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Fabrication and characterization of single walled nanotube supercapacitor electrodes with uniform pores using electrophoretic deposition

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ABSTRACT

Well dispersed aqueous suspensions containing single walled carbon nanotubes (SWNTs) were prepared without surfactants by functionalizing SWNTs in an acid treatment. SWNT coated electrodes were prepared from the SWNT aqueous suspensions using various methods to create uniform nanoporous networks of SWNTs on stainless steel (SST) current collectors. The EPD process was identified as the primary tool for reliably producing uniform SWNT nanoporous networks on SST substrates. Optical and scanning electron microscopic images and the BET surface area analysis were used to evaluate the SWNT dispersion quality of the electrodes. The average SWNT nanopore size produced from the EPD process was found about 1 nm and was nearly unaffected by extended EPD processing times. The SWNT coated electrodes were characterized using the cyclic voltammetry and their capacitance was determined. A correlation between the extended EPD processing time and the electrode capacitance was quantified.

1. Introduction

As energy dependence gradually moves away from fossil fuels, the need to manufacture energy storage devices with large storage capacities and high charge/discharge rates has become more critical, especially to the success of products and technologies requiring electricity [1]. New and innovative materials and processes are being developed in an effort to increase the power storage capacities and improve the charge/discharge performance of batteries and capacitors [2]. Supercapacitors, or Electric Double-Layer Capacitors (EDLC), do not rely on chemical reactions for achieving charge transfer and thus are not limited in the reaction rate or the cyclic lifetime of chemicals [3]. The charge in a supercapacitor is created by the transportation of ions in its electrolyte and the nano thickness layers adjacent to the porous electrode materials [3]. The nano thickness layers allow for increasing the surface area of an electrode pair and their morphologies are critical to achieve the high capacitance of supercapacitors. Recent research has shown, however, that the pore size in the porous electrodes can play an essential role in determining the amount of charges that an electrode can store [4,5]. The literature suggested that there is a critical pore size range of less than 1 nm in diameter which can provide the largest charge storage capability. In comparison, typical porous materials used in some commercially available supercapacitors such as activated carbon, carbon foams and fabrics have pore sizes much larger than this size and in the order of micrometers [6]. Controlling of pore sizes hence becomes critical in order to optimize the ion transport channels and increase the amount of stored charges on supercapacitor electrodes. Single walled carbon nanotubes (SWNTs) have well controlled outer diameters in the range of 1–2 nm and offer excellent electrical properties, chemical stability, and mechanical characteristics [7]. If being processed with a controllable porous structure as either an array or a network, these carbon tubes make an ideal structure for the creation of thin three dimensional nanoporous electrodes. One difficulty exists however in the production of thin films of SWNTs due to the agglomeration of individual nanotubes during suspension processing [8]. The strong van der Walls forces and hydrophobicity of the SWNTs result in the formation of ropes and tangled bundles within aqueous suspensions and can produce non-uniform or uneven SWNT coatings. A process is therefore needed which should be repeatable and can uniformly deposit as-produced SWNTs over a fair large area for a high volume production of SWNT based electrodes, while producing uniform nanopores to create the maximized charge capacity. The investigation of dispersed SWNTs to form nanopores for electrolyte ion transporting and adsorption in supercapacitors enables tailoring of structures for optimum storage capacity [9,10].

Various SWNT structures, as formed through the dispersion of SWNT suspensions and subsequent fabrication onto a metal surface, and their effects on the energy density of supercapacitors

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were investigated in this study. Different SWNT dispersion methods (using the surfactant and the acid treatment, respectively) and coating techniques (such as drop coating, high voltage electrospraying and electrophoretic deposition or EPD [11,12,19]) were studied with a focus of tuning nano-structures for optimizing the energy storage capacity of electrodes. The use of electrophoretic deposition (EPD) to create nanoporous SWNT networks was further characterized to reveal the relationship between the capacitance and the processing parameters. It is worthwhile to mention that in previous works the EPD processing time was limited to 10 min or less and carbon nanotubes were functionalized using a different technique [13,14]. Here the EPD processing times were extended to 1 h and the investigations were conducted to identify a capacitance cap and characterize the effect of extended EPD processing of SWNT electrodes on capacitance gains. This task is very important for the future scale-up production and the optimization of high volume SWNT electrodes. Understanding and optimizing the SWNT structures with the ability to produce large areas of uniform nanoporous networks will help develop manufacturing technologies of supercapacitors with an increased energy density and bridge the gap between high energy density and high power density storage devices.

2. Experimental procedures

Purified SWNTs (97%) obtained from Nano-C Inc. were first acid functionalized using a mixture of concentrated nitric (HNO_3) and sulfuric (H_2SO_4) acid in a ratio of 1:3, respectively (Sigma–Aldrich). 10 mL of the acid mixture was then added to 250 mg of SWNT powder for 30 min to complete the carboxyl functionalization [15,16]. During this process the acid mixture adds —COOH functional groups to these defect sites on the SWNTs [17,18]. This treatment negatively polarizes the SWNTs, which is essential for EPD processing, and allows them to disperse well in pure H_2O without the use of additional surfactants [19]. Our accompanying study found the addition of surfactants can negatively affect the performance of nanotubes and it has been difficult to remove the surfactant from the SWNT network after processing, which agrees with the literature [20]. After acid functionalizing, the SWNT acid mixture was diluted with de-ionized water and washed through a filter to remove the acidity from the nanotubes. The process was repeated until the filtered nanotube slurry reached a pH of 7. The functionalized SWNTs were then washed from the filter into 500 mL of di-water to produce a SWNT aqueous suspension with a nanotube concentration of approximately 0.5 mg mL^{-1} H_2O. The suspension was then placed in a Branson 5210 Ultrasonic cleaner for 30 min at 22 °C. Prior to EPD the suspension is placed in an ultrasonic bath for an additional 5 min and 10 mL of prepared suspension is removed and centrifuged for 30 min at 4000 rpm to remove agglomerated SWNT bundles from the suspension. Fig. 1 shows an image of a bottle of the functionalized SWNT aqueous suspension.

An EPD cell was manufactured with a working distance of 1 cm between two electrodes, shown in Fig. 2. Upon fabrication the electrodes in the EPD cell were used as the current collectors for the characterization of the SWNT electrode in a potentiostat. During EPD processing the stainless steel (SST) 304 (70%Fe, 19%Cr, 11%Ni: wt%) of 0.1 mm thickness from Alfa Aesar were used as the current collectors and substrates for the SWNT deposition. The SST electrodes were cut, numbered, and weighed prior to deposition and then were installed into the EPD cell. The electrodes were lowered into the functionalized SWNT aqueous suspension to a depth of 1 cm. A DC power supply was connected to two electrodes and was used to apply 10–50 V to the EPD cell for the duration of 1–60 min. During EPD processing the negatively charged functionalized SWNTs moved towards the positive electrode and

Fig. 1. Functionalized SWNT aqueous suspension.

uniformly coated the surface. The SWNT coated positive electrode was then removed from the suspension under the applied voltage and disconnected from the voltage supply in air. The SWNT coated electrodes were then dried in an oven at 80 °C for 30 min to remove moisture and to solidify the SWNT network.

In addition to EPD, drop coated and high voltage electro-sprayed (HVES) [21,22] nanotube structures were also processed using the same SWNT aqueous suspension. For drop coating approximately 3–4 mL of suspension was applied to horizontal SST electrodes using a micro-pipette and allowed to dry in air for 24 h before oven

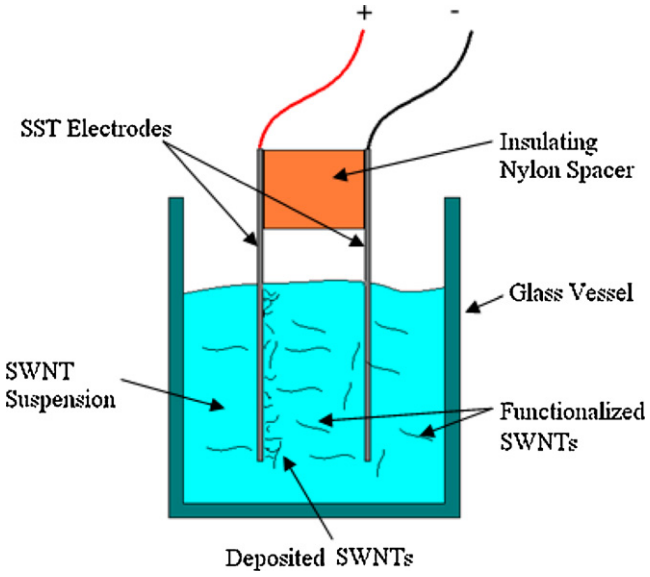

Fig. 2. Schematic diagram of a SWNT EPD cell.