FABRICATION OF A SUPERCAPACITOR USING AN ELECTROSPUN NANOFIBER BASED SEPERATOR AND CARBON NANOFIBER ELECTRODES

Pit Fee Jao, Xiaoyu Cheng, Gloria J. Kim, and Yong-Kyu 'YK' Yoon
Electrical and Computer Engineering, University of Florida, Gainesville, FL, USA.

Abstract: An all-electrospun nanofiber based fabrication process for a supercapacitor is demonstrated, where two electrodes are made of electrospun SU8 derived carbon nanofibers and a separator is made of electrospun SU8 nanofibers. For high throughput production of nanofibers, tube nozzle electrospinning is implemented. Carbon nanofiber based electrodes are advantageous because of the large surface area, chemical resistivity and higher conductivity. Meanwhile, SU8 nanofibers for the separator give faster ion transfer, chemical and mechanical stability. A fabricated supercapacitor with a capacitance density of 450 nF/mm^2 and an overall capacitor thickness of 54 μm is demonstrated. The demonstrated electrospun nanofiber based fabrication process holds promise for next generation flexible high density capacitors and batteries.

Keywords: nanofiber supercapacitor, SU8 nanofiber separator, carbon nanofiber electrodes, compact capacitor

INTRODUCTION

Regenerative energy storage in supercapacitors (SCs) has recently gained popularity primarily due to the rapid charging capability which is extremely useful to capture the large sudden spike in energy generated at short time periods either in automobile regenerative braking or non-conventional energy storage [1]. Also, SCs or electric double layer capacitors have advantages of simple architectures, wide temperature ranges of operation, and good device reliability over a million charge cycles.

Activated carbon powder is one of the most widely used materials in the fabrication of porous electrodes as it has very large specific surface area (SSA) and the relatively low production cost. But not all the surface area is applicable for energy storage as the usable surface area is typically only one-third the SSA [2] and the usage of a binder gives a very high internal resistance. Carbon Nanotube (CNT) on the other hand, is an emerging material for porous electrodes given their high surface area and low resistivity. By growing the CNTs using the catalytic deposition of hydrocarbons directly on the metal, Jiang [3] has shown that highly dense and ordered CNT forests can be grown in an interdigital pattern, to achieve 428 μF/cm^2. But the use of CNT forests is limited by the under utilization of the surface area (40%) due to the highly hydrophobic surface of the CNTs, the requirement of a critical three metal substrate, and the CNT growing process complexity.

While the porous electrode is one of the characteristics of SCs, the necessity of a charge separation mechanism between two electrodes is crucial to prevent the shorting of electrodes. Conventionally, SC separators have been fabricated with cellulose based materials, fluorinated ethylene propylene or sulfonated poly(ether-ether-ketone) [4]. Material selection for separators can help improve electrical performance as well as mechanical, chemical, and thermal stabilities. When compared to conventional polyolefine separators, high permittivity Poly (vinylidene fluoride-co-hexafluoropropene) (PVdF-HFP) separators have been demonstrated to improve ionic conductivities, electrolyte retention and improved pore wetting [5]. Therefore, what is required is a fabrication process to integrate the porous electrode with the separator for a compact SC.

Electrospinning is a technique used to produce polymeric fibers with diameters in the nanometer range and also nanoporous membranes with a very large surface area. Carbonization can be used to transform the polymeric nanofiber to carbon nanofiber (CNF) making it an excellent porous electrode material [6]. A carbon nanofiber electrode based electrolytic capacitor with a conformally coated dielectric layer over the CNF electrode has been demonstrated, to give a capacitive density of 1.78nF/mm^2 [7]. Such carbon nanofibers can be used as electrodes for SCs without dielectric material coated, which in fact provides much higher capacitance density. Meantime, a high throughput nanofiber fabrication process, *Tube Nozzle Electrospinning* (TNE), by using multiple nozzles on an insulated tube channel has been reported by the authors [8], where an improved SU8 nanofiber membrane growth rate has been demonstrated compared to single nozzle electrospinning.

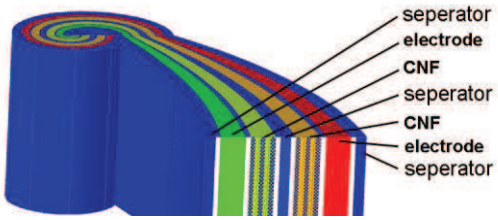

Fig. 1: Schematic of an all-nanofiber based supercapacitor using carbon nanofiber electrodes and an electrospun polymer nanofiber separator.

In this work, we demonstrate a supercapacitor using carbon nanofibers as porous electrodes and an electrospun SU8 nanofiber membrane as the separator. The goal of this work is to demonstrate a fabrication process and to study the improved capacitive density with the thickness of a nanofiber stack. Compared to other SCs, the integrated fabrication procedure allows a compact design which can be scaled up by rolling the ends of the capacitor as shown in Figure 1. Furthermore, the ion transfer length determined by the spacing between the electrodes is minimized with the use of nanofiber separator.

EXPERIMENTAL

Supercapacitor Fabrication

Figure 2 figuratively describes individual steps in the fabrication of the nanofiber based SC. First, a silicon (University Wafers Inc., USA) substrate is insulated with the deposition of silicon dioxide (900nm, 13.56MHz, PECVD, STS 310PC). Then a 7µm SU8 (2005, Microchem Inc., Newton, MA) thin film is spin coated and patterned with the base electrode pattern (a). Non woven SU8 nanofibers are then electrospun on the patterned electrodes by TNE [8] using SU8 with a solid concentration of 60.87 w/v% in a solvent of cyclopentanone (Sigma Aldrich, St. Louis, USA). The process uses an 8-nozzle array with a needle voltage V_N of 15 kV (DEL HVPS MOD 603 30 KV POS, Spellman High Voltage Electronic Corp., USA) and a needle tip to collector distance (TCD) of 15 cm (b). The 8 nozzles have been made on the side wall of a low density polyethylene tube with a nozzle diameter of 0.2mm and a pitch between the nozzles of 5mm using a milling machine (S100 Protomat, LPKF Laser & Electronics, Tualatin, OR). Electrode patterns similar to the base electrode are then photodefined by standard UV lithography using a Mask Aligner (MA-6, Karl Suss) (c). Then the patterned nanofiber stack is then carbonized in a tube furnace (F79345, Thermolyne Inc., USA) in an inert atmosphere to produce the carbon nanofibers (d).

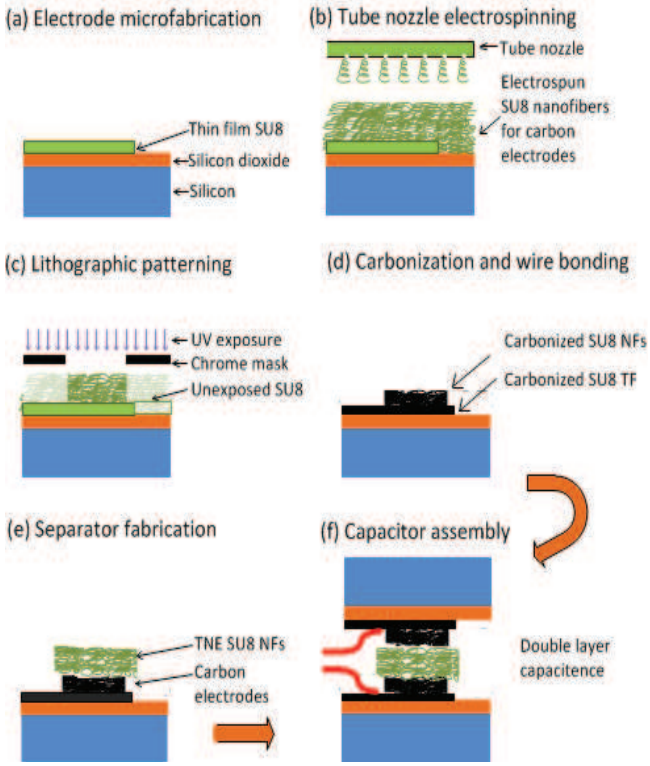

Fig. 2: Super capacitor fabrication process

Steady formine gas (5% H_2, balance N_2) flow in the tube furnace is maintained at 2 slm (Matheson flow meter) with the pyrolysis temperature between 900 - 1000 ^{O}C. On one pair of electrodes, 40µm thick SU8 NFs are then electrospun using the TNE as described above to form the separator (e). Then the two electrodes are sandwiched together and assembled with the separator defining the gap between the electrodes (f). The SC assembly is then immersed into an electrolytic bath (Copper Sulphate/Boric Acid solution) under a modest vacuum to seep the nanofiber electrodes and the separator before packaging and testing.

Nanofiber Characterization

Electrospun SU8 nanofibers are sputtered prior to imaging with a 50 nm copper thin film (KJL CMS-18 Multi-Source, Kurt J. Lesker, Livermore, CA) and imaged using a Field Emission Scanning Electron Microscopy (SU-70, Hitachi Inc., Japan). Carbon nanofibers are imaged without metal coating. Nanofiber membrane height is measured using a profilometer (Dektak 150, Bruker AXS, Tuscon, AZ). The nanofiber diameters on SEM images are measured using image analysis software (ImageJ, National Institutes of Health, USA). Capacitance measurements are performed using a function generator (Agilent 331020A, Santa Clara, CA) and an oscilloscope (Tektronix 2014, Beaverton, OR).

RESULTS AND DISCUSSION

After the carbonization of SU8 nanofibers, the resultant carbon nanofibers are observed to be shrunken in diameter as shown in Figure 3a. Electrospun SU8 nanofibers with an average diameter of 354.8nm decrease in diameter to 178.5nm, 164.5nm and 149.7nm when carbonized at 900^{O}C, 1000^{O}C and 1100^{O}C, respectively. This is attributed to the loss of elemental oxygen and hydrogen during the carbonization, which make up 60% of the polymer as observed in the thin film SU8 analysis [9]. The shrinkage in the carbon nanofiber diameter can be counterproductive in the case of the SC as it reduces the electrode surface area. Thus required is a technique to increase the nanofiber throughput and packing density to compensate the reduced surface area.

TNE is used to increase the nanofiber throughput for the fabrication of thicker nanofiber stacks which counter the carbon shrinkage and also used for the nanofiber separator fabrication. Figure 4a shows the fabrication schematic of the TNE setup wherein, a tube is used as a polymer reservoir and the nozzles fabricated in it act as jetting sources for the electrospinning cones. Compared to the previous a single needle architecture, a higher nozzle count here increases the nanofiber throughput although the nanofiber cones are observed to repel each other as observed in Figure 4b. A measure of the repulsion is the semi-vertical angle (SVA) φ which quantifies the angle of the electrospinning cone to quantify the repulsion. Since the large SVAs imply large repulsion between the cones, a small SVA is desired in the fabrication of thicker membrane stacks needed for the thick porous electrode in a given area.

Nanofiber stacks using the 2, 4, and 8 nozzle architectures are tested and their SVAs are measured by an image analysis tool and tabulated in Table 1. As observed for a 2 nozzle array, the electrospinning cones are very much divergent and similar to single

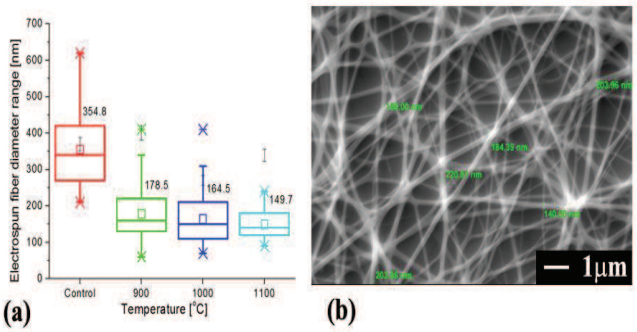

Fig. 3: Carbon nanofiber (a) Diameter shrinkage observed in carbon nanofibers with incremental carbonization temperatures, and (b) SEM image of carbonized SU8 nanofibers.

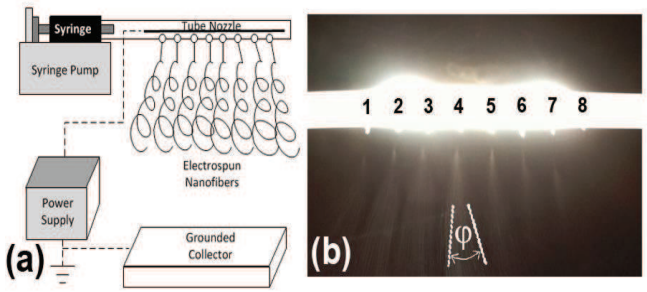

Fig. 4: Tube nozzle electrospinning (TNE) (a) Schematic of TNE setup, (b) Taylor cones observed in the electrospinning of SU8 nanofibers using an 8-nozzle array TNE. φ indicates semi-vertical-angles of the Taylor cones.

needle electrospinning SVAs. For the 4 and 8 nozzle architecture, a decreasing trend in the SVA from the outer nozzles to the inner nozzles is observed. This is attributed to the fiber repulsion observed in the high density nozzle architectures [10]. The higher the nozzle count, the smaller is the SVAs on the Taylor cones, thus the higher density of nanofibers can be deposited in a given electrode area.

While high density nozzles increase nanofiber throughput with decreased SVAs, nanofibers do experience repulsion until they reach the substrate. The thickness of nanofiber stacks is measured as a function of time for 4 and 8 nozzle TNE as shown in Figure 5a. The stack growth rate increases with a higher nozzle count as expected with higher mass throughput. While the stack thicknesses gradually increase, saturation in a growth rate is observed in both nozzle configurations.

Table 1: Semi-vertical-angles (SVA) of TNE Taylor cones

Count	Nozzle position							
2							58	46
4					49	41	42	45
8	38	34	44	43	36	32	30	31

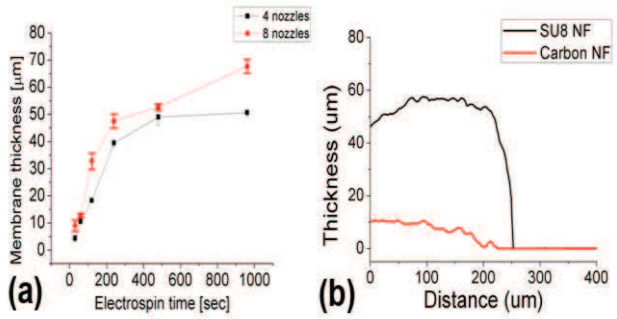

Fig. 5: SU8 nanofiber stack characterization (a) Stack thickness growth chart versus time, (b) Shrinkage of the thickness of the nanofiber membrane with carbonization.

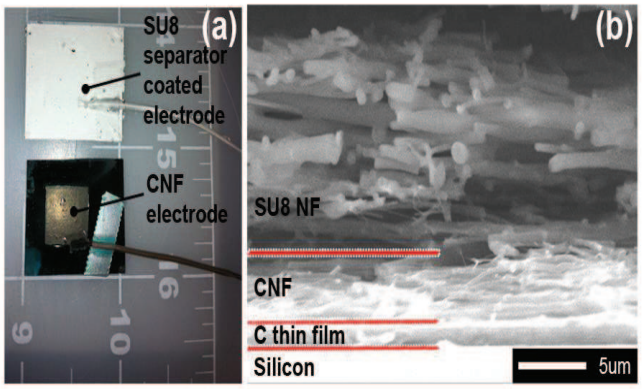

Fig. 6: Nanofiber based supercapacitor (a) Unpackaged supercapacitor (b) SEM image showing the cross-section of the nanofiber layers of a fabricated supercapacitor.

It is be hypothesized to be the effect of repulsion associated with charge accumulation at the collected nanofibers. SU8 nanofiber stacks followed by carbonization are observed to shrink in height as observed in Figure 5b. A 48µm thick SU8 membrane shrinks to 10µm thick when carbonized at 900^{O}C. The shrinkage in thickness of the membrane is attributed to the combination of nanofiber diameter shrinkage and air gap shrinkage.

Figure 6a shows the fabricated carbon nanofiber electrodes alongside the electropsun SU8 nanofiber separator coated carbon electrodes before the final assembly. Figure 6b shows a scanning electron microscope (SEM) image of the cross-section of the fabricated SC, wherein the multiple layers of nanofibers sandwiched tightly to give a compact SC is clearly observed. The overall height of a set of the capacitor including the separator is 54 µm. This is one of the thinnest SCs reported for this capacity range. Capacitance of the fabricated capacitor has been tested using an oscilloscope and a function generator [7], resulting in a maximum 450 nF/mm^2.

CONCLUSION

An all-nanofiber based fabrication process for a supercapacitor using carbon nanofibers for electrodes and electrospun SU8 nanofibers for a separator has been demonstrated. Using a modified tube nozzle electrospinning approach allows higher density of electrospun nanofibers due to smaller SVAs of electrospinning jets resulting in the fabrication of thicker carbon nanofibers. Carbon nanofiber based electrodes are advantageous because of the larger surface area, chemical resistance and higher conductivity. Meanwhile SU8 nanofiber separators give faster ion transfer, chemical and mechanical stability. Thus an all-electrospun nanofiber based super capacitor holds a lot of promise.

ACKNOWLEDGEMENT

This work is in part supported by the National Science Foundation (ECCS 1132413). The authors would like to thanks Dr. Kyoung Tae Kim and Sheng-Po Fang at the University of Florida for valuable discussions.

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