

# Electronic structure of the electrode/electrolyte interface: large-scale tight-binding quantum chemical simulation

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## Abstract

Recently, we have succeeded in the development of new tight-binding quantum chemical molecular dynamics code “Colors”, based on our original tight-binding theory. It realizes 5000 times acceleration compared to the conventional first-principles molecular dynamics method and enables us to simulate huge simulation models. Hence, in the present study we applied our new tight-binding quantum chemical molecular dynamics method to the investigation of the electronic structure of the interface of the  $\text{Li}_{0.5}\text{CoO}_2$  electrode and the ethylene carbonate (EC) electrolyte along with  $\text{LiPF}_6$ . Our electronic structure calculations for the  $\text{Li}_{0.5}\text{CoO}_2/\text{EC}+\text{LiPF}_6$  interface suggest that the  $\text{EC}+\text{LiPF}_6$  electrolyte significantly stabilizes the instability of the  $\text{Li}_{0.5}\text{CoO}_2$  surface. Moreover, the detailed analyses for the electronic structure of the electrode/electrolyte interface were also performed. These analyses cannot be realized by the conventional first-principles approach, since it requests huge computational time for such large and complicated system. Hence, we confirmed the effectiveness of our tight-binding quantum chemical molecular dynamics approach to the investigation of the electrode/electrolyte interface on electronic- and atomic-level.

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## 1. Introduction

Recently, lithium secondary batteries have significantly contributed to the commercial electronic devices owing to their low weight and small volume as well as the high energy density, long cycle life, low self-discharge rates and high operating voltage. At present,  $\text{LiCoO}_2$  [1,2] is widely used as cathode material in lithium secondary batteries because it can

be easily prepared and further it gives a higher voltage compared to other probable cathode materials such as  $\text{LiNiO}_2$  [3] or  $\text{LiMn}_2\text{O}_4$  [4]. In order to achieve a higher efficiency of the lithium secondary batteries, it is indispensable to understand and clarify the atomic and electronic structure of the complicated interface, which consists of anode, cathode and electrolyte. For example, theoretical approaches such as molecular dynamics, Monte Carlo simulation, and quantum chemical calculations have been performed to elucidate the structural and electrochemical characteristics of  $\text{LiCoO}_2$  [5–7]. However, to the best of our knowledge, no theoretical studies have been done for the electrode/electrolyte interface because of its complexity.

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First-principles method is one of the effective candidates to investigate the electrode/electrolyte interface. However, the above method requests huge computational costs and then it cannot be applied to the large and complicated system. Hence, recently we have succeeded in the development of new tight-binding quantum chemical molecular dynamics method, which is based on our original tight-binding theory [8–10]. This method realizes 5000 times acceleration compared to the conventional first-principles approach and hence it enables us to simulate huge simulation model, which cannot be calculated by the conventional first-principles method. Hence, in the present study, we applied our novel tight-binding quantum chemical molecular dynamics method to the investigation on the electronic structure of the interface of  $\text{Li}_{0.5}\text{CoO}_2$  electrode and ethylene carbonate (EC) electrolyte along with  $\text{LiPF}_6$ . In the present study, for the first time, the large-scale quantum chemical simulations on the electrode/electrolyte interface were performed by the development of new tight-binding quantum chemical molecular dynamics methodology.

## 2. Method

### 2.1. Tight-binding quantum chemical calculations

Tight-binding quantum chemical molecular dynamics code “Colors” is based on our original tight-binding approximation [8–10] and the total energy of the system is expressed by Eq. (1).

$$E = \sum_{i=1}^n m_i v_i^2 / 2 + \sum_{k=1}^{occ} \varepsilon_k + \sum_{i=1}^n \sum_{j=i+1}^n Z_i Z_j e^2 / R_{ij} + \sum_{i=1}^n \sum_{j=i+1}^n E_{\text{rep}}(R_{ij}) \quad (1)$$

where  $Z_i$  is the atomic charge,  $e$  is the elementary electric charge, and  $r_{ij}$  is the interatomic distance. In Eq. (1), the first term refers to the kinetic energy of nuclei, the second term is the summation of the eigenvalues of all the occupied orbitals calculated by the tight-binding electronic-states calculation, and the third term represents the Coulomb interaction. The last term corresponds to the short-range exchange-repulsion energy, which is represented by Eq. (2).

$$E_{\text{rep}}(R_{ij}) = b_{ij} \exp[(a_{ij} - r_{ij})/b_{ij}] \quad (2)$$

Here,  $a_{ij}$  and  $b_{ij}$  are the parameters for atom pairs, which represent the size and stiffness of atoms, respectively.

### 2.2. First-principles parameterization

In order to realize the acceleration of the calculation speed, several parameters, such as valence state ionization potential and Slater exponent of atomic orbitals, are

employed in our tight-binding approximation. If the parameters are determined on the basis of experimental results, we cannot apply to the tight-binding quantum chemical molecular dynamics code to unknown system. Hence, we developed new methodology to determine all the parameters on the basis of the first-principles density functional calculation results.

Our tight-binding approximation does not consider apparently the electron correlation and spin state exchange for the acceleration of calculation time, as shown in Eq. (1). However, the parameters for our tight-binding method was determined on the basis of the density functional calculation results, which considers the electron correlation and spin state exchange, and hence those effects are implied in our tight-binding approximation.

For the first-principles parameterization, Amsterdam density functional (ADF) code was employed. The structures of the EC and  $\text{LiPF}_6$  molecules were optimized with the local density approximation level using the Vosko-Wilk-Nusair functional. The energies for optimized structures were calculated with the generalized gradient approximation using the Becke’s exchange and Perdew correlation functionals. The validity of the above methodology was already discussed in the previous paper [11].

## 3. Results and discussion

Before the calculation of the  $\text{Li}_{0.5}\text{CoO}_2$  electrode / EC+ $\text{LiPF}_6$  electrolyte interface, the electronic structure of the  $\text{Li}_{0.5}\text{CoO}_2(100)$  surface was investigated by our tight-binding quantum chemical molecular dynamics code. Here, the  $\text{LiCoO}_2$  structure is obtained from the Ref. [12]. Although both O-terminated and Co-terminated  $\text{LiCo}_{0.5}\text{CoO}_2(100)$  surface are possible, here we employed the O-terminated  $\text{LiCo}_{0.5}\text{CoO}_2(100)$  surface model since the O-terminated surface is energetically more stable than the Co-terminated surface. Moreover, the O-terminated (100) surface was fully relaxed by our tight-binding quantum chemical molecular dynamics calculations. In the present study, we focused on the effect of the Li deintercalation on the electronic structure of the  $\text{Li}_{0.5}\text{CoO}_2(100)$  surface.

Fig. 1 shows the two models employed in the present study. The perfect surface model (a) is composed of 72 atoms and the deintercalated model (b) is composed of 71 atoms. Here, the Li atom marked by a circle in Fig. 1(a) is deintercalated in the model (b). The atomic charges of each atom were evaluated by the Mulliken population analysis. The atomic charges on some specific atoms were also shown in Fig. 1. These figures show that the Li atom in the perfect surface model has atomic charge of 0.10, which is slightly lower than that of 0.13 in the deintercalated model. Likewise, the atomic charges on the Co atom were 0.46 and 0.49 in the perfect model and deintercalated model, respectively, as shown in Fig. 1(a) and (b). On the other hand, no significant difference in the atomic charges on

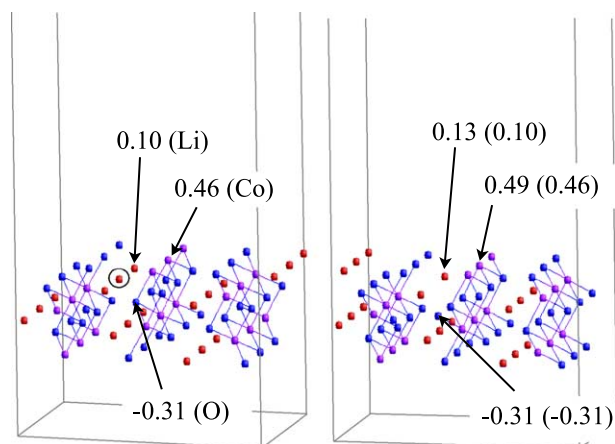


Fig. 1. Charge distribution in the  $\text{Li}_{0.5}\text{CoO}_2$  (100) surface: (a) perfect surface model and (b) model which one Li atom is deintercalated. The values in parentheses represent the charge in the perfect surface model.

oxygen atoms was noted for both these models. Both the atomic charges on oxygen atoms for the perfect and deintercalated models were  $-0.31$ . Since the changes in the atomic charges on the Co atoms were significant compared to those on the O atoms by the Li intercalation, we suggest that the Co atom in the  $\text{Li}_{0.5}\text{CoO}_2$  compensates the atomic charge on the deintercalated Li atom. This result is consistent with the previous experimental knowledge, and hence we confirmed the validity of our tight-binding quantum chemical molecular dynamics method to investigate the huge simulation model of  $\text{Li}_{0.5}\text{CoO}_2$ (100) surface.

The electronic structure of the  $\text{Li}_{0.5}\text{CoO}_2/\text{EC}+\text{LiPF}_6$  interface was investigated by using our tight-binding quantum chemical molecular dynamics method. Fig. 2 shows the employed model for the  $\text{Li}_{0.5}\text{CoO}_2/\text{EC}+\text{LiPF}_6$  interface in the present study. The  $\text{EC}+\text{LiPF}_6$  electrolyte consists of seven EC and one  $\text{LiPF}_6$  molecules. Especially, we focused on the effect of the electrolyte towards the atomic charges on the surface O atoms in the  $\text{Li}_{0.5}\text{CoO}_2$  electrode. Fig. 3(a) and (b) present the atomic charges on some specific O atoms in the  $\text{Li}_{0.5}\text{CoO}_2$ (100) surface model and  $\text{LiCoO}_2$ (100)/ $\text{EC}+\text{LiPF}_6$  interface model, respectively.

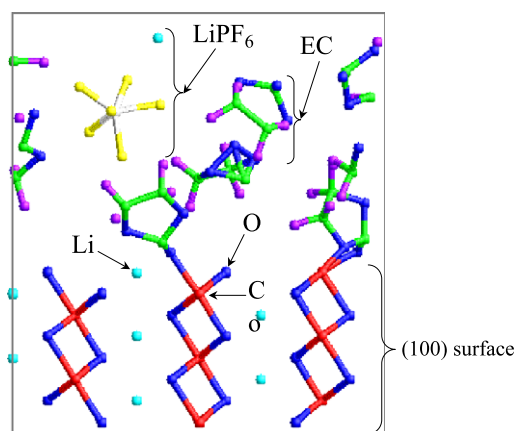


Fig. 2. Interface model of  $\text{Li}_{0.5}\text{CoO}_2$ (100)/ $\text{EC}+\text{LiPF}_6$ .

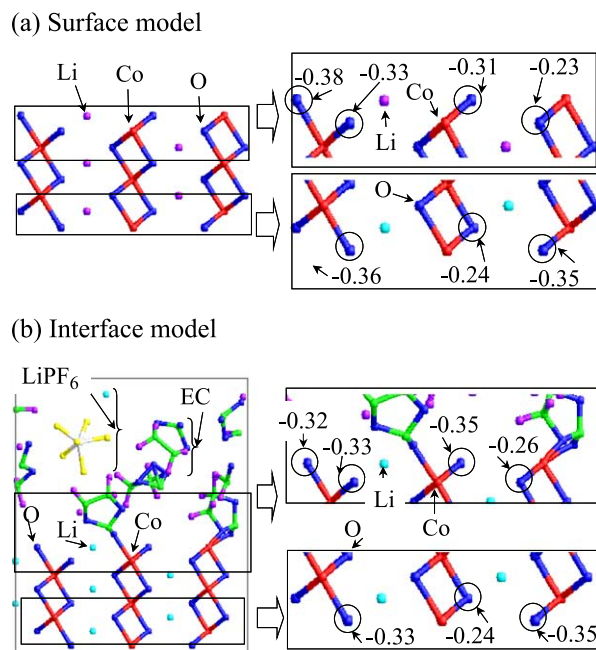


Fig. 3. Charge distributions of the (a)  $\text{Li}_{0.5}\text{CoO}_2$ (100) surface model and (b)  $\text{Li}_{0.5}\text{CoO}_2$  electrode/ $\text{EC}+\text{LiPF}_6$  electrolyte interface model. Atoms marked by circles represent oxygen. Right side of these figures displays the magnified view of the regions marked with the solid rectangle box.

All the oxygen atoms in the bulk  $\text{LiCoO}_2$  have the negative charge of  $-0.23$ . However, as shown in Fig. 3(a), the oxygen atoms at the  $\text{Li}_{0.5}\text{CoO}_2$ (100) surface have wide-range atomic charges of  $-0.23$  to  $-0.38$ . This result suggests that some surface oxygen atoms have highly negative charge compared to those in the bulk  $\text{LiCoO}_2$ . On the other hand, it is very interesting to notice that the range of the atomic charges on the oxygen atoms in the interface model is narrower owing to the interaction of the oxygen atoms with the electrolyte, as shown in Fig. 3(b). The oxygen atoms in the interface model have the atomic charges of  $-0.24$  to  $-0.35$ . In other words, the electrolyte molecules  $\text{EC}+\text{LiPF}_6$  stabilize the atomic charges and electronic states of the oxygen atoms at the  $\text{Li}_{0.5}\text{CoO}_2$ (100) surface.

#### 4. Conclusion

Our novel tight-binding quantum chemical molecular dynamics code “Colors” was successfully applied to the investigation of the electronic structure of the  $\text{Li}_{0.5}\text{CoO}_2$ (100) electrode/ $\text{EC}+\text{LiPF}_6$  electrolyte interface. The calculation results show that the  $\text{EC}+\text{LiPF}_6$  electrolyte stabilize the electronic states of the oxygen atoms at the  $\text{Li}_{0.5}\text{CoO}_2$ (100) surface. These simulation results cannot be obtained by the first-principles molecular dynamics method, since it requests huge computational costs. Hence, the present study also demonstrates the efficiency of our tight-binding quantum chemical molecular dynamics method to

investigate the electronic structures of huge and complicated models.

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