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# Electrochemical characteristics of a composite based on multi-walled carbon nanotubes and manganese oxide doped with silver oxide

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The effect of silver (II) oxide on the electrochemical characteristics of a composite based on multi-walled carbon nanotubes and manganese oxide when it is used as a base for supercapacitor electrodes has been studied. Composite with an Ag content  $\sim 3$  at.% showed higher values of specific capacitance, both at low and high values of the galvanostatic discharge current density, compared with an undoped composite. It is shown that the increase in electrochemical characteristics is due not only to a decrease in electrical resistance, but also to the course of reversible redox reactions involving Ag<sub>2</sub>O oxide.

Keywords: supercapacitors, electrical conductivity, specific capacity, redox reactions.

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Composites based on multi-walled carbon nanotubes (MWCNTs) and manganese oxide (MWCNT/MnO<sub>x</sub>) hold promise for the production of hybrid supercapacitors (SCs) [1]. A combination of high specific surface area and low electrical resistance of MWCNTs and high electrochemical activity of manganese oxide provides elevated specific capacitance values when such composites are used as SC electrodes with aqueous solutions of alkali salts serving as electrolytes [1,2]. MWCNT/MnO<sub>x</sub> composites formed by soaking MWCNTs in an aqueous solution of KMnO<sub>4</sub> have been examined in our previous study [3]. It has been demonstrated that the specific capacitance of the composite formed this way is 3 times higher than the capacitance of initial MWCNTs at low current loads (the composite provides 50-60 F/g, while MWCNTs offer only 21 F/g). However, the rate performance of the composite was substandard, since the conductance of the manganese oxide layer formed on the MWCNT surface was insufficient. The stability of capacitance characteristics was improved by subjecting the composite to thermal processing in an inert atmosphere and doping it additionally with rhenium oxide. In the present study, a promising approach to improving the electrochemical characteristics of a MWCNT/MnO<sub>x</sub> composite, which consists in the introduction of silver into this composite, is proposed. According to the data from [4], silver has the capacity to increase the electrical conductivity of manganese oxide and, consequently, enhance the electrochemical performance. The proposed synthesis method does not involve high-temperature processing in an inert atmosphere. In addition, silver is several times cheaper than rhenium.

MWCNTs produced by the Institute of Catalysis of the Siberian Branch of the Russian Academy of Sciences (Novosibirsk, Russia) were used to form the examined composites. The MWCNT synthesis procedure was outlined in [5]. The specific surface area of these nanotubes was  $\sim 360 \text{ m}^2/\text{g}$ . The conditions for synthesis of MWCNT/MnO<sub>x</sub> composites by soaking in a KMnO<sub>4</sub> solution were detailed in [3]. The composite doped with silver (MWCNT/MnO<sub>x</sub>\_Ag) was synthesized in similar regimes. The differences are that 100 mg of AgNO<sub>3</sub> were added to an aqueous solution of KMnO<sub>4</sub> and MWCNTs were held in this solution at an elevated temperature (60°C).

A JEOL 6610 LV scanning electron microscope (SEM) was used to analyze the morphology and composition of the studied materials. The chemical state of samples was examined via X-ray photoelectron spectroscopy (XPS) with the use of monochromatic  $AlK_{\alpha}$  radiation and a Specs (Germany) laboratory spectrometer, which is a component of the NANOFES station at the Kurchatov Synchrotron Radiation Source (Moscow, Russia). Electrodes with



**Figure 1.** SEM image of the MWCNT/MnO<sub>x</sub>\_Ag composite.



Composition of the MWCNT/MnOx\_Ag composite determined based on the EDX (averaging over five points) and XPS data

**Figure 2.** XPS spectra of the MWCNT/MnO<sub>x</sub> Ag composite. a - Mn2p, b - Ag3d, and c - C1s.

an added polymer binder were fabricated based on the obtained composites under the conditions detailed in [3]. Electrochemical measurements were performed in the threeelectrode setup in accordance with cyclic voltammetry (CVA) and galvanostatic charge–discharge procedures. A 1M solution of Na<sub>2</sub>SO<sub>4</sub> was used as an electrolyte. The specific capacitance was determined by examining galvanostatic discharge curves as a product of the current density and the discharge time divided by the voltage range (0.8 V).

The results of SEM analysis of morphology reveal that manganese oxide in the MWCNT/MnO<sub>x</sub> composite is

distributed uniformly over the surface of carbon nanotubes in the form of continuous layers 10-20 nm in thickness [3]. The SEM image of the MWCNT/MnO<sub>x</sub>\_Ag composite (Fig. 1) also indicates that manganese and silver oxides form layers on the surface of individual carbon nanotubes. The results of energy dispersive X-ray analysis (EDX) suggest that elements are distributed fairly uniformly within the composite (see the table). Potassium in the composite comes from the residual products of reaction of KMnO<sub>4</sub> with MWCNTs and water in the process of synthesis. The EDX data are indicative of a fairly high level of doping of

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manganese oxide with electrically conducting  $AgO_x$ . The oxygen concentration determined by EDX is low (see the table), since this method has a low sensitivity to elements with a small atomic weight. The results of quantitative analysis involving the surface-sensitive XPS method reveal an excess amount of oxygen (see the table). This is likely attributable to MWCNT oxidation in the process of synthesis.

The energy distance between the maxima of the Mn2*p* doublet in the XPS spectrum of the MWCNT/MnO<sub>x</sub>\_Ag composite (Fig. 2, *a*) and the energy position of the Mn2*p*<sub>3/2</sub> and Mn2*p*<sub>1/2</sub> maxima (642.4 and 654.2 eV, respectively) correspond to MnO<sub>2</sub> [6]. However, the results of decomposition of the spectrum (taking into account multiplet splitting, which is typical of 2*p*- spectra of transition metals [7]) suggest the presence of states apparently corresponding to Mn(III) oxide in the low-energy spectral region. The relative integrated area of this component is  $\sim 14\%$ .

The  $Ag_{3d_{5/2}}$  maximum is located at 367.9 eV in the XPS spectrum of the MWCNT/MnO<sub>x</sub>\_Ag composite (Fig. 2, *b*). This position may correspond both to  $Ag_2O$  and to metallic Ag [8]. Since the composite was synthesized in an oxidizing medium,  $Ag_2O$  is more likely to be present in this composite.

The C1s XPS spectrum of the MWCNT/MnO<sub>x</sub>\_Ag composite (Fig. 2, c) was fitted with five components (C1-C5) corresponding to carbon states with different chemical environments. Component C1 (the binding energy is 284.5 eV) corresponds to the states of carbon atoms forming the framework of carbon nanotubes (C=C bonds). Component C2 (the binding energy is 285.0 eV) is associated with defects in MWCNT walls. Components C3, C4, and C5 correspond to carbon forming C-O/C-O-C, C=O, and COOH bonds, respectively (the binding energies are  $\sim$  286.5,  $\sim$  288, and  $\sim$  289 eV) [9]. Since the components representing structural defects and carbon-oxygen bonds of various types (C2-C5) have a high intensity, the interaction of MWCNT surfaces with manganese oxides at interfaces is likely to be fairly strong. Similar processes of oxidation and growth of the defect density on the surface of carbon nanotubes have been demonstrated for an undoped MWCNT/MnO<sub>x</sub> composite in [3].

The capacitance characteristics of electrodes based on MWCNTs and composites were analyzed using the galvanostatic charge–discharge method, and it was found (Fig. 3, *a*) that the MWCNT/MnO<sub>x</sub>\_Ag composite electrode has the highest specific capacitance: 146.0, 106.5, and 65.0 F/g at a current density of 0.1, 0.5, and 1 A/g, respectively. Thus, the specific capacitance of the MWCNT/MnO<sub>x</sub>\_Ag electrode decreases by ~ 56% as the discharge current density increases by a factor of 10. The specific capacitance of the MWCNT/MnO<sub>x</sub> composite electrode decreases by ~ 60%. A fairly rapid reduction of capacitance with an increase in the current load is typical of materials that accumulate charge via redox reactions. The increase in capacitance of the MWCNT/MnO<sub>x</sub>\_Ag electrode may be



**Figure 3.** *a* — Dependences of the specific capacitance on the discharge current density of electrodes based on MWCNTs (*I*), MWCNT/MnO<sub>x</sub> composite (*2*), and MWCNT/MnO<sub>x</sub>\_Ag composite (*3*). Galvanostatic charge-discharge curves measured at a current density of 0.1 A/g are shown in the inset. *b* — CV characteristics of electrodes based on MWCNT/MnO<sub>x</sub> (*I*) and MWCNT/MnO<sub>x</sub>\_Ag composites (*2*) measured at a potential scan rate of 1 mV/s.

attributed to a higher electrical conductivity of manganese oxide doped with Ag<sub>2</sub>O. The specific conductivity of Ag<sub>2</sub>O (10<sup>3</sup> S/m [10]) is much higher than the conductivity of MnO<sub>2</sub> (10<sup>-9</sup> S/m [11]). The cyclic stability of the MWCNMT/MnO<sub>x</sub>\_Ag composite electrode was estimated by cycling in the galvanostatic mode at a current density of 1 A/g, and the specific capacitance was found to decrease by ~ 6% in 1000 charge–discharge cycles.

A pair of peaks (A1 and A2) are present in the charge and discharge CV curves of the MWCNT/MnO<sub>x</sub> electrode (curve *I* in Fig. 3, *b*). These peaks are induced by reversible redox reactions involving manganese oxide

$$\mathrm{MnOOM}_{x}^{+} + n\mathrm{SO}_{4}^{2-} \leftrightarrow \mathrm{MnO}_{2}//(\mathrm{SO}_{4})_{n}^{2-} + xM^{+} + xe^{-},$$

where  $M^+$  are Na<sup>+</sup> cations from the electrolyte or K<sup>+</sup> cations from residual synthesis products in the composite, and two slashes denote the electrical double layer [12]. Peak A1 in the charge CV curve of the MWCNT/MnO<sub>x</sub>-Ag composite (curve 2 in Fig. 3, b) is joined by peak B1 (~ 500 mV). The corresponding peak B2 (~ 240 mV) is also present in the discharge curve. In our view, the presence of peaks B1 and B2 may be attributed to the interaction of Ag<sub>2</sub>O with electrolyte ions. The positive working electrode may support reversible redox reactions

$$Ag_2O + H_2O + 2e^- \leftrightarrow 2Ag + 2OH^-$$

Peak A2 is lacking in the discharge curve of MWCNT/MnO<sub>x</sub>-Ag (presumably, due to the high intensity of peak B2). The obtained results suggest that the enhancement of electrochemical performance of the electrode based on the MWCNT/MnO<sub>x</sub>-Ag composite is attributable both to a higher electrical conductivity and to redox reactions involving silver oxide.

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#### **Conflict of interest**

The authors declare that they have no conflict of interest.

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