



Short communication

Supercapacitor electrodes based on polyaniline–silicon nanoparticle composite

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ABSTRACT

A composite material formed by dispersing ultrasmall silicon nanoparticles in polyaniline has been used as the electrode material for supercapacitors. Electrochemical characterization of the composite indicates that the nanoparticles give rise to double-layer capacitance while polyaniline produces pseudocapacitance. The composite shows significantly improved capacitance compared to that of polyaniline. The enhanced capacitance results in high power (220 kW kg^{-1}) and energy-storage (30 Wh kg^{-1}) capabilities of the composite material. A prototype supercapacitor using the composite as the charge storage material has been constructed. The capacitor showed the enhanced capacitance and good device stability during 1000 charging/discharging cycles.

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1. Introduction

Conducting polymers are an important class of electrode material for supercapacitors [1,2]. Conducting polymers store and release charge through redox processes, resulting in the so-called pseudocapacitance. Charging in a conducting polymer takes place throughout the bulk volume of the polymer, not just on the surface as is the case with carbon, so that the specific capacitance of polymers is high [3]. The fast charge/discharge processes associated with conducting polymers give rise to high specific power [3]. It was demonstrated that the cycle-life of conducting polymer-based supercapacitors can be as high as several thousand cycles [3]. Recently, carbon nanotubes have been incorporated in conducting polymers such as polyaniline and polypyrrole to form composite electrode materials for supercapacitors [4]. Nanotubes played the role of a perfect backbone for the polymers in the composite and therefore prevented the polymers from mechanical changes (shrinkage and breaking) during long cycling. The presence of nanotubes also enabled a high charge/discharge rate due to improved charge transfer.

In this work, we show that a composite material consisting of polyaniline (PANI), a conducting polymer, and ultrasmall silicon nanoparticles provides improved device performance when used as the electrode material for supercapacitors. Because of the hybrid nature of its capacitance, the composite shows a significantly enhanced specific capacitance, which is larger than that of PANI by a factor of 5. The enhanced capacitance results in high power

(220 kW kg^{-1}) and energy-storage (30 Wh kg^{-1}) capabilities of the composite material. The specific capacitance of the composite electrode was observed to be stable during 2000 charging–discharging cycles. A prototype supercapacitor based on the composite has been fabricated and characterized. The supercapacitor's characteristics are similar to that of the composite electrode.

2. Experimental

The silicon nanoparticles were made by electrochemical etching of a (100)-oriented p-type ($1\text{--}10 \Omega \text{ cm}$) silicon wafer in hydrofluoric acid and hydrogen peroxide followed by shaking off the particles from the etched wafer using ultrasound in water or organic solvents such as benzene, isopropyl alcohol and tetrahydrofuran (THF) to form a colloid [5]. This etching technique can be used to prepare 1-nm particles (Si1) and 2.8-nm particles (Si2.8), depending on etching conditions. The surface of the silicon nanoparticles is passivated by hydrogen. Aniline monomers were purchased from Sigma–Aldrich. Polyaniline (PANI) was prepared by electrochemical polymerization on highly oriented pyrolytic graphite (HOPG) electrodes with dimensions of $3 \text{ mm} \times 3 \text{ mm}$ in a solution that contained 0.1 M of aniline and 1 M HCl. The polymerization process was carried out in an electrochemical cell with the HOPG electrode as the working electrode. The deposition of the polymer film was obtained by cycling the cell potential between 0 and 0.8 V at 50 mV s^{-1} for 1000 cycles. The particle–polymer composite was prepared by first mixing a water-based nanoparticle colloid ($10 \mu\text{M}$) with a solution containing 0.1 M of aniline and 1 M HCl followed by cycling the cell potential as described above.

The electrochemical cell was a conventional three-electrode cell, controlled by a potentiostat (CH Instrument 660C). A commer-

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cial Ag/AgCl (3 M KCl) electrode was used as the reference electrode, and a platinum wire was used as the counter electrode. Cyclic voltammetry and galvanostatic charge–discharge measurement were performed using the potentiostat. For CV measurements, the potential was scanned at 50 mV s^{-1} . The charging–discharging measurement was made at different current densities, with cutoff voltages of 0 and 0.8 V. All characterizations were made in $0.5 \text{ M H}_2\text{SO}_4$ aqueous electrolyte. Deionized water ($\rho = 18.2 \text{ M}\Omega \text{ cm}$, 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.

3. Results and discussion

The morphology of polyaniline and the composite material was studied using SEM as shown in Fig. 1. The electrochemically synthesized PANI, as shown in Fig. 1(a), has a fibrillar morphology with a cross-sectional size of about 150 nm as previously noted [6]. In Fig. 1(b), the composite material also appears to have a fibrillar morphology. However, the fibers have a much larger cross-sectional size of about 600 nm, which was the result of incorporating the nanoparticles in PANI during the electropolymerization process.

Cyclic voltammetry of the PANI electrode and the composite electrode was performed in order to show qualitatively the effect of the particle on the capacitance of PANI [1]. Fig. 2 shows the cyclic voltammograms (CVs) of the two kinds of electrodes. CV1 was obtained with a PANI electrode, showing two pairs of redox

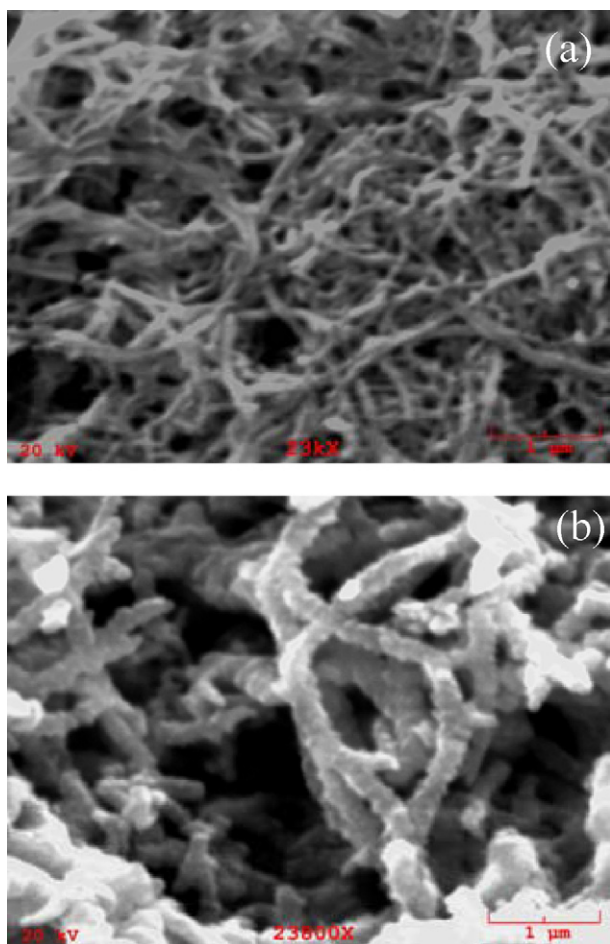


Fig. 1. Scanning electron microscopy image of (a) electropolymerized PANI and (b) the particle–PANI composite material.

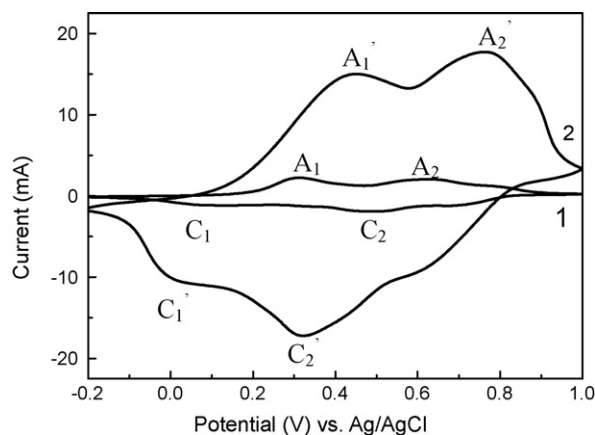


Fig. 2. Cyclic voltammograms of PANI (CV1) and the composite material (CV2) deposited on HOPG. The two pairs of redox peaks are characteristics of PANI.

peaks, A_1/C_1 and A_2/C_2 . A_1/C_1 indicates the transition between leucoemeraldine and emeraldine salt and A_2/C_2 indicates the transition between emeraldine salt and pernigraniline [7]. The redox processes of PANI produce the pseudocapacitance of the electrode [8]. CV2 was obtained with a Si1-based composite electrode. It appears that the two pairs of redox peaks are now superimposed on a plateau to become A_1'/C_1' and A_2'/C_2' . It is obvious that the current level of CV2 in the plateau region is much higher than that of CV1. The higher current level implies a larger electrode capacitance. Comparing the shapes of the two CVs indicates that the contribution of the silicon nanoparticles to the capacitance of the composite electrode is of the double-layer type.

Quantitative information on the capacitances of the electrodes was obtained using galvanostatic charging–discharging cycling of the electrodes as shown in Fig. 3(a). Trace 2 obtained using the Si1-based composite electrode features a significantly increased area under the trace compared to trace 1 obtained using the PANI electrode, therefore reflecting the enhanced capacitance of the composite. The specific capacitances C_s of the electrodes were evaluated using the traces of Fig. 3(a) 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 40 mA cm^{-2} , C_s is evaluated to be 85.07 F g^{-1} and 409.27 F g^{-1} for the PANI electrode and the composite electrode, respectively. The enhanced electrode capacitance is due to the inclusion of the nanoparticles, which contribute a significant double-layer component to the total capacitance as shown above.

Fig. 3(b) shows the relation between C_s and discharging current of the composite electrode obtained from charging–discharging measurements at different current density. As the current density is increased from 10 mA cm^{-2} to 100 mA cm^{-2} , 60% of the capacitance of the composite electrode is retained, indicating a good rate capability. A good rate capability is indicative of high power density. The power and energy-storage capabilities of an electrode are related in the specific power vs. specific energy characteristics of the electrode. Such characteristics for the two kinds of electrodes are plotted in Fig. 3(c). The characteristics indicate that the composite electrode has a superior performance in terms of power capability and stored energy compared to the PANI electrode. In particular, at any given load, the power and energy stored in the composite electrode is about 5 times greater than that of the PANI electrode. The cycling stability of the composite electrode is shown in Fig. 3(d). The specific capacitance of 470 F g^{-1} obtained at 5 mA cm^{-2} of a composite electrode shows a decrease by 78% of the initial value during the first 700 cycles. After that, C_s stays fairly constant all the way to the 1500th cycle.

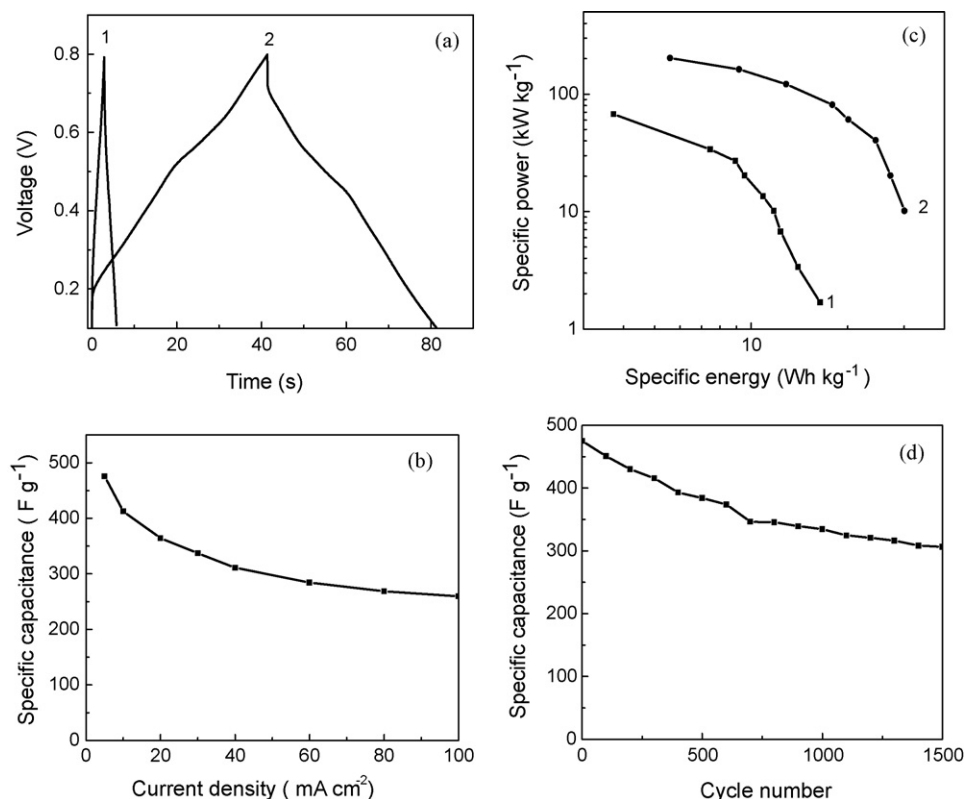


Fig. 3. Characterization of electrodes. (a) Trace 1 and trace 2 are the charging/discharging characteristics of the PANI electrode and the composite electrode, respectively. (b) The relation between the specific capacitance obtained at different current density, (c) specific power vs. specific energy characteristics of the PANI electrode (curve 1) and the composite electrode (curve 2), and (d) charging/discharging cycling stability of a composite electrode.

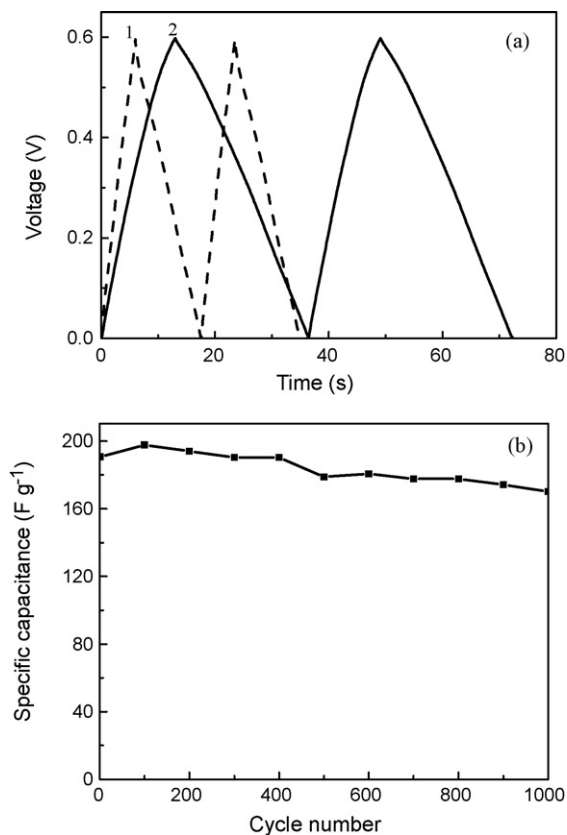


Fig. 4. Characterization of the prototype supercapacitor. (a) Charging/discharging characteristics and (b) capacitor cycling stability.

Silicon forms electrical double layer when in contact with an electrolyte [9]. The silicon nanoparticles were embedded in PANI while being accessed by electrolyte because of the porosity of PANI. Therefore, they make significant contribution to the capacitance of the electrode. The improved electrode performance will become obvious when the power/energy characteristic (Fig. 3(c)) is compared to that of a capacitor made of pure conducting polymer in organic electrolyte of Ref. [10]. With the units of the axes of Fig. 3(c) converted to $mW cm^{-2}$ and $mJ cm^{-2}$, our power capability appears to be 10 times higher and the energy capability 1.6 times higher.

A prototype supercapacitor was constructed using Si2.8-based composite as the electrode material. The supercapacitor was constructed using two 0.3-mm diameter platinum wires as current collector. The composite was deposited on the wires using electropolymerization. The wires were held at 2 mm apart and a length of 2 mm of the wires was dipped in a 0.5 M H_2SO_4 solution. Fig. 4(a) shows the charging–discharging characteristics of a composite capacitor (trace 2) and a PANI-based capacitor (trace 1) having the same geometry. From the traces, the specific capacitances of the composite capacitor and of the PANI capacitor were calculated to be $52.89 F g^{-1}$ and $217.67 F g^{-1}$, respectively, at $80 mA cm^{-2}$. The cycling stability of the composite capacitor was tested by cycling the charging–discharging cycle of the capacitor 1000 times. Fig. 4(b) shows that the charging/discharging voltage of the capacitor remains 90% of the initial voltage after 1000 cycles, indicating good device stability.

4. Conclusion

In summary, the effect of the inclusion of ultrasmall silicon nanoparticles in polyaniline to form a composite material for supercapacitor electrodes has been characterized. The composite

electrode provides enhanced capacitance, which results in superior electrode performance in terms of power and energy-storage capabilities. A prototype supercapacitor based on the composite also indicates the enhanced capacitance as the result of the presence of the nanoparticles in polyaniline. The capacitor exhibits good charging/discharging stability.

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