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Insight into fast Li diffusion in Li-excess spinel lithium manganese oxide

Weiji Xiao, a Chao Xin, a Sibai Li, a Jianshu Jie, a Yue Gu, a Jiaxin Zheng a* and Feng Pan a*

Li-excess cathode materials are expected to have great potential for applications in lithium-ion batteries for their high energy density. Besides the extensive studies on the anionic redox activity in them, their Li-ion diffusion properties have also attracted much interest. Using ab initio calculations, here we systematically explored Li diffusion properties in both stoichiometric and Li-excess phase of spinel lithium manganese oxide (LMO). Our results show that there is a kind of structure unit (six Mn forming a cation ring for Li-ion passing through during migration) to play as "gate sites", and the Li-excess configuration can introduce two kinds of fast Li-ion migration channels to enhance the Li-ion diffusivity. The first kind of fast channels result from that the Li' substitution of Mn can decrease the Coulomb repulsion interactions between the cations at the gate site and the mobile Li-ion. The second kind of fast channels originate from that the excess Li can induce more gate sites with symmetrical distribution of Mn surrounding the Li diffusion channel, which is proved to be able to enhance the Li-ion mobility. Interestingly, it is also found that in the slow Li diffusion channels for both stoichiometric and Li-excess LMO, a simultaneous polaron hopping process around the gate sites will be coupled to the Li migration process, which accounts for the high energy barriers of Li-ion diffusion.

Introduction

Li-excess cathode materials for rechargeable lithium-ion batteries (LIBs) have attracted tremendous attentions. 1-5 In addition to the extra capacity induced by anionic redox activity they can deliver, it is also found that the Li-excess phase is beneficial for Li ion transport. Combining experiments and ab initio calculations, Park et al. 6 demonstrated that the local Li-excess configuration of phosphate Li1.2Fe1.2PO4 unlock the restrictive Li ion diffusion in the olivine structure by providing additional Li diffusion paths. Billaud et al. 7 confirmed experimentally and theoretically that the formation of Li-excess Li2.2Fe1.2SiO4 can enhance the Li ion diffusivity by at least two orders of magnitude in silicate intercalation materials. Using ab initio calculations, Shin et al. 8 proved that pristine layered Li2MnO3 Li-excess material exhibits excellent Li mobility enabling facile Li extraction from both the transition metal layer and Li layer, and thus deduced that the observed inferior rate behavior of this class of cathode materials can’t be blamed on intrinsic bulk ionic mobility. Urban et al. 9 applied Monte Carlo percolation simulations on rocksalt-type lithium metal oxides and found that a critical Li-excess concentration exists at which Li-ion percolation occurs to enhance the Li-ion transport. Yet, there is still a lack of research on Li-ion diffusivity in the spinel Li-excess Li11-xMn2xO4 materials, whose structure ensures three-dimensional diffusion paths other than one- or two-dimensional diffusion for Li-ions in the materials mentioned above.

With its thermal safety, no toxicity, and low cost, spinel lithium manganese oxide (LMO) has been widely used for cathode materials in LIBs. 10 Figure 1(a) illustrates the structure of the spinel LiMn2O4. It crystallizes in the cubic crystal structure of space group Fd3m with O ions at the 32e sites forming a cubic close-packed array. The cation distribution can be described as (Li)(Li)O4, where parentheses () and brackets [ ] denote tetrahedral and octahedral sites, respectively. The tetrahedral 8a sites are occupied by Li ions, while the octahedral 16d sites are occupied by Mn ions. Among all possible ionic defects in LiMn2O4, the lithium antisite created by replacing some of the Mn ions in the 16d sites with Li ions is dominant, 11 resulting in Li-excess phase Li11-xMn2xO4 whose cation distribution is designated by (Li)(Li)O4. The spinels (Li)(Li)O4 are equilibrium phases according to phase diagram research by Paulsen et al. 12, and have been synthesized in various previous studies. 13-16 The remaining half of the octahedral cation sites in the structure are 16c vacancies. The 16c vacancy site is thought to serve as a Li migration path that is connected by two adjacent Li ions at the 8a site. 17, 18 Each 16c site is surrounded by six 16d sites forming a cation ring in the plane that is perpendicular to the Li diffusion path, which is a kind of structure unit to play as "gate sites" for Li-ion passing through during migration, as shown in Figure 1(b). Three-dimensional diffusion paths can be formed inside the structure since each face of 8a site is shared with a 16c site. Therefore, it is reasonable to speculate that LMO

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can deliver high power in spite of its low theoretical capacity of about 148 mAh g⁻¹. However, the pure LiMn₂O₄ is found to have an insufficient rate capability.¹⁹ Taeishi et al.¹⁷ performed a molecular dynamics study on Li migration in LiMn₂O₄ and regarded the Mn atom e_g orbital electron hopping as the trigger of the Li diffusion mechanism. First-principles calculations applied by Nakayama et al.¹⁰ drew the conclusion that the valence state of cations around the Li diffusion path is the dominant factor in determining the migration energy of the Li jump in spinel oxides. And Xu et al.¹⁸ inferred that higher amount of Mn⁴⁺ rather than Mn³⁺ may lower Li diffusion activation barriers in LMO. All these works were focused on the stoichiometric phase, while the intrinsic Li ion diffusivity in Li-excess LMO hasn’t been studied yet.

Herein, using extensive ab initio calculations, we investigate Li ion diffusivity in spinel lithium manganese oxides Li₁ₓMn₂₋ₓO₄ with x = 0 (stoichiometric phase) and x = 0.125 (Li-excess phase). Our calculations reveal that Li-excess configuration does benefit Li-ion mobility by introducing two kinds of fast Li-ion migration channels. The first kind of fast channels result from that the Li⁺ substitution of Mn³⁺ can decrease the Coulomb repulsion interactions between the cations at the gate site and the mobile Li-ion. The second kind of fast channels originate from that the excess Li can induce more gate sites with symmetrical distribution of Mn⁴⁺ surrounding the Li diffusion channel, which is proved to be able to enhance the Li-ion mobility. Moreover, we also found in some categories of Li-ion migration channels in both stoichiometric and Li-excess LMO, the Li-ion diffusion is accompanied with a simultaneous polaron hopping process, which is coupled to the Li migration process and accounts for the high energy barriers for Li-ion diffusion.

Methodology

All calculations were performed using the Vienna Ab-initio Simulation Package (VASP)²¹,²² based on a generalized gradient approximation with Hubbard U correction (GGA+U)²³,²⁴ to the density functional theory (DFT)²⁵. The Perdew-Burke-Ernzerhof (PBE)²⁶ exchange correlation and a plane wave representation for the wave-function with a cut-off of 600 eV were used. The maximum residual of force during geometry optimization is less than 0.01 eV/Å, and energies are converged to within 1 × 10⁻⁵ eV per atom. The Brillouin zone was sampled by 4 × 4 × 4 special k-points using the Monkhorst-Pack scheme.²⁷ According to previous studies on Mn-based compounds,²⁸,²⁹ the Hubbard U value for Mn-d orbitals was set at 4.2 eV. Anti-ferromagnetic (AFM) order was used.²⁸ The climbing image nudged elastic band (cNEB) method³⁰,³¹ was used to investigate the minimum energy pathways of the Li hopping from one lattice site to the adjacent positions. At first, the location of the hopped Li ion and a vacancy at the two potential minima was specified to calculate the initial and end point configurations and the corresponding total energies. Then intermediate configurations between the initial and end points were generated with linear interpolation method. Finally, the intermediate configurations were optimized under the constraint condition that the ions were connected by springs to maintain equal spacing to neighboring configurations. A supercell composed of eight-formula units of LiMn₂O₄ (i.e. Li₈Mn₂O₄) was used for stoichiometric phase, and one lithium antisite was introduced to obtain Li-excess phase Li₁₋ₓMn₁₊ₓO₄ (i.e. Li₉Mn₁ₓO₄). In the cNEB calculations, one lithium vacancy for each supercell was set.

Results and discussion

We started with the stoichiometric supercell Li₈Mn₁₆O₃₂. Then the Li-excess supercell Li₉Mn₁₅O₃₂ was constructed by substituting one Mn ion at the 16d site with a Li ion. Due to the Li-excess configuration, the ratio of Mn³⁺ to Mn⁴⁺ turns from 8:8 into 5:10. Thereupon comes different behavior in structure parameters, electronic structures, as well as Li diffusion properties.

Structure parameters of Li₁₆Mn₂O₄. After structural optimization, the cubic cells transform into tetragonally distorted cells. The calculated lattice constants of stoichiometric supercell Li₈Mn₁₆O₃₂ are a = b = 8.22 Å and c = 8.76 Å, as shown in Table 1, which agrees with the experimental results, 8.11 and 8.65 Å². Lattice constants along the z direction are obviously elongated by about 6.5% compared to the other two directions. As for the Li-excess supercell Li₉Mn₁₅O₃₂, the lattice elongation along the z direction is of about 4.3% with a = b = 8.23 Å and c = 8.58 Å (Table 1). The constants for a and b of

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Figure 1 (a) Crystal structure of spinel LiMn₂O₄. Mn ions reside in octahedrons formed by O ions. Dotted arrow denotes a Li diffusion path. (b) Schematic picture of the Li diffusion channel from a tetrahedral 8a site to the adjacent 8a site through an octahedral 16c vacancy surrounding by six Mn ions in octahedral 16d gate sites. (c) and (d) Valence arrangements and magnetic orderings of Mn ions in stoichiometric Li₈Mn₁₆O₃₂ and Li-excess Li₉Mn₁₅O₃₂, respectively. The arrows across Mn ions denote directions of spin polarization.

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Table 1

<table>
<thead>
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<th>Parameter</th>
<th>Stoichiometric</th>
<th>Li-excess</th>
</tr>
</thead>
<tbody>
<tr>
<td>a (Å)</td>
<td>8.11</td>
<td>8.22</td>
</tr>
<tr>
<td>b (Å)</td>
<td>8.11</td>
<td>8.22</td>
</tr>
<tr>
<td>c (Å)</td>
<td>8.76</td>
<td>8.58</td>
</tr>
</tbody>
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the Mn$^{3+}$/Mn$^{4+}$ ratio is also reflected in PDOS, where the density of Mn$^{3+}$ 3d orbital decreases and that of Mn$^{4+}$ increases for the Li-excess phase, as shown in Figure 3(b). Figure 1(c) shows the valence arrangement and magnetic ordering of Mn ions in Li$_3$Mn$_{16}$O$_{32}$. Anti-ferromagnetic (AFM) Mn$^{3+}$ layers ($\uparrow\downarrow\uparrow\downarrow$) and ferromagnetic (FM) Mn$^{4+}$ layers alternate along the [001] direction. This AFM pattern is the same as one of the stable charge ordering of LiNi$_2$O$_2$ and was proved by Liu et al.$^{28}$ as the most stable configuration in LiMn$_2$O$_4$ since the 90° Mn$^{3+}$-O$_2$-Mn$^{3+}$ in the Mn$^{3+}$-O(001) planes couples via the superexchange interaction. In the case of the Li-excess supercell where the excess Li ion occupies a 16d site as a substitution of Mn ion, various substituted configurations were explored in consideration of valence separation and spin polarization of Mn ions, between which the energy difference is smaller than 0.01 eV, and Figure 1(d) shows the energy favorable configuration. A Mn$^{3+}$ ion is replaced by Li ion, and two Mn$^{4+}$ ions in the same (001) planes are oxidized to Mn$^{4+}$ for charge compensation. The AFM pattern remains unchanged after relaxation while the superexchange interaction ought to be weakened since the amount of Mn$^{3+}$ decreases. By the way, magnetic moments of O ions also changed with the introduction of extra Li$^+$, since electron exchange exists between Mn and O ions. However, the changes of magnetic moments for O ions are smaller than 0.09 $\mu_B$ according to our calculations. This can be explained by the fact that 3d electrons of Mn are far more localized than 2p electrons of O. Based on this, the charge balance was mainly, but not only, accommodated by Mn ion.

### The enhanced Li diffusivity in Li$_{11.75}$Mn$_{12}$O$_{37}$

As mentioned above, Li ion jumps through the 16c octahedron which shares edges with six octahedral cations in 16d sites. In the following, we will refer to these six edge-sharing sites as gate sites (Figure 1(b)), since they determine whether a diffusion channel is open or closed. Figure 4 shows the energy barriers of Li through different diffusion channels and their corresponding cation distributions in the gate sites calculated by the cNEB method. Notice that the Mn$^{3+}$/Mn$^{4+}$ ratios have changed due to the lithium removal in the cNEB calculations. Each supercell contains four Li diffusion paths. According to the gate sites cation arrangements, two categories are untangled in the stoichiometric supercell (a1 and a2), and four in the Li-excess supercell (b1, b2, b3 and b4). Based on the locations of the diffusion paths in the supercells, category a1 is corresponded to

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**Figure 2** Projected density of states of Mn-3d in stoichiometric Li$_3$Mn$_{16}$O$_{32}$ (a) and Li-excess Li$_3$Mn$_{16}$O$_{32}$ (b), respectively.

**Figure 3** Mn-O bond lengths of Mn$^{3+}$/Mn$^{4+}$ in stoichiometric LiMn$_{16}$O$_{32}$ and Li-excess Li$_{11.75}$Mn$_{12}$O$_{37}$.
categories b\textsubscript{11} and b\textsubscript{12}, while category a\textsubscript{2} is mapped to categories b\textsubscript{21} and b\textsubscript{22}.

From Figure 4, we can see that in the stoichiometric supercell, a\textsubscript{1} channel shows a lower energy barrier (0.38 eV) than a\textsubscript{2} channel (0.72 eV) for Li-ion migration. In the Li-excess supercell, b\textsubscript{11} and b\textsubscript{12} show low energy barriers with 0.29 eV and 0.24 eV, respectively, which are significantly lower than the a\textsubscript{1} channel in the stoichiometric phase. Thus, the Li-excess configuration introduces two kinds of fast Li-ion diffusion channels to enhance the Li-ion diffusivity. In the comparison of categories a\textsubscript{1} and b\textsubscript{11}, it can be seen that substituting Mn\textsuperscript{3+} ion with Li\textsuperscript{+} ion lead to lower barriers. This is because the Coulomb repulsion between the gate site Li\textsuperscript{+} (at the 16d site) and the mobile Li\textsuperscript{+} is much weaker than that between the original gate site Mn\textsuperscript{3+} and the mobile Li\textsuperscript{+}. It should be noted that for categories b\textsubscript{11} and b\textsubscript{12}, both of them have four Mn\textsuperscript{4+}, one Mn\textsuperscript{3+}, and one Li\textsuperscript{+} in the gate sites, but b\textsubscript{11} exhibit lower energy barriers. Compared with category b\textsubscript{21}, all Mn\textsuperscript{4+} ions in category b\textsubscript{11} reside in the para-positions of the cation ring. As a result, the coulomb repulsive forces on the migration Li\textsuperscript{+} ion formed by the Mn\textsuperscript{4+} ions counteract with each other in the plane that is perpendicular to the Li diffusion path, which explains the low energy barrier in b\textsubscript{11}. Compared with b\textsubscript{11} channel, the six Mn ions at the gate site are all Mn\textsuperscript{4+} in the b\textsubscript{12} channel, which shows the highest symmetry. Thus, b\textsubscript{12} channel shows the lowest energy barrier of Li-ion diffusion. The appearance of this fast channel with (Mn\textsuperscript{4+})\textsubscript{6} ring gate site can be attributed to that the substituting Mn\textsuperscript{3+} ion with Li\textsuperscript{+} ion leads to the oxidation of Mn\textsuperscript{3+} to Mn\textsuperscript{4+} for charge compensation, which increases the possibility to form the (Mn\textsuperscript{4+})\textsubscript{6} ring gate site. More excess Li\textsuperscript{+} would lead to more Mn\textsuperscript{4+} ions in Li\textsubscript{1+x}Mn\textsubscript{2-x}O\textsubscript{4}. Therefore, according to our calculations, fast Li diffusion channels with either more Mn\textsuperscript{4+} or more Li\textsuperscript{+} in the gate sites will be created. From this view, the greater x is, the better Li diffusion property gets. However, the crystal structure will become unstable when the excess Li\textsuperscript{+} ions

Figure 4 (a) and (b) Valence arrangements of Mn ions and gate-site cation distributions of different Li diffusion channels in stoichiometric and Li-excess supercells with one Li vacancy, respectively. (c) The energy barriers of different Li diffusion channels with different site-gate cation distributions.

Figure 5 The gate-site cation distributions along with the projected density of states of two valence-changing Mn ions before and after the Li hopping in Li diffusion channel a\textsubscript{1} (a) and b\textsubscript{21} (b).
get too many. According to the phase diagram by Paulsen et al., phase Li1+xMn2-xO4 remains equilibrium with $0 < x \leq 1/3$.

Interestingly, the valence states of gate site Mn ions markedly change during the Li migration in category b). The transfer of an electron between a pair of two Mn atoms, Mn$_A$ and Mn$_B$, occurs by hopping between two equilibrium configurations: Mn$^{4+}_A$Mn$^{3+}_B$ and Mn$^{3+}_A$Mn$^{4+}_B$, as described by Figure 5(b). The PDOS of Mn$_A$ transforms from characteristic Mn$^{4+}$ type into Mn$^{3+}$ type, and Mn$_B$ behaves in the other way around. This is also confirmed by the change of magnetic moment: the moment of Mn$_A$ changes from 3.24 $\mu_B$ to 3.88 $\mu_B$, and the moment of Mn$_B$ changes from 3.87 $\mu_B$ to 3.22 $\mu_B$. This electron transfer process in the cation ring of the gate site can be regarded as a polaron hopping process, which was extensively studied in the well-known LiFePO$_4$ cathode materials and other transition metal oxides.35-40 In the polaron migration process, both the electron (or hole) and its associated local distortion move together, which will be coupled to the Li-ion migration process and in turn increase the barriers of Li-ion diffusion. This not only explains the high energy barrier in category b), but also explains the high energy barrier in category a) for Li-ion diffusion in stoichiometric LMO, in which the valence states of gate site Mn ions also markedly change with a polaron hopping process during the Li migration as shown in Figure 5(a). The coupled simultaneous polaron and Li-ion migration process is also observed in LiFePO$_4$ and reported to increase the Li-ion diffusion barriers.35, 36 It should be noted that there is also a similar polaron hopping process during Li-ion migration in other channels, but this polaron hopping process doesn’t happen on the gate site Mn$_B$ ring, which will not affect the Li-ion migration process.

Conclusions

In summary, Li diffusion properties along with charge separation, magnetic orderings, and electronic properties of spinel lithium manganese oxides Li$_{1+x}$Mn$_{2-x}$O$_4$ with $x = 0$ (stoichiometric phase) and $x = 0.125$ (Li-excess phase) were investigated systematically. It is found that there is a kind of structure unit (six Mn forming a cation ring for Li-ion passing through during migration) to play as “gate sites”, and Li-excess configuration in spinel LMO can enhance the Li-ion diffusivity by introducing two kinds of fast Li-ion migration channels. The first kind of fast channels is attributed to that the Li$^+$ substitution of Mn$^{4+}$ can decrease the Coulomb repulsion interactions between the cations at the gate site and the mobile Li-ion. Moreover, the excess Li can induce more gate sites with symmetrical distribution of Mn$^{4+}$ surrounding the Li-ion diffusion channel, which results in the second kind of Li-ion migration channels. Interestingly, in some categories of Li-ion migration channels, Li-ion migration process is accompanied by a simultaneous polaron hopping process, and the coupled effect between them is responsible for high energy barrier for Li-ion diffusion.

Conflicts of interest

There are no conflicts to declare.

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Notes and references


Li-excess configuration can enhance Li diffusion by introducing two fast channels in spinel lithium manganese oxide.