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Composites based on carbon materials and manganese oxide for asymmetric supercapacitors

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The electrochemical characteristics of composite materials based on multi-walled carbon nanotubes (MWCNTs), manganese oxide and carbon black as an electrode material for supercapacitors (SC) are investigated. Composites with a specific capacitance of 120−65 F/g (at a current density of 0.2−1 A/g) were obtained. The asymmetric SC based on one of the obtained composite materials showed high cyclic stability at a maximum voltage of 1.5 V in an aqueous electrolyte, as well as competitive energy and capacitance characterisics.

Keywords: supercapacitors, composites, carbon nanotubes, manganese oxide, carbon black.

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Supercapacitors (SC) are electrochemical current sources with high specific capacitance, cyclic stability, and the ability to quickly accumulate and release the accumulated charge. As a rule, the materials for SC electrodes are various carbon materials that have high chemical stability in various electrolytes. Asymmetric SCs are devices in which charge accumulation occurs not only due to the formation of a electrical double layer (EDL), but also due to reversible oxidationreduction reactions occurring on the surface of the electrode during interaction with the electrolyte [1]. In such devices the positive electrode contains an electrochemically active component (metal oxide, conducting polymer, etc. [2]). One of the most accessible and promising metal oxides is manganese oxide — its specific theoretical capacitance is more than 1300 F/g [2]. However, the low conductivity of manganese oxide limits its wide use as an electrode material for supercapacitors. To solve this problem methods are being developed for producing composite materials in combination with conductive carbon materials [2].

In this paper, the electrochemical properties of composites based on MWCNTs, manganese oxide and carbon black are studied. We used MWCNTs produced by the Catalysis Institute of the Siberian Branch of the Russian Academy of Sciences (Russia, Novosibirsk). To form a composite based on manganese oxide and MWCNTs (Mn/CNT), the method of soaking in an aqueous solution $KMnO_4$ was used under the conditions presented in [3]. In this paper, using electron microscopy and X-ray analysis, it was shown that non-stoichiometric manganese oxide is quite uniformly distributed over the surface of MWCNTs in the form of continuous layers $\sim 10{-}20$ nm thick. According to energy-dispersive X-ray analysis (not presented in this paper), the mass content of MWCNTs in the resulting composite is ~ 45 wt%. The formation of electrodes for electrochemical studies was carried out using polyvinylidene difluoride as a binder (10 wt%). As an active material in the manufacture of electrodes, a mixture of Mn/CNT composite and carbon black (CB) grade „Printex XE-2B“ was used, containing the latter in amounts of 10 and 50 wt%. For comparison, electrodes based on MWCNTs, CB and Mn/CNT composite were also prepared. The used CB grade has a high specific surface area ($\sim 1000\,m^2/g$, versus $\sim 360\,m^2/g$ for MWCNTs), which can improve the capacitive characteristics. Besides, adding CB to the composite reduces the cost of the material. The analysis of the electrochemical characteristics of the electrodes was carried out using the galvanostatic method, as well as cyclic voltammetry (CV) using a three-electrode scheme [3]. The characteristics of asymmetric SC with electrodes based on the obtained composites were studied using a two-electrode circuit in „Swagelok“ type cell. In this case, the positive and negative electrodes had the same weight. Filter paper was used as a separator. For all electrochemical measurements aqueous solution 1M Na_2SO_4 was used as the electrolyte. Electrochemical measurements were carried out using a potentiostat-galvanostat „Elins P-40X“ (Russia, Zelenograd). The specific capacitance (C_s, F/g) of the electrodes, as well as of the asymmetric SC was determined from the discharge curves of galvanostatic charge-discharge as $C_s = (I \cdot \Delta t)/(\Delta U \cdot m)$, where I — discharge current (A), Δt — discharge time (s), ΔU — potential window (V), m — weight of active material. The calculation of the specific energy (W_s, W · h/kg) of the asymmetric SC was carried out using the formula: $W_s = C_s \Delta U^2/7.2$ [4]. For brevity of presentation, electrodes of various compositions were assigned corresponding designations (Table).

Composition and characteristics of work electrodes

Designation	Composition of electrode	R, %*
1P	CB „Printex XE-2B“	70
CNT	MWCNT	86
Mn/CNT	Composite based on manganese oxide and MWCNT	44
Mn/CNT + 0.1P	Composite Mn/CNT with addition 10 wt% CB „Printex XE-2B“	65
Mn/CNT + 0.5P	Composite Mn/CNT with addition 50 wt% CB „Printex XE-2B“	82

Note*: R — ratio of specific capacitance, at current density 1.0 and 0.2 A/g.

CV curves of the 1P and CNT electrodes (Figure 1, *a*) have a quasi-rectangular shape, which is characteristic of charge accumulation in the EDL [1]. These electrodes have a low but stable specific capacitance, which decreases by at least 20% when the current density increases by 5 times (see Figure 1, *b*, as well as the value R in the Table). The area limited by the CV curves of electrodes containing MWCNTs coated with manganese oxide is noticeably larger compared to the CV curves of carbon electrodes (Figure 1, *a*). This indicates a higher specific capacitance of these materials, which is obviously associated with the occurrence of redox reactions during the interaction of manganese oxide with electrolyte ions. CV curve of Mn/CNT electrode has rather high values of peak current density, but its shape differs significantly from quasi-rectangular. This indicates the high electrical resistance of the material. CV curve of Mn/CNT_0.1P electrode (Figure 1, *a*) has maximum area and peak value of current density. It is likely that carbon black globules provide additional channels for the transport of charges formed as a result of reversible redox reactions with the participation of manganese oxide. However, the shape of CV curve indicates that the electrochemical behavior of this material is not satisfactory. For Mn/CNT and Mn/CNT_0.1P electrodes the rapid decrease in specific capacitance is observed with discharge current density increasing (see Figure 1, *b*, as well as the value R in the Table). At the same time, high values of specific capacitance (over 100 F/g) at low values of discharge current density indicate the high electrochemical activity of manganese oxide in these composites. The shape of CV curve of Mn/CNT_0.5P electrode (Figure 1, *a*) is close to quasi-rectangular, which indicates sufficient conductivity of the material for charges formed as a result of reversible redox reactions. This is also confirmed by the high stability of the specific capacitance value with increase in discharge current density (see Figure 1, *b*, as well as the value R in the Table). The relatively low specific capacitance for this electrode is most likely due to the lower content of manganese oxide in its composition.

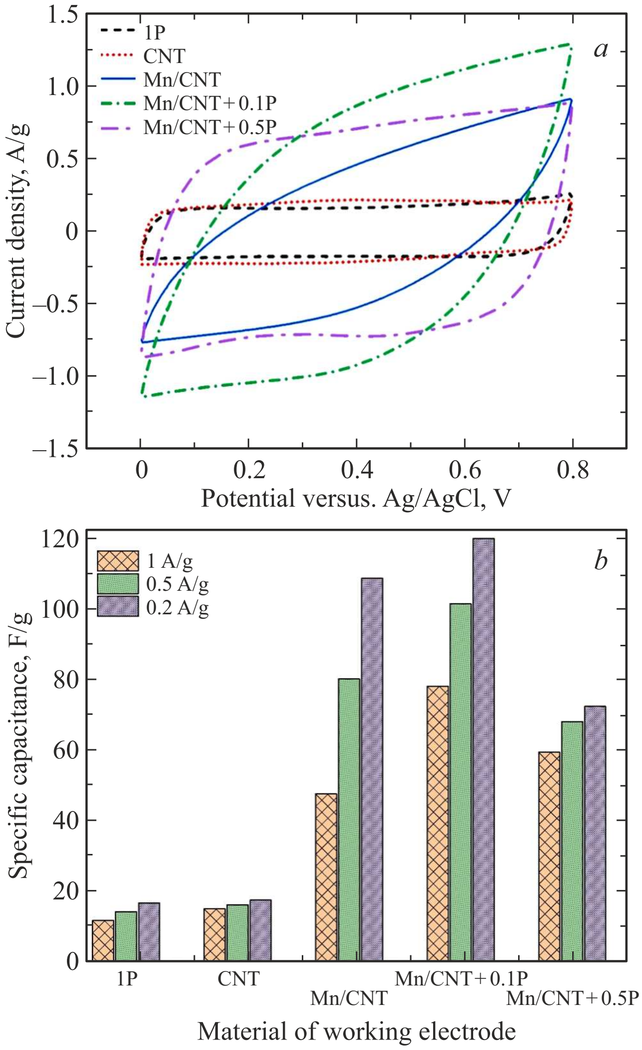

Figure 1. *a* — CV characteristics of the electrodes measured at scan rate of 10 mV/s; *b* — specific capacitance of electrodes at different values of discharge current density.

To manufacture the positive electrode of the asymmetric supercapacitor the Mn/CNT_0.5P composite was used, which showed the greatest stability of the specific capacitance (∼ 75–60 F/g) in the range of discharge current density 0.2–1.0 A/g. Besides, from an economic point of view, such electrode composition is the most beneficial, since it contains the smallest amount of relatively expensive component — MWCNT. The negative electrode was made on the basis of CB „Printex XE-2B“. The combination of electrodes with different nature of electric charge accumulation makes it possible to expand the range of maximum voltage in the cell by increasing the overvoltage of hydrogen/oxygen evolution [4,5]. In this paper the maximum voltage at the terminals of the asymmetrical SC was 1.5 V. During electrochemical measurements the cell was initially stabilized by cycling in the potentiostatic charge/discharge mode for 400 cycles at potential sweep rate of 5 mV/s. Next, CV curves were measured at different

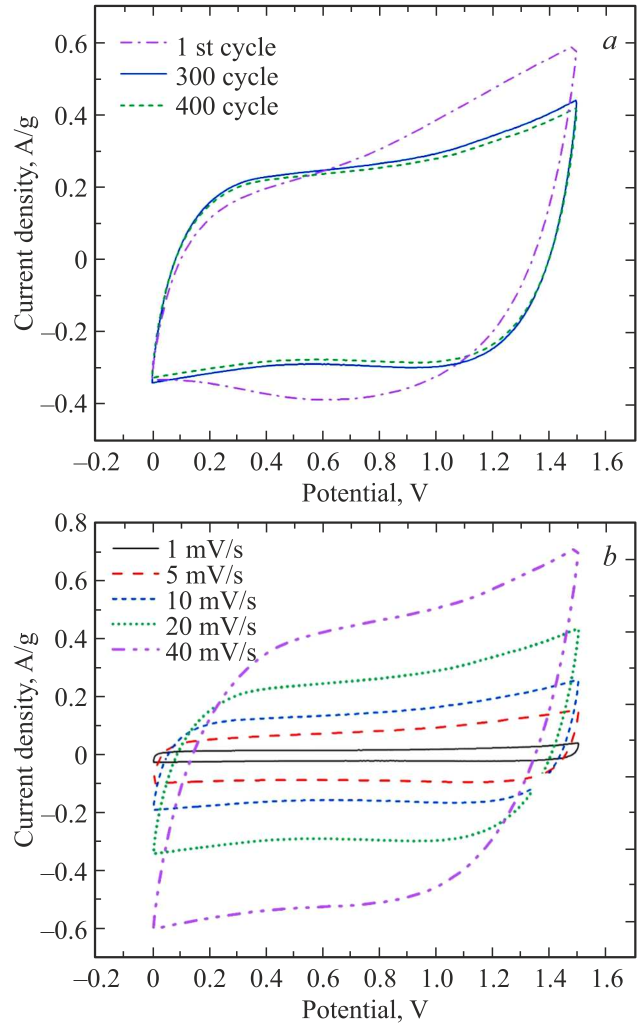

Figure 2. *a* — CV curves of asymmetric supercapacitor cell at the initial stages of measurements (potential sweep rate 5 mV/s); *b* — family of CV curves measured at different potential scan rates.

potential sweep rates in the range 1–40 mV/s. Then a series of measurements was carried out in galvanostatic mode at different current densities.

At the initial stages of CV characteristics measurement on the cathode branch in the potential range from 0.8 to 1.5 V, a sharp increase in current density is observed (Figure 2, *a*), which can be associated with the water decomposition in the electrolyte. However, further change in the shape of the CV characteristic and its stabilization over 400 cycles indicates that most likely, in the initial cycles of potentiostatic charge/discharge, irreversible additional oxidation of non-stoichiometric manganese oxide occurs with the formation of Mn(IV) oxide during interaction with the electrolyte according to the reactions presented in [6]. Further, the stable capacitance of the cell is apparently ensured by the occurrence of reversible redox reactions with the participation of manganese dioxide [4–6]. Analysis of CV characteristics measured at different potential scan rates (Figure 2, *b*) indicates good electrochemical behavior — the proportional increase is observed in the area limited by the CV curve with increase in potential scan rate.

When analyzing the characteristics of the asymmetric SC by the galvanostatic charge/discharge method, we studied the dependence of the specific capacitance and self-discharge rate on the time of additional charge in the potentiostatic mode at maximum voltage (1.5 V) after charging SC to this voltage in the galvanostatic mode. The results showed that the discharge time, and accordingly the capacitance increase with increase in additional charge time (Figure 3, *a* and *b*). With an increase in the current density of the galvanostatic charge/discharge, this effect manifests itself more significantly. Increasing the time of the additional potentiostatic charge also ensures a decrease in the spontaneous discharge of the cell (see insert in Figure 3, *b*). The additional SC charge at constant voltage ensures deeper diffusion of electrolyte ions into the pores of

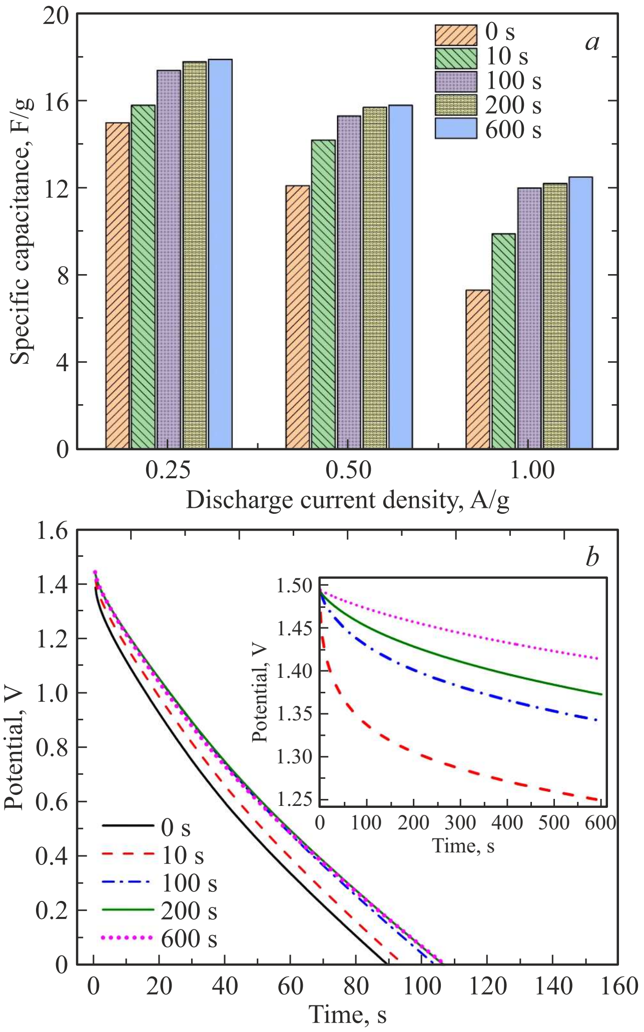

Figure 3. Characteristics of an asymmetric SC vs. the time of additional charge in potentiostatic mode at maximum voltage (1.5 V): *a* — specific capacitance at different current densities; *b* — discharge curves measured at charge/discharge current density of 0.25 A/g (the insert shows the self-discharge curves of asymmetric SC).

the electrodes [7], which increases the charge accumulated in the cell, both due to the formation of EDL and the occurrence of redox reactions.

Thus, the paper shows that composites based on MWCNTs coated with layers of non-stoichiometric manganese oxide can be promising as a base material, as well as electrochemically active additive to other types of carbon materials in the production of supercapacitor electrodes. The specific capacitance of the composites obtained in this paper is $\sim 65-120$ F/g, which is comparable to the specific capacitance of similar materials [4], and is several times higher than the value for the carbon materials used in the formation of the composites ($\sim 15-20$ F/g). The maximum values of the specific capacitance and energy of the experimental asymmetric supercapacitor are ~ 18 F/g and $\sim 6\,\mathrm{W\cdot h/kg}$, respectively, which is comparable to values for currently produced devices [8].

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Conflict of interest

The authors declare that they have no conflict of interest.

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