

Diffusivity of lithium in a graphite intercalation compound by combination of transition state theory and first principles calculations

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In-plane diffusion of lithium atoms in a stage-1 lithium-graphite intercalation compound has been investigated using first-principles calculations. The compound is widely utilized as a negative electrode in lithium-ion rechargeable batteries. The lithium diffusion is of interest in terms of the charge-discharge kinetics of the Li-ion batteries. In the present work, the mean jump frequencies of several types of the atomic jumps via lithium interstitials and vacancies are evaluated to estimate the lithium diffusion coefficient.

A statistical-mechanical approach based on the transition-state theory [1] is employed for the diffusion simulation. In this approach, questions are what types of atomic jumps happen and how often they occur. A mean frequency of atomic jumps in crystals are expressed as

$$\omega = \frac{kT}{h} \exp\left(-\frac{\Delta F}{kT}\right), \quad (1)$$

where k is Boltzmann's constant, h is Planck's constant, and T is the temperature. ΔF is the change in free energy of the system from the initial to the saddle point for the jump. It can be divided into two contributions; the potential barrier and the change in vibrational free energy ($\Delta F = \Delta E^{\text{mig}} + \Delta F^{\text{vib}}$). Figure 1 shows the schematic diagram of the potential hypersurface of an N -atom system, where the configuration coordinates are expressed by two axes; the atomic migration coordinate and the other coordinates ($3N-1$ dimensions). A, B and S denote the initial, final, and saddle point states, respectively. The potential energy of the system is the local minimum for all the coordinates at the initial and final states. At saddle-point state, in contrast, the potential energy is the local maximum for the migration coordinate, while it is the local minimum for the other $3N-1$ coordinates. Note that, for the evaluation of the change in vibrational free energy, the vibrational free energy is evaluated in $3N$ dimensions at the initial state, while that at the saddle point is in $3N-1$ dimensions; the migration coordinate is excluded. The motion along the migration coordinate at the saddle point is regarded as a one-dimensional translational motion with the Maxwell-Boltzmann distribution, leading to the pre-exponential factor kT/h in Eq. (1). The first-principles calculations are performed using the projector augmented wave (PAW) method as implemented in the VASP code [2]. The local density approximation (LDA) [3] is used for the exchange-correlation term.

Figure 2 shows the schematic drawings of the migration path by the vacancy mechanism. A vacancy is surrounded by six lithium atoms, and one of them jumps into the vacancy. As the result of the nudged elastic band method, a lithium atom does not migrate into the vacancy in a straight line trajectory but by way of a first-nearest-neighbor hexagon. The intermediate state in the hexagon is a metastable state, and the migration consists of the two elementary jumps; from the initial regular site to the intermediate site (Jump 1), and from the intermediate site to the final vacant site (Jump 2). The calculated potential barriers of Jumps 1 and 2 are 0.47 eV and 0.26 eV, respectively. The vibrational

free energies are evaluated for Jumps 1 and 2 using the frozen phonon method. The calculated changes in vibrational free energy for Jumps 1 and 2 are shown in Fig. 3. The changes for the two jumps are very similar in the entire range of temperature with a difference of less than 2 meV. This means that the vibrational contributions at the initial and metastable states are almost the same. Once the potential barriers ΔE^{mig} and the changes in vibrational free energy ΔF^{vib} are obtained, the mean jump frequencies can be evaluated from Eq. (1). The calculated mean jump frequency of Jump 1 is much smaller than that of Jump 2, e.g., $4 \times 10^4 \text{ s}^{-1}$ vs. $1 \times 10^8 \text{ s}^{-1}$ at room temperature. This is mainly due to the difference in potential barrier between the two jumps. It is found that the first jump is rate-determining in the vacancy mechanism.

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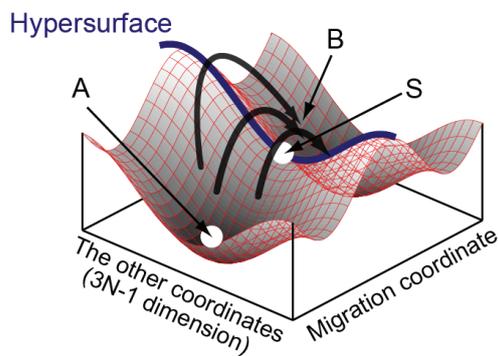


FIG. 1. Schematic diagram of the potential hypersurface of an N -atom system.

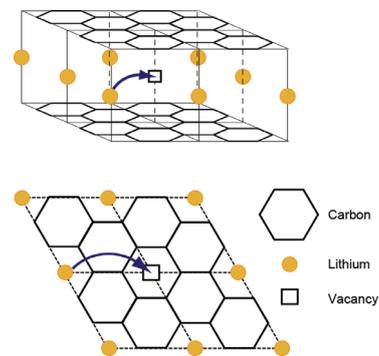


FIG. 2. Schematic drawings of in-plane jump of a lithium atom by the vacancy mechanism.

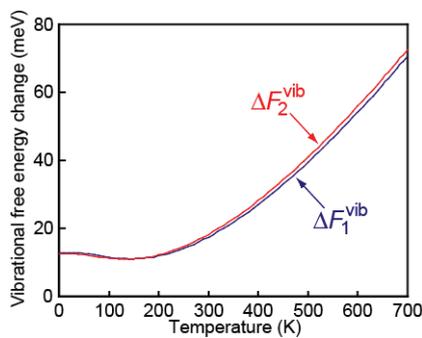


FIG. 3. Changes in vibrational free energy for Jumps 1 and 2.