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Adsorption and Diffusion of Li Atom on Graphene Sheet with V_6 Vacancy: First Principles Calculations

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Abstract

We investigated the adsorption of a Li atom on the graphene with V_6 defect terminated by hydrogens at the edge using first principles electronic state calculations. We found that a Li atom adsorbs more stable on the defect site with less hydrogen atoms since the energy gain is depending on the electrostatic interaction between carbon atoms with dangling bond and a Li ion. The adsorption energy for a Li atom on the hexagonal ring is also depending on the defect termination structures. The reason is explained by the charge transfer from Li 2s states to defect related electronic states. We further estimate the diffusion of a Li atom through the V_6 defect.

1. Introduction

Graphitic carbons are still one of the most fascinating materials for battery anode for its lower standard electrode potential, chemical robustness and ubiquitousness for long life and to maintain a stable supply. Recent experiment[1] shows that the materials obtained by the reduction of graphene oxide has a large capacity with higher charge rate. Here, the reduced graphene should have many defect structures and such defect affect the capacity and charge/discharge rate of Li ion batteries.

In the previous study[2], we investigated the adsorption of Li atom on the graphene with five different defect structures. We found that the adsorption energies are different depending on the defect structure even though the Li adsorbs on the hexagonal rings away from the defect. We explained that the occupation change during the adsorption decide the adsorption energies where the electrons are transferred Li 2s state to defect induced lowest unoccupied state.

In this paper, we investigated the adsorption of Li atom on the graphene with V_6 defect, where a six-membered ring is removed from pristine graphene sheet. We found that the adsorption energies are depending on the number of hydrogen termination at the defect edges and explained the phenomena by the energy of a lowest unoccupied state whose electronic states are distributed near the defect structures.

2. Method and Model

In this study, we investigated the interaction between a Li atom and a graphene layer with/without various defect structures. We performed ab initio electronic state calculations based on the density functional theory[3,4] under a framework with local density approximation (LDA)[5,6] using the STATE code[7]. Plane waves with energies up to 5 and 15 Ry are included in the basis sets of wave functions and charge densities, respectively. We used ultrasoft pseudo potentials[8] for carbon and lithium atoms, and took a 3×3×1 mesh of uniformly spaced k-points for Brillouin-zone integration.

3. Results and Discussions

The adsorption sites of Li atom on the graphene sheet with V_6 defect is shown in Fig.1 schematically. The adsorption site is decided by the electrostatic interaction between negatively charged carbon atoms with dangling bond and positively charged Li ion. The adsorption energies depend on the number and position of hydrogen terminations. The position number of terminations are shown in Fig.2(a).

For the terminations of 2 hydrogen atoms has three different geometries such and a combination of sites (1, 2), (1, 3), (1, 4) as shown in Fig.1. The adsorption energies for Li atom on the V6 defect and on the hexagonal ring is shown in Fig 2(b). It is clear that the adsorption energies are higher for adsorptions with less hydrogen atoms since the number of hydrogen for termination decide the electrostatic potential. Here, higher charge affect the adsorption energy. Interestingly the adsorption energy is depending on the defect termination even when the Li adsorbed on the hexagonal ring away from the V_6 defect. The result is understood by the charge transfer from the Li 2s to defect induced state near the V_6 defect which energy is just above the Fermi level before the Li adsorption.

From the geometries of a Li atom on the V_6 defect, we can estimate that possibility of a Li atom diffusion through the V_6 defect. For several structures of graphene with V_6 defect with partial hydrogen terminations many Li atoms are going into the graphene surface level. Thus, Li atoms may diffuse through the V6 defect without any energy barriers. On the other hand for a Li adsorbed above the graphene surface has some barriers to overcome for diffusion. The result shows most termination structures Li is go into graphene surface level, and it can diffuse barrier less through V_6 defect.

4. Conclusions

From the first principles electronic state calculations, we found that a Li atom adsorbs more stable on the defect site with less hydrogen atoms since the energy gain is depending

on the electrostatic interaction between carbon atoms with dangling bond and a Li ion. The adsorption energy for a Li atom on the hexagonal ring is also depending on the defect termination structures. The reason is explained by the charge transfer from Li 2s states to defect related electronic states. We further estimate the diffusion of a Li atom through the V_6 defect. These calculations show that the diffusion through the atomic scale vacancy can contribute the diffusion of a Li atom perpendicular to the graphene surface. The control of these small defects may enhance the charge/discharge rate of Li ion battery at graphitic electrode without changing the cycle characteristic and capacity.

References

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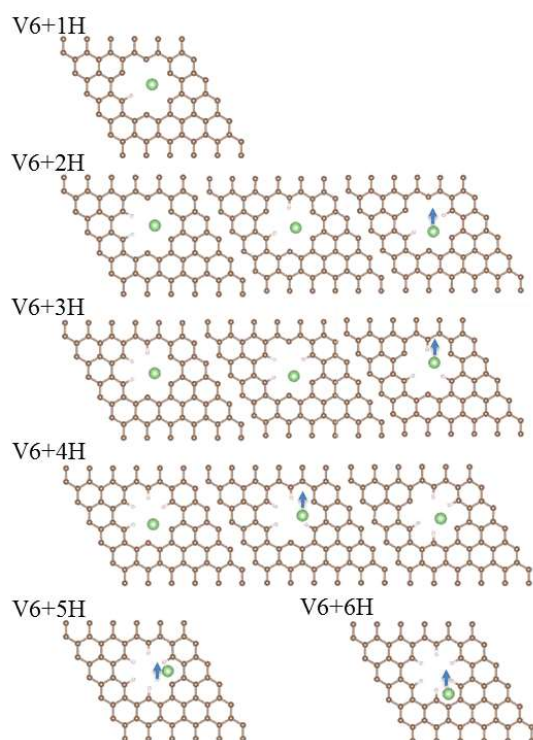[8] sD. Vanderbilt, Phys. Rev. B 41 (1990) 7892.

Fig. 1 Schematic views of a Li atom on a graphene sheet with V6 defect with various hydrogen terminations. Small, middle and large balls indicate hydrogen, carbon and Li atoms, respectively. Arrows indicate the Li atoms are away from the graphene plane. So, the Li atoms with arrows have a diffusion barriers for going through the V_6 defect..
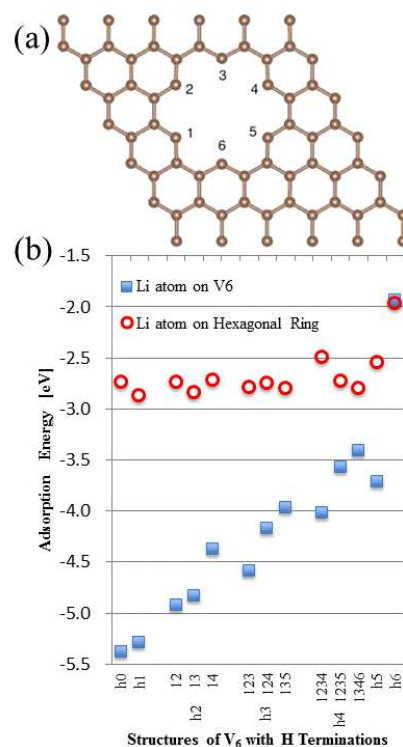

Fig. 2 (a) Schematic view of the graphene with V_6 defect. The balls indicate carbon atoms and numbers near the defect edge carbon atoms indicate the position of hydrogen termination. (b) Adsorption energy for graphene with V_6 defect for various hydrogen termination at the defect edges. The blue squares indicate the energies for Li atom on the V_6 defect and red circles indicate the energies for Li atom on hexagonal rings away from the V_6 defect site.