RELATIONSHIP BETWEEN GRAPHENE STRUCTURE IN BALL MILLED GRAPHITE AND ELECTROCHEMICAL PERFORMANCE OF LITHIUM-ION BATTERY/CAPACITOR

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Introduction

Several types of carbonaceous materials have been examined as anode materials for lithium-ion batteries. The use of carbonaceous materials avoids the dendrite growth associated with metallic lithium upon charging of the battery, thus prolonging the cycle life and improving the reliability of the cells. Yazami et al. indicated that lithium-ions are stored between the graphene layers in the graphite lattice during intercalation [1]. Since the introduction of the Sony lithium-ion battery using hard carbon as an anode materials [2], the trend has been toward the use of graphite due to its high reversibility and flat voltage potential profile. So, in commercial batteries, graphite has been used extensively as anode material due to its excellent cycling performance. However, the theoretical capacity of graphite is limited to 372 mAh/g by the composition of the product LiC_6 [3]. Therefore, alternative materials with high volumetric and gravimetric capacity of lithium are required for replacing the carbon materials as anode materials for lithium ion batteries.

In our group, the physical and chemical properties of the ball-milled graphite have been studied for a hydrogen storage system. The ball-milled graphite was synthesized by a mechanical ball-milling method from high purity graphite under hydrogen atmosphere. The ball-milled graphite has larger specific surface area than original graphite. According to the structural modification of graphite by ball-milling, it seems that the ball-milled graphite has many possible utilities due to its electro-chemical properties. In this work, the relationship between the electrochemical performance and the graphene structure was investigated.

Experimental

Several kinds of ball-milled graphite used in this work were synthesized from polycrystalline carbon powder (purity: 99.999 %) by using a high-energy planetary mill apparatus (Fritsch P6) with different rotation speed (100-370 rpm) for different time (1-4 h) under H_2 or C_2H_6 atmosphere. Here, all kinds of the ball-milled graphite were named as MGs. After the milling treatments, the samples were characterized by Powder X-ray diffraction (XRD, Rigaku, RINT-2100) with Cu Kα radiation. The BET surface area of the samples was measured by using Gemini 2370 (Micromeritics Instrument Corporation). In order to examine the variation of microstructure after by the ball-milling treatments, Scanning Electron Microscope (SEM, JEOL, JSM-6380) was carried out. To evaluate the electrochemical characteristics of MGs, the several kinds of electrodes were coated on Cu foil current collector after mixing of MGs (85 wt.%), conductive filler (Acetylene Black, 5 wt.%), and poly vinylidene fluoride (PVDF, 10 wt.%) as a binder dissolved in 1-methyle-2-pyrrolidinone (NMP) solution. All the MGs electrodes were dried for 1 h at 90 and 120 °C. Here, the weight and thickness of each electrode after the drying were about 10 mg and 100-150 μm. The cells for the charge/discharge tests consisted of Li foil as an anode and the MGs electrodes as a cathode. The Li/MG cells with a polypropylene filter as a separator between anode and cathode were assembled by using a two electrodes cell in an Ar filled glove box. The electrode cells were soaked with liquid electrolyte which was 1 mol/L $LiPF_6$ dissolved in 1:1 volume ratio of ethylene carbonate (EC) and diethyl carbonate (DEC).

The charge/discharge tests of the assembled Li/MG cells were performed with a galvanostatic mode. The cells were discharged (Li insertion) and charged (Li extraction) between 0.02 and 2.5 V. After charge/discharge tests, the MGs electrodes were characterized by XRD and solid-Nuclear Magnetic Resonance (solid-NMR) in order to identify a phase formed.

Results and Discussion

The XRD patterns of prepared MGs are shown in Fig. 1. As shown in the reference, the XRD pattern of original graphite presents the characteristic peaks at 26.4, 42.2, 44.4, 54.5, and 77.2 ° due to hexagonal structure. The (002) peak intensity at 26.4 °, which reflects the structure of graphene layers, was strongly affected by depending on the ball-milling condition, such as rotation speed, time and atmosphere. These results directly indicate the destruction of graphite structure is strongly related to the milling conditions. Especially, the most comminuted layer structure of graphene was shown in the case of MG synthesized with 370 rpm for 4 h under H_2.

Fig. 2 shows the charge/discharge curves of the MGs electrodes. In the Fig. 2, a result corresponding to non-milled graphite was also shown as a comparison. From these results, it was clear that the curves became two steps when the milling condition was set up stronger, e.g. faster rotation speed and longer milling time. First plateau voltage (0.8 V) might indicate growing of Solid Electrolyte Interface (SEI) layer. Then, second plateau voltage (ca. 0.1 V) was caused by the chemical reaction between MG and lithium ion to form Li intercalated graphite LiC_6. In general, the growing of SEI layer was affected by surface properties of the electrode, such as BET specific surface area and functional groups at the graphene edge. Moreover, for all the cells, the initial charge capacity was much larger than the theoretical capacity (372 mAh/g). Especially, the initial capacity of the cell using MG

synthesized by the strongest milling condition (370 rpm, 4 h, H_2) was obtained to be 1388 mAh/g even though its reversible capacity was 443 mAh/g. Therefore, the increasing in the initial capacity was affected with the forms of amorphous carbon, in other words, an active site such as graphene edges and defects generated during the ball-milling treatment would form stable bond with Li or SEI. On the other hand, the reversible capacity is related to crystalline graphite. The electrode of MG with the weaker milling condition (100 rpm, 4 h, H_2) revealed about 567 mAh/g capacity and 74 % of coulombic efficiency at the first cycle. This result indicates that the dispersive crystalline graphite with smaller sized domains would realize higher reversible capacity and coulombic efficiency compared with LiC_6 because of the easier Li intercalation.

Fig. 3 shows ^{7}Li NMR spectra of the MG (100 rpm, 4 h, H_2) electrodes after the full Li insertion, full Li extraction, and Li extraction with at 0.24 V. In addition, Li intercalated graphite (LiC_6) was also measured as reference. For Li intercalated graphite with Li insertion and the MG (100 rpm, 4 h, H_2) with Li insertion, two peaks were observed at around 40 and 0.5 ppm. According to the previous reports, the former peak was explainable by contribution of graphite intercalation compound (GIC). After extracting Li, the peak at 40 ppm disappeared. From the previous NMR result, it was reported that at first Li was bound on the edge of graphene and intercalated into graphene layers [4]. Therefore, the peak at 40 ppm should relate to Li insertion/extraction process to graphite. On the other hand, the peak at around 0.5 ppm would be originated in Li compounds with an ionic bond related compounds such as SEI and lithium carbide. However, it has not identified yet.

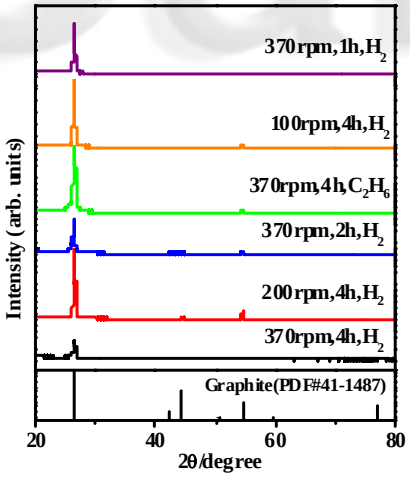

Fig. 1 XRD patterns of milled graphite samples.

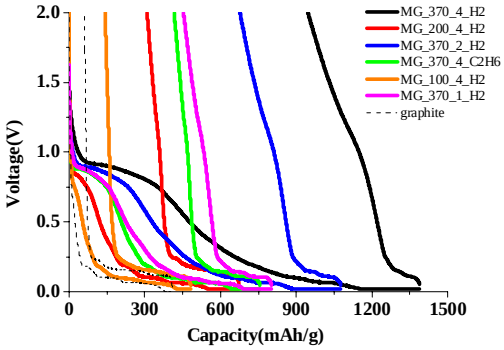

Fig. 2 Charge/discharge curves of milled graphite cells.

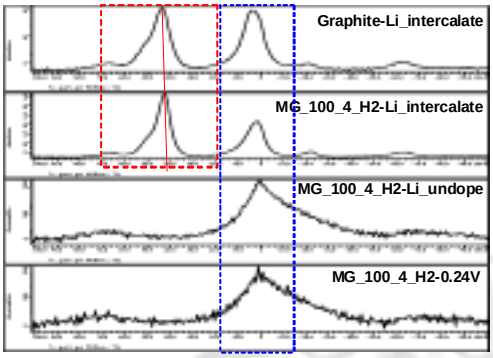

Fig. 3 ^{7}Li NMR spectra of graphite and milled graphite (100 rpm, 4h, H_2).

Conclusions

Several types of carbonaceous materials were prepared from high purity graphite by ball-milling method, and examined their lithium-ion battery performance. After the milling, the ball-milled graphite MG possesses two structures, graphene structure and amorphous structure, and its ratio is varied due to the milling condition. With increase in the milling time (amount of amorphous carbon), irreversible capacity originated in amorphous carbon increased because Li would form the stable ionic bond with the active sites in MG. The electrode of MG with the weaker milling conditions revealed high reversible capacity and coulombic efficiency, 567 mAh/g and 74 %, respectively. Therefore, it was considered that the ball-milled graphite could exceed the theoretical capacity of graphite as an anode material in lithium-ion battery.

References

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