

06.1

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

© S.N. Nesov<sup>1</sup>, P.M. Korusenko<sup>1</sup>, I.A. Lobov<sup>1,2</sup>, K.E. Ivlev<sup>2</sup>

<sup>1</sup> Omsk State Technical University, Omsk, Russia

<sup>2</sup> Omsk Scientific Center, Siberian Branch, Russian Academy of Sciences, Omsk, Russia

E-mail: nesov55@mail.ru

Received July 19, 2023

Revised September 7, 2023

Accepted September 9, 2023

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  $\text{Ag}_2\text{O}$  oxide.

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

DOI: 10.61011/TPL.2023.11.57187.19689

Composites based on multi-walled carbon nanotubes (MWCNTs) and manganese oxide ( $\text{MWCNT}/\text{MnO}_x$ ) 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].  $\text{MWCNT}/\text{MnO}_x$  composites formed by soaking MWCNTs in an aqueous solution of  $\text{KMnO}_4$  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  $\text{MWCNT}/\text{MnO}_x$  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  $\text{MWCNT}/\text{MnO}_x$  composites by soaking in a  $\text{KMnO}_4$  solution were detailed in [3]. The composite doped with silver ( $\text{MWCNT}/\text{MnO}_x\text{-Ag}$ ) was synthesized in similar regimes. The differences are that 100 mg of  $\text{AgNO}_3$  were added to an aqueous solution of  $\text{KMnO}_4$  and MWCNTs were held in this solution at an elevated temperature ( $60^\circ\text{C}$ ).

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  $\text{AlK}_\alpha$  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

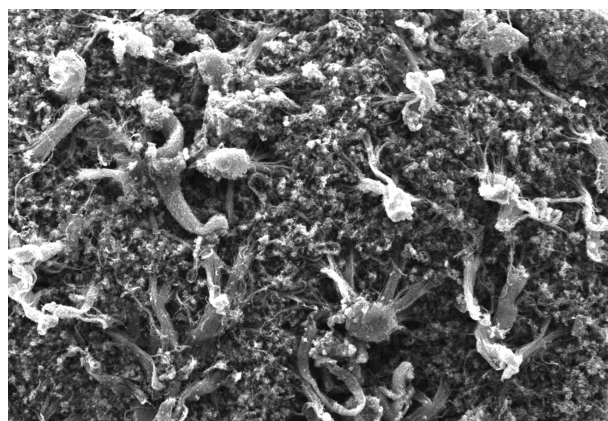
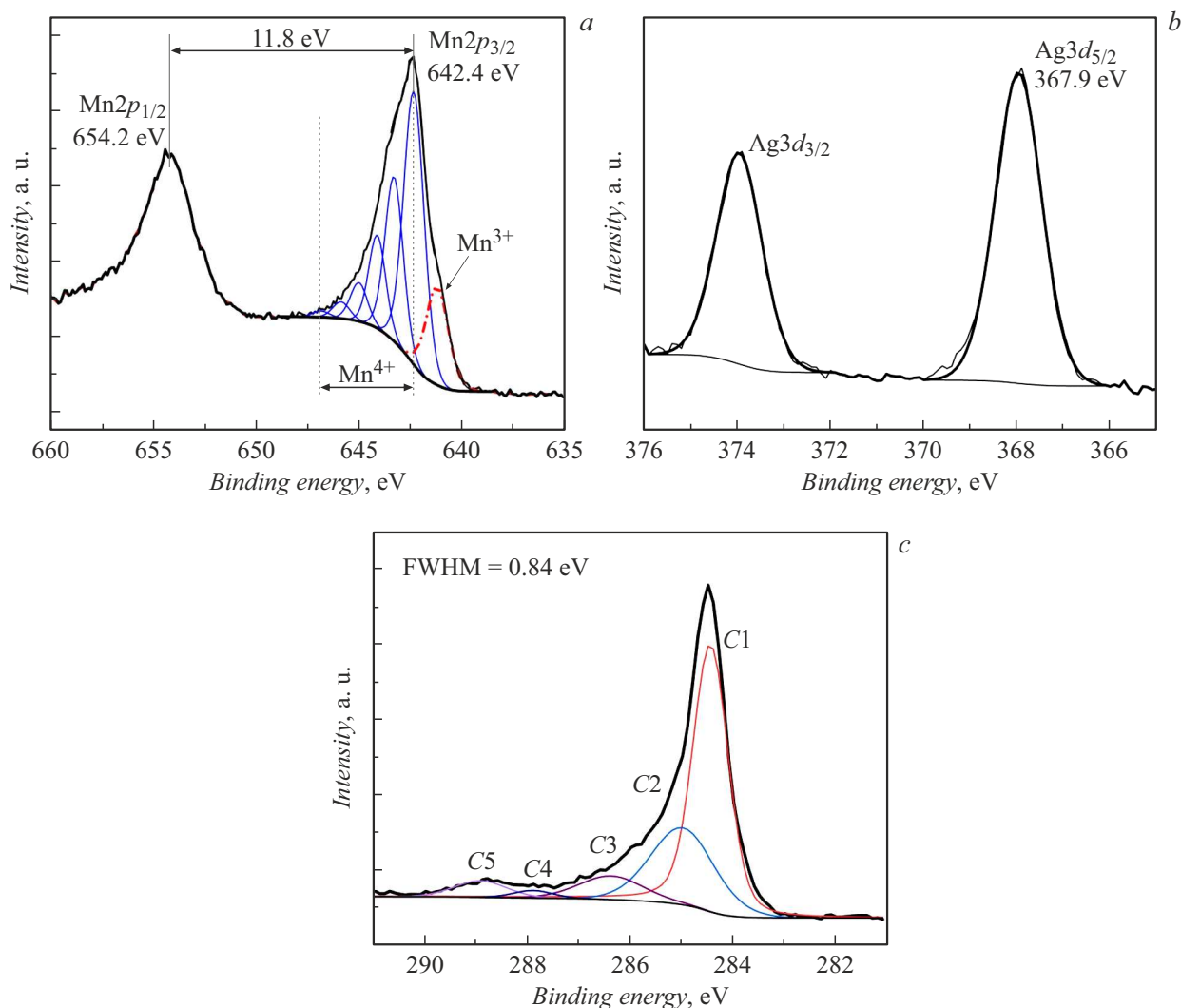


Figure 1. SEM image of the  $\text{MWCNT}/\text{MnO}_x\text{-Ag}$  composite.

Composition of the MWCNT/MnO<sub>x</sub>-Ag composite determined based on the EDX (averaging over five points) and XPS data

Method	Concentration, at.%				
	C	O	Mn	Ag	K
EDX	40.8 ± 7.0	30.1 ± 4.1	22.6 ± 2.0	3.8 ± 0.7	2.7 ± 0.6
XPS	46.3	36.7	11.4	2.8	2.8



**Figure 2.** XPS spectra of the MWCNT/MnO<sub>x</sub>-Ag composite. *a* — Mn2*p*, *b* — Ag3*d*, and *c* — C1*s*.

an added polymer binder were fabricated based on the obtained composites under the conditions detailed in [3]. Electrochemical measurements were performed in the three-electrode 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

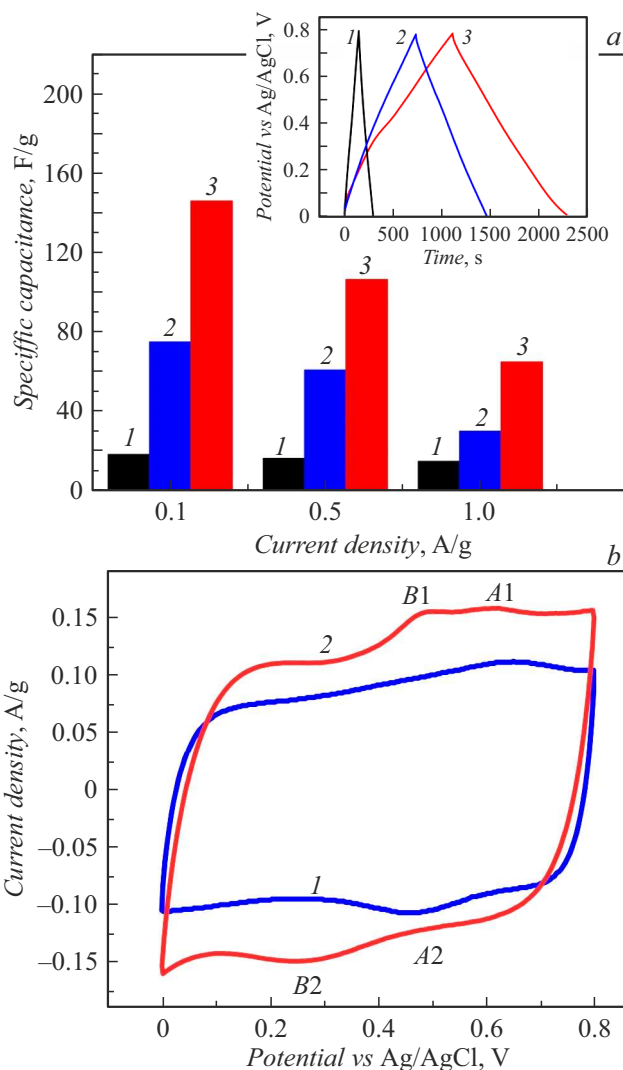
manganese oxide with electrically conducting  $\text{AgO}_x$ . The oxygen concentration determined by EDX is low (see the table), since this method has a low sensitivity to elements with a small atomic weight. The results of quantitative analysis involving the surface-sensitive XPS method reveal an excess 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  $\text{Mn}2p$  doublet in the XPS spectrum of the  $\text{MWCNT}/\text{MnO}_x\text{-Ag}$  composite (Fig. 2, *a*) and the energy position of the  $\text{Mn}2p_{3/2}$  and  $\text{Mn}2p_{1/2}$  maxima (642.4 and 654.2 eV, respectively) correspond to  $\text{MnO}_2$  [6]. However, the results of decomposition of the spectrum (taking into account multiplet splitting, which is typical of  $2p$ - 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  $\text{Ag}3d_{5/2}$  maximum is located at 367.9 eV in the XPS spectrum of the  $\text{MWCNT}/\text{MnO}_x\text{-Ag}$  composite (Fig. 2, *b*). This position may correspond both to  $\text{Ag}_2\text{O}$  and to metallic Ag [8]. Since the composite was synthesized in an oxidizing medium,  $\text{Ag}_2\text{O}$  is more likely to be present in this composite.

The  $\text{C}1s$  XPS spectrum of the  $\text{MWCNT}/\text{MnO}_x\text{-Ag}$  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  $\text{MWCNT}/\text{MnO}_x$  composite in [3].

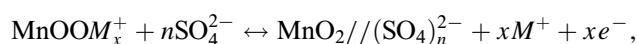
The capacitance characteristics of electrodes based on MWCNTs and composites were analyzed using the galvanostatic charge–discharge method, and it was found (Fig. 3, *a*) that the  $\text{MWCNT}/\text{MnO}_x\text{-Ag}$  composite electrode has the highest specific capacitance: 146.0, 106.5, and 65.0 F/g at a current density of 0.1, 0.5, and 1 A/g, respectively. Thus, the specific capacitance of the  $\text{MWCNT}/\text{MnO}_x\text{-Ag}$  electrode decreases by  $\sim 56\%$  as the discharge current density increases by a factor of 10. The specific capacitance of the  $\text{MWCNT}/\text{MnO}_x$  composite electrode decreases by  $\sim 60\%$ . 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  $\text{MWCNT}/\text{MnO}_x\text{-Ag}$  electrode may be



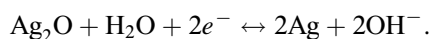
**Figure 3.** *a* — Dependences of the specific capacitance on the discharge current density of electrodes based on MWCNTs (1),  $\text{MWCNT}/\text{MnO}_x$  composite (2), and  $\text{MWCNT}/\text{MnO}_x\text{-Ag}$  composite (3). Galvanostatic charge-discharge curves measured at a current density of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

attributed to a higher electrical conductivity of manganese oxide doped with  $\text{Ag}_2\text{O}$ . The specific conductivity of  $\text{Ag}_2\text{O}$  ( $10^3$  S/m [10]) is much higher than the conductivity of  $\text{MnO}_2$  ( $10^{-9}$  S/m [11]). The cyclic stability of the  $\text{MWCNT}/\text{MnO}_x\text{-Ag}$  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  $\sim 6\%$  in 1000 charge–discharge cycles.

A pair of peaks (A1 and A2) are present in the charge and discharge CV curves of the  $\text{MWCNT}/\text{MnO}_x$  electrode (curve 1 in Fig. 3, *b*). These peaks are induced by reversible redox reactions involving manganese oxide



where  $M^+$  are  $\text{Na}^+$  cations from the electrolyte or  $\text{K}^+$  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/ $\text{MnO}_x$ -Ag composite (curve 2 in Fig. 3, *b*) is joined by peak B1 ( $\sim 500$  mV). The corresponding peak B2 ( $\sim 240$  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  $\text{Ag}_2\text{O}$  with electrolyte ions. The positive working electrode may support reversible redox reactions



Peak A2 is lacking in the discharge curve of MWCNT/ $\text{MnO}_x$ -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/ $\text{MnO}_x$ -Ag composite is attributable both to a higher electrical conductivity and to redox reactions involving silver oxide.

### Acknowledgments

Equipment provided by the Omsk Regional Shared Research Center of the Siberian Branch of the Russian Academy of Sciences and the National Research Center „Kurchatov Institute“ was used in the study.

### Funding

This study was supported by the Omsk State Technical University Development Program („Priority 2030“).

### Conflict of interest

The authors declare that they have no conflict of interest.

### References

- [1] D. Wu, X. Xie, Y. Zhang, D. Zhang, W. Du, X. Zhang, B. Wang, *Front. Mater.* **7**, 1 (2020). DOI: 10.3389/fmats.2020.00002
- [2] M.N. Rantho, M.J. Madito, K.O. Oyedotun, D.J. Tarimo, N. Manyala. *AIP Adv.*, **10** (6), 065113 (2020). DOI: 10.1063/5.0011862
- [3] P.M. Korusenko, S.N. Nesov, *Appl. Sci.*, **12** (24), 12927 (2022). DOI: 10.3390/app122412827
- [4] J.H. Kim, C. Choi, J.M. Lee, M.J. Andrade, R.H. Baughman, S.J. Kim, *Sci. Rep.*, **8**, 13309 (2018). DOI: 10.1038/s41598-018-31611-2
- [5] A.I. Romanenko, O.B. Anikeeva, T.I. Buryakov, E.N. Tkachev, K.R. Zhdanov, V.L. Kuznetsov, I.N. Mazov, A.N. Usoltseva, *Phys. Status Solidi B*, **246** (11-12), 2641 (2009). DOI: 10.1002/pssb.200982267
- [6] N. Yu, H. Yin, W. Zhang, Y. Liu, Z. Tang, M.-Q. Zhu, *Adv. Energy Mater.*, **6** (2), 1501458 (2015). DOI: 10.1002/aenm.201501458
- [7] M.C. Biesinger, B.P. Payne, A.P. Grosvenor, L.W.M. Lau, A.R. Gerson, R.S.C. Smart, *Appl. Surf. Sci.*, **257** (7), 2717 (2011). DOI: 10.1016/j.apsusc.2010.10.051
- [8] *NIST X-ray Photoelectron Spectroscopy Database* [Electronic source], <https://srdata.nist.gov/xps/>
- [9] N.G. Bobenko, V.V. Bolotov, V.E. Egorushkin, P.M. Korusenko, N.V. Melnikova, S.N. Nesov, A.N. Ponomarev, S.N. Povoroznyuk, *Carbon*, **153**, 40 (2019). DOI: 10.1016/j.carbon.2019.06.104
- [10] V. Gaubert, H. Gidik, N. Bodart, V. Koncar, *Sensors*, **20** (6), 1739 (2020). DOI: 10.3390/s20061739
- [11] C.M. Julien, A. Mauger, *Nanomaterials*, **7** (11), 396 (2017). DOI: 10.3390/nano7110396
- [12] D.G. Gromadskyi, *J. Chem. Sci.*, **128** (6), 1011 (2016). DOI: 10.1007/s12039-016-1084-2

*Translated by D.Safin*