Morphology and Electrochemical Properties of Nanostructured Composite Co$_x$Ni$_{(1-x)}$(OH)$_2$/MCNT Based on Carbon Nanotubes

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Abstract

Preparation and properties of nanostructured composites promising for the development of electrode materials for supercapacitors are considered. The composites are based on carbon fibres composed of multilayer carbon nanotubes (MCNT), filled with the nanoparticles of mixed cobalt and nickel hydroxides which are deposited on the surface and in the channels of these nanotubes. The composition and morphology of nanostructured composites were studied by means of transmission electron microscopy and X-ray diffractometry, including the method of small-angle X-ray scattering and X-ray fluorescence analysis. The electrochemical properties of the obtained electrode nanocomposite material were considered. It is shown that variations of the cobalt to nickel ratio in the composition of the mixed hydroxide lead to significant changes in the electrochemical properties of composite electrodes. In general, an increase in their capacitance is due to the contribution of the pseudocapacity of nickel–cobalt hydroxides, and the highest capacitance values are achieved with the Co : Ni ratio close to 1 : 1. Analysis of voltammetric curves also revealed a decrease in the specific electric capacity of the electrode material with an increase in scanning rate for samples having a pseudocapacity component, which was obtained by matrix functionalization and the introduction of cobalt and nickel hydroxides, because redox reactions on the electrodes proceed with lower rates than charge accumulation due to the double electrical layer. The functionalization of carbon nanofibres consisting of multilayer carbon nanotubes was carried out by ozonation, followed by the introduction of a hydroxide filler containing transition metal hydroxides. This treatment caused an increase in their specific electric capacity, thus it is promising for the development of highly efficient electrode materials based on carbon matrices.

Keywords: cobalt hydroxide, nickel hydroxide, carbon matrix, nanostructured composite, carbon nanotubes, electrode materials

INTRODUCTION

During the recent 10–15 years, intense research is carried out in the area of the development of highly efficient devices for the accumulation and storage of electric energy − supercapacitors (ionistors). Progress in this area is to a high extent connected with the use of electrode materials in the form of nanostructured composites (NSC) formed by an electroconductive chemically inert matrix (most frequently carbon) with the nanoparticles of transition metal oxides introduced in the matrix [1].

An attractive idea is to use multilayered carbon nanotubes (MCNT) as an electroconductive matrix. This material combines chemical stability,

relatively high specific surface and electroconductivity, relatively low cost [2, 3]. The major difficulty in developing these electrode nanocomposites is the stage of the introduction of oxide nanophase into the matrix. The regularities of the formation of nanoparticles on the surface of porous carbon materials are insufficiently investigated yet, so researchers have to use complicated and poorly scalable procedures, such as solvothermal synthesis, electrodeposition or sol-gel method [4]. From our point of view, substantial possibilities in governing the distribution of newly formed particles on a porous surface are provided by preliminary preparation (transformation) of this surface. A rather large number of methods are known that can be used to functionalize carbon materials, in particular carbon nanotubes [5]. In a number of cases, a pronounced effect of preliminary treatment on the morphology and dispersion characteristics of the particles of the new phase may be observed. Functionalization may also affect the properties of electric contacts between the materials of the matrix and the extrinsic phase.

In the present work, we consider the effect of functionalization (ozonation) of MCNT on the regularities of the formation of mixed hydroxides of transition metals on their surface. The problems connected with the revelation of a connection between the structure of NSC of the composition $Co_xNi_{(1-x)}(OH)_2$/MCNT and its electrochemical properties, and with the evaluation of the possibility to use the composites as the electrode material in supercapacitors are also considered.

**EXPERIMENTAL**

Reagents and materials

For obtaining NSC, carbon fibres composed of MCNT were used as carbon matrix substrates. The fibres were synthesized at the IC SB RAS and ICCM FRC CCC SB RAS. The outer diameter of the nanotubes is 10−20 nm, their inner diameter is 6−10 nm. Tube walls are 2−5 nm thick; they include 6−14 graphene layers. Filament length reaches 10 μm.

Nanotubes were treated with ozone to functionalize the surface. Ozonation was carried out using an OGVK-02K ozonizer (JSC MELIT, Russia). The ozone-oxygen mixture was supplied into the reactor with a portion of MCNT. Ozonation was carried out at a temperature of 25 °C, the

flow rate of the mixture of ozone and oxygen was 15 L/h, ozone concentration in the mixture was 30 mg/L, process duration was 35 min. The amount of ozone at the inlet and outlet of the reactor was determined with the help of an IKO concentration measuring device (Russia). Ozonation characteristics were: the amount of ozone introduced into the system, 0.26 g; the amount of ozone absorbed by the MCNT material, 0.11 g; the degree of ozone absorption, 42 %; oxygen content in MCNT, 4.15 mass %. The intermediate products of ozone interaction with MCNT components formed during ozonation were destroyed by keeping the ozonized material at a temperature of 105 °C for 1 h. Nanotubes after functionalization were designated as MCNT-2.

It was demonstrated previously for the $Co_{0.5}Ni_{0.5}(OH)_2$/MCNT composite as example [6] that the optimal concentration of the metal of hydroxide phase for obtaining the composites based on MCNT varies within the range 5−10 mass %. Because of this, in the series of experiments with composites filled with mixed hydroxides, their mass concentration equal to 10 mass % was chosen.

To prepare the solutions of reagents for obtaining NSC, we used $CoCl_2 \cdot 6H_2O$, $NiCl_2 \cdot 6H_2O$ and NaOH of Ch.D.A. grade (analytically pure). The electrode composite material was obtained as follows: the weighted portions of the carbon matrix MCNT-2 were placed in weighing bottles and impregnated with the aqueous solutions of cobalt chloride and nickel chloride with molar ratios 1 : 2, 2 : 1, 1 : 4, 4 : 1. Then the material was treated with the aqueous solution of NaOH. The formation of mixed cobalt − nickel hydroxide proceeded according to the exchange reaction

$$xCoCl_2 + (1 - x)NiCl_2 + 2NaOH$$
$$\rightarrow Co_xNi_{1-x}(OH)_2 + 2NaCl \qquad (1)$$
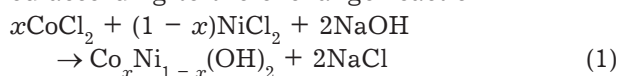
To complete the formation of the mixed hydroxide, the mixture was kept for 20 min at 98 °C. The ratios of cobalt and nickel hydroxides in the resulting composites are indicated in Table 1.

The resulting composite material was transferred to a paper filter in a Buchner funnel conjugated with a Bunsen flask and washed with distilled water to remove sodium chloride. After washing, the composite was dried in a laboratory hood at room temperature to the constant mass.

Methods of investigation

Electron microscopic studies were carried out using a JEOL JEM 2100 transmission electron microscope (Japan).

TABLE 1

Designations of the samples under investigation and the composition of the electrode composite material

No.	Composition of the composite	Co/Ni molar ratio	Mass fraction of metal in composite, mass %
1	$Co_{0.20}Ni_{0.80}(OH)_2/MCNT-2$	1 : 4	10
2	$Co_{0.33}Ni_{0.67}(OH)_2/MCNT-2$	1 : 2	10
3	$Co_{0.67}Ni_{0.33}(OH)_2/MCNT-2$	2 : 1	10
4	$Co_{0.80}Ni_{0.20}(OH)_2/MCNT-2$	4 : 1	10

Specific surface and pore size distribution in the samples were determined using the analyzer of specific surface ASAP 2020 Micromeritics (USA) by means of low-temperature sorption of nitrogen.

X-ray fluorescence and X-ray diffraction measurements were carried out with the help of a Difrey 401 X-ray diffractometer (Russia) using FeK_α radiation ($\lambda = 1.9373$ Å), with the AMPTEK energy dispersive detector (USA).

The intensity of small-angle scattering (SAS) was measured with a KRM-1 diffractometer (Russia) in the transmission mode in the characteristic radiation of iron by counting the pulses in points within the range $0.002-0.35$ Å^{-1}. The functions of particle size distribution in the approximation of uniform spheres were calculated from the SAS curves [7].

The measurements of electric capacity were carried out in a two-electrode asymmetric electrochemical cell with a PARSTAT 4000 potentiostat (USA). Nafion was used as a separator, and 6 M KOH solution was used as the electrolyte. The working electrode was a nanostructured composite, while counter-electrode was a carbon MCNT-2 matrix. The electrode characteristics were determined in the potential window from -1 to 1 V at different potential scanning rates from 10 to 80 mV/s.

The electric capacity was calculated from the area limited by the curves of cyclic voltammetry (CVA) using the equation:

$$C_{cell} = q/Um \qquad (2)$$

where C_{cell} is cell capacity, F/g; q is the charge accumulated in the cell, C; U is the potential difference, V; m is electrode mass, g.

The electrode capacity was determined as

$$C_{el} = C_{cell} C_0/(C_0 - C_{cell}) \qquad (3)$$

where C_{cell} is the capacity of the electrode cell; C_{el} is the capacity of the working electrode; C_0 is the capacity of the counter-electrode.

RESULTS AND DISCUSSION

The electron microphotographs of the carbon substrate MCNT-2 and $Co_xNi_{(1-x)}(OH)_2/MCNT-2$ composite are presented in Fig. 1. One can see that the initial matrix material is composed of fibres which are formed by interlacing multilayer carbon tubes with wall thickness $2-3$ to 12 nm. For some fibres, their opening is observed (see Fig. 1, *c*), which happened most probably during ozonation. Nanoparticles observed in the micrographs of the composite are most probably the particles of the hydroxide phase introduced into nanotubes (see Fig. 1, *a*, *c*).

To reveal the role of ozonation, we carried out a comparative investigation of the characteristics of initial, ozonated carbon matrices and the composite by means of sorption porosimetry. Analysis of sorption isotherms allowed us to relate the materials to the IV type according to the classification adopted by the IUPAC [8], that is, to mesoporous materials.

Results of the calculation of MCNT surface characteristics before and after ozonation are shown in Table 2. The calculation was carried out by means of nonlocal density functional theory taking into account the energy heterogeneity and the geometric distortion of pores 2D-NLDFT (DFT) [9]. The data of sorbtometry point to the fact that ozonation (functionalization) causes partial blockage of micropores, while meso- and macroporosity of MCNT increase, so the total values of specific surface and pore volume change only weakly. The curves of pore size distribution contain extremal points in the regions of $5-8$ and $8-10$ nm, and a mode in the region of $17-20$ nm (Fig. 3).

The results of X-ray fluorescence analysis mainly demonstrate an agreement between the composition of the composites under investigation and the desired composition prescribed for the synthesis. By means of X-ray fluorescence, chlorine is detected as an impurity in an insignificant
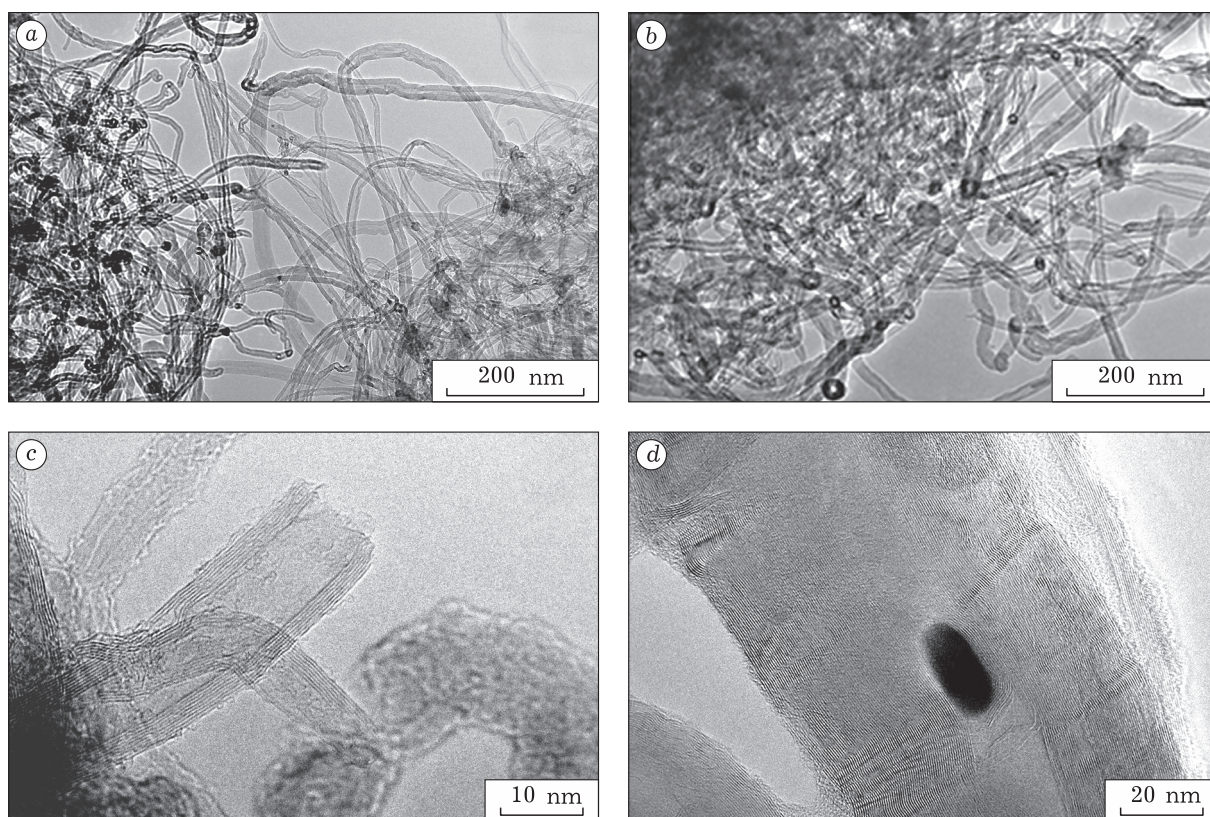
Fig. 1. Electron microphotographs of MCNT-2 (*a*, *c*) and the $Co_{0.67}Ni_{0.33}(OH)_2$/MCNT-2 composite (*b*, *d*).

amount (not more than in the matrices). So, NaCl is removed almost completely at the stage of washing, which is also evidenced by the absence of the line of sodium chloride in the diffraction patterns. Therefore, the procedure used by us allows obtaining multicomponent composite materials using a rather simple method.

The data of the X-ray phase analysis allowed us to refine the composition and structure of the hydroxide phase of the composites. Reflections characteristic of cobalt hydroxide are observed in the diffraction patterns rather clearly. Nickel hydroxide gives much broader peaks, which points to a finer dispersed state of $Ni(OH)_2$ in the composite. The presence of nickel hydroxide may be determined reliably only on the basis of the most intense lines (near 42, 49 and 76°). In general, these results point to the formation of separate hydroxide phases in the case if one of the components dominates, that is, $Co_{0.2}Ni_{0.8}(OH)_2$/MCNT-2 and $Co_{0.8}Ni_{0.2}(OH)_2$/MCNT-2 (see Table 1). In the case when the molar ratio is closer to 1 : 1, a trend to the formation of mixed hydroxide is observed.

An increase in peak broadening points to a higher degree of dispersion when the hydroxide phase of the composite is enriched with nickel hydroxide (a decrease in crystallite size).

The experimental SAS spectra of nanocomposite samples are similar to the spectra of the pure MCNT-2 matrix. In spite of the presence of the metals in the composites (the ratio Co/Ni = 1 : 2 and 2 : 1, see Table 1), their absorption coefficient is lower than that for the pure matrix, which may be explained only by the difference in the apparent density of the materials.

The calculated functions of size distribution $D_m(d)$ for the pure MCNT matrix and for nano-

TABLE 2

Data on the specific volume and specific surface of micro- and mesopores of the carbon material and the composite based on it

Parameter	MCNT	MCNT-2	Composite $Ni_{0.5}Co_{0.5}(OH)_2$/ MCNT-2* [6]
V_{micro}, cm³/g	0.0301	0.0287	0.0224
V_{meso}, cm³/g	0.763	0.8013	0.8172
S_{micro}, cm²/g	103.7	98.54	84.29
S_{meso}, cm²/g	85.28	93.82	93.24

* Mass fraction of metals in the composite: 5 %.
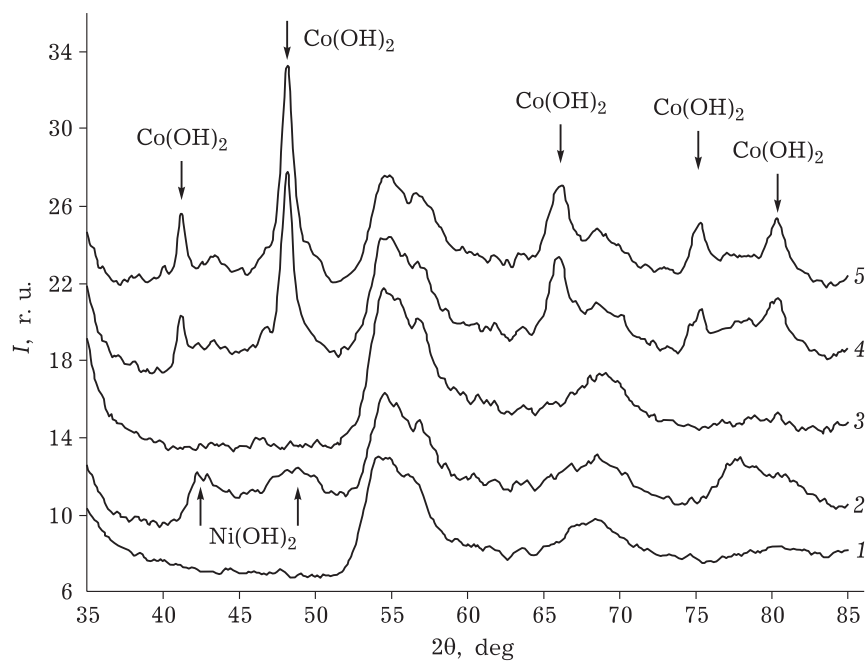
Fig. 2. Diffraction patterns of the matrix (curve *1*) and composite materials $Co_xNi_{(1-x)}$ $(OH)_2$/MCNT-2 with different molar ratios of Co/Ni in the hydroxide phase: 1 : 4 (*2*), 1 : 2 (*3*), 2 : 1 (*4*), 4 : 1 (*5*).
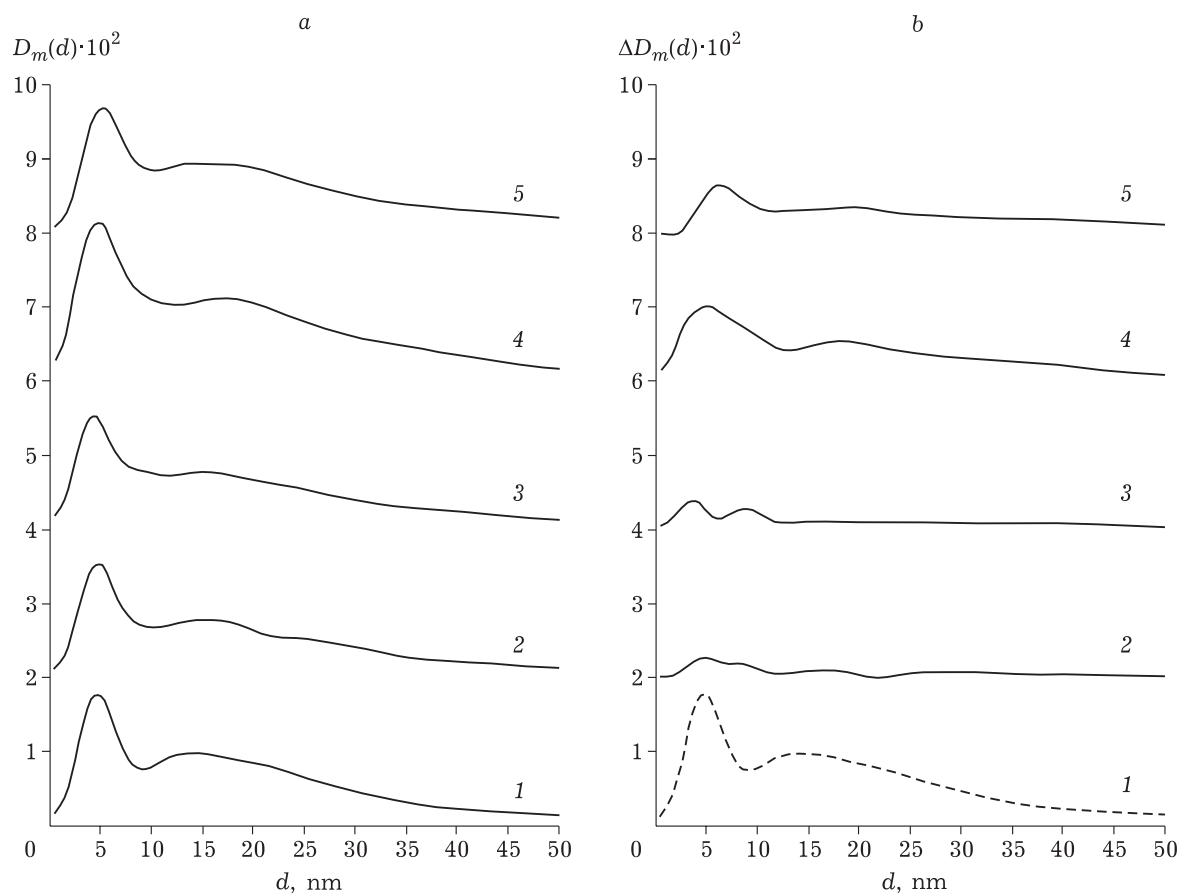

Fig. 3. Calculated mass simple (*a*) and differential (*b*) functions of the size distribution of nonuniformities for the MCNT-2 matrix and nanocomposite samples: *1* − initial MCNT-2 matrix; *2* − $Co_{0.33}Ni_{0.67}(OH)_2$/MCNT-2; *3* − $Co_{0.67}Ni_{0.33}(OH)_2$/MCNT-2; *4* − $Co_{0.20}Ni_{0.80}(OH)_2$/MCNT-2; *5* − $Co_{0.80}Ni_{0.20}(OH)_2$/MCNT-2.
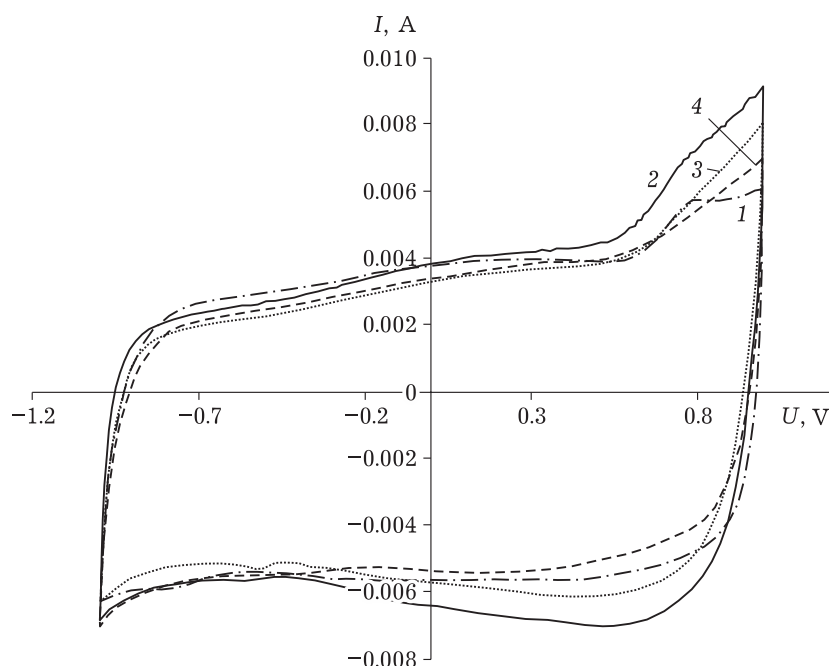
Fig. 4. Dependence of current on voltage for composite electrodes $Co_xNi_{(1-x)}(OH)_2/MCNT-2$ at the rate of potential scanning 40 mV/s. The molar ratio of cobalt to nickel in the hydroxide phase: 2 : 1 (*1*), 4 : 1 (*2*), 1 : 4 (*3*), 1 : 2 (*4*).

composite samples are presented in Fig. 3, *b*. For the MCNT-2 matrix, the curves of nonuniformity size distribution demonstrate pronounced modes in the size regions of 4−8 and 12−18 nm. Nonuniformities of larger size are also recorded. A comparison of the results obtained by means of transmission microscopy, SAS and sorbtometry gives us the reasons to assign nonuniformities in the region of 4−8 nm to hydroxide nanoparticles fixed in the inner channels of nanotubes, while the formations in the region of 12−18 nm relate to the particles on the outer surface of nanotubes.

The difference signal for composite samples with the ratio Co/Ni = 1 : 2 and 2 : 1 is a complicated multimodal curve. For samples with the ratio Co/Ni = 1 : 4 and 4 : 1, the difference function $D_m(d)$ is close to the distribution function for the pure matrix, while the first maximum may be shifted to the larger size region (especially for the sample with the ratio Co/Ni = 4 : 1).

Results of nanocomposite investigation by means of CVA are shown in Fig. 4 (typical CVA curves) and in Fig. 5. The electrochemical properties of the obtained composite electrode materials were compared with the properties of $Co_{0.5}Ni_{0.5}(OH)_2/MCNT-2$ composites obtained in the previous work [6].

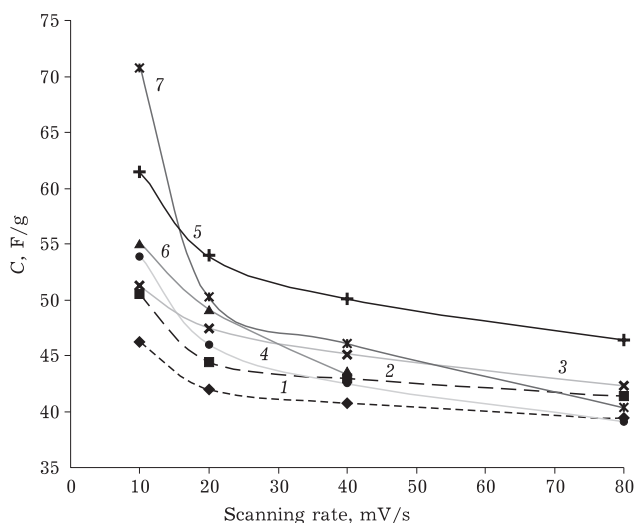
Fig. 5. Dependence of specific capacity on scanning rate for the initial carbon matrix MCNT (*1*) and for MCNT-2 (*2*), for $Co_xNi_{(1-x)}(OH)_2/MCNT-2$ composite with the Co/Ni molar ratio equal to: 1 : 2 (*3*), 1 : 4 (*4*), 2 : 1 (*5*), 4 : 1 (*6*), 1 : 1 (*7*).

The shape of the VA curves of the functionalized matrices and nanocomposites based on mixed hydroxides points to a substantial contribution from pseudocapacity processes into the total capacity of the electrode material. The highest capacity characteristics are observed for the com-

posite $Co_{0.67}Ni_{0.33}(OH)_2$/MCNT-2. Low capacity characteristics are exhibited by the composite with the hydroxide phase, that is, $Co_{0.20}Ni_{0.80}(OH)_2$/ MCNT-2.

It is known that nanocomposites based on carbon matrices filled with mixed hydroxides are better in their electrochemical characteristics that the samples with individual hydroxides. In our case, this is confirmed by the dependences of specific capacity on the scanning rate (see Fig. 5). Among all the studied composites with the composition $Co_xNi_{(1-x)}(OH)_2$/MCNT-2, including the data reported in [6], the maximal capacity (at low scanning rate) is achieved for the mixed hydroxide with the Co/Ni ratio equal to 1 : 1 (see Fig. 5, curve 7).

In general, the introduction of the hydroxide filler causes an increase in the specific electric capacity of carbon matrices and is promising for the development of highly efficient electrode materials based on carbon nanotubes. The maximal electric capacity of the composite electrode material was obtained for the composite $Co_{0.5}Ni_{0.5}(OH)_2$/ MCNT-2 with the concentration with respect to metal 10 mass % [6], it was 70.7 F/g (an increase in comparison with the capacity of MCNT-2 carbon matrix by 40 %).

A rapid decrease in specific capacity with an increase in scanning rate in the samples having the pseudo-capacity component (due to ozonation and the hydroxide component of the composite) is due to the features of morphology and functioning of the composite materials. The capacity characteristics of the matrix are known to be determined by the formation of a double electric layer (DEL). As far as the composite is concerned, along with charge accumulation due to DEL formation, it also accumulates the charge due to electrochemical processes at the interface between the solid hydroxide and the electrolyte. The total capacity at the low rate of potential scanning is to a higher extent determined by the heterogeneous oxidation-reduction processes.

The observed effect of a decrease in capacity with an increase in scanning rate is due to the fact that the electrochemical (electrode) reactions providing additional pseudo-capacity of the electrodes are limited by ion diffusion in the electrolyte and process at a lower rate with respect to DEL formation. Results of microscopy, XPA and SAS reveal aggregation of the crystallites of the filler at the outer surface of the tubes and the formation of some of them in tube channels, which brings complications for the access of the electrolyte to them and thus causes the diffusion hindrance of electrode reactions.

CONCLUSION

The possibility is demonstrated to synthesize nanostructured composite material $Co_xNi_{(1-x)}(OH)_2$/MCNT-2 with different ratios of the components of the hydroxide phase during the formation of the nanoparticles of filler for NSC both in nanotube channels and on the outer surface of the tubes. The morphology of the obtained nanocomposites was studied, and their phase compositions were established. The capacity characteristics of $Co_xNi_{(1-x)}(OH)_2$/MCNT-2 NSC were studied by means of cyclic voltammetry; it was established that the highest specific capacity is achieved at the molar ratio of cobalt to nickel in the hydroxide phase close to 1 : 1, and at the low potential scanning rate. A sharper decrease in capacity with an increase in scanning rate is observed in the presence of the pseudo-capacity component obtained both with the help of matrix ozonation and with the help of the introduction of hydroxide filler, because electrode processes occur at lower rates.

Acknowledgements

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