Electrochemical characteristics of electrode materials based on polyaniline and multi-walled carbon nanotubes decorated with manganese oxide

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In this work, the electrochemical characteristics of polyaniline composites with multi-walled carbon nanotubes (original and decorated with manganese oxide) were studied using cyclic voltammetry and galvanostatic cycling. The composites were synthesized by in-situ chemical oxidative polymerization of aniline in rhenium acid. The composite containing manganese oxide showed higher specific capacitance values (308 versus 238 F/g at 1 A/g) and better self-discharge characteristics (voltage drop 5% versus 20% in 1 h). After 1000 charge/discharge cycles, the specific capacity of both composites decreases by 13% due to the incomplete reversibility of the leucoemeraldine/emeraldine redox reactions.

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

Polyaniline (PANI) has several oxidation-reduction states [1], which makes it a promising material for super-capacitor electrodes. PANI is chemically resistant, stable in air, non-toxic, easy to obtain and low cost. The introduction of carbon nanotubes (CNTs) into the PANI matrix leads to a significant increase in electrical conductivity, specific surface area, and mechanical strength [2,3]. At the same time, CNTs have a low specific capacitance ($10-100$ F/g [3]). Decorating their surface with manganese oxide (theoretical capacity MnO_2 1370 F/g [4]) makes it possible to increase the capacitance characteristics several times [5–7]. It is also known that electrode materials based on PANI and MnO_x show high capacitive characteristics [8]. In this paper, a comparative study of the electrochemical characteristics of composites based on PANI, as well as the original and multi-walled carbon nanotubes (MWCNTs) decorated with manganese oxide nanoparticles, was carried out.

In paper we used multi-walled carbon nanotubes of MWCNT-1 brand (BIC SB RAS) with a characteristic outer diameter of 8 nm and $5-25\,\mu$m long. MWCNTs decorated with manganese oxide ($MWCNTs@MnO_x$) were prepared by the method described in [7].

The synthesis of polyaniline composites with MWCNTs and $MWCNTs@MnO_x$ ($PANI/MWCNT$ and $PANI/MWCNT@MnO_x$) was carried out by chemical oxidative polymerization of aniline in the presence of 1M rhenium acid ($HReO_4$). The choice of rhenium acid is due to the instability of manganese oxide in hydrochloric acid, traditionally used in the synthesis of PANI. Immediately before the synthesis of the composites, the nanotubes were dispersed by ultrasound in an aqueous solution of $HReO_4$ for 1 h. Freshly distilled aniline was added to the suspension and treated with ultrasound for another 30 min. The mass ratio of CNT : aniline is $1:9$. The resulting suspension was cooled in an ice bath to $0°$C. To initiate polymerization, the aqueous solution of ammonium persulfate was added dropwise to this suspension with constant stirring. The molar ratio of ammonium persulfate : aniline $-1:1$. The synthesis was carried out in ice bath with stirring with a magnetic stirrer for 1 h. The reaction product was washed repeatedly with distilled water, ethyl alcohol and acetone, and then dried in air at room temperature.

Electrodes for electrochemical tests were formed by composites pressing on a platinum current collector under a pressure of 10 MPa. Electrochemical measurements were carried out using P-40X potentiostat (Elins, Russia). The studies were carried out in a three-electrode cell with a platinum counter electrode and a silver-chloride reference electrode. 1M HCl was used as the electrolyte. Measurements by cyclic voltammetry (CV) were carried out in the voltage range from 0 to 800 mV (relative to Ag/AgCl). Measurements in galvanostatic mode were carried out at charge/discharge current densities from 0.5 to 5 A/g. After reaching a potential of 800 mV on the electrode when charging in galvanostatic mode, the charge was carried out in potentiostatic mode at a given voltage for 30 min. This is necessary for a more complete charge of the electrode, which has pseudocapacitance. After this, the electrode was discharged in galvanostatic mode to 0 mV. The specific capacitance values based on the results of CV and galvanostatic measurements were calculated using the methods described in [9]. The conductivity of the composites was measured using the four-probe method.

Volt-amperograms of the obtained composites (Figure 1) have peaks characteristic of materials with
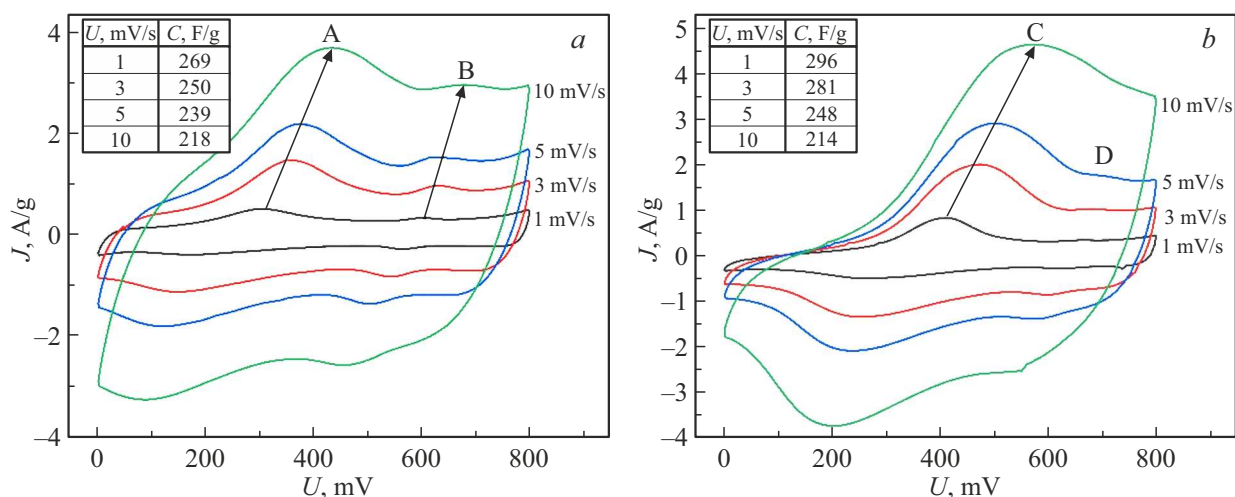
Figure 1. CV dependences measured at different potential scan rates: *a* — PANI/MWCNT and *b* — PANI/MWCNT@MnO$_x$.

pseudocapacitance. For PANI/MWCNTs peaks A and B (Figure 1, *a*) on the charging branch of the CV correspond to the oxidation-reduction reaction leucoemeraldine/emeraldine and the formation of the pair *n*-benzoquinone/hydroquinone, respectively [10]. In the voltamperogram of PANI/MWCNT@MnO$_x$ (Figure 1, *b*) peak C is most likely a combination of redox reactions leucoemeraldine/emeraldine PANI and redox reactions manganese (IV) oxide with electrolyte ions. The latter appeared at 500−600 mV on MWCNT/MnO$_x$ exposed to rhenium acid [7]. Peak C is shifted to the positive potential region by approximately 100 mV relative to peak A in the CV curve of PANI/MWCNT. This shift is due to the strong oxidizing properties of manganese oxide. Peak D (analogue of peak B) is visible only at low potential sweep rates, and it is also shifted to the positive region. As the sweep speed increases, the peaks on the charging branch of CV shift to the right, and on the discharge branch to the left, which is natural. In this case, a linear relationship is observed between the current of oxidation-reduction peaks and the scanning speed. The specific capacitance value for PANI/MWCNT@MnO$_x$ at low sweep speeds is higher than that of PANI/MWCNT (inserts in Figure 1, *a* and *b*). However, at sweep speed of 10 mV/s, the specific capacitance values of the composites are almost identical. This may be due to different redox rates in PANI and MnO$_x$, as well as different conductivity and morphology of the materials.

The cyclic stability of materials was studied in galvanostatic mode at current densities of 5 A/g. The electrode was charged to 800 mV and discharged to 0 V without additional charging in potentiostatic mode. Figure 2 shows the results of these measurements, as well as the appearance of the CV curves at different sweep speeds after testing (Figure 2 inserts). For both composites, the decrease in specific capacity was about 13%. The height of peaks B and D after 1000 charge/discharge cycles remains almost unchanged. At the same time, the height of peaks A and C decreases significantly. This indicates incomplete reversibility of redox data, which manifests itself in a decrease in the specific capacity of the material.

Figure 3, *a* shows the dependence of the specific capacitance of materials on the discharge current density in the galvanostatic mode. The specific capacitance value for PANI/MWCNT@MnO$_x$ is on average by 19% higher than that of the composite based on the original nanotubes. This indicates a significant role of manganese oxide in providing the pseudocapacitance of the electrode material.

Figure 3, *b* shows the decrease in potential on the electrodes during 1 h during self-discharge (in galvanostatic mode in the absence of current load). The measurements were carried out after 30 min of additional charging of the electrode in potentiostatic mode at a potential of 800 mV. As
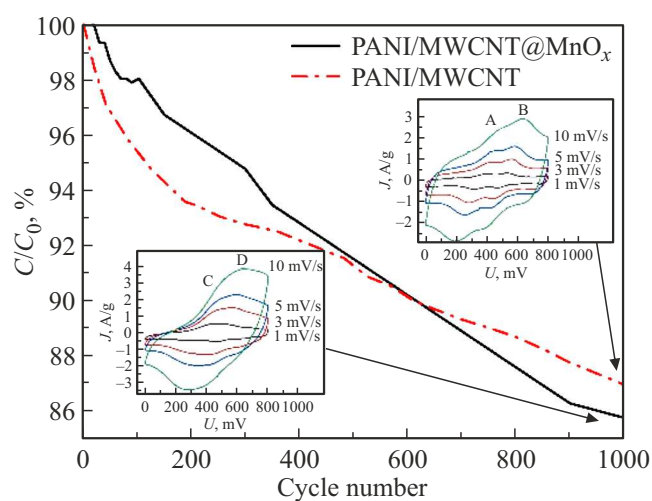
Figure 2. Cyclic stability of PANI/MWCNT and PANI/MWCNT@MnO$_x$ composites. In inserts: CV dependences after 1000 charge/discharge cycles.
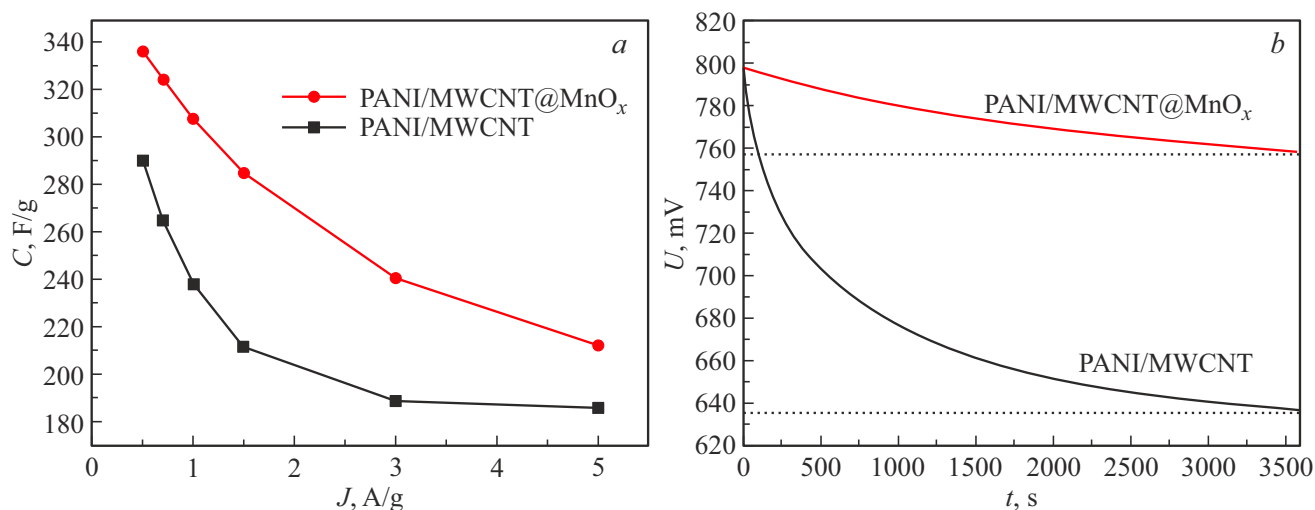
Figure 3. *a* — dependence of the specific capacity of PANI/MWCNT and PANI/MWCNT@MnO$_x$, *b* — self-discharge curves of PANI/MWCNT and PANI/MWCNT@MnO$_x$ electrodes.

can be seen, the voltage drop for PANI/MWCNT@MnO$_x$ was only 5%, while the voltage at the PANI/MWCNT electrode decreased by 20%. Self-discharge of supercapacitors can be caused by Faraday reactions, ohmic leakage or charge redistribution [11]. The specific conductivity of the PANI/MWCNT@MnO$_x$ composite, measured by the four-probe method, is by order of magnitude lower than the specific conductivity of PANI/MWCNT (0.01 and 0.12 S/cm, respectively), which is due to the low conductivity MnO$_x$. This reduces the possibility of ohmic leakage in PANI/MWCNT@MnO$_x$.

Thus, in this paper PANI/MWCNT and PANI/MWCNT@MnO$_x$ composites were synthesized and their main electrochemical characteristics were studied. The specific capacity of both composites decreases by $\sim$ 13% after 1000 charge/discharge cycles due to the incomplete reversibility of the redox reactions of leucoemeraldine/emeraldine in PANI. The use of composite of MWCNT decorated with manganese oxide nanoparticles in the synthesis of the composite provides an increase in specific capacity by 19% on average at various discharge currents due to additional Faraday processes. The improvement in self-discharge performance of PANI/MWCNT@MnO$_x$ may be due to a decrease in the probability of ohmic leakage due to the low conductivity of manganese oxide.

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Conflict of interest

The authors declare that they have no conflict of interest.

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