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Shan Hu, *University of Minnesota*
Rajesh Rajamani, *University of Minnesota*
Xun Yu, *University of North Texas*

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Flexible solid-state paper based carbon nanotube supercapacitor

Shan Hu,[1] Rajesh Rajamani,[1,a)] and Xun Yu[2]
[1]*University of Minnesota, Minneapolis, Minnesota 55455, USA*
[2]*University of North Texas, Denton, Texas 76203, USA*

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This paper presents a flexible solid-state supercapacitor of high energy density. The electrodes of the supercapacitor are made of porous and absorbent cotton paper coated with single-wall carbon nanotubes. To ensure all solid-state configuration, a solid-state polymer-based electrolyte (poly (vinyl alcohol)/phosphoric acid) is used. The as-fabricated supercapacitor can be charged to over 3 V. It has high specific capacitance and high energy density of 115.8301 F/g carbon and 48.8587 Wh/kg carbon. Its performance is comparable to that of commercial supercapacitors, which need to utilize liquid electrolytes. Flexible solid-state supercapacitors offer several significant advantages for use in hybrid electric vehicles. *© 2012 American Institute of Physics*. [http://dx.doi.org/10.1063/1.3691948]

Recently, there has been tremendous interest in using supercapacitors in conjunction with batteries as electrical energy storage devices for hybrid electric vehicles (HEVs).[1,2] However, due to space constraints in the vehicle hood, finding extra room for supercapacitors and other components required in hybrid vehicles is challenging. Thin and flexible supercapacitors can mitigate the problem, because they can fit anywhere and can even be mounted on the inner surfaces of the vehicle body. In other words, they can exploit a lot of space which is inaccessible to the current rigid and bulky energy storage devices. Some prototypes of thin flexible supercapacitors have been developed in literature. Chen *et al.* prepared hybrid In_2O_3 nanowires/carbon nanotubes films on polyethylene terephthalate (PET) substrate to obtain flexible electrodes. Then, supercapacitors were fabricated using the flexible electrodes and a 1 M $LiClO_4$ electrolyte ($LiClO_4$ in a mixture of ethylene carbonate (EC), diethyl carbonate (DEC), and dimethylene carbonate (DMC)).[3] Similar work was done by Yu *et al.* who fabricated supercapacitors using flexible and transparent graphene/PET thin film as electrodes and 2 M KCl solution as electrolyte.[4] Hu *et al.* prepared flexible paper-based electrodes by coating conductive single-wall carbon nanotubes (SWNT) suspension on both sides of a piece of printing paper pre-treated by polyvinylidene fluoride (PVDF). The SWNT/paper electrodes and the electrolyte (1 M $LiPF_6$ in EC and DMC) were encapsulated in a coffee-bag cell to obtain a supercapacitor.[5] The use of liquid electrolyte is a drawback for the above flexible supercapacitor prototypes. Since the electrolyte is usually hazardous to the environment, good sealing of the electrolyte is required. To ensure stable supercapacitor performance, a good housing is also needed to immobilize the electrodes with respect to each other. One example is the coffee bag cell used for both housing and electrolyte-sealing for the supercapacitor in the work of Hu *et al.* discussed above.[5] The sealing and housing materials add a lot of volume and weight to the supercapacitors, making them unsuitable for applications which require thin and light-weight components. Moreover, sealing and housing can reduce the flexibility of supercapacitors as well. To avoid the problems with liquid electrolyte, solid-state electrolyte will be used in this research.

Different kinds of solid-state electrolytes have been studied in literature. As proposed by Ma and Yang, a thin film of metal salt electrolyte (e.g., LiF) could be evaporated on copper electrodes to fabricate solid-state supercapacitors.[6] However, this evaporated electrolyte thin film is fragile and not suitable for use in a flexible device. A polymer based electrolyte is another class of solid-state electrolytes that is very promising for flexible supercapacitors. Examples of polymer based electrolyte include PVDF-co-hexafluoropropylene/1-Ethyl-3-methylimidazolium tetrafluoroborate (PVDF-co-HFP/$EMIBF_4$) and poly (vinyl alcohol) (PVA)/phosphoric acid.[7,8]

In this letter, an easy procedure will be presented to make a flexible and solid-state supercapacitor using SWNT-coated cotton paper as electrodes and PVA/phosphoric acid as electrolyte. The complete fabrication process of the supercapacitor is shown in Figure 1. SWNTs were used as active materials for the flexible electrodes because SWNTs have good electrical and mechanical properties as well as good corrosion resistance. They also provide a large surface area accessible to ions in the electrolyte. For this research, high purity SWNT powder (<10% impurities) synthesized by chemical vapor deposition was purchased from Timesnanoweb (Chengdu, China) and used as received. Then, a solution-based method was used to coat SWNT on compliant substrates. For this, the SWNTs needed to be evenly dispersed into water. Using a surfactant like sodium dodecylbenzenesulfonate for dispersion can risk making the supercapacitor unstable because the surfactant might react with the electrolyte. Instead, we used the acid treatment dispersion method[9]: 200 mg SWNTs were added to 80 ml of acid mixture of sulfuric acid (98 wt. %) and nitric acid (69 wt. %) in a volume ratio of 3:1 and stirred for 2 h on a 110 °C hot plate. The mixture was then diluted to 400 mL, and the SWNTs were collected by membrane filtration and washed by deionized (DI) water to remove residual acids. After acid treatment, the originally hydrophobic SWNTs became hydrophilic because carboxyl groups (-COOH) were attached to SWNT ends. Finally, the acid-treated SWNTs

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[a)]Electronic mail: rajamani@me.umn.edu. Tel.: (612) 626-7961.

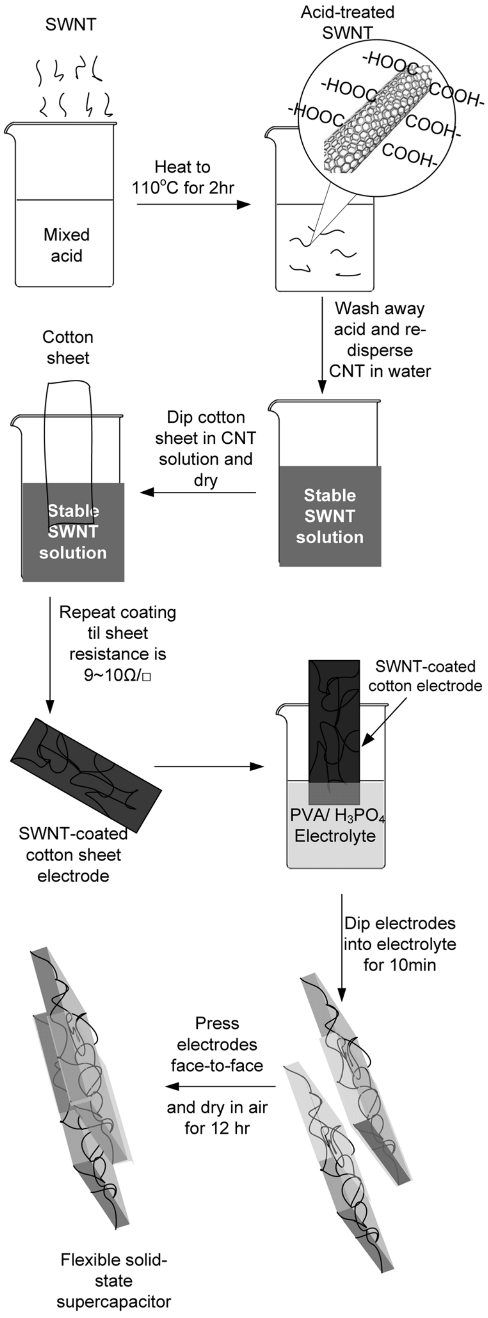


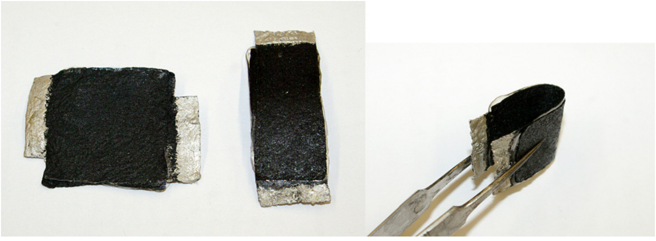
FIG. 1. Fabrication process of SWNT-based, flexible, and solid-state supercapacitor.

were uniformly dispersed into 40 mL of DI water through a 1 h ultrasonic bath. When choosing compliant substrates for the flexible electrodes, paper rather than PET was chosen. Studies have been done to compare the coating of carbon nanotubes (CNT) on PET and xerox printing paper substrates. Results have suggested that the PET substrates showed poor bonding with the CNT, and film delamination was observed, but coating CNT on xerox printing paper was successful.[10] In this research, non-woven 100% cotton paper for cosmetic facial mask was used, because it has rough surface morphology and is lighter and more absorbent than printing paper. Initially, the cotton paper was cut into desired shape. To coat the cotton paper with SWNT, a simple dip-and-dry process was used: The cotton paper was dipped into the SWNT suspension and dried on 120 °C hot plate until excessive water was evaporated. This process was repeated until the sheet resistance of SWNT-coated cotton paper reached 9–10 Ω/□. The acid-treated SWNT bonded to the cotton fibers very well because the cotton fibers have hydroxyl groups that can form strong chemical bounds with the carboxyl groups on the acid treated CNT. For better electrical connection with the testing circuit, a small fraction of the electrodes was covered with silver conductive epoxy.

To make PVA/phosphoric acid, 6 g of PVA powder (Mowiol® 18-88, Sigma Aldrich) and 1.6 g of phosphoric acid (69 wt. %) were added to 40 ml of DI water and stirred on a 85 °C hot plate until the mixture became a clear and glue-like gel. To assemble the supercapacitor cell, two SWNT-coated cotton electrodes were immersed into 85 °C PVA/phosphoric electrolyte. The silver epoxy-coated fraction was carefully kept away from the electrolyte. After 10 min, the electrodes were taken out and assembled together face-to-face to achieve the maximum possible overlapping area. The assembly was dried in room temperature for 12 h. Upon evaporation of excessive water, the original glue-like electrolyte solidified, forming a solid-state flexible supercapacitor. The PVA played two important roles in the fabrication process. It functioned as a binder to hold the supercapacitor assembly as one integrated part. It also acted as a separator to prevent electrode shorting. Figure 2(a) shows the as-fabricated solid-state supercapacitors with different shapes. Figure 2(b) shows that the as-fabricated supercapacitor is very flexible and can be bent by more than 90° without showing any fracture. The supercapacitor is also very thin with a thickness of only 1.3 mm.

The performance of the as-fabricated supercapacitor (the rectangle shaped one in Figure 2(a)) was tested using both cyclic voltammetry (CV) and constant current charging and discharging with a two-electrode setup. Figure 3 shows the cyclic voltammetry of the as fabricated supercapacitor at different scanning rates of 8 mV/s, 4 mV/s, and 2 mV/s. As shown in the CV curves, the supercapacitor has both capacitive and resistive properties mainly due to its not ignorable equivalent serial resistance (ESR).

Five cycles of galvanostat charging-discharging curve at 2 mA are shown in Figure 4. As shown in Figure 4, this supercapacitor can be charged to over 3 V, which is beneficial for high energy density. Specific capacitance, specific energy, and ESR of the supercapacitor were all computed from the discharging curve. Specific capacitance (C_s) was calculated by



(a) (b)

FIG. 2. (Color online) Flexible and solid-state supercapacitors, (a) supercapacitors with two shapes, and (b) supercapacitor bent by more than 90°.

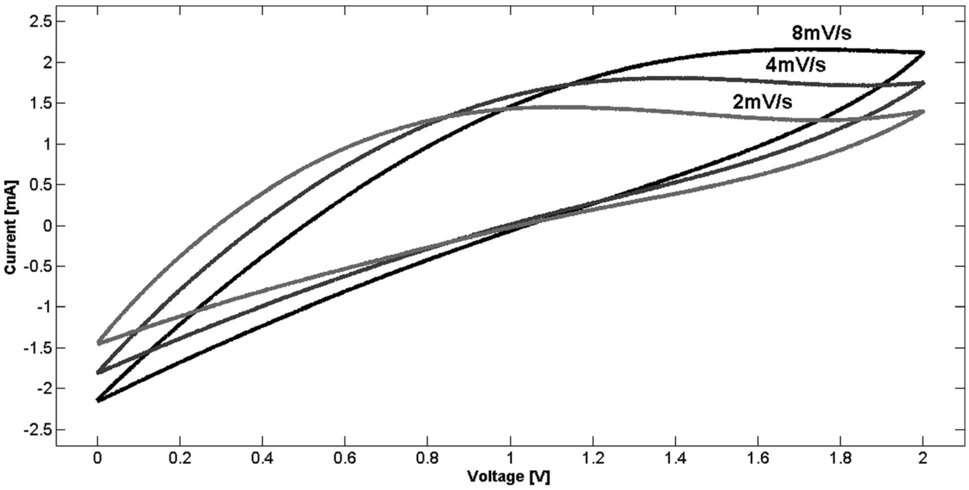


FIG. 3. Cyclic voltammetry of the as fabricated supercapacitor at different scanning rates.

$$C_s = \frac{4I}{m}\frac{\Delta t}{\Delta U}, \tag{1}$$

where I is the discharging current ($I = 2$ mA in Figure 4), t is the discharging time, and U is the discharging voltage. The definition for m varies: In research literature, C_s is usually evaluated with respect to the mass of carbon on the electrodes (in our case, the mass of acid-treated SWNT), whereas for commercial supercapacitors, C_s is calculated with the total weight of the supercapacitor device. In this paper, C_s with respect to both the mass of acid-treated SWNT and the mass of the entire device will be computed. The mass of acid-treated SWNT was obtained by comparing the weight of the cotton paper before and after SWNT coating. Same applies for specific energy (E_s), which can be calculated by $E_s = CU^2/2m$, where C is the capacitance calculated from the discharging curve by $C = I\Delta t/\Delta U$. The ESR was calculated by $ESR = U_{IR}/2I$, where U_{IR} is the initial IR drop at the beginning of the discharging curve.

For the rectangle shaped supercapacitor in Figure 2(a), the total mass of SWNT on both electrodes was 122.40 mg, and the total weight of the supercapacitor was 1.08 g. When only the mass of the SWNT was considered, the specific capacitance of the as-fabricated supercapacitor was 115.83 F/g, and specific energy was 48.86 Wh/kg. Supercapacitors using multi-wall carbon nanotube (MWNT)-based electrodes with specific capacitance in the range of 4-137 F/g were found in literature.[11] For SWNT-based electrodes, a maximum specific capacitance of 180 F/g was found in literature.[12] The specific capacitance of the as-fabricated supercapacitor is in the same range as the best supercapacitors in literature. However, most CNT-based supercapacitors in literature do not have the properties of being flexible and solid-state. When the total weight of the entire supercapacitor was considered, the specific capacitance, specific energy, and ESR of the as-fabricated supercapacitor were calculated and compared with commercial supercapacitors using liquid electrolyte, as shown in Table I. In terms of specific capacitance and specific energy, our flexible and solid-state supercapacitor's performance is superior to the EPCOS cell type B49410B-2506Q000 and is comparable to the ESMA cell type EC303. However, the ESR of our supercapacitor is higher than both commercial supercapacitors. The reason is that the resistance of the SWNT-coated cotton paper electrode (sheet resistance about 9 Ω/□) is much higher compared to that of the metal electrodes in commercial supercapacitors (sheet resistance smaller than 0.1 Ω/□). Thus, coating the cotton paper with higher density SWNT suspension can reduce the ESR. It is also noticed that the ESR is larger than the total resistance of two electrodes

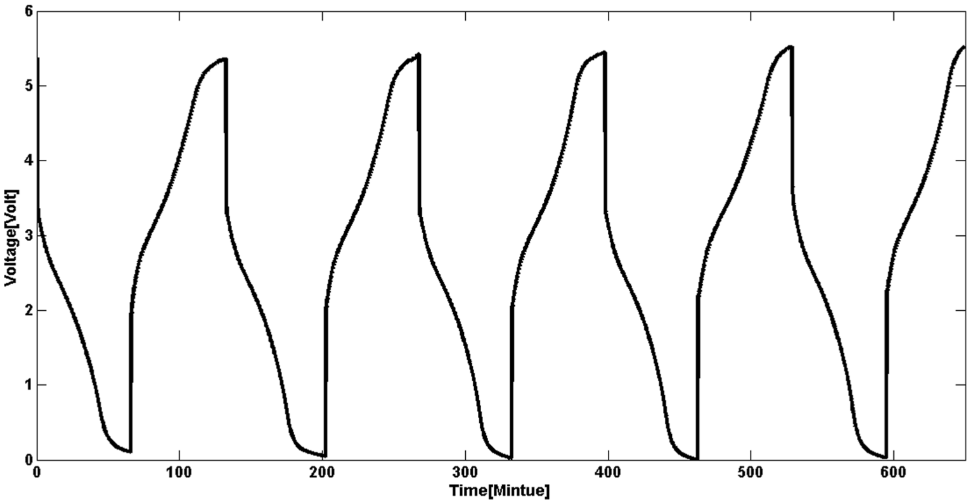


FIG. 4. Galvanostat charging-discharging curve at 2 mA.

TABLE I. Comparison of performance of the new flexible and solid-state supercapacitor with commercial supercapacitors.

Specifications	EPCOS B49410B-2506Q000 (organic electrolyte)[a]	ESMA EC303 (aqueous electrolyte)[a]	Flexible supercapacitor (solid-state electrolyte)
Weight of entire device (g)	1050	2600	1.08
Specific capacitance (F/g)	4.76	17.31	13.15
Specific energy (Wh/kg)	4.1	6.15	5.54
ESR (Ω)	0.35×10^{-3}	0.3×10^{-3}	117.73

[a] Reference 13.

before electrolyte coating, which means the electrolyte also affects the ESR. Since the electrical properties of the electrolyte are determined by the amount of phosphoric acid and water it contains, the ratio of acid and water in the electrolyte should be optimized.

In conclusion, flexible and solid-state supercapacitors have been developed using SWNT-coated cotton paper as electrodes and solid-state PVA/phosphoric acid as electrolyte. The as-fabricated supercapacitor can perform as well as, if not better than, supercapacitors in literature and supercapacitors available in the market. The supercapacitors' flexibility, solid-state configuration, and high energy density make them suitable for applications such as hybrid electric vehicles and portable electronics. Future work needs to be done to optimize the ESR of the supercapacitor in order to achieve better performance in power density.

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