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# Interaction of Lithium Ion ($Li^+$) with Chlorinated Graphene (Cl-Graphene) Surface: A Direct Ab-Initio MD Study

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*Electronic states of lithium ion ($Li^+$) interacting with a chlorinated graphene surface (Cl-graphene) have been investigated by means of hybrid density functional theory (DFT) to elucidate the effect of chlorination of graphene on the diffusion of lithium ion. Also, direct molecular orbital-molecular dynamics (MO-MD) calculation [H. Tachikawa, J. Phys. Chem. C, 112 (2008) 10193] was applied to diffusion processes of the $Li^+$ ion on Cl-graphene. The potential barrier height for movement of $Li^+$ was estimated to be 2.95 kcal/mol on Cl-graphene. The direct MO-MD calculations showed that the $Li^+$ ion diffuses freely on bulk and edge region of Cl-graphene at 300 K. The nature of the interaction between $Li^+$ and Cl-graphene was discussed on the basis of theoretical results.*

**Keywords:** ab-initio MD; charge distribution; chlorinated graphene; diffusion of lithium ion; effect of halogen

## 1. INTRODUCTION

Graphene is a carbon sheet composed of hexagonal carbon units and one of the high performance materials utilized as an electronic

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molecular device. They consist of a hexagonal carbon network arranged disorderly and are close to amorphous carbon. Compared with graphite materials with layered structure consisting of graphite sheets, the amorphous carbon has higher electromotive force and higher energy density. For example, theoretical maximum capacity of normal graphite material for lithium ion ($LiC_6$) is 372 mAh/g [1], whereas the amorphous carbon materials have remarkably high capacities (500–1100 mAh/g) [2]. The characteristics are originated from non-layer structure where Li atom and ion are stored in the edge region of the carbon layer. Therefore, several investigations for the interaction between carbon surface and alkaline metals have been carried out from both experimental and theoretical points of view [3–9].

Recently, the halogen substitution and doping have been examined to develop higher performance graphite materials [10,11]. Delabarre *et al.* used fluorinated graphite as the cathode in primary lithium batteries. The higher capacity values were achieved for low temperature fluorinated graphite [11]. The halogenation of carbon materials is possible to open new materials chemistry. However, the effects of halogen substitution on the electronic structure of the carbon materials are not clearly understood.

In the present paper, we applied density functional theory (DFT) and direct molecular orbital-molecular dynamics (MO-MD) methods to a diffusion dynamics of the $Li^+$ ion on the model surface of chlorinated graphene (denoted by Cl-graphene) to shed light on the development of high performance graphene from quantum mechanical point of view. In particular, we focus our attention on interaction of $Li^+$ ion with Cl-graphene, because this is strongly related to development of high performance lithium secondary battery.

In previous papers [12,13], we have investigated the $Li^+$ ion on the model surface of graphene to elucidate quantum chemically the diffusion dynamics using direct MO-MD method [12–18]. It was found that the $Li^+$ ion diffuses along the node of highest occupied molecular orbital (HOMO) of carbon surface. More recently, diffusion dynamics of $Li^+$ on fluorinated graphene surface (denoted by F-graphene) were investigated by means of direct MO-MD method [19]. The edge of graphene surface is terminated by F atom. The $Li^+$ ion diffuses on the surface, but the ion can not approach the edge region. This is due to the fact that the C-F bond in the edge region is polarized as $C^{\delta+}$-$F^{\delta-}$ and the carbon atom has a positive charge. Therefore, the $Li^+$ ion can not approach the edge region due to positive-positive electrostatic repulsion. In the present work, the similar technique is applied to the $Li^+$ ion on Cl-graphene.

## 2. METHOD OF CALCULATION

As a model of chlorinated graphene, a graphene sheet composed of $C_{96}Cl_{24}$ (denoted by Cl-graphene) was examined in the present study. The structures of Cl-graphene including $Li^+$ ion were fully optimized at the B3LYP/LANL2MB and AM1 levels of theory. It was assumed that one $Li^+$ ion is put on the center-of-mass of Cl-graphene (denoted by site-A), and then the structures of $Li^+$ – F-graphene were fully optimized. It should be noted that AM1 calculation represents reasonably the structural and electronic feature of the lithium-graphite system: charge and activation energy for the diffusion are in good agreement with those of B3LYP/LANL2MB [12,13,19]. For comparison, F-graphene ($C_{96}F_{24}$, F-graphene) was calculated with the same manner.

Diffusion processes of $Li^+$ ion on Cl-graphene were investigated by means of direct MO-MD method. The total energy and energy gradient on the multi-dimensional potential energy surface of the $Li^+$/Cl-graphene were calculated at each time step at the AM1-MO level of theory, and then classical equation of motion is full-dimensionally solved. Therefore, charges and electronic states of the $Li^+$ ion and all atoms are exactly treated within the level of theory by the calculations at each time step. This point is much different from usual classical molecular dynamics (MD) calculation where the charges of all atoms and ion are constant during the diffusion. Hence, one can obtain details of the diffusion processes of $Li^+$ ion on amorphous carbon using direct MO-MD method. All DFT calculations were carried out using Gaussian 03 program package [20]. Details of the method are described in elsewhere [21–23]. Electronic states and atomic charges were investigated by means of natural bond population analysis (NPA) [24].

## 3. RESULTS

### 3.1. Structure and Electronic States of the Cl-Graphene

The geometry of Cl-graphene was fully optimized at the B3LYP/LANL2MB level. It was found that two stable structures of Cl-graphene exist as local minima on the ground state potential energy surface. One is a planar structure where all atoms are located on the molecular plane of Cl-graphene (planar form), while the other one is non-planar structure where Cl atoms of graphene have twist positions from the graphene sheet (twist form). The twist form is 7.1 kcal/mol stable in energy than the planar one. The band gap of Cl-graphene (planar) is calculated to be 2.09 eV, while that of twist form is 2.13 eV which is slightly wider than planar one. The stabilization of twist form is caused by structural change to avoid the electrostatic repulsion between Cl atoms. In the present study, all discussion hereafter was based on the results of twist form. The optimized structure of Cl-graphene is illustrated in Figure 1. The graphene sheet is deformed from the planar structure where adjacent Cl atoms are twisted each other.

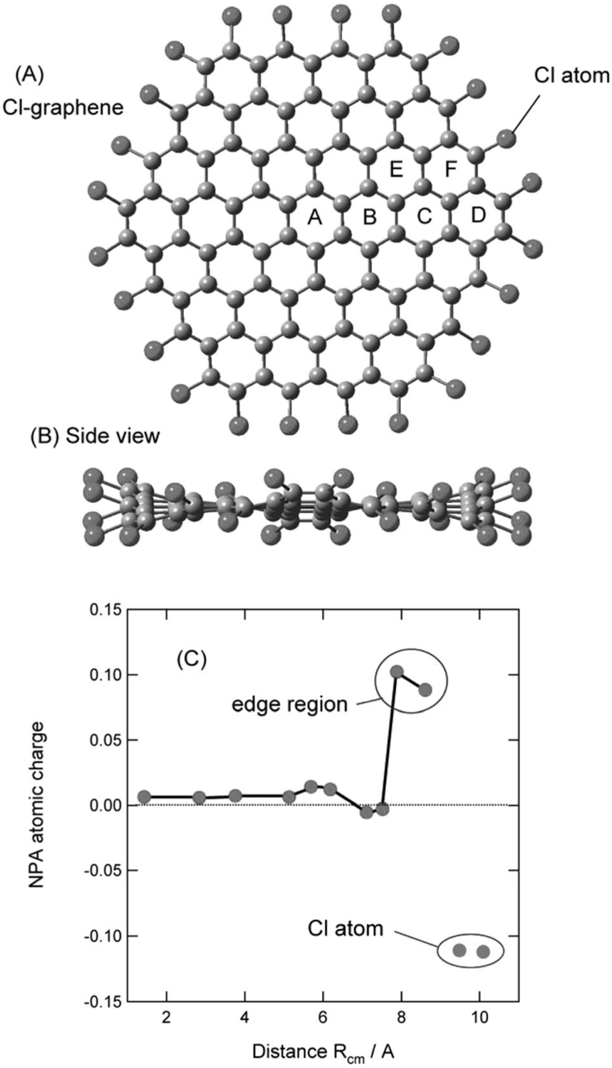

**FIGURE 1** Optimized structures of Cl-graphene ($C_{96}Cl_{24}$) calculated at the B3LYP/LANL2MB level (A) and side view of Cl-graphene (B), and NPA atomic charges of carbon atoms of Cl-graphene plotted as a function of $R_{cm}$ (C).

### 3.2. Binding Structure of Li$^+$ on the Cl-Graphene

There are five positions as trapping sites of Li$^+$ ion on the Cl-graphene surface (denoted by sites A-F). The binding sites are positioned in Figure 1. The geometry optimization indicates that the Li$^+$ ion in all sites are located at about 1.7 Å above the graphene plane. The relative energies of Li$^+$ ion at sites A-F are given in Table 1. The relative energies of all sites were distributed within ±1 kcal/mol. The barrier height between sites A and B was 2.95 kcal/mol, indicating that the Li$^+$ ion can move easily between sites on the Cl-graphene surface.

For comparison, the relative energies of the Li$^+$ ion on F-graphene are given in Table 1. The Li$^+$ ion in sites D and F (near edge of graphene) were 3.6 and 2.0 kcal/mol higher in energy than site A, respectively. In case of Cl-graphene, the energies of sites D and F were −1.9 and 0.3 kcal/mol (site F), which are significantly lower than those of F-graphene. Therefore, the ion can move easily on Cl-graphene.

NPA atomic charges of Li$^+$ on Cl$^-$ and F-graphenes are given in Table 1. In site A, the atomic charges were calculated to be +0.457 (Cl-graphene) and +0.703 (F-graphene). The similar tendencies are obtained in the other sites. These results indicate that magnitude of charge transfer from graphene to Li$^+$ on Cl-graphene is larger than that on F-graphene.

The charges of carbon atoms of the Cl-graphene are plotted as a function of center of mass distance of the graphite ($R_{cm}$). The results are given in Figure 1 (C). In the bulk region of Cl-graphene ($R_{cm}$ = 0.0–7.5 Å), the charges of carbon atoms are close to zero, indicating that the carbon atoms on the bulk surface have neutral charge. The charges are slightly changed to positive in the inner edge region ($R_{cm}$ = 7.6–9.0 Å). Magnitude of positive charges was calculated to be 0.08–0.10. However, this value is significantly smaller than that

**TABLE 1** Relative Energies of Li$^+$ ion on Cl and F-Graphenes (ΔE in kcal/mol) and NPA Charges of Li$^+$ ion Calculated at the B3LYP/LANL2MB

| | Cl-graphene | | F-graphene[a] | |
|---|---|---|---|---|
| Site | ΔE | NPA charge | ΔE | NPA charge |
| A | 0.0 | 0.457 | 0.0 | 0.703 |
| B | −0.5 | 0.453 | 0.0 | 0.698 |
| C | 1.0 | 0.474 | 1.3 | 0.697 |
| D | −1.9 | 0.518 | 3.6 | 0.683 |
| E | 0.9 | 0.467 | 1.5 | 0.702 |
| F | 0.3 | 0.502 | 2.0 | 0.680 |

[a] Cited from our previous paper [H. Tachikawa, *J. Phys. Chem. C*, 112 (2008) 10193].

of F-graphene (0.40–0.50). Therefore, it is expected that the $Li^+$ ion on Cl-graphene can move freely on both surface and edge region.

### 3.1. Diffusion of the $Li^+$ Ion on Cl-Graphene at 300 K

To elucidate the effect of chlorination of graphene, direct MO-MD calculation is preliminary carried out at room temperature (300 K). It is assumed that the $Li^+$ ion is located in the center-of-mass (site A) at time zero. After thermal activation, the $Li^+$ ion moves at 300 K. The trajectory of $Li^+$ ion at 300 K superimposed on Cl-graphene is given in Figure 2. The $Li^+$ ion starting from the center-of-mass (site A) runs against to the edge region of the graphene. The ion reaches the edge region at 0.5 ps. After that, the ion vibrates in bay region of Cl-graphene. The energy of the system was stabilized in this region.

In previous study [19], we showed that $Li^+$ ion on F-graphene can not approach the edge region. This is due to the fact that the charges of carbon atoms of the C-F bond have a large positive value, Hence, $Li^+$ ion does not approach sites D and F at low temperature because of electrostatic repulsion interaction. On the other hand, the $Li^+$ ion

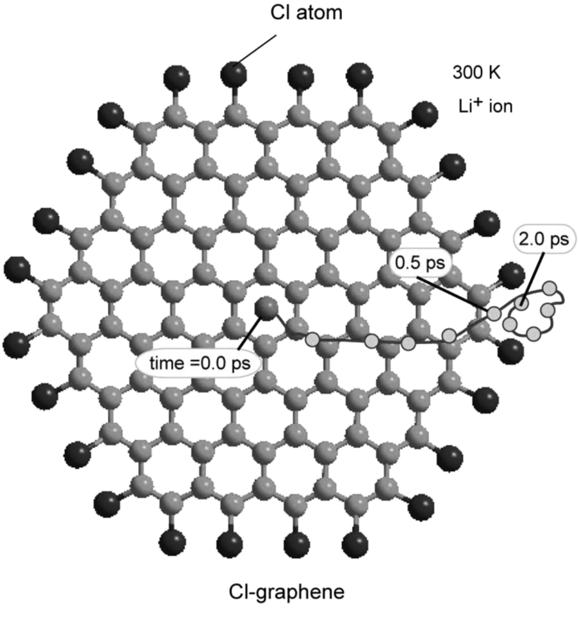

**FIGURE 2** Typical trajectory of diffusion of $Li^+$ ion superimposed on the Cl-graphene at 300 K. The $Li^+$ ion is started from the center-of-mass of Cl-graphene.

can move freely on the Cl-graphene. The electrostatic repulsion between Li+ and positive charge of edge carbon is significantly small in case of Cl-graphene.

## 4. SUMMARY

In the present study, DFT and direct MO-MD calculations have been carried out for the $Li^+$ ion trapped on the chlorinated graphene (Cl-graphene) to elucidate the nature of lithium- chlorinated graphene surface interaction. The B3LYP/LANL2MB calculation showed that the $Li^+$ ion is stabilized in both bulk surface and bay aria of Cl-graphene. The direct MO-MD calculations showed that the $Li^+$ ion diffuses freely surface and edge region at 300 K. This feature is much different with $Li^+$ on F-graphene.

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