

# Effect of the method to form electrodes of supercapacitors based on polyaniline composite with carbon nanotubes at their electrochemical characteristics

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Electrochemical characteristics were studied for the electrodes made by mixing polyaniline composite in the form of a salt and a base reinforced with multi-wall carbon nanotubes, with technical carbon and multi-wall carbon nanotubes with and without a binder. Addition of carbon fillers causes increase in the speed capacity of electrodes by more than 50%. When the technical carbon is added to the composite in the form of a base, the specific capacity grows from the value of 349.7 F/g to 384.6 F/g due to redistribution of the polymer along the surface of the technical carbon.

**Keywords:** carbon nanotubes, technical carbon, specific capacity, pseudocapacity, speed capacity.

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Polyaniline (PANI) composites with multi-wall carbon nanotubes (MWCNT) — are a promising material to be used as supercapacitor (SC) electrodes [1]. Combination of the high electrochemical activity of PANI with the unique electroconductive 1D-structure of MWCNT provides for high capacitance characteristics of composites. Besides, MWCNTs have improved mechanical characteristics, which provides for reinforcement of the polymer and makes it more suitable for technological operations related to making electrodes for SCs. Addition of various carbon fillers (graphene, carbon nanofibers, technical carbon (TC)) and binding components to the composite may additionally improve capacitance and mechanical characteristics and to reduce the cost of the obtained electrode material [2]. Therefore, the search for the optimal combinations of additives to PANI providing for improved capacitance and mechanical properties is a priority task. This paper studies the capacitance characteristics of electrodes based on PANI, MWCNT and TC formed under different conditions.

The paper used MWCNTs of MWCNT-1 grade (Federal Research Center, Institute of Catalysis, Siberian Branch of the Russian Academy of Sciences). PANI composite with MWCNT-1 (PANI/MWCNT-1) was synthesized by method of chemical oxidative polymerization of aniline in hydrochloric acid. MWCNTs in the amount of 1 g were dispersed by ultrasound in 300 ml 1 M HCl for 1 h. Then 10 ml of freshly distilled aniline was added to this suspension, and the reaction flask was placed on a magnetic mixer with an ice bath. After the solution was cooled down to 0°C, 25 g of ammonium persulfate (APS) dissolved in 60 ml 1 M HCl was added thereto in drops. The synthesis was carried out under constant mixing and cooling of the reaction solution on the ice bath for 4 h.

The legend for electrodes and their composition are provided in Table 1. All electrodes for electrochemical tests were produced by material pressing at pressure of 5 MPa. For carbon filler the TC of OMCARB CH-1000 grade (made by LLC „Omsktekhuglerod“) or MWCNT-1 were used in the amount of one-for-one by mass to the composite. Polyvinylidenefluoride (PVDF) used as a binder was dissolved in 1-methyl-2-pyrrolidone (NMP) in the amount of 10 mg per 0.5 ml and was added to 100 mg of the electrode material. PANI/MWCNT composite in the form of a base was obtained by dedoping of the source composite in the aqueous solution of ammonia [3].

Electrochemical studies were performed using potentiostat P-40X (Elins, Russia) in three-electrode cell with platinum counter electrode and silver chloride reference electrode on air at room temperature. HCl with concentration of 1 M was used as electrolyte. Specific capacity  $C_s$  of electrodes was calculated from cyclic current-voltage curves (CVC) using formula [4]:

$$C_s = \frac{\int_{U_0}^U I(U) dU}{2 \cdot m \cdot v \cdot \Delta U}, \quad (1)$$

where  $I$  — current,  $m$  — electrode mass,  $v$  — potential scanning speed,  $\Delta U$  — potential window. The integral in the numerator is numerically equal to full area limited by the current-voltage curve in potential window of 0 to 0.8 V.

SEM-image of the produced PANI/MWCNT is shown in Figure 1. A web of chaotically interwoven MWCNTs coated with a PANI layer with thickness of  $\sim 40$  nm is observed. And PANI agglomerates without tubes are absent at the same time.

Analysis of elemental composition and chemical condition of PANI/MWCNT composite prior to electrochemical tests

Table 1. Composition of electrodes

Electrode	Components	Binder
E1	PANI/MWCNT composite	—
E2	PANI/MWCNT+CH-1000 composite	
E3	PANI/MWCNT+MWCNT-1 composite	
E4	PANI/MWCNT composite	PVDF composite
E5	PANI/MWCNT+CH-1000 composite	
E6	PANI/MWCNT+MWCNT-1	
E7	PANI/MWCNT composite in the form of base+CH-1000	
E8	PANI/MWCNT composite in the form of base+MWCNT-1	

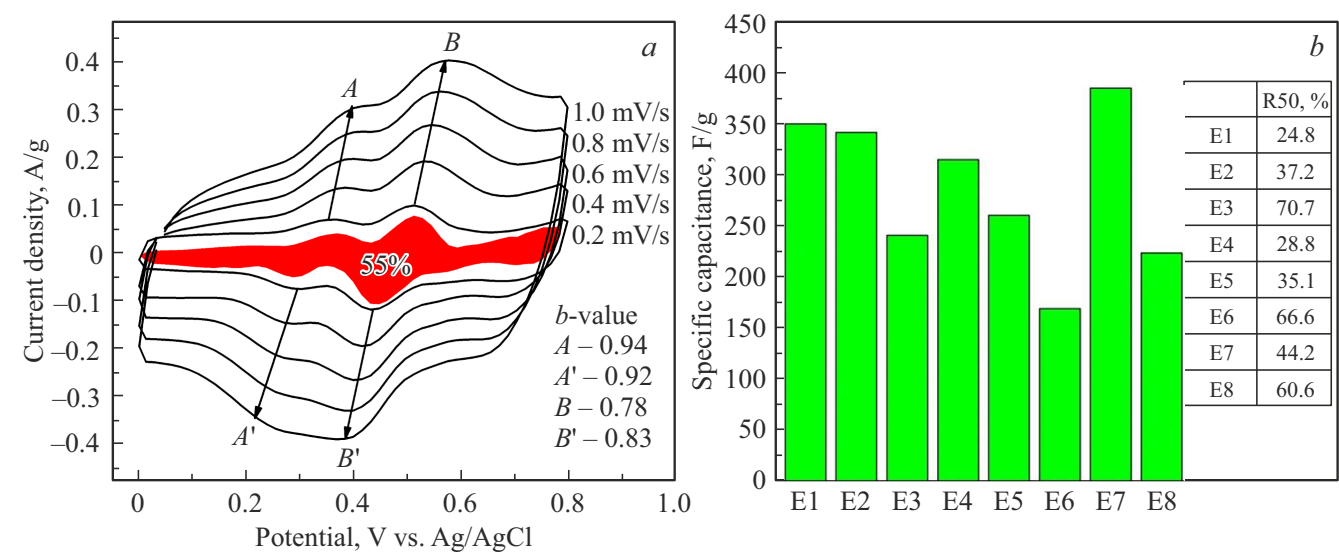


Figure 3. *a* — current-voltage curves of electrode E1 in 1M HCl at various scanning speeds of potential; *b* — values of maximum specific capacity and speed capacity of electrodes.

and after 1000 cycles of galvanostatic charge/discharge at specific current 1 A/g were studied by method of X-ray photoelectron spectroscopy (XPS) (Figure 2). Both presented panoramic spectra show lines of carbon, nitrogen, oxygen and chlorine (Table 2). The source electrode

Table 2. Elemental composition of electrodes by XPS data

Electrode	Concentration, at%				
	C1s	N1s	O1s	Cl2p	S2p
E1	75.4	11.1	10.4	1.1	2.0
E1 after 1000 cycles of charge/discharge	75.3	6.5	14.7	3.5	—

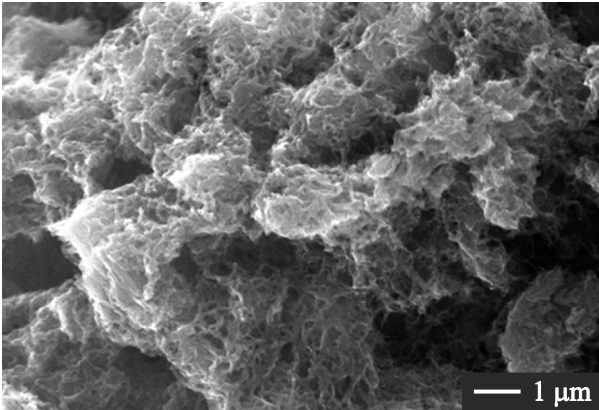
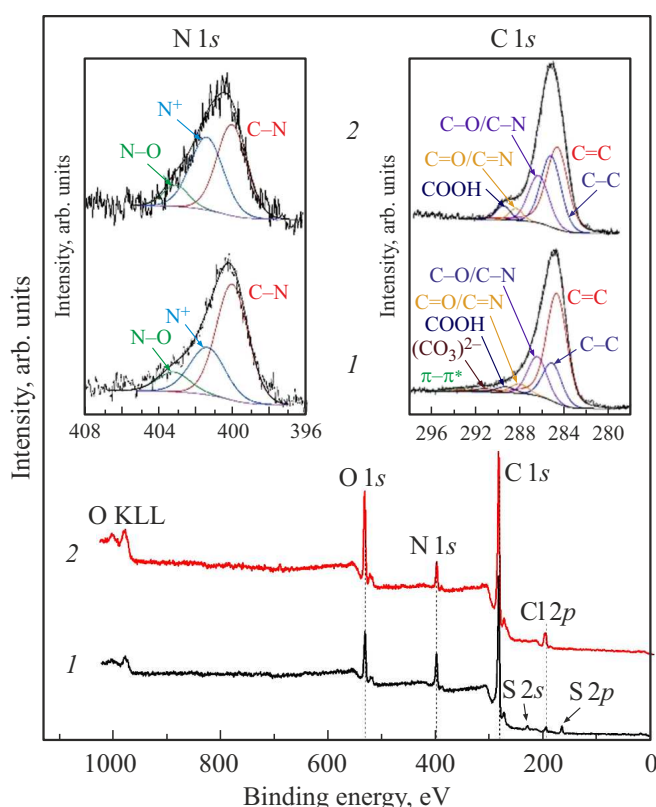


Figure 1. SEM-image of PANI/MWCNT composite.

spectrum contains lines of sulfur, the positions of which comply with SO<sub>4</sub>-conditions that may be related to the APS and aniline reaction products (H<sub>2</sub>SO<sub>4</sub>, (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>). Therefore, practically all oxygen in the initial composite is related to sulfur. After tests of the cyclic stability, the electrode composition demonstrates absence of sulfur, reduction of nitrogen concentration, and oxygen and chlorine concentrations, on the other hand, increase. The detailed analysis of the change in the chemical condition of electrodes was carried out using XPS spectra C1s and N1s (Figure 2, inserts). In C1s spectrum of the source electrodes the components are observed, which correspond



**Figure 2.** XPS-spectra of the initial PANI/MWCNT composite (1) and after 1000 cycles of galvanostatic charge-discharge (2). The inserts show the approximation of N1s and C1s spectra.

to the different chemical conditions of the carbon specific for PANI. Besides, the spectrum demonstrates shake up-satellite, the presence of which is specific for materials with well-ordered  $sp^2$ -structure [5]. C1s spectrum of the electrode after the tests of cyclic stability has a much larger width. The decrease in the relative intensity of the component corresponding to  $sp^2$ -carbon is observed. Components related to carbon-oxygen bonds have higher relative intensity compared to the spectrum of the source sample, which is well matched with the results of the quantitative analysis. N1s spectra demonstrate three components, which correspond to nitrogen within C–N and N–O-bonds, and also cation-radical  $N^+$  [6]. One can see that after the tests of cyclic stability the component related to  $N^+$  increases greatly, which correlates to the increases content of chlorine in the composite. At the same time one may note that the relative intensity of the component corresponding to NO increases insignificantly. Therefore, in the process of cyclic charge/discharge the carbon-oxygen bonds increase greatly, which is seemingly related to the additional irreversible oxidation of carbon in polymer. Such PANI oxidation causes the reduction in the specific capacity by  $\sim 15\%$  after 1000 cycles of galvanostatic charge/discharge.

Electrode current-voltage curves from PANI/MWCNT composite without fillers (E1), measured at different  $v$ , are

given in Figure 3, *a*. The anode branch demonstrates two current maxima, the position of which at  $v = 1 \text{ mV/s}$  is equal to  $U = 0.40 \text{ V}$  (A) and  $U = 0.58 \text{ V}$  (B). They are related to oxidation reactions of PANI leucoemeraldine-emeraldine (A) and hydroquinone-benzoquinone (B) [7]. The cathode branch of current-voltage curves demonstrates two response maxima at  $U = 0.24 \text{ V}$  (A') and  $U = 0.38 \text{ V}$  (B'), corresponding to recovery processes.

For CVA-measurements the current value depends on the potential scanning speed according to the power law:

$$i = av^b, \quad (2)$$

where  $i$  — current,  $v$  — potential scanning speed,  $a$  and  $b$  — coefficients determining the intercalation nature [8]. The value of degree 0.5 corresponds to the electrochemical process limited by diffusion, and value 1 corresponds to the process limited by charging with double electric layer (DEL). Values  $b$  for peaks A and A' are equal 0.93, for peaks B and B' — 0.8, which indicates the considerable share of the charge accumulated at the expense of DEL.

Figure 3, *b* provides the values of maximum specific capacity of electrodes and parameter R50 (speed capacity, %), which numerically characterizes the percentage of the maintained capacity as the scanning speed increases 50 times. Note that the specific capacity of used TCs and MWCNTs is 76 and 17 F/g, accordingly, and hardly depends on the scanning speed. The electrode based on PANI/MWCNT (E1) composite has specific capacity 349.7 F/g at 0.2 mV/s, which decreases down to 86.7 F/g as the scanning speed increases to 10 mV/s ( $R50 = 24.8\%$ ). The reasons for the low speed capacity are the low specific surface area and conductivity of PANI/MWCNT composite. Addition of TC (E2) and MWCNT (E3) to the composite causes increase of R50 by 50 and 180%, accordingly. At the same time the specific capacity E2 is practically the same as E1, and the specific capacity of electrode E3 is noticeably lower and is 240.4 F/g, which may be due to the low specific capacity of MWCNTs as such. TC has higher specific surface area compared to MWCNT (1100 m<sup>2</sup>/g vs 360 m<sup>2</sup>/g), which provides for the high current of DEL charge, hardly depending on the potential scanning speed. Besides, MWCNTs, due to their 1D-structure, help to form the lengthy conductivity channels, providing for high values of R50.

Addition of PVDF as a binding component provides for increase of strength characteristics of electrodes. However, this component, as a rule, causes deterioration of capacitance characteristics of materials. In case of electrodes E4, E5 and E6, the reduction of specific capacity is observed relative to electrodes with the same composition, but without a binder (E1, E2, E3). Besides, the speed capacity of electrodes varies insignificantly. Decrease of the specific capacity in this case is related to the reduction of the available surface reducing DEL.

PANI in the form of a base within PANI/MWCNT composite is highly soluble in NMP. Seemingly, when E7

and E8 electrodes are formed (when PVDF dissolved in NMP is added), the polymer is partially dissolved with subsequent deposition of carbon materials on the surface. This causes the increase in the polymer surface area available for the electrolyte, and accordingly to the growth of the value of the specific capacity relative to E5 and E6 electrodes. Due to the large specific area CH-1000 ( $\sim 1100 \text{ m}^2/\text{g}$ ) compared to MWCNT-1 ( $\sim 360 \text{ m}^2/\text{g}$ ) the effect of PANI redistribution on the surface of the carbon filler for E7 electrode provides for considerable growth of the capacity. The specific capacity and speed capacity of E7 electrode is noticeably higher compared to the electrode based on the composite without the filler (E1). Besides, the availability of the binder in the composition of E7 provides for higher mechanical characteristics of the electrode. Therefore, formation of supercapacitor electrodes with the use of the binder is to be preferably performed from PANI composites in the form of a base with addition of carbon fillers with the large specific surface area.

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### Conflict of interest

The authors declare that they have no conflict of interest.

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