Effect of pyrolysis temperature on carbon obtained from green tea biomass for superior lithium ion battery anodes

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HIGHLIGHTS

- Pyrolytic carbons obtained from green tea leaves are used as LIB anode materials.
- Three different pyrolysis temperatures from 700 to 900 °C were adopted.
- The carbon pyrolyzed at lower temperature exhibits superior rate capability.
- It is attributed to numerous active sites and pores for lithium ion insertion.

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ABSTRACT

Carbonaceous materials pyrolyzed from green tea leaves are fabricated and characterized for their potential application as high-performance anodes in lithium ion batteries (LIBs). Three different pyrolysis temperatures (700, 800, and 900 °C) are employed, and the most efficient pyrolysis temperature is determined through a variety of physical and electrochemical measurements. The carbon pyrolyzed at a relatively low temperature of 700 °C contains numerous functional groups, defects that are different from those in graphitic carbon, and large pores. Consequently, the sample exhibited a relatively large capacity of 471 mAh g^{-1} at the 50th cycle, even though high initial irreversibility was observed. Furthermore, when compared to the extremely low capacity of graphite (12.7 mAh g^{-1}), the carbon specimen pyrolyzed at 700 °C displays an excellent high-rate capability of 131 mAh g^{-1} at 10 C. Such a result is attributed to the relatively isotropic structures and large-size pores in the sample, which facilitates the rapid diffusion of lithium ions.

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1. Introduction

Since lithium ion batteries (LIBs) were commercialized by SONY in 1991, they have become important energy storage systems for mobile electronic devices. Graphite, with a theoretical capacity of 372 mAh g^{-1}, is widely used as a lithium storage material due to its stable structure, excellent electrical conductivity, good cycle ability, and relatively low cost [1,2]. However, the capacity and rate capability of graphite limit its application to electric vehicles and large energy storage systems that require high power and high energy density. Recently, numerous studies have been conducted on next-generation high-capacity anode materials such as Si, Sn, their oxides, and transition metal oxides (CuO, MnO$_2$, Fe$_2$O$_3$, Co$_3$O$_4$) [3–8]. Unfortunately, these materials exhibit significant volumetric changes during charge/discharge processes, which lead to a large irreversible capacity during use when compared to

carbonaceous materials. Such a difficult problem must be resolved so that the commercialization of high-capacity non-carbonaceous materials can be realized. For this reason, carbonaceous materials are still being studied as candidates for high-capacity anodes [9–12].

In a recent study, pyrolytic carbons obtained from biomass precursors such as cotton fibers, rice, coffee, walnuts, sugar, and wood were employed as anode materials in LIBs [13–18]. Pyrolytic carbons are generally regarded as eco-friendly and low-cost materials that can be synthesized by relatively simple methods. In addition, optimization of the pyrolysis temperature, preprocessing procedure, and precursor chemistry allow for the fabrication of carbonaceous materials with capacities higher than that of graphite, though their characteristics vary with the nature of biomass precursors [16–18]. Therefore, it is important to control the physical and chemical characteristics of pyrolytic carbons if they are to be used as anodes in LIBs. The electrochemical performance of the pyrolytic carbons was significantly dependent upon the pyrolysis condition and surface morphology [14,17]. Wang et al. [15]

reported that the reversible capacity of pyrolytic carbons was dependent upon the atomic ratio of hydrogen to carbon. According to their results, the binding energy of C–H is nearly the same as that of C–Li, hydrogen can easily be substituted for lithium, and a high H:C ratio gives rise to an increase in capacity. Control over pore size is also important when fabricating pyrolytic carbons [19]. Carbonaceous materials composed of nano-sized pores generally exhibit high initial capacities because they provide a large number of lithium adsorption sites. However, the initial efficiency decreases due to the low lithium adsorption/desorption reversibility of the pores. Another significant factor affecting the capacity of pyrolytic carbon is the degree of graphitization. A low degree of graphitic carbon leads to a high irreversible capacity with low efficiency during charge/discharge cycles [18].

While research into biomass-derived pyrolytic carbons has yielded some progress, the effect of the structure and pore size of pyrolytic carbons on the reaction mechanism with lithium ions is not yet completely understood. In this study, pyrolytic carbon obtained from green tea as a biomass precursor is prepared at different pyrolysis temperatures. The effects of pore size, functional groups, and crystallinity on both the reaction mechanism and electrochemical properties are subsequently investigated through a variety of characterization techniques.

2. Experiment

Green tea leaves collected from Bosenog in Korea were used as a biomass precursor in this work. First, 5 g of green tea leaves were subject to two retting treatments in 300 mL of deionized water at 100 °C for 5 min to remove impurities in the leaves. The wetted leaves were then dried overnight in a convection oven at 80 °C. The resulting product was pyrolyzed in a furnace at three different temperatures, 700, 800, and 900 °C, for 2 h under a nitrogen atmosphere, as shown in Fig. 1. The specimens produced from pyrolization at 700, 800, and 900 °C are denoted as GT-700, GT-800, and GT-900, respectively. Finally, each of the samples was ball-milled using a vertical mini-mill (Pulverisette 23, Fritsch Co.) with zirconia beads (10 mm: 3 ea and 5 mm: 4 ea) in a zirconia jar at 50 Hz for 30 min.

The biomass-derived pyrolytic carbons were characterized by Fourier transform infrared spectroscopy (FT-IR, Thermo Scientific, Nicolet IR 200), Raman spectroscopy (Thermo, USA, DXR Raman microscope), and X-ray diffractometry (Rigaku, RAD-3C) in order to examine functional groups, crystallinity, and the degree of graphitization. Structural properties such as the specific surface area, pore size, pore volume, and pore distribution were evaluated with a Micromeritics ASAP 2020 adsorption analyzer using the Brunauer–Emmett–Teller (BET) method. Field emission scanning electron microscopy (FE-SEM, Carl Zeiss, Supra40) and transmission electron microscopy (TEM, Jeol, JEM-2100F) were employed to investigate the shape and size of the carbons.

The electrochemical properties of the pyrolytic carbons were evaluated through the use of CR2016 coin cells. The working electrode in the coin cells was prepared by mixing the pyrolytic carbon, super-P, and polyvinylidene fluoride (Solef 5130, Solvay Plastics) binder in a 85:5:10 (wt%) ratio in n-methyl-2-pyrrolidinone, coating copper foil with the mixed slurry, and drying the mixture in a convection oven at 130 °C for 30 min. After pressing to ensure close contact between the carbon particles, the electrode had a thickness of approximately 50 μm. Finally, the electrode was dried in a vacuum oven at 80 °C for 24 h before assembly in an argon-filled glove box. The procedure for assembling the coin cells was described in detail in our previous paper [20]. The coin cells were galvanostatically charged and discharged over a potential range of 0.005–3 V in either a constant current mode of 0.1 C (1 C = 372 mA g^{-1}) or a high rate mode of 0.1–10 C using a battery test system (PNE solution, BCP50). Electrochemical impedance spectroscopy (EIS, Biologic, VSP) measurements were performed in a frequency range of 0.01 Hz–100 kHz. Using the same potentiostat, cyclic voltammetry (CV) data were obtained for the carbons in the range of 0–3 V at a scan rate of 0.5 mV s^{-1} so as to observe changes in the potential by the adsorption/desorption of lithium ions.

3. Results and discussion

The effects of the pyrolysis temperature on the functional groups and degree of crystallization for the pyrolytic carbons were analyzed by FT-IR and Raman spectroscopy; the results are displayed in Fig. 2. Regardless of the pyrolysis temperature, the FT-IR spectra of all samples in Fig. 2(a) showed peaks at 3300, 2925, 2850, and 1573 cm^{-1} corresponding to –OH, C–H, and C–O stretching from surface carboxyl groups of the pyrolytic carbons [20,21]. As the pyrolysis temperature increases, the intensities of peaks assigned to C–H at 2925 and 2850 cm^{-1}, and to C–O–C at 1106 and 875 cm^{-1} decrease. In contrast, the intensities of peaks attributed to double (1166 cm^{-1}) and triple (2350 cm^{-1}) carbon bonds increase with the pyrolysis temperature. Based on this observation, it is clear that the dehydrogenation of C–H bonds and the decomposition of C–O–C bonds result in the formation of unsaturated carbons with sp and sp^2 structures. This in turn leads to a reduction in the H:C atomic ratio as the pyrolysis temperature increases. The degree of crystallization or graphitization according to the pyrolysis temperature was examined from the obtained Raman spectra, as shown in Fig. 2(b). The G-band appearing at 1590 cm^{-1} is attributed to the sp^2 graphitic structure, while the peak of the D-band near 1340 cm^{-1} is related to defects in the graphitic structure. The integrated area ratios of the D-band to G-band peaks (A_D/A_G) are 1.66, 1.59, and 1.42 for GT-700, GT-800 and GT-900, respectively, indicating that a high pyrolysis temperature forms more graphitic structures. Such a conclusion is supported by shifts observed in the Raman peaks deconvoluted by a three band model [22]. As the pyrolysis temperature increases, the G-band peak shifts towards higher frequencies (blue shift), whereas the D-band
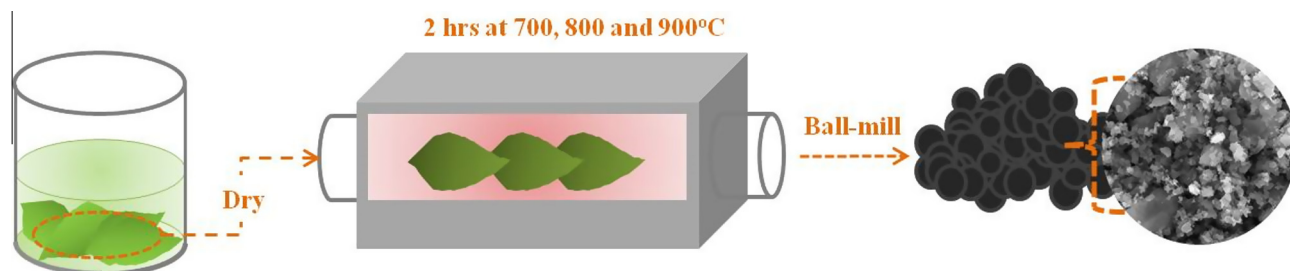

Fig. 1. Schematic illustration of the synthesis procedure used to obtain pyrolytic carbon from green tea.