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Study on thermal behaviors of Li/H atom in the bulk graphite by molecular dynamics method

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Abstract A system with periodical structure of graphite, in which a Li or H atom is set in the center of the supercell, has been simulated by molecular dynamics method to study the thermal diffusion of Li and H in the bulk graphite. It is found that the rates of diffusion of both Li and H atoms increase with the increase of the simulation temperature: from 50 K to 200 K, and the specific diffusive rates and behaviors for Li and H are different according to their trajectories. The diffusive curves for Li can be classified into three types, while H has only one type of diffusive curve, which shows that the interaction between Li and carbon is weaker than that between H and carbon. The conductive band gap of graphite is also calculated by the extended Hückel method. The gap is broadened by about 0.1 eV when graphite is intercalated with H, but the gap remains unchanged when graphite is intercalated with Li. It indicates that the addition of Li does not influence the conduction characteristic of graphite while that of H does. Thus Li-GIC (Graphite Intercalated Compound) is proposed to be a favorable material for the electrode.

Introduction

The continuing and intensive demand for lighter and smaller mobile electronic devices, especially cellular phones and other portable devices, has driven the fast development of higher capacity Li-ion batteries [1–4]. At the same time, the growing interest in hybrid electric vehicles has put emphasis on the development of new anode materials that are safe and have high energy density [5, 6]. Graphite is inherently a semiconductive material with layered structure, which is intercalated by some atoms and molecules to form the stage structures of graphite intercalated compounds (GICs). The typical graphite intercalated compound is Li-GIC, which is widely used in secondary batteries because of its excellent performance such as high storage capacity, high electromotive force and high electron density. And these materials may provide some unique features for those requirements.

There still exist arguments concerning the reason for excess amount of storage of Li in amorphous carbon than that expected in graphite both experimentally and theoretically [7, 8]. One of the effective methods to understand and resolve this question is to study the behaviors of light atom such as Li and H in graphite by calculating in term of molecular dynamics (MD), while such work is not often found [8, 9] for Li/H-GIC. In present paper, the trajectories of Li and H atoms in bulk graphite supercell model in term of MD were calculated at the temperature from 50 K to 200 K. Thermal behaviors of these two kinds of atoms intercalated in the bulk graphite were compared based on the results of MD simulation and calculation. Besides, the band structures of the intercalated graphite by Li and H were also calculated by the extended Hückel method and it is found the changes between the electronic structure of Li-GIC and that of H-GIC are different.

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Method and model of calculation

Molecular dynamics simulation was carried out with the Materials Studio software package [10] using Condensed-phase Optimized Molecular Potentials for Atomistic Simulation Studies (COMPASS) force field. It is a powerful all-atom force field supporting simulations of condensed-phase materials, which is suitable for C, Li and H elements. It is demonstrated that MD method using COMPASS force field is an effective way for simulation and calculation of structures and thermal behaviors of kinds of materials [11–13]. Periodic boundary conditions were used for the MD runs, and after the minimization of energy of system, the system should be heated up to a certain temperature and then the dynamic procedures would be progressed. Thus, the ensemble NVT (Constant Temperature, Constant Volume) was chosen to heat up the system to 50, 100, 150 and 200 K, respectively and then the ensemble NVE was chosen. When NVE (Constant Energy, Constant Volume) was chosen, the system was kept on a constant total energy level and the dynamic process was going on. The thermodynamic behaviors of the system including the intercalated atoms (Li and H) should be obtained. Velocity Verlet was used as the integration method and the initial velocities were gained from Boltzmann distribution. Iteration step time was chosen as 0.2 fs. Trajectories were saved every 20 steps and 20 ps trajectories in total were collected for the analysis.

The model for calculation is a periodical structure of graphite centered with a light atom Li or H, which compose a supercell as shown in Fig. 1. Each supercell is formed by six carbon-stacking layers with each layer having nearly 200 carbon atoms as shown in Fig. 2. The lattice parameter of the supercell is about 20 Å. To simulate the thermal behaviors of Li/H-GIC, a large-sized structure is desired in order to get a high quality calculation, so the periodical structure of Li/H-GIC is adopted in this paper. The distances from the position of Li/H at the beginning time to the positions of Li/H during the simulation are measured. And the distances from Li/H to the nearest carbon atom are also measured during the calculation. In this paper, the mean square distance (MSD) of the light atoms diffusing in bulk graphite is defined as

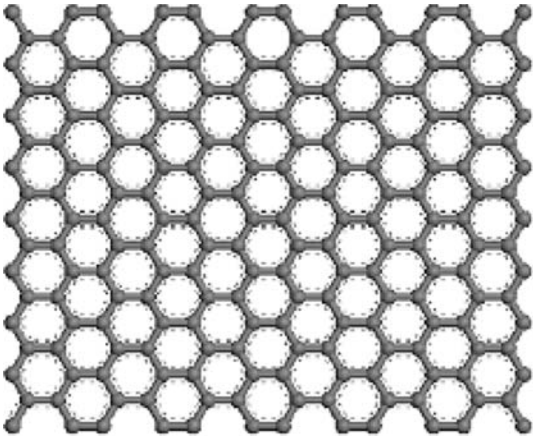

Fig. 2 Carbon layer, six of which compose a supercell together with Li & H

$$MSD = \left\langle \left| \overline{r}_i(i) - \overline{r}_i(0) \right|^2 \right\rangle,$$

among which $\overline{r}_i(i)$ and $\overline{r}_i(0)$ are the position vector versus time, respectively. The diffusion coefficient is defined as

$$D_a = \lim_{t \to \infty} \frac{1}{6t} \left\langle \left| \overline{r}_i(i) - \overline{r}_i(0) \right|^2 \right\rangle.$$

Calculation results

After initial optimization of the supercell structure, the distance between the two layers in the bulk graphite is 3.40 Å, which is very close to the acknowledged value of 3.35 Å [14]. For the supercell intercalated with light atoms Li or H atom, result of the optimization is given in Figs. 3 and 4, where Li and H atom almost are stabilized at the center of mass with the distance to the nearest carbon atom being 2.43 and 2.52 Å, respectively. The basic structure is not destroyed by the intercalation because intercalation of Li or H atom does not influence the attractive force between the upper and lower sets of layers, which are combined with each other through the delocalized Π bonds and the van der Waals forces. But the swelling of layers near Li

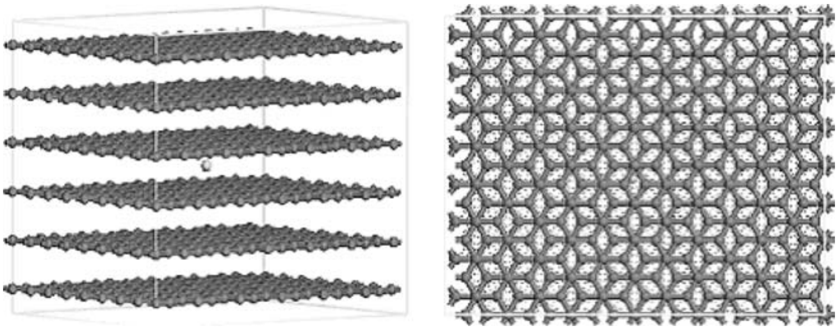

Fig. 1 A supercell of Li/H-GIC with Li/H atom stabilized in the center

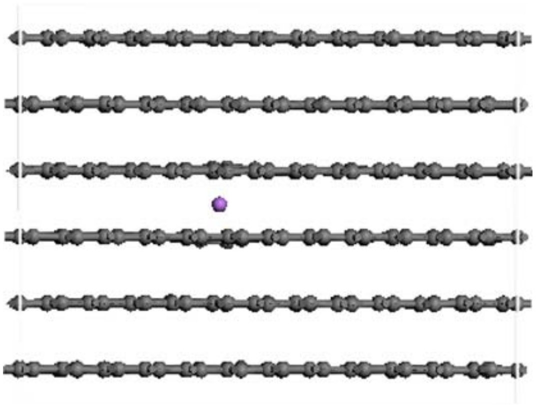

Fig. 3 Optimized structure intercalated with Li in the center

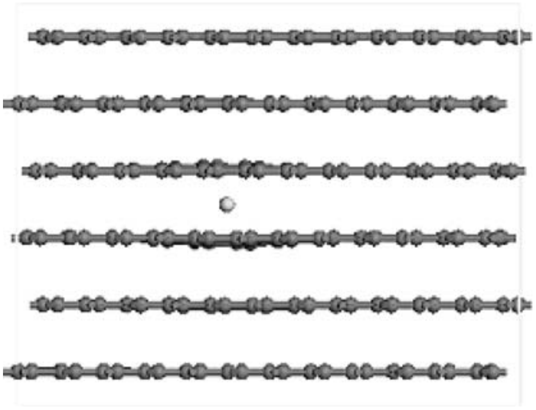

Fig. 4 Optimized structure Intercalated with H in the center

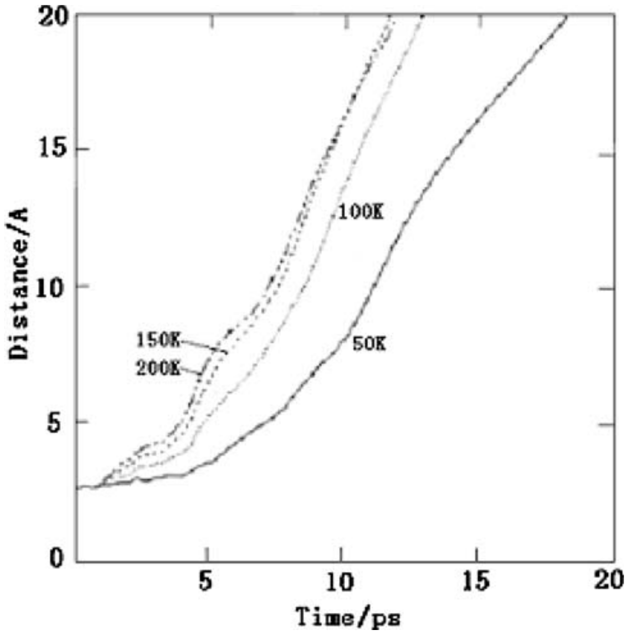

Fig. 5 Trajectories of the distance for H atom intercalated in bulk graphite

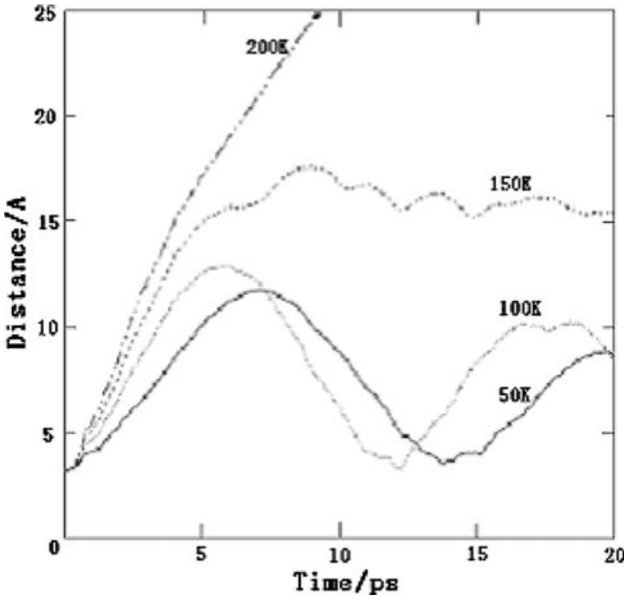

Fig. 6 Trajectories of the distance for Li atom intercalated in bulk graphite

and H atom was found because of the inclusion of Li or H atom. The swelling is strictly limited to the neighborhood of Li and H atom.

Time dependency of the distance for the intercalated H atom is given at various simulation temperatures in Fig. 5. On the basis of the lattice vibration, H atom is found to migrate from the center to the edge parallel to the layers with the lapse of time. The migration rate rises with the increases of the simulation temperature in the range of 50–200 K. The curves have an induction period initially and a flexion point at the distance of about 10 Å where the rate is decreased. Thus, the potential well will also arise in the circumference due to the geometrical arrangement of carbon atoms in the supercell model. The existence of the potential well in the circumference is consistent with the results by Lehnert et al. [15]. On the other hand, the trajectory of the Li atom is given in the same temperature range in Fig. 6. According to Fig. 6, the curves are classified into three types: the distance shows the periodicity below 12 Å for type I at both 50 and 100 K; the distance increases almost linearly up to 15 Å and is kept there for type II at 150 K; and the linear increase in the distance is found for type III at 200 K. For type I, it shows that the moving route for Li atom has a certain periodicity: Li goes forward and backward between the center and the edge on the nearest graphite layer periodically. Such periodicity makes the hitting distance independent of the temperature, but it is obvious that the rate of migration increases with the higher temperature. For type II, the migration of Li atom has taken place away from the center but is retained in a limited region, that is, not beyond the supercell, for this situation. The curve for type III indicates that the migration of Li atom is not restricted in a limited area, contrary to type I and II, will extend from one supercell into another supercell nearby without any obstacles. Comparing both trajectories in Figs. 5 and 6, the migration rates are almost the same. However, the potential well is suggested to be deeper for Li since Li atom cannot escape easily below 150 K as shown in Fig. 6. This can be suggested as the reason why amorphous carbon has a larger storage capacity than graphite: it may be attributable to the tendency that Li atom stabilize and move more easily in amorphous carbon than in graphite because of the deference between the structures of amorphous carbon and graphite. It should be addressed deeply in future research work about the different structures between amorphous carbon and graphite.

Discussion

Concerning the intercalations of Li and H atom in the periodical structure model, calculated results were compared between those of Li and H atom at the same calculation level. It was found that swelling was limited to the narrower central area by Li atom than by H atom. Moreover, based on the translational distance during the initial simulation time ($0 \le t \le 0.3$ ps) in Figs. 5 and 6, the initial rate of Li atom at 200 K was averaged as 2.6×10^3 m/s, which is faster than that of H atom, 6.8×10^2 m/s, calculated in a similar manner at the same simulation temperature. These facts mean that Li atom interacts with host carbon atom weaklier than H atom does, which can be attributed to the fact that the closed shell of $1s^2$ electrons of Li atom restricts the strong attractions of nucleus for p_z electron of carbon lattice. The characteristic high migration rate of Li atom will be due to this shield effect other than the small mass number. According to the shield effect of nucleus, the proton reacts immediately with the environments in solid if the$1s^2$ electrons are absent.

For investigation of the semiconductive property of graphite, variations of the band gap with intercalation of Li and H atom is calculated in terms of the extended Hückel method [16]. The result is illustrated in Figs. 7 and 8. No variations occurred in the band gaps with intercalation of Li. Thus, it indicates Li atom does not influence the conduction mechanism. This is different from the results for H atom, which reduced the electronic conductivity by increasing the band gap by 0.1 eV. In other words, the conductivity of graphite will decrease when intercalated with H, while maintain unchanged when intercalated with Li. Accordingly, Li-GIC is proposed to be a favorable material for the electrode with high conductivity from the present calculations.

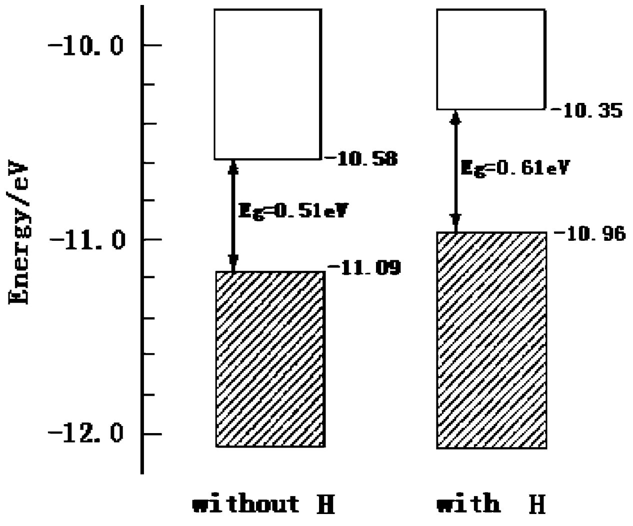

Fig. 7 Schemes of the band gaps for H-GIC

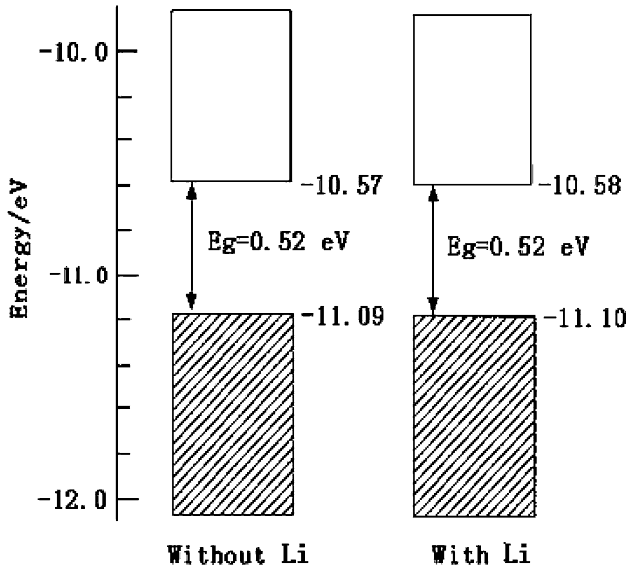

Fig. 8 Schemes of the band gaps for Li-GIC

Conclusions

The simulation studies on the thermal behaviors of Li and H atom intercalated in bulk graphite have been carried out using molecular dynamics method. The simulation results indicate that the interaction between Li and graphite is weaker than that between H and graphite. And because of the intercalation of H, the band gap for H-GIC is broadened by 0.1 eV while this does not happen to intercalation of Li. All of these results point to the fact that Li-GIC is proposed to be a favorable material for the electrode with high conductivity.

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