



Lithium electrochemical intercalation into mechanically and chemically treated Sri Lanka natural graphite

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Abstract

Graphite is a host material for lithium intercalation and can be used as an active anode material in rechargeable lithium cells. The battery performances and cycling depends on the type and morphology of graphite. The advantage of natural graphite is the possibility of enhancing the electrochemical intercalation by simple mechanical or chemical treatments. Sri Lanka natural graphite is found in various morphologies with different structural and physical characteristics. The most abundant morphology, the shiny–slippery–fibrous graphite found in Kahatagaha/Kolongaha mines, has a very high purity of over 98% and high crystallinity. Lithium has been electrochemically intercalated into different morphologies of pure natural graphite as well as into treated graphite. The ball milling facilitates partial conversion of hexagonal into rhombohedral phase, which increases structural defects lowering the tendency to solvent co-intercalation and exfoliation and increasing the reversible capacity. Chemical treatments on graphite show improvements in reversible capacity. The mechanical ball milling and the chemical oxidation in air and $(\text{NH}_4)_2\text{S}_2\text{O}_8$ are simple and effective methods to enhance the electrochemical intercalation of lithium ions into natural graphite.

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1. Introduction

Graphite is one of the most extensively used carbonaceous materials as intercalation anodes in lithium-ion batteries. For battery applications, the electrochemical intercalation and deintercalation capacities are important characteristics of carbon material, which strongly influence the energy density. Highly crystalline graphite is capable of intercalating lithium up to one lithium atom for every six carbon atoms, which is denoted by LiC_6 . The LiC_6 can be obtained via a direct chemical reaction of metallic lithium with graphite [1] or by electrochemical intercalation with a theoretical specific capacity of 372 mAh g^{-1} [2,3].

However, it has been reported that certain types of graphite (flakes, sheets, fibers, micro beads, coke, etc.) give

higher lithium insertion than the theoretical maximum value and improved cycleability [4–10]. However, the lithium intercalations into various Sri Lanka graphite morphologies have not been studied [11].

Both ball milling and chemical oxidation approaches have been attempted to modify the surface properties of natural graphite. The graphite surface can be modified by chemical oxidation [12–16] and the morphology and the texture of graphite can be modified by mechanical ball milling [17,18]. It has been reported that these types of mechanical and chemical treatments have improved the electrochemical properties of graphite [13,15,18,19].

Natural graphite is found in three forms namely amorphous, flake and vein. Sri Lanka is famous for highly crystalline vein graphite, which is mined in large areas in the Central Highlands. Sri Lanka natural vein graphite is found in various morphologies, with different structural and physical characteristics [20]. From the present study, the electrochemical performance of the shiny–slippery–fibrous natural graphite from Kahatagaha/Kolongaha mine (KSSI) is tested. Furthermore, the effect of ball milling and chemical oxidation is investigated.

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2. Experimental

2.1. Material preparation

Natural Sri Lanka vein graphite from the Kahatagaha/Kolongaha mine was used as starting material. The selected graphite samples were first crushed in a ceramic mortar and then powdered by a high-energy vibratory ball-mill (Fritsch Pulverizette) for 50 h in air.

Selected graphite samples having particle sizes less than 63 μm , were used for chemical oxidation. As the first method, oxidation of graphite was performed at 550 $^{\circ}\text{C}$ in a tube furnace under air for 24 h. As the second method of oxidation, the graphite powder was dipped into a 0.1 M solution of $(\text{NH}_4)_2\text{S}_2\text{O}_8$ in 1 M H_2SO_4 , at 60 $^{\circ}\text{C}$ for 24 h, and subsequently washed with water and dried in air.

2.2. Material characterization

X-ray diffraction (XRD) studies were carried out with a Philips X-ray generator, using $\text{Cu K}\alpha$ radiation with a wavelength of $\lambda = 1.5406 \text{ \AA}$. The effect of rhombohedral phase was evaluated, comparing the integrated intensities of hexagonal (101) and rhombohedral (101) reflections. Its lengths of coherence (L_a and L_c) can be quantitatively estimated via conventional structural analysis: the L_c values were calculated on the basis of the d_{002} diffraction line, using the Sherrer's formula, while the L_a values were calculated using the d_{100} diffraction line using the Warren's formula. The chemical characterization was obtained using a Carbon and Sulfur Determinator and an atomic absorption spectrometer (see Table 1).

2.3. Electrochemical characterization

The different varieties of graphite were mixed with 10% of acetylene black as the electronic conducting agent, 15% of PVDF as a binder and dissolved in Dibutyl Phthalate DBP to make thick slurry. The slurry was spread over a polyethylene sheet by Doctor Blade method to obtain a thin film. Those composite electrodes were used to assemble coin-type cells (CR2430) with metallic lithium discs as counter and reference electrode. A solution of 1 M LiPF_6 in ethylene carbonate/dimethyl carbonate with a 1:1 proportion was used as the liquid electrolyte. The electrochemical experiments were performed using a MacPile potentiostat-galvanostat.

Table 1
Percentage of chemical constituents in the shiny–slippery–fibrous natural graphite (KSSI)

| C–S determinator | | Atomic absorption spectrometry (AAS) | | | | | |
|------------------|------------|--------------------------------------|------------------|-----------------------------|------------------|-----------------------------|----------|
| Carbon (%) | Sulfur (%) | SiO_2 (%) | CaO (%) | Fe_2O_3 (%) | MgO (%) | Al_2O_3 (%) | Cu (ppm) |
| 99.20 | 0.01 | 0.05 | 0.004 | 0.06 | 0.173 | 0.21 | 680 |

3. Results and discussion

3.1. Crystallographic characteristics

All the tested graphite samples showed a high crystallinity which was verified by d_{002} interlayer spacing of about 3.35 \AA . According to the diffraction line of d_{100} , the L_a values of ball milled and oxidized KSSI graphite vary between 80 and 90 nm. The L_c values of ball milled and oxidized graphite vary between 30 and 40 nm with respect to d_{002} diffraction line. The average of L_c and L_a values of ball-milled graphite decreases with the duration of the treatment. These decreases are due to the fissure propagation in the graphene layers [21].

Fig. 1 shows the X-ray diffraction results. The $(101)_R/(101)_H$ intensity ratio increases up to 67% with ball milling, showing a very important increase of the rhombohedral phase. However, the rhombohedral phase content remains almost constant after the chemical oxidation. When increasing the rhombohedral phase, it seems that lots of defects were also created, which could affect its electrochemical behavior [7,10,22].

3.2. Discharge and charge profiles of Li/graphite cells

The characterization of lithium/graphite intercalation process was mainly performed using galvanostatic discharge and cyclic voltammetry. The initial discharge–charge profiles were investigated at current rates of C/20, C/40, C/60 and C/80, and cycled between the initial open circuit voltage (Point A in Fig. 2a) and 0.005 V vs. Li/Li^+ . Discharge and charge profiles of untreated, ball milled and oxidized natural vein graphite in the first cycle are shown in Fig. 2. It can be seen that there are several plateaus at B, C, D, and E. The one at 1.45 V vs. Li/Li^+ (B) observed during the first discharge, may be attributed to the reduction of solvents, contaminants or water [23]. In the case of untreated and ball-milled natural graphite, there is a plateau near 0.80–0.90 V vs. Li/Li^+ (C) which is characteristic of a passivation layer formation on the graphite surface.

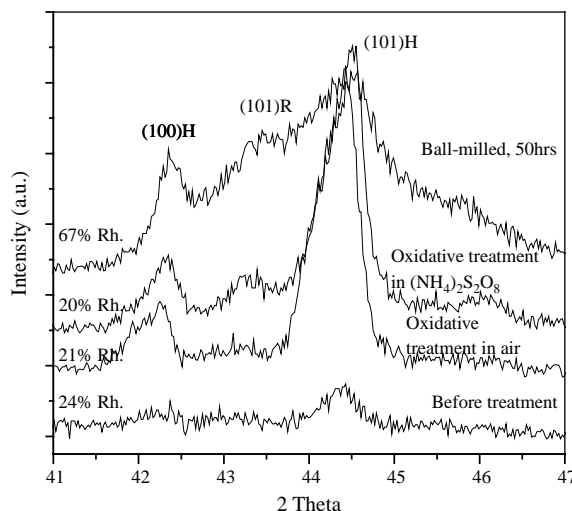


Fig. 1. Variation of rhombohedral phase content of treated and untreated KSSI graphite.

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