



Coating of graphite anode with coal tar pitch as an effective precursor for enhancing the rate performance in Li-ion batteries: Effects of composition and softening points of coal tar pitch



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ABSTRACT

Effects of compositions and softening points of coal tar pitches (CTPs) on the electrochemical performances especially for first cycle Coulombic efficiency and rate performance, of the amorphous carbon coating on the graphite surface were closely examined. CTPs with higher softening points could afford the better homogeneous amorphous carbon coating on the graphite surface, resulting in the better enhancing rate performance of graphite anode without decreasing the first cycle Coulombic efficiency. CTP with almost complete absence of hexane soluble (HS) fraction always showed the good enhancing effect of the rate performance. HS fraction of CTP, which is a reason for inducing surface defects on the coated carbon, hindered the enhancing effect of electrochemical performances. CTP derived amorphous carbon coating could effectively decrease charge transfer resistance on the graphite electrode–electrolyte interface.

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1. Introduction

Over the last two decades, graphite has been used as standard anode material in current Li-ion batteries (LIBs). These are small rechargeable batteries used for cell phones, laptop, and other portable devices due to their excellent performance such as low operating potential, structural stability, moderate cost, and good cycle life [1]. However, the insufficient energy density and rate performance of graphite has restricted their use for future energy storage applications such as electric vehicles (EVs) and large-scale backup power supplies [2]. In an effort to enhance the rate performance as anodic materials in future LIBs, many researchers have reported that graphite based anode materials can achieve high rate performance through the surface modification. The surface chemistry on the interface of electrode–electrolyte has been controlled by modifying the graphite with introducing ion-functional groups, metal oxide, and carbon composite [3–7]. Yeo et al. has reported

enhanced rate performance through the reduction in surface film and charge transfer resistance facilitated by introducing meta-boric acid containing boron oxygen groups on the graphite [4]. The metal oxides, such as SnO, were also achieved with improved electrochemical properties in LIBs [6]. Despite these efforts, the first cycle Coulombic efficiency was degraded owing to a formation of the solid–electrolyte–interface (SEI) film on the graphite surface excessively, resulting in the destruction in repeated charge/discharge process.

To date, a lot of researches have reported that first cycle Coulombic efficiency and discharge capacity can be improved through the surface coating with coal tar pitch (CTP) derived carbon *via* cost-efficiency methods [8–12]. The lithium ion can be transported easily inside carbon by isotropic coating layer on the graphite. Yoon et al. have reported that graphite coated with pitch derived soft carbon showed smaller irreversible capacity and raised Coulombic efficiency enormously, being attributed to a decrease in the surface area due to the coverage of pores of <10 nm *via* coating with coke components [8]. Moreover, Wan et al. reported that the initial Coulombic efficiency could be increased by coating with a thick carbonaceous mesophase layer

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(ca. 2.5 μm thickness) on the surface of spherical natural graphite using CTP [12]. However, most studies on carbon coating with CTPs have focused on improving the first cycle Coulombic efficiency of LIBs by inhibiting excessive formation of the SEI layer and reducing surface area. Although the rate performance is one of the key issues for the application of LIBs to EVs, only a few reports have confirmed the possibility of improving the rate performance by the surface coating [13]. To the best of our knowledge, furthermore, no study has been reported about an influence of the chemical and physical properties of coating materials, which are intrinsic properties that determine the anodic performance. To apply CTP as the coating material for graphite anode in LIBs, it should possess several characteristics; (i) isotropic properties, (ii) a high carbonization yield, and (iii) uniform coating of electrodes [14–16]. In this study, we closely examined the effect of composition and softening point of CTPs on the rate performance and the first cycle Coulombic efficiency of the amorphous carbon coating on the graphite surface. The softening points and soluble components of CTPs were adjusted to afford their best composition as the coating pitch of graphite for improving the electrochemical performances of LIBs.

2. Experimental

2.1. Sample preparations

Synthetic graphite having an average particle size of ca. 10 μm with a core-shell structure was used as-received from RIST in Korea. Emulsions of coal tar were obtained directly from RIST and used as received, which is by-products of the coal carbonization process to make coke or gasified. Quinoline insolubles (QI) of the as-received coal tar were removed by solvent-non solvent methods using toluene as solvent and kerosene as non solvent at 140 °C. To prepare CTP with softening points of 20, 76, 145, and 196 °C, quinoline insoluble free (QI free) coal tar was distilled from 270 to 430 °C under a vacuum of 20–100 torr for 1–3 h.

To prepare the CTP-coated graphite, 900 mg of graphite and 100 mg of CTP were dispersed in 100 ml of THFs. After stirring for 24 h, the solvent was evaporated at 55 °C under vacuum. The resulting CTP-coated graphite was heat-treated at 800 °C for 30 min under Ar flow to remove volatile components of CTP and then heat-treated at 1000 °C for 10 min under vacuum.

Various solvent soluble fractions of pristine CTP were separated using hexane, toluene and tetrahydrofuran (THF) solvents. As-prepared CTP (2 g) was dissolved in 100 ml of hexane solvent with stirring for 3 h. After filtering, the filtered hexane solution (hexane soluble, HS) were heated to evaporate hexane at 55 °C under vacuum, and then dried at 80 °C for 12 h. The remaining samples after filtering were termed hexane insoluble (HI), and were subjected to the same separation method with toluene and THF to generate toluene soluble (TS), toluene insoluble (TI), THF soluble (THFS), and THF insoluble (THFI) fractions.

Platelet carbon nanofiber (PCNF) was prepared through the Fe catalytic pyrolysis under the CO/H₂ gas flow (4:1 v:v, total flow rate 200 ml min⁻¹) at 600 °C for 2 h using iron as a catalyst [17,18]. To analyze the structure of CTP derived carbon coated on the graphite by TEM, CTP derived carbon coated PCNF was prepared with the same conditions and its texture was examined by TEM. 90 wt.% PCNF and 10 wt.% CTP with softening point of 145 °C was dispersed in THF, and stirred for 24 h. After stirring, the solvent was evaporated at 55 °C under vacuum. The prepared sample was heat-treated at 800 °C (heating rate: 5 °C min⁻¹) for 30 min under inert atmosphere (Ar, 200 ml min⁻¹) and then carbonized at 1000 °C (heating rate: 15 °C min⁻¹) for 10 min under vacuum (30 Pa).

2.2. Characterization

Elemental analysis was performed to measure the carbon, hydrogen, and nitrogen contents of the samples using a CHN analyzer (MT-5; Yanagimoto CHN corder). The O content (O_{diff.}) was calculated by subtracting the sum of the contents of C (carbon), H (hydrogen), N (nitrogen), and ash from 100%. Softening points of prepared CTPs were determined using thermo-mechanical analysis (TMA-SS6300, SII NanoTechnologies, Japan). CTP samples were put into an aluminum pan with a diameter of 5 mm, heated to 200 °C at a heating rate of 1 °C min⁻¹ under nitrogen gas flow (100 ml min⁻¹), and then cooled to room temperature. TMA was operated in penetration mode up to 200 °C at a heating rate of 5 °C min⁻¹ under nitrogen gas flow (200 ml min⁻¹).

The relative weight loss of CTPs was measured based on thermogravimetry (TG, EXSTAR6000; SEICO SII NanoTechnology, Japan). CTPs with different softening points were placed in an alumina pan and heated to 800 °C at a rate of 5 °C min⁻¹ under nitrogen gas flow (100 ml min⁻¹).

The molecular weight of soluble components separated from CTP with a softening point of 76 °C (CTP-76) was measured using a TOF-MS spectrometer (JEOL, JMS-3000 with 349 nm Nd: YAG LASER, Japan). Soluble components separated from CTP were dissolved in THF (10 wt.%) without a matrix and then placed on 384 spot target plate.

Charge (Li⁺ intercalation)/discharge (Li⁺ de-intercalation) measurements were performed in a CR2032-type coin cell with two electrodes. Li metal foils were used as the counter electrode. The working electrode was prepared by mixing 90 wt.% active material with 5 wt.% styrene butadiene rubber (SBR) and 5 wt.% carboxy methyl cellulose (CMC) in distilled water. The slurries of the mixture were coated onto a copper foil current collector and then dried in a vacuum oven at 120 °C for 12 h before pressing into a roll-type mill under 100-MPa pressure, cut into discs (size: 12 mm diameter and about 40 μm thickness), and then weighed using an ultra-fine balance to adjust the amount of active material (about 1.5 g cm⁻³). The cell assembly was performed in a glove box with a dew point of -73 °C. The electrolyte solution was 1 M LiPF₆ dissolved in ethylene carbonate (EC)/diethyl carbonate (DEC) (1:1 vol%); Kishida Chemical). These cells were charge/discharge at a current density of 372 mA g⁻¹ between 0.003 and 1.5 V versus Li/Li⁺ using a galvanostatic cyler (Toscat-3100; Toyo System). The assembled coin cells were charged at a 0.1 C rate and discharged at different rates from 0.1 to 5 C between 0.003 and 1.5 V versus Li/Li⁺ (Toscat-3100; Toyo System) to determine rate capability (assuming 1 C = 372 mA g⁻¹) at 25 °C. Electrochemical impedance spectroscopic (EIS) studies were performed by applying a small perturbation voltage of 5 mV in the frequency range of 100 kHz to 10 MHz at 0.7 V using an electrochemical measurement system (HZ-3000, Hokuto Denko Co. Ltd.). Then, all the equivalent-circuit fittings for EIS data were done by EC-Lab software (Bio-Logic).

3. Results and discussion

To confirm a structure of CTP derived carbons coating of graphite, we used the platelet carbon nanofiber (PCNF) as model material of graphite because large size of graphite crystal is very hard to observe by TEM. The size, shape, and layer structure of PCNFs is well-defined and characterized which consisted of perpendicular to the fiber axis [19]. Therefore, well-defined PCNFs can be distinguished easily in order to confirm the coated structure of CTP-derived carbon as possible solutions to a technical problem of TEM. The TEM image clearly shows that the surface of PCNF is coated by CTP derived carbon, which is characteristic of amorphous carbon coating layers (indicated with b region of Fig. S1d).

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