



Thermal diffusion of correlated Li-ions in graphite: A hybrid quantum–classical simulation study



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ABSTRACT

Diffusion of Li-ions in graphite is an essential elementary process in the current lithium-ion battery. The C-layers of graphite deform with Li due to relatively large size of Li-ion, act to confine the Li-ions, and thereby creates correlation between them. We address theoretically the thermal diffusivity of such correlated Li-ions in graphite by the hybrid quantum–classical simulation method. In this method, the quantum-region composed of the Li-ions and surrounding C atoms is treated by the density-functional theory, while it is embedded dynamically in the total system described with an empirical inter-atomic interaction potential. We thereby take into account the long-ranged deformation field in graphite in simulating the Li-ion dynamics. Two kinds of settings of Li-ions are considered for the simulation runs at temperature 443 K: (i) seven Li-ions are inserted in the same inter-layer space of the C-layers to study their intra-plane correlation, and (ii) additional seven Li-ions are inserted in the neighboring space (i.e., fourteen Li-ions totally, 7 Li-ions in upper and 7 Li-ions in lower spaces) to study their inter-plane correlation. As for (i), the Li-ions, concentrated initially with inter-ion distances of 2.5–4.2 Å, scatter due to their mutual Coulomb repulsion. After about 1 ps, the Li-ions and surrounding C atoms thermalize well with deformed C-layers creating a cage of radius about 13.5 Å for 7 Li-ions. Diffusivity of Li-ions inside the cage is much higher than that of the cage itself. The long-time diffusion constant of the cage is the same order as that of an isolated Li-ion in graphite. As for (ii), the Li-ions, concentrated initially in the upper and lower inter-layer spaces of the C-layer, firstly form domains, and then the domains repel each other horizontally. The result is in accord with the experimental finding that the Li-rich and Li-poor planes stack in an alternating sequence in graphite.

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1. Introduction

There exist growing demands for the first-principles (i.e., electronic structure calculation) simulation of realistic interfaces such as the solid-electrolyte interface (SEI) [1] on the graphite anode in the lithium-ion battery (LIB), to investigate chemical reactions in the formation processes and transport properties of ions, electrons, and heat through SEI. In such simulation, the modeling system needs to be sufficiently large to take into account the structural relaxation of environmental atoms at breaking and/or formation of chemical bonds. The hybrid quantum (QM)-classical (CL) simulation [2,3] with the buffered-cluster method (BCM) [4] is one of the multi-scale simulation methods applicable to such a situation.

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In the hybrid QM–CL simulation, the QM regions treated by a QM method as the density-functional theory (DFT) are embedded in the CL system of atoms interacting via an empirical inter-atomic potential. With the BCM, we can treat mechanical coupling of the QM and CL atoms even in a crystalline solid. By varying the size and number of the QM region, one can shift the balance of physical accuracy and computation cost as desired. The hybrid QM–CL simulation method is suited for problems involving moving regions of chemical reactions. The hybrid QM–CL simulation has been applied to the nano-indentation of silicon by diamond-tip with H₂O [5] and the thermal diffusion process of a single Li-ion in graphite [6,7].

The lithium–graphite intercalation compound (Li–GIC) is put to practical use as the negative electrode of the LIB's. In the LIB, Li-ions move from the negative electrode to the positive one during discharge, and back during charging. Transport rate of Li-ions in graphite is related to the output power and fast charging of the

LIB's. Improving LIB's requires theoretical understanding of the Li-ion dynamics in realistic settings with high accuracies. In this connection, we performed the 2400-atom first-principles molecular dynamics simulation [1] and thereby analyzed the Li-ion transfer dynamics through the SEI–electrolyte interface. In the Li-GIC, Li-ion creates a long-ranged stress field around itself by expanding the inter-layer distance by about 10% [6,7]. It is therefore necessary to take into account such distortion of C-layers of graphite, in simulating the diffusivity of Li-ions in graphite.

Since the weak inter-layer interaction of graphite originates from the van der Waals interaction, conventional DFT with the local-density approximation (LDA) or generalized-gradient approximations (GGA) cannot treat it accurately. To overcome the problem, the DFT-D2 [8] and the van der Waals functional DFT such as the vdW-DF2 [9] have been proposed. Empirical inter-atomic terms describing the van der Waals interaction are added to the potential energy in the DFT-D2, and its physical accuracy depends on the parameter values used; that is, it has low transferability. On the other hand, the vdW-DF2 is more accurate and has high transferability at the price of high computational cost. Highly accurate quantum Monte Carlo simulation is applied also to the Li-GIC recently with huge computational cost [10]. In the hybrid QM–CL simulation, the van der Waals inter-layer interaction in graphite can be taken into account through a classical inter-atomic potential for both QM and CL regions, as demonstrated in our former simulations [2–7]. The stress-dependent thermal diffusivity of a single Li-ion in graphite was analyzed in Ref. [6]. In the present study, we will advance the simulation to treat the thermal diffusivity of multiple Li-ions in graphite with both interaction between Li-ions and deformation of surrounding C-layers taking into account explicitly.

Before investigating the thermal diffusivity of Li-ions in graphite, let us consider the ground state configuration of Li-ions at relatively low Li-concentration. It was confirmed that a Li atom ionizes in graphite by transferring the electron to the surrounding six-membered C-ring, which means that the positive charge of Li-ion is screened by its neighboring negatively charged C-atoms [6]. The Li-ion expands the inter-layer space by about 10% and thereby increases the potential energy of the graphite. Such a vertical deformation spreads horizontally to about 5 Å corresponding to the size of a six-membered C-ring. When multiple Li-ions exist in the same inter-layer space of graphite, they gather together with each Li-ion sitting on the center of every two six-membered C-ring, i.e., C₆Li structure, at the ground state; in other words, Li-ions are trapped in a C-cage. It is because the insertion energy of another Li-ion to already expanded C-layers is lower than that without expansion as the positive charge of a Li-ion is screened well by the neighboring C-atoms. In the present study we will investigate possible formation of the C-cage for Li-ions even at an elevated temperature and its effects on thermal diffusivity of Li-ions.

Rest of the present paper is organized as follows. The methodology and modeling will be explained in Section 2. In Section 3, we will show the results of the hybrid QM–CL simulation runs to investigate thermal diffusivity of multiples Li-ions in graphite at various settings. Summary and concluding remarks will be given in Section 4.

2. Methodology and modeling

Fig. 1 depicts a snapshot of a simulation run at temperature $T = 443$ K. The total system contains nine C-layers composed of 12,096 C-atoms. In total, seven Li atoms are inserted into the same inter-layer space. The two C-layers sandwiching the Li-ions are set to the AA-stacking (i.e., the C atoms on the two layers have identical x – y positions), while others the AB-stacking. As the stacking sequence of graphite is known experimentally for two extreme

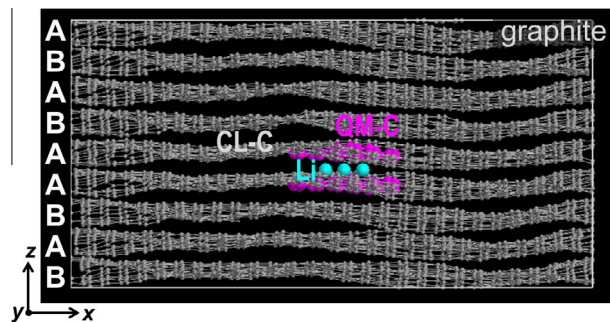


Fig. 1. The simulation system in the C₂Li run at $t = 0$ ps viewed from y -direction. Cyan, magenta, and gray spheres denote Li-ions, QM-C, and CL-C atoms, respectively. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

cases only (AB-stacking for pure graphite, while AA-stacking for the maximally Li-intercalated graphite at C₆Li stoichiometry), we start the simulation with the AA-stacking for the two sandwiching C-layers and then let the stacking sequence relax thermally. As we see in Figs. 1 and 9(b) below, the stacking sequence of the two sandwiching C-layers fluctuates and has substantial chances of assuming both AA and AB-stackings. A region around Li-ions is set as the QM one. The periodic boundary conditions are applied to x , y , and z -directions. The z -axis is perpendicular to the C-layers. The system size is set to $(L_x, L_y, L_z) = (59.57, 58.96, 30.58 \text{ \AA})$. The atomic configuration in Fig. 1 is obtained after relaxation for 1 ps at $T = 443$ K with the x – y positions of Li's fixed. The time step is 0.97 fs with the velocity-Verlet algorithm for the dynamics. The CL inter-atomic potentials used are explained below.

The Brenner's inter-atomic potential [11] is applied to the intra-layer interaction of C-atoms. The parameter values provided in Table 1 in Ref. [11] are employed except for the equilibrium inter-atomic distance, which is changed to 1.33116 Å so as to match with the one obtained by our QM calculation explained below. Such a tuning is necessary to suppress any artificial stress in the hybrid QM–CL simulation. Inter-layer interaction is taken into account by adding an environment-dependent Lennard-Jones-type potential for a pair of C-atoms belonging to two neighbor C-layers as

$$V_{\text{vdW}}(r_{ij}) = 4\epsilon \left[\left(\frac{a}{r_{ij}} \right)^{12} - \left(\frac{a}{r_{ij}} \right)^6 \right] g(r_{ij}), \quad (1)$$

where

$$g = \left\{ 0.98 + \frac{0.07}{\exp\{20[(Z_i + Z_j)/2 - 7]\} + 1} \right\}^6 \quad (2)$$

$$Z_i = \sum_k z_{ik} \quad (3)$$

$$z_{ik} = \begin{cases} 1, & \text{for } x_{ik} \leq 2.59 \text{ \AA} \\ 0.5 \left[1 + \cos \left(\pi \frac{x_{ik} - 2.59 \text{ \AA}}{0.2 \text{ \AA}} \right) \right], & \text{for } 2.59 \text{ \AA} < x_{ik} \leq 2.79 \text{ \AA} \\ 0, & \text{for } 2.79 \text{ \AA} < x_{ik} \end{cases} \quad (4)$$

$$f(r_{ij}) = \begin{cases} 1, & \text{for } r_{ij} \leq 5.4 \text{ \AA} \\ 0.5 \left[1 + \cos \left(\pi \frac{r_{ij} - 5.4 \text{ \AA}}{0.4 \text{ \AA}} \right) \right], & \text{for } 5.4 \text{ \AA} < r_{ij} \leq 5.8 \text{ \AA} \\ 0, & \text{for } 5.8 \text{ \AA} < r_{ij} \end{cases} \quad (5)$$

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