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Capacitive behavior of latex/single-wall carbon nanotube stretchable electrodes

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ABSTRACT

In this report single-wall carbon nanotubes (SWNTs) were coated onto latex using spray coating to produce a stretchable electrode. The electrochemical properties of the electrode were determined using cyclic voltammetry and electrochemical impedance spectroscopy and galvanostatic charge/discharge tests were also carried out. The impedance and charge/discharge curves of the latex/SWNTs electrode showed good capacitive behavior even after repetitive stretching to 100% strain. The highest capacitance value obtained for the unstretched SWNTs electrode was 119 F g^{-1} in 1 M Na_2SO_4 at 5 mV s^{-1}. After the 100th stretch $\approx$ 80% of the original capacitance value was retained.

1. Introduction

The development of novel energy storage devices is of great significance for applications in wearable electronics [1–3]. Amongst the diverse range of energy storage devices available, electrochemical capacitors (ECs) are promising candidates due to their high power density, long life, durability and safety. Such characteristics are desirable for various applications, including high performance sportswear, wearable displays and embedded health monitoring devices [4,5]. Developing technologies such as foldable displays [6], functional electronic eyes [7], transistors [8] and photovoltaic devices [9] also require the continued development of stretchable electrodes. These applications demand power systems with high capacitance but also require the material to be highly flexible and stretchable [10,11]. Two types of ECs, which store charge by electrochemical means, have been developed. The first is the electrochemical double layer capacitor (EDLC) which, instead of having two plates separated by a thick insulator, is based on the operating principle of an electrical double layer that is formed at the interface between an electrode and electrolyte [1,4]. The second type is based on Faradaic pseudo-capacitance where charge is transferred at the surface or in the bulk near the surface of the solid electrode materials [3,5].

Various materials have been used as substrates for stretchable conductors. These include silicone rubber, poly (dimethylsiloxane) (PDMS), nitrile-butadiene rubber (NBR), natural-latex rubber, polyurethane and cotton [12–17]. Among the polymers available, latex rubber is widely available, inexpensive, non-toxic, eco-friendly, highly stretchable and easily processed. Most work to date using latex has focused on sensors and actuators. Sommerdijk et al have developed a biosensor based on a polypyrrole/latex composite [18], while Kim et al have reported a micro-actuator using latex rubber as a membrane [19]. To our knowledge there have been no studies for the capacitive behavior of SWNTs coated onto latex rubber as a stretchable substrate.

Single-wall carbon nanotubes (SWNTs) are highly suitable for preparation of high performance electrochemical supercapacitors due to their high electrical conductivity, thermal and chemical stability and large surface area [20]. In addition, SWNTs possess high flexibility, low mass density and large aspect ratio (typically > 1000), enabling them to maintain conductive pathways by bridging cracked regions under large strain [21–23]. However, a major problem of pristine SWNTs is aggregation due to van der Waals force, which results in poor dispersability of pristine SWNTs in most solvents. In order to overcome this issue, acid treatment has been used to improve dispersability and capacitance

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values of SWNTs in fabricating supercapacitors [24]. Acid treatment using strong acids, including nitric and sulfuric acid, can introduce oxygen containing functional groups such as carboxylic (-COOH) and hydroxyl (-OH) groups on the surface of SWNTs. -COOH groups on SWNTs can enhance surface wettability of SWNTs to improve ionic conductivity between the electrode-electrolyte interface. These functional groups also offer more available sites to enable physisorption of free electrolyte ions. Previous reports have indicated that nitric acid treatment can significantly improve capacitance values of the carbon nanotube based capacitors [25,26].

Initial studies of electrochemical capacitors with SWNTs electrodes [27,28] reported significant increases in electrochemical performance [29–33]. Lee et al. [34] have reported supercapacitors fabricated from SWNTs grown by arc discharge and mixed with poly(vinylidenechloride) as a binder and then dissolved in tetrahydrofuran. They obtained a maximum specific capacitance of 180 F g^{-1} and power density of 20KW kg^{-1} at an energy density of 6.5Wh kg^{-1} in 7.5 N potassium hydroxide (KOH) electrolyte. Pushparaj et al. [2] used nanoporous cellulose composite paper embedded with aligned multi-wall carbon nanotubes (MWNTs) electrodes to achieve an energy density of 13 Wh kg^{-1} with specific capacitance of 36 F g^{-1} and power density of 1.5 Wh kg^{-1}. Yu et al. [11] have reported a stretchable supercapacitor based on buckled SWNTs macro-films on poly(dimethylsiloxane) that has a maximum specific capacitance of 54 F g^{-1} and power density of 0.5 KW kg^{-1} at 4.2 Wh kg^{-1} energy density. The buckled SWNTs films could stretch up to 30% strain.

Established methods for the preparation of carbon nanotube films include vacuum filtration [35,36], dip coating [37,38], ink-jet printing [39] and electro spray deposition [40]. Even though the vacuum filtration method has been widely used to fabricate CNTs films (bucky paper), this method presents practical challenges for scale up of industrial applications and is limited to deposition on porous substrates [38]. Dip and spin coating methods allow the preparation of CNTs films on various substrates at the laboratory scale, but are time consuming when thicker films are required and limited by lack of control of film quality over large areas [35].

In this work, we report on the preparation of a flexible and stretchable electrode using a simple and inexpensive spray coating technique, which is potentially applicable at an industrial scale. Functionalized (carboxylated) single-wall carbon nanotubes (SWNTs) were sprayed onto gold coated latex to create an electrode that displays practically useful electronic properties even after repeated stretching to 100% strain. This is demonstrated through characterization of their electrochemical properties such as changes in specific capacitance under varying mechanical stress and strain. We also describe the surface morphology of SWNTs films on the latex substrate with respect to the capacitance of the stretchable electrode.

2. Experimental

2.1. Materials

Single-wall carbon nanotubes (SWNTs) were purchased from Carbon Nanotechnologies, Inc (Houston, TX). N, N-Dimethylformamide (AR grade), concentrated nitric acid (70%) and sodium sulfate (AR grade) were obtained from Sigma-Aldrich and used as received. The liquid latex was purchased from AA Rubber and Seals. Pty, Ltd (Belmore, NSW, Australia).

2.2. Purification and functionalization of SWNTs

Metallic oxides were removed from pristine SWNTs by nitric acid treatment. Approximately 200 mg of SWNTs were refluxed in 40 mL 5 M nitric acid for 6 hours, then filtered through a polytetrafluoroethylene-coated polypropylene filter (0.2 μm) and rinsed with deionized water. The sample was freeze dried for 2 days [41].

2.3. Preparation of SWNTs coated stretchable electrode

2.3.1. Au modified latex film

A suitable amount of natural liquid latex (with ammonia to prevent bacteria spoilage) was poured into a glass mold (30 cm x 5 cm x 1 mm) and then allowed to dry at room temperature for 24 hrs. To fabricate the electrode, a section of the latex film (1 cm x 5 cm x 1 mm) was transferred to a glass microscope slide, stretched to introduce a 100% uniaxial pre-strain and then held under tension using double-sided adhesive tape. After stretching, a 150 nm thick layer of gold was coated onto the dried latex film by sputter coating (Edwards Sputter Coater AUTO306, BOC Ltd, United Kingdom), allowing it to be used as a current collector.

2.3.2. Carbon nanotube dispersion

Acid treated SWNTs (5 mg) were mixed with 10 mL DMF, then ultrasonicated (Sonics Vibracell ultrasonic processor, 500 watt, 30% amplitude, USA) for 1 hr to create a stable dispersion.

3. Characterization

3.1. Physical and chemical characteristics of the pristine and functionalized (acid-treated) SWNTs

3.1.1. FT-IR spectroscopy

The FT-IR spectra of pristine and functionalized SWNTs samples were measured using a Shimadzu IR Prestige-21 FTIR spectrophotometer with single reflection HATR accessories (Miracle, Pike Technologies). The scanning range of the experiment was 1000–4000 cm^{-1} on transmittance mode with 30 scans and 8.0 resolutions.

3.1.2. Raman spectroscopy

Raman analysis was carried out using a JY-HR800 Raman spectrometer equipped with a visible Raman microscope and Olympus BX41 and CCD detector. The excitation wavelength was 632.81 nm and spectra were obtained over 30 s at 1.0 cm^{-1} resolution.

3.1.3. Morphology measurement of the latex/SWNTs film

Scanning electron microscopy (SEM) images of SWNTs (pristine and functionalized SWNTs on silicon wafer) and SWNTs film on the latex substrate were obtained using a JEOL JSM-7500FA field emission SEM. The accelerating voltage was 5.0 kV and the emission current was 10 μA.

3.1.4. Electrical conductivity measurement

The electrical conductivity measurement of the SWNTs film on the latex was carried out by a JANDEL Four-Point Probe conductometer (Jandel Engineering Ltd, UK). The electrical resistivity could be expressed as [42];

$$\rho = K(\mathrm{V}/\mathrm{I}) * t \tag{1}$$

Where, ρ is the electrical resistivity of the SWNTs film, K is a geometric factor (K = 4.5324), V is the electric potential across the two inner probes, I is the applied current and t is the thickness of the SWNTs film (cm). The electrical conductivity of the SWNTs film is calculated by the following equation;

$$\sigma = 1/\rho \tag{2}$$