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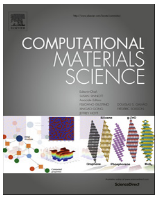

An interatomic potential for the Li-Co-O ternary system

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ABSTRACT

Although large-scale atomistic simulations provide useful insights into various material phenomena, such studies on $LiCoO_2$, which is the most widely used cathode material for lithium ion batteries (LIBs), have rarely been undertaken due to difficulties in developing adequate interatomic potentials. In this study, an interatomic potential (2NNMEAM + Qeq) for the Li-Co-O ternary system is developed to carry out molecular dynamics (MD) simulation studies on lithium cobalt oxides. Potential parameters are optimized so that the potential can successfully reproduce fundamental materials properties (structural, elastic, thermodynamic and migration properties) of various compounds of sub-binary and lithium cobalt ternary oxide systems. Through MD simulations, we investigate lithium diffusion properties (activation energy for lithium migration and diffusion coefficient) in layered $Li_{1-x}CoO_2$ ($0 \leq x \leq 0.5$) of various lithium vacancy concentrations. We find that the lithium vacancy concentration has a significant influence on the activation energy for lithium diffusion and the lithium diffusion coefficient in the $Li_{1-x}CoO_2$ cathode. The developed potential can be further utilized for atomistic simulation studies on other materials phenomena (phase transitions, defect formation, lithiation/delithiation, etc.) in LIB cathode materials.

1. Introduction

$LiCoO_2$ is the most widely used cathode material for lithium ion batteries (LIBs) because of its advantages such as fast Li-ion migration, high voltage and high capacity. However, because of the high material cost and toxicity of the Co element, searching for replacement cathode materials that have a lower cobalt content has attracted recent research interest [1,2]. Although various cathode materials have been proposed including solid solutions of Li-(Co, Mn, Ni, Al, etc.)-O, there have been difficulties in finding a satisfactory replacement cathode material that has sufficiently good performance in the areas of structural stability, capacity, cyclic properties, and so on. One of the most important properties of LIB cathode materials is the lithium diffusion, the main determinant for the charge/discharge rate. However, there is a limit to accurately measuring the Li diffusion coefficient through experiments because of the nature of the very light element and no suitable radioisotope for Li [3]. In addition, investigating properties such as defect formation, lithiation/delithiation and phase transitions in various LIB cathode materials through experiments is difficult because they have atomic-scale origins. Such experiments are also inefficient because the number of possible compounds and doping elements for the cathode materials is almost limitless.

On the other hand, computational approaches can be efficiently utilized for investigations of a wide range of materials phenomena. Among the approaches, the density functional theory (DFT) calculation is a high-level calculation that provides the most accurate information on (sub-)atomic-scale behaviors. However, the DFT calculation is not suitable for investigating dynamic behavior such as diffusion properties because of the limited number of atoms that can be handled. In this case, it is more appropriate to conduct large-scale atomistic simulations using a (semi-)empirical interatomic potential. However, there have been relatively few atomistic simulation studies on the LIB cathode materials. This is because of the difficulty in developing suitable interatomic potential models (and parameterization) for the LIB cathode materials, not because of a lesser importance of atomistic simulations.

The potential model applicable to LIB cathode materials systems should be able to cover various bonding natures (metallic, covalent and ionic bonds) in multi-component lithium transition metal oxide systems. In addition, it should be able to describe how the charge state of individual ions can change in redox reactions during the charge/discharge process. However, most previous studies [4–12] used a simple pair-wise type potential coupled with a fixed charge model. The pair-wise potential cannot cover com-

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plex bonding natures, and the fixed charge model simply considers the charge states of ions to be fixed during simulations. In recent years, to extend the materials coverage of the potential model, many-body type potentials coupled with a variable charge model have been developed: reactive force-field (ReaxFF) [13,14], charge optimized many-body (COMB) [15,16], charge transfer modified embedded-atom method (CT-MEAM) [17,18] and second nearest-neighbor MEAM coupled with charge equilibration (2NNMEAM + Qeq [19]). However, there are only a few applications of that kind of potential model to LIB cathode material systems [17,18,20], and there is no application to the Li-Co-O system, which is one of the most essential cathode material systems.

Our group have developed the 2NNMEAM + Qeq potential model to extend the coverage of the existing 2NNMEAM potential to multi-component metal oxide systems [19]. Based on this potential formalism, we have developed an Li-Mn-O ternary potential recently [20] and are constructing a potential database for LIB cathode material systems. The main objective of this study is to develop the Li-Co-O ternary potential. This is the first achievement for the Li-Co-O system, based on a many-body potential with variable charge scheme. We report the result of MD simulation on lithium diffusion properties in a layered $Li_{1-x}CoO_2$ cathode using the developed potential. Section 2 gives a brief description of the 2NNMEAM + Qeq potential model. Section 3 reports on the evaluation of the developed potentials for the sub-binary systems (Li-Co and Co-O) and ternary Li-Co-O system. Section 4 discusses the results of the MD simulation on lithium diffusion in layered $Li_{1-x}CoO_2$.

2. The 2NNMEAM + QEQ potential

The 2NNMEAM [21,22], one of the latest versions of MEAM [23–25], has been applied to a wide range of materials including metals, covalent elements and their alloys. In particular, it has been successfully applied to essential metallic elements associated with LIB cathode materials, such as Li [26], Co [27], Mn [28], Ni [29], Al [29] and some of their alloys. Recently, our group further extended the 2NNMEAM to cover multicomponent oxide compounds by combining it with a charge equilibration (Qeq [30]) concept (2NNMEAM + Qeq) [19]. Special attention was given to the removal of known problems found in the original Qeq method, during the implementation of the Qeq to the 2NNMEAM.

The total energy of a system in the 2NNMEAM + Qeq potential model [19] is composed of non-electrostatic (2NNMEAM) and electrostatic (Qeq) energy terms, as in the following expression.

$$E^{Total} = E^{MEAM}(\mathbf{r}) + E^{ES}(\mathbf{r},\mathbf{q}) \tag{1}$$

The MEAM energy is calculated as

$$E^{MEAM} = \sum_i \left[F_i(\bar{\rho}_i) + \frac{1}{2}\sum_{j\neq i} S_{ij}\phi_{ij}(R_{ij}) \right] \tag{2}$$

where F_i is the embedding function, ρ_i is the background electron density at site i. S_{ij} and $\phi_{ij}(R_{ij})$ are the screening factor and the pair interaction between atoms i and j separated by a distance R_{ij}, respectively. Full details of the MEAM energy term are not included in this paper, and can be found in the literature [21,22] or in the electronic supplementary information (ESI) of this paper.

The electrostatic energy is expressed as the sum of atomic energy E_i^{atom} (or penalty energy) and the Coulomb pair interaction V_{ij}^{Coul}:

$$E^{ES} = \sum_i E_i^{atom}(q_i) + \sum_{i,j(i\neq j)} \frac{1}{2} V_{ij}^{Coul}(q_i, q_j, R_{ij}) \tag{3}$$

where q_i is the charge state of atom i. The charge state of each atom is not fixed but variable depending on the local environment. Our model use a quadratic spline function of q_i for E_i^{atom} [19], and Coulomb integral between two density functions of the 1s-Slater orbital [31] for V_{ij}^{Coul}. In addition, our potential formalism uses the concept of the split-charge [32], $\bar{q}_{ji}$, which represents the charge flow from the covalently bonded neighbor atom j to the atom i. Full details on the mathematics and algorithms for computing the equilibrium charge using our potential model can be found in Ref. [19] or in the ESI of this paper.

The potential formalism requires the following parameters: fifteen 2NNMEAM parameters (E_c, R_e, α, A, $t^{(1)-(3)}$, $\beta^{(0)-(3)}$, $C_{\min}$, $C_{\max}$, d_{rep} and d_{att}) and seven Qeq parameters (χ^0, J^0, $\Delta E^{(2)-(4)}$, ζ and Z) for each element. Fourteen and six parameters are also required for each pair and triplet, respectively (only the 2NNMEAM part): ΔE_c, R_e, α, d_{rep}, d_{att}, $C_{\min}$ (i-j-i), $C_{\min}$ (j-i-j), $C_{\min}$ (i-i-j), $C_{\min}$ (i-j-j), $C_{\max}$ (i-j-i), $C_{\max}$ (j-i-j), $C_{\max}$ (i-i-j), $C_{\max}$ (i-j-j) and $\rho_0(i)/\rho_0(j)$) for i-j pair, and $C_{\min}$ (i-k-j), $C_{\min}$ (i-j-k), $C_{\min}$ (j-i-k), $C_{\max}$ (i-k-j), $C_{\max}$ (i-j-k) and $C_{\max}$ (j-i-k) for i-k-j triplet. The Qeq part of our model operates only when a charge is assigned to the atoms in the system. This means that unary or metallic alloy systems are described only by the pristine 2NNMEAM formalism. Thus, we use the previously reported 2NNMEAM parameters of Li [26] and Co [27] without any modification. The 2NNMEAM and Qeq parameters for pure O are taken from a previous study on Ti-O and Si-O systems [19]. The Qeq parameters for pure Li and binary 2NNMEAM parameters for the Li-O pair had been determined during the development of the Li-Mn-O ternary potential in another previous study [20], and we use those parameters in this study. Therefore, a total of forty-one parameters (seven Qeq parameters for pure Co, fourteen binary 2NNMEAM parameters for each Li-Co and Co-O pair, and six ternary 2NNMEAM parameters for Li-Co-O triplet) are optimized in this study. The optimization of the parameters is performed using a genetic algorithm (GA). The finally selected potential parameters are listed in Table 1. The cutoff distances for 2NNMEAM and Coulomb interaction are taken as 4.8 Å and 12.0 Å, respectively.

3. Evaluation of the potential development

The reliability of the atomistic simulation results depends on the accuracy of the interatomic potential used in the simulation. In this section, we evaluate whether the developed potential correctly reproduces various fundamental material properties of the relevant material systems (Li-Co, Co-O and Li-Co-O). The reproduced properties are divided into two groups. One includes target properties fitted in a parameter optimization process: lattice parameters, elastic constants, enthalpy of formation and lithium migration energy barrier. The other involves properties calculated to check the transferability of the potential, which are not fitted: redox potential and defect formation energies. In addition, we check whether the developed potential remains reliable in finite temperature simulations as well as in zero K calculations. We use our own in-house code for all calculations, and the source code is included in the ESI of this paper. During all calculations, the charge on individual atoms is automatically determined according to the atomic environment by the Qeq scheme. No charge is assigned to Li and Co atoms in Li-Co alloys. Co atoms have the charge within the range of +1.04 and +1.09, and O atoms between -1.04 and -0.55 in $Co_{1-x}O_x$ ($1/2 \le x \le 2/3$). In Li_xCoO_2 ($0 \le x \le 1$) compounds, the charge of Li, Co and O atoms are between 0 and +0.42, between +1.09 and +1.08, and between -0.55 and -0.74, respectively.