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Physico-chemical and electrochemical properties of pitch-based high crystallinity cokes used as electrode material for electric double layer capacitor

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ABSTRACT

The pitch-based high crystallinity cokes are investigated by evaluating its potential as electrode materials for electric double layer capacitors (EDLCs). After activation process, the high crystallinity cokes-based activated carbon (hc-AC) demonstrates great potential for use as an electrode material for EDLCs. The specific capacitance of hc-AC with the carbon to KOH ratio of 1:3 is 276 F g^{-1}, even with a low specific surface area of 983 m^2 g^{-1}. These results are comparable to that of the most commonly used material for EDLCs, MSP 20 (256 F g^{-1}), which has a high specific surface area of 1807 m^2 g^{-1}.

Introduction

Electric double layer capacitors (EDLCs) have attracted considerable attention as efficient energy storage devices, whose operation is based on the charge accumulation at the electrode [1,2]. EDLCs are popular in the automotive and mobile phone industries due to their high power density (>10 kW kg^{-1}) and long cycle lifetimes (>10^6 cycles) [3,4]. Porous carbon materials have been used as EDLC electrodes due to their unique physical and chemical properties, low cost, and widespread availability [5,6].

Many types of porous carbon materials exist, such as activated carbon (AC) [7], graphite [8], graphene [9,10], activated carbon fibers [11,23], carbon aerogels [12,13], and carbon nanotube [14,15]. Among these carbon materials, activated carbon has often been used as an active material for EDLCs because it possesses a large specific area, adequate pore volume, chemical inertness, and good mechanical stability [6,16]. In general, activated carbon is produced by the activation of carbonaceous source materials, such as nutshells, coconut husk, wood, coal, and petroleum pitch [17–19]. However, activated carbon researchers have recently began using renewable resources, such as aluminum industry waste, bottom ash, peat, steel-plant slag, and beer lees [20–22]. Unfortunately, these resources require additional processes such as heat treatment, sorting, and other chemical treatments to remove impurity.

More than 10 million tons of coke waste is generated per year from petrochemical plants, oil refinery, and steel mills and the uses of these coke wastes are economical and environmentally-friendly from a recycling perspective. However, coke waste has been currently used in only a few applications; thus, finding potential applications for coke waste is significant. Among the various cokes, the pitch-based cokes, which is residual product generated from carbon/carbon composites manufacturing process for high-quality brake discs for F1 automobiles and airplanes is a very fascinating material for EDLCs. To obtain high density of the resulting carbon/carbon composites, pitch is impregnated into the carbon preform and pyrolyzed at temperature lower than 1273 K under extremely high pressure (approximately hundred bar) before graphitization. Hence, the resulting cokes are expected to have high carbon yield, a well-developed crystal structure, and superior electrical conductivity compared to other cokes [23]. Furthermore, the pitch-based high crystallinity cokes have the potential to be used as electrode materials for EDLCs after activation process to develop a porous structure.

This study aims to recycle the pitch-based high crystallinity cokes and evaluate its potential to be used as electrode materials

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for EDLCs. The cokes were activated with various amounts of potassium hydroxide (KOH). The thermal, crystal, textural, and electrochemical properties of the resulting activated carbon materials were then investigated.

Materials and methods

Materials and reagents

The pitch-based cokes used in this study were obtained at temperature lower than 623 K under high pressure of 700 bar for high crystallinity. The size of the cokes was controlled to be under 75 μm using a general pulverizer and a sieve. KOH (95.0%, Samchun, Korea) was used as an activation agent to prepare activated carbon. In preparing electrode for EDLCs, carbon black (Super P, Timcal, Ltd., Switzerland) was used as a conductive material and polyvinylidene fluoride (PVDF, Aldrich) with diluted in N-methyl pyrrolidone (NMP, Aldrich) was used as a binder for electrode material to be stuck on titanium plate.

Preparation of activated carbon

The pulverized cokes were treated with KOH to obtain activated carbon [24,25]. The cokes (2.5 g) were mixed with five different weight ratio of KOH. The cokes-KOH mixtures were heated in an electric furnace. The heat treatments were conducted at 750 °C for 3 h under a nitrogen atmosphere. The untreated cokes samples were named CW, and the treated cokes samples were named CW-P100, CW-P200, CW-P300, and CW-P400, depending on the ratio of carbon to KOH 1:1, 1:2, 1:3, and 1:4, respectively.

Characterizations of the activated carbon

The thermal properties of the prepared samples were investigated using a thermogravimetric analyses (TGA, SDT2960, TA-Instrument, Taiwan). The analyses were conducted between 30 and 1000 °C with increasing temperature at a rate of 5 °C min^{-1} to obtain accurate information regarding materials. The crystal structures of the samples were determined using X-ray diffraction (XRD, D8 DISCOVER, Bruker AXS, Germany) studies. The XRD analyses were conducted using a Cu target. The morphology of the samples was investigated with a field emission scanning electron microscope (FE-SEM, Hitachi, S-5500, the Korea Basic Science Institute (KBSI), Jeonju Center). The textural properties of the samples were evaluated using N_2 adsorption at 77 K with a ASAP 2020 device (Micromeritics, USA) after each sample was degassed at 150 °C for 3 h. The specific surface area of the samples was investigated using the Brunauer–Emmett–Teller (BET) method. The pore volumes and pore size distributions were calculated using a *t*-plot and density functional theory (DFT).

Preparation and electrochemical characterization of the electrodes

The prepared activated carbon was manufactured as an electrode for an EDLC. The electrode material was prepared by mixing 80 wt% the cokes or activated carbon, 10 wt% carbon black, and 10 wt% diluted PVDF to form a slurry. This slurry was then painted onto a titanium plate. After drying the painted plate at 120 °C, the resulting electrodes were pressed at a pressure of 20 MPa for 10 min at 423 K to obtain the final working electrode.

Electrochemical characterization analyses of the prepared electrodes were performed with a Compactstat Electrochemical Interface (Ivium Technologies, The Netherlands) using a three-electrode assembly. AglAgCl and platinum were used as the reference and counter electrode, respectively. Cyclic voltammetry of the electrodes were measured over a potential range of 0–1 V at a scan rates of 5 and 50 mV s^{-1} in a 1 M H_2SO_4 solution. To compare the electrical conductivities of the prepared electrodes, electrochemical impedance spectroscopy (EIS) was also conducted using the same electrochemical device.

Results and discussion

Thermal properties of the cokes

The thermal properties of pitch-based cokes were shown in Fig. 1. The final weight loss of the CW was approximately ~10 wt% under a nitrogen atmosphere. This result indicated that the residual weight is higher than that of other carbon materials due to the severe pressure treatment [5]. Under an air atmosphere, the weight loss curve of the CW exhibited a noticeable decrease starting from 500 to 600 °C, which suggested that the heat treatment temperature of the original cokes are generated in that range. The TGA curve of the CW between 400 and 500 °C slightly increased because of the sudden change in weight of the CW due to air.

Crystallinity of the cokes and activated carbon samples

XRD patterns of the cokes and activated carbon samples are shown in Fig. 2. For the untreated cokes, a strong peak and a weak peak appeared at 26° and 43°, respectively. This result indicated that the cokes primarily had (0 0 2) crystal planes and partially had (1 0 1) crystal planes. Considering the low heat treatment temperature found from the TGA, the crystal structure of the cokes was well developed due to the extremely high pressure treatment. However, the activated carbon samples (CW-P100,

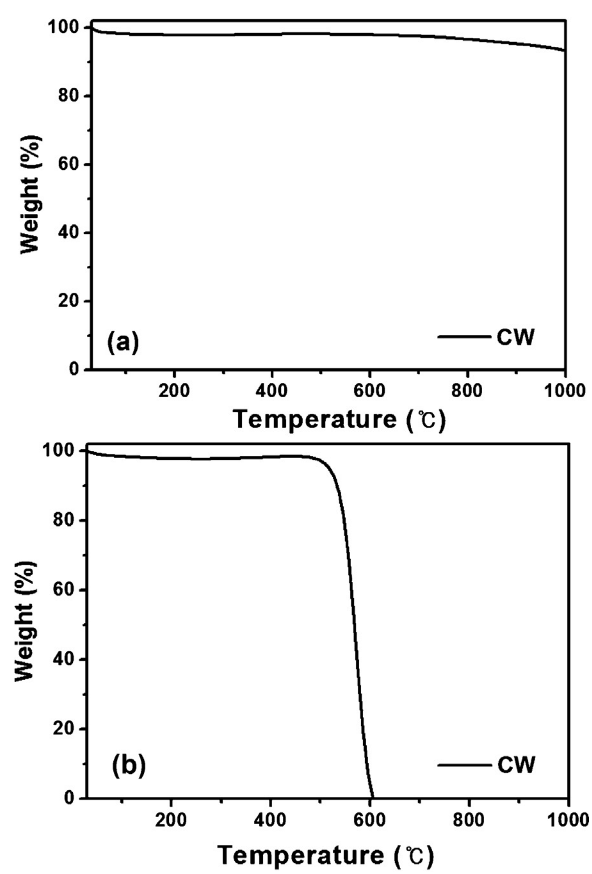

Fig. 1. TGA curves of the pitch-based cokes under increasing temperature, at a rate of 5 °C min^{-1}, under (a) N_2 and (b) air atmospheres.