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First-Principles Calculations for Li Adatom Diffusion on Graphene Surface through V_6 Defect Partly Terminated by Hydrogen Atoms

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Abstract

We investigated diffusion paths and its barriers for Li atom on a graphene sheet through a vacancy defect utilizing density functional electronic states calculations with nudged elastic band method. We found that the Li atom is easily trapped by V_6 defect site, and diffusion barriers from the V_6 adsorption site are very high since the electro static interaction between Li atom and vacancy which consists of carbon atom with dangling bonds or terminated by hydrogen atoms.

1. Introduction

Since nano-carbon materials generally have large pore structures, they have attracted much attention as a negative electrode material for Li ion batteries with high electrical capacity. Recent studies show large battery capacities in comparison with the conventional graphite negative electrode[1]. However, the atomic scale understanding of the Li atom diffusion with some defects is still not clear, where such diffusion through the vacancy defect possibly affect the charge/discharge rate and also increase of the battery capacity. Here, we investigated the adsorption and diffusion of Li atom on the graphene with V_6 defect with various H termination configurations at the defect edge using first principles electronic state calculations.

We calculated Li diffusion path through the defect toward backside of the graphene. For V_6 defect terminated with 4 hydrogen atoms, 0.70eV is required for Li to diffuse through the defect. Although there is little diffusion barrier for clean edge, Li atom could be trapped at the deep potential hollow at the defect due to strong interaction between Li atom and dangling bond. We also investigated the Li atom diffusion through V_6 defect when the Li atoms are trapped at the defect site. We found that the trapped Li atoms reduce the attractive potential for a diffusing Li atom and enable the Li atom to diffuse by way of exchange diffusion.

2. Methods and Models

In this study, we investigated the diffusion of a Li atom through V_6 defect with/without hydrogen termination at dangling bond of carbon atoms. We performed ab initio electronic state calculations based on the density functional theory[2,3] under a framework with local density approximation (LDA) [4,5] using the STATE code[6]. 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 pseudopotentials[7] for carbon and Li atoms, and took a 3×3×1 mesh of uniformly spaced k-points for Brillouin-zone integration.

We modeled all the V_6 defect structures with various H terminations as shown in Fig.1. For description HN_m, "N" indicates number of hydrogen atoms terminating carbon dangling bonds, and subscription "m" indicates the position of terminations, e.g. $H3_{123}$ indicates a V_6 defect terminated by 3 hydrogen atoms at three adjacent sites as shown in Fig.1..

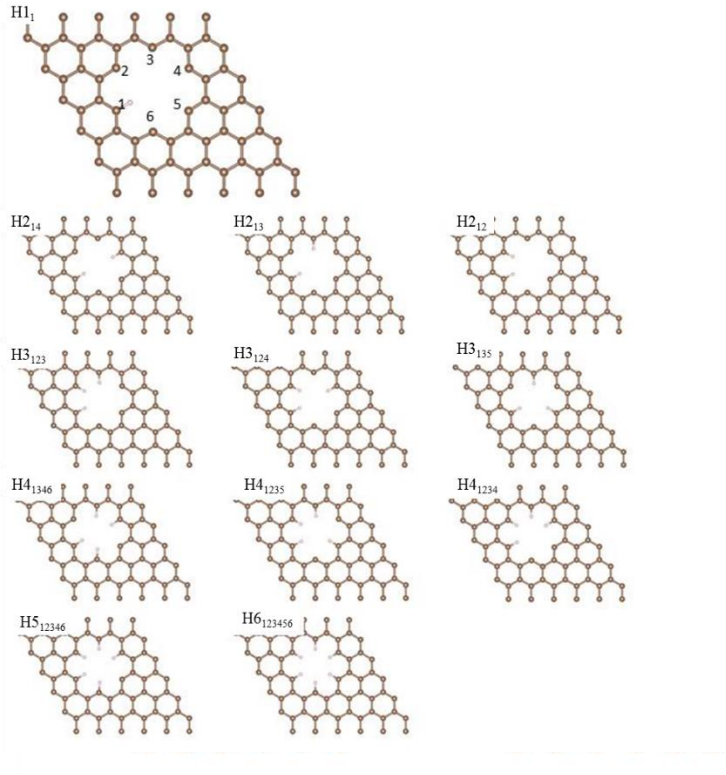

Fig. 1 Schematic views of graphene sheet with a V_6 defect partly terminated by hydrogen atoms.

3. Results

For the diffusion of an individual Li atom, we found that the Li atom easily trapped at the V_6 defect near the dangling bonds due to the electrostatic interaction among them. If there is no H termination attractive potential depth from a Li atom on the HR is about 2.6 eV, which is fairly higher than that without V_6 defect, and it would be very difficult to diffuse from the adsorbed structure at room temperature.

If a carbon atom of V_6 defect edge is terminated by 4 H atoms, adsorption energy is from -4.0 to -3.4 eV, and diffusion barriers are roughly estimated to be 0.6 to 1.5 eV, which is less than those without termination. Using NEB method to calculate the diffusion barrier, we found the diffusion from

HR site to that on the reverse site is almost 0 eV. However, once the Li atom trapped at the defect site, diffusion barrier becomes over 2.3 eV for V_6 without H termination. Even for the V_6 defect with 4 H termination, it require 1.8 eV barrier to diffuse. Therefore, it would be difficult to diffuse a Li atom through the six-membered ring would be difficult at room temperature.

On the other hand, it is well known that exchange diffusion process lower the diffusion barrier, where the Li atoms are adsorbed on the V_6 defect, and a diffusion atom pushes the adsorbed Li atom and it push out the Li atom on the reverse side.

To estimate how many Li atoms can adsorb on the V_6 site, we calculate the adsorption energy for an additional Li atom. The result is shown in Table 1. For V_6 defect 1st and 2nd Li atom obtain ~ 2 eV by the adsorption, however, 3rd Li atom lose 0.16 eV. Then, 2 Li atoms are easily adsorbed on the V_6 defect.

Table 1 Adsorption energy for additional Li atom on the V_6 defect

Number of Li atom	Adsorption Energy [eV]
1	-2.06
2	-2.06
3	0.16

For exchange diffusion, we consider a diffusion of 3rd Li atom from the nearby 6-membered ring to the other one on the reverse side. We found 2 different diffusion path I and II, as shown in Fig.2 and Fig.3, respectively. From the calculation of energy along two exchange diffusion path, we found the path II has a lowest energy barrier, which is less than 1 eV. The energy barrier is less than that of independent Li atom diffusion calculated above, and it would be possible to diffuse at room temperature.

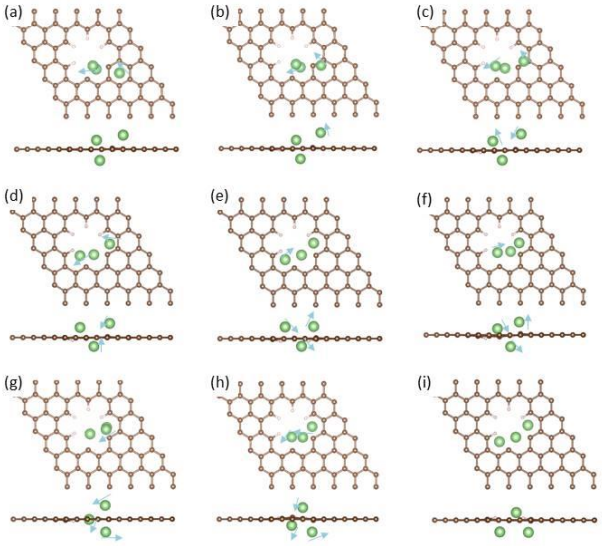

Fig. 2 The schematic top/side view of atomic configuration change for exchange diffusion pathway I, where Li atom diffuse from HR to that on the reverse side nearby V_6 defect.

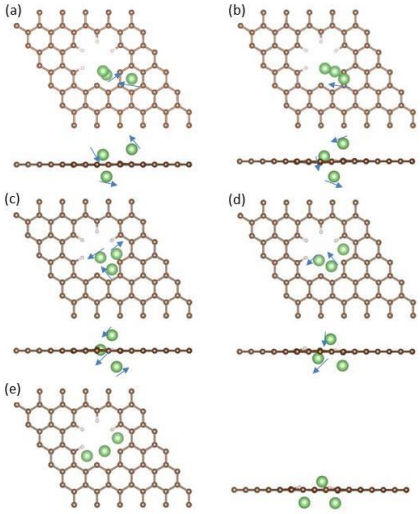

Fig. 3 The schematic top/side view of atomic configuration change for exchange diffusion pathway II, where Li atom diffuse from HR to that on the reverse side nearby V_6 defect.

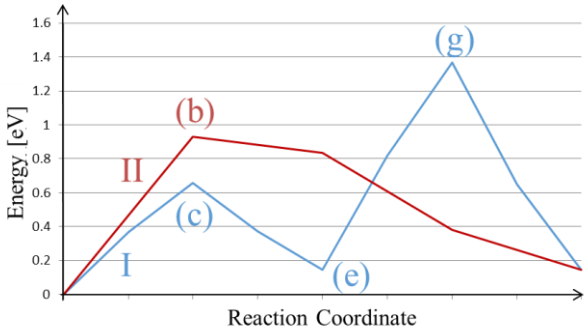

Fig. 4 The energy variation along exchange diffusion path I and II.

4. Conclusions

We calculated Li diffusion path through the defect toward backside of the graphene. Although there is a little diffusion barrier for clean edge, Li atom could be trapped at the deep potential hollow at the defect due to strong interaction between Li atom and dangling bond. We also investigated the Li atom diffusion through V_6 defect when the Li atoms are trapped at the defect site. We found that the trapped Li atoms reduce the attractive potential for a diffusing Li atom and enable the Li atom to diffuse by way of exchange diffusion.

Acknowledgements

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