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Tetsuji Iyama [a], Hiroshi Kawabata [a] & Hiroto Tachikawa [a]

[a] Division of Materials Chemistry, Graduate School of Engineering, Hokkaido University, Sapporo, Japan

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A Direct Molecular Orbital–Molecular Dynamics (MO–MD) Study on the Diffusion of Alkaline Ions on Amorphous Carbon

Tetsuji Iyama
Hiroshi Kawabata
Hiroto Tachikawa
Division of Materials Chemistry, Graduate School of Engineering, Hokkaido University, Sapporo, Japan

Hybrid density functional theory (DFT) calculations have been carried out for the lithium ion-carbon cluster model systems to elucidate the nature of lithium-carbon surface interaction. Also, direct molecular orbital-molecular dynamics (MO–MD) calculation [Tachikawa and Shimizu, J. Phys. Chem. B, 109 (2005) 13255] was applied to diffusion processes of the Li ion on the model surfaces of amorphous carbon. Seven cluster models (n = 7, 14, 19, 29, 37, 44 and 55, where n means numbers of rings in the carbon cluster models) were considered in the present study. The B3LYP/LANL2MB calculations showed that the lithium ion is located at ca. 1.60 Å from the carbon surface. The direct MO–MD calculations showed that the Li ion diffuses freely on the surface above 250 K. At higher temperature (1100 K), the Li ion moves from the center to edge region of the model surface and leaves from the surface. The nature of the interaction between Li^+ and the carbon clusters was discussed on the basis of theoretical results.

Keywords: amorphous surface; charge distribution; DFT; diffusion of lithium and sodium ions

1. INTRODUCTION

Amorphous carbon has ability to accommodate many species on the surface region and also in the edge region of the carbon sheet.

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Address correspondence to Hiroto Tachikawa, Division of Molecular Chemistry, Graduate School of Engineering, Hokkaido University, Sapporo 060-8628, Japan. E-mail: hiroto@eng.hokudai.ac.jp

Actually, 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]. This characteristics is 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].

To elucidate mechanism of lithium battery, Jungblut and Hoinkis investigated experimentally the diffusion kinetics of Li on highly oriented pyrolytic graphite (HOPG) at Li dilute concentration and temperature range from 1000 to 1300 K using isotopes ^{7}Li and ^{6}Li. They found that the Li transport in HOPG is strongly anisotropic, and the Li diffusion coefficient (D) in the direction of carbon plane is measured to be $D = 0.76 \times 10^{-9}$ m^2/s at 1070 K [10]. From the analysis of lattice image and NMR spectra, Sato *et al*. predicted that the Li atom exists in disordered carbon site [11].

The interactions between Li/Li^+ and graphite surface have been investigated theoretically by several groups using lithium-carbon cluster models. Yamabe and his co-workers investigated the interaction of Li atom with polycyclic hydrocarbon molecules (pyrene, anthracene, and phenanthrene) [12], and binding energies for several sites of carbon surface are calculated using the B3LYP/6-31G(d)//HF/6-31G* level. They showed that both the edge and ring-over sites can store the lithium atom. More recently, Suzuki *et al*. investigated the storage state of the Li^+ ion with a $C_{54}H_{18}$ cluster using the PM3 method [13].

Thus, the elucidation of the diffusion processes of the lithium atom and ion on the amorphous carbon is one of the important themes in development of higher performance lithium secondary battery. However, the dynamics feature of the diffusion of the species is scarcely known due to a lack of theoretical method to treat the diffusion dynamics in quantum mechanical level of theory. Recently, we have developed a dynamics method to calculate the trajectory on the full dimensional potential energy surface obtained by ab-initio and semi-empirical molecular orbital (MO) methods [14–18]. This method, called direct ab-initio molecular orbital-molecular dynamics (MO–MD) method, has been applied to chemical reactions, dynamics of molecular clusters, and diffusions of atoms and ions in materials [14–18].

In previous articles [14,19], we investigated the Li^+ ion on the model surface of amorphous carbon to elucidate quantum chemically the diffusion dynamics [14]. It was found that Li^+ ion diffuses along the node of highest occupied molecular orbital (HOMO) of carbon surface.

In the present article, we applied DFT and direct MO–MD methods to a diffusion dynamics of the Li ion on the model surfaces of amorphous carbon to shed light on the mechanism of lithium battery from quantum mechanical point of view. In particular, we focus our attention on interaction of Li ion with the amorphous carbons, because this is strongly related to mechanism of lithium secondary battery.

2. METHOD OF CALCULATION

The structures of Li^+ model clusters 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 the model cluster (denoted by site-A), and then the structures of the Li^+-carbon clusters 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 [14,19].

Diffusion processes of Li^+ ion on the carbon clusters were investigated by means of direct molecular orbital-molecular dynamics (MO–MD) method. The total energy and energy gradient on the multidimensional potential energy surface of the Li^+-carbon clusters 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 atom and all carbon and hydrogen 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 lithium ion on amorphous carbon using direct MO–MD method. Details of the method are described in elsewhere [14–19]. All density functional theory (DFT) calculation was carried out using Gaussian 03 program package [20].

3. RESULTS

3.1. Binding Structures of Lithium Ion on Several Carbon Cluster Models

The structures of the carbon clusters with a Li^+ ion are illustrated in Figures 1 and 2. The optimized parameters are given in Table 1. We assume that the Li ion is located near the center of mass of the cluster model. Although the structure of the carbon cluster without Li^+ ion is purely planar, the Li ion-doped carbon clusters have lens-like

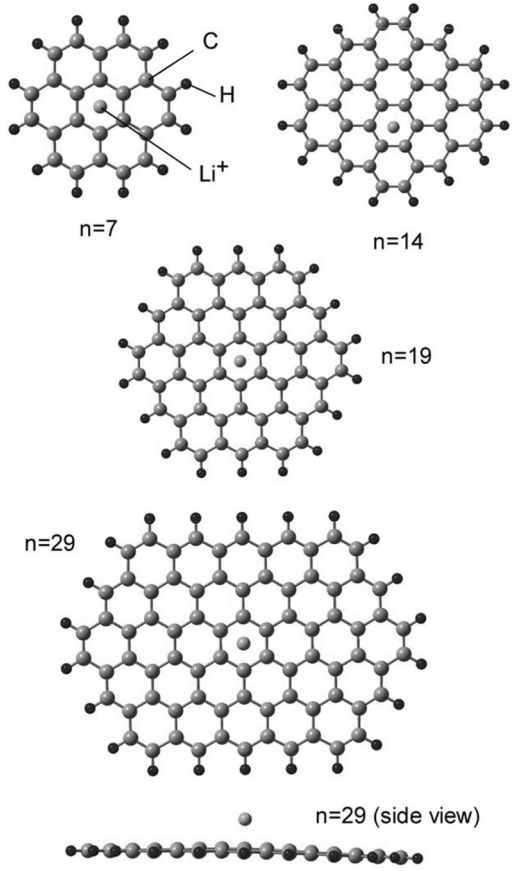

FIGURE 1 Optimized structures of Li^+ ion-carbon model clusters (small-sized clusters, n = 7, 14, 19 and 29) obtained at the B3LYP/LANL2MB calculation.

structure as shown in Figures 1 and 2. In all systems, the Li ions are located in the ranges 1.652–1.691 Å above the carbon surface at the optimized structures, indicating that the distance is hardly affected by the cluster size (n).

The Mulliken atomic charges of Li^+ ion on several carbon clusters are given in Table 1. The charges calculated for n = 7–52 are close to 0.415–0.452 at the B3LYP/LANL2MB level, indicating that about 60 % of hole is transferred from Li^+ to the carbon surface. This is due to the fact that electron transfer occurs efficiently from the carbon cluster to the Li^+ ion. To elucidate the basis set dependency,

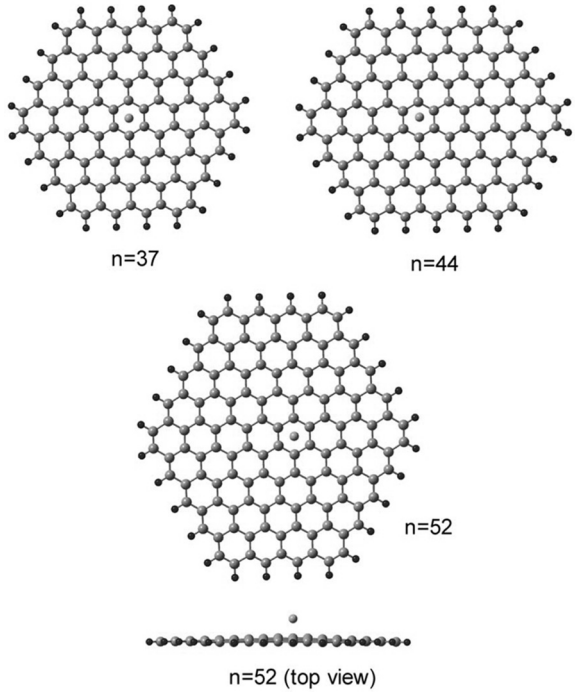

FIGURE 2 Optimized structures of Li^+ ion-carbon model clusters (large-sized clusters, n = 37, 44, and 52) obtained at the B3LYP/LANL2MB calculation.

TABLE 1 Optimized Geometrical Parameters and Charges of Li^+ Ion on Several Carbon Surfaces Calculated at the B3LYP/LANL2MB and B3LYP/6-31G(d) Levels of Theory

		Charge	
n	Distance/Å	B3LYP/LANL2MB[a]	B3LYP/6-31G(d)[a]
7	1.667	0.452	0.409
14	1.691	0.427	0.404
19	1.661	0.421	0.402
29	1.657	0.418	0.401
37	1.652	0.425	0.401
44	1.654	0.420	0.402
52	1.654	0.415	0.400

[a]Structures are optimized at the B3LYP/LANL2MB level.

the B3LYP/6-31G(d)//B3LYP/LANL2MB calculation is carried out for all systems. The charges for n = 7, 19, 37, and 52 are calculated to be 0.409, 0.402, 0.401, and 0.400, respectively. The charge is not dependent on the cluster size and are almost constant to be 0.40, which is in good agreement with that of the B3LYP/LANL2MB level. The 2p-orbital of lithium ion parallel to the carbon surface interacts with the 2p-orbitals of carbon atoms. Therefore, node of HOMO is important in the diffusion of Li^+ ion on the carbon surface.

3.2. Diffusion of the Li Ion at 1100 K

First, the direct MO–MD calculations are carried out at lower temperature below 200 K. However, the Li ion does not move on the surface. It is assumed that the Li^+ ion is located in the center-of-mass at time zero. After thermal activation, the Li ion can move above 250 K.

The trajectory of Li^+ ion at 1100 K superimposed on the carbon surface are given in Figure 3. The Li ion starting from the center-of-mass runs against to the edge region of the carbon cluster. The ion reaches the edge region at 0.3 ps. After that, the ion leaves from the carbon surface.

The diffusion coefficient of the Li ion (D) is calculated to be $D = 0.74 \times 10^{-9}\,m^2/s$ at 1100 K. The corresponding experimental value

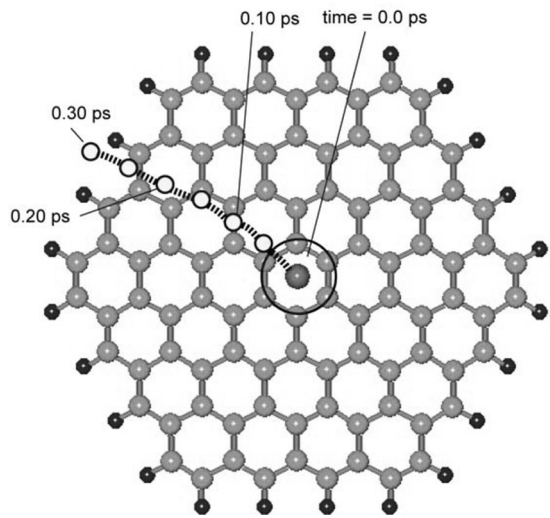

FIGURE 3 Trajectory of Li ion superimposed on the carbon cluster (n = 37) at 1100 K. The Li atom is started from the center-of-mass of the cluster.

for diffusion of Li^+ is $0.76 \times 10^{-9}\,m^2/s$ in graphite at 1070 K [10]. This agreement implies that the present calculation would be valid to simulate the diffusion processes of Li^+-carbon systems.

4. CONCLUSION

In the present study, first, DFT calculation has been carried out for the lithium ion-carbon cluster models to elucidate the nature of lithium-carbon surface interaction. Seven cluster models ($n = 7$, 14, 19, 29, 37, 44 and 55, where n means numbers of rings in the carbon cluster models) were considered in the present study. The B3LYP/LANL2MB calculations showed that the lithium ion is located at ca. 1.60 Å above the carbon surface. The direct MO–MD calculations showed that the Li ion diffuses freely on the surface above 250 K. At higher temperature (1100 K), the Li ion moves from the center to edge region of the model surface and leaves from the surface.

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