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Short Communication

Structural and Electronic Properties of Cation Doping on the Spinel $LiMn_2O_4$: a First-Principles Theory

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The structural and electronic properties of cation doping on the spinel $LiMn_2O_4$ were investigated by the first-principles theory. The calculated results indicate that due to the formation energy of $LiAl_{0.5}Mn_{1.5}O_4$ is the smallest, the structure of $LiAl_{0.5}Mn_{1.5}O_4$ may be the most stable material, so the cycle performance may be the best. Both Cr-O and Sr-O bonds are longer than Co-O and Al-O bonds, thereby the cycle performance of $LiAl_{0.5}Mn_{1.5}O_4$ and $LiCo_{0.5}Mn_{1.5}O_4$ may be better. For $LiCr_{0.5}Mn_{1.5}O_4$ and $LiSr_{0.5}Mn_{1.5}O_4$, the charge density among Sr, Cr, Mn and O atoms decreases, so the partial charge from Sr, Cr, Mn and O atoms is centralized near Li-site atoms, which is beneficial to the transition of lithium. Therefore the electronic conductivity of $LiCr_{0.5}Mn_{1.5}O_4$ and $LiSr_{0.5}Mn_{1.5}O_4$ is improved. For $LiAl_{0.5}Mn_{1.5}O_4$ and $LiCo_{0.5}Mn_{1.5}O_4$, the charge overlap around Mn, Ni and O atoms significantly increased, the charge of Co, Al, Mn and O atoms formed Co-O, Al-O and Mn-O stable bonds, therefore $LiAl_{0.5}Mn_{1.5}O_4$ and $LiCo_{0.5}Mn_{1.5}O_4$ structural stability is dramatically increased and may behave better electronic properties and more capacity.

Keywords: spinel $LiMn_2O_4$, first-principles, formation energy, charge density

1. INTRODUCTION

With many advantages such as no memory effect, high voltage, good cycling stability and abundance in nature, Lithium-ion batteries have been favored in consumer electronics for last 30 years [1-4]. It has been well known that some important factors such as the types of electrolyte used, and the nature of cathode and anode, have great impact on the battery property [5-9]. Compared with $LiCoO_2$, $LiMn_2O_4$ is a good choice for secondary due to its non-toxicity and low cost. It has been well known that $LiMn_2O_4$ has a 120 $mAhg^{-1}$ capacity, and the voltage platform is between 3.5 and 4.5 V, thereby it was a worthwhile study cathode material for new-generation lithium-ion batteries [10,11]. Many previous experimental investigations have revealed that electrochemical properties, such as capacity and intercalation voltage of spinel $LiMn_2O_4$ can be increased through substituting the other transition metal ion for Mn sites [12,13]. There are many types of doping element, such as Ni, Co, Mg, Fe, Li, Al, Ti, Cr, etc. [14-16]. But experiment costs too much and the step is so many that it is easy to affect the accuracy of the results during the experimental process [17]. In recent years, in order to analyze the The essence of the various chemical reaction process, many people are keen to study its microstructure, density of states, charge density and other properties using the first-principles [18]. It is noted that there is close relationship between electronic structures and electrochemical properties in intercalation compounds [19-21]. This paper study mainly on the effect of cation doping on DOS, formation energy$_{\triangle}$E, bonds length and charge density of $LiM_yMn_{2-y}O_4$ (M=Cr, Al, Sr, Co) by means of first-principles theory. Meanwhile, we discussed the impact of these properties on their electrochemical properties such as structural stability and electronic conductivity.

2. METHODS

Computations in this study were performed with CASTEP code (Materials Studio package). Neglecting the 10% Li/Mn site disorder, the initial crystal model was built according to the experimental lattice parameters and ionic positions [22]. Supercells containing eight-formula units with one of Mn atoms substituted by M atom (M=Cr, Al, Sr, Co) are investigated. The generalized gradient approximation (GGA and GGA+U) was employed for the exchange correlation potential [23]. The Hubbard U value of Mn, Cr, Co, Al and Sr atom is 5.0, 4.6, 4.5, 4.5 and 5.0 respectively. Geometry optimization was calculated to fully relax the structures until.

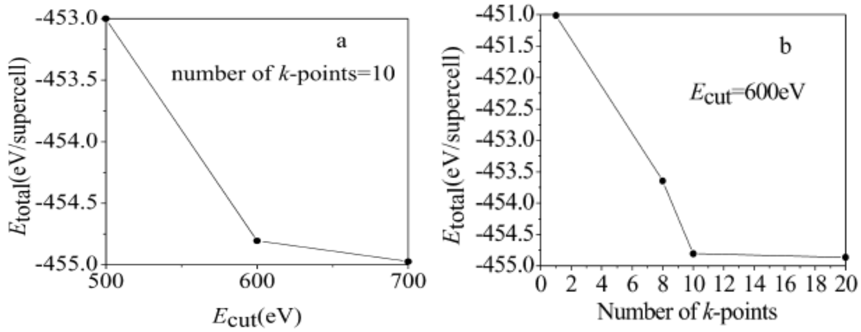

Figure 1. (a)The energy cutoff with ten k-points, and (b) The k-points with energy cutoff of 600 eV.

Then, the total energies and the electronic structures were calculated in the relaxed structures with the same energy cut-off and k-points as those in the geometry optimization. We have carefully carry on the convergence tests for the total energy regarding the k-points sampling and cut-off energy, as shown in Fig. 1. according to the test results, we have chosen 600 eV as the final set of energies, and simultaneously usd ten k-point sampling of Monkhorst-Pack scheme[24]. The total energy was converged to within 10^{-4} eV, while self-consistent field (SCF) convergence per atom is $2\times10-6$ eV, root-mean-square (RMS) displacement of atoms is 0.001 ˚ A, RMS force on atoms is 0.05 eV/ ˚ A and RMS stress tensor are less than 0.1 Gpa [25]. The ionic positions and the lattice parameters were fully relaxed before the calculations, and the final force on each atom is less than 0.01eV/A. Gaussian smearing method with a smearing width of 0.03 eV was chosen in the calculation of the density of states (DOS)and partial density of states(PDOS).

3. RESULTS AND DISCUSSION

3.1. Density of states

The electron density of states (DOS) and projected electron density of states (PDOS) of pure $LiMn_2O_4$ and doped $LiMn_2O_4$ was presented in Fig. 2. From Fig. 2(a), it is interesting to see that the Mn-3d is mainly dispersed in the narrow band near the Fermi level. In this article, to improve the electrochemical performance of $LiMn_2O_4$, we replaced Mn site with Cr for the electronic structures of Cr is similar to Mn. To analyze the electronic distribution nearby the Fermi level, the partial density of states of Cr, Mn and Li atoms were represented as show in Fig. 2(b). The partial density of states of Cr-doped $LiMn_2O_4$ nearby the Fermi level owing to the Mn-3d and Cr-3d. In other words, the presence of Cr atom transform the band gap by altering the electronic structures, and enhanced the electrochemical properties, which is consistent with the experimental results in Refs. [26]. Fig. 2(c) shows the DOS and PDOS of Co-doped $LiMn_2O_4$. The outcome showed that the partial density of states nearby the Fermi level attributed to the Co-3d that hybrids with O-2p and Mn-3d hereabouts. The partial density of states and charge density of $LiCo_{0.5}Mn_{1.5}O_4$ showed that the presence of Co ion and Mn and O ions nearby formed a conducting cluster, therefore electrochemical performance of $LiMn_2O_4$ is improved, which is consistent with the experimental results in Refs. [27]. This is the explanation that the improve of the electrochemical properties of $LiMn_2O_4$ due to Co-doping. Fig. 2(d) shows the DOS and PDOS of Sr-doped $LiMn_2O_4$. The partial density of states near the Fermi level was attributed to Mn-3d, O-2p and Sr-3d states. Facts have proved that the enhance volume is beneficial to the transition of lithium and then resulting in the heighten of electrochemical properties of Sr-doped $LiMn_2O_4$, which is consistent with the experimental results in Refs. [28]. Fig.2(e) shows the DOS and partial density of states of Al-doped $LiMn_2O_4$. The partial density of states at the Fermi level was mainly due to the contributions of Mn-3d and O-2p states. It could also be found that the concentrations of the electronic holes increased, the Fermi level shifted and the DOS around the Fermi level was increased compared with pure $LiMn_2O_4$. Therefore, the Al-doped $LiMn_2O_4$ material behaves a relative better electrochemical properties, which is consistent with the experimental results in Refs. [29].

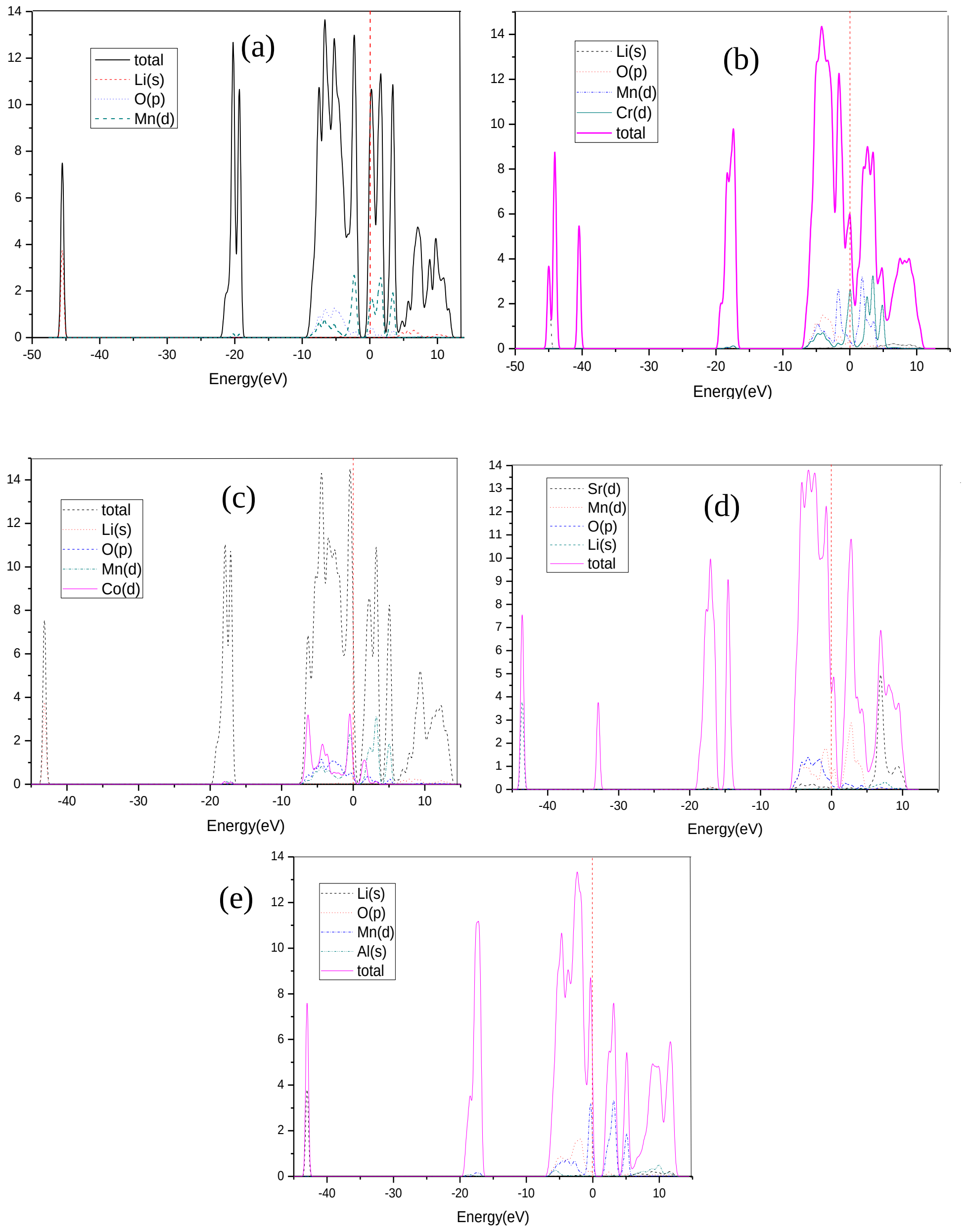

Figure 2. DOS and PDOS of (a)pure $LiMn_2O_4$ (b) Cr-doped $LiMn_2O_4$ (c) Co-doped $LiMn_2O_4$ (d) Sr-doped $LiMn_2O_4$ (e) Al-doped $LiMn_2O_4$. The contributions of Li-s, Mn-s, Mn-p and O-s are small and are not shown. The Fermi level is shifted to 0 eV.

3.2. The formation energy and bonds length

The formation energy $_{\triangle}E$ of Cr-doping is given by $_{\triangle}E = E_{total}(LiCr_{0.5}Mn_{1.5}O_4)+1/2E_{total}(Mn)-1/2E_{total}(Cr)-E_{total}(LiMn_2O_4)$.Where $E_{total}[LiCr_{0.5}Mn_{1.5}O_4]$ and E_{total} ($LiMn_2O_4$) is the total energy per formula unit of $LiCr_{0.5}Mn_{1.5}O_4$ and $LiMn_2O_4$, respectively[30]. E_{total} (Mn) and E_{total} (Cr) are the total energy of metallic lithium and chromium.Similarly, the formation energy$_{\triangle}E$ of $LiCo_{0.5}Mn_{1.5}O_4$, $LiSr_{0.5}Mn_{1.5}O_4$ and $LiAl_{0.5}Mn_{1.5}O_4$ is calculated, respectively. The results were shown in Table 1. From the table, we can see that due to the formation energy of $LiAl_{0.5}Mn_{1.5}O_4$ is the smallest and $LiSr_{0.5}Mn_{1.5}O_4$ is the largest, the structure of $LiAl_{0.5}Mn_{1.5}O_4$ may be the most stable and $LiSr_{0.5}Mn_{1.5}O_4$

may be the most unstable of these four materials, which evidence that $LiAl_{0.5}Mn_{1.5}O_4$ may behave the best electrochemical properties, these are consistent with the experimental results in Refs. [29].

Table 1. Total energy, formation energy of pure and cation doping $LiMn_2O_4$

	$LiCr_{0.5}Mn_{1.5}O_4$	$LiCo_{0.5}Mn_{1.5}O_4$	$LiSr_{0.5}Mn_{1.5}O_4$	$LiAl_{0.5}Mn_{1.5}O_4$
total energy(eV)	-4151	-3437	-3336	-2896
formation energy(eV)	-6	-2	0.54	-9.54

Table 2. Bonds length of pure and cation doping $LiMn_2O_4$

Bond（$LiMn_2O_4$）	Li-O	Mn-O	
average bond length(Å)	1.97	1.95	
Bond（$LiCr_{0.5}Mn_{1.5}O_4$）	Li-O	Mn-O	Cr-O
average bond length(Å)	2.08	1.95	1.99
Bond（$LiCo_{0.5}Mn_{1.5}O_4$）	Li-O	Mn-O	Co-O
average bond length(Å)	1.97	1.95	1.95
Bond（$LiSr_{0.5}Mn_{1.5}O_4$）	Li-O	Mn-O	Sr-O
average bond length(Å)	2.01	2.1	2.41
Bond（$LiAl_{0.5}Mn_{1.5}O_4$）	Li-O	Mn-O	Al-O
average bond length(Å)	1.97	1.95	1.95

Table 2 shows that the average bonds length of $LiAl_{0.5}Mn_{1.5}O_4$ and $LiCo_{0.5}Mn_{1.5}O_4$ are similar to pure $LiMn_2O_4$, indicating the introduced of Al and Co atoms are unsignificant change the crystal structure. The lengths of the Li-O bonds of $LiCr_{0.5}Mn_{1.5}O_4$ and $LiSr_{0.5}Mn_{1.5}O_4$ both enhanced, which reveals that Li-O bonds of $LiCr_{0.5}Mn_{1.5}O_4$ and $LiSr_{0.5}Mn_{1.5}O_4$ are quite weak, and the diffusion coefficient of lithium ion is comparatively large, therefore the electrical conductivity may be comparatively better. Nevertheless both Cr-O and Sr-O bonds are longer than Co-O and Al-O bonds, so the cycle performance of $LiCr_{0.5}Mn_{1.5}O_4$ and $LiSr_{0.5}Mn_{1.5}O_4$ may be relatively poor, while $LiAl_{0.5}Mn_{1.5}O_4$ and $LiCo_{0.5}Mn_{1.5}O_4$ may behave better electronic properties and more capacity[31].

3.3. Analysis of difference of charge density

The difference of charge density is defined as the charge density of a molecule is subtracted by the charge density of the atoms making up of the molecule which are at proper place and aren't disturbed. The difference of charge density of pure and doped $LiMn_2O_4$ are shown in Fig. 3. It is interesting to see that for $LiCr_{0.5}Mn_{1.5}O_4$ and $LiSr_{0.5}Mn_{1.5}O_4$, the charge density among Sr, Cr, Mn and O atoms decrease simultaneously, so the partial charge from Sr, Cr, Mn and O atoms is centralized near Li-site atoms, which is beneficial to the transition of lithium. Therefore the electronic conductivity of $LiCr_{0.5}Mn_{1.5}O_4$ and $LiSr_{0.5}Mn_{1.5}O_4$ is improved enormously. From Fig. 3, it is clear that $LiAl_{0.5}Mn_{1.5}O_4$ and $LiCo_{0.5}Mn_{1.5}O_4$ just in contrast with $LiCr_{0.5}Mn_{1.5}O_4$ and $LiSr_{0.5}Mn_{1.5}O_4$, the charge overlap around Mn, Ni and O atoms significantly increased compared with $LiCr_{0.5}Mn_{1.5}O_4$ and $LiSr_{0.5}Mn_{1.5}O_4$. Meanwhile, it can be found that the charge of Co, Al, Mn and O atoms formed Co-O, Al-O and Mn-O stable bonds, therefore $LiAl_{0.5}Mn_{1.5}O_4$ and $LiCo_{0.5}Mn_{1.5}O_4$ structural stability is dramatically increased and may exhibit better electronic properties and more capacity compared with $LiCr_{0.5}Mn_{1.5}O_4$ and $LiSr_{0.5}Mn_{1.5}O_4$, which is consistent with the experimental results[32].

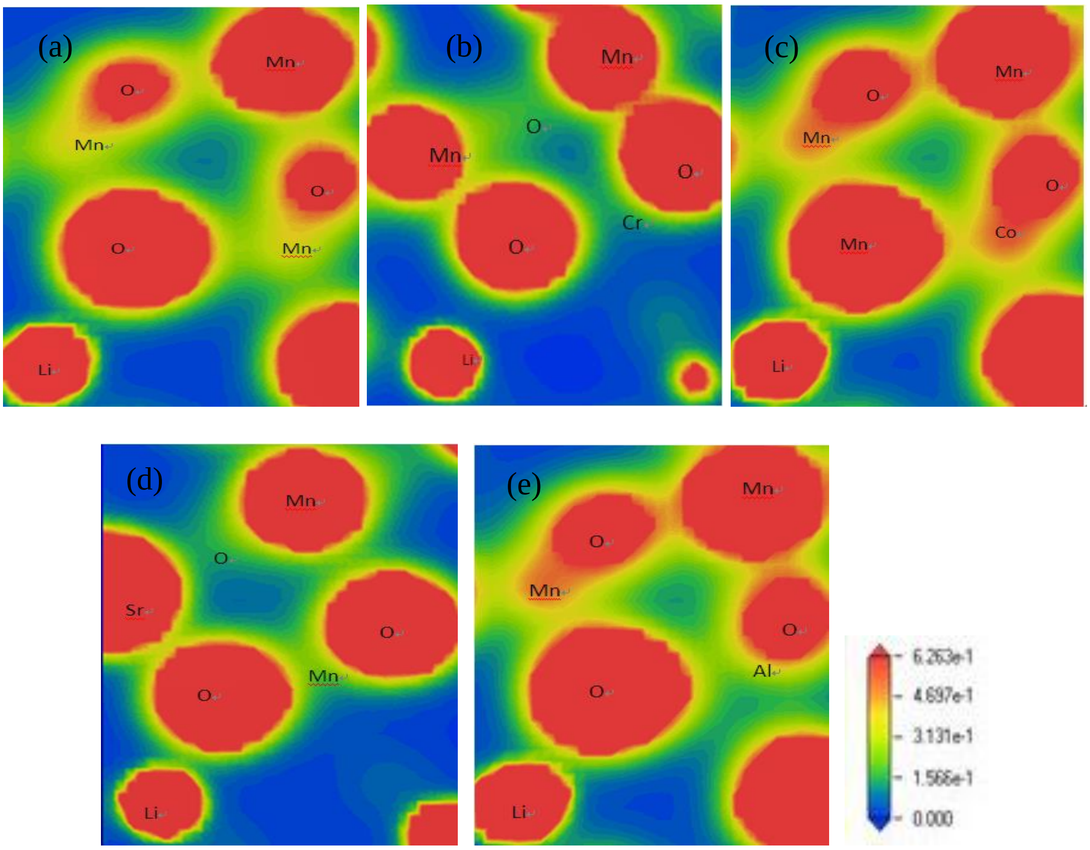

Figure 3. Electric charge density difference of pure and doped $LiMn_2O_4$ respectively: (a) $LiMn_2O_4$ (b) $LiCr_{0.5}Mn_{1.5}O_4$ (c) $LiCo_{0.5}Mn_{1.5}O_4$ (d) $LiSr_{0.5}Mn_{1.5}O_4$ (e) $LiAl_{0.5}Mn_{1.5}O_4$.

4. CONCLUSIONS

In conclusion, we have investigated four types of doped $LiMn_2O_4$ by the first-principles theory. The calculated results indicate that due to the formation energy of $LiAl_{0.5}Mn_{1.5}O_4$ is the smallest, the structure of $LiAl_{0.5}Mn_{1.5}O_4$ may be the most stable, so the cycle performance may be the best. Both Cr-O and Sr-O bonds are longer than Co-O and Al-O bonds, thereby the cycle performance of $LiAl_{0.5}Mn_{1.5}O_4$ and $LiCo_{0.5}Mn_{1.5}O_4$ may be better. For $LiCr_{0.5}Mn_{1.5}O_4$ and $LiSr_{0.5}Mn_{1.5}O_4$, the charge density among Sr, Cr, Mn and O atoms decrease, so the partial charge from Sr, Cr, Mn and O atoms is centralized near Li-site atoms, which is beneficial to the transition of lithium. Therefore the electronic conductivity of $LiCr_{0.5}Mn_{1.5}O_4$ and $LiSr_{0.5}Mn_{1.5}O_4$ is improved. For $LiAl_{0.5}Mn_{1.5}O_4$ and $LiCo_{0.5}Mn_{1.5}O_4$, the charge overlap around Mn, Ni and O atoms significantly increased, the charge of Co, Al, Mn and O atoms formed Co-O, Al-O and Mn-O stable bonds, therefore $LiAl_{0.5}Mn_{1.5}O_4$ and $LiCo_{0.5}Mn_{1.5}O_4$ structural stability is dramatically increased and may behave better electronic properties and more capacity.

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