

Development of an Ultra-Accelerated Quantum Chemical Molecular Dynamics Method and its Application to Ion Transport in Li-ion Battery

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1. Introduction

Because Li-ion batteries have higher-energy and higher-power density than other secondary batteries, they are used for mobile electronics such as cellular phones and laptop computers. Additionally, Li-ion batteries are expected to make practicable for hybrid cars and electric cars. However, Li-ion batteries have two main problems. One is expensive cost and the other is issue of safety. To resolve these problems, computational chemistry like atomic and molecular scale simulation is very useful for analysis of atomic and electronic property.

Theoretical approaches such as first-principles calculations and molecular dynamics (MD) simulations have made an impact on the understanding of materials used in Li-ion battery. For example, Courtney *et al.* [1] calculated the voltage profile of lithium-tin alloy, and Hou *et al.* [2] investigated lithium insertion mechanism and electronic structure of interphase Ni₃Sn in nickel-tin alloy as anode of Li-ion battery by using first-principles calculation. However, their calculated models were limited to several tens of atoms. In addition, electronic structure calculations were performed at absolute zero temperature, so all movement of atoms and molecules in calculation models ceased. Molecular dynamics method made possible by large scale simulation. Borodin *et al.* [3] employed this method to obtain an understanding of Li-ion transport in liquid and polymeric electrolyte. MD method had accuracy issue, and it was not consider the electronic state.

In recent years, quantum chemical molecular dynamics (QCMD) method began to be employed. This method is useful tool for understanding the atomic and electronic structural properties of materials of Li-ion batteries. However QCMD method requires huge computational cost.

In this paper, we show the development of an ultra-accelerated quantum chemical molecular dynamics (UA-QCMD) simulator. This simulation is based on the tight-binding quantum chemical molecular dynamics (TB-QCMD) [4, 5] and molecular dynamics (MD) [6]. It has been successfully applied to the electronic structure calculations advanced materials [7]. An UA-QCMD simulator can perform electronic structure calculations for large scale systems consisted of a few thousands atoms. In this study, we have applied this method to ion transport on Li-ion battery for understanding the change of binding state

between Li-ion and electrolyte, ethylene carbonate.

2. Computational Details

An UA-QCMD was combined two programs. One is a tight-binding quantum chemical molecular dynamics program, "Colors" [4]. The other is a classical molecular dynamics program, "New-RYUDO" [6].

Tight-binding quantum chemical molecular dynamics

Our original TB-QCMD program, "Colors" [4], is based on the original tight-binding approximation, and the total energy of a system is described as follows:

$$E = \sum_{i=1}^N \frac{1}{2} m_i v_i^2 + \sum_{k=1}^{OCC} n_k \varepsilon_k + \sum_{i=1}^N \sum_{j=i+1}^N \frac{Z_i Z_j e^2}{R_{ij}} + \sum_{i=1}^N \sum_{j=i+1}^N E_{REP}(R_{ij})$$

where the first, second, third, and fourth term on the right-hand side refers to the kinetic energy of atom, orbital energy, Coulombic energy, and exchange-repulsion energy, respectively. Electronic structure calculations are performed by solving the Schrödinger equation ($\mathbf{H}\mathbf{C} = \varepsilon\mathbf{S}\mathbf{C}$; \mathbf{H} , \mathbf{C} , ε , and \mathbf{S} refers to the Hamiltonian matrix, eigenvectors, eigenvalues, and overlap integral matrix, respectively) with the diagonalization condition ($\mathbf{C}^T \mathbf{S} \mathbf{C} = \mathbf{I}$; \mathbf{I} refers to the unit matrix). To determine the off-diagonal elements of \mathbf{H} , H_{rs} , the corrected distance-dependent Wolfsberg-Helmholz formula [8] was used.

Classical molecular dynamics

Classical MD program, "New-RYUDO" is our original program. In New-RYUDO code, equations of motions are solved by using Verlet algorithm [9]. Ewald method [10] is applied for calculation of the electrostatic interactions under the three-dimensional periodic boundary condition. In order to control system temperature, New-RYUDO code is implemented the velocity scaling algorithm that is equivalent to Woodcock algorithm [11].

We tuned parameters for "Colors" by first principle quantum chemical molecular dynamics. Then we ran TB-QCMD program, "Colors" by using that parameters. The binding energies and charges get by "Colors" were used for classical MD program, "New-RYUDO". In consideration of process of chemical reaction, the binding energies and charges were calculated every 5 picosecond.

For this dynamics large scale simulation is possible.

3. Results and Discussion

In this study, we applied an UA-QCMD to a calculation model of interface between electrolyte and cathode of Li-ion battery showed in Fig.1. The calculation model has dimensions of $a = 14.041 \text{ \AA}$, $b = 11.264 \text{ \AA}$, and $c = 30.000 \text{ \AA}$. Cathode and electrolyte were used LiCo_2O_4 and ethylene carbonate, respectively. There are 30 ethylene carbonate molecules and there is a lithium ion in electrolyte. Carbonyl oxygen of upper 15 ethylene carbonate molecules and lower layer of LiCo_2O_4 are fixed.

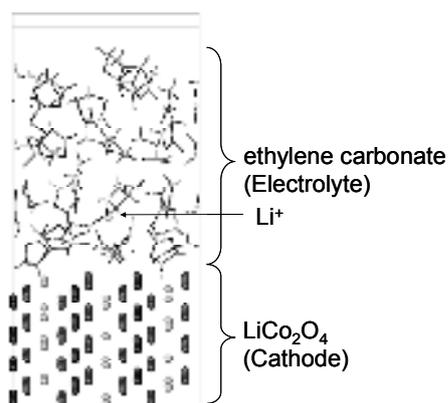


Fig.1 Calculation model of interface between cathode and electrolyte.

We inject Li-ion into neighborhood of cathode and start to simulation. Fig.2 is snapshots of an UA-QCMD simulation during Li-ion transport. Fig.2(a) is a snapshot before starting to simulate of Li-ion transport. In Fig.2, some atoms and molecules changed their conformation and position over time.

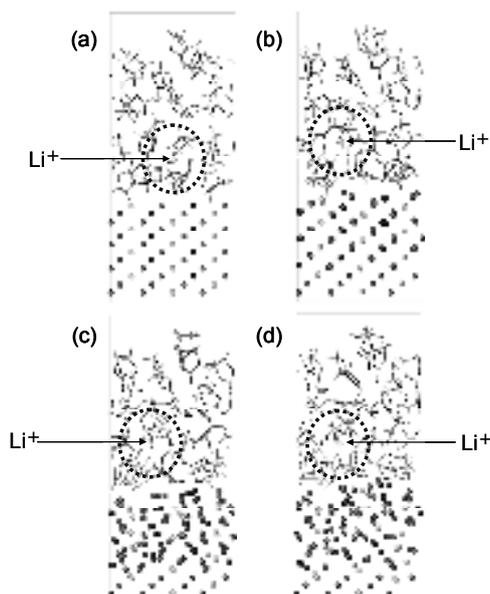


Fig.2 Snapshots of UA-QCMD during Li-ion transport.
(a) before ion transport, (b) after 15 ps,
(c) after 30 ps, (d) after 45 ps

Binding energies between the Li-ion and each carbonyl oxygen in this simulation were shown in Fig.3. Fig.3 showed that the binding energies between Li-ion and carbonyl oxygen atoms gradually decreased with that the ion transport progressed. It indicates that bonds between Li-ion and carbonyl oxygen are weakened by Li-ion moving.

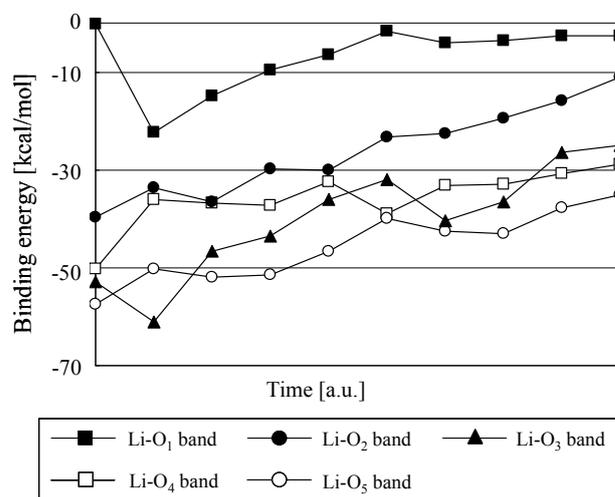


Fig.3 The change of binding energy between Li-ion and carbonyl oxygen during ion transport.

4. Conclusions

We have developed an UA-QCMD simulation. In this study, we have demonstrated that this method can be used to understand the atomic and electronic properties of Li-ion transport at interface between cathode and electrolyte in Li-ion batteries. It is hoped to clarify the mechanism of ion transport and to apply to atomic diffusion by being impressed electric field.

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