

Novel Flexible Supercapacitors Fabricated by Simple Integration of Electrodes, Binders, and Electrolytes into Glass Fibre Separators

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(Received November 3, 2014 : Revised November 18, 2014 : Accepted November 19, 2014)

Abstracts : We report novel and simple structure of supercapacitors fabricated by using flexible glass fibre separators as templates. This method does not require separate electrodes, binders and high pressure/temperature to build the supercapacitor unit cells as required by the conventional technology. The supercapacitors were fabricated by drop-casting solution mixtures of carbonaceous active materials/gel electrolytes onto two sides of glass fibre separators. Two carbonaceous materials (nanoscaled activated carbons, multi-walled carbon nanotubes) were investigated as electrode materials. The electrochemical measurements reveal that the separator-based supercapacitors using ACs successfully demonstrated significant mass specific capacitance (22.3 F g^{-1}) and energy density (9.7 Wh kg^{-1}), indicating this method can be useful in fabricating flexible, wearable and stretchable energy storage devices in more straightforward and cost-effective way than current technology.

Keywords : supercapacitors, activated carbons, carbon nanotubes, glass fiber filters, bending tests

1. Introduction

Supercapacitors or ultracapacitors are next-generation energy storage devices in which charging and discharging process takes place at the electric double layers formed on electrodes. Since the supercapacitors store and release the electrical energy via electrostatic way with high capacitance proportional to the surface area of nano-structured electrodes, they demonstrated extremely high specific capacitances and energy density compared to the conventional dielectric capacitors.¹⁻⁴⁾ Moreover, their high power density could enable us to replace the lithium ion batteries with supercapacitors in the future applications which require high power ratings.^{5,6)}

Due to the recent progress in electronics and microelectronics, there have been numerous reports on device structures, electrode materials and electrolytes of supercapacitors or batteries which could fit

the flexible, wearable and stretchable electronics.⁷⁻¹³⁾ However, in spite of recent progresses, conventional supercapacitors and batteries are still bulky, heavily relying on the rigid substrates and processing technology to circumvent the current trend toward lighter and thinner electronics.¹⁴⁻¹⁶⁾

The conventional unit cell of supercapacitor is comprised of two electrodes prepared by pressing electrodes materials (mainly activated carbons or carbon-based materials) with a binder at high pressure and high temperature such as 500 kg cm^{-2} and 420°C .¹⁷⁾ Two electrodes then are sandwiched together with a polymer-based separator. The electrodes, electrolytes and separators of the supercapacitors are kept under again high pressure such as 16 kg cm^{-2} .¹⁷⁾ Hence, the conventional process to fabricate supercapacitor cell requires high pressures and heating process, which could hinder employment of flexible, wearable, and textile-based substrates for the next-generation electronics. Moreover, simpler processing techniques are preferred for fabricating high efficiency supercapacitors to reduce their manufacturing costs.

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In this regard, it is noteworthy that there have been several reports on new device structures and fabricating methods of supercapacitors. For instance, Hu *et al.*, demonstrated integration of electrodes and separators into commercial papers to build the supercapacitors using carbon nanotubes as electrode materials.¹³⁾ Integration of electrodes, separators and electrolytes into nano-composite units were also reported¹⁸⁾ in the literature.

In this report, we demonstrate an efficient and facile strategy to build supercapacitor unit cells without using electrodes and any processes requiring high temperature and pressure. This new method doesn't need to use any electrodes. Instead, the device structure utilizes only separators. The electrodes are eliminated and formed inside the separators by diffusion of electrodes materials and electrolytes inside the separators. Most of the recent demonstration of the integrations of electrodes, separators and electrolytes utilized carbon nanotubes or similar types of carbonaceous materials. These novel carbon materials are generally expensive. In this work, we investigated possibility of using activated carbons (ACs) as electrode materials for our separator-based supercapacitors. The ACs are currently employed as main electrode materials for the commercial supercapacitors due to their high surface area, wide spectrum of pore structures and cheap price. As a control, we also fabricated the supercapacitors using multi-walled carbon nanotubes (CNTs) as the electrode materials via the same method as that from ACs.

2. Experimental Details

The PVA/H₃PO₄ gel electrolyte was formed by dissolving poly(vinyl alcohol) (PVA) powder (10 g) with water (100 mL) and phosphoric acid (10 g)¹⁹⁾ at 120°C. PVA (Aldrich) was >99% purity with MW of 85000-124000. The gel electrolyte (10 g) was then mixed with 30 mg of AC powder (Duk-san, Korea) using magnetic stirring for 1 h. For control, MWCNT powder (NC 7000, Nanocyl) was dispersed in the gel electrolyte at the same concentration as the solution mixture of ACs in the gel electrolyte. All the chemicals were used as received.

The BET surface areas of ACs and CNTs were measured using TriStar II (Micrometrics) by the adsorption of N₂ at 77 K. Specimens were degassed at 200°C for 2 h before the adsorption.

To fabricate two-electrode test cells with each materials (ACs, CNTs), the mixed slurries containing PVA, H₃PO₄ and ACs or CNTs were drop-casted on the front and back side of a Whatman GF/D glass microfibre filter. The filters or separators of the supercapacitors are typically about 1 cm² in area. The copper wires are attached on two sides of the prepared separators by using a silver epoxy for the electrochemical measurements. A potentiostat (Princeton Applied Research Versastat 4) was used to perform the electrochemical measurements. To examine the surface morphology of ACs and CNTs, a field emission scanning electron microscopy (JEOL) was employed with typical operation voltage of 5 kV.

3. Results and Discussion

The flow process to fabricate the separator-based supercapacitors is presented in Fig. 1. The solution mixture of active materials and PVA/H₃PO₄ gel electrolyte was prepared as described in the experimental section above. The solution mixture of ACs and PVA/H₃PO₄ is shown in Fig. 1a (left vial). It is seen that the ACs are dispersed uniformly in PVA/H₃PO₄ gel electrolyte without precipitation. As a control, we prepared the solution mixture of CNTs dispersed in PVA/H₃PO₄ electrolyte at the same concentration as the solution containing ACs. The picture of the solution containing CNTs also shows well-dispersed solution (right vial in Fig. 2a). These prepared solutions of ACs and CNTs then are drop-casted on the front and back sides of a glass fibre filter (Whatman) (Fig. 1b). Conventionally, the glass fibre filters have been used as separators in supercapacitors in many works reported in literature.^{20,21)} In our fabrication method, the glass fibre filters serve as main flexible templates as well as separators. Instead of sandwiching two electrodes with a separator, the supercapacitor cell assembly is accomplished by coating only one solution mixture on two sides of the separators. The solution in the glass fibre filters will diffuse in the

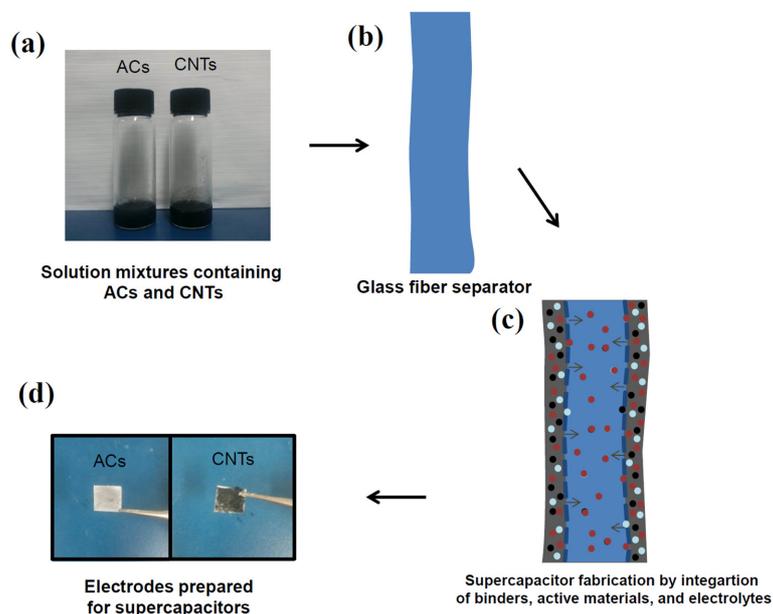


Fig. 1. A flow process to fabricate flexible supercapacitors fabricated by integration of electrodes, electrolytes, and binders into a glass fibre separator. (a) A photo of prepared solution mixtures containing ACs (left vial) and CNTs (right vial). Both mixtures are dispersed in PVA/H₃PO₄ gel electrolyte. (b) A blank glass fibre filter that is used as separator. (c) The glass fibre filter whose front and back side was coated with the solution mixtures. White, black, and red circles represent PVA, ACs (or CNTs), and electrolyte ions from H₃PO₄, respectively in the solution mixture. After the drop-casting, the ions (red circles) diffuse into the separator to form a supercapacitor cell. (d) Photos of the resultant supercapacitor cells.

filter pores after the solution is coated, resulting in transport of electrolyte ions contained in the solution. The electrode materials (ACs or CNTs) in the solution also form the electric double layers at their interface between the electrolytes. The polymers or PVA will prevent the electrical contact between the electrode materials while allowing for ion transport of the electrolytes.¹⁹⁾ Drop-casting of the solution mixture eliminates further processes for electrode formation and pressurizing as is seen in the conventional process of supercapacitor fabrication.

Figure 2 shows SEM images of ACs and CNTs dispersed on Si substrates. For this examination on the surface morphology of ACs and CNTs, each powders of ACs and CNTs were dispersed in acetone with sonication subsequently drop-casted on Si substrates. After drying the acetone, the SEM measurements were performed. Fig. 1a and its inset show thick agglomeration of ACs formed on Si with an irregular form. Fig. 2b shows SEM image of CNTs dispersed on Si. It is seen that the CNTs

can form interwoven structures or networks of bundles of nanotubes on substrates.

The cyclic voltammetry (CV) responses of the two electrode materials (ACs, CNTs) are shown in Fig. 3(a) at a scan rate of 50 mV s⁻¹. The electrolyte used is PVA/H₃PO₄ gel electrolyte. The CV curve from ACs shows clearly asymmetric shape, which is not found in box-shape CVs from ideal supercapacitors using carbonaceous electrodes. The reason for non-ideal shaped CV from our supercapacitors using ACs is currently not clear. However, similar CVs from carbonaceous electrode materials with non-ideal shape were reported in the literature. For instance, CV from CNT electrodes in literature showed a peak at 0.35 V, which can be attributed to pseudocapacitance originated from oxygen containing functional group in the CNTs.^{22,23)} In the literature, the departure of shape of CVs from the ideal shape generally is attributed to the impurities, functional groups on electrodes, and unoptimized conductivity of the cells.²³⁾ The reason for

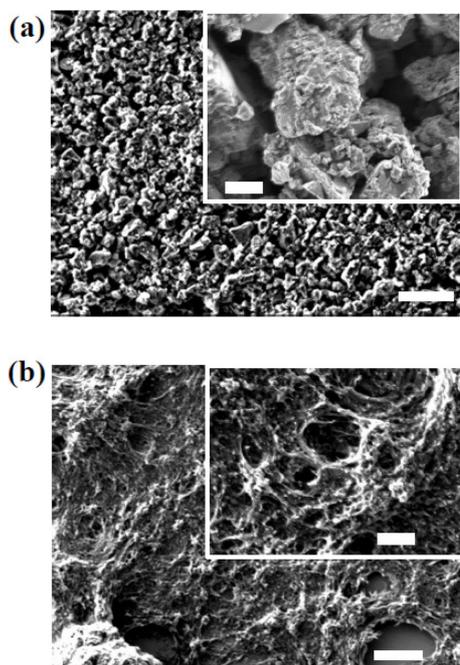


Fig. 2. (a) SEM image of ACs dispersed on Si substrate. Scale bar 100 μm . Inset higher magnification SEM image of the ACs with the scale bar of 5 μm . (b) SEM image of CNTs dispersed on Si substrates. Scale bar 100 μm . Inset higher magnification SEM image of the CNTs with the scale bar of 20 μm .

the significant departure from ideal box like CV curve is attributed to non-uniform distribution of electrolyte ions present inside the glass fibre separator. For our supercapacitors, the electrolyte (H_3PO_4) is mixed with carbon materials and PVAs, and their mixture is drop-casted on front and back side of a separator.

The CV curves at three different scan rates (100,

50, 20 mVs^{-1}) are plotted for ACs-based supercapacitors in Fig. 3(b). For ideal supercapacitors, the currents tend to increase as the scan rates increased. However, our ACs-based supercapacitors showed almost constant level of currents when the scan rate increased up to 100 mVs^{-1} . This behaviour resulted in the low capacitance retention of the supercapacitor cell. In Fig. 3(c), the capacitance retention of the ACs-based supercapacitor is shown. It is seen that the cell retained 56% and 40% of the initial capacitance at scan rates of 50 and 100 mVs^{-1} , respectively. In general, the ions of electrolytes are required to enter the electrode's surface as fast as possible to maintain the capacitance at higher scan rates. This requirement results in high demand of bigger pores in the electrodes.²⁴⁾ Our results of capacitance retention suggest that pore size distribution needs to be improved to enhance the retention of ACs-based supercapacitors. The investigations for improving the retention are currently in progress.

The specific capacitances can be obtained from the CV curves using the equation:^{25,26,27)}

$$C_m = \frac{Q}{S(V_1 - V_2)m}$$

where C_m , m , S , V_1 , V_2 , and Q are the mass specific capacitance, the mass of the active materials in the cell, scan rate, upper and lower limit of the potential window, and the charge stored in the capacitors. The charge Q can be obtained by the voltammetric discharge integrated over the potential window.²⁵⁾ In our works, the maximum charges measured by the potentiostat are used to determine the charge Q . The above equation reveals that the

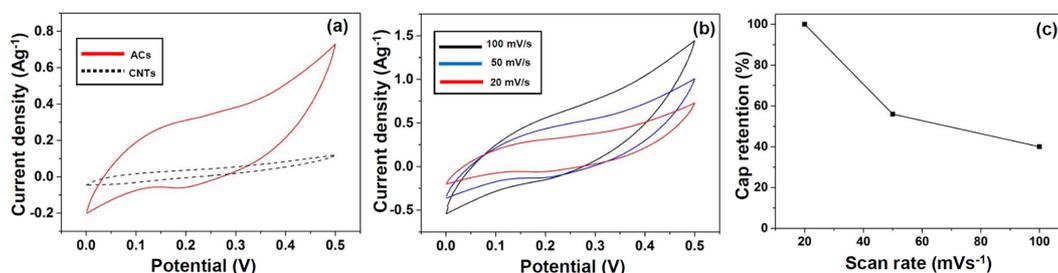


Fig. 3. (a) CV plots of the supercapacitors using the solution mixtures containing ACs and CNTs. The scan rate is 50 mVs^{-1} . (b) CV curves at three different scan rates (100, 50, 20 mVs^{-1}) are plotted for ACs-based supercapacitors. (c) The capacitance retention of the ACs-based supercapacitor at the different scan rates.

mass specific capacitances of our separator-based supercapacitors using ACs and CNTs in the gel electrolyte are 22.3 and 3.6 Fg^{-1} , respectively. The scan rates are 20 mVs^{-1} .

This value of specific capacitance particularly from ACs-based supercapacitors is comparable to those reported in the literature. For example, ACs-based supercapacitors using the conventional methods and binders were reported to exhibit about 20 Fg^{-1} .²⁸⁾ In contrast, when compared to recently reported ones from carbonaceous materials such as graphenes-based supercapacitors exhibiting 160 - 220 Fg^{-1} , our supercapacitors need further optimization.^{29,30)} The previous works on the graphenes suggest that tailoring micro- or nano-structures of our ACs or active materials/binders/electrolyte solutions could enhance the specific capacitance.

Figure 4 shows the results of the galvanostatic charge-discharge measurement on the separator-based supercapacitors using ACs and CNTs. The applied currents are 0.08 mA while the potential range is between 0 and +0.5 V. Both active materials in the plot demonstrate symmetry of the charging and discharging behaviour, indicating good capacitive characteristics. The typical triangular shapes evident in the curves also suggest that the capacitive behaviour of the supercapacitors is originated from the effective ion adsorption at the interface of electrolytes and the active materials.

The coulombic efficiencies of the supercapacitors were calculated to test their capacity to retain charges.³¹⁾ The coulombic efficiency (η) is calcu-

lated according to the equation, $\eta = \Delta t_d / \Delta t_c$, where Δt_d and Δt_c are discharging and charging time.^{32, 33)} The coulombic efficiencies of the supercapacitors from ACs and CNTs are determined to be 52% (ACs) and 63% (CNTs). The coulombic efficiencies of ACs and CNTs-based supercapacitors are lower than those from other supercapacitors fabricated by conventional method using binders and pressing the electrodes with high pressure. For example, manganese oxide/activated carbon capacitors were reported to show the coulombic efficiency of up to 97%.³²⁾ The low coulombic efficiency of our supercapacitors is evident in the charging-discharging plot showing short discharging time compared to the charging time. It indicates that the charges stored in the capacitors are discharged faster than charging process. These poor charge-retaining capacities of our separator-based supercapacitors are currently attributed to the absence of charge collectors (metal substrates) which are available in the conventional two-electrode-supercapacitors. Our separator-based supercapacitors employed silver paste attachments of electrodes on the two sides of the supercapacitors without any current collectors. This absence of current collectors may be responsible for the low coulombic efficiency. Works are in progress to improve the coulombic efficiency of separator-based supercapacitors.

Figure 5 shows stability characteristics of the ACs-based supercapacitors. In Fig. 5(a), galvanostatic charge-discharge measurements were performed on the supercapacitor for 500 cycles at the current density of 0.09 mA. This result demonstrates reliable and stable charging and discharging characteristics of supercapacitors using our novel fabrication method. To test mechanical stability and flexibility of the supercapacitors, mechanical bending test was also conducted on the ACs-based supercapacitors. The supercapacitor was bent at the angle from 0 to 95°, and the ratio (C/C_0) of capacitance (C) to initial capacitance (C_0) was calculated (Fig. 5(b)). It is seen that the capacitance rather increases at the bending angle of 20-65°. After the bending angle of 65°, the capacitance is observed to be in the trend of decreasing. The surge or increase of the capacitance at the angle range (20-65°) may have been caused by increase of pressure on the electrodes, resulting in the

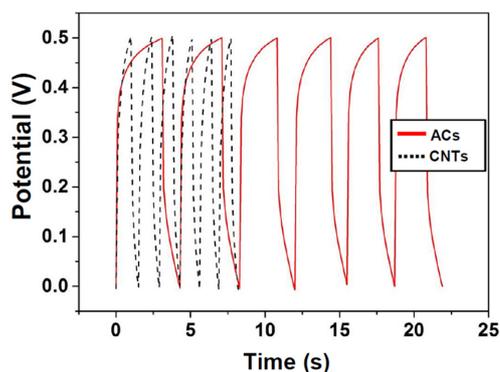


Fig. 4. Galvanostatic charge-discharge curves from the supercapacitors using the solution mixtures containing ACs and CNTs.

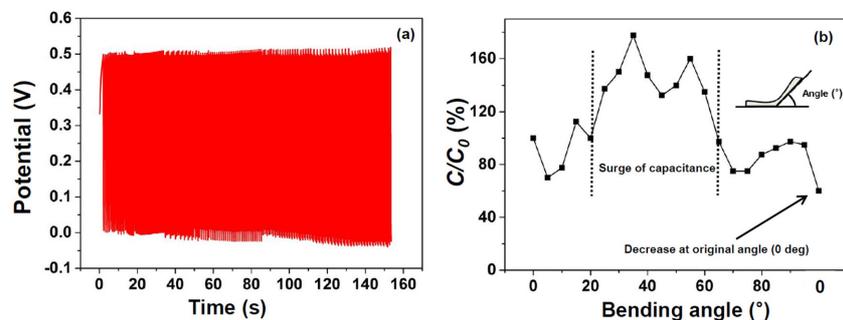


Fig. 5. Stability tests performed on the ACs based supercapacitors. (a) Galvanostatic charge-discharge measurements performed for 500 cycles. (b) Evolution of the mass specific capacitances during the mechanical bending test.

increase of electrolyte transport in the glass fibre filter. When the capacitor was released from the bending, we found the significant decrease of the capacitance ($C/C_0 = 60\%$) compared to the original capacitance (C_0). The capacitance change is 40%. This bending tests suggest that significant damage has occurred to the supercapacitor cell after 95° .

The device characteristics and materials properties of the supercapacitors are presented in Table 1. To evaluate their performance as energy storage devices, the energy density (E) of the supercapacitors are calculated by using $E = 0.5 C V^2$, where V is the potential difference in the CV curve, and C_m is the mass specific capacitance of the supercapacitor. Using the equation above, the maximum energy densities of ACs and CNTs-based supercapacitors are determined to be 9.7 and 2.9 Wh kg^{-1} , respectively. These values are comparable to the energy densities of carbon-based supercapacitors reported in the literature. For example, An *et al.*, reported the maximum energy density of supercapacitor using single-walled CNTs as 7 Wh kg^{-1} .³⁴⁾

The higher mass specific capacitance and energy density of ACs-based supercapacitors is attributed to their higher surface area compared to CNTs. Fig. 5 shows N_2 adsorption isotherms from ACs and

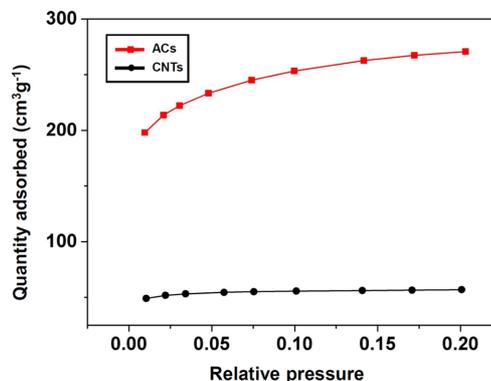


Fig. 6. N_2 adsorption isotherms of ACs and CNTs.

CNTs performed at 77 K. As is seen in Fig. 5, ACs exhibited higher gas adsorption capacity than CNTs, therefore resulting in the higher BET surface area. The surface areas of ACs and CNTs are measured to be 1012.4 and 223.7 m^2g^{-1} , respectively, resulting in the higher electrochemical performances of the supercapacitors from ACs as compared to those from CNTs.

4. Conclusion

In summary, novel integration of the electrodes, binders and electrolytes into separators were suc-

Table 1. Summary of the supercapacitor cells using ACs and CNTs as electrode materials

Specimens	BET Surface Area (m^2g^{-1})	Weight of Active Materials (mg)	Mass Specific Capacitance, C_m (Fg^{-1})	Coulombic Efficiency (%)	Energy Density, E (Wh kg^{-1})
Activated Catbons (ACs)	1012.4	0.22	22.3	52	9.7
Carbon Nanotubes	223.7	0.13	3.6	63	2.9

cessfully demonstrated to fabricate supercapacitors using ACs and CNTs as active electrode materials.

The simple structure of supercapacitors by using flexible glass fibre separators as templates is found to be useful in eliminating separate electrodes, binders and high pressure/temperature which are typical in the current supercapacitor fabrication process. The electrochemical measurements on the supercapacitors from ACs and CNTs using this method reveal that the supercapacitors using ACs successfully demonstrated significant mass specific capacitance (22.3 Fg^{-1}) and energy density (9.7 Wh kg^{-1}). Our method could provide useful strategy to realize fully flexible, wearable and stretchable energy storage devices by simpler and more cost-effective ways than conventional technology.

Acknowledgments

This research was supported by Basic Science Research Program through the National Research Foundation of Korea (NRF) funded by the Ministry of Science, ICT & Future Planning (2013R1A1A1008436).

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