

Lithium Diffusion in Layered Li_xCoO_2

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The results of a first principles investigation of lithium diffusion within the layered form of Li_xCoO_2 are presented. Kinetic Monte Carlo simulations predict that lithium diffusion is mediated through a divacancy mechanism between $x = 0$ and $x < 1$ and with isolated vacancies at infinite vacancy dilution. The activation barrier for the divacancy migration mechanism depends strongly on lithium concentration resulting in a diffusion coefficient that varies within several orders of magnitude. We also argue that the thermodynamic factor in the expression of the chemical diffusion coefficient plays an important role at high lithium concentration.
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The layered nature of the O3 form of Li_xCoO_2 , a material used as the cathode in rechargeable lithium batteries, is well suited for the rapid removal and reinsertion of lithium ions. Within Li_xCoO_2 , the lithium ions reside in octahedral sites forming a two-dimensional triangular lattice between O-Co-O sheets. A variety of phase transformations occur in Li_xCoO_2 as the lithium concentration, x , is varied. These include a large two-phase region^{1,2} induced by a metal-insulator transition,^{3,4} order-disorder¹ and staging⁵ reactions, as well as structural transformations of the CoO_2 host.⁶ In a typical lithium battery, x is varied only between 1 and 0.5 because the c lattice parameter contracts significantly below $x = 0.5$.^{2,3,6}

Although thermodynamic and equilibrium properties have been studied extensively from first principles,^{3,5,7,8} only limited insight exists about the kinetic properties of lithium transport through the CoO_2 host.⁹ Lithium diffusion in the oxide is a key factor that determines the rate at which a battery can be charged and discharged. With increasing interest in higher power density, understanding the mechanisms of diffusion in insertion electrodes becomes important. In this paper, we present the results of a systematic theoretical study of lithium diffusion within the O3 form of Li_xCoO_2 (*i.e.*, having the $\alpha\text{-NaFeO}_2$ structure). We have used first-principles electronic structure methods in combination with Monte Carlo simulations to investigate the atomistic mechanisms of lithium diffusion. The technical details of these calculations will be published in a forthcoming paper.

The chemical diffusion coefficient D_c , as defined by Fick's first law, can be expressed as a product of a thermodynamic factor Θ and a jump diffusion coefficient D_j ¹⁰

$$D_c = \Theta D_j \quad [1]$$

where

$$\Theta = [\partial(\mu/kT)/\partial \ln x] \quad [2]$$

and

$$D_j = \lim_{t \rightarrow \infty} \left[\frac{1}{4t} \left\langle \frac{1}{N} \left(\sum_{i=1}^N \vec{r}_i(t) \right)^2 \right\rangle \right] \quad [3]$$

In Eq. 2, k is the Boltzmann constant, T is the temperature, x is the lithium content in Li_xCoO_2 , and μ is the lithium chemical potential. D_j is similar to a tracer diffusion coefficient but includes the effect of correlation in the motion of particles. N in Eq. 3 corresponds to the number of diffusing lithium ions and $\vec{r}_i(t)$ is the displacement of the i th lithium ion after time t . We have approximated

the rate Γ with which lithium ions hop to vacant neighboring sites by transition state theory¹¹ according to

$$\Gamma = \nu^* \exp(-\Delta E_b/kT) \quad [4]$$

where ν^* is an effective vibrational frequency and ΔE_b is 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. Typically, the prefactor ν^* is on the order of 10^{13} s^{-1} ; however, a first-principles investigation of two-dimensional diffusion on germanium surfaces¹² has indicated that ν^* can be on the order of 10^{11} s^{-1} .

As a result of interactions between lithium ions, the activation barrier depends on the presence and arrangement of other lithium ions. Activation barriers for lithium migration in different lithium vacancy environments of Li_xCoO_2 were calculated with the first-principles pseudopotential method (as implemented in the Vienna *ab initio* simulation package code¹⁵) within the local density approximation (LDA) of density functional theory. Calculations were performed in supercells containing 37-47 ions, and the locations of the activated states were determined with the elastic band method.¹³ The calculated activation barriers were used to parameterize a local lattice model that characterizes the activation barrier for arbitrary lithium vacancy arrangement. This lattice model in combination with the lattice model for the configurational energy of the O3 host of Ref. 3 was implemented in kinetic Monte Carlo simulations¹⁴ to calculate the lithium diffusion coefficient with Eq. 1-4. The procedure, therefore, takes into account the necessary thermodynamic (*i.e.*, lithium-lithium interactions) and kinetic information (activation barriers) affecting diffusion.

The first-principles calculations indicate that lithium migration to an adjacent vacant octahedral site occurs according to one of two mechanisms depending on the lithium-vacancy arrangement around the hopping ion. The migration paths of the two mechanisms are illustrated in Fig. 1a and b. If a lithium ion hops into an isolated vacancy (Fig. 1a), the minimum energy path involves the squeezing past a dumbbell of oxygen ions O(1) and O(2) (Fig. 1a) by the hopping lithium ion. We refer to this migration mechanism as an oxygen dumbbell hop (ODH). If the lithium ion hops into a vacancy that is part of a divacancy (Fig. 1a) then the minimum energy path passes through the tetrahedral site centered between the two vacancies and the initial site of the hop. Note that both vacancies of the divacancy are simultaneous neighbors of the migrating lithium ion. We refer to this migration mechanism as a tetrahedral site hop (TSH). The TSH mechanism also occurs when lithium hops into a vacant site that is part of a cluster of more than two vacancies. A hopping mechanism similar to the TSH has also been conjectured to occur based on the results of molecular dynamics simulations.⁹

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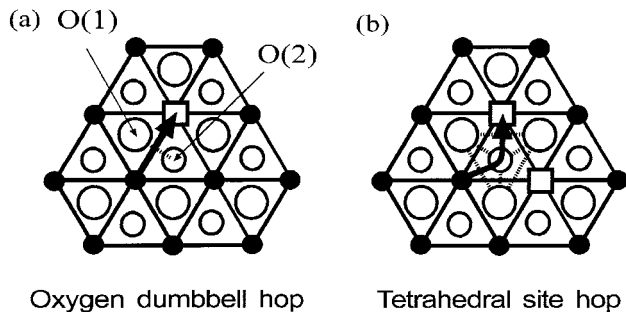


Figure 1. The two lithium migration paths as seen looking down on the Li_xCoO_2 crystal structure along the c axis. The triangular grid corresponds to the lithium sites, the filled circles are lithium ions, the large empty circles are oxygen ions in the plane directly above the lithium plane and the small empty circles are oxygen ions directly below the lithium plane. \square refer to lithium vacancies. (a) Oxygen dumbbell hop (ODH). (b) Tetrahedral site hop (TSH).

Figure 2a shows the activation energy calculated with the pseudopotential method for the TSH and ODH mechanisms at different concentrations. Two main trends can be observed: The activation energy for the TSH (between 230 and 600 meV) is always considerably lower than that for the ODH (~800 meV) and the activation barriers increase as Li_xCoO_2 is delithiated. Although the TSH activation energies are significantly less than those for the ODH mechanism, a TSH requires the presence of a divacancy, a phenomenon less likely to occur as x approaches 1. This suggests that a concentration should exist below which the TSH mechanism dominates and above which the ODH mechanism dominates. Our Monte Carlo simulations indicate that such a transition occurs only at infinite dilution of vacancies, *i.e.*, as x approaches 1.

Figure 2b illustrates the average activation barrier $\langle\Delta E_B\rangle$ overcome by hopping lithium ions as calculated with the Monte Carlo simulations.⁴ A comparison with Fig. 2a clearly illustrates that lithium ions hop exclusively according to the TSH mechanism between $x = 0$ and 1. This means that lithium diffusion within Li_xCoO_2 occurs through the motion of divacancies. It is only at infinite vacancy dilution, where the divacancy concentration vanishes, that lithium diffusion occurs according to the ODH mechanism. In real systems, some amount of intrinsic vacancy defects will always be present so that the regime where the ODH mechanism dominates may never be attained. The prediction that lithium migration is mediated through divacancies is a result of the large difference in activation barriers between the TSH and ODH mechanisms.

The origins of the variation of the TSH activation barriers with x can be traced to two factors. The dramatic rise in $\langle\Delta E_B\rangle$ at low x is in large part caused by a rapid drop in the c lattice parameter of the O3 host below approximately $x = 1/3$, a feature of Li_xCoO_2 that is both observed experimentally^{2,6} and predicted from first principles.³ A drop of the c lattice parameter is accompanied by a reduction of the distance between the oxygen planes, and hence, a contraction of the tetrahedral site along the TSH migration path. A second factor contributing to the rise in $\langle\Delta E_B\rangle$ with decreasing x is the change in effective valence of the cobalt ions with x . The tetrahedral site along the TSH migration path shares a face with an oxygen octahedron around a cobalt ion. A lithium ion in the tetrahedral site therefore experiences a large electrostatic repulsion from the positively charged Co ion. As x is reduced, the effective positive charge on Co increases causing the activation barrier to simultaneously increase.

Figure 3 illustrates calculated values for the jump diffusion coefficient D_j , the thermodynamic factor Θ , and the chemical diffusion

⁴ Note that this is not the same as the activation energy for diffusion in an Arrhenius approximation as the latter contains the temperature dependence of the divacancy concentration.

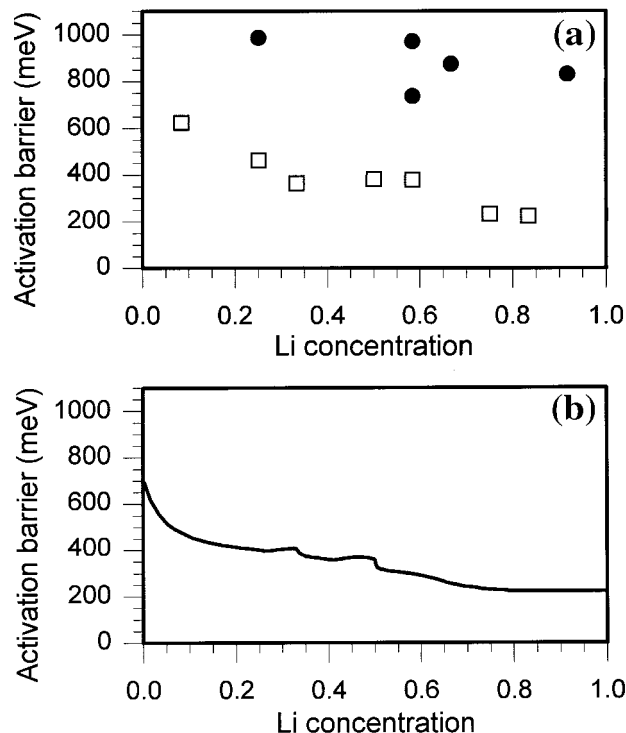


Figure 2. (a) First-principles activation barriers for the TSH (\square) and ODH (\bullet) mechanisms at several different lithium concentrations x as calculated within LDA. (b) Variation with x of the average activation barrier overcome by hopping lithium ions in the Monte Carlo simulations.

coefficient D_c at 300 and 400 K as a function of x . Because of the uncertainty in the prefactor v^* , $(10^{13}/v^*)D$ (where D refers to either D_c or D_j) is plotted which should correspond to the real D within one to two orders of magnitude. D_c varies by several orders of magnitude with x . For small x , D_c is low as a result of the high activation barrier $\langle\Delta E_B\rangle$. The reduction of $\langle\Delta E_B\rangle$ by 300 meV with increasing x (Fig. 2) causes an increase in D_c at intermediate values of x . The dips in D_c at $x = 1/3$ and $x = 1/2$ at 300 K and at $x = 1/2$ at 400 K are produced by the lithium ordering predicted by the first-principles lattice model³ used in this study. Lithium ordering energetically locks the lithium ions at their sublattice sites, thereby reducing their mobility. Above $x = 0.65$, D_c drops by several orders of magnitude despite a more or less constant and low value of $\langle\Delta E_B\rangle$.

The significance of a divacancy diffusion mechanism is especially pronounced at intermediate to high lithium concentration. The Monte Carlo simulations predict that the equilibrium divacancy concentration within Li_xCoO_2 decreases more rapidly with increasing x than the concentration of isolated vacancies. This results in a sharper decrease in D_c with x than would be the case if diffusion occurred with a single-vacancy mechanism and with the same and constant activation barrier. The divacancy mechanism has important consequences on how diffusion should be modeled in simpler theories. For a single-vacancy mechanism, diffusivity in the dilute vacancy limit becomes proportional to $1-x$ (the concentration of vacancies). For a divacancy mechanism with randomly distributed vacancies, D_c is proportional to $(1-x)^2$, leading to a much stronger concentration dependence. Lithium-lithium interactions reduce the divacancy concentration even further than the $(1-x)^2$ dependence.

Several experimental investigations of the lithium diffusion coefficient in Li_xCoO_2 have been performed,¹⁷⁻¹⁹ all exhibiting essentially the same qualitative concentration dependence: as x is lowered from 1 to 0.95, D_c drops by one to two orders of magnitude. As x is lowered from 0.75 to 0.5, it increases by one to two orders of mag-

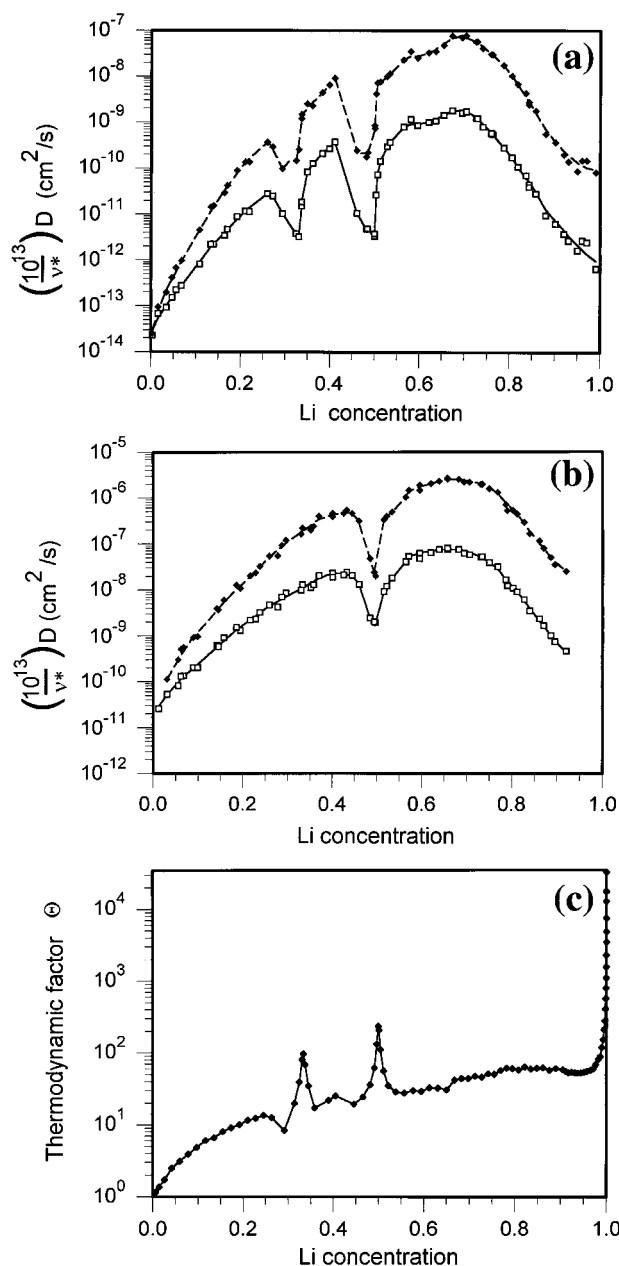


Figure 3. Calculated values for D_c (\blacklozenge) and D_j (\square) as a function of x at (a) 300 and (b) 400 K (lines serve as guide for eye). Because of the uncertainty in v^* of Eq. 4, we plot $(10^{13}/v^*)D$ where D corresponds to D_j or D_c . (c) Calculated thermodynamic factor at 300 K.

nitude. Between $x = 0.75$ and 0.95 , a two-phase region exists and a value for D_c cannot be defined.

The rise in D_c as x approaches 0.5 is clearly reproduced by the calculations Fig. 3. This is especially true at $T = 400$ K where the predicted width of the ordered phase at $x = 1/2$ closely approximates the experimentally measured width at room temperature. The experimentally observed initial decrease in D_c as x is lowered from 1 to 0.95 is not reproduced by the calculations.

We attribute the sharp drop in D_c between $x = 1$ and 0.95 observed experimentally to the rapid change in the thermodynamic factor, Θ , in this concentration range. The thermodynamic factor is a measure of the deviation of the chemical potential from that for an ideal solution. Its role is to ensure that the flux as calculated with

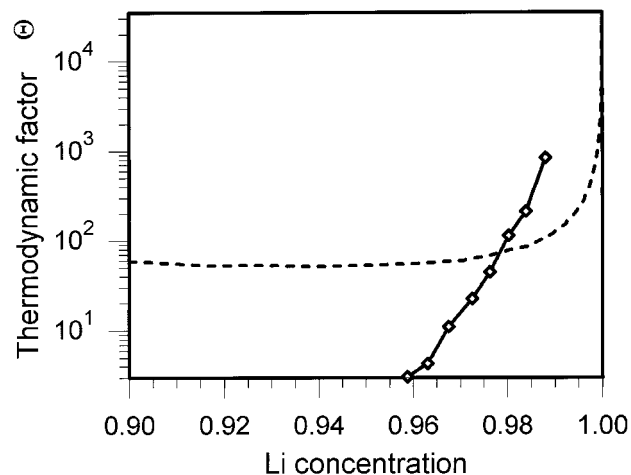


Figure 4. Comparison between calculated (-----) and experimental (\diamond) thermodynamic factors Θ of Li_xCoO_2 .

Fick's first law using D_c correctly reflects the fact that the true driving force for lithium diffusion is a gradient in chemical potential and not a gradient in concentration as is assumed explicitly in Fick's law. As x approaches 1 , at which point Li_xCoO_2 becomes a stoichiometric compound, the lithium chemical potential deviates strongly from ideality. In this regime, a small gradient in concentration has an enormous amplifying effect on the gradient in chemical potential. This is reflected by a large thermodynamic factor.

Although the calculated D_c between $x = 1.0$ and 0.95 does not exhibit the experimentally observed decrease as the lithium concentration is lowered from $x = 1.0$, inserting values for Θ determined from the experimental open-circuit voltage⁴ along with the calculated D_j into Eq. 1, however, does result in a drop in D_c . We therefore conclude that the qualitative discrepancy between calculated and experimental D_c above $x = 0.95$ is of a thermodynamic origin. A comparison of the calculated Θ and that approximated from the experimental voltage curve⁴ between $x = 0.9$ and 1 is illustrated in Fig. 4. The calculated value of Θ above $x = 0.95$ differs from experiment because our lattice model fails to account for the localized electron holes present in Li_xCoO_2 in this concentration range.^{3,4} It is also for this reason that the first-principles model is unable to predict the two-phase region between $x = 0.75$ and 0.95 .³ Because of the two-phase region, where Θ is zero, the experimental Θ spans a much larger interval than the calculated quantity between $x = 1.0$ and 0.95 and more than compensates for the increasing trend of D_j with decreasing x .

In conclusion, our major findings can be summarized as follows. (i) For most values of x , lithium migration to adjacent vacant octahedral sites is mediated through a divacancy mechanism and the migration path of this mechanism passes through a tetrahedral site; (ii) The activation barrier associated with the divacancy hop mechanism increases with decreasing lithium concentration; (iii) We have argued that the drop in D_c at high x as x is reduced from 1.0 to 0.95 is a result of the thermodynamic factor which expresses the deviation of the lithium chemical potential from ideality.

Although the results in this paper were derived for Li_xCoO_2 , similar conclusions are likely to hold for other layered materials with the $\alpha\text{-NaFeO}_2$ structure such as Li_xNiO_2 and layered Li_xMnO_2 . The understanding that the concentration of divacancies, the variation of c lattice parameter and the change in valence of the transition metal with x are factors that affect lithium transport may lead to strategies to improve the diffusivity in these materials.

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