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# Intercalation of Hexagonal Boron Nitride and Graphite with Lithium by Sequential Process of Ball Milling and Heat Treatment

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## ABSTRACT

Recently, intercalation compounds with various intercalants between hexagonal boron nitride (h-BN) layers have been studied, where lithium BN intercalation compound (Li-BNIC) is one of such compounds successfully synthesized. They are expected to exhibit similar properties to lithium graphite intercalation compounds (Li-GICs) that are known as the anode material for lithium ion batteries. It is difficult, however, to apply Li-BNIC for the batteries due to its returning to an insulator when Li is deintercalated. In this study a Li–BN–graphite ternary system has been focused because it is reported that graphite-like BC<sub>2</sub>N is a promising material for rechargeable Li batteries. The primary purpose of this study is thus to investigate combined reactivity of BN and graphite with Li through milling and heating processes, and possible intercalation of Li into the matrix: h-BN, graphite or B–C–N. The pieces of lithium metal, h-BN and graphite powders were ball-milled using a vibratory ball-mill machine and heat-treated at 700 °C for 2 h under argon atmosphere. The samples were then characterized by X-ray diffractometry, X-ray photoelectron spectroscopy, <sup>7</sup>Li nuclear magnetic resonance and Differential thermal analysis study. Li-GICs were mainly produced by milling, while post-annealing caused their eliminations and instead produced Li-BNICs with small amount of other lithium compounds. In terms of thermal stability, Li-BNIC is more stable than Li-GICs. In a Li–BN–graphite system, an activation energy of Li-BNIC was estimated to be 119.6 kJ/mol, which is higher than reported activation energies for Li-GICs.

**Keywords** Lithium; Intercalation; Boron Nitride; Graphite; Ball Milling; Thermal stability

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## 1. Introduction

Graphite is known to exhibit intercalation compounds with its layered structure, and graphite intercalation compounds (GICs) have been intensively studied due to their interesting properties, such as superconductivity and electrochemical characteristics [1]. Among various GICs, lithium GICs (Li-GICs) have been actively studied due to their application for anode material of lithium ion batteries. The overall stoichiometry of Li-GICs has been classified into stages such as gas-like stage 1', dilute LiC<sub>9n</sub> type, dense LiC<sub>6n</sub> type [2-10] and super-dense LiC<sub>2.3</sub> [11-14], where n is the number of graphene planes between two layers of intercalated Li. These Li-GICs have been synthesized through various methods, such as electrochemical method [2-5, 7, 9, 15], mechanical milling [10, 12-14] and heat treatment with/without pressure control [8, 10, 11]. In case of heat treatment, temperatures below 400 °C have been usually selected to suppress synthesis of Li<sub>2</sub>C<sub>2</sub>, which is not an intercalation compound. Direct production of Li-GICs might be possible even at room temperature under high pressures (10~20 kbar), while in vacuum or under low pressures they can only be synthesized by annealing [6]. Except for LiC<sub>6</sub>, which is a "stage-one" compound of dense LiC<sub>6n</sub> type, the stoichiometry is thus sensitive to temperature when synthesized under lower pressures, whereas it becomes sensitive to pressure (less sensitive to temperature) under high-pressure preparative methods. As the thermodynamic stability of Li-GICs is controversial, there is no consensus on the temperature of their deintercalation(s) [3, 8, 15, 16], and it might depend on the methods of synthesis. In case of an electrochemical method, deintercalation of Li-GICs occurs at ~80 °C [15]. Drüe et al. reported that it has been produced by annealing at 330 °C, though LiC<sub>6</sub> was thermodynamically unstable above the temperature (330 °C), and suggested a metastable Li–C phase diagram [8, 16]. As for thermodynamic stability of Li-GICs synthesized by mechanical milling there has not been a detailed report until

now.

Hexagonal boron nitride (h-BN) is also known to exhibit similar layered structure to graphite, and the intercalation compounds with various intercalants, such as alkali metals [17-22], transition metals [23] or molecules (Br<sub>2</sub> [24], S<sub>2</sub>O<sub>6</sub>F<sub>2</sub> [25], Brønsted acids [26]) into h-BN layers, have been studied for prospective similar (or even better) properties to Li-GICs. Also, lithium BN intercalation compound (Li-BNIC) was synthesized using heat treatment by Sumiyoshi et al. [19, 21], or using the sequential process of ball milling and heat treatment in our previous study [22], and the structural investigation has been carried out [20-22]. It is difficult, however, to define stoichiometry of Li-BNIC, due to the irregular arrangement of Li ions in the BN host. Unlike Li-GICs, the interlayer distance of Li-BNICs did not change even with different ratios of Li and BN [22]. The layered structure of Li-BNIC have been suggested to exhibit "1L model", but not "2L model", that is, possessing "a structure without two-layer stacking periodicity" of pristine h-BN structure [21]. It is supposed that Li could be intercalated into the defective BN host structure. Sumiyoshi et al. have also reported that electrical conductivities of Li-BNICs are higher than pristine h-BN [19, 21], however, it is still difficult to apply Li-BNIC for lithium ion batteries due to its easiness of returning into an insulator when Li is deintercalated.

In this study, a Li–BN–graphite ternary system has been then focused to overcome this problem, as there is a paucity of available research on the field, particularly Li intercalation into a BN–graphite binary system. In the B–C–N system, graphite-like BC<sub>2</sub>N has been reported as a promising material for rechargeable Li batteries [27], and, among various methods of BC<sub>2</sub>N synthesis, ball-milling was reported as one of the useful processes, using h-BN and graphite powders as starting materials [28, 29]. Therefore, the purpose of this study is to investigate firstly intercalation of combined BN–graphite with Li through milling and heating processes, which were used in our previous study

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