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Effects of Na-substitution on structural and electronic properties of Li₂CoSiO₄ cathode material

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Abstract: Na-substituted dilithium orthosilicate Li_2CoSiO_4 was investigated by performing density functional theory calculations within the GGA+U framework. The effects of Na-substitution on the electronic structures and structural properties of Li_2CoSiO_4 were presented. The results show that the Na-substitution on Li sites in Li_2CoSiO_4 induces a lowering of the conduction bands and a narrowing of the band gap, which could be helpful for enhancing the electronic conductivity. On the other hand, the Na-substitution on the Li ions in Li_2CoSiO_4 leads to the expansion of interlayer space of the adjacent corrugated layers. This lattice expansion effect would benefit the Li ion diffusion.

Key words: dilithium cobalt orthosilicate; Na-substitution; structural properties; electronic structures

1 Introduction

Polyanionic cathodes such as olivine type LiMPO₄ (M=Mn, Fe, Co, Ni, etc)[1-3] have attracted considerable attention as next-generation cathodes due to their better safety characteristics compared with the more commonly used metal oxides, which act as strong oxidizers in charged state in direct contact with an organic electrolyte [4]. More recently, an entirely new class of lithium intercalation compounds based on silicates, Li₂MSiO₄, where M=Mn, Fe, Mn/Fe, Co, Ni, has been described [5-15]. Compared with phosphate materials in which only one lithium ion can be reversibly cycled, dilithium orthosilicate materials, i.e. Li2MSiO4, would allow reversible extraction of two lithium ions in principle, thus they should deliver higher capacity (e.g. Li₂CoSiO₄, 325 mA·h/g) than phosphates. This makes them very attractive new cathode materials for lithium ion batteries. these compounds, Among the dilithium cobalt orthosilicate (i.e. Li2CoSiO4) has been prepared successfully by a solution route and hydrothermal reaction[9]. However, the pristine Li₂CoSiO₄ prepared by solution route shows poor electrochemical performance due to its poor conductivity[9]. Even coated with carbon, reversible electrochemical extraction was limited to 0.46 Li per formula unit[9]. Further studies are essential to seek possible approaches to improve the electrical conductivity and the electrochemical performance. In the present work, we focus on the analysis of Na-substituted Li₂CoSiO₄, in order to characterize the structural properties and electronic structures of Li_{2-x}Na_xCoSiO₄ (0 < x < 2), and to understand the effects induced by the Na-substitution on the related properties, including the electrical conductivity and lithium ion diffusion.

2 Computational details

All calculations on $\text{Li}_{2-x}\text{Na}_x\text{CoSiO}_4$ were carried out by using the projector augmented wave(PAW) method [16] within the density functional theory(DFT) as implemented in the Vienna *ab initio* simulation package (VASP)[17–18]. The exchange and correlation energy was treated within the spin-polarized generalized gradient approximation(GGA) and parameterized by Perdew-Burke-Ernzerhof formula (PBE)[19]. Furthermore, the

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effects due to the localization of the d electrons of the transition metal ions in the silicates were taken into account with the GGA+U approach of DUDAREV et al[20]. Within this approach, an effective value of $U_{\text{eff}} = (U-J)=6$ eV was used for $\text{Li}_{2-x}\text{Na}_x\text{CoSiO}_4$. Such a value was recently used to analyze the electronic structures and voltage of the $\text{Li}_2\text{MSiO}_4[15]$. The GGA+U approach has been proved to be able to well determine the structural and electronic properties of the Li_xMSiO_4 (M=Mn, Fe, Co, Ni) compounds[15]. Wave functions were expanded in plane waves up to a kinetic energy cut-off of 500 eV. Brillouin-zone integrations were approximated by using special *k*-point sampling of Monkhorst-Pack scheme[21] with a $9 \times 9 \times 9$ grid.

3 Results and discussion

The unit cell of Li₂CoSiO₄ has an orthorhombic structure in the $Pmn2_1$ space group with corrugated layers of SiO₄ and CoO₄ tetrahedra lying on the *ac*-plane and linked along the *b*-axis by LiO₄ tetrahedra. This structure can also be described by a ZnS-type arrangement (in a distorted form of hexagonal close packing), within which the Zn sites are occupied by Li, Co and Si cations while the S sites are occupied by O anions. All the tetrahedra point in the same direction, perpendicular to the close-packed planes, and share only corners with each other[10]. Especially, Li ions occupy tetrahedral sites located between the two [SiO₄-CoO₄] corrugated layers (Fig.1). A path for lithium extraction/ insertion exists in this structure since the LiO₄ tetrahedron is arranged in rows running along the *a*-axis by sharing corner. Also, the diffusion of Li ions in the corrugated layers is possible. There are two formula units per unit cell of Li₂CoSiO₄, i.e., each unit cell contains 4 lithium, 2 cobalt, 2 silicon, and 8 oxygen atoms. The structural stabilities, electronic structures and Li deintercalation for the dilithium orthosilicate Li2CoSiO4 have been investigated in our previous work[15].

For the Na-substituted compounds, i.e. $Li_{2-x}Na_xCoSiO_4$, the initial crystal structures were obtained via replacing Li by Na in the corresponding optimized Li_2CoSiO_4 unit cells, then the crystallographic cell parameters (the cell shape as well as the lattice constants) and the atomic fractional coordinates were relaxed until the forces on all atoms were less than 0.01



Fig.1 Structure of Li_{2-x}Na_xCoSiO₄ (CoO₄ tetrahedra: light gray; SiO₄ tetrahedra: dark gray; Li/Na atoms: light (smaller/larger); O atoms: dark)

eV/Å. The calculated lattice parameters, equilibrium volumes for $\text{Li}_{2-x}\text{Na}_x\text{CoSiO}_4$, with x=0, 0.5, 1 and 2, are listed in Table 1. To be more precise, the expansions of lattice parameter due to Na-substitution are also shown in Fig.2. The lattice parameters and equilibrium volume of $\text{Li}_{2-x}\text{Na}_x\text{CoSiO}_4$ are well described by the VEGARD's law[22] as shown in Fig.2. It is obvious that smaller x (the smaller amount of Na-substitution) would have less influence on the structural properties. This tendency also applies to the electronic structures, which will be discussed later. Furthermore, under the aim to improve

Table 1 Lattice parameters and equilibrium volumes for $Li_{2-x}Na_xCoSiO_4$ (*x* =0, 0.5, 1, 2)

Tuble I Buttlee parameters and equilibrium volumes for El2=gr (u costo 4 (v o, o.s., 1, 2)								
Li _{2-x} Na _x CoSiO ₄	x	a/Å	$b/{ m \AA}$	$c/\text{\AA}$	α	β	γ	$V/\text{\AA}^3$
Li ₂ CoSiO ₄	0	6.195	5.443	4.988	90	90	90	168.20
Li1.5Na0.5CoSiO4	0.5	6.231	5.617	5.072	90.4	90.2	89.7	177.50
LiNaCoSiO ₄	1.0	6.246	5.781	5.158	90	90.4	90	186.25
Na ₂ CoSiO ₄	2.0	6.296	6.093	5.344	90	90	90	204.99



Fig.2 Expansion of lattice parameters and volumes due to Na-substitution compared with VEGARD's prediction (dashed lines)[22]

conductivity of Li₂CoSiO₄, the electrical the predominance of the theoretical capacity is expected to be kept. Therefore, in the following we would focus mainly on the case of Li1.5Na0.5CoSiO4 and the comparison between the substituted Li1.5Na0.5CoSiO4 and the pure Li₂CoSiO₄. For the stable structures of Li_{1.5}Na_{0.5}CoSiO₄, small deviations from the perfect orthogonality have been found, as listed in Table 1. Moreover, all the three lattice parameters of Li_{1.5}Na_{0.5}CoSiO₄ are larger than those of Li₂CoSiO₄. This can be understood from the fact that the ionic radius in four-coordination of Na (0.99 Å) is larger than that of Li (0.59 Å)[23]. With respect to those of Li₂CoSiO₄, the deviations of the lattice parameters of Li₁₅Na₀₅CoSiO₄ are 0.6% and 1.7% for a and c, respectively. Whereas, a more significant deviation (3.2%) has been found for the parameter b. The optimized cell volume is found to about 5.5% increase by from Li₂CoSiO₄ to Li15Na05CoSiO4.

On the other hand, as mentioned above, the corrugated layers should be two-dimensional(2D) pathways for lithium ion diffusion. Therefore, the interlayer space of the corrugated layers should be an important factor for the Li ion diffusion. According to the symmetry, three distances d_1 , d_2 and d_3 as shown in Fig.1(b) can be used to characterize the interlayer space of the corrugated layers. Table 2 lists the distances d_1 , d_2 and d_3 for Li₂CoSiO₄ and Li_{1.5}Na_{0.5}CoSiO₄. It is obvious

Table 3 Bond lengths for $Li_{2-x}Na_xCoSiO_4$ (x=0, 0.5) (Å)

that all the three distances, i.e. the interlayer spaces, are enlarged when partial Li is replaced by Na. This means that the expansion of structural parameters leads to the expansion of interlayer space of the adjacent corrugated layers. This would benefit the lithium ion diffusion and may also further improve the electrochemical performance.

Another way of quantifying the structural differences is in terms of the bond lengths. The bond lengths of Co-O, Si-O, Li-O and Na-O for Li₂CoSiO₄ and Li_{1.5}Na_{0.5}CoSiO₄ are listed in Table 3. Both the average bond lengths of Co-O and Si-O for Li15Na05CoSiO4 are almost the same as those for Li₂CoSiO₄, with a tiny increase of 0.3% and 0.1%, respectively. However, larger spread has been found for the Co-O bond lengths in Li₁₅Na₀₅CoSiO₄, whereas the bond lengths of Si-O still keep a small spread. Although Na-substitution has an influence on the local environment, the Si - O bonds in $Li_{1.5}Na_{0.5}CoSiO_4$ should still be strong covalent and afford the same lattice stabilization effect as in the Li₂CoSiO₄[14–15]. Besides, we can find that the average Li-O bond length of Na-substituted Li₂CoSiO₄ is slightly larger (1.5%) than that of the pure material. This indicates a wider Li ion pathway and lower Li-O interactions in Li15Na05CoSiO4.

In order to understand the effects of Na-substitution on the electronic structures, we calculated the band structures (Fig.3) and the density of states (DOS) (Fig.4) for the Li_{1.5}Na_{0.5}CoSiO₄ and the pure Li₂CoSiO₄. In Fig.3, we can observe that the valence band maximum (VBM) and conduction band minimum (CBM) both occur at Γ -point, making both compounds to be direct gap materials. The gap value is about 3.74 eV for the pure Li₂CoSiO₄, and a smaller one (3.39 eV) for Li_{1.5}Na_{0.5}CoSiO₄. This indicates that the Li_{1.5}Na_{0.5}CoSiO₄ material has better electronic conductivity than the Li₂CoSiO₄ material. It is found that the Na-substitution induces the CBM's shifting toward the Fermi level, especially for the Co projected-DOS (Fig.4(b)). The

Table 2 Distances d_1 , d_2 and d_3 as described in Fig.1(b) for $Li_{2-x}Na_xCoSiO_4$ (x=0, 0.5)

$\underline{\mathbf{H}}_{2} = \underline{\mathbf{J}}_{1} \cdot \mathbf{u}_{1} \in \mathbf{O} \setminus \mathbf{O} + \mathbf{U}_{1} \in \mathbf{O} $	0.0)			
Li _{2-x} Na _x CoSiO ₄	x	$d_1/\text{\AA}$	$d_2/\text{\AA}$	$d_3/\text{\AA}$
Li2CoSiO4	0	4.388	5.443	4.423
Li1.5Na0.5CoSiO4	0.5	4.604	5.617	4.575

Bond		Li2CoSiO4			Li1.5Na0.5CoSiO4	
	Min.	Max.	Average	Min.	Max.	Average
Со—О	1.995 4	2.023 0	2.012 1	1.964 3	2.041 9	2.017 7
Si—O	1.652 8	1.660 0	1.656 8	1.642 6	1.666 9	1.658 6
Li—O	1.949 3	1.998 7	1.980 1	1.911 0	2.076 5	2.008 9
Na—O	_	_	_	2.167 3	2.253 9	2.195 6



Fig.3 Band structure of Li₂CoSiO₄ (a) and Li_{1.5}Na_{0.5}CoSiO₄ (b) (Solid lines are for majority spin and dash lines for minority spin. Points are labeled as Γ =(0, 0, 0), X(B)=(1/2, 0, 0), S(A)=(1/2, 1/2, 0), Y(F)=(0, 1/2, 0), Z(G)=(0, 0, 1/2), U(D)=(1/2, 0, 1/2), R(E)=(1/2, 1/2, 1/2), and T(C)=(0, 1/2, 1/2) with respect to (b_1 , b_2 , b_3) for orthorhombic structure (a) and triclinic structure (b). Dash dot lines mark Fermi level (top of valence band))



Fig.4 Total and projected density of states (PDOS) for $Li_{2-x}Na_xCoSiO_4$ (*x*=0, 0.5): (a) Total DOS; (b) Co-PDOS; (c) Li/Na-PDOS; (d) Si-PDOS; (e) O-PDOS

Li/Na, Si and O also contribute to the CBM and their CBM is also found to shift down, but the magnitude of their corresponding density of states is quite small compared with Co projected-DOS as shown in Figs.4(b)–(e). This means that the shifting of Co conduction bands would play an important role in the improvement of electronic conductivity when partial Li is substituted by Na. In addition, as shown in Fig.4(b), the Na-substitution has more significant influence on the Co2 atom, which has a smaller distance from the substituted Na than the Co1. The lowering of conduction band may be due to the expansion of the lattice and the distortion of the local environment (especially the CoO₄ tetrahedra) caused by Na-substitution.

4 Conclusions

1) The effects of Na-substitution on the electronic structures and structural properties of Li_2CoSiO_4 are presented. When Li ions in Li_2CoSiO_4 are substituted (fully or partially) by Na ions, the lattice parameters expand especially for the parameter *b*. This lattice expansion effect benefits the Li ion diffusion due to the widening of the diffusion pathways.

2) The Na-substitution on Li sites in Li_2CoSiO_4 induces a lowering of the conduction bands and a narrowing of the band gap, which could be helpful for enhancing the electronic conductivity.

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186