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Abstract

Wearable electronics offer the combined advantages of both electronics and fabrics. Being an indispensable part of these electronics, lightweight, stretchable and wearable power sources are strongly demanded. Here we describe a daily-used cotton fabric coated with polypyrrole as electrode for stretchable supercapacitors. Polypyrrole was synthesized on the Au coated fabric via an electrochemical polymerization process with p-toluenesulfonic acid (p-TS) as dopant from acetonitrile solution. This material was characterized with FESEM, tensile stress, and studied as a supercapacitor electrode in 1.0 M NaCl. This conductive textile electrode can sustain up to 140% strain without electric failure. It delivers a high specific capacitance of 254.9 Fg⁻¹ at a scan rate of 10 mV s⁻¹, and keeps almost unchanged at an applied strain (i.e. 30% and 50%) but with an improved cycling stability.

Keywords

polypyrrole, fabric, electrodes, supercapacitor, stretchable, synthesized, electrochemically

Disciplines

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Electrochemically synthesized stretchable polypyrrole/ fabric electrodes for supercapacitor

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ABSTRACT

Wearable electronics offer the combined advantages of both electronics and fabrics. Being an indispensable part of these electronics, lightweight, stretchable and wearable power sources are strongly demanded. Here we describe a daily-used cotton fabric coated with polypyrrole as electrode for stretchable supercapacitors. Polypyrrole was synthesized on the Au coated fabric via an electrochemical polymerization process with *p*-toluenesulfonic acid (*p*-TS) as dopant from acetonitrile solution. This material was characterized with FESEM, tensile stress, and studied as a supercapacitor electrode in 1.0 M NaCl. This conductive textile electrode can sustain up to 140% strain without electric failure. It delivers a high specific capacitance of 254.9 F g⁻¹ at a scan rate of 10 mV s⁻¹, and keeps almost unchanged at an applied strain (i.e. 30% and 50%) but with an improved cycling stability.

KEYWORDS: Polypyrrole, e-textile, electrodeposition, supercapacitors, stretchable electrode.

1. Introduction

Intelligent and wearable electronic items have demonstrated significant advances in terms of miniaturisation, functionality and comfort. The flexibility, stretchability, and lightweight of such wearable electronics allow for many new applications and designs which are previously impossible with traditional electronics or textile technology. Continuous personal health monitoring, wearable displays and new class of portable power are some examples of these novel applications [1-5]. To

power these wearable electronics, stretchable and wearable energy conversion/storage devices including batteries and supercapacitors become a necessity. To be conformal to the curved surface and sustain its function during the body movement, the ideal wearable power sources would be made into breathable textile formats with stretchability.

Supercapacitor possesses the advantages of high power densities, excellent reversibility and long cycle life [6]. Recently, there has been an emerging interest in stretchable supercapacitors and batteries [7-11]. Single-walled carbon nanotubes (SWNT) integrated with poly (dimethylsiloxane) (PDMS) [7, 9] or textile substrate [8] is one type of stretchable supercapacitor electrodes. Buckle-structured stretchable SWNT macrofilms on PDMS exhibited a much similar specific capacitance, 54 F g^{-1} at 0% strain vs. 52 F g^{-1} at 30% strain at a current density of 1 A g^{-1} [7]. The stretchable SWCNT-coated textile supercapacitor delivered a specific capacitance of 62 F g^{-1} at a current density of 1 mA cm^{-2} , and no notable capacitance fade was observed after 100 cycles at 120% strain [8].

Inherently conducting polymers (ICPs) are interesting candidates for flexible energy storage devices due to their relatively high theoretical capacity, fast redox properties, lightweight and mechanical flexibility [12-16]. ICPs are well-suited for the fabrication of conductive textiles [5, 17, 18], and ICPs coated textiles have been studied in energy storage [19-21]. Very recently we have demonstrated that Polypyrrole coated Nylon Lycra fabric can be used for stretchable supercapacitor [22]. This stretchable PPy electrode was chemically synthesized on Nylon Lycra fabric and delivered a specific capacitance of 108.5 F g^{-1} at 1 A g^{-1} in 1.0 M NaCl , which increased to 125.1 F g^{-1} at 60% strain.

Here we report a stretchable supercapacitor electrode material based on polypyrrole (PPy) coated cotton fabric via electrochemical deposition. Compared with the chemical process, electrochemical polymerization can provide cleaner products, better control of film thickness and morphology [23-25]. PPy coated cotton fabric via electropolymerization delivered a much higher specific capacitance of 255 F g^{-1} at a scan rate of 10 mV s^{-1} in 1.0 M NaCl , in comparison with that of 123 F g^{-1} reported for chemically synthesized PPy on fabric [22]. This electrode delivers slightly higher specific capacitance and improved cycling stability at 30% and 50% strain.

2. Experimental section

2.1 Preparation of PPy coated fabric

The stretchable knitted fabric with 90% cotton and 10% Lycra was purchased from Spotlight Stores Pty Ltd. Before coating, the cotton fabric was treated with an aqueous solution of scouring agent and sodium hydroxide for 1 h to remove the grease and impurities attached, followed by rinsing with H_2O till neutral pH.

Pre-strained (50%) cotton fabric was treated with plasma prior to the sputter coating. A layer of gold (approximately 200 nm) was coated on such fabric using an Edwards Auto 306 Sputter Coater. Released the strain and a uniform and coherent gold coating was obtained. Polypyrrole films were electropolymerized galvanostatically at a current density of 2 mA cm^{-2} on re-elongated (50%) Au coated cotton fabric from acetonitrile solution containing 0.1 M monomer (pyrrole) and 0.1 M *p*-toluenesulfonic acid (*p*-TS) at room temperature. The solution was de-oxygenated with nitrogen prior to the electrodeposition, and the pyrrole was electrodeposited to a charge density of 0.8 C cm^{-2} .

2.2 Characterization of Au/PPy coated fabric

The surface morphologies of the conductive fabric were investigated by means of a cold-field-gun field emission microscope (FESEM, JEOL JSM7500FA). The surface resistance was determined according to the American Association of Textile Chemists and Colorists Test Method 76-1995. Two rectangular copper electrodes were placed on the fabric sample and the surface resistance (R_s) was given by:

$$R_s (\Omega/\square) = \frac{W}{D} R'$$

Where, R' is the resistance measured by the Multimeter, and W and D are the width of the sample and the distance between the two copper electrodes, respectively.

The fabric sample with a size of 20 mm (length) $\times$ 10 mm (width) was used for the stress-strain test using a Shimadzu EZ mechanical tester. It was elongated / released at a controlled speed of 3.3% s^{-1} . The concomitant resistance was measured by an Agilent 34410A digital multimeter during the stretching cycles.

2.4 Electrochemical properties of PPy coated fabric

Cyclic voltammetry were carried out in a standard three-electrode system using a Pt mesh counter electrode, a Ag/AgCl (3M NaCl) reference electrode, and a PPy coated cotton fabric attached onto reticulated vitreous carbon (RVC) as working electrode. The electrolyte was 1.0 M NaCl. Cyclic voltammetry was performed using a Solartron SI 1287 and scanned between -0.4 V to 0.5 V.

The specific capacitance of PPy coated cotton fabric was calculated using the following equation [26]:

$$C = \frac{A/2}{f \times v \times m}$$

Where C is the specific capacitance, A is the integral area of the cyclic voltammogram loop, f is the scan rate, v is the voltage window, and m is the mass of electroactive material (PPy). The loading mass of polypyrrole on the cotton fabric was 0.14 mg cm^{-2} .

3. Results and Discussion:

3.1 Surface morphology

The surface morphology of the Au coated cotton fabric is shown in Fig.1a and b. It can be seen that gold was uniformly deposited onto the fibre surface. The resultant Au-coated cotton fabric displayed a good electronic conductivity with a surface resistance of $50 \Omega/\square$, and could be used as substrate for PPy electrodeposition. After electrochemical polymerization, the cotton fibre was covered with a layer of PPy (Fig. 1c). PPy shows a cauliflower-like nodule structure composed of microspherical grains (Fig. 1d) as reported previously [27].

3.2 Tensile test

The mechanical properties of the original cotton fabric, Au coated fabric and PPy coated fabric were tested and the stress strain responses at wale direction are shown in Fig. 2. They all exhibited a much similar stress-strain response with a large hysteresis being observed between the first and the rest cycles. It can be explained by the non-reversible structural changes when the fabrics were subjected to external force. And the system approached steady state after 2 cycles for all three samples. The Au-coated fabric exhibited a plastic deformation when a 50% strain was maintained for ~1 h. The fabric did not return to the original dimensions with a 25% increase in length observed.

Au and PPy coated fabrics exhibited increased drawing forces when compared with the uncoated fabric, as shown in Fig. 2d. A stress of 64 N m^{-2} was required for uncoated fabric to be

stretched to 50% elongation at the wale direction compared to that of 107.5 N m^{-2} for Au coated fabric. A much higher stress of 144.5 N m^{-2} was required for PPy coated fabric. Such higher stress required can be ascribed to the increased stiffness induced by the Au or PPy coating.

The electrical resistance of the Au and PPy coated cotton fabrics was investigated with strains up to 140% applied in the wale direction (Fig. 3a). Both electrode structures exhibited excellent stretchability and sustained their conductivity even at 140% elongation. The commonly recognized break strain for PPy films is just 10% [28]. The normalized electrical resistance of Au coated cotton fabric increased rapidly with a strain between 3% and 25% applied. Then the resistance decreased and gradually stabilized. The resistance change of the Au coated fabric might be due to the fabric structural change itself rather than the Au film coating. When the fabric was stretched, those fibers inside threads were firstly straightened and then slipped along the elongation direction, causing an increase in the electric resistance. Simultaneously, the threads with Au coating got closer resulting in a conductivity increase. Compared with the Au coated cotton, PPy coated cotton fabric showed a much smaller initial resistance increase with strain applied before it gradually stabilized. It is also noticed that PPy coated fabric showed a higher R/R_0 than the Au coated fabric at the stable state.

To avoid the irreversible elongation induced with large strains, a maximum strain of 50% was applied for further work. The stretchability of the PPy coated cotton fabric was investigated with 1000 stretching cycles at 50% strain. The normalized resistance initially increased and then decreased when it was stretched (Fig. 3b). When the strain was released, the resistance was also increased first and then decreased. Such double peak phenomenon, same as that observed for the chemically polymerized PPy coated fabric, can be due to the slow strain recovery of the fabric at

large elongation [22, 29]. The normalized electrical resistance was found to be irreversibly increased after stretching, from $\sim 105 \Omega/\square$ to $\sim 1645 \Omega/\square$ after 1000 stretching cycles.

The morphology of the PPy coated cotton fibre after 1000 stretching cycles was investigated and showed in Fig. 4. No cracks can be found on the surface of PPy coated cotton fibre. This may be explained by that the applied strain was accommodated by the fabric structural change rather than the fiber elongation itself. It is also indicative of the strong adherence of PPy coating on the fabric.

3.3 Electrochemical properties

The electrochemical properties of PPy electrode were tested in 1.0 M NaCl. The choice of NaCl as supporting electrolyte is based on that the use of edible NaCl as electrolyte will not cause any damage to our body in the case of electrolyte leakage, which is highly desirable for wearable power sources. In addition, NaCl is of high ion conductivity and commonly used for characterizing PPy [30, 31].

The PPy coated fabric exhibits typical capacitor-like characteristics in the form of a nearly rectangular CV behavior even at 100 mV s^{-1} (Fig. 5a). These results indicate that the charge-discharge responses of the electric double layer are highly reversible and kinetically facile. This may be attributed to the high rate of electrochemical process that can be achieved in thin layer PPy film. The rectangular shape of CV curves became distorted at the scan rate of 200 mV s^{-1} . This phenomenon is common for the electrochemical capacitive materials [32, 33]. It could be attributed to the delayed charge transfer following change of the electric field caused by the penetration and diffusion of electrolytes barrier into a relatively poor electronic or ionic conductive material [34].

The electrochemical properties of this PPy coated fabric were also investigated with a strain of 30% and 50% applied. The results obtained at 30% strain are shown in Fig. 5b. They all displayed nearly identical rectangular shape CV responses up to the scan rate of 300 mV s⁻¹. Such phenomenon was also observed for PPy coated fabric at 50% strain (not shown). To give a clear view, Fig. 5c shows the CV curves of the PPy coated fabric at a scan rate of 100 mV s⁻¹ with different strain applied. No notable difference was observed between these CVs, which clearly demonstrate that our fabric can endure up to 50% strain without loss of electrochemical properties.

Fig. 5d shows the specific capacitance of PPy coated fabric obtained at different scan rates in 1.0 M NaCl for electrodes prepared with or without strain applied. It can be seen that the specific capacitance of the PPy coated fabric increased slightly after the strain was applied. It delivered a specific capacitance of 255, 217, 197, 166 and 145 F g⁻¹ at 0% strain at a scan rate of 10, 50, 100, 200 and 300 mV s⁻¹, respectively. The corresponding specific capacitance slightly increased to 256, 225, 203, 175 and 150 F g⁻¹, respectively at 30% strain. When the applied strain increased to 50%, the specific capacitance increased again to of 260, 218, 206, 177 and 151 F g⁻¹ respectively. This might be due to the easy accessibility of ions at the electrolyte-electrode interface induced by the applied strain, same as in the case of the chemically deposited PPy coated fabric [22].

The cyclic stability was also investigated, and the results are shown in Fig. 6. Polypyrrole coated fabrics with or without elongation were cycled at a scan rate of 100 mV s⁻¹. PPy coated fabric at 0% delivered a specific capacity of 71 F g⁻¹, only about 36% of its initial capacitance after 500 cycles. In comparison, with 30% strain applied the electrodes retained a specific capacitance of 103 F g⁻¹, about 51% of the initial capacitance. This may be attributed to the PPy on elongated fibres being oriented in a more ordered structure, leading to more homogeneous stress distribution and less stress

concentration during the oxidation/reduction cycles [35]. In consequence, the reversibility and stability of the PPy coated fabric was improved. With 50% strain applied the electrode showed a similar result, a capacitance of 103 F g^{-1} , about 50% of its initial value was retained after 500 cycles.

4. Conclusion

In summary, we have demonstrated that highly stretchable and conductive textile could be prepared by simple electrochemical deposition on pre-strained Au coated cotton fabric. PPy coated fabric exhibited a surface resistance of $105 \text{ } \Omega/\square$, and this increased to about $1645 \text{ } \Omega/\square$ after 1000 stretching cycles at 50% strain. This material demonstrates a good capacitive behaviour, even up to the scan rate of 300 mV s^{-1} . A specific capacitance of 255 F g^{-1} was obtained at a scan rate of 10 mV s^{-1} . This increased slightly to 260 F g^{-1} at 50% strain. In addition, PPy coated cotton fabric exhibited improved cycling stability with strain applied. It might be ascribed to the more oriented and ordered structure of PPy induced by the applied strain, which led to more homogeneous stress distribution and less stress concentration during oxidation/reduction cycles.

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Captions:

Fig. 1 FESEM images of Au (a, b) and PPy (c, d) coated cotton fabric.

Fig. 2 Strain stress curves of original cotton (a), Au coated cotton (b) and PPy coated cotton fabric. (d) The first cycle of the stress strain response of all three samples when stretched to 50%.

Fig. 3 (a) Normalized electrical resistance *versus* tensile strain of Au coated fabric and PPy coated fabric. (b) Normalized electrical resistances under cyclic elongation of 50% for PPy coated fabric (first 5 cycles).

Fig. 4 FESEM images of PPy coated cotton fabric after 1000 stretching at 50% strain.

Fig. 5 Cyclic voltammograms of PPy coated fabric with 0% (a) and 30% (b) strain at different scan rates in 1.0 M NaCl. (c) Cyclic voltammograms of PPy coated fabric with or without strain at the scan rate of 100 mV s⁻¹. (d) Specific capacitance *versus* scan rate of PPy coated fabric with or without strain.

Fig. 6 Specific capacitance versus cycle number at a scan rate of 100 mV s⁻¹ for PPy coated fabric with or without strain.

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6