



The effect of mild activation on the electrochemical performance of pitch-coated graphite for the lithium-ion battery anode material

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ABSTRACT

In order to improve the rate performance of a graphite anode for lithium-ion batteries (LIBs), mild activation was applied after a coating process to deposit unique coating layer with additional sites where lithium ions are able to be inserted on the graphite anode. In this study, we coated the pitch onto spherical natural graphite (SG) by using toluene and drying, before mild activation to control the coating layer structure, which contributes to preserving the intact structural integrity of graphite anodes during the repeated charging and discharging process. The crystal structure and surface of pitch-coated graphite with mild activation was observed using XRD, Raman spectra, TEM, SEM analyses to verify the formation of the coating layer. The pitch-coated graphite with mild activation can provide improved cycle stability (86.3% after 30 cycles at 0.5 C-rate) and high rate capability (91.0% at 1 C-rate/0.1 C-rate). Notably, complicated voltage profiles of as-prepared samples demonstrate that mild activation can be utilized to establish the lithium-ion insertion sites, such as partially charge transferring surface sites (Type 1), edges of carbon hexagon clusters (Type 3), and micro-void structures by hexagonal planes (Type 4).

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1. Introduction

Lithium-ion batteries (LIBs) have been recognized as the most important energy storage system because of huge advantages such as high energy density, long cycling lifetime, environmental benignity and portability [1–3]. In particular, carbon materials for general anode materials of LIBs are artificial graphite and natural graphite. When natural graphite is used in a low-cost PC-based electrolyte, poor cycle performance and a low initial coulombic efficiency is presented as a result of a phenomenon in which graphite is exfoliated and lithium insertion/de-insertion via co-intercalation. Thus, spheroidization and pitch coating processes are applied in commercial natural graphite anodes for LIBs to overcome this issue [4,5,21]. Pitch-coated spherical natural graphite is widely known as a secondary battery anode material having an outstanding voltage flatness, constant discharge voltage in the discharge process, and excellent initial coulombic efficiency [6,7,22].

Soft carbon, which has high initial capacity and excellent rate capability as an anode material for LIBs, has been extensively researched, but has not been commercialized due to a rapid decrease in the cyclability. Mabuchi et al. reported a mechanism whereby lithium ions are stored depending on heat treatment of the soft carbon [8]. Mochida et al. investigated the charge and discharge mechanism of hard carbon prepared from isotropic pitch [9,10]. In previous papers, five sites by which lithium ions are stored in soft and hard carbon have been reported as micro-voids surrounded by a hexagonal plane (0–0.13 V), a charge transferred surface (0.25–2 V), a sp^2 graphite layer structure (0–0.25 V), a cluster gap (discharge potential 0–0.1 V, charge potential 0.8–2 V) and atomic defects in the hexagonal plane (discharge potential 0–0.1 V, charge potential 0.8–2 V) [10–14]. Thus, pitch, which is one of the soft carbons, exhibits a higher discharge capacity than the theoretical capacity of graphite due to the micro-voids and a disordered carbon structure. However, this anode material exhibits low initial coulombic efficiency and severe deterioration [4,9].

In this paper, micro-voids and several sp^3 structures of pitch coated on graphite were controlled through mild activation, and an anode material with improved cyclability and excellent rate performance was investigated via a mechanism analysis to store the lithium ions.

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