopy, X-ray small angle scattering, confocal micro-Raman spectroscopy, infra-red and Mössbauer spectroscopy. Fe²⁺- and Er²⁺-intercallative modifications of nanoporous carbon were performed. It was found that the modification process characteristics correlated with the structure parameters of the EDL.

Keywords: *Fe- and Er-intercalative modifications; small angle X-ray diffraction; specific capacity; nanocluster; nanoporous carbon; supercapacitor*

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1. Introduction

Up-to-date knowledge and understanding of the physical-chemical processes determining new ways to obtain the effective systems for energy accumulation and storage is rather poor. For that reason the main characteristics of such systems as working voltage has been increased to 4.5 to 4.7 V but their specific capacitance still reminds low. The latter disadvantage can be overcome using the so-called supercapacitors with a capacitive or pseudocapacitive mechanism of energy accumulation. This way is effective only in case when the optimal porous structure and the electron structure, both responsible for the unblocking of Helmholtz capacitance by capacitance of the space charge re-

gion (SCR) in the solid phase, are related to each other. The chemical methods developed for this purpose and already used for porous structure modification [1–10] are not efficient in obtaining desirable change in the electron structure. In a previous paper [11] we described a simultaneous modification of porous and electron structures by nickel ion intercalation into activated carbon, significantly improving the supercapacitor parameters. It is interesting to study the modification of carbon materials by another transition metals and compare with the results obtained for Ni²⁺ intercalation. For that reason the main aim of this work was to study the changes caused by Fe²⁺- and Er²⁺-intercallative modifications.

2. Background

We focus on the EDL structure, formed at the interface between the electrolyte and the solid phase. The simplest equivalent electric circuit con-

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sists of SCR capacitance for the solid phase – C_{SC} – which obviously can block the Helmholtz capacitance [11]. The total capacitance of EDL is:

$$C^{-1} = C_{SC}^{-1} + C_H^{-1} + C_G^{-1}, \quad (1)$$

where C_H is the Helmholtz capacitance. The Gouy-Chapman capacitance of diffusive layer in electrolyte, C_G , is commonly significantly larger than the capacitance of the carrier-rich part of the EDL (Helmholtz layer) that allows neglecting its contribution to C^{-1} in this equation. The unblocking of the Helmholtz capacitance does not occur for metallic electrodes, but the Debye screening radius can reach a large value and the unblocking takes place for carbon-graphite electrodes. It is clear that the unblocking of the Helmholtz capacitance, due to extending of the spatial charge region in the solid constituent of the system, is related to the change in density of states of delocalized electrons at the Fermi level, $D(E_F)$, according to [12]:

$$C_{SC} = e \{ \epsilon_{SC} \epsilon_0 D(E_F) \}^{\frac{1}{2}}, \quad (2)$$

where ϵ_{SC} is the relative permittivity of SCR, ϵ_0 is the dielectric constant of vacuum, and e is the elementary charge.

We suggest that C_{SC} should increase due to both the technology modification and an increase in the carrier concentration (enhancement of screening) that narrows the EDL and thus increases the Helmholtz layer capacitance. In order to obtain better parameters, the intercalation of the material into the unoccupied graphitized regions or into its nanopores together with $(\text{HSO}_4)^+$ and Fe^{2+} or Er^{2+} cations is supposed to be used. Introducing graphite inclusions significantly develops a porous structure and increases its hydrophilicity [13]. It should be noted that an increase in the free charge concentration by means of incorporation of 3d- or 4f-metals into the structure of activated carbon is impossible.

3. Experimental

The samples under investigation were prepared by the following procedures: at first, $\text{K}_2\text{Cr}_2\text{O}_7$ (0.19 g) was diluted in concentrated H_2SO_4 (4 ml)

and then added to carbon (1 g), finally being diluted in concentrated H_2SO_4 . We used the lamellar carbon which was obtained by means of activated carbonization of birch wood. The mean size of the carbon particle was equal to 45 μm and the amount of impurities was less than 2 %. Upon mixing for 10 to 15 min., the FeSO_4 salt (0.1 or 0.5 g) was added and then once again mixed for 10 to 15 min. The prepared mixture was subjected to thermal treatment at 250 °C for 2 hours. Finally, a modified in such way carbon was purified from the products of chemical reactions as well as from unreacted ingredients [11]. A similar method was used to prepare the $\text{Er}_2(\text{SO}_4)_3$ (0.1 or 0.5 g) samples.

The traditional methods, such as X-ray diffraction (XRD) and small angle X-ray diffraction (SAXRD) were used for structure studies. A triode cell with a chlorine-silver reference electrode was a principal measuring unit to obtain the electrochemical data. Important experimental information was obtained by means of impedance measurements (10^{-2} to 10^5 Hz frequency range). The electron structure of the nanoporous carbon before and after ultrasonic modification was investigated by X-ray photoelectron spectroscopy using a Kratos Axis Ultra X-ray photoelectron spectrometer and combination of Raman spectroscopy (Horiba Jobin Yvon T64000 triple spectrometer) with Mössbauer spectroscopy (using MS 1104EM). Confocal micro-Raman measurements were carried out at room temperature using a Horiba Jobin Yvon T64000 spectrometer equipped with an Olympus BX41 microscope for micro-Raman sampling and with a thermoelectrically-cooled charge-coupled (CCD) detector. An Ar+/Kr+ laser (488.0 nm) was used as the excitation source.

4. Results and discussion

Analysis of diffraction patterns for Fe^{2+} -intercalated sample shows the presence of amorphous phase (Fig. 1). A drastic increase in scattered intensity within the region $2\theta = 5$ to 15° is an evidence of highly developed porous structure. Another feature of the principal peak is

its asymmetry which can be interpreted considering the total curve as an additive sum of particular curves corresponding to the structural units of various structures. The diffused profile maxima can be regarded as a weighted superposition of two symmetric maxima, which correspond to the scattering from microregions with different types of a short range order (Fig. 2). The first of these maxima is shifted towards lower scattering angles and has a significantly larger half-height width, which most probably corresponds to the scattering from the less ordered amorphous carbon phase whereas the second one has a lower half-height width and its position is the same as the one in polycrystalline graphite. Therefore, all these features allow us to suggest the formation of nanoclusters with graphite like short range order. The diffraction patterns were used to determine the main structure parameters, which are listed in Table 1. Such parameter as density of nanoclusters was determined as described in [14] and another one – a volume fraction was determined by comparison of integral scattered intensities from amorphous and nanocrystalline phases. The mean grain size L of ordered nanoporous carbon regions was determined using the Debye-Scherrer formula [15]. Analysis of these parameters showed that the treatment resulted in an increase in both the density and size of nanoclusters with a simultaneous decrease of interlayer distance. One of the reasons for the latter change was the intercalation of Fe-atoms into the interlayer region.

Small angle intensity curves (Fig. 3), represented in logarithmic coordinates, reveal linear behavior, which allowed us to describe them by power dependence $I(s) \sim s^{-\alpha}$, ($1 < \alpha < 3$) that is an evidence of fractal aggregates formation. It was also shown that these aggregates are the volume fractals with the fractal dimension $D_v = \alpha < 3$. It should be noted that the slope α of the linear dependences increased to 4 at the values of a wave vector larger than s_o (marked by arrows in Fig. 3), which allowed us to interpret the scattered intensity with the Porod law for scattering on homogeneous nanoparticles with a smooth surface. Due to the aggregation of initial nanocrystals, the inhomogeneous

Fig. 1. Scattered intensities for carbon versus scattering angles 1 – initial sample; 2 and 3 – after intercalation with 10 % of FeSO_4 and 50 % of FeSO_4 , respectively.

fractal aggregates were formed at length scales of $L > 2\pi/s_o$. It should be noted here that a decrease in the linear dependence slopes to $\alpha = 3.50$ and $\alpha = 3.25$ was observed in the intercalated samples. Since $3 < \alpha < 4$, scattering by carbon nanoclusters with an unsmooth interface and fractal dimension of surface fractals $D_s = 6 - \alpha$ was observed within the mentioned angle region. In this case the value of a specific surface depends on the size and fractal dimension of the nanocluster surface and can be calculated according to the formula:

$$S = \frac{3}{\rho_0 R_s^3} r_0^2 \left(\frac{R_s}{r_0} \right)^{D_s} \quad (3)$$

where r_0 , ρ_0 are the average size and density of initial nanocrystals, R_s is the radius of fractal clusters. The calculations (Table 1) revealed a significant increase in the specific surface area, S , in the intercalated samples (up to $990 \text{ m}^2/\text{g}$), which can be attributed mainly to the changes of the carbon clusters surface.

The behavior of the Er^{2+} -intercalated samples is contrary to that of Fe^{2+} -intercalated ones. The increase in the slope of the linear dependences to $\alpha = 4.67$ and $\alpha = 4.88$ at the wave vector values larger than s_o (marked by arrows in Fig. 4a, 4b) was observed. For this case the calculated parameters are listed in Table 2.

Fig. 2. Approximation of diffraction maxima (a) for initial carbon (b) for carbon intercalated with 10 % $FeSO_4$ and (c) for carbon intercalated with 50 % $FeSO_4$.

Table 1. Structure parameters of carbon nanoclusters after intercalation with $FeSO_4$.

Material	L_o nm	ρ_0 g/cm ³	D_v	D_s	s_o nm ⁻¹	L nm	S m ² /g
Initial carbon	1.4	2.05	2.80	2.00	1.0	6.3	467
Intercalated with 10 % $FeSO_4$	1.6	2.10	2.2	2.50	1.1	5.2	990
Intercalated with 50 % $FeSO_4$	1.4	2.20	2.1	2.75	1.0	5.4	790

Table 2. Structure parameters of carbon nanoclusters after intercalation with $Er_2(SO_4)_3$.

Material	L_o nm	ρ_0 g/cm ³	D_v	D_s	s_o nm ⁻¹	L nm	S m ² /g
Initial carbon	1.4	2.05	2.80	2.00	1.0	6.3	467
Intercalated with 10 % $Er_2(SO_4)_3$	2.0	2.00	2.85	—	1.25	5.0	980
Intercalated with 50 % $Er_2(SO_4)_3$	1.5	2.10	2.78	—	1.25	5.0	1060

The presence of Fe^{2+} cations in the carbon structure was confirmed by elemental electronography using the REM 106 I (Ukraine) electron scanning microscope. The obtained images and elemental analysis results are shown in Fig. 5 and Table 3.

The Mössbauer spectroscopy was used to answer the question in which state iron atoms existed in the carbon matrix. The obtained value of the quadrupole splitting (Fig. 6) proved that they existed as Fe^{2+} ions. Thus, two electrons of each atom can form delocalized states, increasing the free carrier concentration and the C_{SC} capacity.

Fig. 3. Determination of fractal dimension from SAXS data (1 – initial carbon; 2 and 3 – after intercalation with 10 % and 50 % FeSO_4 , respectively).

Table 3. Redistribution of elements in the surface layer of carbon after modification.

Element	Weight %	
	initial carbon	after modification with 10% FeSO_4
C	98.46	62.29
Al	0.96	–
Ca	0.58	–
O	–	34.60
Si	–	1.23
S	–	1.39
Fe	–	0.49
Total	100	100

(a)

(b)

Fig. 4. Plots of X-ray scattered intensity versus wave-vector before and after its intercalative modification at (a) 10 % and (b) 50 % $\text{Er}_2(\text{SO}_4)_3$, respectively.

The galvanostatic charge-discharge curves (Fig. 7) illustrate the increase in specific capacitance after Fe^{2+} -intercalative modification. Similar curves were obtained for carbon materials, intercalated with erbium salt. The results of galvanostatic measurements indicated an increase in the specific capacity from 52 F/g to 177 F/g (10 % FeSO_4 precursor) and to 174 F/g (50 % FeSO_4 precursor) for Fe^{2+} -intercalation, whereas for Er^{2+} -intercalation, the corresponding values were 196 F/g (10 % $\text{Er}_2(\text{SO}_4)_3$ precursor) and 145 F/g (50 % $\text{Er}_2(\text{SO}_4)_3$ precursor). The fact that

Fig. 5. Microstructure image for carbon after 10 % Fe²⁺-intercalative modification.

Fig. 6. Mössbauer spectrum of carbon after 10 % Fe²⁺-intercalative modification.

the observed specific capacitance increase was not caused by surface redox-groups was proved by IR-spectroscopy (Fig. 8) which excluded the contribution to pseudocapacitance from surface functional groups formed during the ultrasonic treatment: after the latter process the intensities of all the absorption bands were reduced (without the appearance of any new bands). In particular, we registered a decrease in the CH and OH content in the sample after the treatment (in the vicinity of 3450 cm⁻¹ and from 2800 to 3000 cm⁻¹, respectively) as well as enhancement of the absorption in the region of 2150 to 2250 cm⁻¹ (triple CC bond). The changes in the position of the C=O

band and its shift from 1742 cm⁻¹ to 1729 cm⁻¹ could be connected with drastic changes in the environment of the C=O groups. We suppose that the bands in the region 1100 to 1300 cm⁻¹ with the maximum at 1240 and 1125 cm⁻¹ could be assigned to the C=S and the C–O vibrations, respectively. The band at 1575 cm⁻¹ seem to be of the C=C origin. After the treatment sulfur bands appeared while the number of different functional groups and their intensities decreased (1100 to 1700 cm⁻¹ region).

Fig. 7. “Charge-discharge” galvanostatic cycles before (1) and after intercalative modification of carbon with 10 % FeSO₄ (2) and 50 % FeSO₄ (3).

Fig. 8. Infrared spectra of carbon: 1 – initial sample; 2 – after intercalative modification with 10 % FeSO₄.

The structural and vibrational properties of nanostructured carbon with *sp*, *sp*² and

sp^3 hybridization were investigated by Raman spectroscopy. In Fig. 9 the Raman spectra for untreated (curve 1) and intercalated with 10 % $FeSO_4$ (curve 2) nanoporous carbon can be divided into three main regions. The first-order Raman spectrum of the nanoporous carbon displayed in Fig. 9 reveals two intense and narrow G (graphitic) and D (disorder) bands at about 1360 cm^{-1} and 1580 cm^{-1} , respectively. For the sake of realistic comparison, the spectra were normalized with respect to the G band. The relative intensity and full widths of D and G bands characterize the disorder degree of the material (broader lines correspond to more disordered materials). Secondly, the remarkably asymmetric and wide vibrational features in the 1900 to 2200 cm^{-1} spectral region refer to sp -enriched carbon structures (so-called C band [16]) and correspond to C–C stretching vibrations of linear sp hybridized carbon structures. Fitting this band with Gaussian shapes, we obtained two components corresponding to the presence of sp/sp^2 cluster-assembled carbon. As a consequence, this Raman features provide a strong support for the interpretation of the observed signal as related to the C–C stretching vibrations, together with polyvinyl structures (i.e. involving the stretching of both single and triple bonds in the chain) of the cumulenlic structure (i.e. cumulated double bond only) [16]. This band consists of two components and is attributed to a contribution of a different environment of the C–C functional groups in our structure. Vibrations in the region of 1900 to 2200 cm^{-1} were also registered in the exfoliated graphite [17]. Within the third spectral region, almost all kinds of graphitic or sp^2 carbon materials exhibit strong Raman band in the 2300 to 3500 cm^{-1} , which corresponds to the second-order Raman spectra with overtones and combination of the first order phonon band [18].

After subtracting the linear background, the Raman spectra were fitted with Lorentz and Gaussian line-shapes using non-linear square fitting [19]. The first-order spectra of our porous carbon could be successfully fitted using five components, i.e. G, D_1 , D_2 , D_3 , and D_4 bands (Fig. 10). The high wave number in G band at ~ 1580 to 1600 cm^{-1} region is associated with the tangential C–C or

Fig. 9. Raman spectra of initial – 1 – and after intercalative modification with 10 % $FeSO_4$ – 2 – nanoporous carbon.

tangential displacement mode of E_{2g} symmetry. These features can be assigned to the E_{2g} symmetry of sp^2 graphite that results from splitting of the interlayer stretching mode. The D_1 band at $\sim 1350\text{ cm}^{-1}$ in sp^2 carbon is a disorder-activated band of A_{1g} symmetry in the first-order scattering process, arising from the in-plane substitution heteroatoms, vacancies, grain boundaries (edge of graphene layer) and fine size effects [20]; D_2 band, centered at $\sim 1620\text{ cm}^{-1}$ activated by a disordered graphitic lattice, is observed as a G band wing (surface of graphene layer, E_{2g} symmetry) [21]; D_3 band, centered at ~ 1500 to 1530 cm^{-1} is caused by amorphous carbon; D_4 band centered at ~ 1200 to 1220 cm^{-1} is attributed to a disordered graphitic lattice (A_{1g} symmetry), polyenes (sp -hybridized carbon chains) and ionic impurities.

When comparing the obtained spectra with each other (Fig. 10) it can be seen, first of all, that there is no intensity increase for D and G bands of initial nanoporous carbon after the Fe^{2+} -intercalative modification, showing the stability of ordering in carbon bonds. However, a drastic (about fivefold) increase in the intensity for D_2 band centered at $\sim 1620\text{ cm}^{-1}$ can be observed in the first order spectra that correspond to the graphite lattice, activated by structural disordering. This increase

Fig. 10. First-order micro-Raman spectra of nanoporous carbon: (a) before and (b) after intercalative modification with 10 % FeSO₄.

Fig. 11. Second-order micro-Raman spectra of nanoporous carbon: (a) before and (b) after intercalative modification with 10 % FeSO₄.

in intensity correlates well with the conclusion on the intercalation of graphite nanoclusters with the Fe²⁺-cations, which follows from the X-ray diffraction investigation. Consequently, this leads to a change in the electron structure of the activated carbon, particularly to an increase in the free carriers concentration. In addition to the above mentioned facts, the change in the phonon spectrum and thus in the current carrier scattering mechanism, caused by the Fe²⁺-intercalative modification is confirmed also by the second order Raman spectrum (2200 to 3700 cm⁻¹), attributed to the totality of overtones at 1350 and 1550 cm⁻¹ modes and their combination. Simulation of this second order spectrum can be successfully carried out us-

ing a combination of five Lorentzian-shaped bands (Fig. 11), from which the increase in the intensity of the 2D₃ band follows. Unfortunately, at the moment we can only state this fact, the origin of which is still unclear.

5. Conclusions

1. It has been shown that Fe²⁺- and Er²⁺-intercalative modifications of carbon are similar to intercalation of this material with Ni²⁺ ions studied earlier. Therefore 3d- and 4f-metals show no difference in ability to hydrophilize the activated carbon effectively with increasing

the current carriers density.

2. As in case of Ni^{2+} intercalation the remarkable increase in the specific surface area, mainly due to the size reduction of graphite nanoclusters, is also observed for intercalation by Fe^{2+} - and Er^{2+} .
3. The intercalative modification with Fe^{2+} - and Er^{2+} -elements increased the specific capacitance by more than 3.5 times, which is due to improvement of “charge-discharge” process kinetics in an EDL, thus also leading to an increase in the supercapacitor power that is of the same order as for Ni^{2+} intercalation.

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