Structural and electronic properties of $LiMnO_2$ doped with transition metals: A first-principles study

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Abstract. A spin density functional calculations of structural and electronic properties of $LiMnO_2$ doped with several transition metals (Sc, V and Tc) are reported. The physical properties of $LiMnO_2$ material are sensitive with the transition-metal dopants. Transition metal dopants enhance the lattice parameters and volumes, thus increasing the Li diffusion channel. The computations underscore that d orbitals of transition metals are located around the Fermi level. V doping in $LiMnO_2$ demonstrates the enhancement in the electronic conductivity due to the volumetric expansion. Finally, these results deliver a valuable information for the transition-metal doped $LiMnO_2$ cathode materials to improve the performance of lithium batteries.

1. Introduction

The environmental contamination and gradual exhaustion of oil resources have recently grown much attention. To overcome these concerns, the area of energy storage system has been substantially developed. The lithium-ion batteries have been utilized extensively in various application such as mobile phones, computers, cameras, electrical automobiles and hybrid electrical automobiles. The focus of this paper is on $LiMnO_2$ compound which constitutes the active component of the cathode. For the utilization of lithium-ion batteries, the performance of the cathode materials needs to be improved. To do so, several schemes have been implemented to solve this problem such as mixing carbon with the particles, formation of submicron or nanometer dimension and transition-metal doping to improve the electrochemical properties. [1-3] The $LiMnO_2$ has been a pronounced systematic consideration in the last years. [4, 5]

Here, this theoretical investigation reports the electronic properties of $LiMnO_2$ doped with Technitium (Tc), Vanadium (V) and Scandium (Sc) because there is no report of these transition metals doping in this cathode. Here, we utilize the generalized gradient approximation (GGA) with the Perdew, Burke, and Ernzerhof (PBE) [6] exchange-correlation functional as executed in CASTEP [7, 8] to convey the atomistic information. When doping with transition metals, the Broyden-Fletcher-Goldfarb-Shanno minimization algorithm [9-12] is used for the optimization. These computations can provide a better understanding and support the experimental works.

2. Theory

The spin polarized generalized gradient approximation (GGA) with PBE exchange correlation functional is used to determine the electronic structures in all systems of $LiMnO_2$. The magnetic states in all systems are antiferromagnetic (AFM). For the doping presentation, one of Mn atoms in the unit

cell is replaced by Tc, V and Sc. The structural optimization is computationally achieved by the Broyden-Fletcher-Goldfarb-Shanno minimization algorithm. The criterion of the algorithm is given as energy of 2.0×10^{-6} eV/atom, force of 1.0×10^{-5} eV/Å, stress of 0.05 GPa and displacement of 0.001 Å. For all calculations, the plane-wave basis set with a cut-off energy of 520 eV is employed. The total energy within 2.0×10^{-6} eV/atom is calculated for the convergence. A $4 \times 4 \times 4$ Monkhorst-Pack mesh is described for Brillouin zone integration.

3. Result

Here, $LiMnO_2$ structure is Pmmn. The structural parameters of $LiMnO_2$ doped with Scandium, Vanadium and Technetium atom are itemized in table 1. The calculations demonstrate that all transition metals doping in $LiMnO_2$ increase the lattice constants and their volumes. The changes of lattice constants and volumes are reported when doping with the transition metals due to the different ionic radius between Mn and dopants. These calculations highlight that the escalation of volume by transition-metal impurity can improve channels of lithium-ion diffusion.

Table 1. The computed lattice parameters, volumes of $LiMnO_2$ with Mn replacement by Sc, V and Tc.

	$LiMnO_2$	$Li(Mn, Sc)O_2$	$Li(Mn, V)O_2$	$Li(Mn, Tc)O_2$
a (Å)	2.926894	3.164833	3.124775	3.107963
b (Å)	9.268949	8.263267	8.307039	8.206066
c (Å)	5.832507	6.276250	6.456483	6.247384
Volume ($Å^3$)	155.089668	163.857134	167.264277	159.334211

The formation energies of $LiMnO_2$ doped with Scandium, Vanadium and Technetium atom are computed from this relation,

$$E^f(TM) = E_{dope}(TM) - E_{pure} - (\mu_{TM} - \mu_S) \quad (1)$$

Here, $E^f(TM)$ is the formation energy of the transition-metal doped cathodes. $E_{dope}(TM)$ is the total energy of the cathode with a transition-metal dopant (TM) and E_{pure} is the total energy of the pure cathode. μ_{TM} is the chemical potential of transition metals and μ_S (S=Mn or Co) is the chemical potential of Mn or Co atom in these cathodes. The chemical potentials (μ) are computed as the free atom energy. For the calculations, the free atom is placed in the center of a very huge empty cubic box with lattice constant of 30 atomic units. Table 2 lists the formation energies of $LiMnO_2$ doped with Sc, Tc and V atom. The calculations demonstrate that all transition metals doping in $LiMnO_2$ can be experimentally synthesized at the regular conditions. The highest value of the formation energies is observed in V doping in this cathode material.

Table 2. The calculated formation energies of $LiMnO_2$ with Mn substitution by Sc, Tc and V atom.

Material	Formation energy (eV)
$LiMnO_2$	-
$Li(Mn, Sc)O_2$	-5.6956
$Li(Mn, Tc)O_2$	-6.6503
$Li(Mn, V)O_2$	-7.8395

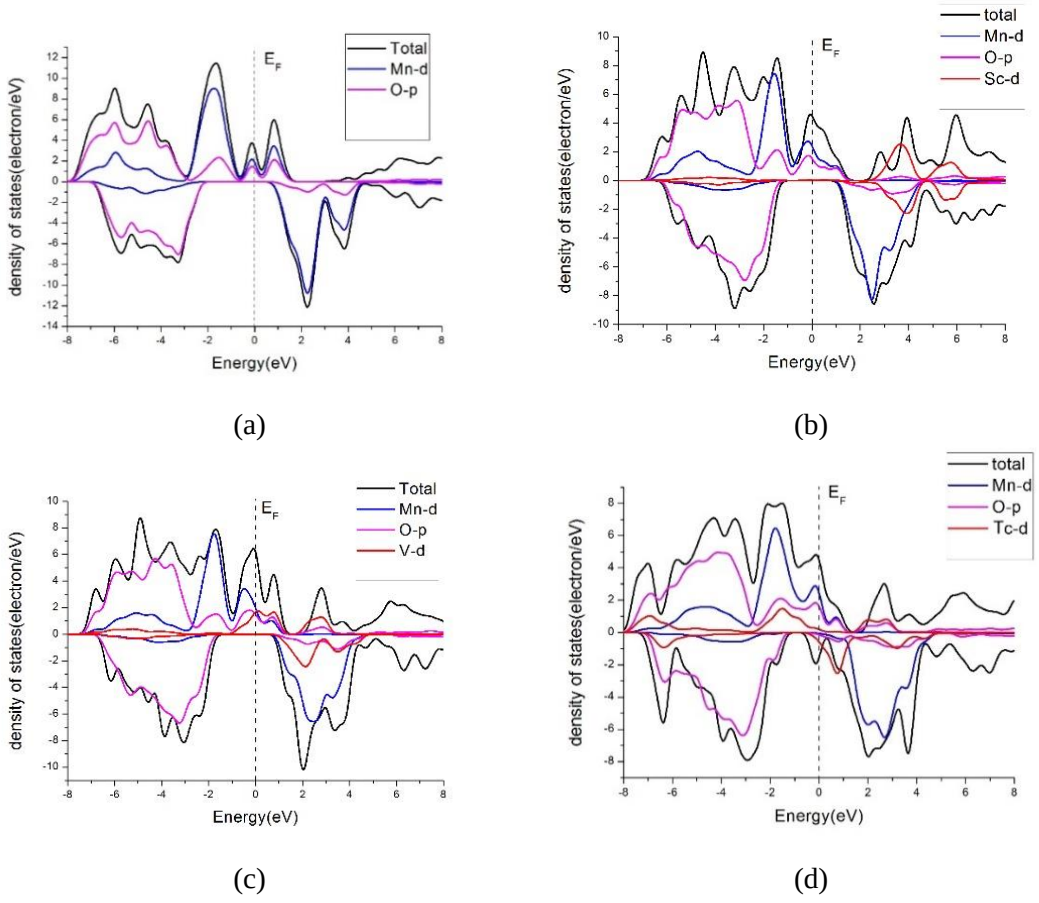

Figure 1. (a) Density of states of $LiMnO_2$ (b) $LiMnO_2$ doped with Sc (c) $LiMnO_2$ doped with V (d) $LiMnO_2$ doped with Tc.

Finally, figure 1 demonstrates the density of state of all studied materials. The dopants with d orbitals are mainly introduced around the Fermi level. Besides, all doped $LiMnO_2$ compounds are characterized as metal.

4. Summary and conclusion

In this work, the result shows that $LiMnO_2$ doped with Vanadium atom is the best material to synthesis a new battery because of the highest volume. This means Lithium ions can move easily in this cathode.

All transition metals doping in $LiMnO_2$ can be experimentally synthesized at the normal conditions. The highest value of the formation energies is observed in $Li(Mn, V)O_2$. All doped $LiMnO_2$ compounds are considered as metal. Finally, these computational results mainly provide the suggestion of transition-metal doped $LiMnO_2$ cathode for the novel lithium batteries.

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