Materials Science and Engineering B 184 (2014) 34–43

Contents lists available at ScienceDirect

Materials Science and Engineering B

journal homepage: www.elsevier.com/locate/mseb

Flexible supercapacitor yarns with coaxial carbon nanotube network electrodes

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ARTICLE INFO

Article history:
Received 3 September 2013
Received in revised form
10 December 2013
Accepted 20 January 2014
Available online 2 February 2014

Keywords:
Flexible
Energy storage
Supercapacitor
Carbon nanotube
Yarn

ABSTRACT

Flexible supercapacitors with a yarn-like geometry were fabricated with coaxially arranged electrodes. Carbon nanotube (CNT) network electrodes enabled the integration of the electronic conductor and active material of each electrode into a single component. CNT yarns were employed as the inner electrode to provide the supporting structure of the device. These part integration strategies eliminated the need for inactive material, which resulted in device volumetric energy and power densities among the highest reported for flexible carbon-based EDLCs. In addition, the coaxial yarn cell design provided a robust structure able to undergo flexural deformation with minimal impact on the energy storage performance. Greater than 95% of the energy density and 99% of the power density were retained when wound around an 11 cm diameter cylinder. The electrochemical properties were characterized at stages throughout the fabrication process to provide insights and potential directions for further development of these novel cell designs.

1. Introduction

Improvements in electrical energy storage (EES) devices are critical as our society continues to become more reliant on electricity as an energy source for applications requiring mobility such as portable electronic devices and transportation [1]. In addition to the need to increase energy and power densities, novel device architectures are needed to support applications such as flexible and wearable electronics for both consumer and military applications [2–5]. The unique versatility of carbon in electrochemical systems has been utilized for decades in fuel cells, batteries and electrochemical capacitors [6]. Carbon nanotubes greatly enhance this versatility not only in terms of their physical properties but also in the plethora of macroscopic formats and fabrication methods that can be utilized to create electrodes for electrochemical devices. The capability to tailor CNT networks to achieve properties such as high electrical and mechanical properties, controlled porosity and surface chemistry make them an attractive platform for constructing novel electrochemical devices. This is evident in the large amount of research utilizing planar networks of CNTs (*e.g.* sheets, buckypapers, thin films) in various electrochemical capacitors [7], batteries [8], and fuel cells [9]. Macroscopic porous networks of CNTs can also be formed into a yarn or fiber morphology; however, there are considerably fewer studies using carbon nanotube yarns/fibers in electrochemical applications. These high aspect ratio morphologies offer unique capabilities compared to their planar counterparts, particularly for next generation flexible electrochemical devices with novel property requirements [10,11]. It should be noted that the terms 'carbon nanotube yarn' and 'carbon nanotube fiber' are used in the literature without any apparent differentiation of one another and in this manuscript the original terminology used by each author is maintained when referencing the literature.

Kozlov et al. measured the capacitance of CNT fibers fabricated using a polymer-free flocculation spinning method [12]. They reported specific capacitances for the as-spun and annealed fibers of 48 F g^{-1} and 100 F g^{-1}, respectfully. Similar results were obtained by Shin et al. from DNA assisted wet-spun CNT fibers [13]. These results are on the high end of the typical range of reported capacitances of CNT electrode. Large variability exist in these results due to the large variations inherent to as-produced CNTs and CNT assemblies due to factors such as sample purity, bundling effects [14], network density [15], surface chemistry [16], surface area [17], porosity [18], and electrical conductivity [18]. Capacitance results in the literature for planar assemblies of CNT networks can range from anywhere less than 20 F g^{-1} to greater than 100 F g^{-1} [19].

In addition to the half-cell characterization, Kozlov et al. also fabricated a solid-state supercapacitor from two CNT fibers. Two fibers were coated with a polymer electrolyte, twisted together and the final device was obtained after the drying of a final polymer electrolyte coating on the pair of twisted fibers. They conducted

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http://dx.doi.org/10.1016/j.mseb.2014.01.013

a 5 mV s^{-1} cyclic voltammetry test and reported a device capacitance of 7 F g^{-1}. This same twisted two-fiber cell design was more recently used by several groups to fabricate flexible supercapacitors with the fiber-like geometry [20–22]. These studies took advantage of the ability of CNTs to function as a highly conductive, large surface area substrate and deposited polyaniline (PANI) onto the CNT fiber. The reversible redox capabilities of PANI provided large psuedocapacitive responses and high gravimetric (274 F g^{-1}) [22] and volumetric (299 F cm^{-3}) [23] electrode capacitances were achieved for CNT-PANI fibers.

Indeed, the fiber-like cell geometry is very attractive for flexible devices as both Wang and Cai showed the ability to maintain high capacitance while undergoing repeated bending stresses [21,22]. However, the twisted fiber cell design used thus far to create these fiber-geometry cells has a number of potential disadvantages for EES devices. A primary concern for any EES device is the non-uniform current and electric potential distributions created due to the helical interaction between the two electrodes. In general, non-uniform currents can, lower cell efficiencies due to the poor utilization of the electrode materials, decrease cycle life because of the detrimental effects of non-uniform stresses on electrode stability, and induce local hot-spots [24].

To overcome these disadvantages we have utilized carbon nanotube yarns as the backbone for solid-state flexible supercapacitors with a coaxial electrode design. The CNT yarns are the inner electrode and supporting structure for a polymer electrolyte coating which also functions as the separator between the two electrodes. The polymer coated CNT inner electrode is then wrapped with thin CNT sheets, creating a concentric cylinder outer electrode of porous CNT networks with the CNT yarn inner electrode at its center axis. The coaxial cell design allows for uniform primary current distribution because of the radial ion transport between electrodes. The symmetric area moment of inertia of the circular cross-section simplifies predictions of stress distributions due to mechanical deformation of the cell. This system provides a design that is easily tailored to match the locations and characteristics of the coaxial components with the linear, radially symmetric stress distribution. In fact, nature has utilized the same methodology to optimize the structure of plant stems to provide robust mechanical properties while protecting the delicate living cells responsible for transport of water and nutrients between the leaves and the roots [25].

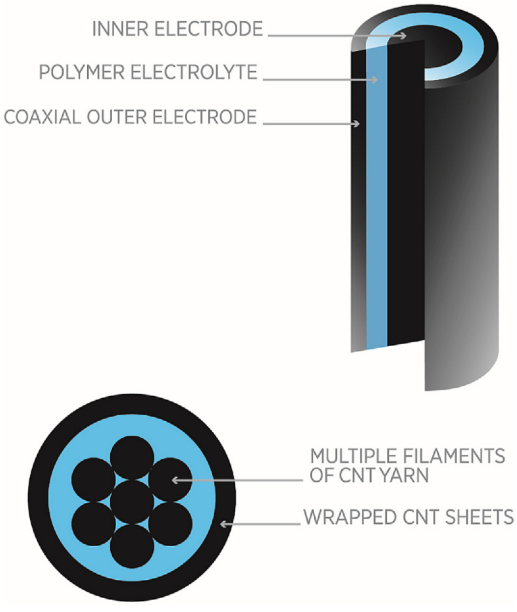

Fig. 1. Top: Schematic of the coaxial electrode design for flexible electrochemical cells. Bottom: Cross-section of the multifilament CNT yarn cells fabricated in this report.

Fig. 1 shows a graphical representation of the coaxial cell design. The experiments discussed in the current report utilized a multifilament inner electrode in order to achieve a more manageable mass and size for reduce measurement errors and ease of fabrication. During the preparation of this manuscript Chen et al. published their work on the fabrication of carbon nanotube based coaxial electrode double-layer capacitors [26]. Indeed, this work demonstrates the attractiveness of the design including excellent electrochemical properties and impressive mechanical robustness. Additionally, Chen et al. showed provided quantitative examples of the benefits of the coaxial electrodes as compared to the twisted pair design. However, the details and effects of the fabrication process of the coaxial cells are not discussed. Additionally, the commercial viability and large scale production of CNT sheets and yarns obtained by drawing/spinning from CNT forests are questionable. This report details the investigations into the fabrication of these fiber EES devices and demonstrates the feasibility of obtaining this unique architecture using commercially available materials. Electrochemical characterization was conducted at various steps throughout the fabrication process in order to obtain quantitative information on the influential factors affecting the final device performance.

2. Materials and methods

2.1. Materials

CNT yarns and nonwoven sheets were purchased from Nanocomp Technologies, Inc. and contain typically few-walled tubes (*e.g.* double, triple-walled), specific surface areas of 150–200 m^2 g^{-1}. The sheets have area densities of 10 g m^{-2} and the linear density of the yarns were ~1.6 mg m^{-1}. A mild purification process was performed to remove catalyst particles, amorphous carbons, and residual resins or other contaminants from the manufacturing process. While purity is always critical in electrochemical experiments, the mechanical integrity of the yarns was a priority due to the device-oriented goals of the research. Extensive purification can lead to breakdown of the CNT network structure, and thus, a mild purification process was used on the CNT yarns to ensure the mechanical integrity was preserved. The samples first underwent a 400 °C heat treatment in a tube furnace with both ends open to the atmosphere. Following the heat treatment the samples were soaked overnight in acid baths of 1 M HCl, followed by a 3:1 mixture of 1 M H_2SO_4 and 1 M HNO_3.

2.2. Equipment

All electrochemical characterization was conducted with the VersaSTAT3-400 with FRA upgrade. An Olympus BX40 optical microscope with CCD camera was used to measure the device diameter. The cross-section was obtained by ion beam milling using the TIC 3X from Leica Microsystems and imaged with a JOEL 7401F FE-SEM.

2.3. Device fabrication

A polyvinyl alcohol (PVA) and phosphoric acid (H_3PO_4) polymer gel electrolyte was prepared as described in numerous literature reports and functioned as both the electrolyte and separator [27,28]. The inner electrode consisted of multiple filaments of CNT yarn. The filaments were twisted together using small amounts of aqueous solution to aid in the adhesion between yarns. After drying overnight a ~2 cm region at one end of the multifilament strand was coated with silver paste to create a region for electrical connection.