Electrochemical Properties of Activated Polyacrylonitrile/pitch Carbon Fibers Produced Using Electrospinning

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The electrospinnability of pitch was improved by blending in a solution of polyacrylonitrile (PAN) resulting in the reduction of the average fiber diameter from 2000 to 750 nm. Activated carbon fibers (ACFs) derived by stabilization, carbonization and steam activation at 700, 800, and 900 °C of the PAN/pitch electrospun fibers for 60 min were investigated as electrodes for supercapacitors. The Brunauer, Emmett, Teller (BET) specific surface area ranged from 732 to 1877 m^2g^{-1} and the specific capacitance from 75.5 to 143.5 Fg⁻¹, depending on the activation conditions. Electrodes from the electrospun web activated at 900 °C exhibited a particularly quick response showing a high frequency of 5.5 Hz at a phase angle of -45° of the impedance spectroscopy.

Key Words: Electrospinnability, Blend, Activated carbon fiber, Supercapacitor, Electrochemical test

Introduction

With the worldwide increase in energy demand on finite fossil fuel resources, energy storage systems such as fuel cells, supercapacitors, and batterries are seen as potential solutions. Among them, the supercapacitor is a very promising candidate due to its long shelf life and ability to deliver energy at high rates. Supercapacitors have a wide range of applications, either alone or in conjunction with fuel cells, batteries, and solar cells.¹

To improve the electrochemical properties of carbonaceous supercapacitors, researchers have been developing various types of advanced materials by controlling the pore size distribution, modifying the electrical conductivity, introducing electroactive polymers or metals, and optimizing device construction. Electrospun activated carbon fibers (ACF) are attractive materials for electrodes in electrical double layer capacitors (EDLC) due to their submicron diameter, high specific surface area, shallow pore depth, and the 3-D connection of the constituent fibers.²⁻⁷ We have previously reported the fabrication and electrochemical characterization of polyacrylonitrile (PAN)-, pitch-, polyimide (PI)-, and polybenzimidazole (PBI)-derived carbon fibers.⁸⁻¹⁷

Among them, fibers obtained from pitch exhibit high surface area (> 2000 m²g⁻¹), a high electrical conductivity (> 50 Scm⁻¹), and a high carbon yield (60%) at 1000 °C. However, pitch-based fibers showed poor electrospinnability due to problems of low molecular weight and/or low solubility in solvents such as tetrahydrofuran (THF)/dimethylformamide (DMF). This can be improved by blending with a polymer with excellent electrospinning ability such as PAN. Accordingly, we reasoned that carbonized PAN/pitch blends might be a promising electrode material that could take advantage of the excellent fiber-forming ability of PAN and the conductivity and high surface area of pitch.¹³⁻¹⁷

The fabrication of PAN/pitch blends by electrospinning is a novel approach, and the derived PAN/pitch activated carbon fiber webs can open new avenues for their industrial application

as supercapacitor electrode material and catalyst support. In this work, the unique combination of PAN/pitch improved the electrospinnability than the pitch only: carbon yield and response time for EDLC application than PAN only. The potential to achieve industrially acceptable energy density is also being explored by hybridization with metal oxides in the ACF.¹⁸⁻²¹

Experimental Section

Materials. PAN (molecular weight = 160,000), DMF (\geq 99.9%) and THF were obtained from Aldrich Chemical Co. (USA). The solvents were used without further purification. Pitch was supplied by Anshan East Asia Carbon Fiber Co., Ltd., China.

Solution Preparation and Electrospinning. Pitch was dissolved in a binary solvent (DMF:THF = 1:1) and a previously prepared solution of PAN in DMF was added. This mixture was continuously stirred at 60 °C for 12 hours until a homogeneous solution was obtained and then cooled down to room temperature. These solutions were fed into a positively charged spinneret attached to an electrospinning apparatus operating at 25 kV (NT-PS-35 K, NTSEE Co., Korea). Electrospun fibers were collected as a web on a negatively charged metal drum electrode wrapped with aluminum foil with a linear speed of 85 m/min.

Preparation of Activated Carbon Fiber (ACF). The electrospun fiber web was stabilized in air at 300 °C for 1 hour at a heating rate of 1 °C/min. The stabilized fiber was then carbonized in N₂ atmosphere and activated in a steam/N₂ (1:1) atmosphere at 700, 800, and 900 °C for 1 hour (heating rate: 5 °C/min) using an electrical furnace. The activated carbon fibers were characterized by scanning electron microscopy (SEM. Hitachi, S-4700. Japan), thermogravimetric analysis (TGA)/differential thermal analysis (DTA) (Mettler, STAR SW) analyses, and BET specific surface area (Micrometrics, ASPS2020, USA).

Electrochemical Tests. The EDLC cell was constructed with two activated PAN/pitch carbon fiber electrodes separated by a polypropylene membrane (Cellgard 3501, 25 µm) sandwiched

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between a pair of nickel plates (thickness 50 μ m) as current collectors. The electrodes were prepared in square form with an area of 2.25 cm². The performance of the electrodes was measured in a 6 M KOH aqueous electrolyte solution at room temperature. Cyclic voltammograms (CV) of the unit cell were performed over the potential range of 0 to 0.9 V, varying the scan rate from 10 to 500 mVsec⁻¹ (Jahner Electrik IM6, Germany). The capacitance of the electrodes was measured by charge-discharge in the potential range of 0 - 0.9 V and varying the current density of 1 - 10 mA/cm⁻² by using a WBCS 3000 battery cycler system (WonA Tech Co., Korea). The specific capacitance was compared with the respective specific capacitance obtained fro CV.

$$C = \frac{4(i \times \Delta t)}{W \times \Delta V} \tag{1}$$

where *i* is the current (ampere). Δt is the discharging time from 0.54 to 0.45 V (*ca*, 60 ~ 50% of the initial voltage), ΔV is the voltage shift at a given discharge time, and W is the total weight of both electrodes. The AC impedance behavior of the EDLCs over the frequency range of 1 MHz to 10 mHz was measured by using an electrochemical impedance analyzer (Jahner Electrik IM6, Germany).

Results and Discussion

Characterization of the Electrospun Fiber. These PAN/pitch fibers show improved spinnability compared to that of pitch $(2 \sim 3 \,\mu\text{m} \text{ diameter in Figure 1a})$. resulting in a smooth surface.



Figure 1. SEM images of (a) electrospun pitch fiber (b) PAN/pitch fiber web.

continuous length, and reduced fiber diameter to 750 nm (Fig. 1b) without the appearance of beading.

The carbonization reduced the average fiber diameter from 750 to 500 nm as shown in Figure 2. The spinnability is normally determined by the material parameter, which is calculated by the ratio of surface tension to viscosity of the fluid with an inverse relationship between spinnability and material parameter.

The TGA and DTA (Figure 3a) of PAN/pitch fibers measured in air show that mass was maintained up to 300 °C. Mass loss was seen at 324 and 524 °C, arising from dehydration accompanied by cyclization of PAN and the evolution of CO, CO₂, and H₂. In order to evaluate the effect of blend ratio on the carbon yield. TGA was performed for electrospun PAN and PAN/pitch fibers in N₂ atmosphere. As presented in Figure 3b, the carbon yield increased with an increase in pitch concentration.

Activation Behaviors. The activated PAN/pitch carbon fibers maintained their original shape despite further mass loss when the activation temperature was increased from 700 to 900 $^{\circ}$ C as shown in Figure 4. During carbonization, the mass of the fiber decreases by the evolution of H₂O. NH₃, HCN, CO, CO₂,



Figure 2. Diameter distribution of fiber diameter in (a) electrospun fibers and (b) carbonized fibers derived from PAN/Pitch.

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Figure 3. TGA/DTA profiles of electrospun PAN/Pitch fibers (a) PAN/ Pitch = 5/5 under air; (b) PAN/Pitch = 0/10, 5/5, 7/3, 10/0 under N₂.



Figure 4. SEM micrograph of activated PAN/pitch carbon fibers with 1 hour activation as a function of activation temperatures: (a) 700, (b) 800, (c) 900 °C.



Figure 5. N2 adsorption of activated PAN/Pitch-based carbon fibers.

 N_2 , H_2 and possibly CH_4 .²² After steam activation, the fiber diameter decreased by half from 750 to approximately 400 nm.

Pore volume increases when the activation temperature is increased from 700 to 800 $^{\circ}$ C, and this is mainly from the result micropore formation. On the other hand, activation at 900 $^{\circ}$ C brings an increase pore volume from mesopore formation (Figure 5).

Pore size and specific surface area were calculated on the basis of the BET equation and are summerized in Table 1. As the activation temperature rises from 700 to 900 $^{\circ}$ C, the fraction

of micropores decreases from 71.1 to 49.2% whereas that of mesopores increases from 28.9 to 50.8%. There is also an increase in the surface area from 732 to 1877 m^2g^{-1} . The specific surface area of carbon fiber would be considered unexpectedly large if it came only from the PAN component but is reasonable if a larger portion was contributed by pitch. The specific surface area of activated PAN carbon fiber was less than 1500 m^2g^{-1} as measured from a previous experiment.²³

Electrochemical Behavior. The electrochemical behavior of activated PAN/pitch carbon fiber electrodes was examined by CV and impedance spectroscopy. As shown in Figure 6, the rectangular CV curve comes from EDLC behavior, and not from pseudo-capacitance of oxygen-containing functional groups on the surfaces of the electrodes. Particularly, as the activation temperature increased from 700 to 900 °C, the shape of CV curve becomes more rectangular even at the highest scan rate (500 mVs^{-1}) for the ACF. The incline of the CV curve implies that a resistive component is involved in the charging process. The resistive component could be due to a hindered mobility of ions in micropores and/or a low electrical conductivity of the electrode. The resistive component's impact became smaller as the activation temperature increases. It is noteworthy that the PAN/pitch carbon fiber web activated at 900 °C shows the lowest resistance and the highest capacitance. The incline of the PAN/pitch ACF activated at 900 °C is surprisingly small even at a high scan rate of 500 mVs⁻¹, when compared with the

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Table 1.	Surface	characterizat	ion and cap	pacitance of	the activated	PAN/1	oitch carbon	fibers electrode

A attinution town (00)	DET $\mathcal{O} \mathcal{O} = \{m^2/m\}$	Total pore volume	Pore volume fraction (%)		Aver, pore size	Capacitance (F/g)
Activation temp. (C)	BET 5.5.A. (m/g)	(cm^3/g)	Micro	Meso	(nm)	$(at l mA/cm^2)$
700	722.9	0.3244	79.5	20.5	1.79	75.5
800	1220.2	0.7674	71.1	28.9	1.89	123.5
900	1724.8	1.1138	49.2	50.8	2.58	143.5



Figure 6. CVcurves of PAN/Pitch-based ACFs-web electrodes obtained from various activation temperatures (a) 700 (b) 800 (c) 900 °C in 6.0 M KOH aqueous solution recorded at various scan rates. Arrows indicate CV at decreasing scan rates (from 500 mV/s to 10 mV/s).



Figure 7. The specific capacitances of the activated heat-treated electrodes at various temperatures as a function of the discharging current density at a charging voltage of 0.9 V for 10 min.

large incline observed for activated carbons such as MSC-25 carbon even at 20 $\,mVs^{-1}.^{24}$

Approaching the more rectangular shape of the CV curve, which occurs with an increase in activation temperature, and the simultaneous increase in capacitance can be related to the increase in the volume fraction of mesopores (Table 1). As this volume fraction increases, the ions in the electrolyte can easily move into or out of the mesopores, thus decreasing the resistance associated with ionic mobility. In addition, a higher mobility of ions will certainly lead to an increase in the effective surface area of the studied carbonaceous materials, and thus an increase in electrical double layer capacitance, as shown in Table 1.

The capacitance of the activated PAN/pitch carbon fiber web activated at 700 °C decreases as the scan rate becomes larger. Because the pores in the activated PAN/pitch carbon fiber web are predominantly microporous (Table 1). the ions need a longer time to diffuse into or out of the pores. Figure 7 shows the specific capacitance as a function of current density at various activated temperatures, where the data were taken from the samples charged at 0.9 V for 10 min.

A slower scan rate affords more time for this diffusion, so that the effective surface area increases and enhances the capacitive behavior. As the activation temperature becomes higher, the pore size increases, thus reducing the time for ions to penetrate into the pores, so that the slopes of the plots in Figure 8 become smaller. Taken together, the data in Figure 6 and 8 demonstrate that the volume of micropores is the resistive component in the capacitive charging process of the activated PAN/pitch carbon fiber web.

The Nyquist plots for the activated PAN/pitch carbon fiber webs show typical capacitive behavior (Figure 9). At a very high frequency region $(1.00 \text{ E} + 05 \sim 6.00 \text{ E} + 04 \text{ Hz})$, there is pure resistance²⁵ for all the studied carbon webs, which corresponds to the solution resistance (R_s).^{26,27} In the semicircular

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Figure 8. Specific capacitance of samples treated at (a) 900 (b) 800 (c) 700 $^{\circ}$ C as a function of scan rate.



Figure 9. (a) Complex-plane impedance plots of the activated PAN/pitch carbon fiber web at an AC voltage amplitude of 10 mV. Z^{**} : imaginary impedance, Z^{**} : real impedance. The inset section is the equivalent circuit representing the supercapacitor cell behavior on the whole frequency range, (b) Bode phase plot by AC impedance method in 6 M KOH aqueous solution.



Figure 10. Ragon plot for PAN/Pitch-derived supercapacitor obtained at a constant current and from galvanostatic measurements (Current = 2 mA): (a) 700 °C, (b) 800 °C, (c) 900 °C.

loop in the lower frequency region $(R_s + R_F)$, resistance is due to solution resistance (R_s) plus charge transfer resistance (R_F) represented by inter-fiber electronic resistance and a resistance related to the porous structure of carbon materials.²⁸ The resistance component as a function of activation temperature in Figure 9(a) is reasonably and consistently assigned to the resistance of ions to diffuse into or out of pores. As the diameter of the semicircle in the lower frequency region becomes smaller, the slope of the capacitive component becomes more vertical. revealing that higher activation temperatures lead to more efficient capacitive charging for the activated PAN/pitch carbon fiber web. The frequencies at phase angle -45° are the measure of the charge transfer rate to the applied potential. The electrode activated at 900 °C shows the highest response frequency of 5.5 Hz among the electrodes activated at three temperatures (Figure 9). This behavior further shows that the diffusion of ions into the pores becomes faster as the proportion of mesopores increases, which reduces resistance.

The power density and energy density of the unit mass of the supercapacitors were evaluated from the discharge curves of galvanostatic cycles using the following equation (2):

$$P = \frac{I \times U}{w}$$

$$E = \frac{I \times U \times \Delta t}{w}$$
(2)

where *I* is the discharging current in amperes, *U* is the working voltage of supercapacitor in volts. Δt is the discharging time in hours, and *w* is the weight of a pair of electrodes in kilograms.²⁸

In this Figure 10, at the low power density in the range of $0 \sim 50$ W/kg, the energy densities are nearly same for all samples. However, they drop very swiftly with increasing power density, especially for the samples having large ESR due to low specific surface area and large hindrance. In the case of 700 °C-sample, the slope of Ragon curve is lowest and the smallest specific energy is reached just at about 300 W/kg of specific power comparing to 600 W/kg and 1300 W/kg for 800 and 900 °C-sample, respectively. Obviously, all electrochemical tests show good agreement results and lead to a conclusion that PAN/Pitchbased electrode heated at 900 °C performs highest efficiency of electrochemical properties.

Conclusion

The combination of highly spinnable PAN and high surface area pitch were combined to prepare electrospun fiber webs that could be subsequently activated and used as electrodes for supercapacitors. The activated PAN/pitch carbon fiber electrode obtained by activating at 900 °C for 1 hour shows the best performance in electrochemical tests for EDLC. CV indicated that the electrodes were stable in 6 MKOH aqueous solution within the potential range employed, and Faradaic reactions did not occur in these capacitor cells. The 900 °C-electrode, which was expected to possess high electrical conductivity. large specific surface area (1877 m²g⁻¹), and a highly mesoporous structure, provided the highest specific capacitance (143.5 Fg^{-1}) and highest power density of 1300 Wkg⁻¹ as well as the lowest cell resistance. Therefore, we have succeeded in combining the advantageous properties of PAN and pitch precursors in the electrospinning process, followed by suitable stabilization and activation, to form submicron carbon fiber web electrodes for supercapacitors with increased energy and power densities.

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