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RESEARCH PAPER

Preparation of a carbon nanofiber/natural graphite composite and an evaluation of its electrochemical properties as an anode material for a Li-ion battery

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Abstract: A carbon nanofiber (CNF)/natural graphite (NG) composite was prepared to improve the rate capability of as-received NG to be used as the anode material in a Li-ion battery. Optimum control over both the amount and shape of the CNFs to enable their growth on NG remarkably improved the cycle performance and rate capability of the as-received NG. The first-cycle discharge capacity of the CNF/NG composite was 95% of that of the as-received NG. The amount of grown CNFs was controlled to be less than 15% of the as-received NG. CNF growth on the surface edges of NG in an ivy leaf shape proved to be most effective in improving the rate capability by controlling the extent of volumetric expansion and shrinkage occurring in the charge and discharge processes. Schematic structural models of the as-received NG and CNF/NG composite were proposed to account for the volumetric stability of the electrode in repeated charge-discharge processes. The improved rate capability is ascribed to the thin solid electrolyte interphase and reduced volumetric change of the anode in the charge/discharge processes, both of which are achieved by growing ivy-like CNFs over the graphite surface.

Key Words: Natural graphite; Li-ion battery; Carbon nanofiber; Rate capability; Volumetric stability

1 Introduction

Since artificial graphites such as graphitized petroleum coke, needle coke, carbon fibers, and meso-carbon microbeads, are known to be highly efficient in enhancing intercalation and de-intercalation rates of lithium (Li) ion, those carbon materials are well adopted commercially as anodic materials for Li-ion battery. The properties of artificial graphite anodes such as cycle efficiency, reversible discharge capacity, and cyclability have been improved by certain factors including the degree of graphitization, purity, and optimum particle size distribution. Although they have been adopted in commercialization, it is still bothering us with their high production cost and lower discharge capacity compared with natural graphites (NGs)[1].

Still, NG is regarded as one of the most feasible anodic material candidates for Li-ion batteries based on its high reversible discharge capacity, lower discharge potential, and cost competitiveness. However, its limitations such as low coulombic efficiency at first cycle, poor cyclability, and rate capability are the main disadvantages for its commercialization[2-3].

Recently, the use of Li-ion battery in the electric vehicle (EV) gets a public interest. Its application in transportation is expected to play an important role in promoting the effective utilization of renewable energy in preserving the environment. To use the NG as anodic material in Li-ion batteries in the EV, it must perform under severe automobile conditions. The NG must undergo low temperature down to -20 ºC to maintain a continuous high discharge rate at 1.0 C as well as high discharge capacity and better cyclability[4]. Considering this, improving the rate capability of NG is one of the most critical issues for its further application into EV.

The problem found with NG is its morphological anisotropy resulting from graphene layer alignment[5]. Its unique flaky shape makes it expand in unilateral direction, which makes it difficult to efficiently engage in the repetitive charge and discharge. Critical edges of NG flakes allow the electrolyte molecules to decompose into thick layers of solid electrolyte interphase（SEI）, which brings about a high irreversible capacity and decreases the rate capability[6].

Many researchers have made efforts to develop a proper NG treatment method to improve the cyclability and coulombic efficiency at first-cycle[7-10]. Herstedt et al.[8] suggested that jet milling was a good method to improve the rate capability of the Swedish NG. Kottegoda et al.[9] found that zirconia-coated NG improved the rate properties. Zhao et al.[10] proposed that a NG modified by phenol resin encapsulation

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was effective for its electrochemical performance. Guo et al.[7] reported that the cycle performance of NG with polyacrylonitrile coating was improved by radiation-initiated polymerization, although the initial irreversible capacity was increased by the thick amorphous carbon layer with a number of micropores and/or nanochannels.

In this study, a novel form of CNF–NG composite was prepared through the selective catalytic pyrolysis of carbon source gas on the edges of the as-received NG. We implemented this process because the higher rate capability of NG can be accomplished in the EV application. The optimized condition, that is, controlling the shape and amount of the grown CNFs over the NG, for the CNF–NG composite was found by improving the rate capability. The limited expansion of graphite while charging is expected to improve the stability of the anodic electrode. The grown CNF covering the edges of graphite can help prevent the undesirable decomposition of electrolyte by reducing the edges.

2 Experimental

2.1 Materials

Two NGs of SP (Nippon graphite, Japan) and HFP (Tsinghua Univ., China) were used as starting materials in this study. Also commercialized artificial graphite (MAG, Hitachi Chemical Co. Ltd., Japan) was used as reference. The graphites were all used as received themselves.

Pure helium (He, 99.99%), carbon monoxide (CO, 99.9%), and hydrogen (H_2, 99.999%) (Asahi Sanso Japan) were used to prepare CNF–graphite composites. Iron nitrate enneahydrate ($Fe(NO_3)_3{\cdot}9H_2O$) (Wako chemical Co. Japan) was used as catalyst precursor for the growth of CNFs without further purification.

2.2 Preparation of CNF–graphite composites

The CNF–graphite composites were prepared by the catalytic pyrolysis of carbon source gas on the surface of the graphite as follows. Iron catalyst was impregnated on the surface of graphite, and CNFs were grown through the catalytic pyrolysis of CO gas on the iron catalyst.

$Fe(NO_3)_3{\cdot}9H_2O$ (0.723 g) and graphite (10 g) powder were put into ethanol (50 ml). The solution was stirred at 60 ºC in a rotary evaporator to remove ethanol. The resulting solid powders were filtered and dried at 105 ºC for 6 h under vacuum. The amount of $Fe(NO_3)_3{\cdot}9H_2O$ was controlled to impregnate precisely 1% iron(mass fraction) on the surface of graphite on the weight basis of iron.

The CNF–graphite composites were synthesized in a fixed reactor (quartz tube of 50 mm diameter, 80 cm long in a horizontal electric furnace). The quartz boat containing 0.5 g of graphite with 1% (mass fraction) iron was placed in the center of the reactor and was heated up to 650 ºC at a heating rate of 10 ºC·min^{-1} under He (flow rate: 200 mL·min^{-1}) flow. The reactor was initially purged with He at room temperature for 30 min prior to the start of the reaction. After the temperature reached 650 ºC, a gas mixture of CO, H_2, and He (total flow rate: 200 mL·min^{-1}) was introduced over the catalyst for 30 min. The reactor was cooled down to room temperature after the reaction was completed. The amount of grown CNFs was controlled to be less than 15% on the weight basis of graphite. The CNF-grown graphite should be characterized and electrochemical property should be evaluated.

2.3 Characterization of CNF–graphite composites

The surface area was determined by BET through N_2 adsorption using specific surface area analyzer (Belsorp-max S, Nippon bell, Japan). The surface morphology was observed by SEM (JSM-6700F, JEOL, Japan). Crystallographic properties were measured by X-ray powder diffractometer (CuKα, Ultima-III, Rigaku, Japan) and calculated according to JSPS (The Japan Society for the Promotion of Sciences) procedure[11].

The galvanostatic charge-discharge performance was carried out using a coin-type cell with two electrodes system. A weighed amount of active materials (85%)was mixed with polyvinylidene fluoride (PVDF, 15%) and then coated on a copper foil (18 μm thick). The coated foil was then dried at 120 ºC under vacuum for 12 h before roll-pressing under a pressure of 100 MPa. The pressed foil was cut into discs (*D*12 mm, 60 μm thick) and the exact amount of active material was weighed by ultra-fine balance. Coin-type cells (CR2032) were assembled in a humidity-free glove-box (humidity is less than 0.05 %) using polyethylene film (16 μm thick) as a separator, 1 mol/L $LiPF_6$ in ethylene carbonate (EC)/diethyl carbonate (DEC) (1:1 % volu fraction, Ube Kosan, Japan) as electrolyte solution, and Li foil as a counter electrode. A current density of 30 mA·g^{-1} was applied, and the potential cut-off range was fixed at 0–1.5 V vs. Li/Li$^+$. For the determination of reversible discharge capacity, the test was performed under constant current and constant voltage method (CC-CV) at charge (cut-off current is 1/10 of charged current) and CC at discharge using galvanostatic charge/discharge apparatus (Toscat-3100, Toyo system, Japan). For the evaluation of rate capability, on the other hand, the tests were performed under CC condition with the same current density. All the electrochemical experiments were carried out at ambient temperature.

3 Results

3.1 Preparation of CNF–graphite composites

Table 1 summarizes the preparation conditions of CNF–graphite composites and the amount of grown CNF on the weight basis of graphite. Because the NGs of SP and HFP and synthetic graphite of MAG have their own different surface properties, the preparation conditions were delicately designed and controlled so that each graphite obtained almost the same amount of CNFs. Especially, the amount of CNFs was controlled to be less than 15% of the original graphite by weight.