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Factors that affect Li mobility in layered lithium transition metal oxides

Kisuk Kang and Gerbrand Ceder*

Center for Materials Science and Engineering and Department of Materials Science and Engineering, Massachusetts Institute of Technology, 77 Massachusetts Avenue, Cambridge, Massachusetts 02139, USA

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The diffusion constant of Li in electrode materials is a key aspect of the rate capability of rechargeable Li batteries. The factors that affect Li mobility in layered lithium transition metal oxides are systematically studied in this paper by means of first-principles calculations. In close packed oxides octahedral ions diffuse by migrating through intermediate tetrahedral sites. Our results indicate that the activation barrier for Li hopping is strongly affected by the size of the tetrahedral site and the electrostatic interaction between Li^+ in that site and the cation in the octahedron that shares a face with it. The size of the tetrahedral site is determined by the *c*-lattice parameter which has a remarkably strong effect on the activation barrier for Li migration. The effect of other factors such as cation mixing and doping with nontransition metal ions can be interpreted quantitatively in terms of the size and electrostatic effect. A general strategy to design high rate electrode materials is discussed.

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I. INTRODUCTION

New applications for rechargeable lithium batteries, such as hybrid electric vehicles (HEV), or power tools require high charge and discharge rates, and tradeoffs between energy and power density in battery materials are often made. High power requires that Li diffusion in and out of the electrode materials takes place fast enough to supply the electrical current. In cells with liquid electrolytes, diffusivity in the electrode material and through the porosity of the composite electrode are usually among the rate limiting factors.[1–4] While electrode porosity can be engineered, the Li diffusivity in an active compound is an intrinsic property of the material. In this paper we investigate the factors that affect Li mobility in the O3-type layered structure, common for electrode compounds. In this structure it is believed that Li diffusion takes place in the Li layer by hopping from octahedral to octahedral site through intermediate tetrahedral sites (Fig. 1).[5,6]

The oxygen distance across the Li layer, cation mixing, and the nature of the metal ion in the transition metal layer have all been proposed to influence the Li mobility in the layered structure.[7–10] Using first-principles methods to calculate the energy of Li in the activated state, as a function of all these variations, the extent to which each of these impacts diffusion can be studied.

II. METHODOLOGY

All energies are calculated with the spin-polarized generalized gradient approximation (SGGA) to the density functional theory (DFT), using a plane-wave basis set and the projector-augmented wave (PAW) method[11] as implemented in the Vienna *ab initio* simulation package (VASP).[12] A plane-wave basis with a kinetic energy cutoff of 400 eV was used, and reciprocal-space *k*-point grids were $3\times3\times5$ or $3\times3\times3$ depending on the supercell size. In order to minimize interactions between Li-vacancy images arising from the periodic boundary conditions, a supercell of $12\times Li_{1-\delta}MO_2$ formula units has been used[5,13] except for the cation-mixed $LiNiO_2$ system for which a larger supercell of $24\times Li_{1-\delta}MO_2$ has been used to avoid out-of-plane interactions between Ni defects in the Li layer. Two out of 12 lithium sites are vacated in a unit cell for Li motion. Two lithium vacancies are adjacent in a triangular lattice.[5]

In the layered O3 structure, there are several possible pathways for Li ions to hop. Previous work has identified the most likely pathway as one in which an octahedral Li moves through the tetrahedral site by means of a divacancy (Fig. 1).[5,13] The other pathways require so much higher activation energy that their contribution to Li motion is negligible.[5,13] Therefore, in this study, we investigate Li motion in the octahedral-tetrahedral-octahedral pathway. Li activation energies were calculated in supercells with two adjacent vacancies out of 12 Li sites. The activation barrier is approximated to be the difference in energy between Li in the octahedral and intermediate tetrahedral site. It was previously shown that Li in the tetrahedral site is very close to the maximum energy along the migration path.[5,6]

III. RESULTS

A. Effect of Li slab distance

Since Li movement is constrained to a two-dimensional (2D) layer, the spacing of the oxygen layers around the Li layer is critical to Li motion.[8] The idea is related to the free-volume ideas of diffusion in a large class of materials: more open space facilitates atomic motion. To investigate the effect of Li slab distance, calculations are performed on a representative layered system such as $LiCoO_2$ (Fig. 2). The Li slab distance is varied in the calculations by expanding or contracting the *c*-lattice parameter. Because transition metal (Co)-O bonding is much stiffer than Li-O bonding, the majority of change in the *c*-lattice parameter is accommodated by the Li slab distance (86%). Slab distances were varied around the equilibrium value by about ±4%, which is typical of variations observed in layered lithium transition metal ox-

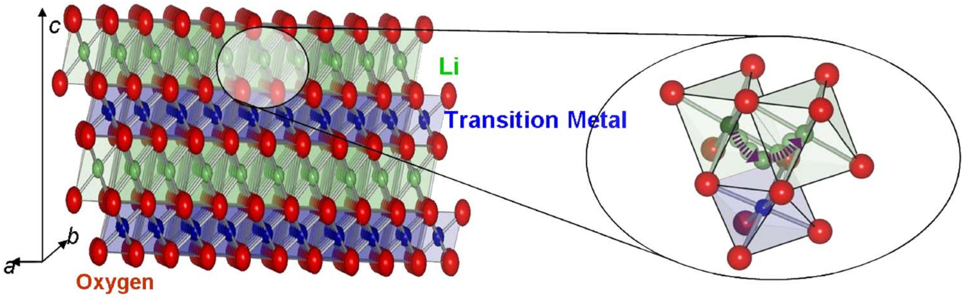

FIG. 1. (Color online) In layered lithium transition metal oxides Li hops between octahedral sites through an intermediate tetrahedral site. The activated tetrahedral site shares an oxygen face with a transition-metal octahedron below.

ide depending on Li content and transition metal species. Our calculated equilibrium Li slab distance for fully lithiated $LiCoO_2$ (2.64 Å) is in good agreement with the experimental value (2.64 Å).[14,15] Also, the calculated activation barrier obtained at the equilibrium Li slab distance agrees well with previous computational studies.[5,13] The results shown in Fig. 2 indicate that activation barriers for Li migration vary considerably with Li slab distance, changing by more than 200% for a 4% change in Li slab distance. Since diffusivity is inversely proportional to the exponential of the activation barrier, this variation will result in a dramatic change in the macroscopic rate of Li diffusion.

To understand this remarkable variation more thoroughly, Fig. 3 shows how the energy of octahedral (initial state) and tetrahedral (activated state) Li positions individually vary with Li slab distance. Both energy curves follow a harmonic behavior with Li slab distance but their minima are located at different slab spacings. The minimum energy for Li in a tetrahedral site lies at a larger Li slab distance than the equilibrium structure. Therefore, for the equilibrium lattice parameters, Li is under relative compressive stress when positioned in a tetrahedral site. As the Li slab distance gets larger, compression on the activated Li site is released, leading to a lower activation barrier. At very high Li slab distances the tetrahedral and octahedral site energy cross over, and in this regime diffusion in the slab resembles surface diffusion with no considerable strain contribution to the activation energy.

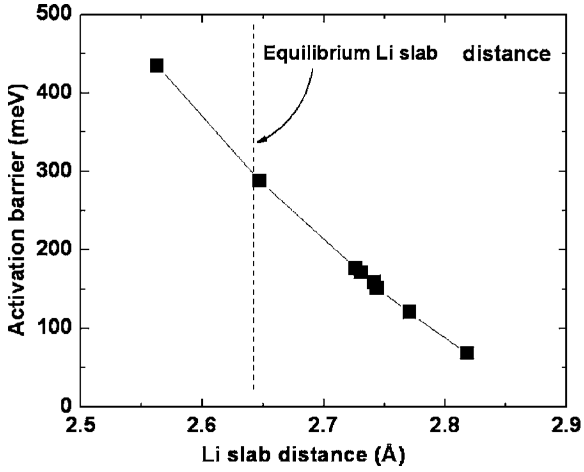

FIG. 2. Activation barrier (squares) for Li migration in $LiCoO_2$ as a function of Li slab distance. The dashed line shows the calculated equilibrium Li slab distance at a fully lithiated state.

B. *a* and *b* lattice parameter

One can vary the size of the activated tetrahedral sites by changing not only the *c*-lattice parameter (Li slab distance) but also the *a (or b)*-lattice parameters. If compression in the tetrahedral site is uniform in all directions, a change in the *a (or b)*-lattice parameter should give similarly large variations in E_a as the ones observed for the *c*-lattice parameter. However, as shown in Fig. 4, the calculated activation barrier is considerably less sensitive to *a (or b)*-lattice parameter variations. Although the calculated activation barrier decreases with *a (or b)*-lattice expansion, this dependency is considerably smaller than the dependence on *c*-lattice parameter.

A closer look at atomic arrangements around a Li tetrahedral site reveals that the volume of the tetrahedron increases with *a (or b)*-lattice expansion but the shortest Li-O distance in the tetrahedron, which is along the *c* direction, changes very little. This indicates that the compression in the activated Li tetrahedral site is mainly along the *c* direction (perpendicular to the Li slab) and the expansion of the tetrahedron along the *a (or b)* direction does not release the compression to a significant degree. Also, we note that Li resides far from the tetrahedral face that is shared with a Co octahedron. This is due to the strong electrostatic repulsion between Li^+ and Co^{3+} along the *c* direction.

C. Nontransition metal (Al or Mg) substitution

Successful performance enhancements of commercial Li batteries utilize a strategy of doping nontransition metals into

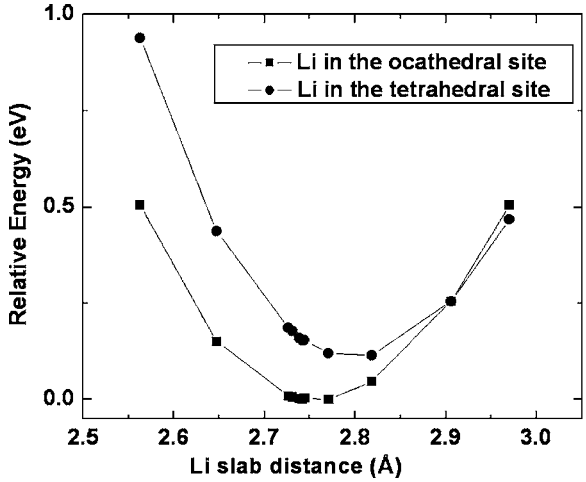

FIG. 3. Energy for Li in the octahedral (squares) and tetrahedral (circles) site as a function of Li slab distance.

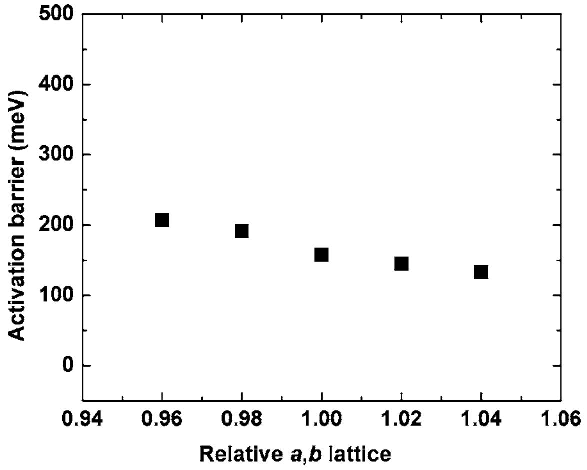

FIG. 4. Activation barrier for Li migration in $LiCoO_2$ as a function of *a* (or *b*)-lattice parameter.

lithium transition metal oxides. By substituting nontransition metals into the layered structure, various electrochemical properties such as voltage, structural integrity, electronic conductivity, and safety of the electrode are greatly enhanced.[16–19] It has recently been reported that Li diffusion might be deteriorated by doping nontransition metals into $LiCoO_2$,[10] and as such, we investigate the effect of nontransition metal element addition on Li mobility.

Nontransition metal substitution is studied by calculating activation barriers in a system where two Al or Mg ions replace two Co ions in a supercell containing 12 transition metal sites. The doping ions are placed next to one another to observe their effect more clearly, and Li is allowed to move through the tetrahedral site face-sharing with the Al or Mg octahedron. Activation barriers for Al and Mg-doped systems are shown in Fig. 5 at two different Li slab distances, and compared with undoped $LiCoO_2$. The doped materials show consistently higher activation barriers than undoped $LiCoO_2$. For the Al-doped system, the activation barrier is higher by about 100 meV and for the Mg-doped system, it is higher by about 30 meV than that of the undoped $LiCoO_2$ at the equivalent Li slab distance. This increase of the activation barrier by nontransition metal doping of $LiCoO_2$, especially by Al-doping, may result in an appreciable decrease in the macroscopic rate of Li diffusion.

The variation of activation barriers with nontransition metal substitution cannot be explained in terms of structural parameters such as the size of the Li tetrahedron, since no appreciable difference in the size of each tetrahedron is observed. The tetrahedron that face-shares with Mg is actually slightly larger than in undoped $LiCoO_2$. However, a clear difference between the undoped and the nontransition metal doped system can be observed in the electronic structure of the oxygen ions near the migrating Li. Figure 6 shows the electron charge integrated around three oxygen atoms that form the shared triangular face between the tetrahedron that Li is migrating through and the adjacent octahedron containing Al [Fig. 6(a)], or Mg [Fig. 6(b)]. For comparison, the same charge integrations for undoped $LiCoO_2$ are shown as a dashed line in each figure. The graph shows the number of electrons as a function of the sphere radius around an oxygen

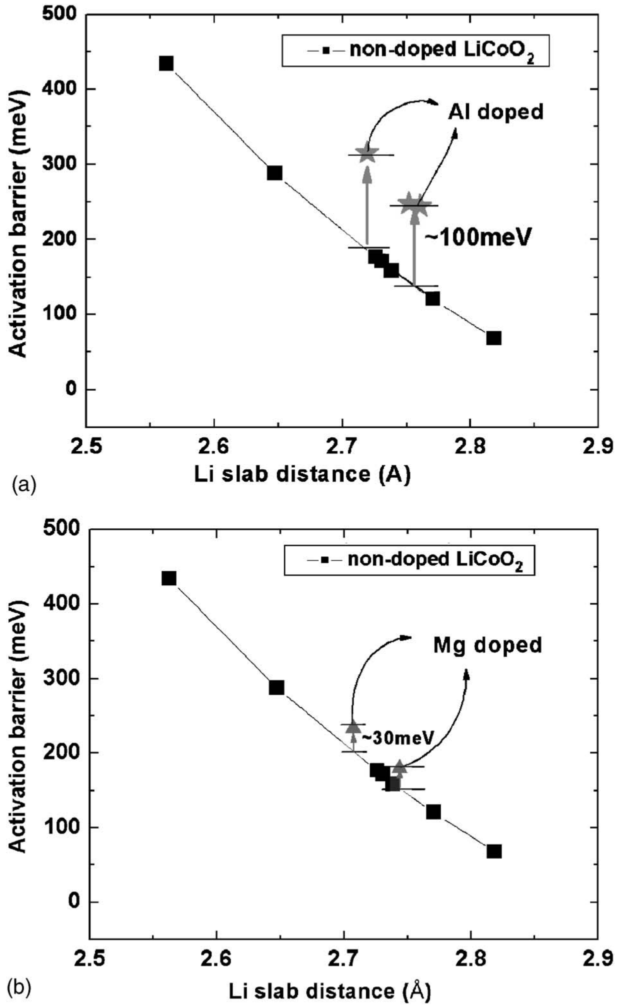

FIG. 5. (a) Activation barriers (stars) obtained for Al-doped $LiCoO_2$. (b) Activation barriers (triangles) obtained for Mg-doped $LiCoO_2$.

atom. Figures 6(a) and 6(b) indicate that oxygens between the migrating Li and Al or Mg have less electron density on them than in the undoped case. Upon closer inspection we find that the electron density around oxygen systematically decreases with an increasing number of nontransition metal nearest neighbors. Oxygen electron density plays an important role in screening the electrostatic interactions between cations, as was already noticed previously.[5,13] Hence, a reduction of that screening will lead to a more bare interaction between Li in the activated state and the face-sharing cation, and consequently a higher activation barrier.

Note that Mg substitution increases the activation barrier less than Al. Because of its lower charge, Mg^{+2} will cause less repulsion for Li in the tetrahedral site than an ion with a +3 valence state. Hence, the activation barrier increases due to the less effective screening by oxygen but is somewhat offset by the weaker electrostatic repulsion with Li.

D. Transition metal species

We further investigated the effect of doping on the Li migration barriers by performing additional calculations for

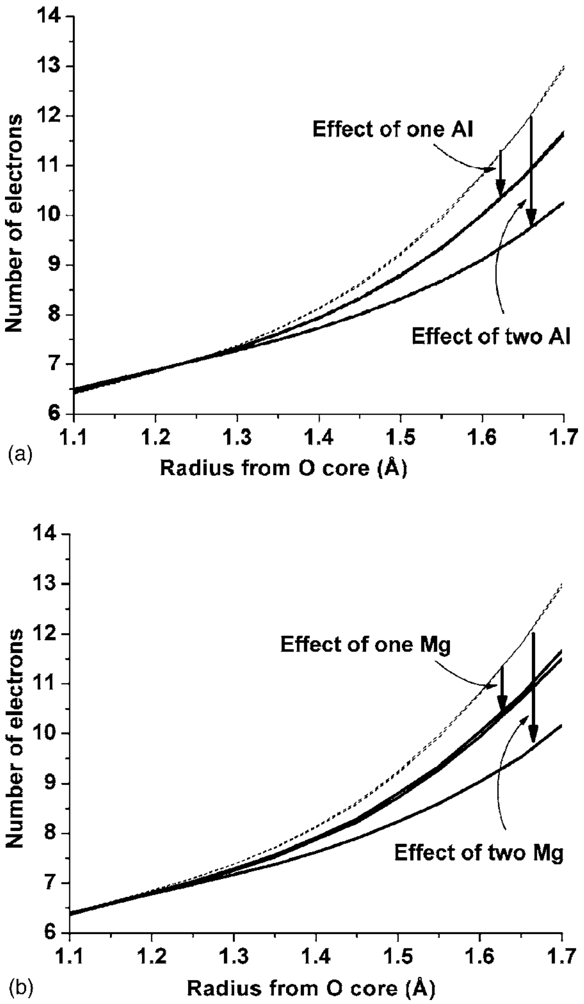

FIG. 6. Electron charge density integrated around oxygen atoms near Li in the tetrahedral site for (a) Al-doped $LiCoO_2$ (b) Mg-doped $LiCoO_2$. The dashed lines give the electron charge density integrated in undoped $LiCoO_2$ for comparison.

layered $LiVO_2$, $LiCrO_2$, $LiTiO_2$, $LiNiO_2$ and $LiFeO_2$. Some of these compounds can be synthesized in the layered structure, while others are purely hypothetical. All systems show a similar dependence of Li mobility on the Li slab distance (Fig. 7). Similar slopes in each system indicate that the dependency is rather general in layered structures. However, activation barriers for a given slab distance vary from Ti to Ni. While Ni and Fe oxides behave similarly to $LiCoO_2$, V, Cr and Ti layered oxides show substantially higher activation barrier. This result is somewhat consistent with what was observed for nontransition metal doping. Generally, the early transition metals tend to induce less electron density around oxygen than the late transition metals leaving the oxygen ions with less screening power. The observation that late transition metal layered oxides exhibit a relatively low activation barrier for Li motion explains in part why most useful layered oxide electrodes contain late transition metals.

E. Valence of transition metal

We further investigated the effect of transition metal valence on the Li migration barrier. It has already been speculated that the valence of the transition metal ion that face-shares with the activated state significantly influences the Li migration barrier.[5] Activation barriers are calculated for several important transition metals in different valences at a fixed Li slab distance. The calculations are performed for various chemistries and Li contents. For example, activation barriers for +3 ions are obtained using the lithiated form of Li_xMO_2 (M is transition metal), while activation barriers for +4 ions are obtained using the delithiated form of Li_xMO_2 except Mn^{4+} whose activation barrier is calculated in $Li_x(Ni_{0.5}Mn_{0.5})O_2$ along with Ni^{2+}. Lastly, the activation barrier for Cu^{2+} is obtained in Li_xCoO_2 with a small amount of Cu doping. Some of these differences in Li concentration and chemistry may affect the results but we believe our main conclusion will hold. The results in Fig. 8 clearly show that low valent cations lead to a lower migration barrier for Li. This is not surprising given that the lower (higher) valent cations exhibit weaker (stronger) electrostatic interaction with the migrating Li. Since the valence of the transition metal ion in the electrode compound changes with Li content upon charge and discharge, the effect of transition metal valence plays a role in the charge/discharge process. Indeed, the oxidation of Co^{3+} to Co^{4+} is one contributing factor to the observed variation of the Li diffusivity with Li content in $LiCoO_2$.[3,5,20] The decrease in Li diffusivity at the end of charge of the cell is in part explained by stronger electrostatic interaction with the Co^{4+}.

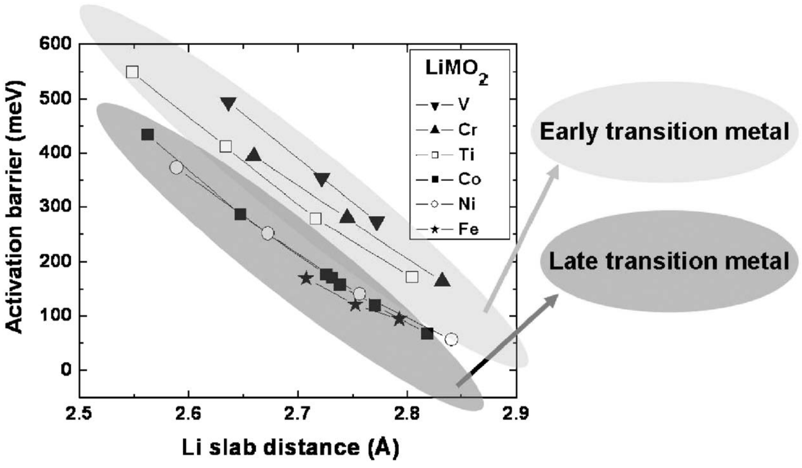

FIG. 7. Calculated activation barrier as a function of Li slab distance for various layered lithium transition-metal oxides.

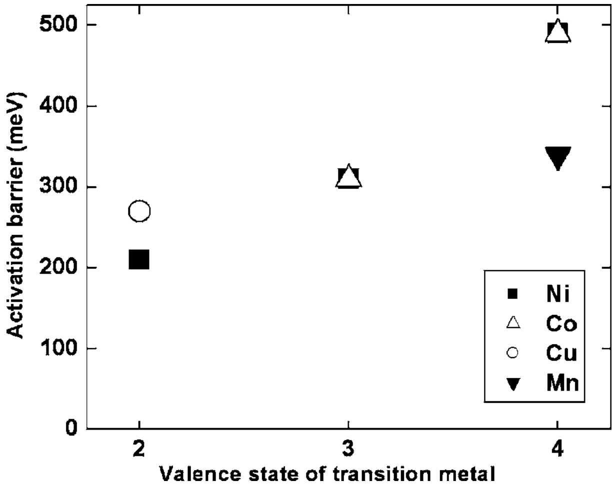

FIG. 8. Activation barriers for Li motion for various transition metals. The values were calculated at a fixed Li slab distance for various chemistries and Li contents.

F. Cation mixing (defects in Li layer)

Layered lithium transition metal oxides especially those including Ni^{+2} or Ti^{+4} are often observed to have cation mixing in the structure. Cation mixing is believed to be a result of the similar ionic size of Li^{+} and Ni^{2+} (or Ti^{+4}), since the major driving force for layering is the size difference of the cations.[21,22] For $LiNiO_2$ it has been demonstrated that the amount of Ni in the Li layer is critical to the electrochemical performance of the electrodes.[23] To investigate how and to what extent the presence of Ni in the Li layer affects the Li mobility, we calculated the Li migration barrier in $LiNiO_2$. Cation mixing is commonly observed in this material and the activation barrier in well-ordered $LiNiO_2$ is similar to that in $LiCoO_2$. Li/Ni disorder is simulated by occupying one out of 12 Li sites with excess Ni and calculating the activation barrier for a Li hop near this Ni in the Li layer.

Figure 9 shows that cation mixing affects the activation barrier primarily by changing the equilibrium Li slab distance. Systems with and without cation mixing lie on the same curve, but the effect of Li/Ni disorder is to reduce the Li slab distance. In particular, when the Li slab distance is relatively large, the contraction induced by Ni in the Li layer is rather severe, implying that the effect of Ni in the Li layer will be more dramatic in the partially delithiated state. The rate limiting effect of Ni in the Li layer may therefore be particularly pronounced in the initial charge process. Upon charging, the outer shell of electrode particle is delithiated first. The concomitant Li slab opening and increase in Li mobility facilitates further transfer of Li through this layer. This effect can also be observed in the dependence of Li diffusivity on Li concentration.[3,20] When Ni is present in the Li layer, the increase in Li mobility upon charging will be considerably less, which may result in less deintercalation of the active material.

It is interesting to observe that the amount at which the activation barrier increases with cation mixing is almost exactly the same as for a perfectly layered material under the same Li slab contraction. This indicates that other potential factors, such as electrostatic repulsion between Li and Ni in the Li layer, are not significant.

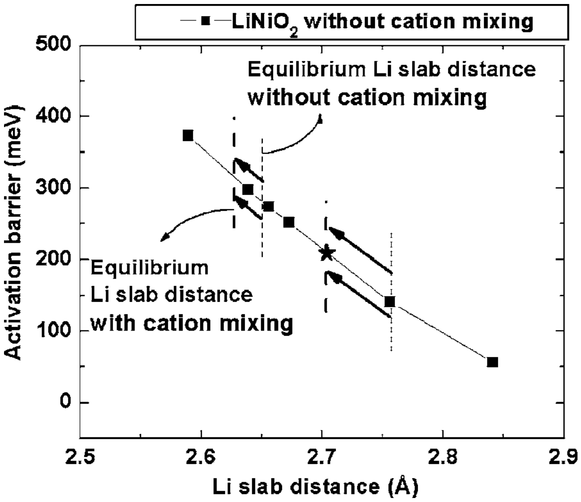

FIG. 9. The calculated activation barrier for Li migration in $LiNiO_2$ with cation mixing (stars) and without cation mixing (squares). The Li slab distances with and without cation mixing are indicated with thick and thin dashes at different Li contents, respectively. The shift on the left is from fully lithiated state and the one on the right is from partially delithiated state.

G. Anion effect

The effect of anions on Li mobility is investigated by studying how the activation barrier for Li migration is different between an oxide and sulfide within the same layered structure. Typically the 3*d*-metal sulfides and oxides rarely have the same structure, but we keep the structure in our work the same in order to capture purely chemical effects. The study is performed for two representative transition metal oxide/sulfide systems, hypothetical layered $LiCoS_2$ and $LiTiS_2$ in comparison with $LiCoO_2$ and $LiTiO_2$. Because the Li slab distance is calculated by averaging z of the sulfur layer above and below each metal and subtracting them, the comparison with the oxide systems is only possible after considering the size difference of oxygen and sulfur ion. All slab distance of the sulfides are shifted (by about 0.8 Å, approximately the difference in ionic diameters of oxygen and sulfur) so that the equilibrium Li slab distance of sulfides coincides with the equilibrium one in the oxide system.

Activation barriers obtained for sulfides with adjusted Li slab distances are plotted with the results for oxides in Fig. 10. Similar to what we observed with oxides, the Li slab distance appears to be a critical factor, affecting the activation barrier in the sulfide system. However, the activation barriers significantly decrease from oxide to sulfide. For both Ti and Co, it decreases by about 200–250 meV at the equilibrium Li slab distance. This is not unexpected, because in a sulfide the migrating Li can be farther away from the transition metal due to the bigger ionic size of the sulfur ion. Indeed, the Li-Ti distance at the equilibrium Li slab distance increases from 2.39 Å in oxide to 2.78 Å in sulfide. This confirms that the electrostatic interaction between cations

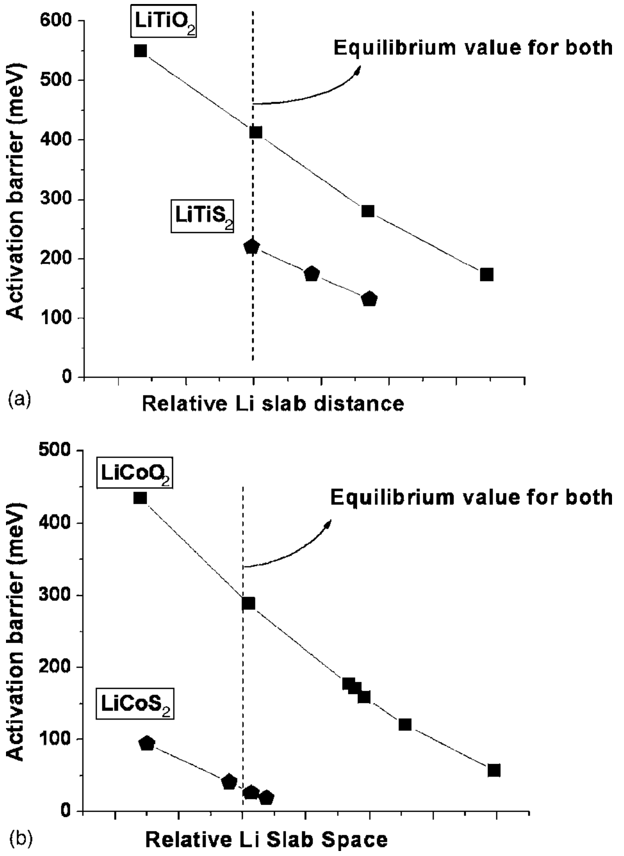

FIG. 10. Activation barriers of Li migration for sulfides as a function of normalized Li slab distance compared to oxides. Slab distances of the sulfides are shifted so that the equilibrium Li slab distance of sulfides coincides with the equilibrium one in the oxide system. (a) $LiTiS_2/LiTiO_2$ and (b) $LiCoS_2/LiCoO_2$.

during Li migration is a critical factor. Additional contributions in reducing the activation barrier may come from more effective screening by sulfur. A larger electron density on the sulfur ion can provide better shielding between a migrating Li and a transition metal ion.

The difference in activation barriers for Ti and Co systems is also observed in the sulfides. We attributed the difference in oxides to the less effective screening role of oxygen in a Ti system. The investigation of the electron charge density near the migrating Li also reveals that a similar phenomenon controls the activation barrier in sulfide systems (not shown here).

Interestingly, the activation barrier at an equilibrium Li slab distance is less than 50 meV in $LiCoS_2$. With this low activation barrier, the Li migration in the electrode is not likely to be the rate limiting factor for the battery operation, even though it needs to be stressed that this compound is purely hypothetical. The low activation barrier found for $LiTiS_2$ at the equilibrium Li slab distance seems to *a posteriori* justify the use of this compound as one of the first positive electrodes in Li battery technologies.[8,24]

IV. DISCUSSION AND CONCLUSION

We systematically investigated several factors that influence the migration barrier for Li motion in layered oxides with the O3 structure. The two dominant effects are the Li slab spacing determining the compressive stress on Li when it is in the tetrahedral site, and the electrostatic repulsion Li experiences there from the transition metal ion. These two effects are coupled to some extent. As the tetrahedral site becomes expanded in the c direction, Li in the tetrahedral site can move farther away from the face-sharing transition metal cation. The structural and compositional aspects that may contribute to high rate capability are therefore conceptually straightforward: (1) Create materials with large Li slab distance over the relevant Li composition range, and (2) Create a percolating network of tetrahedral sites in contact with low valent metal cations. The Li slab criterion may be difficult to engineer, as the distance between oxygen layers around Li is largely determined by the ionic size of Li^+ and the electron density on oxygen. The latter aspect is particularly important at high levels of delithiation ($x<0.5$ in Li_xMO_2 where M is a transition metal) where O-O interactions across the slab lead to a contraction which is very pronounced as x approaches zero.[25,26] Attempts to covalently bond groups across the Li slab in order to keep it open have been made.[27] The requirements on these groups (chemically inert, immobile…) limit the chemistries that can be used. The limit of Li slab spacing is ultimately a free surface, and nanotubes or small nanofibers may approach this diffusion limit.[28]

The second important factor, namely the electrostatic interaction between Li in the tetrahedral site and the face-sharing transition metal may be easier to engineer. Our calculations show that low valent cations are clearly effective in lowering the migration barrier for Li. Since the average valence in the transition metal layer is +3, lower valent cations need to be compensated by higher valent ones. Although the latter would create sites with high barriers, this is not a problem as diffusion in landscapes with variable barriers is dominated by the low barriers not the large ones. Percolation of paths with low barriers will provide fast Li diffusion pathways in Li layer unless local features from mixed transition metals trap Li or vacancies. In this respect, a material such as $Li(Ni_{0.5}Mn_{0.5})O_2$[29–31] is particularly interesting. There is substantial evidence that Ni is +2 and Mn is +4 in this material[31,32] so that at least in the beginning of the charge a large number of high rate pathways should exist. Indeed, recent work by us demonstrated that when the Li/Ni disorder is reduced in $Li(Ni_{0.5}Mn_{0.5})O_2$ the material does achieve much higher rate capability.[33]

The other factors investigated here (nontransition metal doping, Li-metal site exchange) can be reduced to the effect they have on the electrostatic and Li-slab factor. The presence of small, high valent cations in the Li layer increases the activation barrier by reducing the slab space. The effect of nontransition metal doping is to modify the screening ability of oxygen and, hence, modify the electrostatic interaction in the tetrahedral site. We showed that Al, in particular, may have a negative effect on Li mobility.

Our study has been limited to layered materials with the O3 structure though the two generic factors that we find are likely to transfer to other materials. For example, spinels are known to be high-rate materials. While this is often attributed to the 3-dimensional network of tunnels for Li diffusion, it is more likely due to the fact that in the spinel structure, the Li cation can on average stay farther away from the other cations along its migration path. It should not be surprising that similar criteria have been identified for the diffusion of protons in the different polymorphs of MnO_2.[34] Ramsdellite, which is well known to be one of the best proton diffusers among the MnO_2 structures, allows the proton to migrate from oxygen to oxygen without ever coming near the high valent Mn^{4+} ions.

We hope that these guidelines will contribute to the design and optimization of high rate electrode materials.

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*Corresponding author. Email address: gceder@mit.edu

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