Ab Initio Calculations for Li$^+$ Solvation in Ethylene Carbonate near the Graphite Edges with Hydrogen/Oxygen Terminations

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Abstract

We performed ab initio calculations for configurations and electronic states of Li$^+$ solvation in a solvent of ethylene carbonate. The solvation of Li$^+$ ion with four ethylene carbonates is found to raise the energy of lithium 2s atomic orbital, and then the ionic state of the lithium become stabilized. The energy difference in tetrahedral and square coordination structure is less than 0.3 eV. Thus, the coordination structure is flexibly deformed depending on the environment at around room temperature. We further investigated the interaction between a solvated Li$^+$ ion and graphite edge terminated by hydrogen or oxygen atoms. The energy gain by the adsorption is larger for graphite edge with the oxygen termination than that with hydrogen termination due to the large interaction of polarized graphite edge and solvated Li$^+$ ion. Then, the oxidative edge termination would enhance the concentration of Li$^+$ ions near the graphite edge.

1. Introduction

Lithium ion battery is one of indispensable key devices for leading to a better balance between supply of electricity from environmentally-friendly sources and power demand changing with every moment. Because the lithium ion batteries have a large electric power capacity with a little degradation during repeated use. Along with further development of these properties, rapid charge/discharge ability is required to respond flexibly to the supply and demand.[1,2]

To realize the rapid charge/discharge of batteries, it would be important to understand an atomic scale mechanism of lithium ion diffusion from a solvated configuration in a solvent to an intercalated structure at a graphite anode. However, the atomic scale mechanism is not clearly understood especially for solvation/desolvation process at the graphite edges depending on the edge terminations.

Previously, we performed the ab initio calculations to estimate the diffusion barriers of a lithium atom from the step edge to interlayer sites of graphite depending on the edge termination.[3,4] We found that oxidative edge termination attract the lithium atom at the step edge. The lower potential energy for the lithium ion at the step edge increases the barrier for a further diffusion. However, the

barrier is lowered by the applied voltage during the charging process.

In this study, we investigated the interaction between lithium ion and an ethylene carbonates (ECs) as an electrolyte. We also investigated the interaction between solvated lithium ion (Li(EC)$_4$) and graphite edge with a hydrogen/oxygen atom terminations.
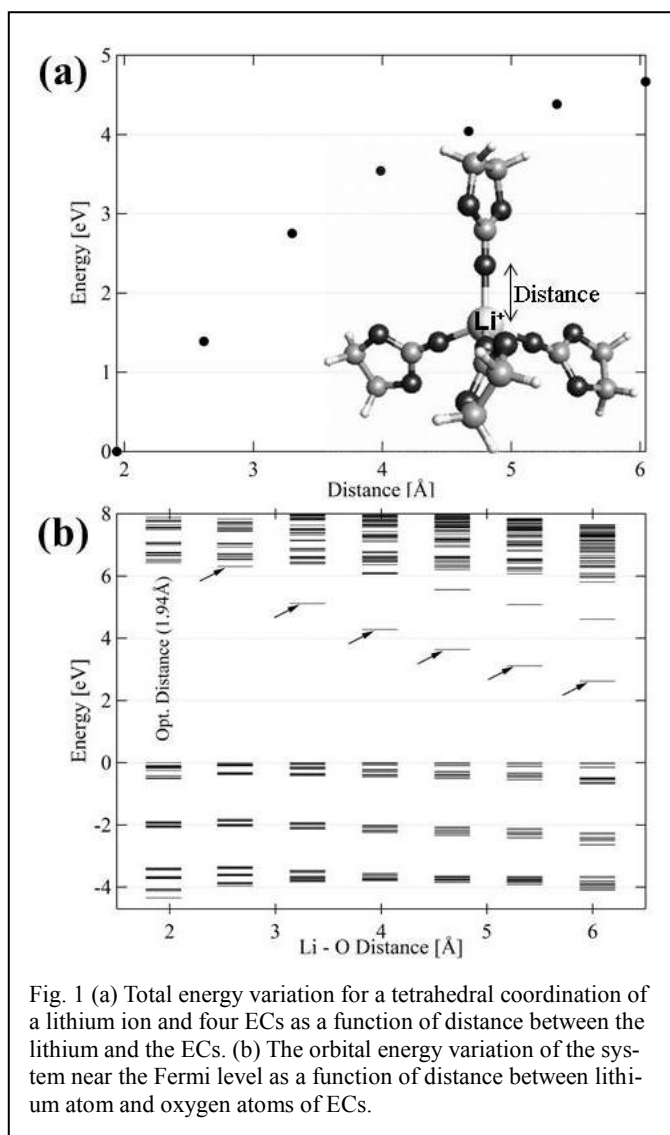

Fig. 1 (a) Total energy variation for a tetrahedral coordination of a lithium ion and four ECs as a function of distance between the lithium and the ECs. (b) The orbital energy variation of the system near the Fermi level as a function of distance between lithium atom and oxygen atoms of ECs.

2. Models and Theoretical Tools

We performed ab initio electronic states calculations within density functional theory under the framework with generalized gradient approximation (GGA) including van der Waals interaction 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.

For the calculations of interaction between a lithium ion and ECs, four-coordinated configurations are used. 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 coordination is considered to be most stable for the system.[6,7] We found, however, that the total energy difference between the tetrahedral coordination and the planar square coordination is less than 0.3 eV, and there is no reaction barrier between those structures. Then, we consider that the planar square coordination structure is often realized as a transition state during the diffusion of $Li(EC)_4$.

3. Results

To investigate the interaction between lithium ion and ECs, the total energy is calculated as a function of a distance between lithium atom and top oxygen atoms of ECs. The energy gain by forming a tetrahedral configuration is over 4 eV. The energy gain of solvation is attributed to an electrostatic interaction between lithium ion and polarized ECs. The change in a molecular orbital energy by approaching the ECs to lithium ion is shown in Fig.1(b), where the HOMO level is taken as a Fermi level. It is shown clearly that unoccupied 2s orbital energy at the energy gap of ECs (indicated by arrows in Fig.1(b)) is significantly raised up by approaching the ECs to the lithium atom so that the anion state is stabilized for $Li(EC)_4$.

Next, we consider an interaction between $Li(EC)_4$ and graphite edges with hydrogen/oxygen termination because the interaction affect the diffusion of lithium ions significantly. We consider the interaction between the graphite edge and $Li(EC)_4$ in planar square coordinate as shown in Fig.2(a), because the diffusion barrier for the lithium ion intercalation is lowered by approaching the solvated lithium ion to the graphite edge as much as possible. The total energy variation as a function of distance between graphite edge and $Li(EC)_4$ is shown in Fig. 2(b). The energy gain by adsorption for graphite with oxidative edge termination is larger than that with hydrogen termination due to the large interaction of polarized graphite edge and solvated Li ion. However, the distance between the surface and molecule become large for graphite with oxygen edge termination due to the interaction between graphite edge and polarized EC molecules. Then, the oxidative edge termination would enhance the concentration of Li+ ions.

References

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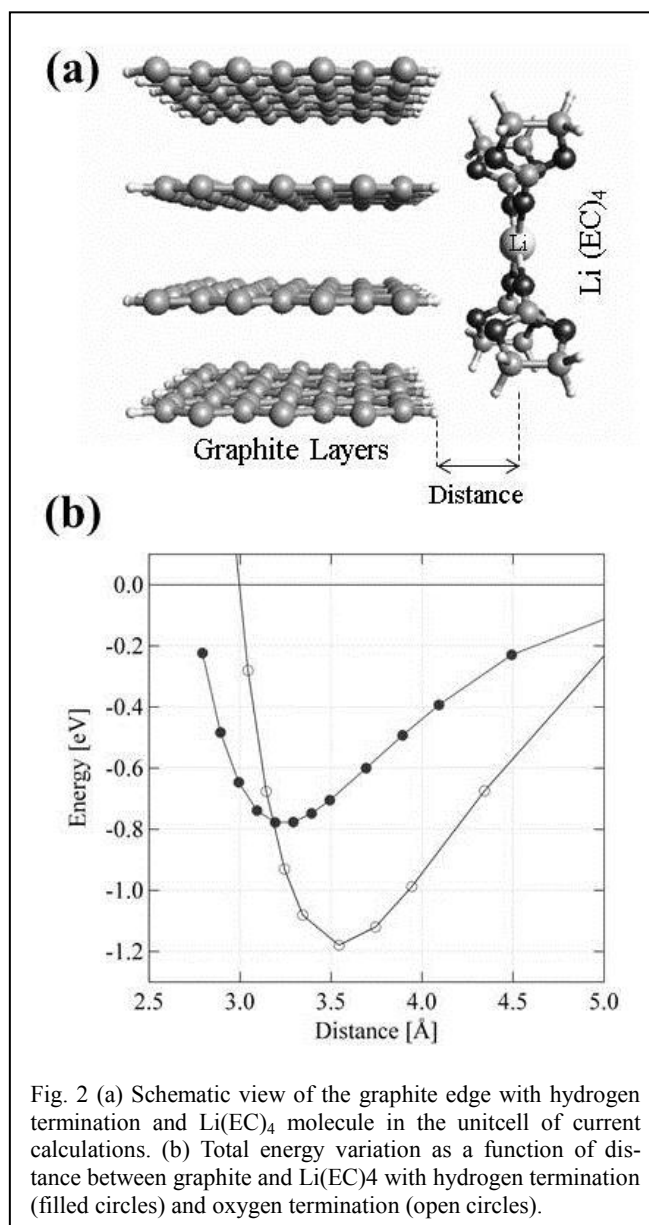Fig. 2 (a) Schematic view of the graphite edge with hydrogen termination and $Li(EC)_4$ molecule in the unitcell of current calculations. (b) Total energy variation as a function of distance between graphite and Li(EC)4 with hydrogen termination (filled circles) and oxygen termination (open circles).