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

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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.

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 Brod-
yden-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 periodic 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 gra-
phene 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 elas-
tic band method (NEBM) depending on the edge termina-
tion of graphite. We considered 4 different termination
dges, i.e., (a) hydrogen termination, (b) hydroxyl termina-
tion, (c) carboxyl termination, and (d) carboxyl termina-
tion 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 a hump when Li atom go over the C-C bond per-
pendicular 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 bar-
errier is consistent with previous works [5]

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

For carboxyl termination, the interaction between the Li
atom and oxidized graphite edge lower the energy signifi-
cantly. 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 edge step of oxida-
tive will disturb further Li intercalation. Then the progress
of oxidation at the edge of graphite would affect the per-
formance of batteries.

3. Conclusions

Insertion of Li atom from the graphite edge with vari-
ous 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 barri-
ers 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 carboxyllic 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.

References
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