Pore size distribution control of pitch-based activated carbon for improvement of electrochemical property

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ABSTRACT

Activated carbon has been prepared using coal tar pitch as a precursor with a simple NaOH activation process. The effect of the activation on the porosity and the specific surface area is characterized by nitrogen adsorption–desorption isotherms. The highest specific surface area of $1409.7 \text{ m}^2\text{ g}^{-1}$ is obtained with a NaOH to pitch ratio of 6. Its specific capacitance is 287.43 F g^{-1} at the scan rate 50 mV s^{-1}, 197.78 F g^{-1} at the current density 1 A g^{-1}, and it has outstanding energy density of 16.34 Wh kg^{-1}. Thus, pitch-based AC is a promising material for various energy storage devices.

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Introduction

International Union of Pure and Applied Chemistry (IUPAC) defines pitch as the residue obtained after pyrolysis of organic materials or distillation of tar [1]. It is also means that pitch is a complex form consisting of aromatic hydrocarbons and heterocyclic compounds.

Pitch obtained from coal tar or petroleum. Both pitch types are complex mixtures of organic molecules that primarily consist of polycyclic aromatic hydrocarbons (PAH) [2]. This polycyclic aromatic structure of pitches results in isotropic or anisotropic semicokes formation during heat treatment processes. Due to this chemical property of pitches, main applications rely on their chemical characteristic structure.

Commercially, petroleum and coal-tar pitches turned from worthless wastes into important raw materials of carbonaceous materials. Manufacturing of graphite electrodes, carbon fibers, carbon–carbon composites, activated carbons, and mesophase carbon fibers can be obtained by pyrolysis and carbonization processes of pitch [3,4], and this conjugation can create a high added value.

Electrochemical capacitors (ECs) are energy storage devices that expected as a secondary electric power supplier for the automobiles with hybrid engine or fuel cell motor due to their high power density, long cycle life and short charge time [5]. However, compared with usual batteries, electrochemical capacitors have much lower energy densities. In order to overcome this shortage and to improve the performance of capacitor, the selection of electrode materials is important.

Electrical double layer capacitors (EDLCs) use carbonaceous materials such as carbon aerogels, carbon fibers, graphite, and activated carbons obtains by physical activation or chemical activation from different precursors [6]. As EDLCs stores the electric power by adsorbing electrolyte ions at the interface between electrode and electrolyte, the activated carbon (AC) having properties that high specific surface area and porous structure has been considered as an electrode material for EDLCs among the many types of active materials, without doubt.

Generally speaking, the higher surface area of the electrode, the more energy can be stored because of much electrochemical reaction sites [7,8]. Strictly speaking, but relationship between the specific capacitance and total surface area is not clearly linear [9]. The pore size distribution plays a crucial role in the performance of EDLCs, because surface of micropores must be accessible to electrolyte ions and a suitable amount of mesopores help a rapid mass transport of ions within the electrode enabling

the charging and discharging the double layer [10]. Therefore, an appropriate ratio of micropore and mesopore leads to an improved capacitance.

In this study, coal tar pitch was used as the precursor of activated carbon for electrode of EDLC. The pitch-based activated carbon by NaOH has advantages that a low cost, well developed porous structure, and high activation yield. A series of activated carbon from pitch using NaOH of various amounts was prepared to understand the relationship between porosity characteristics and electrochemical properties.

Experimental details

Materials

Coal tar pitch (purchased from Ansan Co., SN-280#), was used as the raw material to prepare ACs. Pitch has carbon content of 90–93 wt% and ash content of 0.1%. Softening point is 280 °C. Sodium hydroxide (NaOH, bead, 98%, Samchun Co.) was sued as a chemical agent for activation.

Chemical activation of coal tar pitch

The activation of coal tar pitch was carried out by NaOH at 750 °C for 3 h under N_2 flow in tube furnace. The NaOH/Pitch weight ratio (control variable) was 1, 2, 4, and 6. The obtained ACs were washed with distilled water several times, and dried at 100 °C in vacuum oven (MVP 12, Woosung Vacuum Co., 5×10^{-4} torr) for overnight. The prepared ACs were denoted as AC1, AC2, AC4, and AC6 (named by NaOH/Pitch weight ratio).

Morphology and structure analyses

The crystalline structure of the samples was determined by a X-ray diffraction (XRD) analysis (D8, Germany) with Cu Kα (λ = 1.54056 Å).

Fourier transform infrared spectrometry (FT-IR) was carried out with a Spectrum GX over the wavenumber range of 4000–400 cm^{-1}.

Nitrogen adsorption analysis was conducted at 77 K to examine the changes in the specific surface areas and pore structures of the pitch-based activated carbon by NaOH activation.

The specific surface area and the total pore volume were calculated using the Brunauer–Emmett–Teller (BET) equation. The micropore volume was calculated using the Dubinin–Radushke-vitch (D–R) equation, and the pore volumes of the mesoporous were investigated according to the Barrett–Joyner–Halenda (BJH) method. The pore size distribution was calculated using the density functional theory (DFT).

The microstructures of the samples were investigated using field emission scanning electron microscopy (Tescan Mira 3 LMU FEG).

Electrochemical measurements

Electrochemical measurement such as cyclic voltammetry (CV) and Galvanostatic charge–discharge was carried out on potentiostat/galvanostat (IviumStat, Netherland) in a potential window from −0.9 to 0.0 V in 6 M KOH electrolyte. The three electrodes test cell was composed of nickel foam as a working electrode, saturated calomel electrode (SCE) as a reference electrode, and platinum wire as a counter electrode. The working electrode was prepared by mixing pitch-based activated carbon, carbon black, and polyvinylidene fluoride (PVDF) in a mass ratio of 85:10:5 with a small amount (3–5 ml) of N-methyl-2-pyrrolidone (NMP) solvent. The prepared mixture was pasted onto nickel foam (1 cm × 1 cm)

current collector, and dried in oven at 100 °C for 12 h to remove solvent.

Results and discussion

Material characterization

XRD patterns of the pitch-based activated carbon samples are shown in Fig. 1. NaOH-activated carbon appeared a relatively strong peak at 26° and this result indicated that the activated carbon had (002) crystal planes, graphitic structure.

FT-IR spectra were recorded to evaluate the functional groups on the activated carbon and are shown in Fig. 2. The peak around 3440 cm^{-1} is the O–H stretching of the hydroxyl functional groups [11], and the adsorption peak at 1600 cm^{-1} is aromatic C=C stretching vibrations [12]. The peak at 1440 cm^{-1} is for aliphatic C–H bending vibrations [13], and the peak at 3300 cm^{-1} is the IR adsorption peak of alkyne C–H vibration [14]. The peaks appeared at activated carbons tend to decrease as amounts of NaOH increase. This result indicates that cleaning effect occurred on the surface of material during activation process.

Characterization of the porous structure

The N_2 adsorption isotherms of the samples are presented in Fig. 3. Non-activated sample Pitch shows the quite low N_2 adsorption relatively, showing the non-developed pore structure. The isotherm of AC1 shows type I showing the characteristic of micropores according to IUPAC classification [15,16]. The others show type I at relatively low pressures (less than 0.1 P/P$_0$), and simultaneously appear some mesopores behavior of type IV over the range of the relatively high pressures. The isotherms of the samples except AC1 increase remarkably in lower than 0.4 P/P$_o$, and show a typical hysteresis loop in the intermediate relative pressure range. These results suggest that the samples typically have bottleneck shaped pores containing both the micropore and mesopore region, it is also show in SEM image of Fig. 4.

As shown in Table 1, the total pore volume and specific surface area increased gradually with higher amount of activation agent, NaOH. The AC6 has the highest values for specific surface area and total pore volume of 1409 $m^2 g^{-1}$ and 0.79 $cm^3 g^{-1}$, respectively.
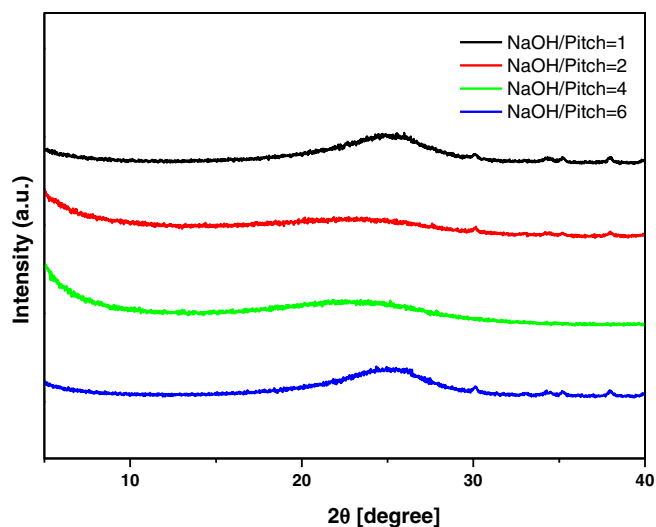

Fig. 1. X-ray diffraction of the pitch-based activated carbon by NaOH of various amounts.