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Enhanced performance of a flexible supercapacitor due to a combination of the pseudocapacitances of both a PANI/MWCNT composite electrode and a gel polymer redox electrolyte

G. P. Shumakovich,[a] O. V. Morozova,[a] M. E. Khlupova,[a] I. S. Vasil'eva,[a] E. A. Zaitseva[b] and A. I. Yaropolov*[a]

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In this paper, a combination of the pseudocapacitances of both an enzymatically synthesized polyaniline/multi-walled carbon nanotube (PANI/MWCNT) composite with a core shell structure and a gel polymer redox electrolyte was used to improve the specific characteristics of a supercapacitor (SC). The gel of polyvinyl alcohol in sulfuric acid containing sodium 1,2-naphthoquinone-4-sulfonate (PVA/H_2SO_4/NQS) was used as a gel polymer redox electrolyte. Electrochemical studies have shown that the redox behavior of NQS is a diffusion-controlled and quasi-reversible process. The PANI/MWCNT composite in 13 mM NQS solution had a high specific capacitance of *ca.* 1100 F g^{-1} at a scan rate of 5 mV s^{-1} (three electrode cell configuration). The symmetrical flexible SC device based on the PANI/MWCNT composite and the PVA/NQS gel redox electrolyte had a power density of 1.8 kW kg^{-1} and an energy density of 23.3 W h kg^{-1}. After 3000 cycles of potential scanning, the specific capacitance of the SC device decreased by less than 7%.

1. Introduction

Energy accumulation and storage is a problem fundamental to the further development of various technical devices, such as hybrid electric vehicles, mobile electronic devices, solar panels, memory backup systems, medical appliances, *etc.*

Supercapacitors (SC) are currently the most promising devices for this purpose. A classic SC is an electrochemical double electric layer capacitor in which carbon materials with a high specific surface area are used as electrodes.[1–3] Such SCs have high power density, whereas their energy density is much lower than that of Li-ion batteries. Certain metal oxides or conducting polymers which ensure the faradaic reaction were added to carbon materials to enhance the specific capacitance and energy density of SC devices.[4–8] The combination of the double electric layer capacitance and the faradaic reaction can significantly improve the specific characteristics of SC devices. However, such devices based on conducting polymers show an insufficient stability in charge/discharge cycles. Therefore, it is essential to increase the stability of SC and improve its characteristics. The cycling stability of the composite can be enhanced by forming a thin polyaniline film on the surface of carbon nanomaterials.[9]

Another way of increasing the energy density and the device stability is to add redox active compounds into the electrolyte.[10–18] The method originally developed for carbon-based double layer supercapacitors with electrochemically inert electrodes[14,15] has recently been used to enhance the capacitance of polyaniline-based supercapacitors.[16–18] The introduction of hydroquinone into the conventional electrolyte H_2SO_4 reported in[16] resulted in a 2-fold increase in the specific capacitance of polyaniline supercapacitors and in a dramatic enhancement of their cycling stability, which in the authors's opinion can be explained by: firstly, the additional pseudocapacitance of hydroquinone–quinone couples; secondary, the improvement of the ionic conductivity of the electrolyte, and finally, the reactions proceeding between the redox electrolyte components and electrochemically active material of the composite electrode. A similar effect was observed with the benzoquinone-hydroquinone redox couple.[17] High pseudocapacitance of this polyaniline–benzoquinone–hydroquinone supercapacitor is attributed to the fast and reversible charge-transfer process between the polyaniline-modified electrodes and the quinones. Simultaneously, the enhancement of the long-term stability can be explained by a lower extend of unfavorable redox processes in polyaniline. Thus, quinones show promise as redox-additives to electrolytes.

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[a] Bach Institute of Biochemistry, Research Center of Biotechnology of the Russian Academy of Sciences, Leninsky Ave. 33, bld. 2, 119071 Moscow, Russia. E-mail: yaropolov@inbi.ras.ru; Fax: +7 495 954 2732; Tel: +7 495 954 4477

[b] Department of Chemistry, Lomonosov Moscow State University, Leninskie Gory 1/3, 119991 Moscow, Russia

To improve the characteristics of a flexible supercapacitor we used sodium 1,2-naphthoquinone-4-sulfonate (NQS) as a redox-active additive.

2. Experimental section

2.1 Materials

Aniline (Labtech, Russia) was distilled under reduced pressure before use. Poly(vinyl alcohol) (hydrolyzed 99+%, M_w 89 000–98 000), *N*-phenyl-*p*-phenylendiamine, ABTS, sodium 1,2-naphthoquinone-4-sulfonate (Sigma-Aldrich), *p*-toluenesulfonic acid monohydrate (Acros Organics), H_2SO_4, HNO_3 (Chimmed, Russia) were used without further purification. Flexible graphite foil (thickness 0.2 mm) was purchased from Unichimtek (Russia). Multi-walled carbon nanotubes "Taunit M" (NanoTechCentre Ltd, Tambov, Russia) were used after treatment with hot 70% nitric acid (MWCNT). PANI/MWCNT composite was obtained by *in situ* enzymatic aniline polymerization. The laccase from the fungus *Trametes hirsuta* (Wulfen) Pilát CF-28 was purified to homogeneity as described previously.[19] The specific activity of the enzyme was *ca.* 160 U mg^{-1} of protein using ABTS as a chromogenic substrate.[20]

2.2 Preparation of PANI/MWCNT composite

PANI/MWCNT composite was obtained by *in situ* enzymatic aniline polymerization with atmospheric oxygen as terminal oxidant. The fungal laccase catalyzed aniline polymerization in the presence of aniline dimer as a redox enhancer of enzymatic polymerization. The reaction of aniline polymerization was carried out under conditions described in our previous work[21] using toluenesulfonic acid as a dopant.

2.3 Preparation of a flexible supercapacitor

The supercapacitor was fabricated from two identical thin flexible electrodes coated with enzymatically synthesized PANI/MWCNT composite as an electroactive material. The PVA/H_2SO_4/NQS gel polymer redox electrolyte was employed as both electrolyte and separator.

2.4 Characterization

The morphology of PANI/MWCNT composite was characterized by scanning electron microscopy (SEM, Supra 40 VP, Carl Zeiss) and transmission electron microscopy (TEM, LEO 912 AB OMEGA, Carl Zeiss). FTIR spectra were recorded using KBr pellets on a FTIR spectrometer (IRPrestige Fourier, Shimadzu, Japan). Four-point conductivity measurements were carried out with a Loresta GP (Mitsubishi, Japan).

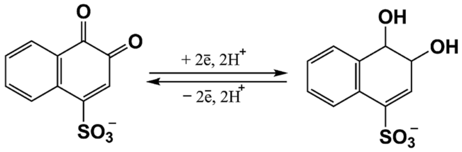

Fig. 1 Structure of NQS and the schematic drawing of its electrochemical reaction mechanism.

The characterization of the PANI/MWCNT composite in the redox electrolyte (1 M H_2SO_4/13 mM NQS) was performed by cyclic voltammetry (CV) using a BAS CV-50 W voltammetric analyzer (Bioanalytical System, USA). An electrochemical cell with a commercial Ag/AgCl electrode (Bioanalytical System, USA) as a reference electrode and platinum sheet as a counter electrode were used for electrochemical studies. Either a glassy carbon electrode (Bioanalytical System, USA) or flexible graphite foil coated with PANI/MWCNT composite served as a working electrode. The specific capacitance (C_s) of the composite was calculated using the formula $C_s = \frac{\int I\mathrm{d}E}{\nu \Delta E m}$ where I is the current, ΔE is the potential range, ν is the potential scan rate, m is the mass of electroactive composite.

Electrochemical characteristics of the SC device were recorded using a galvanostatic charge/discharge test

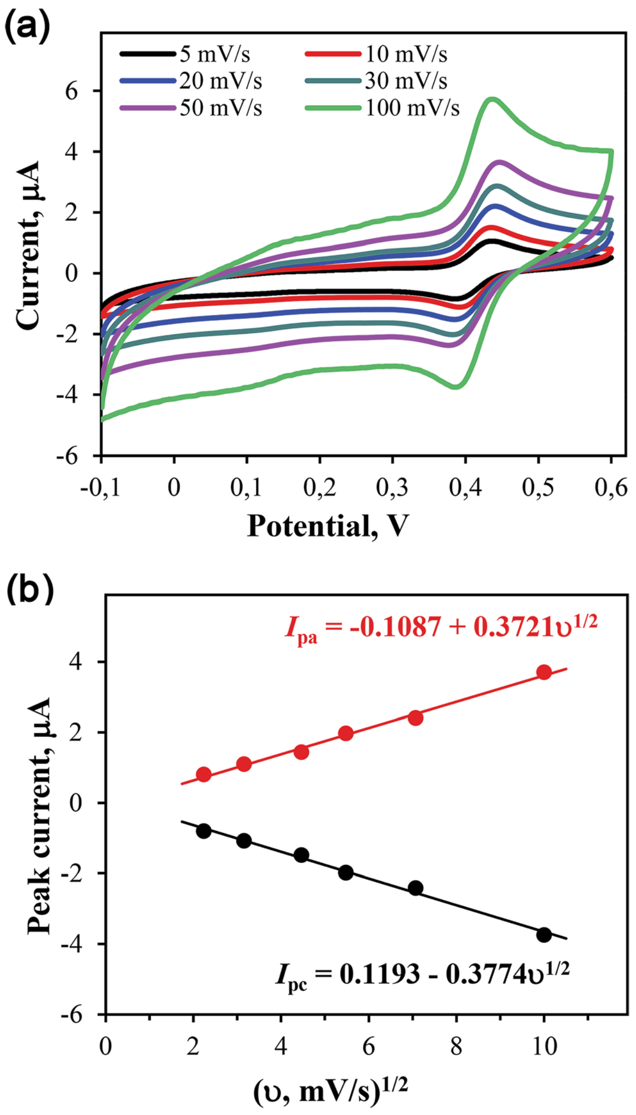

Fig. 2 (a) Cyclic voltammograms of 0.1 mM NQS in 1 M H_2SO_4 at different scan rates. (b) Linear relationships between the oxidation and reduction peak currents of NQS and the square root of the scan rate.

(MetrohmAutolab, Holland) and calculated according to the formulas described in ref. 22.

3. Results and discussion

To increase the specific capacitance and cyclic stability of the SC device, we used a combination of two redox systems, *i.e.* an enzymatically synthesized PANI/MWCNT composite with improved morphology was combined with the redox-active compound NQS, whose formula is shown in Fig. 1.

NQS was studied in detail in 3-electrode experiments by cyclic voltammetry using a glassy carbon electrode. Cyclic voltammograms recorded at different scan rates in 1 M of H_2SO_4, containing 0.1 mM NQS, are shown in Fig. 2a. At a potential scan rate of 5 mV s^{-1}, the middle point potential and ΔE were 415 mV and *ca.* 33 mV, respectively. Therefore, the redox behavior of NQS on the glassy carbon electrode was almost reversible. Both the oxidation and reduction peak currents of NQS showed a linear relationship with the square root of the scan rate (Fig. 2b), which is characteristic of a diffusion controlled process.

The number of transferred electrons in the course of the NQS electroreduction reaction was calculated by the Randles-Sevčik equation[23] using the diffusion coefficient of 0.58×10^{-5} cm^2 s^{-1} (ref. 17) was *ca.* 1.9. The peak currents of NQS did not change within the potential range from −0.1 to +0.6 V after 100 cycles of the potential scanning with a scan rate of 100 mV s^{-1}, which indicates a high electrochemical stability of NQS.

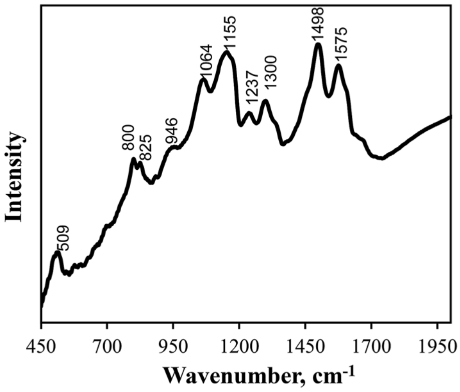

Fig. 3 FTIR spectrum of enzymatically synthesized PANI/MWCNT composite.

PANI-based materials have high electrochemical capacitance and high electrical conductivity, but the poor stability in charge/discharge cycles hampers their use as electrode material for SC devices. The stability of these materials depends on the morphological homogeneity of PANI/MWCNT composite and can be improved by forming a uniform thin layer of the conducting polymer on carbon nanomaterials. The amount of the functional polymer not bound to the MWCNTs, should be minimal, which is difficult to achieve using traditional chemical synthesis, since the monomer polymerization occurs not only on the MWCNTs but also in the reaction medium. The enzymatic approach reported in the given paper enabled us to improve the morphology of the composite.

We performed *in situ* laccase-catalyzed aniline polymerization using aniline dimer (AD, *N*-phenyl-*p*-phenylendiamine) as an enhancer of aniline enzymatic polymerization[24] in order to obtain a uniform thin PANI layer on the surface of MWCNTs. The composite was synthesized as follows. AD was pre-adsorbed on MWCNTs by incubating 5 mg of acid-treated MWCNTs in 5 ml of 1 mM AD solution for 1 h. The required amount of MWCNTs with the adsorbed AD was dispersed in a solution (pH 2.8) containing equimolar concentrations of aniline monomer and toluenesulfonic acid (65 mM). Aniline polymerization was initiated by adding the laccase stock solution. The specific activity of the enzyme in the reaction mixture was 4.0 U ml^{-1}. The reaction was carried out at room temperature for 24 h with magnetic stirring under aerobic conditions.

The PANI/MWCNT composite was separated by centrifugation, washed with ethanol and dried to a constant weight. The content of PANI in the composite was *ca.* 46 wt%. The FTIR spectrum of PANI/MWCNT (Fig. 3) exhibits characteristic absorption bands arising from the vibration mode of both C═N and C═C stretching of the quinoid diimine unit near 1575 cm^{-1}, while the band near 1498 cm^{-1} is attributed to C═C aromatic ring stretching of the benzenoid diamine unit.[25] Absorption bands near 1300 cm^{-1} and 1155 cm^{-1} belong to N–H and –N = stretching, respectively.[26] The 1,4-disubstituted aromatic rings vibrate at 825 cm^{-1} and 800 cm^{-1}.[27]

The morphology of the PANI/MWCNT composite was studied by transmission electron microscopy (TEM). As is seen in the TEM (Fig. 4) a core–shell structure composite was formed on MWCNTs on laccase-catalyzed aniline polymerization, *i.e.* a uniform thin, rough layer of PANI coated the surface of MWCNTs. Besides, the composite had no PANI not bound to the

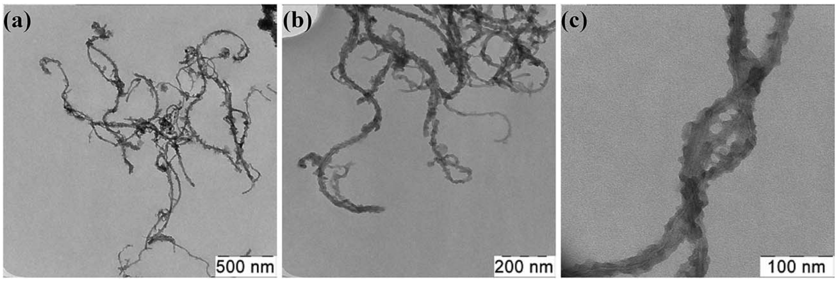

Fig. 4 TEM images of PANI/MWCNT composite under different magnifications.

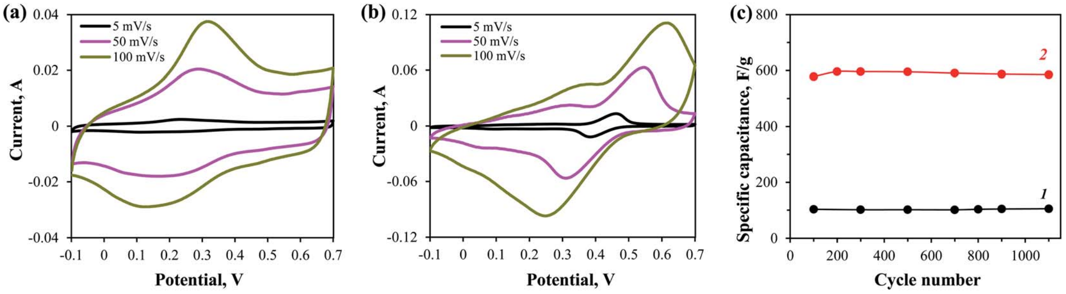

Fig. 5 Cyclic voltammograms of PANI/MWCNT composite at different scan rates in 1 M H_2SO_4 aqueous electrolyte (a) and in 1 M H_2SO_4/13 mM NQS aqueous redox electrolyte (b). The dependence of the specific capacitance of PANI/MWCNT electrodes on CV cycle numbers (c) within a potential range of −0.1 to +0.7 V at a potential scan rate of 100 mV s^{-1}: (1) 1 M H_2SO_4; (2) 1 M H_2SO_4/13 mM NQS.

surface of MWCNTs. The conductivity of the composite measured by the four-point probe method at room temperature was 11.2 ± 1.2 S cm^{-1}.

Electrochemical characteristics of the PANI/MWCNT composite were examined in 1 M H_2SO_4 by cyclic voltammetry using a three electrode cell configuration at various scan rates (Fig. 5a). The specific capacitance of the composite was *ca.* 420 F g^{-1} (5 mV s^{-1}) and after 1100 scanning cycles at a potential scan rate of 100 mV s^{-1} decreased by about 3% (Fig. 5c, curve 1). Cyclic voltammograms of the PANI/MWCNT composite electrode in 1 M H_2SO_4/13 mM NQS are shown in Fig. 5b. The cyclic voltammograms demonstrate current peaks corresponding to the redox behavior of both PANI and NQS. The specific capacitance of PANI/MWCNT electrode in 1 M H_2SO_4/13 mM NQS redox electrolyte was *ca.* 1100 F g^{-1} at a potential scan rate of 5 mV s^{-1}. Fig. 5c presents the stability of PANI/MWCNT composite electrode in 1 M H_2SO_4 (curve 1) and 1 M H_2SO_4/13 mM NQS (curve 2). It is seen that the electrode stability hardly varies in both solution. However, the specific capacitance of the PANI/MWCNT electrode in H_2SO_4/NQS redox electrolyte is ~6 times as high.

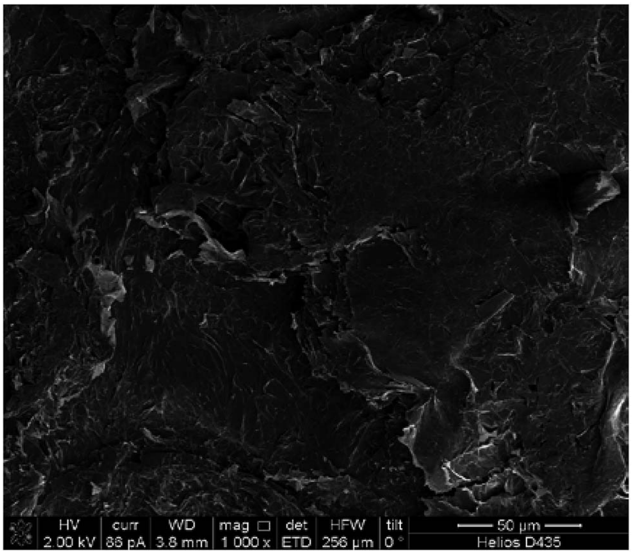

Fig. 6 SEM image of graphite the current collector.

A flexible supercapacitor of symmetric architecture was fabricated from two identical thin flexible electrodes with the enzymatically synthesized PANI/MWCNT composite as an electroactive material. First, a current collector was formed as follows. Some regular Scotch tape was stuck to the graphite foil and then peeled off. As a result, a thin graphite layer was formed on the sticky side. Sheet resistance of the carbon layer was 5–8 Ω

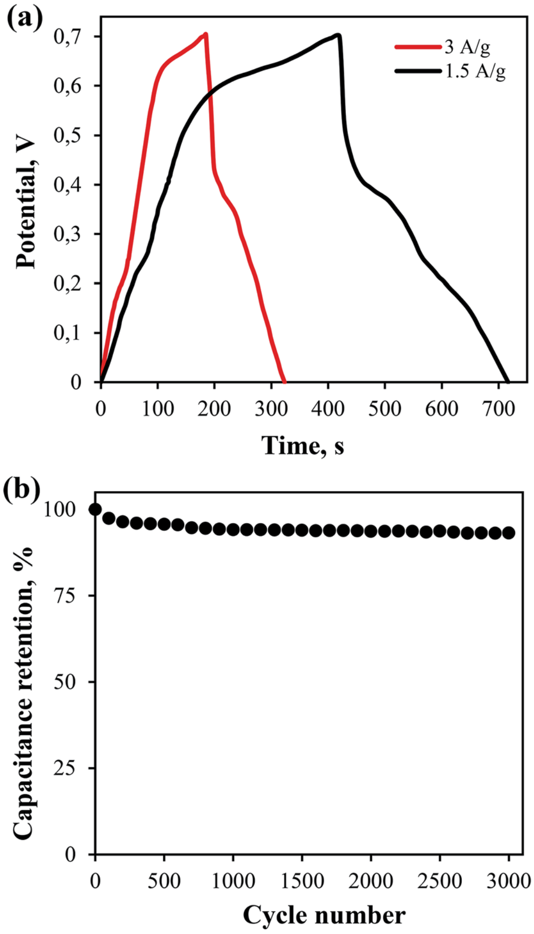

Fig. 7 (a) Galvanostatic charge/discharge curves of the SC device with PVA/1 M H_2SO_4/13 mM NQS gel polymer electrolyte at different current densities (2); (b) cycling stability of the SC device measured in a two electrode configuration.

$\square^{-1}$. The SEM image of the graphite layer is shown in Fig. 6. Then, an alcohol dispersion of PANI/MWCNT composite was deposited on the graphite current collector. The gel polymer redox electrolyte (10 wt% PVA/1 M H_2SO_4/13 mM NQS) was "sandwiched" between the electrodes to fabricate a thin flexible supercapacitor.

Electrochemical studies of the flexible symmetric SC were performed by the galvanostatic method in a two electrode configuration. Fig. 7a shows the dependence of the SC voltage change on time with a given current density. The discharge curve at 1.5 A g^{-1} was used to calculate the power and energy densities, which were 1.8 kW kg^{-1} and 23.3 W h kg^{-1}, respectively. The loss of the SC capacitance after 3000 cycles was less than 7% of the initial value (Fig. 7b).

4. Conclusions

In the present study two redox systems (polyaniline as an electrochemically active electrode material and sodium 1,2-naphthoquinone-4-sulfonate as a redox additive to the electrolyte) were combined to improve the supercapacitor performance. An enzymatic approach enabled us to obtain a PANI/MWCNT composite with a core–shell structure and minimize the formation of the functional polymer not bound to the surface of the carbon nanomaterial. The resulting composite electrode showed a better long cycling stability.

Electrochemical studies have shown that the redox behavior of NQS used as a redox-active additive to the electrolyte is a diffusion controlled and reversible process involving the transfer of two electrons *via* the electrode/electrolyte interface. A thin flexible SC device with high specific characteristics was constructed on the basis of the PANI/MWCNT composite and the PVA/H_2SO_4/NQS gel polymer redox electrolyte.

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