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Improvement of supercapacitor parameters by nickel ion intercalation into activated carbon^{*}

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The relation between the porous structure and the electron structure in carbon materials was investigated in order to optimize the efficiency of the physical-chemical processes in an electric double layer (EDL) formed at the boundary between the carbon material and the electrolyte (KOH 30 % aqueous solution). In particular, an Ni^{2+} intercalative modification of nanoporous carbon resulted in more than a triple increase in the specific capacitance and a significant improvement of the charge-discharge kinetics in the EDL.

Keywords: Ni-intercalative modification; small angle X-ray scattering; nanocluster; nanoporous carbon; supercapacitor

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1. Introduction

Recent progress in electric vehicle construction and non traditional power engineering has stimulated the design and production of effective highpower energy accumulation and storage systems. Many previous investigations have allowed the operational voltage to be increased to 4.5-4.7 V, but the power of such systems has not been increased and continues to remain low. Supercapacitors with capacitive or pseudocapacitive mechanisms of energy storage are commonly used to overcome the latter disadvantage. However, this solution can be successful only if the optimal porous structure is suitably combined with the electron structure, so the Helmholtz capacitance is unblocked by the space charge region (SCR) capacitance. Unfortunately, the chemical methods commonly used for the surface modification of the porous structure [1-3] are unable to produce the desired change in the electron structure. Most publications on improvement of active materials in supercapacitors suggest two major main methods only - porous structure modification

[4-7] or grafting some suitable redox-groups to the surface with any method [8-10] in order to form the desired electron structure. In the present paper we attempt to develop new methods of surface modification.

2. Background

The conceptual approach to the solution of the above mentioned problem is based on the structural features of the electric double layer (EDL) formed at the electrolyte – nonmetallic solid phase interface (Fig. 1a). The total capacitance of the EDL, C, can be determined from the relation (cf. Fig. 1b):

$$C^{-1} = C_{SC}^{-1} + C_H^{-1} + C_G^{-1} \tag{1}$$

where C_G is the Gouy-Chapman capacitance of the diffusive layer, C_H is the Helmholtz capacitance and C_{SC} is the capacitance of the SCR in the solid phase. It should be noted that C_G is usually greater than C_H . Coulomb blocking is negligible for metallic electrodes, but it is substantial for carbon-graphite electrodes, since in the latter case the Debye screening radius usually assumes large values. C_{SC} is proportional to the density of delocalized states at the Fermi level, thus, an increase in C_{SC} promotes the unblocking of the Helmholtz capacitance. Our modification of technology is aimed at achieving an

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Fig. 1. Electric double layer model for nonmetallic electrodes (a) and related electric circuit (b).

increase in the density of states. At the same time, the higher the concentration of the current carriers, the higher the degree of the charge screening, which leads to an elevated charge concentration within the EDL, thus increasing the Helmholtz layer capacitance. Taking into account these facts we propose to use the intercalative mechanism of modification, the main idea of which is to introduce various materials with $(HSO_4)^+$ - and Ni^{2+} -cations into graphitized regions (whose content can reach 30 %) or into their nanopores. Intercalation of graphite by impurities develops the porous structure and increases its hydrophilicity [11], while the increase in the free charge carrier concentration is achieved by injection of 3d elements into the activated carbon structure.

3. Experimental

The samples were prepared in the following way. $K_2Cr_2O_7$ (0.19 g) was added to carbon (1 g) diluted in concentrated H_2SO_4 . Then, the composition was mixed for 10–15 min. Then, NiSO₄ (0.1; 0.5 g) salt was added and the new composition was mixed once more for 10–15 min. The prepared mixture was heated to 250 °C and held at this temperature for 2 hours. The carbon modified in the aforementioned procedure was purified both from the absorbed products of chemical reactions and the un-reacted ingredients in the following way:

• 22–24 hour treatment in concentrated HF at room temperature with subsequent washing in distilled water until pH reached 5.5;



Fig. 2. Angular dependences of scattered intensity for carbon (1 – initial sample; 2 and 3 – after intercalation with 10 % and 50 % of NiSO₄).

- 22–24 hour treatment in concentrated HCl at room temperature with subsequent washing in distilled water until pH reached 5.5;
- 22–24 hour treatment in the 30 % HNO₃ solution at room temperature with subsequent washing in distilled water until pH reached 5.5.

The final drying was accomplished at the temperature of 110 °C until the mass was constant.

The X-ray diffraction studies were carried out using a DRON-3 diffractometer in a wide scattering angle range ($2\Theta = 5 \div 70$ degree) in the Θ -2 Θ scanning regime with the step of $\Delta 2\Theta = 0.05$ degrees. An LiF single crystal was installed in the incident beam in order to obtain the Cu K α radiation with a wavelength of 1.5418 Å. The scattered intensities were recorded with a high accuracy with a high-precision goniometer and an NaJ(Tl) perfect crystal as the scintillation detector. The experimental data were analyzed with the DHN_PDS software package.

Small angle X-ray scattering data were obtained over the scattering range of $2\Theta = 0.2$ -4.0 degrees with a special collimation system both for incident and scattered beams. In order to reduce the parasite scattering from the crystalline monochromator, a special slit system was arranged at the front of the sample at a distance within the 3.5-4.0 cm range. A similar system was installed also at the front of the receiving slit of the detector, what reduced the background scattering. The usage of a perfect LiF



Fig. 3. Partial diffraction maxima for carbon: a) initial sample; b), c) intercalated with 10 % and 50 % of NiSO₄.

crystal and the above described collimation system permitted us to carry out investigations within a small angle region, starting from $2\Theta = 0.2-0.25$ degrees. The resolution of the detector was estimated to be 0.03 degrees. The scattered intensities were measured in the transmission regime with a step of $\Delta 2\Theta = 0.05$ degrees and the exposition of 100 s.

The electrochemical studies of activated carbon were performed in a triode cell with a chlorinesilver reference electrode. The impedance measurements were carried out over the frequency range of 10^{-2} – 10^5 Hz by means of the AUTOLAB (ECO CHEMIE, the Netherlands) measuring set, driven by the FRA-2 and GPES software. The cyclic voltammograms for the electrochemical cells were recorded with a sweep voltage rate of 0.01 V/s. The charge-discharge galvanostatic cycles were performed by means of an electronic galvanostatic device.

4. Results and discussion

The diffraction patterns showed diffuse maxima typical for amorphous or nanocrystalline materials (Fig. 2). Some features were observed at angles smaller than 10 degrees. The intensity increased sharply for decreasing scattering angles, indicating the presence of a porous structure. A detailed analysis of the principal peak profile showed its asymmetric form for all the curves. The left hand side of this peak was flatter than the right hand one allowing us to deduce the presence of other peaks which could be fitted to the left branch of the principal maximum. By means of a computer procedure the experimental principal maximum was fitted to the sum of two partial maxima, assumed to be corresponding for the scattering from structural units with a different kind of structure (Fig. 3).

As can be seen from the figure, the maximum located at the higher value of the scattering angle (2) was more than twice lower than the maximum (1)and its position was close to the position of the (002)reflex for polycrystalline graphite. Therefore, the existence of nanoclusters with a graphite-like structure can be supposed. The partial maximum (1) is shifted to small 20-values and reveals a greater half-height width. Such behavior enabled us to conclude that this maximum corresponded to the scattering from structural units with either a smaller degree of ordering or a smaller size. The integral analysis of the intensity curves profile allowed us to determine the structure parameters which are listed in Table 1. The density of graphite-like nanoclusters was determined using the method described in [12]. The size of the structural units was determined according to the Debye formula:

$$L_0 = \frac{\lambda}{\beta \cos \theta} \tag{2}$$

where λ , β , and θ are the X-ray wavelength (1.5406 Å), the half height of the graphite (002) diffraction peak, and the Bragg diffraction angle,

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Material	<i>s</i> ₁ ,	<i>d</i> ,	$L_o,$	ρ,	α	s_o ,	<i>L</i> ,	<i>S</i> ,
	nm^{-1}	nm	nm	g/cm ³		nm^{-1}	nm	m ² /g
Initial Carbon	16.9	0.371	1.4	2.04	2.8	1.0	6.3	467
Intercalated with	17.5	0.358	1.7	2.11	2.2	1.3	4.8	592
10 % NiSO ₄								
Intercalated with	17.5	0.359	2.0	2.11	2.1	1.6	3.9	729
50 % NiSO ₄								

Table 1. Structure parameters of carbon nanoclusters.

 $(s_1 - \text{first maximum position in intensity curve}; d - \text{interlayer distance in carbon structure}).$



Fig. 4. Scattered intensity as function of wave vector: 1 – initial carbon; 2 and 3 – after intercalation with 10 % and 50 % NiSO4.

respectively. The Ni²⁺ intercalative modification of carbon results both from the increased density and size of graphite nanoclusters, simultaneously reducing the interlayer distance (Table 1). It is reasonable to suppose that these changes are due to the interlayer volume occupation by Ni-atoms.

Small angle scattering curves for various intercalative modification regimes are shown in Fig. 4. Since the curves in the logarithmic scale are linear, the scattered intensity obeys a power dependence on the wave vector $I(s) \sim s^{-\alpha}$. The fact that index α satisfies the inequality $1 < \alpha < 3$, indicates the formation of volume fractals. It should be noted here that the slope of linear dependences changes up to $\alpha = 4$ at the vector values larger than s_o (marked with arrows in Fig. 4). It follows from the theory of small angle scattering that the experimental data in our case can be interpreted by Porods law for scattering from homogeneous smooth nanoparticles. The

Table 2. Elemental analysis of carbon materials: initial – a); after modification – b).

	(a)	(b)				
Element	Weight %	Element	Weight %			
С	98.46	С	50.87			
Al	0.96	0	48.16			
Ca	0.58	S	0.73			
Total	100.00	Ni	0.24			
		Total	100.00			

application of this law enables us to conclude that the aggregation of initial nanocrystals resulted in the formation of inhomogeneous fractal structures at the space scale *L* of $L > 2\pi/s_o$. The experimental curves obtained in the diffraction studies were used for estimation of the mean size of graphite nanoclusters according to the formula:

$$L \approx \frac{2\pi}{s_0} \tag{3}$$

where L is the cluster size.

Another important parameter – the specific surface – can be easily determined from the equation:

$$S \approx \frac{6}{\rho L}$$
 (4)

where ρ is the microscopic density of carbon clusters (Table 1). As it is seen, there was a significant increase in the specific area of carbon upon intercalative modification. It follows from the fractal structure analysis that the increase is due to the reduction in the size of the initial structural units (nanographite clusters).

The presence of Ni²⁺ in the carbon structure was confirmed by an elemental analysis that was



Fig. 5. Microscopic structure of carbon after Ni-modification.



Fig. 6. Charge-discharge galvanostatic cycles for initial carbon (1) and upon Ni²⁺ intercalative modification with 10 % (2) and 50 % (3) of nickel sulfate precursor.

carried out by means of a scanning electron microscope (REM 106 I, Ukraine). The compositions were different before and after the Ni^{2+} intercalative modification (Tables 2a,b). It should be noted that the initial structure of carbon persisted after modification and did not depend on the kind of modification, which changed its electron structure as well as porosity. Such a typical structure after modification is shown in Fig. 5.

We used the Mössbauer spectroscopy to understand in what charge-state the Ni atoms existed inside the activated carbon. The obtained quadrupole splitting proved the existence of the Ni²⁺ charge state. Consequently, two electrons from each atom could be delocalized what increased the free carries concentration and consequently C_{SC} .



Fig. 7. Nyquist plots for initial carbon (1) and after Ni²⁺intercalative modification with 10 % (2) and 50 % (3) content of nickel sulfate precursor. Equivalent electric circuit is shown in inset.

The galvanostatic "charge-discharge" curves (Fig. 6) revealed a specific capacitance increase upon Ni^{2+} intercalative modification from 52 F/g to 165 F/g and 178 F/g at 10 % and 50 % of the precursor (nickel sulfate).

The results of the X-ray porometry (Table 1) suggested that:

- the estimated value of the active surface approached a limit value, which was responsible for the EDL capacitance in aqueous solutions [13]. Thus, significant development of the active surface would not be recommended, since this could worsen the electron structure due to the decrease in the concentration of the free current carriers [8];
- a significant increase in the specific capacitance upon Ni²⁺ intercalative modification was not adequate to the surface area increase that was an evidence of a significant contribution of the electron structure to the modification process of the EDL structure.

We analyzed the impedance spectroscopy data in order to clarify the hierarchy of the influences of SCR thickness in carbon and the screening radius for the electric field of ions on the EDL (Fig. 7). As can be seen all the curves for the three materials behaved in a similar way, while their quantitative parameters for the capacitances of the related EDLs

Material	R_1 ,	$\sum R_i$,	$\sum C_i$,	<i>C</i> ₅ ,	R_5 ,	<i>C</i> ₆ ,	<i>R</i> ₆ ,	<i>C</i> ₇ ,	R_7 ,
	Ohm	Ohm	F	μF	Ohm	F	Ohm	F	Ohm
Initial carbon	1.25	21.78	0.11	78.28	1.17	0.03	4640	0.04	3.66
Intercalated with	0.74	4.13	0.29	99.46	0.70	0.09	3786	0.07	1.74
10 % NiSO ₄									
Intercalated with	0.98	4.95	0.34	113.88	0.76	0.10	3852	0.07	2.63
50 % NiSO ₄									

Table 3. Results on computer parametric identification for impedance model.



Fig. 8. Cyclic voltammograms for initial carbon (1) and after Ni²⁺intercalative modification with 10 % – (2) and 50 % – (3) sulfate precursor content of nickel.

were different. This, as well as the necessity to account for the SCR capacitances requires the usage 1. of the Levie approach [14], modified by serial attaching of a parallel $R_{SC}C_{SC}$ chain (here modeled with three serially connected R_5C_5 , R_6C_6 and R_7C_7 chains, see inset in Fig. 7) in order to formulate the impedance models. The first of the chains limits the SCR capacity, what is due to the charge transfer. The second and third chains correspond to the current transfer through inter-granular barriers and the energy release of individual particles, respectively. The results of computer parametric identification using the ZView 2.3 (Scribner Associates) software package for the case of zero shifts are listed in Table 3.

As can be seen from Table 3 and the Nyquist plots (Fig. 7), there is a double or triple (for 10 % and 50 % of the nickel sulfate precursor content, respectively) increase in the specific capacitance

of the Helmholtz layer (due to increasing of free charge-carries concentration) and a significant decrease in the resistance (due to the SCL capacitance increase). It is worth noting that the above mentioned behavior is not identical with a possible increase in the area of the hydrophilizated surface. Taking into account the fact that the values R_5 , R_6 , R_7 and C_5 , C_6 , C_7 are similar for materials with 10 % and 50 % of the nickel sulfate precursor content, we can suppose that a reduction in the Coulomb repulsion between the charges forming the EDL is due to more efficient screening. As a result, we obtain not only an increase in the specific capacitance but also an improvement of the capacitive energy storage process that is clearly evidenced by the cyclic voltammograms presented in Fig. 8.

5. Conclusions

- 1. It is shown that the Ni²⁺ intercalative modification is effective for hydrophilization of an activated carbon structure and a simultaneous significant increase in the current carrier concentration due to the intercalation of graphitized impurities and Ni-injection into the carbon structure.
- The small angle X-ray scattering data have confirmed that the Ni²⁺ intercalative modification of carbon promotes a significant increase in the specific surface area that is caused by a reduction in the size of both graphite nanoclusters and initial building units of fractal aggregates.
- 3. It follows from the impedance spectroscopy data that the effect of the Coulomb repulsion (decreasing the interaction between the charges forming the EDL) must be taken into account in the estimation of the specific capacitance. An

increase in the SCR capacitance results in an increase in the specific capacitance and improves the kinetics of the charge-discharge process in the EDL, leading to an increase in the supercapacitor power.

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