

Short communication

# Influence of the microstructure on the supercapacitive behavior of polyaniline/single-wall carbon nanotube composites

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## Abstract

Polyaniline/single-wall carbon nanotube (PANI/SWCNT) composites were prepared by in situ potentiostatic deposition of PANI onto SWCNTs at the potential of 0.75 V versus SCE, with the aim to investigate the influence of microstructure on the specific capacitance of PANI/SWCNT composites. It was found that the specific capacitance of the PANI/SWCNT composites is strongly influenced by their microstructure, which is correlated to the wt.% of the PANI deposited onto the SWCNTs. The optimum condition, corresponding to the highest specific capacitance, 463 F g<sup>-1</sup> (at 10 mA cm<sup>-2</sup>), was obtained for 73 wt.% PANI deposited onto SWCNTs. The specific capacitance of the PANI/SWCNT composite electrode was highly stable, with a capacitive decrease of 5% during the first 500 cycles and just 1% during the next 1000 cycles, indicative of the excellent cyclic stability of the composite for supercapacitor applications.

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## 1. Introduction

Supercapacitors or electrochemical capacitors are electrical-energy storage systems that have higher power-densities than batteries. Their cycle lives are 10<sup>2</sup> to 10<sup>3</sup> times higher than those of conventional batteries, because they rely on charge-storage mechanisms that do not involve chemical reaction-derived energy. Supercapacitors can be divided into two categories based upon the charge-storage mechanism, i.e. (i) electrical double-layer capacitance, which arises from the charge separation at an electrode/electrolyte interface, and (ii) redox capacitance, which arises from Faradaic reactions occurring at the electrode surface. Supercapacitors have potential applications in several systems, such as electrical vehicles, portable computers, cellular devices and nano-electronics [1–5].

The main materials that have been studied for the supercapacitor electrode are (i) carbons, (ii) metal oxides and (iii) conducting polymers. Current research has been centered mainly on carbon-based materials such as carbon nanotubes (CNTs), due to their high surface area and excellent electrical conductivity [6–9]. There are currently two types of CNTs under consideration for electrochemical capacitors: (i) single-wall carbon nanotubes (SWCNT) and (ii) multi-wall carbon nanotubes (MWCNT). Both types of nanotubes have high conductivity, but the use of SWCNT is more advantageous as compared to the MWCNT in supercapacitor applications, mainly due to the higher surface area, higher conductivity and interconnectivity of SWCNTs. All of these properties are essential for obtaining high specific capacitance. The diameter of the SWCNT is an order of magnitude lower than that of the MWCNT, which accounts for the significant increase in surface area. Moreover, high surface area is important for hybrid composites in which the SWCNT is used as a template. The interconnectivity of SWCNTs allows higher conductivity of the electrode. Therefore, the specific

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capacitance of the SWCNT is generally higher than that of the MWCNT. It has been shown that the specific capacitance of SWCNT (ca.  $50 \text{ F g}^{-1}$ ) in aqueous electrolytes [9] can be increased by polymer wrapping. Among the polymers, such as polymethyl methacrylate (PMMA) [10], *p*-phenylenevinylene (PPV) [11], polypyrrole (PPy) [12–16] and polyaniline (PANI) [16–18], polyaniline is one of the more promising, due to its ease of polymerization, as well as good supercapacitive characteristics [19].

The supercapacitive characteristics of PANI/CNT composite were reported recently [16–18], and the specific capacitance of  $312 \text{ F g}^{-1}$  was achieved for SWCNT deposited with 92 wt.% PANI [18] and  $400 \text{ F g}^{-1}$  for MWCNT deposited with 80 wt.% PANI [16] over a similar (positive) potential range. However, these preliminary studies were not highly informative in terms of the prospects for such composites as supercapacitors over a wide range of compositions, as they were performed only for several arbitrary compositions. For the use of such composites in supercapacitors and to obtain specific compositions for optimum specific capacitance, it is vital to study the microstructure and its relationship with the specific capacitance of the composites. Here, we report a study of the microstructures and the specific capacitances of PANI/SWCNT composites. The PANI/SWCNT composites showed that the specific capacitance depends strongly upon the microstructure of the PANI/SWCNT composite, as detailed below.

## 2. Experimental

### 2.1. Starting materials

SWCNTs were synthesized in-house by the electrical arc-discharge method with Ni/Y (4/2 atomic ratio) as a catalyst, according to a procedure reported earlier [20]. In brief, SWCNTs were prepared under a helium atmosphere ( $\sim 700$  mbar). The cathode consisted of an ultrapure graphite rod (15 mm diameter, 15 mm length). The anode consisted of an ultrapure graphite rod having an outer diameter of 6 mm (10 cm long), into which a large hole (5.3 mm diameter, 7 cm depth) was drilled, and which was subsequently filled with a mixture of graphite with catalysts (2 at.% Y as  $\text{Y}_2\text{O}_3$  and 4.2 at.% Ni as NiO). A current of 60 A was passed between anode and cathode to produce an arc-discharge plasma. The distance between anode and cathode was kept constant at 2 mm, and a voltage of 30 V was maintained during the consumption of the anode and subsequent production of SWCNTs. The duration of this process was 120 s, after which  $\sim 1$  g of SWCNTs soot was obtained.

The poly(vinylidene difluoride) (PVDF), dissolved in 1-methyl-2-pyrrolidone solvent ( $\text{CH}_3\text{NC}_4\text{H}_6\text{O}$ ), was obtained from Kureha Chemicals. The 1 M  $\text{H}_2\text{SO}_4$  and aniline were obtained from Aldrich and Wako, respectively. Research grade stainless-steel (SS, grade 304, 0.2 mm thick) was obtained from the Nilaco Corp. SS was polished with emery

paper to a rough finish, washed free of abrasive particles and then air-dried.

### 2.2. Preparation and characterization of PANI/SWCNT composites

First, the working electrode was prepared by mixing SWCNTs (90 wt.%) with PVDF binder (10 wt.%) and applying on the SS sheet (1 cm  $\times$  1 cm) at a thickness of a few hundred micrometers, as determined by scanning electron microscopy (SEM, JEOL, JSM-6340F). This electrode is referred to simply as the SWCNT electrode in the subsequent discussion. The SWCNT electrode was dried at  $80^\circ\text{C}$  for 24 h to remove the solvent. The electrochemical cell used in the present study was a three-electrode-cell in which the counter electrode was platinum and the reference electrode was a saturated calomel electrode (SCE). The working electrodes were the SWCNT electrode for PANI deposition and PANI/SWCNT for characterization.

An electrolyte solution of 1 M  $\text{H}_2\text{SO}_4$  + 0.05 M aniline was used for the electrochemical deposition of PANI onto SWCNT. The potentiostatic deposition of PANI onto the SWCNT electrode was carried out at 0.75 V versus SCE. This potential was chosen, because PANI changes its form from emeraldine (EM) to pernigraniline (PE) above this potential [21]. Subsequent to the deposition of PANI onto the SWCNT electrode, the electrode was washed in distilled water and then dried in an oven at  $40^\circ\text{C}$  for 1 day. The mass of the active electrode material was measured in all the cases by subtracting the mass of SS from the total weight. The mass of PANI deposited onto the SWCNT electrode was estimated from the weight difference before and after PANI deposition. All electrochemical depositions and measurements were performed with an Autolab PGSTAT 30 instrument (Eco-Chemie, The Netherlands) connected to a three-electrode cell. The 1 M  $\text{H}_2\text{SO}_4$  electrolyte was used in all electrochemical charge–discharge cycling measurements. The specific resistance was measured by means of the ac complex impedance method. The microstructure of the composite electrodes was observed by means of SEM.

## 3. Results and discussion

### 3.1. Microstructure of the SWCNT and PANI/SWCNT composites

Fig. 1 shows an SEM micrograph of the original SWCNTs. These are distributed in the form of an extended network over a large area. Fig. 2 shows SEM micrographs of PANI/SWCNT composites for various wt.% of deposited PANI. The morphologies of the PANI/SWCNT composites are found to vary with the deposited wt.% of PANI. Initially deposited PANI is mostly wrapped around the SWCNTs (Fig. 2(a)). As the wt.% of deposited PANI increases, the diameter of the wrapped PANI increases continuously

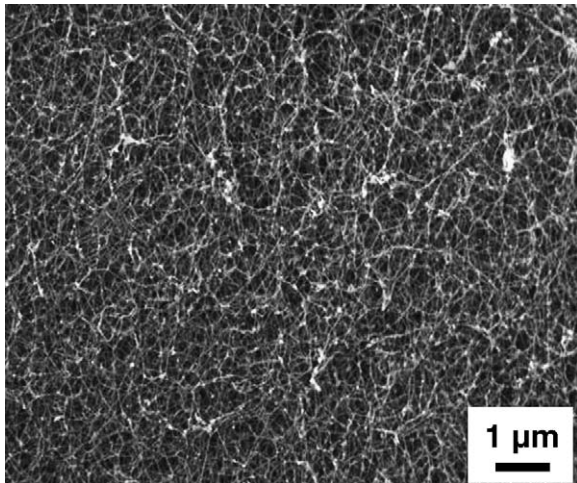


Fig. 1. SEM image of the original SWCNT.

(Fig. 2(b)). Beyond 73 wt.%, PANI is no longer deposited around the SWCNTs but tends to be deposited independently around the surface of the composite, as shown in Fig. 2(c), with the thickness of the composite remaining a few hundred micrometers in all the cases, as observed by SEM. This implies that the microstructure of the PANI/SWCNT composites is dependent on the weight of deposited PANI. This behavior has profound implications on the specific capacitance of the PANI/SWCNT composite, as discussed in the next section.

### 3.2. Charge–discharge behavior of the SWCNT, PANI and PANI/SWCNT composites

The specific capacitance (SC) values were evaluated from charge–discharge cycling measurements, which are considered to be the most reliable. SC values can be calculated by the following relationship, i.e.  $SC = i\Delta t / \Delta E m$ . Here,  $i$  is the discharge current,  $\Delta t$  the discharge time corresponding to the voltage difference ( $\Delta E$ ), and  $m$  is the electrode mass. Fig. 3(a) and (b) shows the charge–discharge cycling data of the original SWCNT and pure PANI, respectively. SC values of 50 and 230  $F g^{-1}$  were obtained for SWCNT and PANI, respectively. These results are in good agreement with those previously obtained [17,18].

Fig. 4(a)–(c) shows the charge–discharge cycling of the PANI/SWCNT composites with 57, 73 and 85 wt.% deposited PANI onto the SWCNTs, respectively. The SC values of the PANI/SWCNT composites are estimated to be 325, 463 and 317  $F g^{-1}$ , respectively, for 57, 73 and 85 wt.% of deposited PANI. By comparing SC values and the corresponding microstructure of the PANI/SWCNT composites (Fig. 2), it is clear that the SC depends on the microstructure of the PANI/SWCNT composite. A general relationship between wt.% of PANI deposited onto SWCNT and specific capacitance is shown in Fig. 5(a). There is an increase in the SC of the PANI/SWCNT composite with an increase

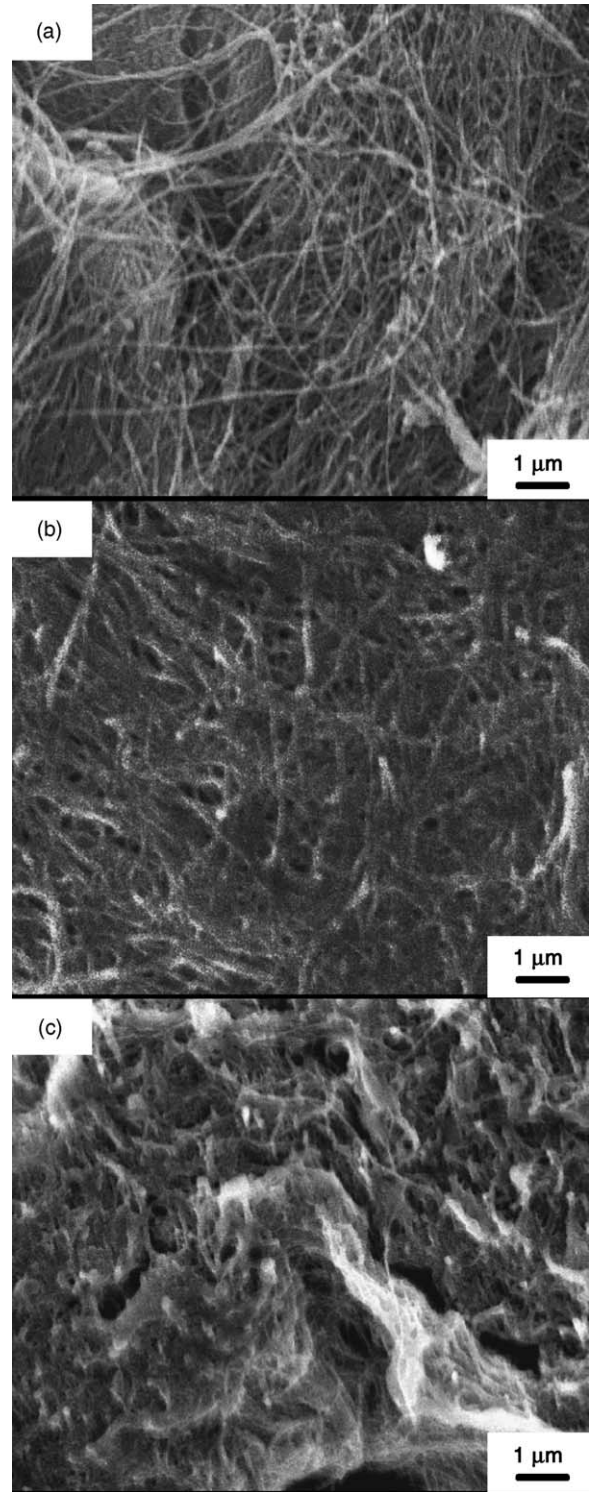


Fig. 2. SEM images of the PANI/SWCNT composites with (a) 57 wt.% PANI, (b) 73 wt.% PANI and (c) 85 wt.% PANI.

in the deposited mass of the PANI, up to 73 wt.%. Thereafter, there is a decrease in the SC. From this relationship, it can be inferred that the highest specific capacitance can be obtained for 73 wt.% PANI deposited onto SWCNT. This characteristic is independent of the configuration of the cell

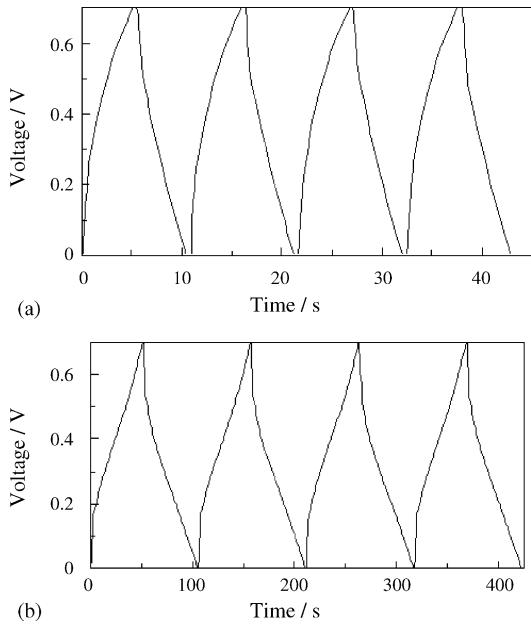


Fig. 3. Galvanostatic charge/discharge curves of the (a) original SWCNT (electrode wt. = 1.85 mg) and (b) PANI (electrode wt. = 4.2 mg) in 1 M  $\text{H}_2\text{SO}_4$  electrolyte.

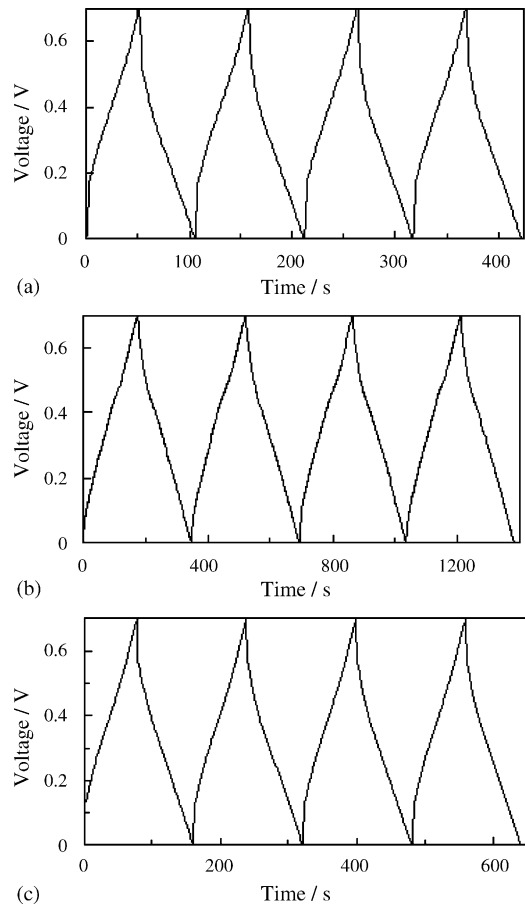


Fig. 4. Galvanostatic charge/discharge curves of the PANI/SWCNT composite with (a) 57 wt.% PANI (electrode wt. = 3.2 mg), (b) 73 wt.% PANI (electrode wt. = 6 mg) and (c) 85 wt.% PANI (electrode wt. = 4.8 mg) in 1 M  $\text{H}_2\text{SO}_4$  electrolyte.

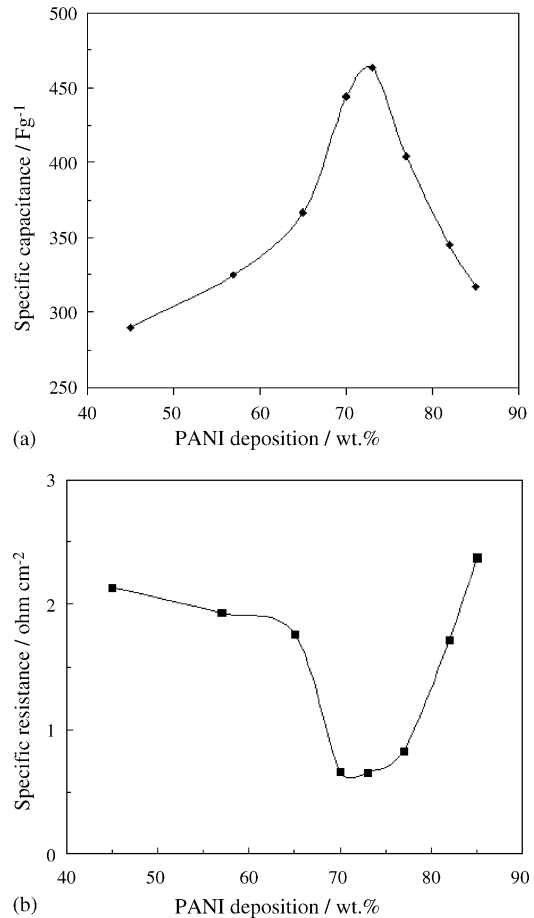


Fig. 5. Relationship of wt.% of the deposited PANI with the (a) specific capacitance (at  $10 \text{ mA cm}^{-2}$  in 1 M  $\text{H}_2\text{SO}_4$  electrolyte) and (b) specific resistance of the PANI/SWCNT composite.

(qualitatively). Therefore, this relationship is of significant importance.

An increase in the SC in the PANI/SWCNT composite was previously observed by Zhou et al. [18]. They obtained a specific capacitance value of  $312 \text{ F g}^{-1}$  for PANI/SWCNT composites with a PANI content of 92 wt.%. It was shown that this rise in the SC value was due to the formation of a charge-transfer complex in the PANI/SWCNT composite and the increase in the active sites for Faradaic reactions for the charge transfer complex of the composites. The extensive study performed here indicates that the increase in the SC value due to such a mechanism is closely related to the microstructure of the PANI/SWCNT composite, with the highest SC value of  $463 \text{ F g}^{-1}$  obtained for 73 wt.% PANI. This can be understood as follows. Initially, the deposited PANI is mostly wrapped around the SWCNTs, as shown in Fig. 2(a). PANI continues to be deposited onto the SWCNTs until 73 wt.% PANI is wrapped around the SWCNTs. This condition is shown in Fig. 2(b). Thereafter, the additional PANI tends to deposit independent of the SWCNT in the form of small aggregates, as shown in Fig. 2(c). This morphology has a direct effect on the SC of the PANI/SWCNT composites,

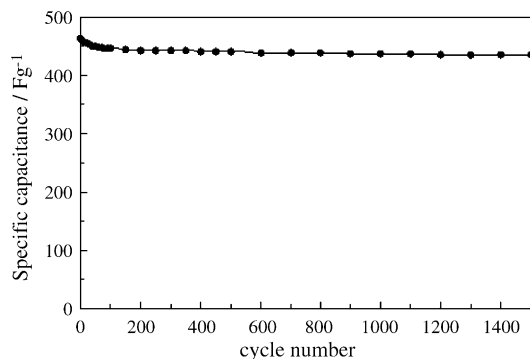


Fig. 6. Cyclic-life data of the PANI/SWCNT composite (73 wt.% PANI). The specific capacitance was calculated for the charge–discharge cycling at the current density of  $10 \text{ mA cm}^{-2}$  in  $1 \text{ M H}_2\text{SO}_4$  electrolyte.

because the optimum condition of specific capacitance can be effectively achieved for PANI wrapped around the SWCNTs because of the fact that the rise in the specific capacitance is due to charge-transfer complex. The PANI deposited independent of the SWCNTs not only gives lower SC values (Fig. 3(b)) but also decreases the effective surface area for the Faradaic reactions. This is the reason for the decrease of the SC value above 73 wt.% deposited PANI in the present case as well as in the previous studies [17,18].

Fig. 5(b) shows the relationship between the resistance of the PANI/SWCNT and the deposited PANI. Initially, there is decrease in the specific resistance of the PANI/SWCNT composite with increasing wt.% of deposited PANI, up to 73 wt.% deposited on SWCNT. Thereafter, there is an increase in the resistance of the PANI/SWCNT composite. The resistance values of the original SWCNT and PANI were  $2.70$  and  $4.12 \Omega$ , respectively. The decrease in the resistance for the PANI/SWCNT composites (73 wt.% PANI deposited on SWCNTs) is more than six times as compared to PANI. This indicates the role of the conductivity of the electrode in obtaining the observed higher SC for 73 wt.% deposited PANI. The cyclic stability of the PANI/SWCNT composite was observed by continuous charge–discharge cycling, as shown in Fig. 6. Initially, there is a decrease in SC by 5% during the first 500 cycles, after which it stabilizes. After the initial 500 charge–discharge cycles, the decrease in SC was about 1% during the next 1000 charge–discharge cycles. This indicates the high cyclic stability of the PANI/SWCNT composites for supercapacitor applications.

#### 4. Conclusions

PANI/SWCNT composite electrodes were prepared and characterized for microstructure as well as specific capacitance for the supercapacitor application. The highest reported specific capacitance ( $463 \text{ F g}^{-1}$ ) was obtained for 73 wt.% PANI deposited onto the SWCNT electrode. Excellent cyclic stability of the PANI/SWCNT composite was observed. The

results suggest that the specific capacitance of PANI/SWCNT can be significantly controlled by carefully controlling its microstructure.

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