THIN-FILM PAPER SUPERCAPACITOR

N.S. Korivi, M. Vangari, D. Mohammed, B. Etzioni, K. Henry and L. Jiang
Department of Electrical Engineering, Tuskegee University, Tuskegee, USA

Abstract: This manuscript reports on the development of a thin-film paper supercapacitor, based on paper electrodes sandwiching an integrated solid electrolyte and separator layer. A typical finished device with total weight of 0.3 gm exhibits a planar capacitance of approximately 87 μF/cm^2 and a specific capacitance estimated to be 100 F/gm. The developed paper supercapacitor is an improvement over some of the state-of-art paper supercapacitors reported till date, which show similar specific capacitance but have more mass than our device. The low total weight of our finished device arises from a new combination of materials. The structural characteristics of the developed device in conjunction with its electrical behavior make it a candidate for portable and micro-electro mechanical systems (MEMS).

Keywords: supercapacitor, flexible supercapacitor, energy storage

INTRODUCTION

In the recent years, there has been considerable interest in developing supercapacitor technology and employing it in conjunction with battery technology for electric energy storage applications [1]. This combination of supercapacitor and battery technologies is of particular interest for portable and micro-electro mechanical systems (MEMS) applications where limited space availability necessitates the need for thin and lightweight device structures. There are advantages to thin and lightweight supercapacitors, primarily in stacking a large number of them to increase capacitance and the capacitance-to-volume density. Such supercapacitors can be realized by using paper materials in their structures. A very limited number of reports exist on thin film supercapacitors employing paper type materials [2, 3]. These reported devices are primarily based on using a liquid electrolyte with carbon nanotube based composite electrodes prepared by coating carbon nanotubes on fabric and paper by relatively complex processes [4]. We propose an innovative supercapacitor device that employs paper electrodes sandwiching a free-standing solid electrolyte. The electrodes are based on carbon micro-fiber paper with its surface modified by active materials. The surface modification process involves incorporating silver nano-particles in the carbon micro-fiber paper, followed by attachment of multi-walled carbon nanotubes. An integrated solid electrolyte/separator layer is sandwiched by the surface modified paper electrodes to complete the device (Fig. 1). This electrolyte layer is a composite material of polyvinyl alcohol (PVA) and phosphoric acid (H_3PO_4). Evaluation of this device showed a capacitance performance comparable to existing state-of-art. Improvements on existing state-of-art include reduced device thickness and total mass. Another positive attribute is the relative ease of development due to the use of commercially available carbon paper as the base material for the electrodes.

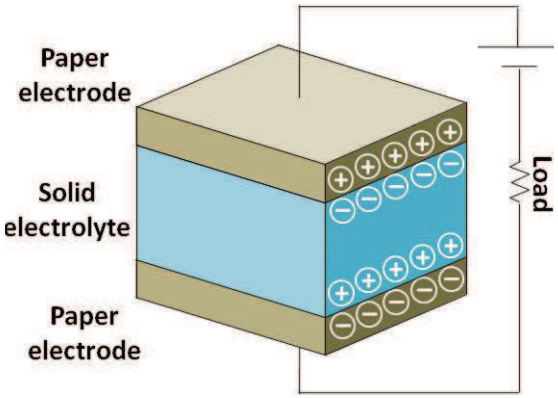

Fig. 1. Schematic representation of the developed thin film paper supercapacitor. The electrodes are carbon papers incorporated with silver nano-particles and multi-walled carbon nanotubes. The solid electrolyte layer is a composite of PVA and H_3PO_4. The figure is not to scale.

EXPERIMENTAL

Electrode Fabrication

The base material for the electrodes was a commercially available carbon micro-fiber paper (Toray TGP-H-060, Fuel Cell Store, www.fuelcellstore.com). The thickness of this paper was 190 μm. The surface of the carbon paper was modified by spin-coating a layer of silver (Ag) nano-

particles (Fig. 2). For this purpose, silver nano-particles in the form of a nano-particulate ink (UT Dots Inc) were employed as obtained. Following the spin-coating process, the silver nano-particulate ink was allowed to cure at room temperature. In the next step, a layer of multi-walled carbon nanotubes (MWCNTs) was spin-coated on the carbon paper (Fig. 2). The MWCNTs (diameter from 110-170 nm, length 5-6 μm) were obtained from Sigma-Aldrich Corporation. The MWCNTs were dispersed in acetone by sonication in an ultrasonic bath. Subsequently, the MWCNTs in acetone were spin-coated on the carbon paper, followed by room-temperature curing.

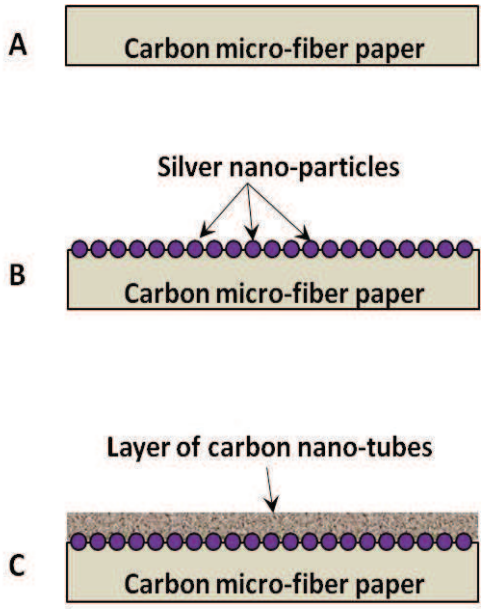

Fig. 2. Schematic diagram of paper electrode fabrication procedure, showing (A) a carbon micro-fiber paper as the base substrate; (B) silver nano-particles incorporated on the micro-fiber paper by spin-coating silver nano-particulate ink; (C) a layer of carbon nanotubes spin-coated on the surface, over the silver nano-particles. The figure is not to scale.

Electrolyte Fabrication

The PVA/H_3PO_4 composite electrolyte layer also functioned as a separator between the electrodes. To fabricate this layer, PVA (MW 10,000 – 13,000) and H_3PO_4 (≥85 wt% in water, ACS reagent quality) were obtained from Sigma-Aldrich Corporation. An aqueous solution of PVA is prepared by dissolving PVA in water (1:10 ratio by volume) with the aid of magnetic stirring for 40 minutes at 75-80 °C. This is followed by preparing a solution phase blend of PVA and H_3PO_4 at a temperature of 70 °C with magnetic stirring. Subsequently, the PVA/H_3PO_4 blend is cast on a surface modified polyethylene teraphthalate (PET) substrate and cured overnight at room temperature to form a solid layer of electrolyte. This solid layer is peeled off from the underlying PET sheet after the curing process (Fig. 3).

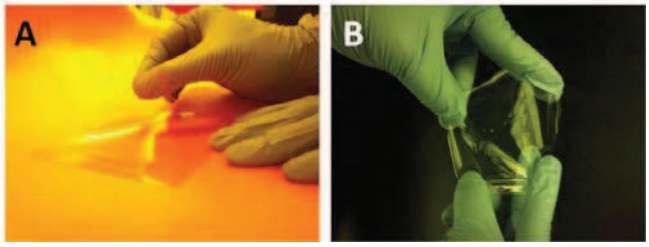

Fig. 3. Photographs of (A) a solid PVA/H_3PO_4 electrolyte layer formed on a PET surface and being manually peeled off after its curing process; (B) a released solid electrolyte layer.

Device Assembly and Testing

Following the fabrication of the electrodes and electrolyte layer, these components were assembled together to realize the supercapacitor. The electrolyte layer was sandwiched between the electrodes and the stack was placed in a specially designed mechanical vise made of plastic (Fig. 4). The vise held the individual layers together. The device was now ready to be tested electrically. The testing of the assembled devices was done by studying their capacitance characteristics. This was accomplished by connecting the two electrodes of an assembled device to a precision LCR meter (Hewlett Packard 4284A) and measuring capacitance as a function of frequency. The precision LCR meter was used at a setting of 0 V DC voltage bias.

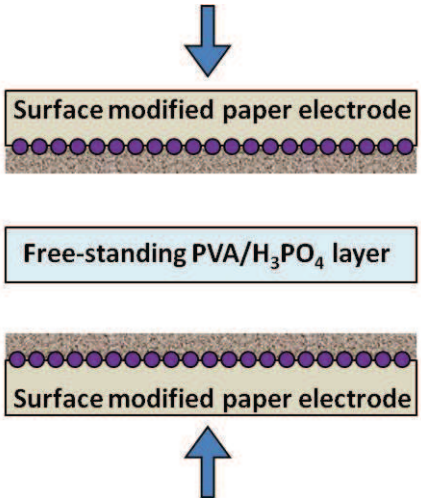

Fig. 4. Schematic diagram of the paper supercapacitor device assembled and held together in a mechanical vise. The figure is not to scale.

RESULTS

Device Development

The fabrication processes described in the preceding sections were successfully employed to realize functional supercapacitors. A finished device is shown in Fig. 5. A typical embodiment of the developed supercapacitor had a total weight of 0.3 gm with dimensions of 1 cm x 1 cm. This total mass of the device is lower than that of similar devices reported elsewhere where the total mass was more than 1 gm [5]. The typical thickness of our device ranged from 450 - 480 µm thick. This is thinner than similar devices reported elsewhere [6]. The reduced mass and thickness of the developed device make it a candidate for portable and MEMS applications.

In reports of similar devices, only the mass of active materials was considered while calculating specific capacitance and energy density [5, 6]. Considering the mass of only Ag nano-particles and MWCNTs in our case, the specific capacitance of the developed device is estimated to be approximately 100 F/g, which is in the range of similar devices.

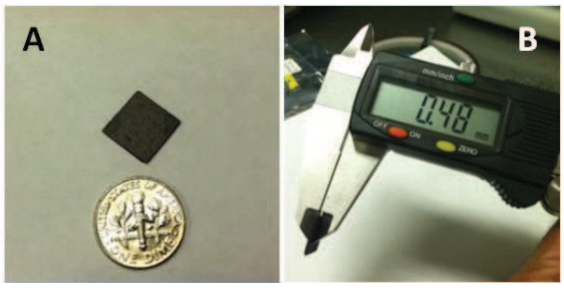

Fig. 5. Photographs of (A) a finished paper supercapacitor with dimensions of 1 cm × 1 cm and a total weight of 0.3 gm; (B) a vernier calipers showing thickness (0.48 mm) of same device.

Capacitance Characteristics

The capacitance characteristics of the developed supercapacitor were studied as a function of frequency. The highest planar capacitance recorded was 87 µF/cm^2 for electrodes employing Ag nano-particles and MWCNT layer, and sandwiching a PVA/H_3PO_4 layer of 70 µm thickness (Fig. 6). Our experiments clearly indicated the importance of employing carbon nanotubes as an active material. This was further illustrated by our studies on the effect of Ag nano-particles on capacitance behavior of the supercapacitor. Devices with electrodes made by a sole coating of Ag nano-particles on carbon paper showed lower planar capacitance, as compared to electrodes with both Ag nano-particles and carbon nanotubes (Fig. 7).

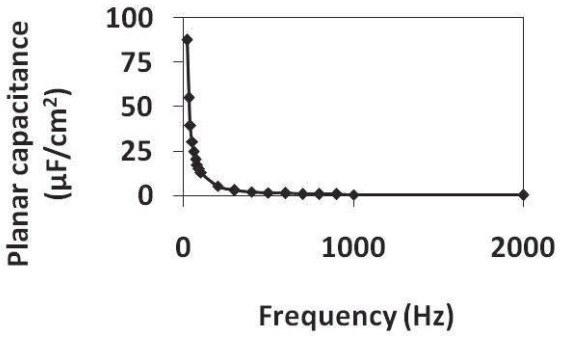

Fig. 6. Planar capacitance of the developed supercapacitor as a function of frequency. The electrodes were 190 µm thick carbon micro-fiber papers coated with Ag nano-particulate ink and MWCNTs.

In control experiments, supercapacitors were made with plain carbon micro-fiber papers serving as electrodes. These devices showed almost negligible capacitance values (Fig. 7). This indicated the role played by Ag nano-particles in improving the capacitance characteristics of the developed supercapacitor. It is evident from Fig. 6 and Fig. 7 that the presence of MWCNTs considerably improves the electrical behavior of the device. This is a reason why similar thin-film or paper based supercapacitors have employed carbon nanotubes [7, 8].

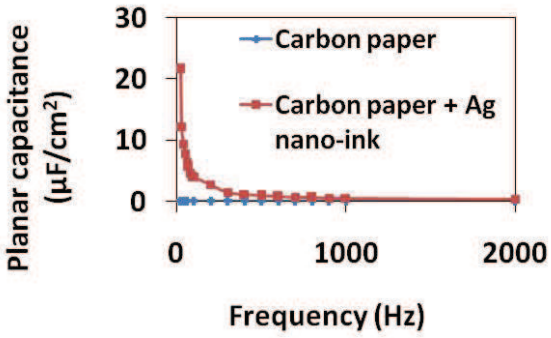

Fig. 6. Planar capacitance of the developed supercapacitor as a function of frequency. The figure shows a comparison between two cases. The electrode was a plain 190 µm thick carbon micro-fiber paper in one case and coated with Ag nano-particulate ink in the other case. In both cases, a 70 µm thick PVA/H_3PO_4 electrolyte layer was employed.

DISCUSSION

The main aspect of the electrode fabrication is the surface modification processes i.e. the incorporation of silver nano-particles, followed by MWCNTs. It was challenging to deposit these materials on the carbon paper by regular spin-coating processes. A

regular spin-coating scheme involves dispensing a certain amount of material on a stationary substrate and spinning the substrate at a pre-set rpm. In the present case, when either Ag nano-particulate ink or MWCNTs in acetone were dispensed on a stationary carbon paper, the paper was immediately soaked with these nano-materials and became sodden with loss of structural rigidity. In some cases, this resulted in insufficient active material being retained on the surface of the carbon paper. To overcome these problems, a modified spin-coating process was used to deposit the active materials. The carbon micro-fiber paper was initially rotated at a certain rpm and active material was dispensed on the rotating surface. This allowed the active material to be incorporated on the paper's surface without seeping through its bulk.

The fabrication processes developed for the supercapacitor allow for easy scaling up or down of dimensions, if required by the application at hand. The nature of the developed supercapacitor allows for stacking multiple devices to obtain the desired electrical performance.

On the aspect of fabrication of the PVA/H_3PO_4 layer, it must be noted that PET surfaces are typically hydrophobic, preventing effective solution casting on these surfaces. Therefore, prior to solution casting, the PET surfaces are modified by physical abrasion that renders them hydrophilic.

The device assembly method used in this work involves stacking the individual layers of the supercapacitor and holding them together by a mechanical vise. This method is relatively crude and may not create a uniform electrode-electrolyte interface over the area of contact. An effective approach to bond the individual layers can involve the electrolyte layer spin-coated on one electrode, cured partially and placed over the other electrode. Upon further curing, the electrolyte layer functions to hold the two electrodes together. This method can address the electrode-electrolyte interface aspect.

In a different set of experiments, we fabricated and tested supercapacitors with carbon micro-fiber paper of different thicknesses. It was observed that paper thickness influenced the capacitance behavior. Devices made on thicker papers yielded higher planar capacitance. The thickness of the carbon paper directly impacts its role as a current collector.

CONCLUSION

A thin-film paper supercapacitor was successfully developed and evaluated. This device is based on modifying the surface of a commercially available carbon micro-fiber paper. An important consequence of the surface modification processes is the incorporation of nano-structured active material and the consequent enhanced surface area of the carbon micro-fiber paper. This contributes directly to the electrical behavior of the device. The importance of the surface modification processes is underscored by the capacitance characteristics of the supercapacitor which clearly show the influence of both silver nano-particles and carbon nanotubes as active materials.

ACKNOWLEDGMENTS

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REFERENCES

[1] Burke A. 2000 Ultracapacitors: Why, How, and Where is the Technology? *J. Power Sources* **91** 37-50

[2] Zheng G., Hu L., Wu H., Xie X., Cui Y. 2011 Paper Supercapacitors by Solvent-free Drawing Method *Energy Environ. Sci.***4** 3368-3373

[3] Yuan L., Lu X-H., Xiao X., Zhai T., Dai J., Zhang F., Hu B., Wang X., Gong L., Chen J., Hu C., Tong Y., Zhou J., Wang Z.L. 2012 Flexible Solid-state Supercapacitors Based on Carbon Nanoparticles/MnO_2 Nanorods Hybrid Structure *ACS Nano* **6** 656-661

[4] Hu L.B., Wu H., Cui Y. 2010 Printed Energy Storage Devices by Integration of Electrodes and Separators into Single Sheets of Paper *Appl. Phys. Lett.* **96** 183502

[5] Hu S., Rajamani R., Yu X. 2012 Flexible Solid-state Paper Based Carbon Nanotube Supercapacitor *Appl. Phys. Lett.* **100** 104103

[6] Kang Y.J., Chung H., Han C-H., Kim. W. 2012 All-solid-state Flexible Supercapacitors Based on Papers Coated with Carbon Nanotubes and Ionic-liquid-based Gel Electrolytes *Nanotechnol.* **23** 065401

[7] Chen P., Chen H., Qiu J., Zhou C. 2010 Inkjet Printing of Single-walled Carbon Nanotube/RuO_2 Nanowire Supercapacitors on Cloth Fabrics and Flexible Substrates *Nano Res.* **3** 594-603

[8] Kaempgen M., Chan C.K., Ma J., Cui Y., Gruner G. 2009 Printable Thin Film Supercapacitors Using Single-walled Carbon Nanotubes *Nano Lett.* **9** 1872-1876