

# Lithium diffusion mechanisms in layered intercalation compounds

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## Abstract

We investigate the mechanisms of lithium diffusion in layered intercalation compounds from first-principles. We focus on  $\text{Li}_x\text{CoO}_2$  and find that lithium diffusion in this compound occurs predominantly with a divacancy mechanism. First-principles calculations predict that the activation barrier is very sensitive to the lithium concentration due to the strongly varying  $c$ -lattice parameter of the host and the change in effective valence of the cobalt ions. This translates into a diffusion coefficient that varies by several orders of magnitude with state of charge. © 2001 Elsevier Science B.V. All rights reserved.

**Keywords:** Lithium diffusion;  $\text{Li}_x\text{CoO}_2$ ; First-principles

## 1. Introduction

Rechargeable lithium batteries with a  $\text{Li}_x\text{CoO}_2$  cathode are currently used to power many electronic devices such as cell-phones and laptop computers. Compared to other lithium transition metal oxides including  $\text{Li}_x\text{MnO}_2$  and  $\text{Li}_x\text{NiO}_2$ ,  $\text{Li}_x\text{CoO}_2$  is still widely ranked among the best cathode material due to its good cycling properties when variations in  $x$  are limited between 1 and 0.5. Nevertheless, the power density of  $\text{Li}_x\text{CoO}_2$  is low making it unsuitable for automotive applications. The power density is in part determined by the lithium mobility within the lithium layers of the  $\text{Li}_x\text{CoO}_2$  host. To optimize power density in layered  $\text{Li}_x\text{CoO}_2$  as well as in other layered transition metal oxides, a clear understanding of the lithium diffusion mechanisms within these compounds must be obtained. In this paper, we describe the results of a first-principles investigation of lithium diffusion in  $\text{Li}_x\text{CoO}_2$ .

Extensive experimental and theoretical work have elucidated much about the thermodynamic properties of layered  $\text{Li}_x\text{CoO}_2$  which has the  $\alpha\text{-NaFeO}_2$  structure. As lithium is initially removed from  $\text{LiCoO}_2$ , the compound passes through a two-phase region where two crystallographically identical forms of  $\text{Li}_x\text{CoO}_2$  with  $x = 0.75$  and  $0.95$  coexist [1,2]. This first-order phase transformation is driven by a metal insulator transition that occurs at high lithium concentration [3,4]. Upon further lithium removal,  $\text{Li}_x\text{CoO}_2$  undergoes an ordering reaction at  $x = 0.5$  [1], a staging

transformation at low lithium concentration [5] and a structural transformation upon complete deintercalation in which the host changes from O3 to O1 [6]. The  $c$ -lattice parameter, more or less constant between  $x = 1$  and  $0.5$ , drops dramatically at low lithium concentration [2,3,6].

The diffusion coefficient, which is determined by the rate at which lithium ions can migrate through the host, depends on several factors. Li hopping requires at least an adjacent vacancy for it to hop to. A lithium ion will have more freedom to migrate if it is surrounded by many vacancies. This depends on the overall lithium concentration and the equilibrium degree of short or long range order. The rate  $\Gamma$  at which an individual hop occurs can be approximated by transition state theory [8] according to

$$\Gamma = \nu^* \exp\left(\frac{-\Delta E_B}{kT}\right) \quad (1)$$

where  $\nu^*$  is an effective vibrational frequency and  $\Delta E_B$  the activation barrier defined as the difference in energy at the activated state and the energy at the initial equilibrium state of the hop. The activated state is located at the maximum energy point along the minimum energy path between the end points of the hop.

Using first-principles, total energy calculations within the local density approximation of density functional theory, we investigated the different types of migration paths and their corresponding activation barriers for lithium diffusion within  $\text{Li}_x\text{CoO}_2$  [7]. We find that two qualitatively different migration paths are available depending on the local lithium-vacancy arrangement around the endpoints of the hop. The first hopping mechanism occurs when the two lithium sites

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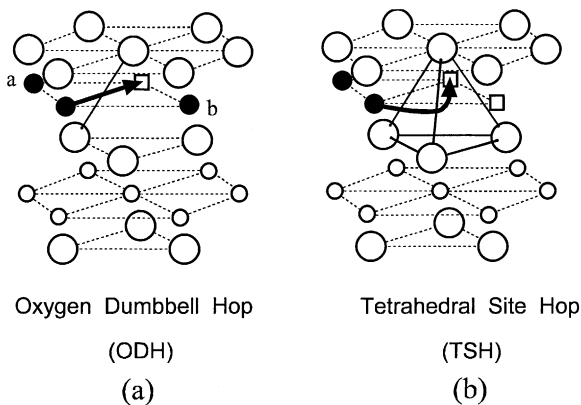


Fig. 1. The two lithium migration paths in layered  $\text{Li}_x\text{CoO}_2$ . The filled circles are lithium ions, the empty squares are lithium vacancies, the large empty circles are oxygen ions and the small empty circles are cobalt ions. (a) The oxygen dumbbell hop (ODH) occurs when the sites *a* and *b* adjacent to the end points of the hop are simultaneously occupied by lithium ions. (b) The tetrahedral site hop (TSH) occurs when one or both of the sites adjacent to the endpoints of the hop are vacant.

(sites *a* and *b* in Fig. 1(a)) immediately adjacent to the endpoints of the hop are simultaneously occupied by lithium ions. The diffusing lithium ion then migrates along the shortest path connecting the initial site of the hop and the vacancy. This path denoted by the arrow in Fig. 1(a) passes through a dumbbell of oxygen ions. We refer to this migration path as an oxygen dumbbell hop (ODH). This is the mechanism by which isolated vacancies exchange with lithium. When either one or both of the sites immediately adjacent to the endpoints of the hop are vacant, lithium migrates along a curved path which passes through a tetrahedral site as illustrated in Fig. 1(b). Notice that for this migration mechanism to occur, the destination of the hopping lithium ion must be part of a divacancy (it could also be part of a cluster of vacancies containing more than two vacancies).

The activation barriers for both the ODH and TSH mechanism vary significantly with lithium concentration. Fig. 2 illustrates calculated activation barriers for the TSH and ODH mechanisms plotted as a function of lithium concentration. It should be realized that the activation barrier can vary with the arrangement of lithium ions and vacancies surrounding the migrating lithium ion. At a given lithium concentration, many different lithium-vacancy arrangements can occur and therefore more than one activation barrier can be calculated at each lithium concentration corresponding to a different local environment. The activation barriers for the ODH mechanism is much larger than for the TSH mechanism. Since the hopping rate depends exponentially on minus the activation barrier, this result indicates that lithium migration should occur much more frequently with the TSH mechanism than with the ODH mechanism. Nevertheless, the TSH mechanism requires the presence of a divacancy which becomes increasingly less likely at high lithium concentrations. In fact, kinetic Monte Carlo simulations [7] predict that the TSH mechanism dominates at all

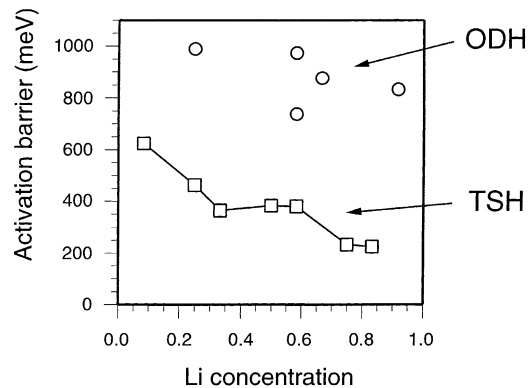


Fig. 2. First-principles activation barriers for the TSH (squares) and ODH (circles) mechanisms at several different lithium concentrations  $x$  as calculated from first-principles. Note that several different activation barriers can be calculated at a given lithium concentration since activation barriers depend on the local arrangement of lithium ions and vacancies around the migrating lithium ion, and many different such arrangements exist at fixed lithium concentration.

lithium concentrations. Only at infinite dilution is lithium forced to migrate according to the ODH mechanism. This means that lithium diffusion in layered  $\text{Li}_x\text{CoO}_2$  is mediated by divacancies (or more precisely clusters of two or more vacancies) at all practical lithium concentrations. At high lithium concentrations, the diffusion coefficient, therefore, scales approximately as  $(1-x)^2$ , the divacancy concentration in an ideal solid solution of lithium ions and vacancies. Monte Carlo simulations predict that the divacancy concentration in  $\text{Li}_x\text{CoO}_2$  at high  $x$  is actually less than  $(1-x)^2$ , since vacancies repel each other due to electrostatic interactions.

Not only is the activation barrier very different for the two hopping mechanisms, but it also varies significantly with concentration for a given hopping mechanism. Fig. 2 shows that the activation barrier for the TSH mechanism increases by more than 300 meV as  $x$  is reduced from 1 to 0. Two effects contribute to this concentration dependence. The dramatic increase of  $\Delta E_B$  at low  $x$  is a result of the drop in *c*-lattice parameter of the  $\text{Li}_x\text{CoO}_2$  host. This drop is accompanied by a contraction of the space along the path of the TSH mechanism, making it energetically more difficult for the hopping lithium ion to pass through the tetrahedral site. The general increasing trend of  $\Delta E_B$  with decreasing  $x$  over the whole concentration range can be attributed to the change in effective valence of Co with  $x$ . The tetrahedral site along the TSH migration path shares a face with the octahedral site containing a Co. As  $x$  is reduced from 1 to 0, the effective valence of Co changes from +3 to +4. Hence as  $x$  is lowered, the electrostatic repulsion between a lithium in the tetrahedral site and Co increases.

Both the significant concentration dependence of the activation barriers and the dominance of the divacancy mechanism ensures that the diffusion coefficient in  $\text{Li}_x\text{CoO}_2$  varies several orders of magnitude with lithium concentration. Fig. 3 illustrates the diffusion coefficient at

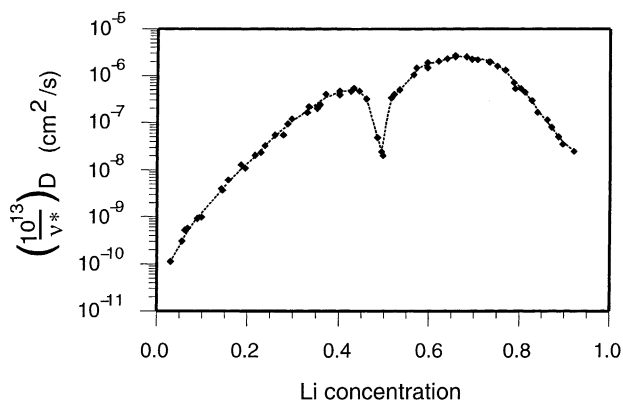


Fig. 3. Calculated value for  $D$  as a function of  $x$  at 400 K (lines serve as guide for eye). Because of the uncertainty in  $v^*$  of Eq. (1), we plot  $(10^{13}/v^*)D$ .

400 K calculated with kinetic Monte Carlo simulations. Since a rigorous first-principles calculation of the hop prefactor  $v^*$  is currently beyond practical computational capabilities, we have normalized the diffusion coefficient in Fig. 3 by  $10^{13}/v^*$ , where  $10^{13} \text{ sec}^{-1}$  is typically a good approximation for  $v^*$ . Values as low as  $10^{12}$  have been reported [9], though, implying that the calculated diffusion coefficient in Fig. 3 should correspond to the real diffusion coefficient within one to two orders of magnitude. Fig. 3 shows that the diffusion coefficient initially increases by several orders of magnitude with  $x$  as a result of the decrease in the activation barrier with  $x$ . Lithium ordering, at  $x = 0.5$  (which is still predicted to be stable at 400 K from first-principles [3]) produces a dip in the diffusion coefficient. As  $x$  is increased beyond 0.65, the diffusion coefficient drops as a result of the decreasing concentration of divacancies. This trend is observed experimentally [10–12].

In conclusion, first-principles calculations predict that diffusion in layered  $\text{Li}_x\text{CoO}_2$  occurs predominantly via a

divacancy mechanism. Furthermore, the activation barrier for diffusion is predicted to be very concentration dependent due to important variations in  $c$ -lattice parameter with  $x$  and the change in the effective valence of cobalt with  $x$ .

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