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Enhancing the rate performance of graphite anodes through addition of natural graphite/carbon nanofibers in lithium-ion batteries

Tae-Hwan Park[a], Jae-Seong Yeo[a], Min-Hyun Seo[b], Jin Miyawaki[b], Isao Mochida[c], Seong-Ho Yoon[a,b,*]

[a] *Interdisciplinary Graduate School of Engineering Sciences, Kyushu University, Fukuoka 8168580, Japan*
[b] *Institute for Materials Chemistry and Engineering, Kyushu University, Fukuoka 8168580, Japan*
[c] *Research and Education Center of Carbon Resources, Kyushu University, Fukuoka 8168580, Japan*

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ABSTRACT

Mesophase pitch-derived synthetic graphite was hybridized with natural graphite/carbon nanofiber (NG/CNF) composites prepared by mechanical mixing, carbonization, and graphitization processes. Addition of the NG/CNF composites introduced effective internal pores inside the synthetic graphite matrix, thereby improving the rate performance, 1st cycle coulombic efficiency, and cyclability. Hybridized graphite with 10 wt% of added NG/CNF composite exhibited the best rate performance, with a discharge capacity retention rate of over 90% after a 5 C discharge test.

1. Introduction

Recently, lithium-ion (Li-ion) batteries have attracted attention because of their high specific energy density and long life cycle. Several requirements, such as high rate performance and safety, are essential for the practical use of Li-ion batteries. These performance requirements are principally related to the characteristics of the carbon material used as the anode material in the batteries. Graphitic materials are commonly used as anodic materials in commercial Li-ion batteries due to their low, flat potential at discharge, stability, and safety in long-life use [1].

Graphite can be divided into two categories: (i) natural micro- or macrocrystalline graphite (found as an earth mineral) and (ii) synthetic graphite obtained through high-temperature treatment of graphitic material, usually at around 3000 °C [2,3]. Natural graphite (NG) is regarded as one of the most attractive anodic materials for Li-ion batteries because of its high discharge capacity, lower discharge potential, and cost competitiveness. However, its limitations, such as low 1st cycle coulombic efficiency, poor cyclability, and poor rate performance, are its main weaknesses for commercialization [4]. Synthetic graphite has been industrially produced in large amounts mainly from petroleum coke and has been used for electrodes in steel refining and electrical discharge machining [5]. The cyclability, discharge capacity, and 1st cycle coulombic efficiency of synthetic graphite are related to its degree of graphitization, purity, and optimum particle size distribution. Synthetic graphite suffers from poor rate performance at high hourly rates (C-rates), which limits its broad application in Li-ion batteries for electric vehicles. Carbon nanofibers (CNFs) have been proposed and studied as anodes for Li-ion batteries [6]. CNFs are very interesting due to their high electrical conductivity of around 10^5 S cm^{-1} [7]; however, their low first cycle coulombic efficiency, which is induced by their high surface area, remains an obstacle to their use in real-world battery applications.

In this study, we attempted to improve the rate performance of synthetic graphite by using NG/CNF composites to introduce nanoscale internal pores into the mesophase pitch-derived synthetic graphite matrix. Our results suggested that the internal pores, which were artificially introduced into the synthetic graphite matrix using specially designed NG/CNF, play a significant role in improving the rate performance of the material when used in battery anodes. The quantity of internal pores was controlled by varying the amount of NG/CNF introduced into the synthetic graphite matrix. The electrical conductivity and the expansion of the electrodes were carefully examined to explain the role of the internal pores in improving the rate performance.

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* Corresponding author at: Institute for Materials Chemistry and Engineering, Kyushu University, Fukuoka 8168580, Japan. Tel.: +81 925837959; fax: +81 925837897.
E-mail address: yoon@cm.kyushu-u.ac.jp (S.-H. Yoon).

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2. Experimental

2.1. Materials and synthesis

Aromatic resin (AR) mesophase pitch (Mitsubishi Gas Chemical Co. Ltd. Japan) was used as a precursor for synthetic graphite [8]. NG (SPR, Nippon Graphite, Japan) of size *ca.* 5 μm was used as a support for CNF composite. High-purity helium (He, 99.95%), carbon monoxide (CO, 99.95%), and hydrogen (H_2 99.99999%) (Ashahi Sanso Co. Ltd., Japan) were used for CNF growth on the natural graphite. Reagent-grade iron nitrate enneahydrate [$Fe(NO_3)_3{\cdot}9H_2O$] (Wako chemical company, Japan) was used as a precursor for the CNF growth catalyst. The NG particles were dispersed into $Fe(NO_3)_3{\cdot}9H_2O$/ethanol solution, and then the slurry was stirred for 3 h at room temperature. The amount of catalyst was carefully controlled to 1 wt% of Fe. After evaporating ethanol at 50 °C, these mixtures were dried at 105 °C for 12 h under vacuum. The NG with Fe (1 wt%) was placed in the center of a horizontal tube furnace and heated to 650 °C at a heating rate of 10 °C min^{-1} under He gas flow. Then, CO and H_2 were introduced as a mixed gas and allowed to flow over the mixture for 30 min. The reactor was cooled to room temperature under He gas after the CNF synthesis [9]. The amount of CNF growth was 12 wt%, based on the NG weight.

The composites of NG/CNF and mesophase pitch were prepared as follows. The mesophase pitch was proportionally mixed with NG/CNF in tetrahydrofuran (THF) in a glass reactor; the NG/CNF content in raw pitch was 0%, 10%, 20%, 30%, and 50%. Then, the mixtures were held at 350 °C for 3 h to obtain uniform mixtures. During the heat treatment, agitation at 150 rpm was maintained. Next, a N_2 flow of 0.1 $m^3\,h^{-1}$ was applied to remove THF and volatile compounds, and then the mixtures were grounded. The resulting mixtures were stabilized with air gas up to 300 °C and then cooled to room temperature. Stabilized composites were carbonized at 800 °C for 1 h to remove volatile compounds. Carbonized composites were then heat treated (*via* graphitization) up to 2800 °C at a heating rate of 10 °C min^{-1} and maintained for 10 min under inert argon (Ar) gas flow. Prepared specimens were designated as AR from the AR mesophase pitch, NC from the synthesized NG/CNF, and AR/NC*x* from the composites, where *x* indicates the mixing ratio of NG/CNF on a weight basis. Fig. 1 shows a schematic model of NG/CNF particles and the hybridized material (AR/NC) of NG/CNF with AR synthetic graphite matrix.

2.2. Sample characterizations

Brunauer–Emmett–Teller (BET) specific area was measured by nitrogen absorption using automatic specific surface area measuring equipment (4200e, Nova, Japan). Crystallographic properties were measured by an X-ray powder diffractometer (XRD, CuKα, Ultima-III, Rigaku, Japan). The electrical conductivity of graphite materials was evaluated from volume resistivity using disk-shaped samples in a four-probe method at room temperature. The morphology of graphite materials was observed using a scanning electron microscope (SEM, JSM-6700F, JEOL, Japan).

2.3. Cell preparation and electrochemical tests

Galvanostatic charging and discharging were carried out using coin-type cells of CR2032 with two electrodes, where Li metal foil was used as a counter electrode, styrene–butadiene rubber (SBR, trade name BM-400B, ZEON, Japan) as a binder, and carboxy methyl cellulose (CMC) as a thickening agent. To form the anode, the mixed slurry was coated on a copper foil (18 μm thick), dried at 120 °C under vacuum for 12 h, pressed using a roll-type mill under 100 MPa of pressure, cut into discs (12 mm in diameter and about 40 μm thick), and then weighed using an ultra-fine balance to adjust the amount of active material. Coin-type cells were assembled in an Ar-filled glove box using a polyethylene film (16 μm thick) as a separator and 1 M lithium hexafluorophosphate ($LiPF_6$) in ethylene carbonate (EC)/diethyl carbonate (DEC) (1:1 vol%, Ube Kosan, Japan) as an electrolyte. The electrochemical measurements were performed through constant current and constant voltage method (CC–CV) at charge (cut off current is 1/10 of charged current) and CC at discharge, under charge at 30 mA g^{-1} and discharge at variable current in the potential range of 0.003–1.5 V *versus* Li/Li^+ (Toscat-3100, Toyo-system, Japan) at room temperature.

3. Results and discussion

3.1. Physical properties of AR and AR/NC composites

The surface areas of the AR and AR/NC composites are shown in Table 1. BET surface areas are similar and have low values from 1.1 to 1.9 $cm^2\,g^{-1}$ for all composites. X-ray density of the AR and AR/NC composites was evaluated from XRD data, as shown in Table 1 [10]. The d_{002} interlayer spacing values of the AR and AR/NC composites were similar and range from 3.3579 Å to 3.3661 Å. The AR/NC50 composite had the lowest d_{002} value with an interlayer spacing of 3.3579 Å [11]; the AR/NC50 composite also exhibited the most crystalline graphite structure due to the high quantity of NG on the NG/CNF composite. The electrical conductivities of the AR and AR/NC composites were estimated and are shown in Table 1. As shown in Table 1 and Fig. 2, the electrical conductivity increased with increasing NG/CNF composite addition from 457 S cm^{-1} (AR, 0%) to 1618 S cm^{-1} (AR/NC10, 10%) and decreased with increasing NG/CNF composite addition from 1618 S cm^{-1} (AR/NC10, 10%) to 206 S cm^{-1} (AR/NC50, 50%). The profound increase in electrical conductivity was attributed to the presence of CNFs in the AR/NC sample, which bridged mesophase pitch-derived graphite and NG, thus lowering the contact resistance.

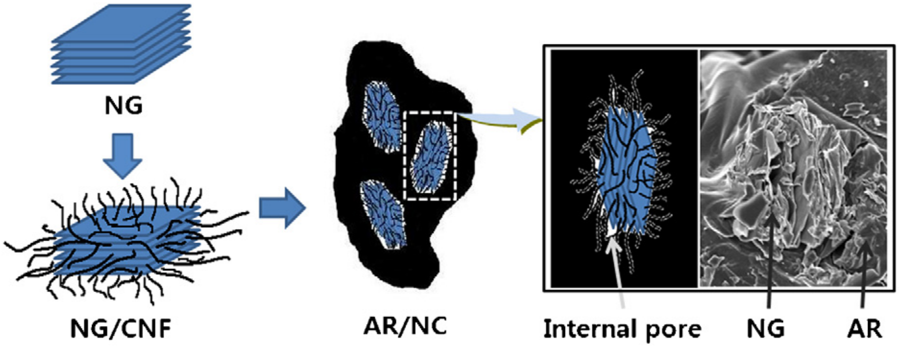

Fig. 1. Schematic model of NG/CNF particles and the hybridized material of NG/CNF with the AR graphite matrix (AR/NC).