



Molecular dynamics simulation of lithium ion diffusion in LiCoO₂ cathode material

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ABSTRACT

In this study, lithium ion (Li⁺) diffusion inside lithium cobalt oxide (LiCoO₂) as a cathode material is investigated using molecular dynamics (MD) simulation. The effect of some important parameters such as voltage, Li⁺ content, and diffusion axis on Li⁺ diffusion coefficient value is explored and compared with the experimental data. The results show that Li⁺ diffusion coefficient in LiCoO₂ material is in the order of 10⁻¹² to 10⁻¹³ cm²/s, which is in agreement with the experimental data. Increased voltage value and decreased Li⁺ content raise the Li⁺ diffusion coefficient. In addition, the comparison of the Li⁺ diffusion coefficient along different axes of the crystal layer reveals that transporting lithium ions in a direction perpendicular to the layers of cathode material is more difficult than transporting them in a direction parallel to the layers. It can decrease the diffusion coefficient of Li⁺ by about 20%, especially at high voltage value and low Li⁺ content. But the diffusion coefficient in both directions has the same order of magnitude, which may explain different values of Li⁺ diffusion coefficient in various experimental methods. Replacing Co³⁺ with Fe³⁺ for increasing the capacity and stability of cathode material may slightly diminish the values of Li⁺ diffusion coefficient, which is in agreement with the experimental results.

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1. Introduction

Lithium cobalt oxide (LiCoO₂) has been the subject of growing attention worldwide especially because of its application as a cathode material in rechargeable lithium ion batteries. It has unique properties such as high specific capacity and energy, low self-discharge, and excellent cycle life [1]. Since in lithium ion batteries, the rate of charge and discharge is related to the Li⁺ diffusion in the electrode materials, it is necessary to calculate the diffusion coefficient of Li⁺ [2,3]. Many studies have focused on investigating the lithium ion transport properties, especially Li⁺ diffusion coefficient in various electrode materials. Most of these studies are experimentally performed on composite electrode materials such as LiCoO₂ [4–7], LiNiO₂ [8], and LiCo_xNi_{1-x}O₂ [9–14]. Also, it is difficult to conduct the detailed analysis of diffusion coefficient for composite electrodes, which is due to the non-uniform potential distributions of lithium ions on composite electrodes and unknown electrode surface area [2,3]. Moreover, another obstacle is the long time required to complete the electrochemical diffusion experiment. Furthermore, there are significant discrepancies in the calculation of Li⁺ diffusion coefficient values reported by various methods due to the limitations of each measurement [15]. As such, these samples and methods introduce ambiguities in the diffusion measurement and make it

difficult to determine an intrinsic diffusion constant. Computational methods such as molecular simulations may help solve some of these problems. By knowing the crystallographic structures of electrode materials, it is possible to simulate diffusion process in each complicated composite electrode and investigate the effect of some important parameters on the diffusion coefficient.

The aim of this study is to calculate Li⁺ diffusion coefficient in LiCoO₂ cathode material using molecular dynamics simulation method. Moreover, the effects of Li⁺ content (x), voltage (V), and diffusion axis on the diffusion coefficient are investigated in detail.

2. Methodology

Molecular dynamics simulation was applied to calculate Li⁺ diffusion coefficient inside LiCoO₂ under different conditions. Generally, two important factors affect the Li⁺ diffusion coefficient:

- Available vacancy sites for Li⁺ jump: The concentration of vacancy sites is related to the lithium concentration [8,16].
- Activation barrier for Li⁺ jump: The activation barrier depends on two parameters: C-lattice and effective valence of cobalt ions [2].

According to these parameters, simulations are set up in different categories to investigate the effects of voltage, lithium ions content, diffusion plane orientations, and cobalt ions charge on Li⁺ diffusion

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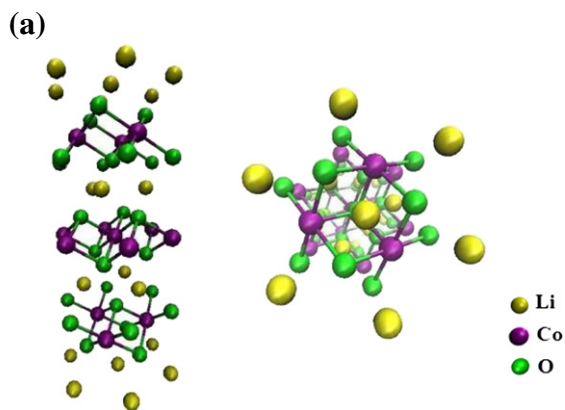


Fig. 1. Schematic diagram of the hexagonal structure of LiCoO_2 unit cell from (a) parallel view to CoO_2 layers, (b) perpendicular view to CoO_2 layers.

(b) coefficient in LiCoO_2 cathode. The important requirements of simulations are as follows:

2.1. System preparation

LiCoO_2 cathode material has a hexagonal crystallography structure with lattice parameters of $a = b = 2.8161\text{\AA}$ and $c = 14.0536\text{\AA}$ [17]. The space group of this material is $R\bar{3}m$ [9–11,18–20]. $\text{O}_3\text{-LiCoO}_2$ is adapted as the initial structure among various types of this cathode material. This structure is thermodynamically stable and usually obtained in the synthesis process. Fig. 1 shows the scheme of LiCoO_2 unit cell adopted in this study. The final structure of the crystal for MD simulation is constructed by repeating one unit cell in x, y, and z axes in a simulated box with $3 \times 3 \times 3$ nm dimensions. A schematic diagram of the structure is illustrated in Fig. 2a. Also, CoO_2 layers without Li^+ ions are shown in Figs. 2b and c. Other structures of cathode materials are constructed by removing Li^+ from the crystal lattice according to Ceder et al. [21] method. Fig. 3 shows the procedure of removing Li^+ from

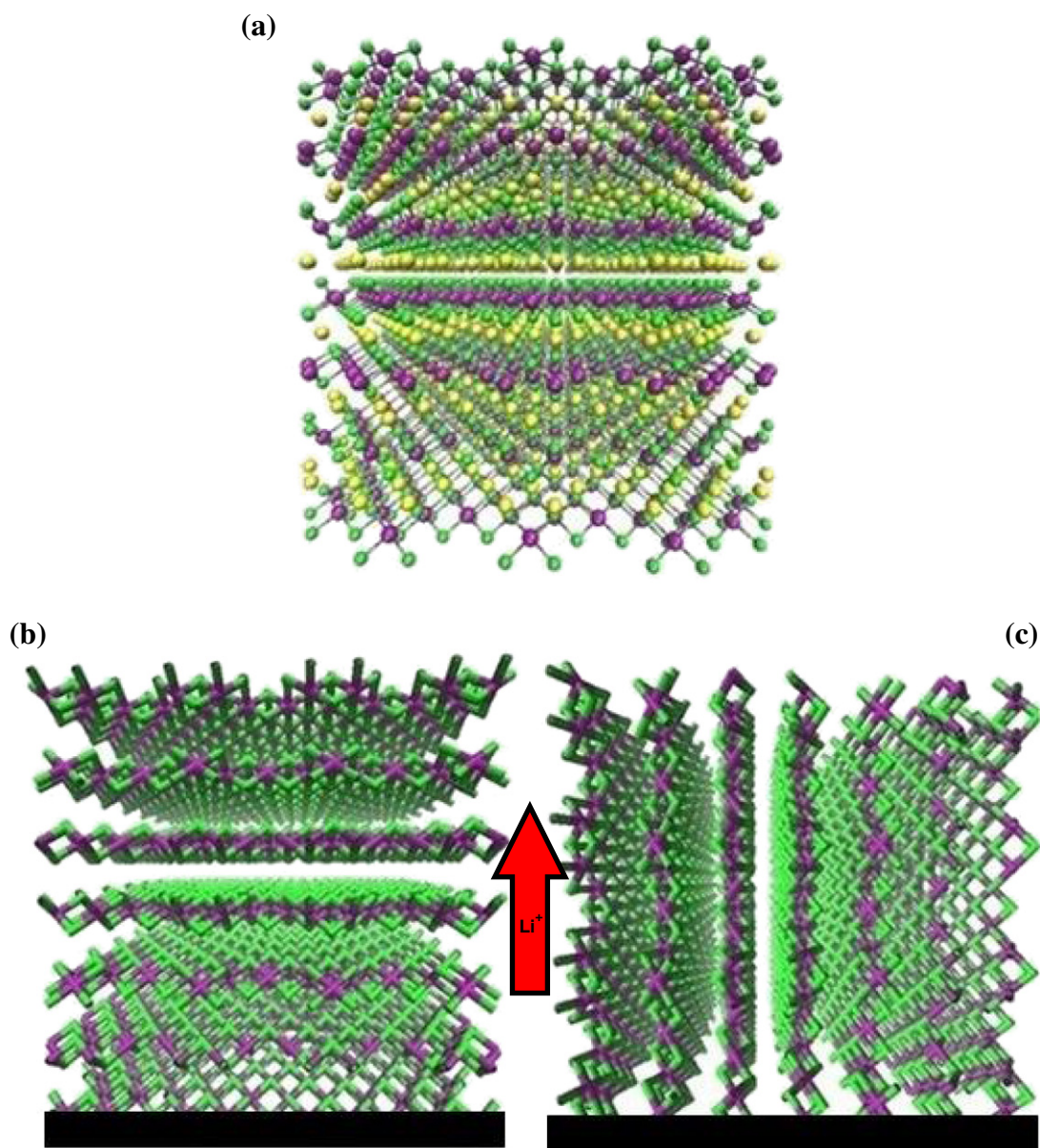


Fig. 2. Schematic model representing (a) the final structure of the simulated box, (b) the orientation of Li^+ diffusion perpendicular to CoO_2 layers, and (c) the orientation of Li^+ diffusion parallel to CoO_2 layers. (Arrow represents the direction of the Li^+ diffusion and different colors are selected according to Fig. 1.)

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