

First-Principles Calculations for Diffusion Mechanism of Li atom from Li(EC)₄ to Interlayer of Graphite with Hydrogen/Carbonylic Edge Terminations

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Abstract

The configurations for Li(EC)₄ and the diffusion barriers for the intercalation of a Li atom are calculated using first principles electronic states calculations. We found that the carbonylic edge terminations attract solvated Li atoms near the graphite edge, which would enhance the rapid charge/discharge of the Li ion batteries. We will further discuss the diffusion barriers and electronic states during the intercalation of Li atom from solvated configuration in ECs.

1. Introduction

It is required to utilize electric power efficiently by distributing it on demand to shift into a world with sustainable energy. The request is not so easy to achieve mainly because 1) the electric power generations by natural energy such as solar power and wind power depends on weather and not stable, and 2) the demand for electricity changes drastically depending on the time and factory utilization in the area. To realize the goal, the batteries are important key devices to store electric power as required.

For such large scale applications, the electric batteries are highly demanded to have large capacity and long lifetime. The large capacity save a space for installation and administrative expenses, and long life save a time and money for maintenance. These properties are also attractive for other applications such as electric/hybrid vehicles and heavy industrial machines.

To respond quickly to demands in smart grid and automobiles, fast charge/discharge is also an important challenge. Because we need more storage and space to utilize the slow rate batteries to correspond to the drastic change of demand from smart grid or electric/hybrid vehicles. The fast charge/discharge is also achieved by a combination with electric capacitors, although such system needs more space and money. Here, the cost is another important factor for large batteries.

Here, we focus on Li atom diffusion near the negative electrode, which is rate-limiting reaction and affects the charge/discharge rate of the battery. Recently, various ma-

terials such as graphene oxides are suggested in several papers.[1-3] Although those progresses are also fascinating and worth studying, the atomic scale mechanisms of surface reactions are complicate and not clear even for the most simple graphite edge with Li atom solvated in ethylene carbonates (ECs).[4]

Before studying the diffusion of Li atom, we studied the solvated state of Li with ECs and physisorption of Li(EC)₄ on graphite edge terminated by hydrogen or carbonyl group. In this paper, we further evaluated the energy barriers for Li atom diffusion near the graphite edges with hydrogen/carbonylic terminations. Initially solvated Li atom with ethylene carbonate is finally intercalated into graphite from the edge.

2. Theoretical Tools and Models

We performed ab initio electronic states calculations within density functional theory under the framework with generalized gradient approximation (GGA) including van der Waals interaction (DFT-D) using the Quantum Espresso/PWscf code.[5] We used the Perdew-Burke-Ernzerhof (PBE) version of exchange-correlation functional for the electron-electron interaction, and Vanderbilt ultrasoft pseudopotentials. The cutoff energy of 46 Ry was used for the plane wave basis set to expand the wave functions.

We also used Effective Screening Media (ESM) method to include the effect of a constant chemical potential for electron during the Li atom diffusion.[6,7]

As a model for solvated Li atom in ECs, We used four-coordinated configurations, i.e., Li(EC)₄. A schematic view of the tetrahedral coordination of the Li(EC)₄ is shown in an inset of Fig. 1(a). The coordination number and the tetrahedral configuration is considered to be the most stable for the Li in EC solvent.[8,9] We also found the 4 coordinated tetrahedral configuration is rather stable. Furthermore, it is found that the total energy difference between the tetrahedral coordination and the planar square coordination is less than 0.3 eV. There is no extra barrier for the transformation between those structures. Then, we consider that various intermediate structure between tetra-

hedral coordination to the planar square coordination structure is realized as a transition state during the diffusion of $\text{Li}(\text{EC})_4$ and intercalation of Li atoms.

We consider that the planar square coordination is more appropriate compared to the tetrahedral configuration of $\text{Li}(\text{EC})_4$ for the diffusion of a Li atom due to two reasons. One reason is that an energy barrier of desolvation for the tetrahedral configuration would be higher due to the steric hindrance. The other reason is a distance between a solvated Li atom and graphite edge surface. For the planar square configuration, a Li atom approaches the graphite edge surface closer than that with tetrahedral one. Then, we chose the planar square configuration $\text{Li}(\text{EC})_4$ for the initial structure of intercalation after calculating stability of the configuration at the graphite edge.

3. Results

The appropriate distances for the planar square configuration of $\text{Li}(\text{EC})_4$ is calculated on graphite edge terminated by hydrogen or carbonyl group. We found that the potential energy for $\text{Li}(\text{EC})_4$ near graphite edge with carbonylic terminations are deeper than that of hydrogen terminations. The potential profile for graphite edge with carbonylic terminations will enhance the density of Li ions near the graphite edge. Then, the Li ions intercalate into graphite edge from rather short distances. We assume that the difference of terminations affect the charge/discharge rate dramatically, because the distance from solvated Li atom and graphite interlayer position affect the diffusion barriers, which affect the diffusion rate exponentially.

We are now calculating the diffusion barriers for the diffusion of a Li atom from planar square configuration to a graphite interlayer space as shown in Fig.1(b) and (c). The barrier height is 0.75 eV for termination with hydrogen atoms. The potential energy variation for that with carbonylic termination is rather complicate because the Li atom is trapped near the oxygen atoms at the edge of graphite. We will discuss the effect of the termination of graphite from the electronic states and atomic configurations.

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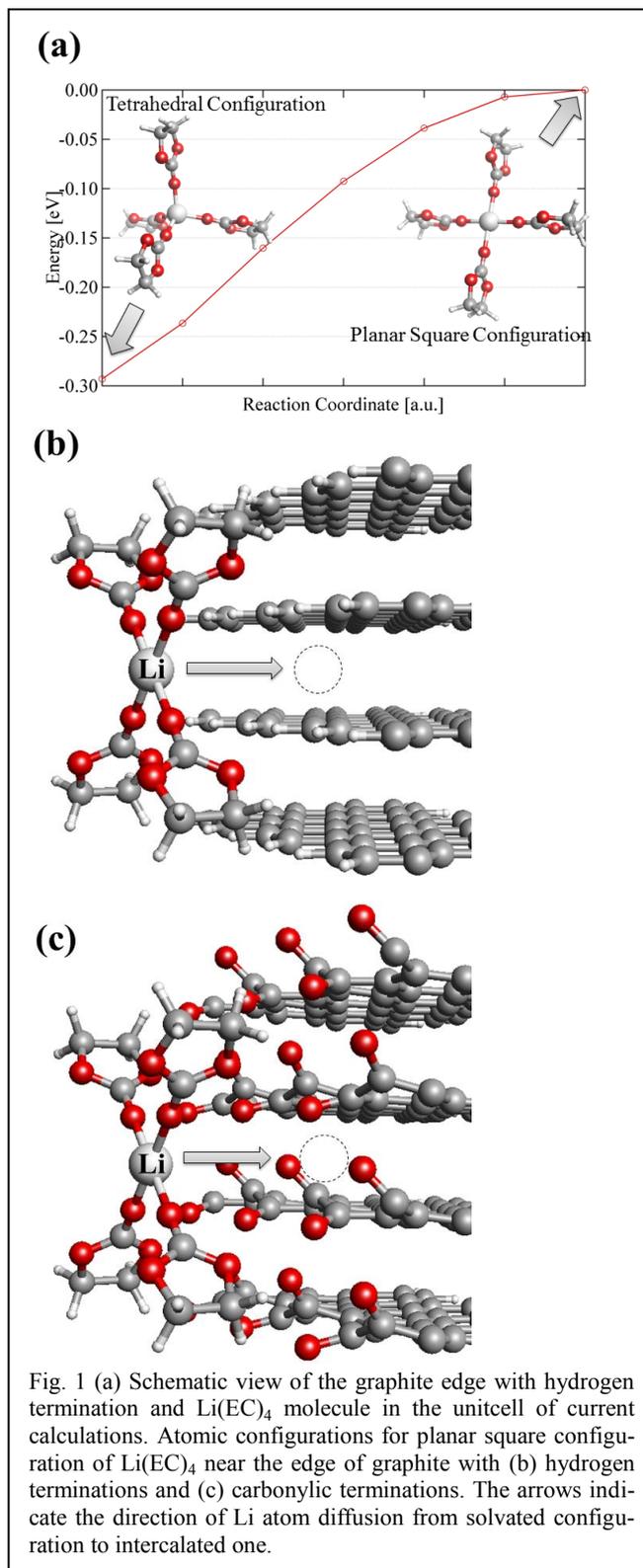


Fig. 1 (a) Schematic view of the graphite edge with hydrogen termination and $\text{Li}(\text{EC})_4$ molecule in the unitcell of current calculations. Atomic configurations for planar square configuration of $\text{Li}(\text{EC})_4$ near the edge of graphite with (b) hydrogen terminations and (c) carbonylic terminations. The arrows indicate the direction of Li atom diffusion from solvated configuration to intercalated one.

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