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Short communication

Effect of Mg-doping on the structural and electronic properties of $LiCoO_2$: A first-principles investigation

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Abstract

The electronic structures of Mg-doped $LiCoO_2$ have been investigated by the first-principle pseudopotential method. The effect of Mg-doping content on the band structure and structural stability of $LiCoO_2$ is presented. The results obtained via a full relaxation of the crystalline structure show that a rational amount of Mg-doping in $LiCoO_2$ is helpful to enhance its electronic conductivity. However, the doping magnitude should be controlled within 15 mol% of $LiCoO_2$ in order to keep its crystalline structure unchanged. By combining total energy calculations with basic thermodynamics, the average intercalation voltages of this doped system have been predicted.
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1. Introduction

Lithium-ion batteries are undergoing a period of intense commercialization due to their intrinsically energy density superior to other rechargeable batteries such as nickel metal-hydride. In the last decades of study, the research on the cathode materials for lithium-ion batteries has been focused on four materials: $LiCoO_2$, $LiNiO_2$, $LiMn_2O_4$, $LiFePO_4$ and their derivatives though there are some other materials as promising candidates. Of these materials, $LiCoO_2$ is considered the most stable among the family of α-$NaFeO_2$ structured materials and is the only member that has been commercialized on a large scale. In an attempt to extend the reversibility and enhance the capacity of the electrochemical Li/$LiCoO_2$ cells, numerous cations have been substituted for cobalt, including Ni [1–3], Mn [4,5], Cr [6], Al [7,8], and Fe [9]. Tukamoto and West [10] and Carewska et al. [11] reported that substitution of Mg for Co can enhance the cycling properties of $LiCoO_2$ by strongly increasing the electronic conductivity of the pristine $LiCoO_2$. Julien et al. [12] prepared $LiMg_{0.5}Co_{0.5}O_2$ with a pure layered structure using sol–gel method. Very recently, Levasseur et al. [13] studied the structure of Mg-doped $LiCoO_2$ by X-ray diffraction and Li MAS NMR spectroscopy, and detected a lot of MgO in annealed $LiMg_{0.06}Co_{0.94}O_2$. These authors all proposed that Mg-doping in $LiCoO_2$ always leads to the simultaneous presence of Co^{4+} ions (sharing an itinerant electronic hole with the neighboring Co^{3+} ions). Moreover, they hypothesized that Mg-substitution corresponds to the $2Co^{3+} \rightarrow Co^{4+} + Mg^{2+}$ process and thereby leads to the appearance of electronic holes in the cobalt t_{2g} band. However, to our knowledge, the theoretical explanation of the electronic conductivity's increase has not been reported yet.

Computational experiments have the advantage in supplementing the real experiments that one has full control over the relevant variables. What is especially worth mentioning is that first-principles calculations have made an impact on the understanding of practical lithium-ion batteries materials. For example, Ceder et al. [14] demonstrated that new materials can be pre-screened before attempting their synthesis

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through the first-principles prediction voltages. Wolverton and Zunger [15] performed the first-principles prediction of vacancy order–disorder and intercalation battery voltages in Li_xCoO_2. Actually, by first-principles calculations, we have elucidated the relation between the electron transfer, the valence change and the change of the average intercalation voltage of Cr-doped $LiMn_2O_4$ [16,17], and that the electronic conductivity can significantly enhanced with the displacement by Cr^{3+} [18]. In the present paper we focus on the electronic structure analysis of Mg-doped $LiCoO_2$, in order to characterize the structural stability and electronic conductivity of the Mg-doped $LiCoO_2$.

2. Computational details

The first-principles calculation has been performed using the Vienna *ab inito* simulation package, VASP [19]. All the calculations are performed in a 12 formula unit $LiCoO_2$ supercell with partial Co atoms replaced by Mg atoms. The Monkhorst-Pack scheme [20] with $4 \times 4 \times 2$ k points has been used for integration in the irreducible Brillouin zone. Energy cutoff for the plane waves is 700 eV. Fermi level is smeared by the Gaussian method [21] with a width of 0.1 eV. This set parameters assures a total energy convergence of 2 meV per atom. In structure search, all cell-internal structural parameters are fully relaxed. The search is stopped when forces all relaxed atoms are less than 0.02 eV Å. We used the Vanderbilt ultrasoft pseudopotentials [22] and the generalized gradient approximation by Perdew and Wang [23] for the exchange-correlation energy.

The theoretical procedure to calculate the average intercalation voltage through first-principles has been established [14]. The intercalation voltage V_{AVE}, is given by

$$V_{AVE} = \frac{-\Delta G}{F} \quad (1)$$

where ΔG is the change in Gibbs free energy for the intercalation reaction, and F is the Faraday constant. Assuming that effects of the changes in volume and entropy associated with the intercalation on the Gibbs free energy are negligibly small. ΔG can be approximated by the internal energy term ΔE, i.e.

$$V_{AVE} \approx \frac{-\Delta E}{F} \quad (2)$$

where ΔE is given by the difference in total energies between $LiMg_xCo_{1-x}O_2$ and the sum of oxide $Mg_xCo_{1-x}O_2$ and metallic lithium, for which the lattice parameters and atomic internal coordinates are fully relaxed, i.e.

$$\Delta E = E_{total}[LiMg_xCo_{1-x}O_2] - E_{total}[Mg_xCo_{1-x}O_2] - E_{total}[Li] \quad (3)$$

3. Results and discussion

3.1. Structural stability

In this calculation, full relaxation is performed for $LiMg_xCo_{1-x}O_2$. It is found that the lattice parameters vary with the Mg-doping content in $LiCoO_2$, as shown in Table 1. At the 1/12 (8.33%) mole Mg-doping, the change in the value of lattice parameters of c and a are 0.35% and −0.18%, respectively, although the latter reaches half of the former. It is natural that the larger ionic radius of Mg^{2+} than Co^{3+} results in the larger interlayer distance (the increase of c value). On the other hand, the increase of c value with Mg-doping should be related to the difference between the electronic structures of Co and Mg. There exists a d_{z^2} orbital for the former although three p orbitals are symmetrical for the latter. On the reason why the a axis shrinks slightly with Mg-doping, it is still unclear. However, it can be said that this will provide the more open channel and the shorter diffusion path along the a–b plane for the Li ions, thus lowering the activation energy during the intercalation and deintercalation of the Li ions. Kang et al. [24] also reported that Li motion is so sensitive to the spacing between oxygen layers that this very small change (∼0.02 Å) results in a 20–30 meV increase in the activation barrier. However, for the 1/6 (16.7%) mole Mg-doping, it is found that the crystalline structure is obviously distorted. In fact, we also examine the case of 1/8 (12.5%) mole Mg-doping through doping three Mg atoms in the $2 \times 1 \times 1$ supercell with 24 Co atoms, and find that there is no lattice distortion even at the 12.5% mole Mg-doping. Thus, we use the average value (∼15%) of 12.5% and 16.7% as the critical point of theoretical doping. The distortion becomes severe as the doping magnitude is further increased. This is harmful to the intercalation and deintercalation performance of the material and thereby reduces the capacity of the battery.

Table 1
Variation of the lattice parameters and average intercalation voltages and Mg content in $LiCoO_2$

x in $LiMg_xCo_{1-x}O_2$	a (Å)	c (Å)	c/a	Average voltage (V)
0	2.8396	14.0538	4.95	3.963
1/12	2.8346	14.1033	4.98	4.170
1/6*	2.8331	14.1347	4.99	4.441

* The lattice is distorted at this Mg content.

3.2. Electronic structure

The electronic conductivity of semiconductor depends on the charge carrier concentration at constant temperature. The charge carriers are created by impurity ionization or intrinsic excitation. Usually, electronic holes are created in the bulk material and thus its electronic conductivity is enhanced when low-valence atoms are introduced.

A one-to-one correspondence among the Fermi level, the charge carrier concentration and the electrical conductivity was established in a recent research [25]. Based on this relationship, the Fermi level shift due to redox reactions determines the electrical conductivity of the doped bulk material, i.e., the Fermi level shift was proportional to the variation of conductivity. This indicates that the conductivity can be notably altered by adjusting the position of the Fermi level and thus doping-induced charge transfer.

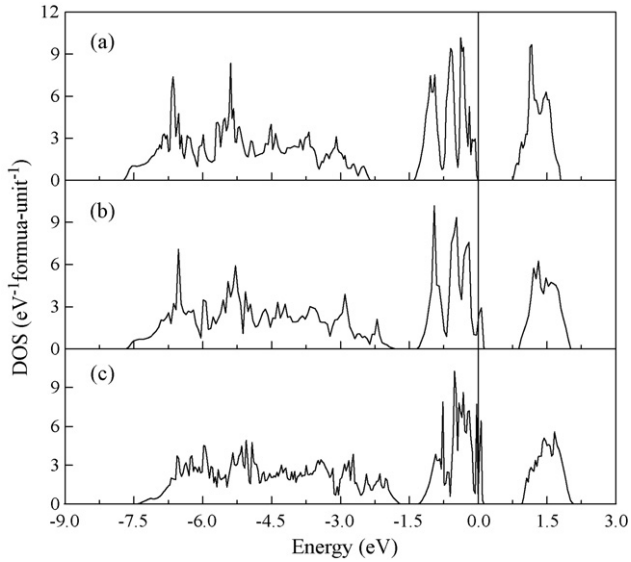

Fig. 1. Density of states of $LiMg_xCo_{1-x}O_2$: (a) $x = 0$; (b) $x = 1/12$; (c) $x = 1/6$. The vertical line at zero point represents the Fermi level.

Fig. 1 shows the density of states (DOS) of $LiMg_xCo_{1-x}O_2$. It can be clearly seen that $LiCoO_2$ is a typical semiconductor with a gap of 0.765 eV from the valence band top to the conduction band bottom as shown in Fig. 1(a). The calculated value is considerably smaller than the experimental band gap of 2.7 eV [26], which is known to be due to the GGA. For the case of Mg-doping, the concentration of the electronic holes is significantly increased and the Fermi level shifts into the valence band after Mg is doped in $LiCoO_2$, displaying the remarkable p-type conductivity. That is to say, the DOS around the Fermi level is increased with Mg-doping. This is consistent with the hypothesis that the substitution of Mg for Co corresponds to the $2Co^{3+} \rightarrow Co^{4+} + Mg^{2+}$ as mentioned above.

The DOS's of $LiMg_xCo_{1-x}O_2$ are composed of two main peak groups; one located around −18 eV (not shown in figure) and the other between −7 and 0 eV. The peak group around −18 eV results from the contribution of the O 2s orbit while the peak group between −7 and 0 eV is mainly attributed to the mixture of O 2p and Co 3d states. With the increase of Mg-doping, the overlapping becomes more significant, implying that the communization of the electrons is enhanced. Therefore, the Mg-doped $LiCoO_2$ becomes easily conducting.

Fig. 2 shows the valance electron density of the $LiMg_xCo_{1-x}O_2$ in α-$NaFeO_2$ structure. The crystallographic plane shown in this figure is $(1\,1\,\bar{2}\,0)$, which is parallel to the *c* axis. We can find that the remarkable charge overlap between the Co and O atoms compared to the nearly pure ionic state of Li. The layered characteristics of the structure are also clearly seen.

The difference in the electron densities before and after lithium deintercalation is compared in order to study the effect of Li deintercalation on the charge transfer. For the purpose of analyzing the difference in the electron densities both $LiMg_xCo_{1-x}O_2$ and $Mg_xCo_{1-x}O_2$ are calculated in the same geometry with the relaxed $LiMg_xCo_{1-x}O_2$ so that the electron densities can be subtracted point by point. The difference in the

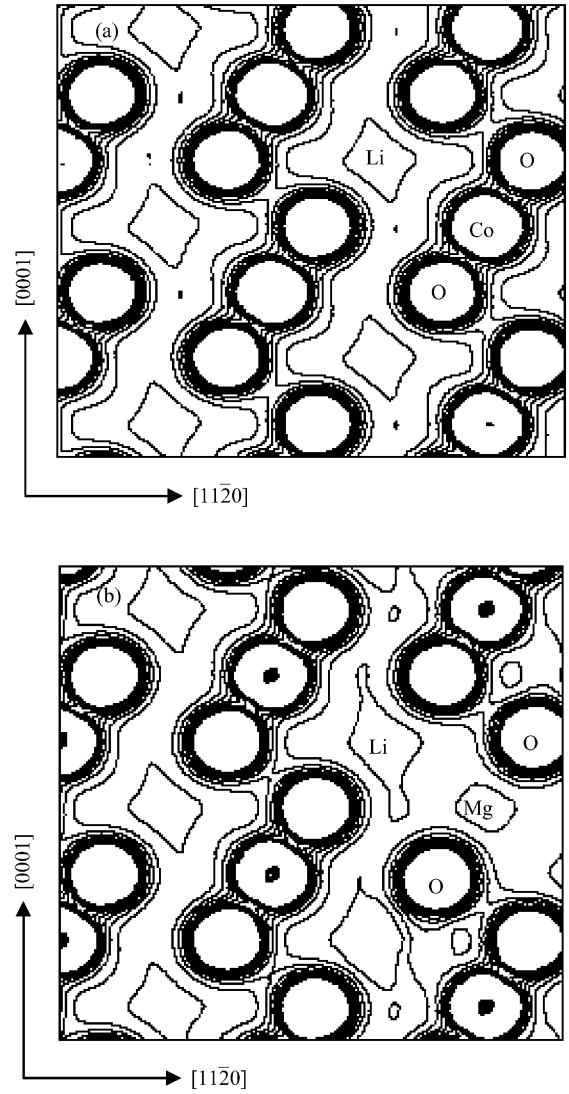

Fig. 2. Valence charge density in layered $LiMg_xCo_{1-x}O_2$: (a) $x = 0$ and (b) $x = 1/12$.

electron densities is due to the intercalation of Li. The positive part of the difference in electron density in the α-$NaFeO_2$ structure (that of relaxed $LiCoO_2$ and $LiMg_xCo_{1-x}O_2$) is shown in Fig. 3. The value of the negative part has some minor charge depletion around Co and O, but is not shown here because it is very small. It is revealed that oxygen as well as Co loses some electrons during the process of Li deintercalation. This is in contrast to the viewpoint of the classical inorganic chemistry that only the valence state of Co is changed from Co^{3+} into Co^{4+}.

3.3. Average intercalation voltage

It is well known that the Fermi level E_F of the electrode material is closely related to the average intercalation voltage (open-circuit voltage) of the battery. Several groups [14,16] have recently performed first-principles calculations on the average intercalation of various electrode materials. Here, we calculate the theoretical average intercalation voltages of $LiMg_xCo_{1-x}O_2$ in terms of Eqs. (2) and (3) and calculated total energies, as listed

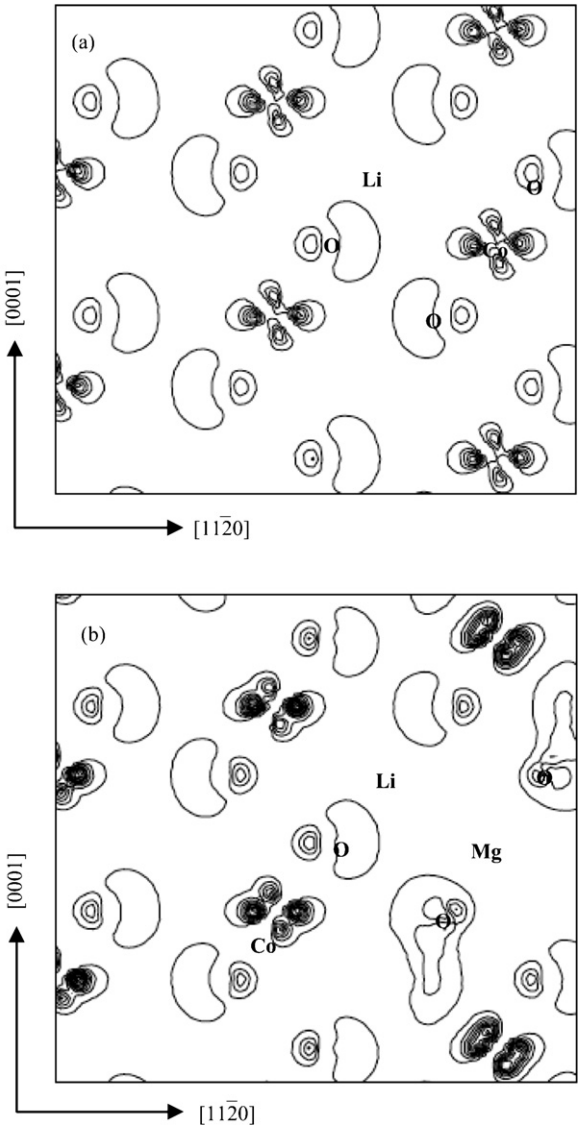

Fig. 3. Positive part of the difference in valence charge between $LiMg_xCo_{1-x}O_2$ and $Mg_xCo_{1-x}O_2$: (a) $x = 0$ and (b) $x = 1/12$.

in Table 1. These calculations do not require any experimentally measured input data. Interestingly, the theoretical average intercalation voltage of the pure $LiCoO_2$ agrees well with the experimental one (3.95 V) [27]. It is shown that the average intercalation voltage increases with Mg-doping. This similar tendency is also observed in the Al-doped $LiCoO_2$ [14] and Cr-doped $LiMn_2O_4$ [16] systems.

As Mg-doping gives rise to partial $Co^{3+} \rightarrow Co^{4+}$ transformation, the corresponding charge transfer while charging in $LiMg_xCo_{1-x}O_2$ is smaller than in $LiCoO_2$. This will result in decrease of the electrochemical capacity of $LiCoO_2$. As for the compensation of the charge in the calculation, it is found that Co ions near the doped Mg ion shows the higher valence state. This is consistent with the experimental proposal that Mg-doping in $LiCoO_2$ always leads to the simultaneous presence of Co^{4+} ions [10–13]. On the other hand, the conductivity of the material increases, and the transport of the Li^+ ions into and out of the layered structure becomes easier. Therefore, the overall electrochemical performance of the material does not necessarily become worse in a practical Mg-doped $LiCoO_2$ cathode material. This interpretation explains why a small quantity of substitution of Mg for Co can enhance the cycling properties of $LiCoO_2$ as observed in the experiment [11].

4. Conclusions

The electronic structures, structural stability and average intercalation voltages of Mg-doped $LiCoO_2$ systems are studied by the first-principles calculations. It is found that Mg-doping into $LiCoO_2$ gives rise to the shift of the Fermi level into the valence band due to the increase of Co^{4+} concentration. With the increase of Mg-doping, the overlapping of the Co 3d with the O 2p electrons becomes more significant, implying that the communization of the electrons is enhanced. Therefore, its conductivity is obviously increased and the average intercalation voltage of the battery is elevated. As the electrochemically active Co is replaced with inactive Mg, the theoretical capacity of $LiMg_xCo_{1-x}O_2$ will be lower than that of $LiCoO_2$. On the other hand, because of the bigger ionic radius of Mg^{2+} than Co^{3+}, the interlayer distance of Mg-doped $LiCoO_2$ becomes bigger than of pristine $LiCoO_2$. This will make it easier for the transport of the Li^+ ions into and out of the layered structure. Therefore, the general electrochemical performance of the material does not necessarily become worse in a practical Mg-doped $LiCoO_2$ cathode material. Of course, Mg-doping will result in the lattice distortion and the significant decrease of theoretical capacity of $LiCoO_2$ if the dopant content is very high. Therefore, the Mg-doping content is suggested to the less than 15% mole of $LiCoO_2$, considering the above two factors. In such a range of Mg-doping, the substitution will be beneficial to the enhancement of both the practical capacity and the rate performance of the cathode material.

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