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Effect of finely dispersed carbon black on the polyaniline electrochemical properties

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Received July 11, 2024
Revised August 6, 2024
Accepted August 8, 2024

In this work, three-component electrode materials based on a composite of polyaniline with multi-walled carbon nanotubes and carbon blck were obtained, which are promising for supercapacitor electrodes. The method proposed in the work allows achieving a uniform distribution of polyaniline over the surface of carbon black particles in the form of layers with a thickness of $\sim 5\,\mathrm{nm}$, which ensures high porosity and specific surface area. It is shown that the presence of carbon black in the material composition leads to a decrease in the degree of defectiveness of the polymer structure. With an increase in the proportion of carbon black, the electrochemical characteristics of electrode materials increase: the speed capacity of the electrodes (up to 81%) and their cyclic stability (92%) compared to a composite that does not contain carbon black (25% and 78%, respectively).

Keywords: composites, XPS, cyclic voltammetry, specific capacitance.

DOI: 10.61011/PSS.2024.09.59225.188

1. Introduction

Development of high-efficiency devices for energy accumulation and storage is one of ways to overcome energy crises and to solve ecological problems. Supercapacitors (SC) have high specific power, long service life, operation and ecological safety due to possibility of using non-toxic and non-flammable components. Due to their capacity characteristics SCs are inferior to lithium-ion batteries. The difference in characteristics can be reduced by use of the materials having pseudocapacitive properties. In such materials energy is accumulated due to inversible Faraday redox reaction [1,2].

The conductive polymer polyaniline (PANI) is one of such materials. Its polymer chain comprises N-phenyl-p-phenylenediamine and quinonediimine blocks. Depending on their ratio three main form of PANI are distinguished: leucoemeraldine (unoxidized form), emeraldine (semi-oxidized form) and pernigraniline (fully oxidized form). Transition between these forms leads to charge accumulation. Maximum theoretical capacity of PANI is about 2000 F/g [3], but in practice it is not achievable due to some reasons. One of the main reasons is insufficiently high specific surface area and relatively low conductivity. Besides, PANI use is limited by its physical properties: low plasticity, mechanical stability, poor solubility in major of solvents [4]. Creation of composites based on PANI and various conductive carbon materials with high specific surface area ensures more efficient use of the polymer for different applications, including for SCs [5,6]. The conductive carbon materials, like PANI, have interfaced π-system of electrons ($sp2$-carbon). This facilitates the formation of non-covalent-bonds between composite components during their interaction ($\pi-\pi^*$-stacking) [7]. At that morphology and structure, as well as properties of PANI significantly depend on structure of carbon template, on which polymerization occurs.

In present paper we suggested a two-stage method of formation of electrode materials for SC based on PANI, multi-wall carbon nanotubes (MWCNT, CNT) and highly dispersive conductive carbon black (CB). At the first stage the aniline is polymerized on surface of MWCNTs having rather high degree of orderliness of carbon $sp2$-structure. At the second stage the formed PANI is transferred on CB surface. Such approach ensures formation of composites comprising low-defect PANI and having high specific surface area and conductivity.

2. Experiment

PANI/CNT composite was synthesized by method of *in situ* chemical oxidative polymerization of aniline in hydrochloric acid. MWCNT of grade MUNT-1 (BIC of SB RAS) was dispersed by ultrasound in 1 M HCl for 1 h to separate MWCNT bundles formed during nanotubes synthesis. Fresh-distilled aniline in amount by 10 times exceeding weight of MWCNT was added to the suspension.

Then test jar with reagents was loaded on the magnetic stirrer with ice water bath. After the solution cooling to 0°C upon continuous stirring ($1000\,\mathrm{min}^{-1}$) the ammonium persulphate (APS) dissolved in 1 M HCl was added to it by droplets. The solution temperature and stirring rate were maintained permanent for entire time of composite synthesis. After 4 h the reaction product was filtered through a Buchner funnel and washed with distilled water, ethyl alcohol and acetone to remove low-molecular PANI oligomers and unreacted reagents. The obtained powder was dried at pressure ~ 1 Pa and temperature 80°C for 4 h.

In obtained composite PANI presents in form of conductive emeraldine salt, which has extremely low solubility in most solvents. To transform PANI into soluble form of emeraldine base the composite was dedoped in a weak ammonia solution for 24 h at room temperature. Further the composite was washed with water until complete removal of the ammonia, and dried at pressure ~ 1 Pa and temperature 80°C for 4 h.

Then in quantity of obtained composite in glass-tube 1-methyl-2-pyrrolidone (NMP) was added to solve the polymer. After 15 h to solution that differs by fark-blue tint the technical carbon of grade OMCARB CH-1000 (Omsk Carbon group) was added in amount of 200, 300 and 500% relative to compposite. This grade of superconducting technical carbon has the following characteristics: specific surface area $\sim 1100\,\mathrm{m}^2/\mathrm{g}$ and particles size ~ 28 nm. For carbon black dispersion the obtained suspension was subjected to ultrasound action for 1 h and further held in air at room temperature with periodic stirring. After 24 h in all three glass tubes the transparent solvent was observed. This confirms that complete solved PANI was redistributed over surface of carbon black. The obtained three-component composites PANI/MWCNT/CB (designated as C+2CB, C+3CB and C+5CB, which corresponds to carbon black content 200, 300 and 500%) washed through Buchner funnel and dried at pressure ~ 1 Pa and temperature 80°C for 4 h. In case of composite with minimum content of carbon black (C+2CB) after washing on filtered paper we can observe a slight, almost imperceptible blue tint, indicating trace amounts of PANI dissolved in NMP. Thus, addition of such amount of CB to composite PANI/CNT used in study is minimum required for sedimentation of complete polymer from solution under given conditions.

To form electrodes from composites PANI/CNT and PANI/MWCNT/CB as a binder polyvinylidenfluoride in amount of 10% was added, preliminary solved in NMP. Electrodes were manufactured by mass rolling using roller. The obtained layer about 0.5 mm thick was cut to electrodes with size 5×10 mm, they were dries at pressure ~ 1 Pa and temperature 110°C for 16 h. Just before electrochemical tests the electrodes were held in 1 M HCl for 30 min wot wetting, and doping of PANI.

Electrochemical studies were performed by method of cyclic voltammetry (CV) using potentiostat P-40X (Elins, Russia) in three-electrode cell with platinum counter electrode and silver chloride reference electrode. 1 M HCl was used as the electrolyte. Before measurements of CV curves the electrodes were stabilized in potentiostatic mode at potential sweep rate 40 mV/s. Measurements were performed are potential sweep rate of 0.2 to 10 mV/s in potential window of 0 to 0.8 V. The specific capacitance (C_s) of electrodes was calculated by formula

$$C_s = \frac{\int I dU}{2 \cdot m \cdot v \cdot \Delta U}, \tag{1}$$

where I — current (A), m — electrode weight (g), v — potential sweep rate (V/s), ΔU — potential window (V) [8]. Here integral is numerically equal to full area limited by CV curve in potential window of 0 to 0.8 V.

Morphology of obtained materials was studied by method of scanning-electron microscope (SEM) using microscope JSM 6610-LV (Omsk Regional Shared Equipment Centre SB RAS) at accelerating voltage 20 kV.

The chemical state and composition of the composite were analyzed using X-ray photoelectron spectroscopy (XPS). XPS spectra were measured using non-monochromatic X-ray Al-Kα-radiation with photon energy 1486.6 eV (Spectrometer LAS 3000, OSC SB RAS) at pressure in analysis chamber $\sim 2 \cdot 10^{-6}$ Pa. Effective depth of analysis was ~ 5 nm. The obtained spectra were analyzed using special software CASA XPS. During decomposition of C1s-spectra the component corresponding to states of *sp*2-hybridized carbon was approximated using Doniak–Sundzhik function [9], rest components — using mixed Gaussian–Lorentz function.

3. Results and discussion

The morphology of composite PANI/CNT (Figure 1, *a*) is presented by mesh of randomly intertwined fibers, comprising MWCNT coated with polymer layer 30−50 nm thick. In composite no large agglomerates of polymer not associated with MWCNT are observed. Formation of polymer layers on surface of low-defect carbon nanotubes ensures supposition of their positive effect on the degree of ordering of the polymer structure.

Morphology of all three composites PANI/MWCNT/CB is similar (Figure 1, *b*) and repeats the morphology of carbon black. This allows us to talk about the polymer redistribution from the MWCNT surface to the surface of the carbon black particles. At average size of CB particles ~ 28 nm (specified by manufacturer), the particles size in composites reaches ~ 50 nm. This indicates the polymer redistribution over CB surface.

Figure 2 shows survey XPS-spectra of analyzed samples. The results of the quantitative analysis performed using the spectra data by method of elemental sensitivity coefficients are listed in Table.

In survey spectrum of CB (Figure 2, curve *1*) lines C1s (~ 285 eV) and O1s (~ 532 eV) are observed. Oxygen content in the surface layer of this sample as per results

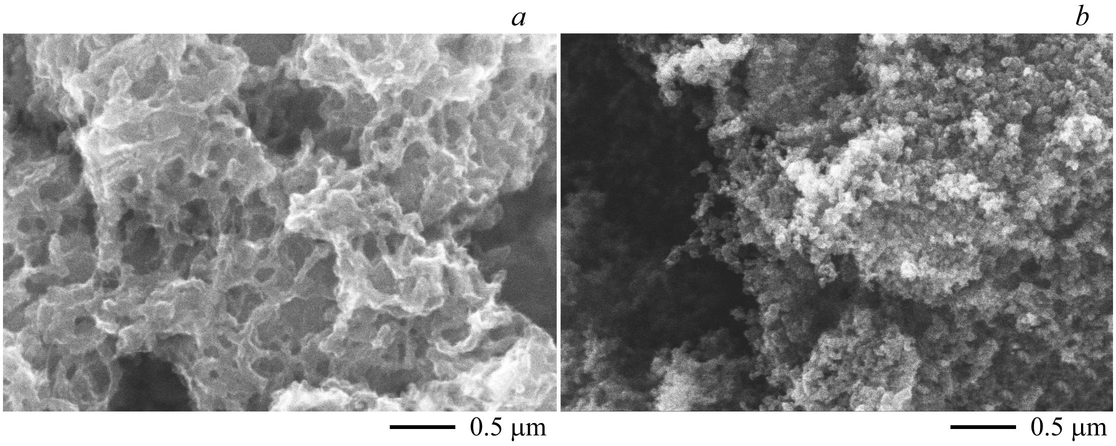

Figure 1. SEM-images *a*) of composite PANI/CNT and *b*) composite C+5CB.

Element composition of samples according to XPS data

Sample	Concentration, at.%				
	C1s	O1s	N1s	Cl2p	S2p
Carbon black	96.0	4.0	–	–	–
PANI/CNT	75.0	10.3	11.6	1.1	2.0
C+2CB	92.6	4.0	3.2	−0.2	
C+3CB	94.3	2.6	2.9	–	0.2
C+5CB	95.8	1.7	2.4	–	0.1

of quantitative calculation is 4.0 at.% (see Table). In survey spectrum of sample PANI/CNT (Figure 2, curve *2*) additionally to lines of oxygen and carbon also line N1s (~ 398 eV), Cl2p (~ 198 eV) and lines S2s and S2p (~ 230 and 168 eV respectively) are observed. Chlorine presence is associated with its embedding into PANI structure in form of emeraldine salt [10]. Sulfur presence in sample is due to presence in PANI of residues of APS used during aniline polymerization. Considering thickness of PANI layer on MWCNT surface in composite PANI/CNT, we can state that XPS-spectra in this case characterize the composition and chemical state of polymer.

The relatively high sulfur content of PANI/CNT sample suggests that the bulk of the oxygen present is likely due to the presence of residual APS ($(NH_4)_2S_2O_8$), and only small part of oxygen is associated with partial oxidation of PANI, see Table). In spectra of three-component composites (Figure 2, curves *3–5*) less intense photoelectron lines of nitrogen and sulfur, as compared to spectrum PANI/CNT (Figure 2, curve *2*) are observed. At that with increase in amount of carbon black in materials the proportional decrease in nitrogen concentration is observed (see Table). This, together with SEM data, indicates PANI distribution over surface of carbon black particles in form of rather thin layer (about thickness of layer analyzed by XPS method, which is several units of nanometers).

Figure 3 presents photoelectron spectra of line C1s of „pure“ PANI samples (which polymerization was performed under conditions described in Section 2, but without MWCNT use) and composite PANI/CNT. Spectra have same asymmetric form typical for *sp*2-hybridized carbon full width at half maximum (FWHM) in spectrum of „pure“ PANI by more than 0.2 eV is higher (Figure 3, *a*), as compared to spectrum of PANI/CNT (Figure 3, *b*). Besides, in both spectra local maximum and bond energy ~ 291.5 eV is observed, it is satellite of „shake up“ ($\pi-\pi^*$), presented in XPS-spectra of carbon materials consisting of aromatic rings [11,12]. Intensity of this satellite characterizes the degree of ordering of carbon crystalline structure. In composite spectrum this maximum has the highest intensity (Figure 3). Spectra comprise components corresponding to different chemical states of carbon: comprising C=C-bonds (bond energy

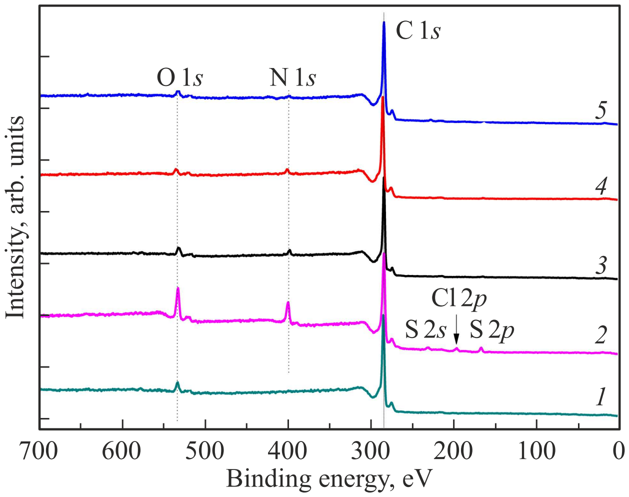

Figure 2. Survey XPS-spectra: curve *1* — carbon black; *2* — PANI/CNT; *3* — C+2CB; *4* — C+3CB; *5* — C+5CB.

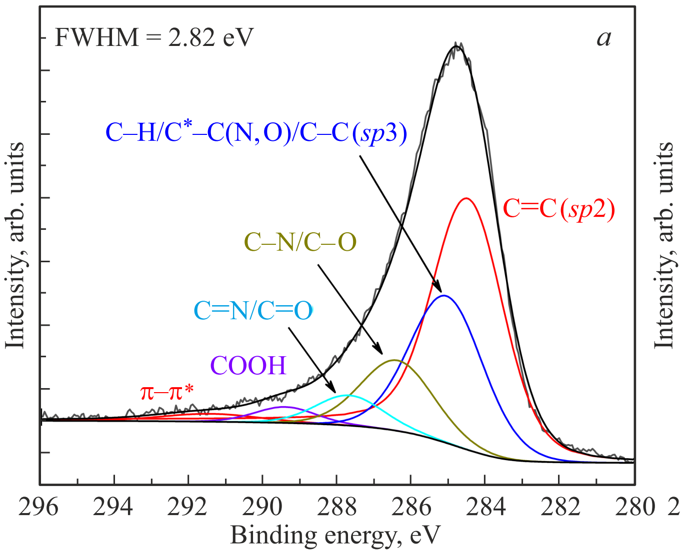

Figure 3. XPS-spectra C1s *a*) of sample PANI and *b*) composite PANI/CNT.

284.5 ± 0.1 eV, C1); comprising C−H-bonds, and located near heteroatoms ($C^*-C(O,N,H)$) and comprising C=C-bonds with *sp*3-hybridization of valence electron shells (bond energy 285.1 ± 0.1 eV, C2); comprising single C−N-(amines) and C−O-bonds (bond energy 286.4 ± 0.1 eV, C3); comprising double C=N- (imines) and C=O-bonds (bond energy 287.8 ± 0.1 eV, C4); COOH-groups (bond energy 288.5 ± 0.1 eV, C5) [12–16]. We see that spectrum of „pure" PANI (Figure 3,*a*) differs from spectrum of composite PANI/CNT, first of all, by high relative intensity of component at 285.1 ± 0.1 eV, associated, particularly, with „defect" in polymer structure. Set of XPS data (value FWHM, intensity of „shake of" satellite and results of decomposition) indicate more higher degree of ordering of the structure of polymer formed on surface of carbon nanotubes as compared with „pure" PANI.

Figure 4 presents XPS-spectra C1s of „pure" carbon black, and three-component composites. Spectrum of CB has asymmetric form, and „shake up"-satellite (291.5 eV), this indicates rather high degree of carbon graphitization in this material. The decomposition results indicate that portion of carbon in composition of C=C-bonds is ∼ 55%.

The decomposition results indicate that relative content of graphitized carbon (component C1) in spectra of three-component composites is higher as compared with carbon black (Figure 4). We also see that FWHM values in spectra of three-component composites are comparable, and even somewhat lower as compared to FWHM value in spectrum of carbon black. This fact is rather noticeable, as increase in portion of heteroatoms in the carbon material (determined by deposition of nitrogen-containing polymer on surface of carbon black) shall lead to increase in FWHM value relative to spectrum of „pure" CB. We assume that FWHM value decreasing and increase in relative portion of C=C can indicate the deposition on surface of carbon black particles

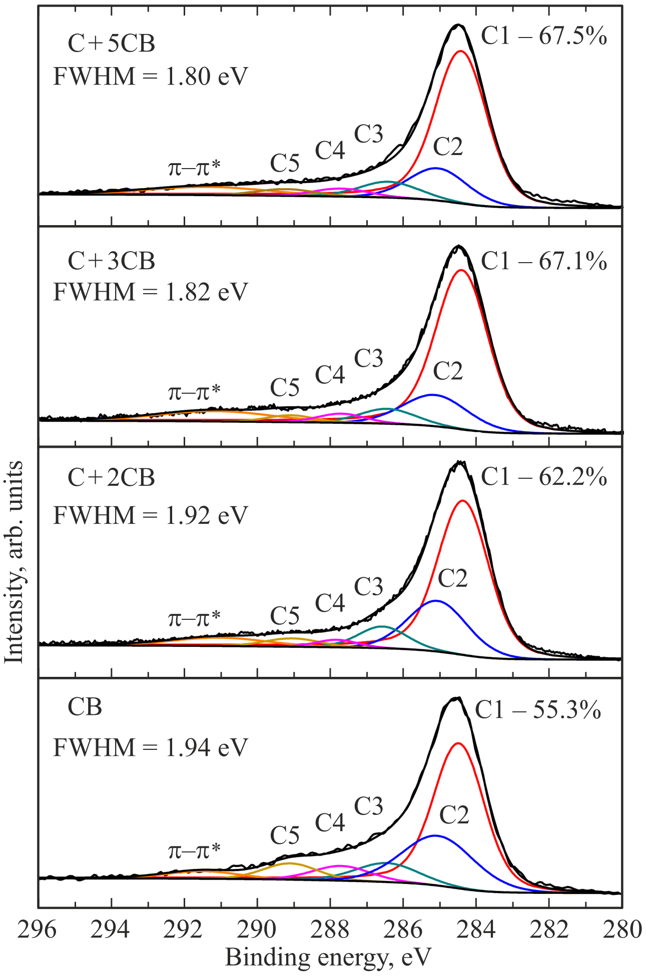

Figure 4. XPS-spectra C1s of materials based on PANI/CNT and CB.

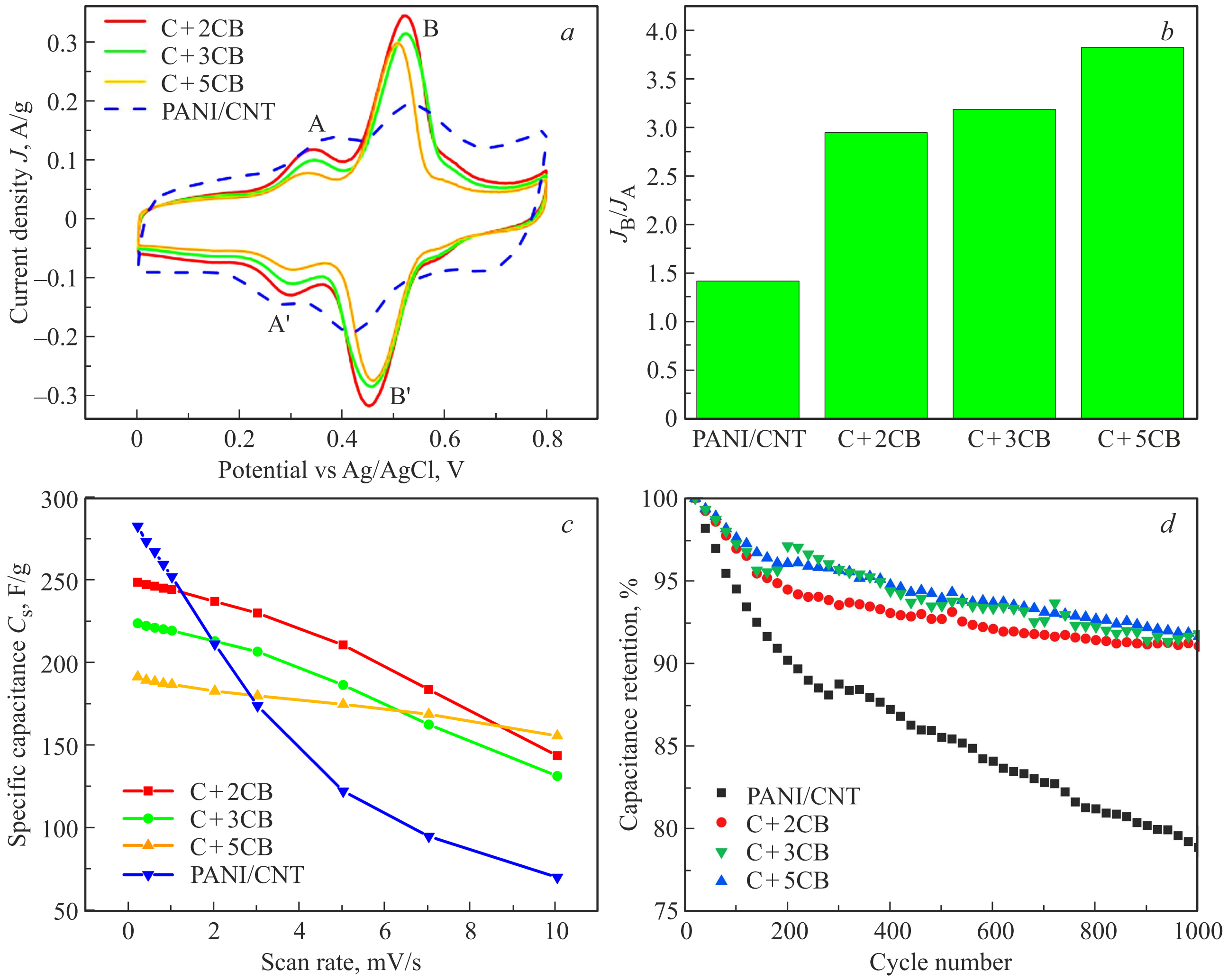

Figure 5. Results of electrochemical measurements of characteristics of electrodes PANI/CNT, C+2CB, C+3CB and C+5CB by CV method: *a*) CV curves measured at sweep rate 0.4 mV/s; *b*) values of ratios of current densities J for peaks B and A on CV curves; *c*) specific capacitance C_s vs. potential sweep rate; *d*) relative cycle stability.

of well structured layer of PANI pre-formed on surface of low-defect MWCNT. It was shown previously [17,18] that decrease in FWHM value in the C1s XPS spectrum indicates increase in the electrical conductivity of the carbon material.

Voltamperograms for composite PANI/CNT and composites PANI/MWCNT/CB are given in Figure 5, *a*. Symmetrical form of CV curves indicates reversibility of reaction running on electrode surface. On all curves we see peaks typical for redox reactions processes running with the participation of PANI in acid electrolytes, that correspond to transformation of leucoemeraldine-emeraldine (A and A′) and crosslinking reactions between polymer chains, as well as oxidation-reduction reactions of hydroquinone-benzoquinone (B and B′) [19–21]. In CV curves of composites containing carbon black these peaks are more clear, this indicates data of oxidation-reduction reaction in more narrower window of potentials. This, most likely, is associated with increase in accessibility of PANI surface for electrolyte ions, and increase in the material conductivity due to polymer distribution over surface of porous matrix of high-conductivity carbon black. The latter assumption is in good agreement with the fact that the greatest offset of the oxidation peaks A and B to the region of low potential values (reduction peaks A′ and B′ — to the region of high potential values) if observed on CV curve of composite C+5CB, which has maximum content of carbon black (Figure 5, *a*).

In CV curves of three-component composites the peak values of current density for the peak B (B′) are higher by more than three times as compared to peak A (A′), but in case of PANI/CNT the ratio of appropriate peaks is close to 1 (Figure 5, *b*). We see that this ratio increases with increase in content of carbon black in material (Figure 5, *b*). This, obviously, indicates the most intense running of reversible reactions of hydroquinone-benzoquinone or crosslinking of polymer chains due to PANI distribution over the surface of carbon black particles. The above experimental data on the structure and composition of three-component composites suggest that increase in the amount of charge stored due to these reactions (B/B′) (as compared to composite PANI/CNT), occurs due to increase in contact area of the polymer, distributed over surface of carbon black, with electrolyte. We suppose that on interphase interfaces the reaction is also possible of crosslinking the polymer chains with graphitized areas on the surface of carbon black particles. This may be indicated, in particular, by noticeable increase in the ratio of peak currents A and B for the composite with the maximum content of CB (Figure 5,*a* and *b*). Fir this composite, having, presumably, minimum thickness of PANI, the interface PANI-CB covers major portion of bulk material participating in electrochemical interaction with electrolyte.

The capacity characteristics of electrodes were measured in range of sweep rates of 0.2 to 10 mV/s (Figure 5,*c*). The speed capability of the electrodes was estimated as the portion of the preserved specific capacity with increase in the potential sweep rate by 50 times (from 0.2 to 10 mV/s). Composite PANI/CNT has specific capacity (C_s) 282 F/g at potential sweep rate 0.2 mV/s, which significantly decreases at increase in potential sweep rate by 50 times (to 70 F/g). The speed capability in this case is 25%. Value C_s at 0.2 mV/s for three-component composites decreases proportionally to the increase in the content of carbon black in the composition of the materials and is 248.1, 223.3 and 191.0 F/g for electrodes C+2CB, C+3CB and C+5CB respectively (Figure 5,*c*). However, it is clearly seen that with increase in the potential sweep rate to 3 mV/s and more, the values of specific capacity for all three-component composites are higher compared to the composite PANI/CNT. Moreover, the highest value of the specific capacity (155.4 F/g) at high potential sweep rate (10 mV/s) is observed for the composite with maximum content of carbon black (C+5CB). The speed capability for electrodes C+2CB, C+3CB and C+5CB is $\sim$ 58, 59 and 81% respectively.

The cyclic stability of the electrodes was estimated as the portion of the retained specific capacity after 1000 cycles of potentiostatic charge/discharge at potential sweep rate of 10 mV/s (Figure 5,*d*). Electrode PANI/CNT keeps 78%, but electrodes containing carbon black keep over 92% of the initial value C_s. Thus, CB in three-component composites additionally leads to stability increasing.

4. Conclusion

Structure and electrochemical properties are studied of composites based on composite PANI/CNT and high-conductive fine carbon black obtained by two-stage method. At first stage the aniline polimerization is performed on MWCNT surface, this ensures PANI formation with higher degree of structure ordening as compared to polymer formed without MWCNT use as template. In the second stage, the dedoped polymer was rather uniformly re-deposited from the solution from MWCNT surface onto the surface of the technical carbon while maintaining the high porosity and surface area typical for the latter. By XPS method we show that PANI deposition on surface of carbon black particles, apparently, leads to increase in degree of ordering of PANI structure itself.

By CV method the significant increase in contribution of redox reactions of polymer chains into charge accumulation for the three-component composites was determined. It is suggested that this may be due to increase in the area of the electrochemically active surface of PANI, as well as the possible occurrence of crosslinking reaction at PANI-CB interfaces. Value of specific capacity of composite PANI/CNT at the potential sweep rate 0.2 mV/s (282 F/g) is higher than in three-component composites (248.1, 223.3 and 191.0 F/g for electrodes C+2CB, C+3CB and C+5CB, respectively). But, upon increase in potential sweep rate to 10 mV/s the maximum value C_s (155.4 F/g) is observed for electrode with maximum content of carbon black (C+5CB), but C_s of composite PANI/CNT is 70 F/g. So, speed capability of three-component composites ($\sim$ 58, 59 and 81% for electrodes C+2CB, C+3CB and C+5CBrespectively) is significantly higher then in PANI/CNT (25%). Tests of cycle stability also show the advantages of composite PANI/MWCNT/CB as compared to PANI/CNT. After 1000 cycles of potentiostatic charge/discharge composites C+2CB, C+3CB and C+5CB keep over 92% of initial value C_s, but for composite PANI/CNT — only 78%.

The obtained in study three-component composites are promising when developing stable SC with high energy-capacity characteristics. In this case, the main component (by mass content) of the composites is carbon black (up to 500 wt%), which increases the mechanical characteristics of materials for carrying out technological operations, and also reduces their cost (relatively to „pure“ polymer).

Funding

The study was performed under framework of State Assignment of Omsk Scientific center of Siberian Branch of Russian Academy of Science (state registration number of project 121021600004-7). In study equipment of Omsk Regional Shared Equipment Centre of the Siberian Branch of RAS was used.

Conflict of interest

The authors declare that they have no conflict of interest.

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Translated by I.Mazurov