Effects of Na Substitution on Li Ion Migration in Li$_2$CoSiO$_4$ Cathode Material

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Li$_2$MSiO$_4$ (M = Mn, Fe, Co, Ni) family$^{1-11}$ has been intensively investigated due to its potential applications as the cathode materials for the next generation rechargeable Li ion batteries. Many attractive aspects have been reported, including the high safety arising from the strong Si-O bond and the theoretical high capacity (e.g. 325 mAh/g for Li$_2$CoSiO$_4$) due to the possibility of reversibly cycling two Li ions per Li$_2$MSiO$_4$ unit. Of these silicates, Li$_2$CoSiO$_4$ has been prepared successfully by solution route and hydrothermal reaction.$^3,4$ However, the poor electronic and ionic conductivities of bare Li$_2$CoSiO$_4$ become a major barrier to hinder the further applications of this material as the cathode for Li ion batteries. Even coated with carbon, the reversible electrochemical extraction was limited to 0.46 Li per formula unit of Li$_2$CoSiO$_4$ ($\text{Ref. } 4$). Thus, further studies are essential to seek possible approaches to improve the electrochemical performance of Li$_2$CoSiO$_4$, including the electronic and ionic conductivities of the material. In our previous work,$^7$ we found that Na substitution on Li sites in Li$_2$CoSiO$_4$ could induce a lowering of the conduction bands and narrowing of the bandgap, which may be helpful to enhance the intrinsic electronic conductivity. Moreover, the expansion of the interlayer space of the adjacent [CoO$_4$]$_x$ corrugated layers was observed, when one of the four Li atoms in the unit cell (Li$_{1.5}$Na$_{0.5}$CoSiO$_4$) was substituted by one Na atom, which was anticipated to benefit the Li ion migration.$^1$ Although the Na substitution decreases the intrinsic capacity of Li$_2$CoSiO$_4$, the reversible capacity of the material is expected to be increased due to the enhanced electrochemical performance benefitted from the substituted Na ions. Moreover, for the Na substitution compound Li$_{x}$Na$_{3-x}$CoSiO$_4$, the theoretical capacity is ca. 230 mAh g$^{-1}$, which is still much higher than that of LiFePO$_4$ (ca. 170 mAh g$^{-1}$). Thus, the Na substitution in Li$_2$CoSiO$_4$ is attractive, if it can increase the Li ion diffusion in the material. In the present work, detailed studies of the effects of Na substitution on the diffusion of Li ions in the Li$_2$CoSiO$_4$ material are investigated. The Na substitution on Li sites has shown to increase the Li ion diffusivity. In addition, the investigations of Na substitution on Li sites may also be helpful in giving some preliminary knowledge for designing better Li ion and/or Na-Li hybrid ion batteries.

**Computational Details**

We present first-principles results on the possible Li ion migration pathways and the diffusion barriers for the Li$_{2-x}$Na$_x$CoSiO$_4$ ($x = 0, 0.5$) based on the structure with $Pmmm_2$ symmetry, by using the projector augmented wave (PAW) method$^{12}$ within the density functional theory (DFT) as implemented in the Vienna $ab$ $initio$ simulation package (VASP).$^{13,14}$ The exchange and correlation energy was treated within the spin-polarized generalized gradient approximation (GGA) parameterized by Perdew-Burke-Ernzerhof (PBE).$^{15}$ To address on-site Coulomb interactions in the localized $d$ electrons of Co ions, the GGA+$U$ method with an additional Hubbard-type U term ($U_{eff} = U-J = 6$ eV) was employed.$^{16}$ Wave functions were expanded in plane waves up to a kinetic energy cutoff of 500 eV. Brillouin-zone integrations were approximated by using special $k$-point sampling of Monkhorst-Pack scheme$^4$ with a $9 \times 9 \times 9$ grid. Activation barrier calculations are performed by using the climbing nudged elastic band (NEB)$^{18}$ method in a supercell ($2a \times 2b \times 2c$) containing 16 formula units (the primitive cell contains 2 formula units). The images of the migrating Li are then more than 8 Å apart. The large supercell isolates hopping atoms from their periodic images, providing accurate calculations for the diffusion barriers in the dilute limit. The activation barriers in the dilute vacancy limit with 31 Li and 1 Li vacancy for Li$_2$CoSiO$_4$, while 23 Li (with one Li vacancy) and 8 Na for Li$_{1.5}$Na$_{0.5}$CoSiO$_4$. During the NEB calculations, all the lattice parameters are fixed at the relaxed values of the fully lithiated structure, with all the other internal degrees of freedom relaxed.

**Results and Discussion**

The crystal structure of Li$_{1.5}$Na$_{0.5}$CoSiO$_4$ ($x = 0, 0.5$) can be described as built up of infinite corrugated layers having the composition [CoSiO$_4$]$_x$ linked along $b$-axis direction by the Li(Na)O$_4$ tetrahedra (see Fig. 1). Within these layers, each SiO$_4$ tetrahedron shares its corners with four neighboring CoO$_4$ tetrahedra, and vice versa. Li (Na) ions occupy the tetrahedral sites located between two [CoO$_4$]$_x$ layers. As shown in Fig. 1, if a single Li ion is removed from the crystal,

Figure 1. (Color online) (a) Li ion migration pathways, and (b) Li sites along these pathways, in the Li$_{1.5}$Na$_{0.5}$CoSiO$_4$ ($x = 0, 0.5$). The blue and purple tetrahedra represent the SiO$_4$ and CoO$_4$, respectively. The red, green and yellow balls represent O, Li, and Na ions in Li$_{1.5}$Na$_{0.5}$CoSiO$_4$; while in Li$_2$CoSiO$_4$, both green and yellow balls represent Li ions.
there are several neighboring Li ions that can hop into the vacancy site and contribute to a three dimensional diffusion. For Li$_{2-x}$Na$_x$CoSiO$_4$, three possible Li migration paths are identified: (a) pathway A - channels along the $a$-axis direction, (b) pathway B - zigzag trajectory in the $bc$ plane, and (c) pathway C - across the [CoSiO$_4$]$_{x=0}$ layer through a small void. Other paths with longer Li-Li hop distances should yield high migration batteries and thus be highly improbable.

The migration steps along the pathway A are schematically shown in Fig. 2a. The calculated activation barriers along the pathway A for Li$_{2-x}$Na$_x$CoSiO$_4$ ($x = 0, 0.5$) are given in Fig. 2b and 2c, respectively. Actually, the migration of Li ion is the motion of vacancy along the opposite direction. Since there are two inequivalent Li tetrahedra in the pathway A, the Li ion migration involves two different kinds of steps with different potential barriers, i.e. hopping between sites 10 and 18 and that between sites 18 and 14. As shown in Fig. 2b, for the Li$_2$CoSiO$_4$, the migration potential barrier is 0.74 eV and the jumping distance is 3.50 Å when Li ion goes from site 10 to site 18. For the moving of Li ion from site 18 to site 14, the migration barrier is then 0.65 eV and the jumping distance is 3.75 Å. When the Li ions are substituted by Na near the site 18 as in the case of pathway A, the total energy of the system with Li ion occupying the site 18 becomes lower, as shown in Fig. 2c. As a result, jumping into site 18 is energetically easier than jumping out of site 18. For Li$_{1.5}$Na$_{0.5}$CoSiO$_4$, the potential barriers along pathway A for jumping out of site 18 are 0.66 and 0.56 eV, respectively, while barriers for jumping into site 18 are 0.62 and 0.53 eV, respectively. The calculated barriers are both about 0.1 eV lower than the counterparts of Li$_2$CoSiO$_4$. The hopping distances of Li ions in Li$_{1.5}$Na$_{0.5}$CoSiO$_4$ along pathway A are 3.75 Å for the first hop and 3.90 Å for the second hop, which are both slightly larger than those in the Li$_2$CoSiO$_4$.

As shown in Fig. 1, Li ion migration along the pathway B consists of identical steps, i.e., jumping from site 1 to site 10 and then from site 10 to site 2. The calculated activation barriers for Li$_{2-x}$Na$_x$CoSiO$_4$ ($x = 0, 0.5$) are given in Fig. 3b and 3c, respectively. For Li$_2$CoSiO$_4$, the activation barrier between two sites is 0.72 eV, with a hopping distance of 3.65 Å. Upon Na substitution, since more Na ions are located near site 1 and the distance between the Na ions and site 1 are also smaller, as in the case of pathway B, the total energy of the system with Li ion occupying site 1 becomes significantly lower, as compared with that in pathway A. As a result, jumping of Li ion into site 1 is energetically easier than jumping out of site 1. For Li$_{1.5}$Na$_{0.5}$CoSiO$_4$, the potential barrier along pathway B for jumping out of site 1 is 0.79 eV, while the barrier for Li ion jumping into site 1 is 0.52 eV. Moreover, a longer hopping distance of 3.85 Å is observed in Li$_{1.5}$Na$_{0.5}$CoSiO$_4$, compared with the case of Li$_2$CoSiO$_4$.

Li ion migration along the pathway C again consists of two identical steps, i.e., jumping from site 3 to site 10 and then from site 10 to site 4 (see Fig. 1). As shown in Fig. 4a, in the pathway C, Li ion has to migrate through a small void in the [CoSiO$_4$]$_{x=0}$ layer which induces a large repulsive interaction between the diffusion ion (Li$^+$) and the ions in the [CoSiO$_4$]$_{x=0}$ layer. It can be seen from Fig. 4b and 4c that such a diffusion leads to activation barriers of ca. 2 eV for both the Li$_2$CoSiO$_4$ and Li$_{1.5}$Na$_{0.5}$CoSiO$_4$, which is substantially higher than those in the pathway A and B. The distances between the two neighboring sites in pathway C are 5.0 Å and 5.25 Å for Li$_2$CoSiO$_4$ and Li$_{1.5}$Na$_{0.5}$CoSiO$_4$, respectively, which is also larger than those found in the pathway A and B. Accordingly, Li ion migration along the pathway C is suggested to be more difficult than that along the pathway A and B. Therefore, we can infer that the Li$_{2-x}$Na$_x$CoSiO$_4$ ($x = 0, 0.5$) compounds have a two-dimensional pathway for Li ion diffusion.

The calculated migration barriers and estimated diffusion coefficients are summarized in Table I. The Li diffusion barriers in Li$_2$CoSiO$_4$ are shown to be significantly higher (with lower conductivity) than those in other common cathode materials (as listed in Table I), which implies a relative poor rate capacity of this material. Interestingly, the calculated results show that Na substitution can lower the activation barrier along the pathway A (see Fig. 2b–2c).
Table I. Calculated activation barriers, $E_m$, and the estimated diffusion coefficients, $D$, for the Li ion migrations in various cathode materials.

<table>
<thead>
<tr>
<th>System</th>
<th>Space group</th>
<th>$E_m$ (eV)</th>
<th>$D$ (cm$^2$s$^{-1}$)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li$_2$CoSiO$_4$</td>
<td>Pmn2$_1$</td>
<td>0.74$^\text{A}$/0.72$^\text{B}$</td>
<td>$10^{-14}$</td>
<td>This work</td>
</tr>
<tr>
<td>Li$<em>{1.5}$Na$</em>{0.5}$CoSiO$_4$</td>
<td>Pmn2$_1$</td>
<td>0.66$^\text{A}$/0.79$^\text{B}$</td>
<td>$10^{-13}$</td>
<td>This work</td>
</tr>
<tr>
<td>LiCoO$_2$</td>
<td>R3m</td>
<td>0.23</td>
<td>$10^{-9}$</td>
<td>Van der Ven et al. $^{19}$</td>
</tr>
<tr>
<td>Li$_2$FeSiO$_4$</td>
<td>Pmn2$_1$</td>
<td>0.83/0.75</td>
<td>$10^{-13}$/10$^{-13}$</td>
<td>Liivat et al. $^{20}$</td>
</tr>
<tr>
<td>LiFePO$_4$</td>
<td>Pnma</td>
<td>0.27/0.55</td>
<td>$10^{-7}$/10$^{-5}$</td>
<td>Morgan et al. $^{21}$</td>
</tr>
<tr>
<td>$\beta$-Li$_3$PO$_4$</td>
<td>Pmn2$_1$</td>
<td>0.55</td>
<td>0.55</td>
<td>Du et al. $^{23}$</td>
</tr>
</tbody>
</table>

A, B: Li migration pathway A, B.

$D = d^2 v \cdot \exp(E_m/k_BT)$, where $v = 10^{13}$ Hz, $T = 300$ K, and $d$ is the hopping distance.

Figure 3. (color online) (a) Li ion migration steps; the calculated activation barriers for (b) Li$_2$CoSiO$_4$ and (c) Li$_{1.5}$Na$_{0.5}$CoSiO$_4$ along the pathway B.

Figure 4. (color online) (a) Li ion migration steps; the calculated activation barriers for (b) Li$_2$CoSiO$_4$ and (c) Li$_{1.5}$Na$_{0.5}$CoSiO$_4$ along the pathway C.
and thus enhance the Li ion migration. A detailed study of the structural variation upon Na substitution in Li$_2$CoSiO$_4$ has been reported previously. We found that the lattice parameters expands by 0.6%, 1.7% and 3.2% along $a$, $b$ and $c$ direction, respectively, when 1/4 Li ions are substituted by Na. This should be ascribed to the larger ionic radius of substituted Na ions, compared with Li. The structural expansion of Li$_{1.5}$Na$_{0.5}$CoSiO$_4$ relative to the pure Li$_2$CoSiO$_4$ cannot only increase the interlayer space between the two adjacent [CoSiO$_4$]$_n$ layers, but also make the [CoSiO$_4$]$_n$ layers less corrugated. This could weaken the interactions between the migrating Li ions and the adjacent [CoSiO$_4$]$_n$ layers (especially for the configuration with maximum activation barrier), which would lower the activation barrier and enlarge the hopping distance. On the other hand, the substituted Na ions render the adjacent Li ions bonded with O ions more tightly than those far from them. The calculated results show that, in Li$_{1.5}$Na$_{0.5}$CoSiO$_4$, the average Li-O bond lengths at the sites near the substituted Na ions are smaller than those at the sites far from Na (e.g., Li-O bond lengths at site 1 and site 10 are ca. 1.97 Å and 2.04 Å, respectively). As a result, it is easier for the Li ion to hop into the sites near Na ions, as compared to the hopping of Li ion out of the same sites.

Conclusion

In summary, first-principles calculations on the effects of Na substitution on the Li ion migration in cathode material Li$_2$CoSiO$_4$ have been performed based on the density functional theory. The Li ion diffusion in three main pathways in Li$_{1-x}$Na$_x$CoSiO$_4$ ($x = 0, 0.5$) with space group $Pmm2_1$ have been identified. The present results show that Na substitution can influence significantly the Li ion migration by decreasing the activation barriers and enlarging the hopping distances along the diffusion paths. Our results suggest that the chemical modification, i.e. Na substitution on Li site, could be a promising route to improve the electrochemical performance of the Li$_2$MSiO$_4$ family of compounds. The present findings may also encourage the use of hybrid Li/Na ion materials as cathode for Li ion batteries.

Acknowledgments

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References