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Controlling the electrochemical properties of an anode prepared from pitch-based soft carbon for Li-ion batteries

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ABSTRACT

A petroleum residue-based carbon electrode for use in a lithium-ion battery was prepared through the thermal reaction of pyrolyzed fuel oil. The samples were characterized by their softening point, crystallinity and battery performance. The softening point and pitch crystallinity increased with higher reaction temperatures and longer reaction times. The prepared pitch-based carbon had a 300–350 mAh/g capacity and 71–78% initial efficiency. Notably, the high-softening-point pitch resulted in the developed crystallinity through polymerization and condensation. In conclusion, the high-softening-point pitch had a better initial efficiency and rate capability based on its high crystallinity.

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Introduction

Carbon-based materials are used as negative active materials, most of which are based on graphite and disordered carbon. Disordered carbon (referred to as soft carbon) has been evaluated for its long-term charging and discharging rate characteristics to meet the requirements of electric vehicles (EVs) [1]. However, the reversible capacity of soft carbon is 250 mAh g⁻¹, which is lower than that of graphite (372 mAh g⁻¹). Several criteria exist for the anode material [2,3]. Specifically, low-temperature processing and low-cost precursors are mandatory. When the carbon precursor is carbonized at high temperatures (above 1000 °C), the initial efficiency and rate capability are higher than those of disordered carbon (below 1000 °C). However, carbonaceous materials manufactured at high temperatures consume more energy and have

higher associated costs. Thus, investigating the low-temperature preparation of carbonaceous materials with outstanding electrochemical properties is needed [4–8].

The petroleum residue derived from the naphtha reforming process is referred to as pyrolyzed fuel oil (PFO) and has an abundant polyaromatic content that adds value to the product [9]. Its low price and abundant sources (1 million tons per year in the Republic of Korea) are the main advantages of PFO. Therefore, PFO has the potential to become a high value product if it is converted into other valuable products. In fact, the price of anode material manufactured using petroleum residue is evaluated at \$8/kg, and \$12/kg using commercial soft carbon. Pitch is a valuable PFO product that can be prepared by the thermal condensation, polymerization, aromatization and polymerization of aromatic compounds [10,11]. Pitch can be further carbonized to soft carbon (PFO → pitch → soft carbon).

Chung et al. [12] used two types of pitch with different carbon crystallite lattice parameters (L_c and L_a). These researchers compared the initial irreversible capacity of the electrode active material after carbonization. The prepared coke, which was carbonized from the pitch with different softening points, exhibited different crystallite lattice parameters. Kinoshita et al. [13] reported that the irreversible capacity of carbon sources could

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be explained using the crystallite lattice parameter equation. Therefore, the lattice parameters (L_a and L_c) can be used to control the initial irreversible capacity of the soft carbon. These carbonaceous materials of the anode can be controlled based on the pitch softening.

The irreversible capacity is believed to be important for full cell performance because of the influence of the reduction of usable lithium on the overall battery capacity. The primary reasons for the decreased electrochemical characteristics involve electrolyte decomposition and the hysteresis phenomenon caused by the nanopores in the prepared carbon [14–20]. Because of the thermodynamically unstable state, a solid electrolyte interphase (SEI) layer forms on the surface of the carbon material via electrochemical reaction accompanied by electrolyte decomposition in the low potential region (approximately 0 V).

Graphite is primarily used as a carbonaceous anode material. However, graphite has disadvantageously poor rate properties. To overcome this disadvantage, graphite is used in anode materials as pitch-coated graphite [21].

In this study, we prepared a pitch-based soft carbon using PFO. The pitch was manufactured using different process temperatures and holding times to study the relationship between various pitch characteristics and the electrochemical properties of the pitch-based carbon. For the first time, the electrochemical characteristics of pitch-based carbon with a softening point of 100–150 °C were studied. The softening point of the petroleum-based pitch may be a variable that can be used to control the electrochemical properties of pitch-based soft carbon.

Experimental details

Materials

PFO-based pitch preparation

PFO derived from the naphtha cracking process was obtained from YNCC (Yeochun NCC CO. LTD), Republic of Korea, and used as the precursor to the anode material. This PFO had 78.6% aromatic and 21.6% resin contents, as determined by SARA (saturates, aromatics, resins, and asphaltenes) analysis. The pitch was prepared via the thermal reaction of PFO in a 5 L autoclave reactor. The PFO was heated at 350, 360 and 370 °C for 1, 2 and 3 h, respectively. Heating was performed in an N_2 atmosphere, and the heating rate was set to 2.5 °C/min. The details of the conditions used are tabulated in Table 2. The pitch prepared at 350 °C for 1 h was named '3501', and the other samples were named using the same protocol.

Carbonization

Carbonization was performed at 900 °C for 1 h under an N_2 atmosphere in a tubular furnace, and the heating rate was 3 °C/min. Each sample was ground using stainless balls and then passed through a sieve with 25 μ m openings to produce a powder for analysis of its electrochemical properties as an anode material for Li-ion batteries.

Characterization

Elemental analysis

Elemental analysis was performed to confirm the H/C ratio of the carbonized samples using a Thermo Scientific FLASH EA-2000 organic elemental analyzer. The results are tabulated in Table 1.

X-ray diffraction (XRD) analysis

The crystalline structure of the samples was determined by XRD analysis using a Rigaku Ultima IV diffractometer with Cu $K\alpha$ radiation. The d-spacing was estimated using the Bragg equation. To obtain more information of the crystalline structure, L_a and L_c

Table 1
Elemental analysis results.

Sample	C	H	O	N	H/C
3501	96.4	0.7	2.9	–	0.09
3502	95.7	0.9	3.4	–	0.11
3503	95.8	0.7	3.5	–	0.09
3601	96.9	0.7	2.4	–	0.09
3602	97.3	0.6	2.1	–	0.07
3603	97	0.7	2.3	–	0.09
3701	97	0.7	2.3	–	0.09
3702	97.1	0.6	2.3	–	0.07
3703	97.4	0.6	2	–	0.07

(the lattice parameters of the lateral size and stacking height, respectively) were calculated using the following equations [16,17]:

$$L_a = \frac{1.84\lambda}{B_a \cos \theta} \quad (1)$$

$$L_c = \frac{0.89\lambda}{B_c \cos \theta} \quad (2)$$

where λ is the wavelength, with a value of 1.54056 Å, and B_a and B_c are the half-widths of the (1 0 0) and (0 0 2) signals, respectively.

Softening point measurements

The softening point of the prepared pitches was measured using a DP-70 (Mettler Toledo) instrument according to ASTM D3416. The prepared pitch samples were placed on an aluminum plate and heated to 300 °C at a heating rate of 3 °C/min under an N_2 gas flow of 10 L/min.

Electrochemical measurements

The electrochemical properties of each carbon sample were estimated using 2032 coin cells. The mixing ratio of carbon and a polyvinylidene fluoride (PVdF) binder solution (NMP) was 96:4. The conductive materials were excluded to evaluate the performance of the as-prepared sample by itself. After mixing with a Thinky Mixer (MDbros Co.), the resulting slurry was coated onto Cu foils that were used as anode current collectors. The coated electrode was dried at 120 °C in a vacuum oven overnight to remove volatiles. Then, the dried electrode was pressed to a thickness of 70 μ m and porosity of 34–5%. Next, a disk with a diameter of 14 mm was punched out from the electrode material. The half cells were assembled in an argon-filled glove box. Li foil was used as the counter electrode. Additionally, 1 M LiPF₆ was dissolved in a mixture of ethylene carbonate (EC), dimethyl carbonate (DMC) (1:1 in volume), and 3 wt% vinylene carbonate (VC) and used as the electrolyte. For the electrochemical test, the aging time of the assembled cells was set to 12 h. The cells were charged at 0.1 C mA from 1.5 V to 0.01 V vs. Li/Li⁺, followed by a constant-voltage charge at 0.01 V. The cut-off current was 0.001 C mA. The discharge rate was 0.1C, 0.2C, 0.5C, 1C, and 2C for 5 cycles per current rate, for which we assumed that the specific capacity of each carbon sample was 250 mAh g⁻¹ for the 1C rate.

Results and discussion

Structural and elemental analysis

The lattice parameters L_a and L_c of the carbonaceous material, which were calculated from the XRD measurements, were also reported by other researchers. Matumura et al. [18] reported that L_c of a disordered carbon material is proportional to the heat treatment temperature and inversely proportional to the half-cell test capacity. In their report, L_c rapidly increased from 1000 °C to 1500 °C, but the specific capacity decreased from 300 mAh g⁻¹ to

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