



# Electrical structure, magnetic polaron and lithium ion dynamics in four mixed-metal oxide multiple-phase electrode cathode material for Li ion batteries from density functional theory study



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## ABSTRACT

This study presents results derived from first-principles calculations, at density functional level, and molecular dynamics simulations. Calculations of perfect  $\text{LiMO}_2$  ( $M = \text{Mn, Co and Ni}$ ) and their mixed-metal oxide ( $\text{LiMn}_{1/3}\text{Co}_{1/3}\text{Ni}_{1/3}\text{O}_2$ ) were performed by PBE with the GGA method in the VASP Package. Atomistic simulation calculation was used for searching the electrical structure, magnetic polaron and lithium ion dynamics properties. The results were suitable for the measured valence-band structure, also with the magnetic and electrical properties of the Li-transition metal oxide. The band gap is determined by the charge-transfer and the main contributions from the magnetic polaron produced spin electron-hole pairs that were smaller than that of the states of the M3d and O2p orbitals. When anisotropic O2p-M3d orbital hybridization occurs, a highly-delocalized characteristic was shown in the M3d hole state owing to the states mixing. The extended M4p orbital improved the exchange interaction between Mn3d and Op which led to an asymmetric charge distribution in the M–O bonds. The delocalized characteristic of Mn3d holes is a vital part of the mechanism of spin-dependent ligand ( $\text{O}^{2-}$ ) hybridization. Due to the decrease in inter-molecular attractive forces, a decrease in the order parameter of crystalline was derived from the increase of temperature. Moreover, the transition metal-oxygen and lithium-oxygen radial distribution functions (RDF) at temperatures of 300 and 900 K were compared to each other. The results indicate that the height of the peaks decrease and the system becomes more stable due to increasing temperature. Overall, because of the increase of thermal motion with increasing temperature, lithium ions showed a gradual evolution of mobility.

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## 1. Introduction

Recently, lithium ion batteries have been researched actively due to diverse applications such as storage devices [1–3] and have gradually become one of the most potential energy sources. Detailed investigation of many electrode materials have been carried out to become more compatible with future versions which have superior characteristics of rechargeable batteries [4,5]. Among these electrode materials, Li-transition metal oxide multiple-phase electrode cathode material based on a layered-structure, such as  $\text{LiMO}_2$  (here M represents transition metals, such as Co, Ni, and Mn) and their mixed-metal oxide  $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ , are widely studied as cathode electrode materials for lithium ion batteries [6,7]. Their excellent chemical properties such as high

specific capacity, lower cost, high safety alternatives, and environmentally friendly performance compared to some common cathode materials like  $\text{LiFePO}_4$  make them potential materials [8,9]. The structure can be considered as a mixed-metal oxide layering of  $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$  because of the layered structure of the  $\text{LiMO}_2$  and R-3mH spatial symmetry space group. One of these composite electrodes ( $\text{Li}_2\text{MnO}_3\text{–LiMO}_2$ ) has been proven to be consistent [10,11] and is represented by two voltage plateaus observed at about 3.8 and 4.5–4.6 V at the first charge process. Also, the first charged or discharged voltage of the cell of electrodes ( $\text{LiCoO}_2$ ) was investigated at about 3.0 or 4.35/eV using the target rate [12,13]. However, there are several problems which interrupts their potential to be used for lithium ion battery applications. The methods for synthesizing these materials are very complicated and they have poor thermodynamic stabilities under frequent charge and discharge. Some works demonstrated the electronic structure of  $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$  by using first-principles calculations. By

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considering the magnetic polaron effect and spin-electron coupling, anti-ferromagnetic (AFM) electron spin polarization became a crucial part in transition metal oxides [14,15]. Layered lithium transition metal oxides improve  $\text{Li}^+$  ion mobility thoroughly, but their low electron conductivity and poor lithium ion diffusion coefficient are still needed to be enhanced. Meanwhile, there were several researches about substituting Mn with alternative transition metals to  $\text{LiMnO}_2$ . For example,  $\text{LiNiO}_2$  or  $\text{LiCoO}_2$  has been investigated because of several disadvantages of  $\text{LiMnO}_2$  and as a potential replacement for  $\text{LiMnO}_2$ . The double electron exchange interaction of asymmetric electron hopping of magnetic polarized of M-deg (M = Mn, Co and Ni) states that produces a polar charge distribution [16,17] drives the transition metal atom induced magnetism dipole. Based on the strong spin-orbit coupling, the spin-dependent electrons of atomic orbitals ( $3d^m4s^n$ ) with oxygen (2p) orbitals hybridization proves the microscopic mechanism of magnetically induced ferroelectricity in mixed-metal oxides. It shows similar behavior compared to the procedure in the charge transfer model and the electron density via the p-d hybridization.

Because  $\text{LiMO}_2$  (M = Mn, Co and Ni) and their mixed-metal oxide ( $\text{LiMn}_{1/3}\text{Co}_{1/3}\text{Ni}_{1/3}\text{O}_2$ ) have remarkable chemical features of lithium-metal oxides such as the high specific capacity, lower cost, high safety alternatives, and environmentally friendly characteristics, it can be expected to be commercially widely used as the cathode electrode materials for Li ion batteries. Thus, the understanding of their electrical structure, magnetic polaron and lithium ion dynamics in four mixed-metal oxide multiple-phase electrode cathode material for Li ion batteries from density functional theory study are gradually required. In addition, the benefits of the first-principles calculation by using a molecular dynamics (MD) simulation to study the thermal stability of these materials can be obtained.

In this work, for perfect  $\text{LiMO}_2$  (M = Mn, Co and Ni) and their mixed-metal oxide ( $\text{LiMn}_{1/3}\text{Co}_{1/3}\text{Ni}_{1/3}\text{O}_2$ ), the electronic structure, magnetic structure, and physical properties are investigated through the calculation and simulation of the lithium ion dynamic properties at the atomic level from first-principles density functional theory (DFT) calculation with the combination of *ab initio* molecular dynamics (AIMD) simulation [18,19]. As complex structure, thermal stability, and lithium ion transport mobility properties of these systems at different temperatures have been changed and evolved rapidly, thus they are taken into consideration in the first-principles density functional theory (DFT) simulation. The effect of structural disorder of Li-transition metal oxides structural and transport properties are demonstrated [20,21] by MD simulation with the bond valence force fields [22].

## 2. Methodology

The calculations were performed using the Perdew Burke Ernzerh (PBE) method and Generalized Gradient Approximation (GGA + U) [23] exchange-correlation function as implemented in the (VASP) package [24]. U was set to 3.81 eV, 4.30 eV, and 4.93 eV, corresponding to Mn3d, Co3d, and Ni3d, respectively. The valence configurations were fixed to ( $3d^m4s^n$ ) and  $2s^22p^4$  for the valence shell atomic orbitals of M (Mn, Co and Ni) and O, respectively. All calculations were carried out on a super cell of ( $2 \times 2 \times 1$ ) that contains 12 formula units. Band structure and electronic structure calculations were performed by spin-polarization using formal spin as the initial [25]. The structure was optimized by both lattice parameters, and the position of the atoms full relaxation until forces converge was assumed to be  $1.0 \times 10^{-6}$  eV/cell. The cut-off energy was set to 380/eV, the k-point was set for meshes of a ( $5 \times 5 \times 5$ ) scheme for the density of states (DOS) calculations, and the electronic structure and magnetic properties of perfect

$\text{LiMO}_2$  (M = Mn, Co and Ni) and their mixed-metal oxide ( $\text{LiMn}_{1/3}\text{Co}_{1/3}\text{Ni}_{1/3}\text{O}_2$ ) were discussed. Also, Molecular Dynamics (MD) simulations were used to study the transformation process of crystal ordering and the evolution of the micro-structure as implemented in the VASP code. All work was performed in an NPT ensemble with a ( $2 \times 2 \times 1$ ) super-cell, which lasted for 100 ps with a time step of 0.2 ps, and the temperature was controlled using the Nose-Berendsen method [26].

## 3. Results and discussion

### 3.1. Electronic structure analysis

According to the Crystal Field Theory (CFT) [27], the continuous state of the electronic level set level split composition [28] such as  $t_{2g}$  and  $e_g$  of M3d (Mn, Co and Ni) orbitals, generates energy level fission. The crystal field altered the electronic structure of the transition metal atoms which influenced the electronic properties. The splitting of energy levels was the most influential factor in the crystal field on the density of states of metal [29]. A liquid crystal model was constructed using a ( $2 \times 2 \times 1$ ) super-cell which contains 48 atoms to verify the phenomenon. And the electronic properties were studied in perfect  $\text{LiMO}_2$  (M = Mn, Co and Ni) and their mixed-metal oxide ( $\text{LiMn}_{1/3}\text{Co}_{1/3}\text{Ni}_{1/3}\text{O}_2$ ) bulk. Fig. 1 shows the structural models, while Fig. 2 shows the total DOS and partial DOS of the four perfect systems proving that the band of perfect structure was located near the Fermi level (EF). By analyzing the band structure of crystals, the existence of a partial band gap was proven. The band gap is defined as an energy difference between the top of the valence band and the bottom of the conduction band which is similar to the HOMO/LUMO gap in chemistry. Therefore, some properties such as electrical conductivity of crystalline solid is determined by the band gap. Due to the overlap of valence bands and conduction bands, the band gap is assigned as an indirect band gap of 1.01/eV in  $\text{LiMn}_{1/3}\text{Co}_{1/3}\text{Ni}_{1/3}\text{O}_2$  (shown in Fig. 2d). Compared with the other three compounds, we found that the high symmetry points from G and A shifted to between the F and G points, as shown by the arrow in Fig. 1. The energy ranged from -6 to 6 eV. The bands located at the bottom of the conduction band correspond to the occupied M3d- $t_{2g}$  (M = Mn, Co and Ni) and O2p bands [30]. And those at the top of the valence band belong to the unoccupied M3d- $e_g$  bands.  $\text{LiMO}_2$  are identical for both projections of DOS, in which the transition metal ions are surrounded by octahedron anion clusters  $[\text{MO}_6]^-$  with the valence shell of O2p bands. The  $\text{Mn}^{2+}$  band state transits to the neighboring O atom due to the donation of its two electrons [31] which shows a negative divalent state. The calculated band gap of  $\text{LiMnO}_2$  showed a high value of 2.21/eV which is higher than other materials and lower than the experimental value of 3.45/eV. This was due to the electronic structures calculated without considering some correlated effects. Fig. 2 shows the total DOS and partial DOS of the perfect systems.

O2p and M3d orbitals usually form a valence band, but Mn4s, Co4s and Ni4s orbitals form a conduction band. The electronic band structure shows both total and partial DOS of the systems indicating that the main contributions are from the transition metal atoms M3d (M = Mn, Co and Ni) and O2p atomic orbitals. The band gap of  $\text{LiMn}_{1/3}\text{Co}_{1/3}\text{Ni}_{1/3}\text{O}_2$  (shown in Fig. 1d) has the smallest value (1.01/eV) compared to other materials and this was because the bands are mostly filled near the Fermi level band. The O2p band is filled with the valence electron that is mainly built by electronic states M4s, localized at the metal atoms. The role as an indirect semiconductor with an indirect band gap to the conduction band at the same symmetry points [32] without  $\text{LiMn}_{1/3}\text{Co}_{1/3}\text{Ni}_{1/3}\text{O}_2$  was proven by the results of the electronic structure.

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