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ARTICLE

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Polyaniline-Coated Electro-Etched Carbon Fiber Cloth Electrodes for Supercapacitors

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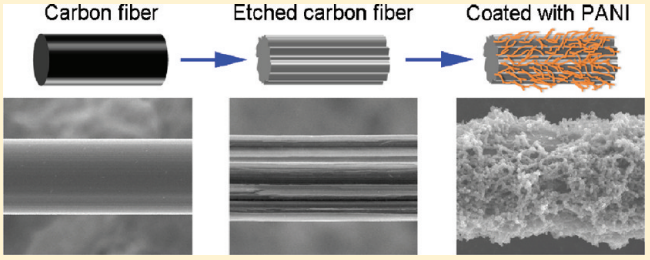
ABSTRACT: Carbon fiber clothes are a promising material for electrodes of supercapacitors owing to their unique 3-D structure, high surface area, remarkable chemical stability, and electrical conductivity. In this Article, electro-etched carbon fiber cloth is explored as an electrode for supercapacitors by coating polyaniline nanowires. The as-prepared electro-etched carbon fiber cloth and polyaniline nanowires, which were characterized by scanning electron microscopy and transmission electron microscopy, were assembled into supercapacitors. The polyaniline nanowires can reach a mass-normalized specific capacitance of 673 F/g and an area-normalized specific capacitance of 3.5 F/cm^2. We also studied the etching and coating of single carbon fibers using the same processing method. The single fiber shows almost the same specific capacitance as the carbon fiber cloth of the same coating density, indicating good accessibility of etched carbon fiber cloth electrode. This work suggests that our polyaniline-based etched carbon fiber cloth electrodes can be a low-cost and scalable solution for the high-performance energy storage devices.



INTRODUCTION

Supercapacitors, also known as electrochemical capacitors or ultracapacitors, offer a promising alternative approach to meet the increasing power demands of energy storage systems.[1,2] Supercapacitors have attracted much attention in recent years because of their pulse power supply, long cycle life (>100 000 cycles), simple operational mechanism, and high dynamic of charge propagation.[3] The high power capability and relatively large energy density compared with conventional capacitors can enable supercapacitors to be used in energy storage systems. The electrode material for supercapacitors can be divided into three major categories. The first category is carbon material, including activated carbon,[4,5] carbon nanotubes,[6] and graphene.[7−9] The use of carbon material is based on the mechanism of double-layer capacitance. It stores the charges electrostatically by reversible adsorption of ions in the electrolyte into active materials that are electrochemically stable and have high accessible surface area.[10] The second category is redox-based electrochemical capacitors using transition-metal oxides such as MnO_2[11−13] and RuO_2,[14,15] which have fast, reversible redox reactions at the surface of the active materials. But metal oxides usually have large electrical resistance and this usually leads to a low power density. The third category is conductive polymers with polyaniline[16−18] or polypyrrole[19−21] being typical examples. The conducting polymer such as polyaniline (PANI) has advantages in terms of low cost, ease of synthesis, good stability in air, and high conductivity.[22] The PANI used for supercapacitors usually has good electrochemical properties with a specific capacitance of 233−1220 F/g.[9,18,23,24] The PANI-based supercapacitors could offer a high-performance and low-cost alternative source of energy to replace rechargeable batteries for various applications, such as electrical vehicles and high power tools.[25] Currently, supercapacitors have already been used in the fields of memory back-up systems, consumer electronics, industrial power, and energy management.[2] A more recent application is the use of supercapacitors in emergency doors on Airbus A380, highlighting their safe and reliable performance.

However, there are also several major issues of fundamental importance to be addressed. The supercapacitor electrodes usually need metal current collectors to conduct electrons, and they decrease substantially the weight-normalized specific capacitance in the final product. Furthermore, in practical applications, the area-normalized capacitance is a very important indicator of the performance of a supercapacitor. A lower area-normalized specific capacitance means more area is needed to reach the desired capacitance and this in turn leads to the use of larger current collector and therefore lower weight-normalized capacitance in the final product.[24,26−29]

In this study, we propose to use a simple and convenient route to fabricate PANI nanofibers onto an electro-etched carbon fiber cloth by electrodeposition. Carbon fiber cloth was selected because of its high conductivity, chemical stability, 3-D structure

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of high porosity, and low cost. The porous structure of carbon fiber cloth is expected to facilitate the diffusion of electrolyte into the electrode material and to provide more channels for rapid ion transport. To examine the performance of carbon fibers, we also performed electro-etching and PANI coating of isolated single carbon fibers. Moreover, by growing PANI directly onto the electro-etched carbon fiber cloth electrodes, the electrodes are binder-free, and this can further reduce the interfacial resistance and enhance the electrochemical reaction rate. Most important of all, the carbon fiber cloth of high conductivity can also be used as the current collector to avoid using metal current collectors to increase the specific capacitance in practice.[28]

RESULTS AND DISCUSSION

Our strategy is shown schematically in Figure 1. A carbon fiber cloth is first etched electrochemically to form a highly conductive substrate with high surface area. Then PANI nanofibers are coated onto the surface-etched carbon fiber cloth to form a 3-D structure. We expect this kind of nanostructured electrodes to have both high weight-normalized and area-normalized specific capacitance.

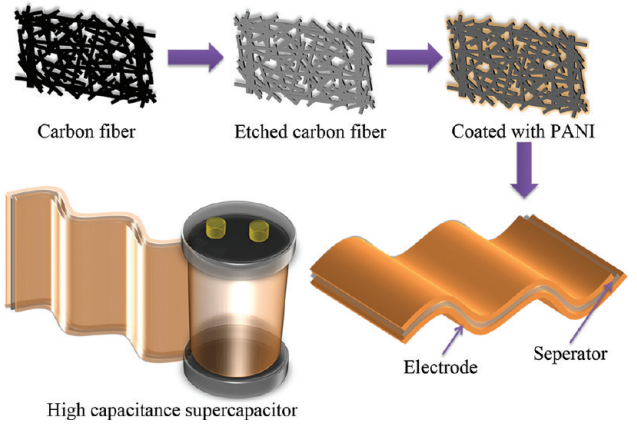

Figure 1. Procedure for preparation of carbon electrodes and supercapacitor. Carbon fiber cloth was first etched by electro-etching. The etched carbon fiber cloth was then coated with PANI by electrodeposition. This kind of electrodes can be made into flexible structure that can be rolled into coiled foils.

Scanning electron microscope (SEM) observations of PANI coated electro-etched carbon cloth are shown in Figure 2. Figure 2a is an SEM image of the carbon fiber cloth before etching. We can see that the carbon fibers are densely packed but randomly oriented to form a macroscopically open structure. This kind of open structure can offer better accessibility to the electrolyte. Furthermore, the carbon fiber cloth of high conductivity can also be used as flexible electrodes. Figure 2b shows a typical structure of the carbon fibers in the fiber cloth after electro-etching. The etched grooves will greatly increase the surface area. The electro-etched carbon fibers are easier for nucleation of monomers. Moreover, we also found that the electro-etched carbon fiber cloth is more hydrophilic than the one without etching. Figure 2c is the SEM morphology after PANI coating. The PANI nanofibers were grown on the electro-etched carbon fibers quite uniformly. We can control the thickness of the PANI coating by adjusting the coating time. Figure 2d shows the PANI nanofibers at high magnification. The as-grown PANI nanofibers have an average length of 1 to 2 μm. The PANI nanofibers are packed randomly to form a mesoporous structure that would increase the rate of ion exchange. Figure 2e is a transmission electron microscope (TEM) image of a single PANI nanofiber. Figure 2f shows the nanofiber at higher resolution. We can see that the PANI nanofiber actually consisted of many small PANI nanorods. This is an ideal structure with high surface area for ion absorption.

We found that etching is a very necessary step for making high-performance carbon fiber cloth electrodes. The comparison of electrochemical performance is shown in Figure 3a. The same PANI coating was carried out on two pieces of same carbon fiber clothes: one is electro-etched and the other is not. The electro-etched piece exhibited a much larger cyclic voltammetric (CV) current than the pristine piece (Figure 3a), indicating a much larger specific capacitance. This is because the electro-etching process has increased the hydrophilicity that resulted in a more uniform coating on the whole carbon fiber cloth. This uniform coating would then enhance the accessibility of electrolyte. As a result, almost every PANI nanofiber can access the electrolyte and take part in the reactions with electrolyte. The carbon fiber

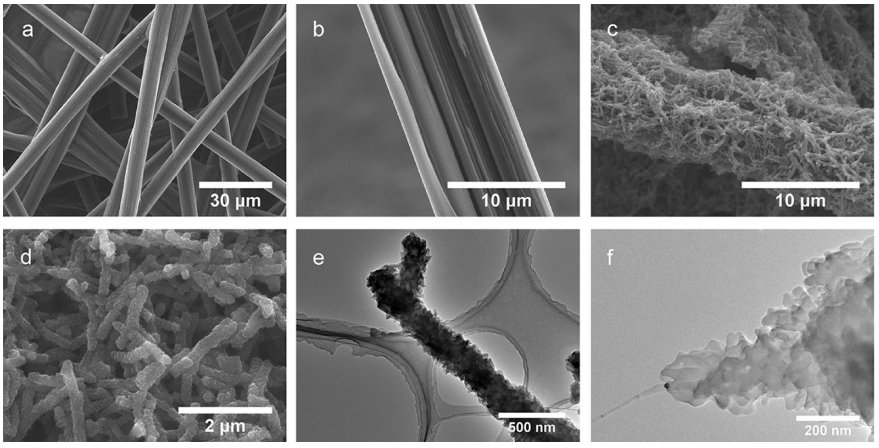

Figure 2. (a) SEM image of the carbon fiber cloth. (b) Carbon fiber cloth after electro-etching. Grooves on the carbon fiber are due to electro-etching and the surface area is enlarged. (c) SEM image of electro-etched carbon fiber cloth after PANI coating. (d) SEM image reveals that the PANI coating is composed of tiny nanorods of PANI. (e) TEM image of a PANI nanowire. (f) High-resolution TEM image of PANI nanowire revealing that it is noncrystalline and is porous at the nanoscale.

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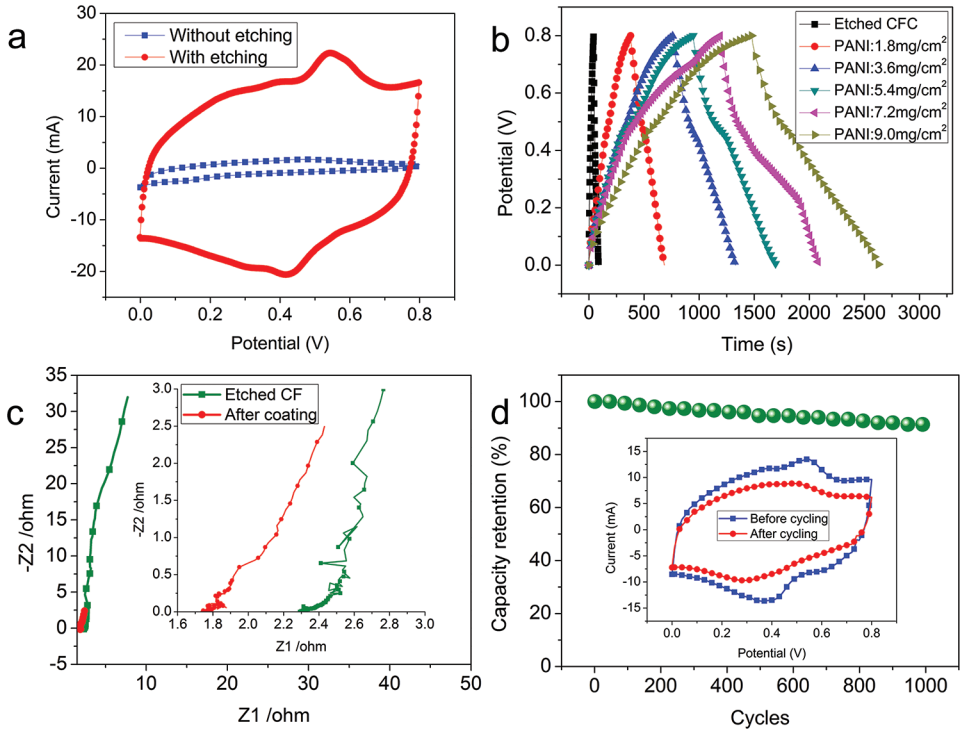

Figure 3. (a) CV comparison of same amount of PANI coated on electro-etched and unetched carbon fiber cloth. (b) Charging and discharging curves of electro-etched carbon fiber cloth under various PANI coatings at constant charging current of 2 mA. (c) EIS curve of electro-etched carbon fiber cloth with and without PANI coating. (d) Cycling of PANI coated electrode under constant charging current of 20 mA. Inset is the CV curves before and after cycling.

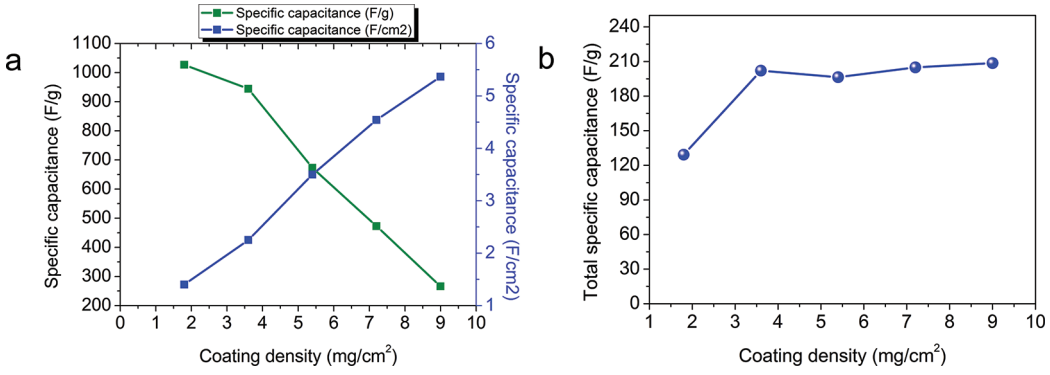

Figure 4. (a) Comparison of mass- and area-normalized specific capacitance under various PANI coating. (b) Specific capacitance with the carbon fiber cloth of various coating.

cloth without electro-etching has poor hydrophilicity in the coating solution, and a thick PANI film is coated just on the carbon fiber cloth. This kind of thick film has poor efficiency in the use of the electrode material and results in a smaller CV current and therefore a lower specific capacitance.

The coating density of the PANI coating can be controlled by the coating time. The charging and discharging curves at different coating densities are shown in Figure 3b. The discharge curves are almost linear in the total range of potential, which shows a very good capacitive behavior.[30] In the case of an electrochemical double-layer capacitor that only has an excess or deficiency of electron charges on the electrodes, no chemical changes are involved; therefore, symmetrical charging and discharging curves are expected. However, for a pseudocapacitor using material like conductive polymers or transition-metal oxides, redox reactions or insertion/removal of counterions must take place. Although the overall energy change can be conducted in a relatively reversible process thermodynamically, the charge and discharge processes in a pseudocapacitor often involve irreversibility in interconversion. Moreover, oxidation and reduction often take place at different potentials. As a result, we usually do not observe symmetrical charging and discharging curves for pseudocapacitors. In our case, the efficiency of pure carbon fiber cloth is ~100% (electrochemical double-layer capacitance). The efficiency of PANI-coated carbon fiber cloth is 81.5%. We calculated the mass- and area-normalized specific capacitance, and the results are displayed in Figure 4a.

Figure 3c is the Nyquist plot of impedance for the etched-electrode before and after PANI coating. In the complex-plane, Z2, the imaginary component (vertical), represents the capacitive properties,

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and Z1, the real component, represents the ohmic properties. Both components were studied in the frequency range between 100 kHz and 0.1 Hz. These plots usually consist of one or more semicircles in the complex plane, sometimes with the center of a semicircle depressed below the Z1 axis. Ideally, a Nyquist plot of a supercapacitor consists of three regions that are all dependent on the frequency. At high frequency, the supercapacitor behaves like a pure resistor. At low frequency, the imaginary part sharply increases and a vertical line is observed, indicating a pure capacitive behavior. In the medium frequency domain, the influence of the electrode porosities can be observed. When the frequency decreases, starting from the very high frequency, the electrolyte penetrates deeper and deeper into the porous structure of the electrode, then more and more electrode surface becomes available for ion adsorption. This medium frequency range is related to the electrolyte penetration inside the porous structure of the high porosity electrode, and this region is usually called the Warburg curve.[31] Both of the two lines in Figure 3c are nearly linear in the low-frequency region and show a very small arc in the high-frequency region. This loop shift is related to the electric resistance between the PANI and carbon fiber cloth. The semicircular loop has been observed routinely in carbon-based supercapacitors. There is usually a very large loop in the supercapacitors of activated carbon electrodes, which means large intergranular electric resistance between the activated carbon particles. It mainly depends on the electrode surface area and the interparticle resistivity. The use of thin active layers or adding some low surface area conductive additives can reduce this value but will lead to a low capacitance per area or per weight. The loop may also reveal correlations between the active material and the current collector. The very small loop regions in Figure 3c indicate a very low electrical resistance between the PANI nanofibers and good interfacial conductivity between the PANI nanofibers and the carbon fibers of the cloth. The Warburg curves in Figure 3c are very short, indicating good accessbility of electrolyte ions to the PANI nanofibers. The equivalent series resistance (ESR) is obtained from the Z1-intercept in the Nyquist plot (Figure 3c), and they are 2.3 Ω and 1.75 Ω, respectively. We noticed that the ESR decreased after we made PANI coating on the carbon fiber cloth. The conductivity of carbon fiber cloth is one order of magnitude greater than PANI. However, in the carbon fiber cloth, because the carbon fibers are stacked together and the point of contact of the carbon fiber may increase the resistance, the coating of conductive polymer could enlarge the contact area for each fiber, which would in turn decrease the resistance. The ESR data determined the rate that the supercapacitor can be charged and discharged, and it is a very important factor to determine the power density of a supercapacitor.

Figure 3d shows the cycling property of PANI-coated carbon fiber cloth under the charging current of 20 mA. We coated different densities of PANI onto the etched carbon fiber cloth of 1.8, 3.6, 5.4, 7.2, and 9.0 mg/cm^2. The cyclicity shown in Figure 3d is obtained with a coating density of 1.8 mg/cm^2, which is the smallest coating density. The capacitance dropped less than 10% after 1000 cycles, indicating good cyclability of the electrodes. The inserted graph is the CV curve before and after long time cycling. It should be noted that in the first 500 cycles a large drop in specific capacitance is usually observed, and the specific capacitance becomes relatively stable afterward. In our case, the specific capacitance dropped around 7% in the first 500 cycles, and it dropped less than 3% in the last 500 cycles. We also

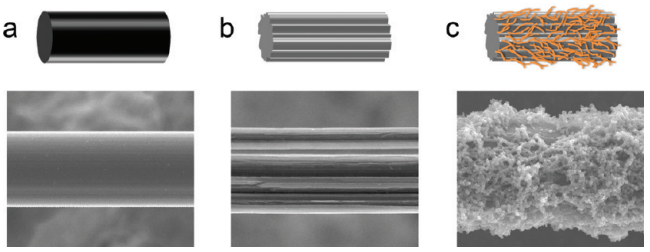

Figure 5. (a) SEM image of a single carbon fiber without etching. (b) SEM image of the same carbon fiber after electro-etching. (c) Etched carbon fiber after PANI coating.

tested the cyclicality of larger coating densities, which exhibited almost the same behavior, but we should note that the cyclicality of high coating density like 9 mg/cm^2 became a little worse; it dropped ∼15% after 1000 cycles. This is because for a thick PANI coating, some PANI may have fallen from the carbon fiber cloth to the separator to result in a lower capacitance.

The mass- and area-normalized specific capacitance under different coating densities were calculated from the charging and discharging curve, which is shown in Figure 4a. We could see that the mass-normalized capacitance decreased when the coating density is increased. The higher coating density means thicker PANI coating. We obtained a high mass-normalized specific capacitance of 1026.8 F/g at the PANI coating density of 1.8 mg/cm^2. However, we only reached 265.9 F/g when the coating density was 9 mg/cm^2. This is because only the PANI on or near the surface could participate the redox reactions. Some of the PANI was not utilized when the PANI coating layer is thick. The area-normalized specific capacitance, which is a very important indicator of the performance of supercapacitor, is also studied in this work. Most electrodes with low loading of active materials can achieve high mass-normalized specific capacitance but often poor area-normalized capacitance. This kind of supercapacitor is not suitable for practical applications. Achieving both high mass-normalized capacitance and area-normalized capacitance for electrodes is crucial for practical applications. We obtained specific capacitance of 5.4 F/cm^2 when the PANI coating was 9.0 mg/cm^2. We optimized the coating time to 10 min and obtained a mass-normalized specific capacitance of 1026.8 F/g and an area-normalized specific capacitance of 1.4 F/cm^2 with a coating density of 1.8 mg/cm^2. We also obtained mass-specific capacitance of 673 F/g and area-normalized specific capacitance of 3.5 F/cm^2 when we controlled the coating time to 30 min with a coating density of 5.4 mg/cm^2. The high conductive carbon fiber cloth can also be used as the current collector to avoid using metal current collectors.

It is interesting to compare our electrodes with PANI-carbon nanotube composite electrodes. Gupta et al. successfully synthesized a PANI and single-walled carbon nanotube (SWCNT) composite electrode and obtained a mass-normalized specific capacitance of 463 F/g of and an area-normalized specific capacitance of 2.7 F/cm^2.[18] PANI and multiwalled carbon nanotube composite electrode was synthesized by in situ chemical polymerization, and a high initial mass-normalized specific capacitance of 606 F/g was obtained.[24] Zhang et al. successfully deposited PANI onto vertically aligned carbon nanotubes for preparing supercapacitors, and a high mass-normalized specific capacitance of 1030 F/g was obtained, although it could only reach a rather low area-normalized specific capacitance of 1.4 F/cm^2.[23] As previously

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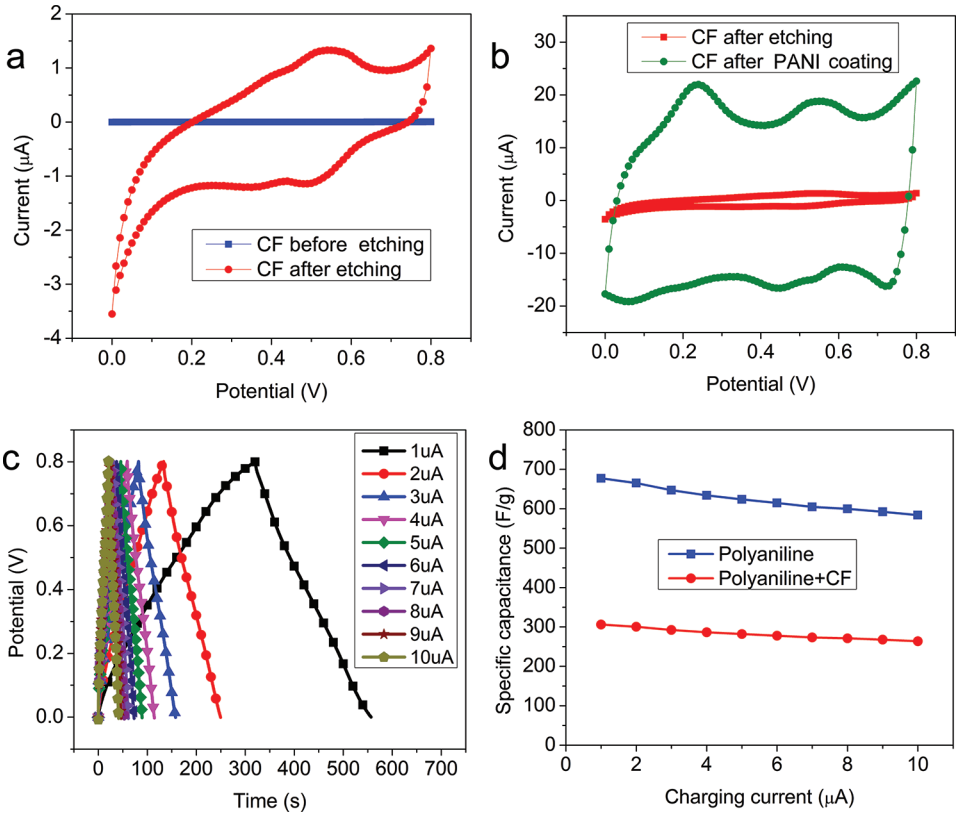

Figure 6. Electrochemical properties of a single carbon fiber. (a) CV curves of the carbon fiber before and after electro-etching. (b) CV curves of the single fiber before and after PANI coating. (c) Charging and discharging curves of PANI-coated single carbon fiber under different charging current. (d) Specific capacitance of the PANI coating and the PANI coating together with the carbon fiber under different charging current.

mentioned, the carbon fiber cloth can also be used as the current collector to avoid using metal current collectors. The total specific capacitance with carbon fiber cloth under different coating densities is shown in Figure 4b. The specific capacitance is nearly 200 F/g using the carbon fiber cloth as current collector, underlining the potential for practical applications of the electrodes.

To understand and evaluate the performance of carbon fibers, we also applied the same processing to isolated single carbon fibers, as illustrated in Figure 5. A single carbon fiber was first picked up and mounted onto the platinum substrate. The morphology of the pristine carbon fiber is shown in Figure 5a. The single fiber was etched in the same acid solution for the same amount of time, leading to the structure shown in Figure 5b. The electro-etched carbon fiber was then coated with the same PANI nanofibers, as shown in Figure 5c.

The electrochemical performance of the single carbon fiber before and after PANI coating is shown in Figure 6. As previously reasoned, the etched carbon fiber increased the surface area to raise the double-layer capacitance, and this is confirmed by the electrochemical properties of the structure shown in Figure 6a. The carbon fiber before etching shows very small current response in the CV curve. In contrast, the carbon fiber after etching shows a much larger current than the one without etching. In the case of a pure carbon material, the specific capacitance, which is proportional to the CV current, is only dependent on the surface area. This means that the surface area has increased greatly after etching. Figure 6b is the CV curve of the single carbon fiber before and after PANI coating at the density of 5.4 mg/cm^2. The CV current increased greatly after PANI coating, indicating an increase in the capacitance because the PANI coating and the redox reaction of PANI are the main contributions to the whole capacitance. The shape of the CV curve is close to rectangular, indicating an excellent capacitance behavior and a low contact resistance. The charging and discharging curves in different charging currents are shown in Figure 6c. The specific capacitance of the PANI coating alone as well as the PANI coating together with the carbon fibers was calculated on the charging and discharging curves, which are shown in Figure 6d. The specific capacitance of the PANI is 677 F/g, almost the same as that of the carbon fiber cloth with PANI coating (673 F/g) of the same coating parameter. We know that the single fiber can be fully accessed by and reacted with the electrolyte. The almost same specific capacitance of the single fiber compared with carbon fiber cloth electrode indicates a very good accessibility of the PANI-coated carbon fiber cloth electrode. This result is attributed to the 3-D macroscopically open structure of the carbon fiber cloth and the mesoporous structure of PANI nanofibers.

Charged supercapacitors, like charged batteries, are in a state of high free energy relative to that of the discharged state, so there is a pseudodriving force for their self-discharge. The self-discharge characteristics of a supercapacitor device are important in evaluating its performance and commercial specifications. When supercapacitors or batteries are charged and then left on open circuit for some time, a certain degree of self-discharge can set in, which depends on the chemistry and electrochemistry of the system, the purity of reagents and electrolytes, and so on. Charged supercapacitors usually exhibit greater rates of self-dicharge than most

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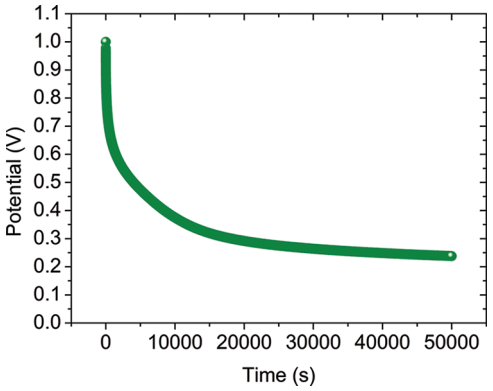

Figure 7. Self-discharge of PANI-coated carbon fiber cloth supercapacitor.

batteries at a given temperature. This difference in stability of voltage is attributable to the fact that the potential of battery electrodes is usually thermodynamically determined at some equilibrium open-circuit value that is characterized by an exchange current density corresponding to an electrostatically determined potential difference that has no mechanism thermodynamically and kinetically stabilizing it. Hence the potential can be easily disturbed by some adventitious depolarizing process set, for example, in impurities or surface redox groups. In the case of a charged pseudocapacitor, the self-discharge mechanism must involve a dissipation of the double-layer charge coupled to diminution of the coverage on the electrode surface because the charge for formation or removal of such an electroactive species is normally substantially larger than that for charging or discharging the double-layer capacitance.[32] We charged our PANI-coated carbon fiber cloth supercapacitor to 1.0 V and then left on open circuit for 50 000 s (~14 h) at room temperature; the self-discharge associated with a fall in potential takes place over a long period, which can be seen in Figure 7. It dropped ~50% after the first 1 h and eventfully reached a steady potential of ~0.24 V.

Our results indicate that the carbon fiber cloth electrode can be a promising candidate for uses in electric or hybrid vehicles. Furthermore, the results are also of potential use for the preparation of PANI-based electrodes with varied properties to meet diverse applications, such as lithium ion batteries, electrochemical sensors, and solar cells.

CONCLUSIONS

We have successfully fabricated PANI-coated electro-etched carbon fiber cloth electrodes for supercapacitors that give rise to a remarkable result of weight-normalized specific capacitance of 673 F/g. What's more, the high value of area-normalized specific capacitance of 3.5 F/cm^2 is crucial for their practical applications. The electro-etching process is very important for making the carbon fiber cloth electrodes effective and efficient. First, the electro-etching process can greatly increase the surface area of the carbon fiber cloth. Second, the etching process can increase the hydrophilicity of the carbon fiber cloth and make it easier for uniform PANI coating. Moreover, the coating of PANI can decrease the electrical resistance of the electrodes. We also studied single carbon fibers under the same processing procedure. The single carbon fiber showed almost the same specific capacitance as the carbon fiber cloth with the same coating density, indicating the good accessibility of the etched carbon fiber cloth electrodes.

METHOD

The carbon fiber cloth with a thickness of 0.19 mm was purchased commercially from TORAY. The mass density of the carbon fiber cloth is 0.44 g/cm^3. The average diameter of each carbon fiber is 8 μm. The aniline and sulfuric acid were of analytical reagent grade from Sigma-Aldrich.

The electro-etching of carbon fiber cloth was conducted using a potentialstat operated at 2 V for 10 min in 1M H_2SO_4 electrolyte. The electro-etched carbon fiber cloth (0.5 × 2 cm) was used as the working electrode, and a platinum sheet (1 × 2 cm^2) was used as the counter electrode. All potential values were recorded versus the saturated Ag/AgCl reference electrode. The distance between the working electrode and counter electrode was fixed at 1.5 cm. Anodic deposition was controlled by an electrochemical station (IVIUM Technologies) in a 1 M HCl electrolyte containing 0.3 M aniline monomer.[26] The PANI nanowires were synthesized by a two-step method on a conventional three-electrode system. The first step is the nucleation of PANI, performed at a constant potential of 0.8 V for 1 min at room temperature. After that, the nanowires were grown under a constant current condition with current density of 5 mA/cm^2.

The electrochemical properties and capacitance measurement of the supercapacitor electrodes were studied in a three-electrode system by CV and electrochemical impedance spectroscopy (EIS) using CompactStat of Ivium Technologies. The CV response of the electrodes was measured at different scan rates varying from 10 to 100 mV/s. Voltammetry testing was carried out at potentials between 0 and 0.8 V in 1 M H_2SO_4 aqueous electrolyte solution. Impedance spectroscopy measurements were carried out without DC bias sinusoidal signal of 0.005 V over the frequency range from 100 kHz to 0.1 Hz.

We calculated the area-normalized specific capacitance by using the total electrode capacitance divided by the apparent carbon fiber cloth area, which is 1 cm^2. The weight-normalized specific capacitance is calculated by the total capacitance divided by electrode weight, which is measured by an analytical balance (XP205, 0.01 mg).

The morphology and structure of the electrodes were examined by SEM (JSM-6500F, JEOL) and TEM (JEM-2100, JEOL).

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This manuscript was originally published on the web on November 1, 2011, with errors to the Results and Discussion Section and the caption of Figure 2. The corrected version was reposted on November 4, 2011.