Electrochemical Behaviors of PAN/Ag-based Carbon Nanofibers by Electrospinning

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In this work, silver nanoparticles-containing polyacrylonitrile (PAN) solutions in *N,N*-dimethylformamide (DMF) were electrospun to be webs consisting of nanofibers. The inputted voltage and PAN content in the solution were fixed at 15 kV and 10 wt.% in DMF with 10 cm of tip-to-collector distance (TCD). The PAN/Ag nanofiber webs were stabilized by oxidation at 250 °C for 2 h in air and carbonized at 1000 °C for 2 h in N_2. The resultant diameter distribution and morphologies of the nanofibers were evaluated by scanning electron microscope analysis. The electrochemical behaviors of the nanofiber webs were also observed by cyclic voltammetry tests. It was found that the presence of silver nanoparticles in carbon nanofiber webs led to the increase of specific capacitance and the decrease of fiber diameters.

Key Words : PAN-based carbon nanofibers, Electrical conductivity, Capacitor

Introduction

Polymer nanofiber webs have been fabricated using an electrospinning process driven by an electrically charged jet of polymer solution.[1,2] One advantage of nanofiber webs is the high specific surface area developed through the creation of pores on the nanofiber surface.[3,4] Also, the mechanical strength of an individual nanofiber is expected to be enhanced by decreasing its diameter.[5] This material has been widely applied to filters,[6] scaffolds,[7] protective clothing,[8] and sensors.

Polyacrylonitrile (PAN) has been widely used to fabricate nanofiber webs owing to the easy carbonization process.[9] PAN nanofiber webs, unlike other types of polymers, can be used directly as electrode materials after stabilization and carbonization. Despite the fact that the electrical conductivity of individual PAN nanofiber webs, after carbonization, is increased, the electrical conductivity of such carbon nanofiber webs is yet expected to be low, owing to the sparse nanofiber network.

Recently, many kinds of electronic communication devices have been becoming smaller, more lightweight, and advanced. Electric double-layer capacitors (EDLCs) are in demand as sources of electricity for electronic devices. The EDLC is a new source of high-power production. The electrode materials of EDLCs normally employed are carbon alloys, aerogel carbons, and activated carbons. More recently, conductive polymers and polyacenic semiconductors (PASs) have been introduced.

Electrospinning has been shown to be a powerful and effective method for the preparation of fibers of nano-size diameter.[4,10] It is a process for producing non-woven webs of nano-size fibers through the introduction of instability into a polymeric solution or melt by applying opposing high-direct-current (high DC) charges at the spinneret and at the ground.[1,2] Initially, the polymer solution is held by its surface tension in the form of a droplet at the tip of the spinneret. As the voltage is increased, a charge is introduced onto the surface of the droplet, which charge distorts the droplet. Above the critical voltage, a single jet, commonly termed the Taylor cone, is ejected from the tip of the spinneret. Electrospun fibers have received a great amount of attention for their wide application range in the fields of tissue engineering, sensors, protective clothing, high-performance filters, and carbon materials.[6-8]

Silver is one of the most interesting materials form the standpoint of nanotechnology and nano-devices, owing to their superior structural, thermal, and electrical properties. Incorporation of silver into electrospun nanofiber webs has been demonstrated to enhance electrical conductivity.

PAN-based carbon nanofiber webs can be used directly as supercapacitor electrodes.[9] However, their power density is poor, due to their large electrical resistivity. Higher electrical conductivity has always been desired as the means to high-capacitance and high-power-density supercapacitors. For this reason, PAN/silver-based nanofiber webs have recently been introduced. A previous paper has reported the electrochemical and structural properties of carbon fibers electrospun using PAN precursors.[11] However, the electrical conductivity of the fibers was not sufficient for capacitor electrode use. Therefore, in the present work, we prepared silver-nanoparticle-containing PAN-based carbon nanofibers in order to evaluate their electrical conductivity and EDLC behaviors.

Experimental

Preparation of PAN/silver nanofiber webs. PAN and N,N-dimethylformamide (DMF) were purchased from Aldrich Co. The silver powders (particle size is 5-10 nm and silver content 10 wt.%) that were dissolved in ethanol solution in this study were acquired from ABC nanotech of Korea. Silver powders of 0, 1, 3, and 5 wt.% were mixed in DMF and strongly stirred for 5 h in a bath-type sonicator. All of the reagents were used without further purification. PAN, with an average molecular weight of Mw = 86,200 g/mol,

was dissolved in slightly stirred silver-dispersed DMF to yield a 10 wt.% solution.

The electrospinning technique is based on the mechanics of electrostatic forces drawing a jet of polymer solution, which experiences high extension due to an electro-statically driven bending instability, forming nanofibers. In the present study, the solutions were electrospun from a 5 mL syringe with an MN-22G needle (negative). An aluminum wheel was used as the collector (positive). The distance between the needle tip and the collect wheel (TCD) was 10 cm, and the applied voltage was 15 kV.[12,13]

Preparation of carbon nanofiber webs contain silver nanoparticles. The electrospun PAN/silver-based nanofiber webs were collected on aluminum foil that was attached to the edge of the collector. The 10×10 cm webs were stabilized in an air-circulating furnace supplying 30 mL/min air, raising the temperature from room temperature to 250 °C at a rate of 1 °C/min and holding that final temperature for 2 h, and then the webs were carbonized for 2 h in nitrogen to 1,000 °C at the same 1 °C/min rate.[14] The samples were stored in a desiccator until they were used for analysis. The sampling process is shown in Figure 1. The fiber distribution and morphology of the electrospun nanofibers were determined using a scanning electron microscope (SEM, JEOL JXA 840A).

Electrochemical measurements. Cyclic voltammetry (CV) on the unit cell was performed in the potential range of 0-0.9 V at a scan rate of 10 mV/s. The discharge capacitance of the electrodes in the EDLCs were calculated on the basis of equation (1),[15]

$$C = \frac{2(i \times \Delta t)}{(W \times \Delta V)} \qquad (1)$$

where i is the current, Δt is the discharging time from 0.54 to 0.45 V, ΔV is the voltage variation in the time range measured, and W is the weight of the two electrodes.

Electrochemical measurements were carried out in a conventional three-electrode electrochemical cell at 25 °C. A piece of Pt wire was used as the counter electrode, and KCl-
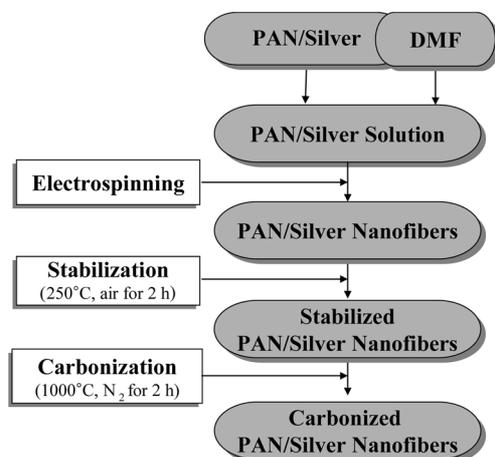

Figure 1. Sampling process for electrospun PAN/silver-based carbon nanofibers.
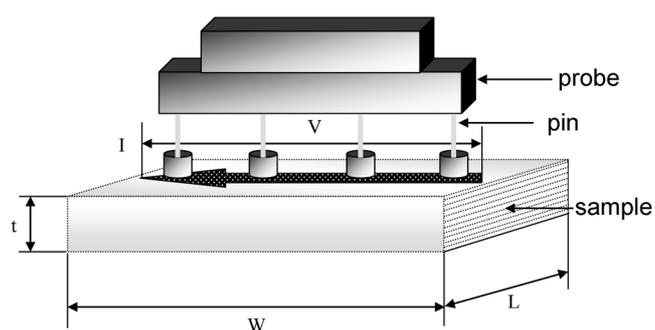

Figure 2. Schematic diagram of specific resistivity measurement.

saturated Ag/AgCl was used as the reference electrode. The above-mentioned fiber electrodes were used as working electrodes. All of the solutions were prepared with ultra-pure water. Electrochemical experiments were performed using an Autolab with a PGSTAT 30 electrochemical analysis instrument (Eco Chemie B.V.; The Netherlands).

Electrical resistance measurements. The electrical resistance behaviors of the carbonized PAN/silver were evaluated by a four-probe volume resistivity tester (MITSUBISHI Chemical Co., MCP-T610). Wang *et al.*'s initial four-probe design[16] for a strip specimen is shown in Figure 2. The outer and inner pairs of electrodes were used as current and voltage contacts, respectively. Because the two quantities of voltage and current are independent of the resistances caused by electrodes, wires, and imperfect electrode bonding, the measured resistance is accurate. Based on the measured resistance, the specific resistance (or electrical conductivity) can then be obtained by equation (2):

$$\text{Specific resistance} = \frac{\Omega \cdot L \cdot t}{W} \qquad (2)$$

Results and Discussion

Electrospinning. Electrospinning is a special electrostatic atomization process that was explored in detail by Zeleny in 1917.[17] Michelson[18] provides an excellent overview of electrostatic atomization theory and modern applications. Electrostatic atomization occurs when the surface tension of a liquid is overcome by an applied electric field, thereby ejecting tiny droplets from the surface. Polymeric solutions behave differently from monomeric liquids during electro-static atomization, in that they persist as elongated jets over a much greater distance.

Taylor[19] identified the critical electric potential for the electrostatic formation of a cone of liquid (now known as a Taylor cone) at the end of a capillary tube. His derivation began with the expression for the equilibrium state of a droplet at the end of a pressurized tube, and the coefficients for the electrostatic potential were calculated, by observing the deflection of charged solutions at the end of an inverted capillary, on the basis of equation (3),

$$V_c^2 = 4\frac{H^2}{L^2}\left(\ln\frac{2L}{R} - 1.5\right)(0.117\pi R\gamma) \qquad (3)$$

where V_c is the critical voltage, H is the separation between the capillary and the ground, L is the length of the capillary, R is the radius of the capillary, and γ is the surface tension of the liquid.

A similar relationship was developed by Hendricks *et al.*[20] for the potential required for electrostatic spraying, from a hemispherical drop pendant from a capillary tube, on the basis of equation (4),

$$V = 300\sqrt{20\pi\gamma r} \qquad (4)$$

where r is the radius of the pendant drop.[20]

In each case, the conducting drop was assumed to be surrounded by air, and suspended in a stable position from the capillary tube. These equations are appropriate physical models for droplet formation for slightly conducting, monomeric fluids. By examining a small range of fluids, Taylor determined that a 49.38 deg equilibrium angle balanced surface tension with electrostatic forces, and used this value in his derivation. However, it has been shown that conductivity and viscosity both play vital roles in the electrostatic atomization process, and can influence the equilibrium angle and other aspects of that process.[18] The dependence on conductivity and viscosity is missing from these two equations, but the relationship between surface tension and critical voltage serves as a useful guide for slightly conducting, medium-to-low viscosity solutions. Taylor cones are important to electrospinning in that they define the onset of extensional velocity gradients in the fibres-forming process.[21] Other important aspects of electrospinning that have been examined include the different modes of droplet formation as a function of several process variables,[22] and the scale-up of atomization using a linear array of Taylor cones.[23]

Surface tension and critical voltage. Table 1 summarizes the characteristics of the solutions. The surface tensions ranged from 0.0364 to 0.0367, 0.0375, and 0.0386 N/m when the concentration of silver was increased from 0 to 1, 3, and 5 wt.%, respectively. The critical voltages were calculated from equation (3) and increased from 14.68 to 14.92 kV as a function of the silver concentration. This result indicates that the presence of silver nanoparticles leads to the increase of surface tension of PAN/NMP solution due to the high polarity of metal nanoparticles. The reason of increase in critical voltages is probably related in the electroconductivity of silver/PAN solutions, but the conductivity changes were not significant to evaluate in this work.

Morphology. Figure 3 shows SEM micrographs of the

Table 1. Surface Tension and Critical Voltage of PAN/silver-based Nanofibers

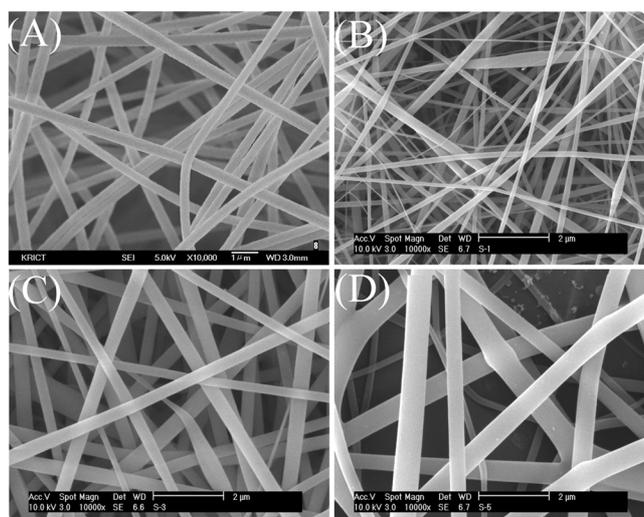| Concentration (wt.%)	Surface tension (N/m)	Critical voltage (kV)
0	0.0364	14.68
1	0.0367	14.72
3	0.0375	14.89
5	0.0386	14.92

Figure 3. SEM images of PAN/silver-based nanofiber webs with silver contents ranging from (A) 0 wt.%, to (B) 1 wt.%, (C) 3 wt.%, and (D) 5 wt.%.
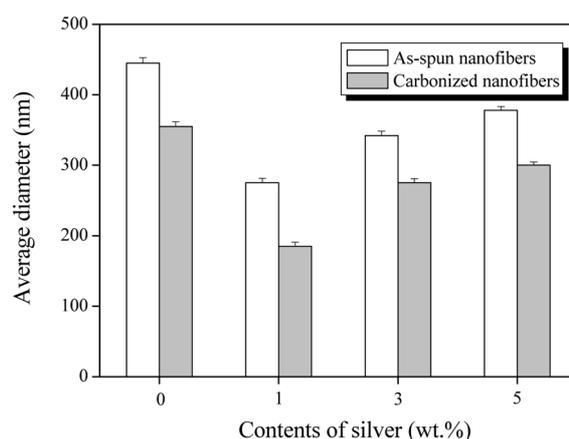

Figure 4. Diameter distribution of PAN/silver-based carbon nanofibers before and after carbonization process with different silver contents.

PAN/silver-based nanofibers. Figure 3(A) illustrates the electrospun PAN nanofiber webs. Figures 3(B), (C), and (D) show the nanofiber webs as a function of the PAN/silver solution content. It was found that the average diameter of the PAN/silver-based nanofiber webs ranged from 200 to 500 nm. As shown in Figure 4, the diameter of the as-spun PAN/silver fibers ranged from 275 to 445 nm (average: 360 nm). The average diameter of the carbonized nanofibers decreased after the carbonization process. This reduction in diameter was a consequence of the carbonization process, by which the amorphous structure of the polymeric fiber webs was significantly changed to the graphitic crystalline, resulting in the shrinking of fiber diameter. It is interesting to note that the fiber diameter of 1 wt.% of silver content showed the smallest. Normally, the fiber diameter of electrospun fibers could be controlled by several factors, such as critical voltages, temperature, humidity, viscosity and electro-conductivity of polymeric solution, TCD, and etc. In this system, surface tension of polymeric solution could be a
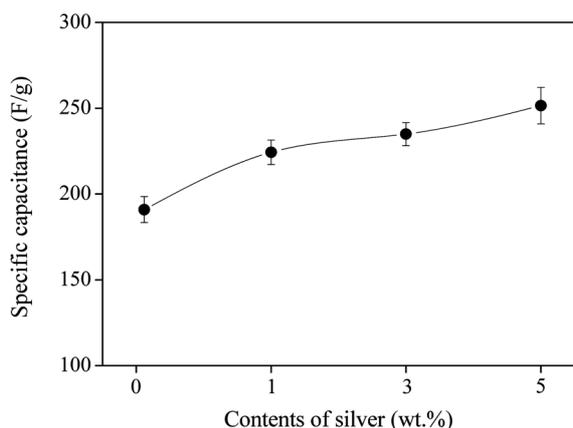
Figure 5. Specific capacitance of PAN/silver-based nanofibers with different silver contents.

main factor to determine final fiber diameters, indicating that low surface tension led to the narrow fiber diameter due to the needs for high force to break polymeric droplet on the needle tip, resulting in the high tension to nanofibers. Meanwhile, the presence of metal nanoparticles might play a role to reduce fiber diameter in the respect of electro-conductivity or electric network in PAN webs.

Electrochemical properties of PAN/silver-based carbon nanofibers. The electrochemical properties of the carbonized PAN/silver nanofibers were investigated by reference to CV curves in 0.5 M H_2SO_4 aqueous solution. Figure 5 shows the specific capacitance of the carbonized PAN/silver nanofibers with different silver contents. In the case of the 0 wt.% silver concentration, the capacitance was 190.85 F/g. For the 1 wt.% silver concentration, the value was 224.26 F/g., for 3 wt.%, it was 234.91 F/g, and for 5 wt.%, it showed the highest specific capacitance among the samples. These results indicate that the silver concentration can have a positive influence on the electrochemical properties of nanofibers. In order to evaluate the real content of silver in PAN/silver webs, the elemental analysis (EA) method was used. From the EA results, it was found that real content was not significantly different with ideal content of silver, and it was
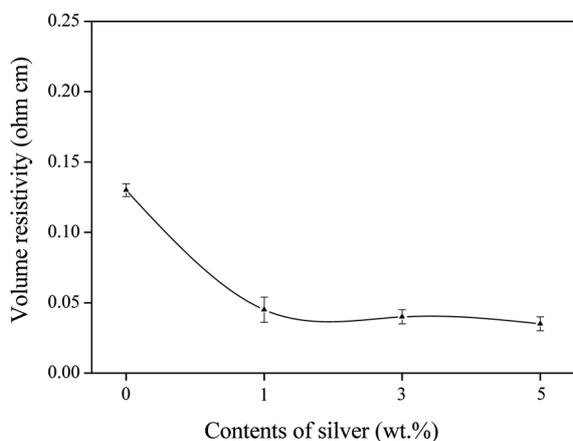
0.98, 2.87, and 4.85 wt.%.

Electrical resistance properties of carbonized PAN/silver-based fibers. Figure 6 shows the volume resistivities of the carbonized PAN/silver-based nanofibers for different silver contents. The electrical resistance decreased with increasing silver concentration. Specifically, in the case of the 0 wt.% silver concentration, the average volume resistivity was 1.3×10^{-1} Ω·cm. For the 1 wt.% silver concentration, it was 4.5×10^{-2} Ω·cm, and for 3 wt.% and 5 wt.%, it was 4.0×10^{-2} Ω·cm and 3.5×10^{-2} Ω·cm, respectively. These results indicate that the graphitic region as well as the silver-particle concentration in carbonized PAN/silver nanofibers can influence the electrical resistance properties. It is also worth to note that excessively silver-loaded carbon nanofibers didn't show lower electric resistance than that of the 1 wt.% sample. This result indicates that percolation threshold could be placed in 1 wt.% of silver content.

Conclusions

Electrospun PAN/silver-based carbon nanofiber webs were successfully prepared by carbonization at 1000 °C. The diameter distribution of the nanofiber webs was found to be influenced by silver contents and the carbonization process. The diameters of the electrospun nanofiber webs ranged from 275 nm to 445 nm. After carbonization, the carbon nanofiber web diameters ranged from 185 to 355 nm. The electrical resistivity slightly decreased with increasing silver content. The specific capacitance properties of the electrospun nanofibers already containing silver were increased with increased silver contents. It was also found that the PAN/silver-based carbon nanofiber webs showed a much better electrochemical performance than the as-spun PAN carbon nanofiber webs. In conclusion, the addition of silver nanoparticles was found to be an effective means of improving the energy-storage capacities of carbon nanofiber webs.

Figure 6. Volume resistivity of PAN/silver-based carbon nanofibers with different silver contents.

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