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Short communication

Brushed-on flexible supercapacitor sheets using a nanocomposite of polyaniline and carbon nanotubes

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ABSTRACT

A simple, two-step method for constructing flexible sheets of supercapacitors is described. The construction is based on painting a sheet of flexible plastic electrolyte with a composite material made of a conducting polymer and carbon nanotubes. The total capacitance of the supercapacitor consists of pseudocapacitance produced by the polymer and electrical double-layer capacitance produced by carbon nanotubes. Stacks of the capacitor sheets were used to light up a system of three light-emitting diodes. The method suggests an inexpensive and potentially high-throughput approach for making flexible supercapacitors.

1. Introduction

Energy storage for portable electronic devices, which are becoming increasingly important to the present society, forms by far the largest mobile energy storage market today and is experiencing innovation for future applications such as flexible/printed electronics and display [1,2]. To operate flexible devices, flexible energy storage needs to be integrated with the active devices. Electrochemical supercapacitors with high energy and power capabilities are potentially capable of powering flexible devices. In order to be integrated with flexible electronics, supercapacitors should be made flexible with sheet-like structures, which are lightweight [3,4]. Also, the fabrication method of the supercapacitors should be inexpensive and high-throughput.

Recently, a paper-like nanocomposite material was used as the basic unit for assembling flexible capacitors [5]. The first step was to grow films of vertically aligned carbon nanotubes (CNT) on silicon substrates using thermal–chemical vapor-deposition. Then, cellulose dissolved in an ionic liquid that was also used as electrolyte was infiltrated into the CNT to form a film of cellulose and electrolyte, embedding the CNT. After solidification on dry ice, the resulting nanocomposite paper was peeled from the substrate. A supercapacitor was made by bonding two pieces of the nanocomposite papers back-to-back. Flexible supercapacitors were also fabricated using a spraying technique [6]. CNT dissolved in water was sprayed on plastic substrates to form flexible electrodes. The supercapacitor was formed by sandwiching a flexible gel/solid electrolyte with two flexible electrodes.

This paper reports a simple approach for constructing flexible sheets of supercapacitor. The construction is based on painting a sheet of flexible plastic electrolyte with a composite material made of a conducting polymer and carbon nanotubes. To fulfill the requirements of flexible electronics applications, solid electrolytes are preferred over liquid electrolytes, which evaporate and therefore require enclosures. Carbon nanotubes were used to reduce the internal resistance of the conducting polymer. The fabrication approach is inexpensive and potentially high-throughput. Stacks of capacitor sheets were used to light up a system of light-emitting diodes.

2. Experimental

The two-step construction of the capacitor sheet is schematically described in Fig. 1(a). Polyvinyl alcohol (PVA) powder (Sigma–Aldrich) was mixed with water with a ratio of 1:9 by weight. The PVA mixture was then mixed with phosphoric acid (H_3PO_4, 85%) with a ratio of 1:1 by volume. Films of PVA were formed by first casting the final mixture on a glass surface and then peeling the cast off from the surface after water had evaporated. The free-standing films had a thickness of about 0.3 mm. A volume

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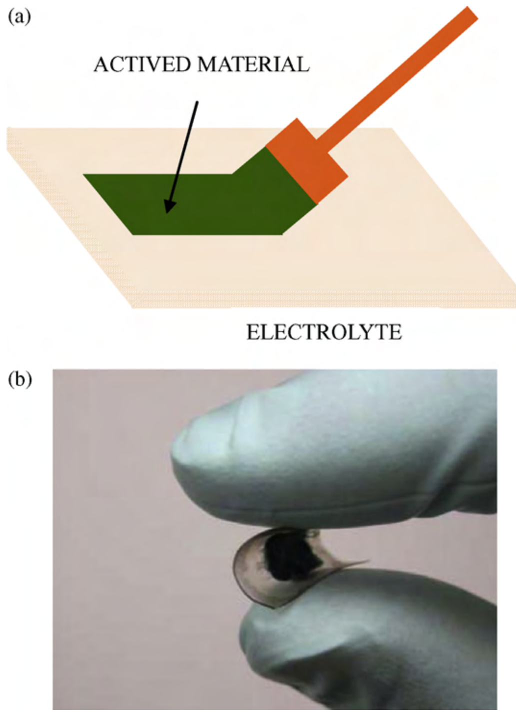

Fig. 1. (a) Schematic illustration of the two-step construction of the supercapacitor sheet. The first step is the formation of the free-standing electrolyte sheet. The active material is then painted on both sides of the electrolyte using a brush. (b) A capacitor sheet.

of 0.1 ml of polyaniline (PANI) dispersed in xylene (Sigma–Aldrich) and 0.003 g of single-walled carbon nanotubes (CNT) (Carbon Solutions) were mixed in N-dimethylformamide. Both materials were used as purchased. A painting brush was used to transfer the PANI–CNT aqueous mixture on both sides of a PVA film to form and define the shape of a capacitor. Painted sheets were put in an oven at 40 C for water to be evaporated. Fig. 1(b) shows a capacitor sheet. The two-dimensional size of the capacitor was about 5 mm × 5 mm. Electrical contacts were made by either using metallic clips or copper sheets.

Cyclic voltammetry of PANI and galvanostatic charging–discharging measurements of capacitor sheets were performed using a commercial potentiostat (CH Instrument 660C). The electrochemical cell used was a conventional three-electrode cell with a commercial Ag/AgCl (3 M KCl) electrode as the reference electrode and a platinum wire as the counter electrode. For voltammetry measurements, the cell potential was scanned at 50 mV/s. Charging–discharging measurements were made at different current densities, with cutoff voltages of 0 and 0.8 V. Voltammetry measurements were made with electrodes immersed in 0.5 M H_2SO_4 aqueous electrolyte. Deionized water (ρ = 18.2 MΩ cm, Direct Q3, Millipore) was used to prepare solutions. Phosphate buffer solution (PBS, 100 mM) was prepared for general use. Scanning electron microscopy was performed using an Amray 1820 instrument.

3. Results and discussion

The morphology of the PANI–CNT composite material was studied using SEM as shown in Fig. 2(a). The composite material shows a fibrillar structure with a cross-sectional size of about 250 nm, which has been observed previously [7]. The absence of CNT in the morphology indicates that CNT was embedded in the PANI layer. Cyclic voltammetry of the purchased PANI was performed. Fig. 2(b) shows the cyclic voltammograms (CVs) of PANI and the PANI–CNT

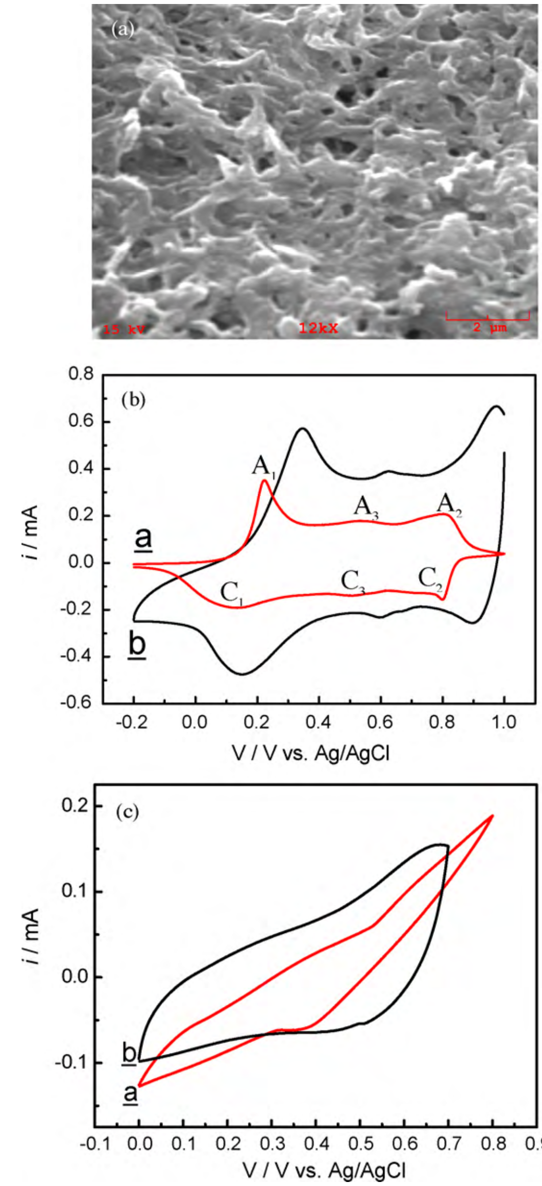

Fig. 2. (a) SEM of the PANI–CNT composite. (b) CVs of PANI and the PANI–CNT composite in 1 M H_2SO_4. (c) CVs of PANI and the PANI–CNT composite at pH 4.

composite material deposited on highly oriented pyrolytic graphite (HOPG) electrodes. Both CVs were obtained with the electrodes immersed in 1 M H_2SO_4. CV *a* of PANI shows three pairs of redox peaks, namely, A_1/C_1, A_2/C_2 and A_3/C_3. A_1/C_1 and A_3/C_3 indicate respectively the transition between leucoemraldine and emeraldine salt the transition between emeraldine salt and pernigraniline [8]. A_2/C_2 has been attributed to either the presence of ortho-coupled polymers [9]. The appearance of the redox peaks indicates that the purchased PANI was functional as conducting polymer and therefore the redox processes of PANI gave rise to pseudo-capacitance of the electrode [10]. The evidence that CNT was in the composite is indicated by CV *b* taken with the PANI–CNT composite. The three pairs of redox peaks still appear in CV *b* with a positive 100 mV shift in potential. Comparing the two CVs indicates that the total current level the PANI–CNT composite was enhanced due to the presence of CNT, which contributes an electrical double-layer capacitance [11] component to the total capacitance of the electrode.

Initially capacitor sheets made of PANI only were fabricated and tested. Trace *a* of Fig. 3(a) is the charging–discharging characteristic

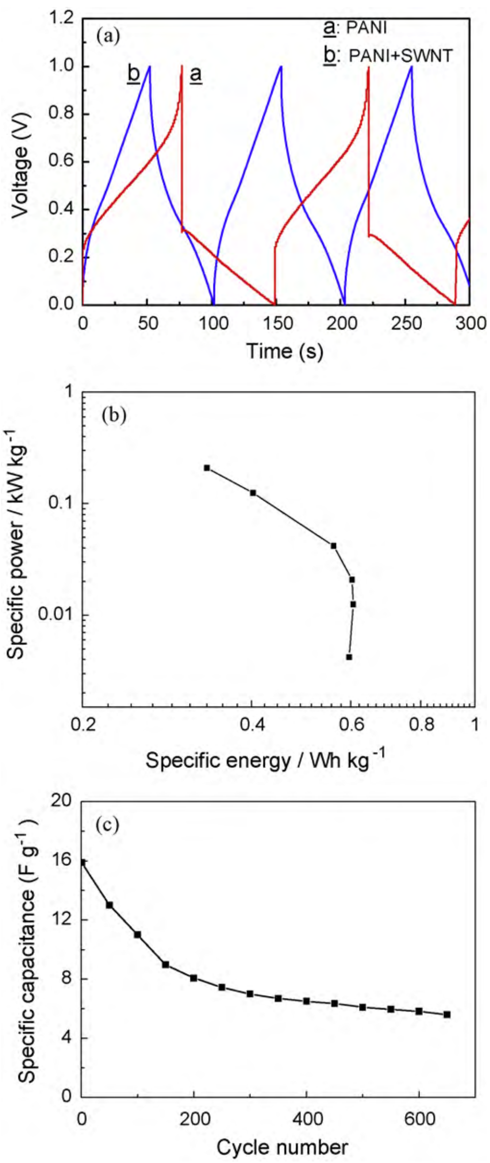

Fig. 3. (a) Trace *a* and trace *b* are the charging/discharging characteristics of the PANI electrode and the composite electrode, respectively. (b) Ragone plot of the capacitor sheet. (c) Charging/discharging cycling stability of a composite capacitor sheet.

of the PANI capacitor sheet. The trace indicates a large equivalent series resistance (ESR), which in principle reduces the power output of the capacitor sheet [12]. To reduce the observed large ESR, CNT was introduced into PANI to form the composite. Trace *b* of Fig. 3(a) was obtained with the composite capacitor sheet and it shows that ESR is almost absent in the composite. The specific capacitance C_S of the composite capacitor sheet was evaluated using Trace *b* according to $C_S = I/(m \times dV/dt)$, where I is the discharging current, m is the mass of the electrode material and dV/dt is the rate of change in the discharging potential obtained from the charging–discharging trace. For a discharging current density of 0.16 mA/cm^2, C_S was evaluated to be 16 F/g.

The Ragone plot of the capacitor sheet, which shows the relation between the energy storage and power capabilities of a supercapacitor, is shown in Fig. 3(b). The plot shows that the capacitor sheet has a maximum specific energy of 0.5 Wh kg^{-1} and a maximum specific power of 0.3 kW kg^{-1}, which are much lower than those observed previously with flexible supercapacitors [5,6]. The low energy and power capabilities are attributed to the fact that

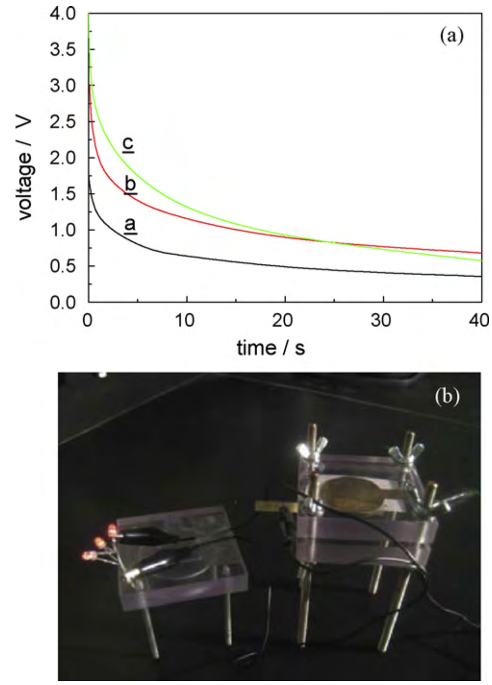

Fig. 4. (a) Discharging characteristics of three difference stacks of capacitor sheets. (b) Three LEDs powered by a stack of three capacitor sheets.

a mild acid, H_3PO_4, was used in the preparation of the solid electrolyte. Fig. 2(c) shows the CVs of PANI (CV *a*) and the PANI–CNT composite (CV *b*) measured at pH 4. Two effects are indicated by the CVs: disappearing redox peaks and diminished current levels of the two materials compared to those obtained in strong acid such as H_2SO_4 (see Fig. 2(b)). Thus, the capacitance, the energy storage and power capabilities of the PVA-based capacitor sheet were affected accordingly. The cycling stability of the capacitor sheet is shown in Fig. 3(c). The specific capacitance of 16 F/g obtained at 0.16 mA/cm^2 of a capacitor sheet shows a fast decrease by 50% of the initial value during the first 200 cycles. After that, C_S shows a mild decrease all the way to the 650th cycle. The fast decrease in the specific capacitance with the cycle number is likely to be caused by the swelling and shrinking of conducting polymers, which are known to cause degradation during cycling [12].

The potential application of the capacitor sheet is demonstrated by using the capacitor sheet to power light-emitting diodes (LED). A problem encountered in the demonstration was the low operation voltage (~1 V) provided by the sheet. To satisfy the operating requirement of LEDs, a stack of several capacitor sheets connected in series was used to increase the voltage. Fig. 4(a) shows the discharging characteristics of stacks of one (curve *a*), two (curve *b*), and three (curve *c*) capacitor sheets. The initial voltages of the stacks are proportionally higher, reaching 4 V. A stack of three capacitor sheets was used to drive three red LEDs as shown in Fig. 4(b).

4. Conclusion

In summary, we have demonstrated a simple, two-step method for constructing flexible sheets of supercapacitors. The construction is based on painting a sheet of flexible plastic electrolyte with a composite material made of a conducting polymer and carbon nanotubes. The total capacitance of the supercapacitor consists of pseudocapacitance produced by the polymer and electrical double-layer capacitance produced by carbon nanotubes. The use of solid electrolyte has resulted in considerably small energy and power capabilities as reflected in the Ragone plot of the capacitor sheet. However, we have used stacks of such capacitor sheets to light up a system of three light-emitting diodes in order to demonstrate the potential applications of the capacitor sheet. Our future work will focus on improving the energy and power capabilities and the stability of the capacitor sheet.

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