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Engineered carbon fiber papers as flexible binder-free electrodes for high-performance capacitive energy storage

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ABSTRACT

A binder-free electrode for flexible supercapacitor applications was fabricated using carbon fiber papers (CFPs) via a facile paper making method. CV curves and galvanostatic charge/discharge profiles exhibited ideal capacitive behavior and linear voltage–time function with small *IR* drop. O_2 activation process greatly affected the porosity and surface structures. The CFP electrodes activated at 325 °C for 45 min by O_2 oxidizing gas showed highest specific capacitance of 156.9 F g^{-1} and excellent cycle stability (~90.2%) after 5000 cycles at 1.0 A g^{-1} in 1.0 M H_2SO_4, which presented the possibilities as flexible electrodes with excellent electrochemical performances for EDLCs.

Introduction

The supercapacitor plays an important role in electrochemical energy storage because of its combined relative advantages, such as lower price and more environmentally friendly properties, higher power density, and longer cycle life [1]. Supercapacitors, electrochemical double-layer capacitors (EDLCs), and ultracapacitors are generally utilized names for the classification of electrochemical energy storage devices that store energy by electrostatic attraction in double-layer. These energy storage devices are suitable for the rapid charge and discharge of energy, which are highly dependent on the specific surface area of electrode materials [2,3]. EDLCs have both the fast-response performance of capacitors and the energy storage capability of secondary batteries. They also have rapid charge/discharge performance, high energy efficiency, and long cyclic life-time of over 100,000 cycles, because the electrical energy is stored by charge separation in electric double-layers. Due to environmental issues attributed to the use of fossil fuels, great interest has recently been generated in fuel cell vehicles, electric vehicles, and hybrid electric vehicles in combination with the internal combustion engine and secondary batteries. In the case of electric vehicles that momentarily require large power, the performance has been improved through the development of EDLC with high energy efficiency [4–6].

Currently, activated carbons (ACs) and activated carbon fibers (ACFs) with high specific accumulation capacity are mainly used for the EDLCs as electrode materials that have excellent properties, such as high specific surface area, high electronic conductivity, good corrosion resistance, and low thermal expansion [7,8]. ACFs are novel fibrous adsorbents that have been developed by the carbonization and activation of organic fibers [9]. The beneficial properties of ACFs are the thinner diameter of the fiber (which can minimize diffusion limitations, and allow rapid adsorption/desorption), narrower pore size distribution, and superior adsorption capacity at low concentration of adsorbates, compared to conventional ACs powder. The porosity of ACFs is developed through activation process, normally by partial gasification in carbon dioxide, and/or steam and they are affected by many conditions, such as the degree of activation and carbonization. Typically, ACFs are a kind of micro-pore carbonous adsorbent that

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exhibits slit-shaped pores. These properties of porosity, surface area, and surface structure affect the high adsorption capacity of ACFs, and therefore they play an important role in an electrode material for EDLCs as well as hybrid supercapacitors [10–12].

ACs [13,14] and ACFs [15–17] have been extensively used as electrode materials for EDLCs, because of their high specific surface areas and electric conductivities. However, the use of insulating binder during electrode fabrication, such as poly(tetrafluoroethylene) (PTFE) and poly(vinylidenefluoride) (PVDF), will increase the internal resistance of the electrodes, and thus deteriorate the rate performance of the EDLCs [18]. Moreover, such binder may block some pores of the porous carbons, resulting in the decreased capacitance [19]. Among the electrodes employed in EDLCs, great interest in binder-free electrodes, such as cloth, fabric, sheet and paper forms, have recently emerged [20–22], which show superiority over carbon fibers or powders, and can be directly used as electrodes. Therefore, they are expected to show higher capacitance and better rate performance [18].

Ishikawa et al. [23] have achieved ACFs cloth electrode (surface area of 1300 $g\,m^{-2}$, thickness of 0.62 mm) with a discharge capacitance of 20 $F\,g^{-1}$, through cold plasma treatment generated in an Ar-O_2 atmosphere. The capacitance value was shown to increase with the cold plasma treatment by increasing the micropores on the surface of the ACFs cloth electrode. Xu et al. [18] have fabricated binder-free electrode through carbonization and activation of PAN-based carbon fiber cloths, and reported that moderate carbonization at 600 °C resulted in higher specific capacitance value of 208 $F\,g^{-1}$. Hsieh and Teng [21] prepared capacitor electrode (surface area of 1300 $g\,m^{-2}$, thickness of 0.4–0.6 mm) using a PAN-based carbon cloth with different O_2 activation times at 250 °C, which showed slightly increased specific capacitance with increasing activation time. For instance, the sample activated at 250 °C for 6 h showed a specific capacitance value of 130 $F\,g^{-1}$ in 1 M H_2SO_4 aqueous electrolyte, retaining excellent cyclic stability of 99.5% after 100 cycles. So far, several efforts have been devoted to develop binder-free electrodes based on the carbon cloths, and most of the research efforts have focused on the form of woven electrodes using carbon fibers. To the best of our knowledge, there was no research effort on the form of paper electrodes using both a facile paper making process and an O_2 activation at low temperature.

In this study, for the purpose of reducing the equivalent series resistance (ESR) of EDLC, we have fabricated the ACF papers (ACFPs) using a paper making method, and used the ACFPs as a flexible binder-free electrode for EDLC. This strategy enables the paper electrodes to be lighter, thinner, and easier to manufacture than conventional binder-free electrodes. The physical activation under O_2 as oxidizing gas at a relatively low temperature was also carried out to enhance the specific surface area and the electrochemical performance of ACFPs. One of the advantages of this method is that it is available at relatively lower temperature than the several other methods. The surface morphologies, porosity analysis, and electrochemical performances of the flexible binder-free ACFPs were performed to evaluate the possibilities as binder-free electrode materials for EDLC.

Experimental

Materials

ACFs (BET surface area: 1200 $m^2\,g^{-1}$, fiber length: 6 mm) were purchased from An Shan Sino Carbon, China, and used to fabricate ACFPs as received, without further purification. Phenolic resin as a binding material was kindly provided by Phenolite KC-6301, Kangnam Chemical Co., Ltd., Republic of Korea. All of the reagents were analytical grade, and were used without further purification. All of the aqueous solutions were prepared with distilled water.

ACFPs fabrication

For the dimensional stability of ACFPs, physical bonding between the fibers in the ACFPs was induced by mixing with aqueous phenolic resin as a binder, according to a previous papermaking method [24]. In order to prepare uniformly dispersed ACFs slurry, ACFs (1.4 g) were added into aqueous phenolic resin solution of 10 wt% (1000 ml), and then stirred using a mechanical stirrer for 10 min. The resultant slurry was positioned to head box of hand sheet former, followed by filtration and dehydration on screen mesh. The circular-shaped ACFPs with base weight of 70 $g\,m^{-2}$, diameter of 160 mm, and thickness of 0.85 mm were obtained by these procedures. After dehydration, the obtained ACFPs were dried at 80 °C for 60 min, and then further pressed using a hot-pressing machine with a load of 500 kg at 130 °C for 5 min. The hand sheet former, shown in Fig. 1, manufactured in our

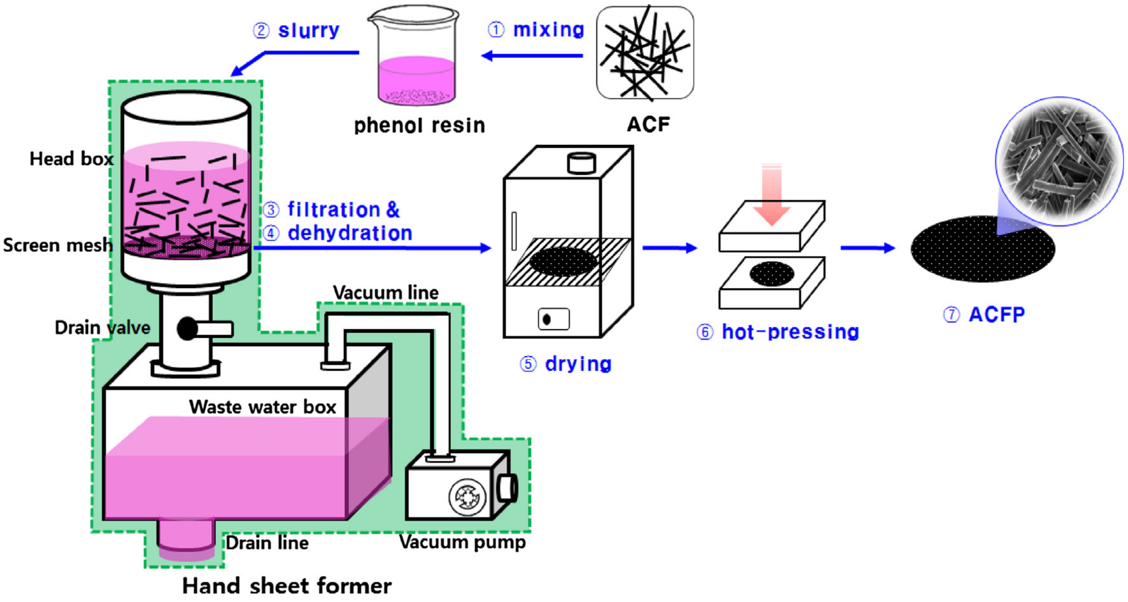

Fig. 1. Schematic illustration for the procedure to fabricate activated carbon fiber papers using a hand-sheet-former.

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