Brief Report

Hybrid Quantum-classical Simulation of Intercalation Compounds

Nobuko Ohba and Shuji Ogata

1. Introduction

Layered materials such as graphite have the ability to incorporate ions and thus form intercalation compounds. In order to understand the materials properties of graphite intercalation compounds, it is important to investigate both the dynamics of the inserted ions and the nature of the bonds they form with graphite. In particular, Li-graphite intercalation compounds (Li-GICs), in which Li ions are inserted between graphite layers, are used as the negative electrode in Li-ion batteries. In these batteries, the migration characteristics of Li ions in graphite are directly related to the battery output power. Thus, to improve the battery performance, an accurate understanding of the atomic motion of Li is essential. In this study, the hybrid quantum (QM)-classical (CL) simulation method is applied to a Li-GIC in order to determine the thermal diffusion mechanism of Li ions in graphite.

2. Method

In our hybrid QM-CL simulation, a cluster consisting of Li and surrounding carbon (C) atoms is selected as the QM region where the quantum mechanical calculation is adopted, and the atoms in the QM region are embedded in the whole system described in the classical interaction model.

2. 1 Buffered Cluster Method

At the boundary between the QM and CL regions, interatomic bonds are severed and dangling bonds form. Since these dangling bonds are not originally there, it is necessary to subtract their effect on the electronic structure and on the atomic forces. In the present study, we use the buffered cluster method (BCM)[1] as a model for the boundary between the QM-CL regions. In the BCM, additional atoms (called buffer atoms) are introduced in order to terminate the dangling bonds. In the QM calculation, the buffer atoms are fixed at the positions determined through the CL calculation. Thus, the BCM suppresses artificial surface relaxation of the QM region, and as such, it is a general and highly precise model.

2. 2 QM Calculation

The real-space grid-based density functional theory (RGDFT) is adopted for the QM calculation, because it is suitable for parallel computation of the large-scale model and allows us to set boundary conditions flexibly. The details of the algorithm are described in Refs. (2) to (4). For the interaction between the valence electrons and nuclei (ions), Troullier-Martins type norm-conserving pseudopotentials[5] are used. The generalized gradient approximation parameterized by Perdew, Burke and Emzerhof (GGA-PBE)[6] is applied to the exchange-correlation energy term. The fourth-order finite difference scheme is used for the Laplacian operation. A mesh size of $h = 0.55$ a.u. (1 a.u. ≈ 0.5292 Å) is used. A finer grid spacing of $h/3$ is used only around the atoms.

2. 3 CL Calculation

A periodic boundary condition is imposed in the CL molecular dynamics calculation, and a velocity Verlet algorithm is applied to integrate Newton's equations of motion. The Brenner potential[7] is adopted as an inter-atomic potential between the C atoms. The cutoff distance of the interaction in the Brenner potential is 2.0 Å. In the case of a layered structure like graphite,

only the interactions between the nearest-neighbor C atoms belonging to the same layer are considered; inter-layer van der Waals interactions are ignored. The following potential (V_{vdW}) is added to correct for the inter-layer interactions:

$$V_{vdW}(r) = 4\varepsilon \left\{ \left(\frac{\sigma}{r}\right)^{12} - g(Z)\left(\frac{\sigma}{r}\right)^{6} \right\} f(r) \qquad (1)$$

The basic formula is the Leonard-Jones potential, and r denotes the atomic distance between C atoms belonging to different layers. The parameters ε and σ are set to 2.84 meV and 3.35 Å in order to reproduce the experimental inter-layer energy and distance of graphite, respectively. $f(r)$ is a cutoff function of a suitable form that approaches zero at a long distance. We introduce the parameter Z, which expresses the coordination number of atoms in a neighboring layer, and the function $g(Z)$ varies depending on whether the degree of similarity of the stacking structure of graphite is of type AA or AB.

3. Results

A hybrid QM-CL simulation run is conducted on a Li-GIC consisting of a single Li ion and nine graphene layers, each of which is composed of 336 C atoms. The temperature is set to 398 K. In this simulation, the QM region is selected adaptively, following the migration of the Li ion in order to minimize the number of atoms included in the QM region within the physical accuracy tolerance. **Fig. 1** shows a snapshot of the Li diffusion process obtained from the hybrid calculation. The diffusion coefficient estimated on the basis of the present hybrid dynamics is 7×10^{-5} cm^2/s. This is in good agreement with the experimental value, which is on the order of 10^{-5} cm^2/s in the dilute case of Li density.[8] The calculated diffusion coefficient without the inter-layer interaction, i.e., in the case of a Li ion on a graphite surface, is ten times larger than that with the inter-layer interaction. Clearly, the inter-layer interaction in graphite has a significant effect on the thermal diffusion of Li ions in Li-GICs.

References

(1) Ogata, S., *Phys. Rev. B*, Vol. 72, No. 4 (2005), pp. 045348 -1-045348-17.
(2) Ogata, S., Lidorikis, E., Shimojo, F., Nakano, A., Vashishta, P. and Kalia, R. K., *Comput. Phys. Commun.*, Vol. 138, No. 2 (2001), pp.143-154.
(3) Ogata, S., Shimojo, F., Kalia, R. K., Nakano, A. and Vashishta, P., *Comput. Phys. Commun.*, Vol. 149, No. 1 (2002), pp. 30-38.
(4) Shimojo, F., Campbell, T. J., Kalia, R. K., Nakano, A., Ogata, S., Vashishta, P. and Tsuruta, K., *Future Gen. Comp. Sys.*, Vol. 17, No. 3 (2000), pp. 279-291.
(5) Troullier, N. and Martins, J. L., *Phy. Rev. B*, Vol. 43, No. 3 (1991), pp. 1993-2006.
(6) Perdew, J. P., Burke, K. and Ernzerhof, M., *Phy. Rev. Lett.*, Vol. 77, No. 18 (1996), pp. 3865-3868.
(7) Brenner, D.W., *Phys. Rev. B*, Vol. 42, No. 15 (1990), pp. 9458-9471; Vol. 46, No. 3 (1992), p. 1948(E).
(8) Funabiki, A., lnaba, M., Ogumi, Z., Yuasa, S., Otsuli, J. and Tasaka, A., *J. Electrochem. Soc.*, Vol. 145, No. 1 (1998), pp. 172-178.
(9) Ohba, N., Dr. Thesis, Nagoya Institute of Technology, (2012).
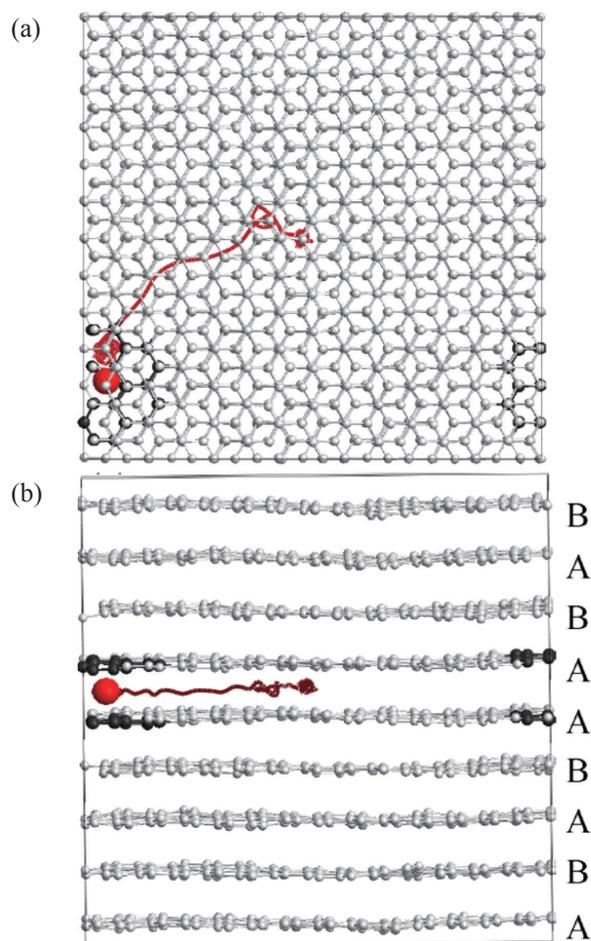
Fig. 1 A snapshot of the Li diffusion process obtained from hybrid calculations at temperature of *T=398* K. The red, black, and white spheres are Li, QM-calculated C, and CL-calculated C atoms, respectively. The trajectory of Li is also shown. (a) Top view, (b) Side view. The letters A and B denote the stacking structure of C-layers.[9]

Nobuko Ohba
  Research Fields:
    - First-principles Calculations for Solid
      Materials
    - Hybrid Simulation Combined the
      Electronic Structure Calculations and Classical
      Molecular Dynamics
  Academic Degree: Dr.Eng.
  Academic Societies:
    - The Physical Society of Japan
    - American Physical Society
    - The Japan Institute of Metals and Materials
    - The Japan Society of Mechanical Engineers
  Award:
    - Certificate of Merit for Best Technological
      Presentation, JSME the 22nd Computational
      Mechanics Division Conference, 2009

Shuji Ogata*
  Research Field:
    - Development of Algorithms and
      Codes for Large-scale Electronic
      Structure and Atomic Dynamics
      Calculations
  Academic Degree: Dr.Sci.
  Academic Societies:
    - The Physical Society of Japan
    - The Japan institute of Metals and Materials
    - Materials Research Society
  Awards:
    - Best Technical Paper Award in Supercomputing 2001,
      IEEE/ ACM, 2001
    - Certificate of Merit for Best Technological
      Presentation, JSME the 22nd Computational
      Mechanics Division Conference, 2009

*Nagoya Institute of Technology