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Electrochemical behavior of pitch-based activated carbon fibers for electrochemical capacitors

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ABSTRACT

In the present study, electrode materials for electrochemical capacitors were developed using pitch-based activated carbon fibers with steam activation. The surface and structural characteristics of activated carbon fibers were observed using scanning electron microscopy and X-ray diffraction, respectively. Pore characteristics were investigated using N_2/77 K adsorption isotherms. The activated carbon fibers were applied as electrodes for electrical double-layer capacitors and analyzed in relation to the activation time. The specific surface area and total pore volume of the activated carbon fibers were determined to be 1520–3230 m^2/g and 0.61–1.87 cm^3/g, respectively. In addition, when the electrochemical characteristics were analyzed, the specific capacitance was confirmed to have increased from 1.1 F/g to 22.5 F/g. From these results, it is clear that the pore characteristics of pitch-based activated carbon fibers changed considerably in relation to steam activation and charge/discharge cycle; therefore, it was possible to improve the electrochemical characteristics of the activated carbon fibers.

1. Introduction

Electric double-layer capacitors (EDLCs) have attracted considerable attention as efficient energy storage devices [1]. Their operation is based on charge accumulation at the electrode. EDLCs are very attractive as potential energy storage systems because of their high energy density (>10 kW/kg) [2], quick charge/discharge rate [1], and long, maintenance-free operation life (>10^6 cycles). Characteristics of supercapacitors make them a very suitable option for energy storage in both power applications [3] and electric vehicles [4].

Charge storage in EDLCs utilizes electrostatic adsorption of electrolyte ions at the electrode–electrolyte interface [5]. An ideal electrode material is expected to possess a high specific surface area [6], an optimal pore size distribution [7], electric stability, and electric conductivity for fast transport of the electrolyte ions and charges.

Porous carbonaceous materials with tunable porosities, including activated carbon (AC) [8], activated carbon fibers (ACFs) [9], ordered mesoporous carbons [10], carbon nanotubes (CNTs) [11], and graphene-based materials [12] have been used extensively as electrode materials in commercial EDLCs.

ACFs make up a porous carbon material that possesses unique electrochemical properties due to qualities such as a well-developed porous structure [9], high specific surface area, and high pore volume [13]. Pores of the ACF open directly to the outer surface, and the size of the pores falls within a narrow distribution.

Currently, research in supercapacitors is focused on increasing their energy densities further and lowering their overall production costs by finding suitable electrode materials [14]. Carbon nanotubes (CNTs) based electrodes were proposed to overcome the above limitation because of CNT's large electrical conductivity [15]. Despite this advantage, the use of CNTs in supercapacitors has been limited due to the presence of a high contact resistance between the supercapacitor electrode and current collector.

Pitch-based AC is expected to have a high carbon yield [9], a well-developed crystal structure [16], and superior electrical conductivity [17], compared to other forms of activated carbon. Furthermore, pitch-based high-crystallinity AC has the potential to be used as electrode material for EDLCs after an activation process to develop a porous structure [17]. Pitch-based ACFs exhibit high specific surface area showing adsorption/desorption with negligible hysteresis. Therefore, manufacture of EDLCs using ACF is expected to improve electrochemical stability [18].

Consequently, in the present study, steam was used to activate pitch-based ACFs to develop their pore structure. The textural properties of the well-developed ACF pores were investigated,

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including their specific surface area and pore structure. Also investigated were the electrochemical characteristics of electrodes fabricated with the ACF so produced, and of supercapacitors made of organic electrolytes. In this way, the effect of steam activation on the electrochemical characteristics of pitch-based ACF electrodes was determined.

2. Experiment details

2.1. Sample preparation

In the present study pitch-based CF (GS Caltex, Korea) was activated using steam. For the activation process, the temperature was elevated from room temperature (25 °C) to 900 °C at 10 °C/min in N_2 gas in a custom-made cylindrical steel tube (SiC heater; 1300 mm × 100 mm). The reactor tube was maintained in a steam atmosphere for either 10 min (ACF-10), 20 min (ACF-20), 30 min (ACF-30), or 40 min (ACF-40), and then cooled down once again to room temperature, still in N_2 gas.

2.2. Characterizations

The pore structure of the ACs was characterized by N_2 adsorption/desorption at 77 K using a BELSORP-max (BEL JAPAN, Japan). All ACFs were degassed at 300 °C for 6 h prior to measurement. The specific surface area was calculated within the relative pressure interval of 0.01–0.2 using the Brunauer-Emmett-Teller (BET) method [19]. Pore size distribution in the mesopore range was obtained by the Barrett-Joyner-Halenda (BJH) method [20]. The microstructure of the ACFs was determined using a wide-angle X-ray diffractometer (WAXRD), employing a Rigaku SmartLab X-ray diffractor with customized auto-mount and a Cu Kα radiation source. Diffraction patterns were collected within the diffraction angles from 5° to 90° with a speed of 2 °/min. The morphology of the ACFs was explored using a field emission scanning electron microscope (FE-SEM, S-4800, HITACHI, Japan). To reduce charging during FE-SEM imaging, the samples were first placed on a sample holder and coated with platinum.

2.3. Electrochemical measurements

The electrodes were prepared by coating aluminum foil with an aqueous ACF suspension (87 wt%) mixed with carboxy-methyl-cellulose binder (CMC, 4 wt%), a plasticizer (styrenebutyrene rubber (SBR), 3 wt%), and a conductive agent (carbon black, 10 wt%). A coin-type capacitor cell was used to examine the electrochemical performance of the ACF electrodes, which consisted of a carbon film (diameter 14 mm, ~200 μm thick) and Al foil as the current collector. This cell consisted of two, facing carbon electrodes, sandwiching a cellulose filter paper as the separator. All electrochemical measurements were carried out using organic electrolyte 1 M $(C_2H_5)_4NBF_4$/propylene carbonate at room temperature.

To verify the charge and discharge characteristics of the cells produced, a charge/discharge tester (Maccor 4300 k desktop; Maccor, USA) was used for charging and discharging via the galvanostatic method. Measurements were made at a driving voltage of 0.1–2.5 V, and a current density of 2 mA/cm^2, during charge and discharge. The produced cell was measured based on the capacitance per unit weight combining conductive material and binder (F/g). It is necessary to confirm definitely the electrode capacity evaluation method. This is due to the fact that many numbers quoted are not electrode mass and quite often relate only to the active material and do not include the mass of the binders, conductive carbon fillers. Again, this makes comparison of numbers in the literature often difficult.

The cyclic voltammetry (CV) and electrochemical impedance spectroscope (EIS) measures were collected using an electrochemical device (VSP; Biologic, USA). The CV was found to be 30 mV/s at 0.1–2.5 V, and the Nyquist plots were recorded potentiostatically (0 V) by applying an alternating voltage of 10 mV amplitude in the 10 MHz–300 kHz frequency range.

3. Results and discussion

3.1. Surface morphology analysis

Fig. 1 presents the FE-SEM images of the ACF, which were used to investigate the effects of steam activation on the surface morphology. All images were taken at a magnification of 10,000× or 200,000×. For the as-prepared CF and all ACF samples (Fig. 1a–i), the fiber shape was maintained despite the severe conditions of the activation process. The CFs (Fig. 1a) prepared through the melt-spinning process were round with a smooth surface. The pores that developed on the surface due to activation can be seen in Fig. 1c–j. The high-magnification images (Fig. 1f, h, and j) show that the number of pores increased with the time of steam activation. In addition, as the activation time increased, micropores developed into mesopores, which then collapsed and developed into macropores.

3.2. Adsorption isotherm and textural properties

Fig. 2 shows the typical N_2 adsorption/desorption isotherms for CFs and ACFs prepared in this work. The ACFs showed a mixture of IUPAC Type I and Type IV [21]. The data about N_2 adsorption at 77 K were listed in Table 1.

The specific surface area of the ACFs increased with increasing activation time. It is clear that the surface area and pore structure were significantly influenced by the activation time. The specific surface area and the pore volume of the as-received CF were about 5 m^2/g and 0 cm^3/g, respectively. However, the specific surface area of the ACFs varied between 1520 and 3230 m^2/g. It reached a maximum value of 3230 m^2/g at 40 min, indicating that continuous activation is beneficial for obtaining ACFs with the greatest specific surface area.

Based on the literature for pitch-based ACFs, it was expected that the specific surface area would increase with burn off. The specific surface area of ACF was increased by activation with a corresponding decrease in carbon yield. ACF-20 resulted in 1750 m^2/g specific surface area and 64% (w/w) yield (36% burnt off). The specific surface area and the carbon yield of ACF-30 changed remarkably (2650 m^2/g and 34%, respectively).

Fig. 3 shows the mesopore distribution of the prepared ACF, calculated using the BJH method. When the mesopore distribution curve according to the BJH equation was examined (Fig. 4), it was possible to obtain results identical to those in Table 1. All the ACFs had their highest intensity peak around 2.0 nm. The ACNF-45 sample showed better-developed mesopores than did other ACFs. This means that increasing activation time results in larger pore size. Clearly, steam activation played an effective role in the development of mesopores.

3.3. X-ray diffraction

The crystallography of ACF produced from carbon fiber using steam activation, was characterized by means of X-ray diffraction (XRD). This information, for the CF and ACF prepared during this work, is presented in Fig. 5 and Table 2. It is well known that the oxidation of carbonaceous materials has a higher probability of occurring in the amorphous region and graphite edges [22].

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