First Principles Calculations for Diffusion Barriers of Lithium intercalation into Graphite with various Edge Terminations

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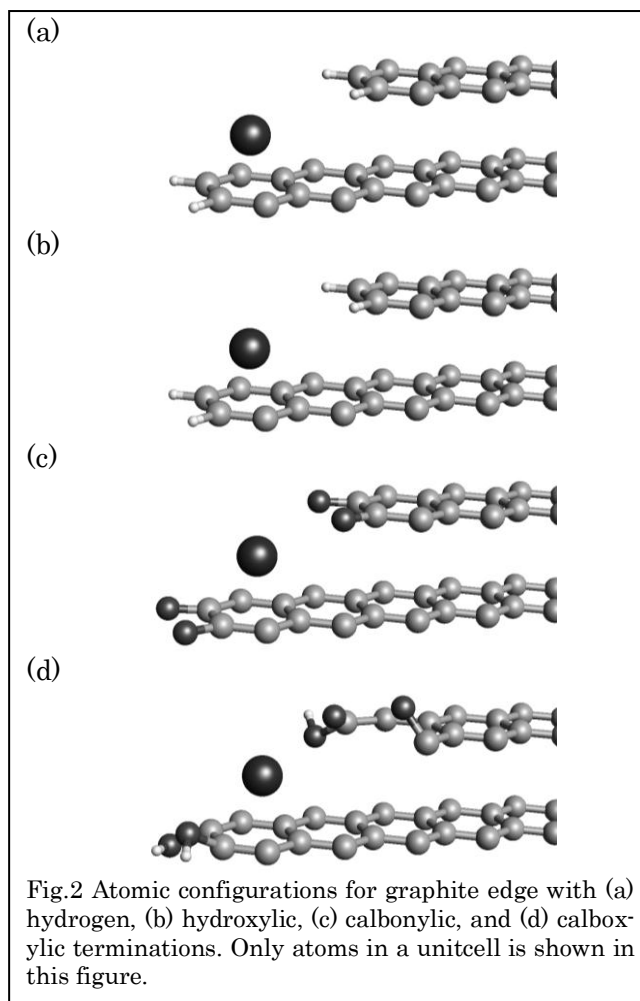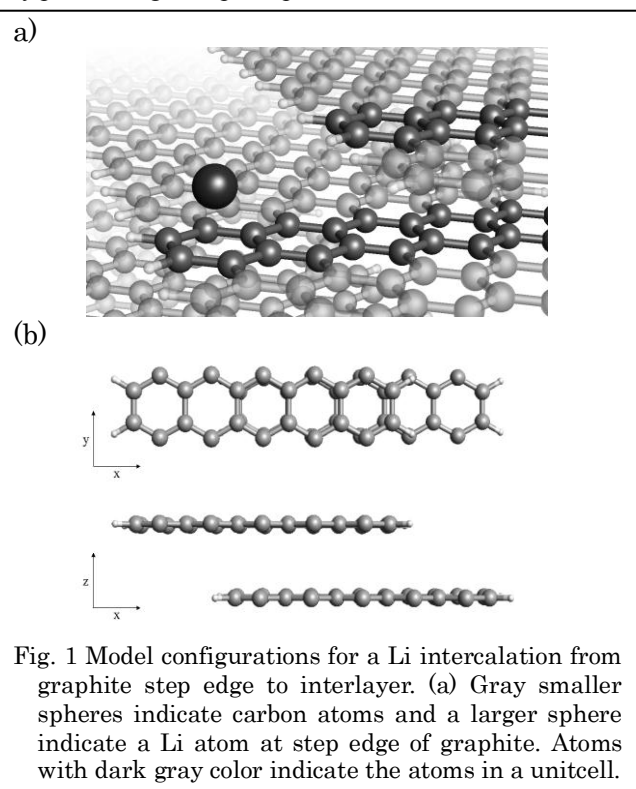Phone: +81-29-850-1554 E-mail: t-kawai@da.jp.nec.com
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1. Introduction

The lithium ion rechargeable battery (LIB) is one of the most important and indispensable devices to utilize the green energy such as solar and wind power generation. This is because the LIB can store the supplied energy and minimize the volatility of the energy supply from those green energies, where the LIB can work as a buffer for unstable electric power consumption. For such applications, LIB is required to have longer life time and to be secure [1].

However, the degradation mechanism of LIB is not known clearly, yet. Currently, the reasons for the degradation by long term use are considered that 1) the formation of solid-electrolyte interphase (SEI) consumes the Li ion in electrolyte which is indispensable for charge and discharge of battery, and 2) increase of SEI film thickness blocks the diffusion of Li ions at graphite surface of anode. Thus, the chemical reaction at surface of electrode (especially for anode) is getting more attention, recently.

In this article, we focus on the effect of graphite edge termination on the Li atom diffusion into graphite interlayer by performing first-principles electronic state calculations.

Fig. 1 Model configurations for a Li intercalation from graphite step edge to interlayer. (a) Gray smaller spheres indicate carbon atoms and a larger sphere indicate a Li atom at step edge of graphite. Atoms with dark gray color indicate the atoms in a unitcell.

Fig.2 Atomic configurations for graphite edge with (a) hydrogen, (b) hydroxylic, (c) calbonylic, and (d) calboxylic terminations. Only atoms in a unitcell is shown in this figure.

2. Calculation Models and Theoretical Tools

To investigate the diffusion barrier heights for a Li atom diffusion from step edge to interlayer of graphite as shown in Fig.1, we performed first-principles total energy calculations within the density functional theory framework with generalized gradient approximation (GGA) including van der Waals interactions using Quantum Espresso/PWSCF code[2]. We used Perdew-Burke-Ernzerhof (PBE) version of exchange-correlation functional[3] for the electron-electron interaction and Vanderbilt ultrasoft pseudopotentials[4] and the valence wave functions are expanded in plane-wave basis set with cutoff energy of 46 Ry,

while the cutoff of charge density is 200 Ry. The Broyden-Fletcher-Goldfarb-Shanno (BFGS) method is used for geometry optimization, and we used gamma point for the k-point integration. In this calculation model shown in Fig.1, we used periodical boundary conditions and the unitcell including two stepped graphene layer where each layer consists of 22 carbon atoms terminated by 2 hydrogen atoms on each side of the edge. The stacking of two layers in this model is AA-stacking where six membered ring of two layers overlapped each other. This stacking realized when the Li atoms are already intercalated enough[5].

The most stable configuration for Li atom on a graphene plane is when the Li atom sits on the center of six-membered ring. Here, we perform the diffusion path optimization for Li atom from a step edge of graphite as shown in Fig.1 to interlayer of graphite using nudged elastic band method (NEBM) depending on the edge termination of graphite. We considered 4 different termination edges, i.e., (a) hydrogen termination, (b) hydroxylic termination, (c) carbonylic termination, and (d) carboxylic termination as shown in Fig.2. These termination structures would be realized by native oxidation of graphite edge after long term charge-discharge processes [6].

3. Results and Discussions

For graphite edge terminated by hydrogens, the total energy has hump when Li atom go over the C-C bond perpendicular to the diffusion path. The barrier height for the diffusion is about 0.5 eV. The barrier height is not change significantly as shown in Fig.3.This value of diffusion barrier is consistent with previous works [5]

For graphite with hydroxylic termination, an interaction between Li atom and the edge lower total energy and the diffusion barrier height becomes lower than that of hydrogen termination. Thus, the initial barrier for the intercalation of Li atom into graphite is lowered by the hydroxylic termination. The diffusion barrier heights for Li atom inside graphite layers are similar to that of hydrogen termination.

For carbonylic termination, the interaction between the Li atom and oxidized graphite edge lower the energy significantly. In other words, the Li atom is trapped at the edge of graphite before the intercalation. The energy barrier for the diffusion from the trapped configuration is over 2.0 eV, which is 4 times higher than those for hydrogen termination. The diffusion barrier with carboxylic termination is as large as 1.5 eV. The trapped Li atoms at the step edge of oxidative will disturb further Li intercalation. Then the progress of oxidation at the edge of graphite would affect the performance of batteries.

3. Conclusions

Insertion of Li atom from the graphite edge with various oxidative terminations is investigated by first-principles electronic states calculations. Using the graphite step model as shown in Fig.1 and 2, we calculated the diffusion barriers for a Li atom from the step edge to the interlayer of graphite. Our calculation results show that the diffusion barriers are increased by the oxidative terminations since the Li atom is trapped at the oxidative edge of graphite. The diffusion barrier of ~0.5 eV for hydrogen termination is increased to ~2.0 eV for carbonylic termination. These values of activation barriers are comparable or larger than those of desolvation energy of Li in electrolyte solution, which is another rate limiting process for charge-discharge process of rechargeable batteries.

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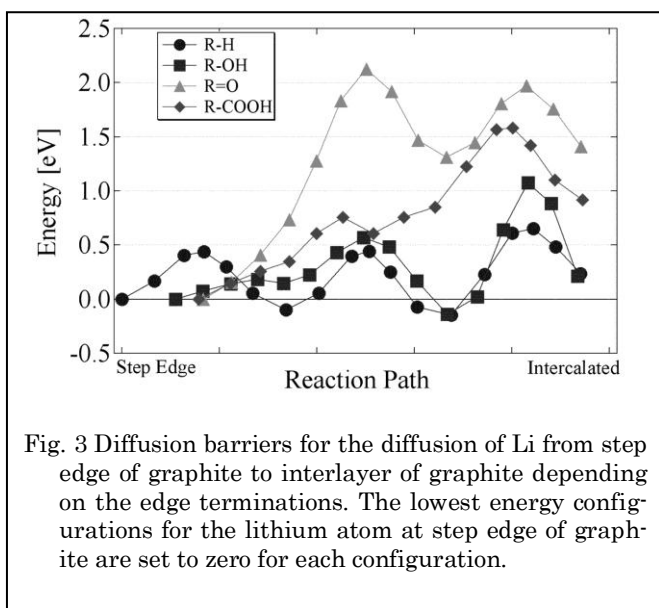[6] J.L. Figueiredo, et al, Carbon 37 (1999) 1379.

Fig. 3 Diffusion barriers for the diffusion of Li from step edge of graphite to interlayer of graphite depending on the edge terminations. The lowest energy configurations for the lithium atom at step edge of graphite are set to zero for each configuration.