Intrinsic Defects in LiMn$_2$O$_4$: First-Principles Calculations
Xu Li, Jianchuan Wang,* Shiwei Zhang, Lixian Sun, Weibin Zhang, Feng Dang, Hans J. Seifert, and Yong Du

ABSTRACT: Spinel LiMn$_2$O$_4$ has attracted wide attention due to its advantages of a high-voltage plateau, good capacity, environmental friendliness, and low cost. Due to different experimental synthesis methods and conditions, there are many intrinsic point defects in LiMn$_2$O$_4$. By means of first-principles calculations based on a reasonable magnetic configuration, we studied the formation energies, local structures, and charge compensation mechanism of intrinsic point defects in LiMn$_2$O$_4$. The formation energies of defects under the assumed O-rich equilibrium conditions were examined. It was found that O, Li, and Mn vacancies, Mn and Li antisites, and Li interstitial could appear in the lattice at some equilibrium conditions, but Mn interstitial is hard to form. The charge was compensated mainly by adjusting the oxidation state of Mn around the defect, except for the defects at the 8a Wyckoff site. The binding energies between point defects were calculated to shed light on the clustering of point defects. Furthermore, the diffusion of Li ions around the defects was discussed. Cation antisites led to a decrease of the Li diffusion barrier but O vacancy caused an increase of the barrier. This study provides theoretical support for understanding point defects in spinel LiMn$_2$O$_4$.

1. INTRODUCTION
Spinel LiMn$_2$O$_4$ is a typical manganese-based cathode material.1−3 Thackeray et al. first proposed it as a cathode material for lithium-ion batteries.4 In terms of battery performance, spinel LiMn$_2$O$_4$ has a high-voltage plateau (>4 V), good theoretical capacity density (148 mAh/g), and great thermal safety. More importantly, Mn has obvious advantages of low cost and nontoxicity. Consequently, LiMn$_2$O$_4$ is considered to be a substitute for layered LiCoO$_2$ on the electrodes of lithium-ion batteries.5−8

The cubic spinel structure of LiMn$_2$O$_4$ belongs to the Fd$ar{3}$m space group. Oxygen atoms, which are at 32e sites, are arranged in a cubic close-packed arrangement, lithium ions are located at 8a tetrahedral sites, and manganese ions occupy half of the octahedral positions, which are 16d sites. The other half of the octahedral void is 16c sites, which reside halfway between neighboring tetrahedral sites and serve as a channel for the migration of Li.9−11 The average oxidation state of Mn in LiMn$_2$O$_4$ is +3.5, which is caused by a mixture of Mn$^{3+}$ and Mn$^{4+}$ in equal proportion, and its charge−discharge activity is the contribution of Mn$^{3+}$/Mn$^{4+}$ redox.12,13 The existence of the orbital-degeneracy Mn$^{3+}$ ions will cause the Jahn−Teller (JT) effect during charging and discharging,14−16 leading to unique properties such as structural distortions and phase transitions. On this account, the spinel LiMn$_2$O$_4$ transforms into an orthogonal phase when the temperature drops below 280 K,17,18 and its magnetic ground state is antiferromagnetic (AFM).19−21

It is difficult to obtain the exact stoichiometric LiMn$_2$O$_4$ because of various synthetic methods and the synthetic environment. There would be various types of intrinsic point defects within the material, such as vacancies, interstitials, and metal antisite defects. Using powder X-ray diffraction and thermogravimetry analysis (TGA), Tarascon et al. found that some Mn ions are located in the tetrahedral sites of the spinel and a significant number of oxygenes are lost,22 suggesting that Mn antisites and O vacancies appear in LiMn$_2$O$_4$. Paulsen et al. also found that a certain amount of metal ion antisite defects, i.e., the antisites of Li and Mn, exist in Li$_2$MnO$_4$ at a wide range of temperatures.23 Oh’s group first applied differential pulse polaroigraphy to analyze the dissolved Mn$^{3+}$ ions, which are generated by the disproportionation reaction 2Mn$^{3+} \rightarrow$ Mn$^{4+}$ + Mn$^{2+}$ in the electrolyte.24 They found that Mn dissolution was the primary reason for the capacity loss. With the dissolution of Mn, Mn vacancies are present in the 16d octahedral sites.

Following the formation of defects in the lattice, the spatial geometric environment and chemical environment of the surrounding atoms will change. As a result, the structure and...
charge distribution of LiMn$_2$O$_4$ will change, which further affects the structure stability, charge voltage, and diffusion of ions in the material. Sugiyama et al. studied the effect of O vacancies (i.e., O deficiency) on the phase transition from cubic to the tetragonal phase of LiMn$_2$O$_4$ using differential scanning calorimetry (DSC), magnetic susceptibility, $^7$Li nuclear magnetic resonance, and electronic resistivity. Xia et al. studied the effects of Li defects and O vacancies on the structure and electrochemical properties of LiMn$_2$O$_4$. They found that the capacity loss rate of anoxic materials is much faster, which is related to the phase transition in the cyclic process, in comparison with intact LiMn$_2$O$_4$. Besides experimental studies on defect-related properties in cathode materials, theoretic calculations, especially first-principles methods based on density functional theory (DFT), have been demonstrated to be a powerful tool for addressing defects in solid. Some researchers have studied point defects in LiMn$_2$O$_4$ through computational methods. As early as the 1990s, Islam’s group has studied Li- and Mn-related interstitials and vacancies in LiMn$_2$O$_4$ using interatomic potential models. Koyama et al. studied O vacancy, Li and Mn interstitials, Mn antisite, and some defect complexes in LiMn$_2$O$_4$ using the first-principles method. They revealed that metal interstitials have lower formation energy compared with that of O vacancy. The excess Li are prone to occupy the 16$d$ site other than the 16$c$ site. Hoang has investigated cation point defects in LiMn$_2$O$_4$ through computational methods. As early as the 1990s, Islam’s group has studied Li- and Mn-related interstitials and vacancies in LiMn$_2$O$_4$ using interatomic potential models. As early as the 1990s, Islam’s group has studied Li- and Mn-related interstitials and vacancies in LiMn$_2$O$_4$ using interatomic potential models. As early as the 1990s, Islam’s group has studied Li- and Mn-related interstitials and vacancies in LiMn$_2$O$_4$ using interatomic potential models.

As mentioned above, point defects are common in LiMn$_2$O$_4$ and may affect the electrochemical performance of LiMn$_2$O$_4$. Although there are some studies on point defects in LiMn$_2$O$_4$, by experimental or/and theoretic calculation methods in the literature, point defects are still not understood. For example, how is the distribution of point defects? What are the effects of defects on the charge distribution and charge compensation in the delithiation process? And how is the migration of Li when defects exist in the lattice? On the other hand, previous theoretic calculations have not carefully dealt with the magnetism of Mn in the lattice, except for the work of Xiao et al. The spinel LiMn$_2$O$_4$ may have various magnetic configurations. Ouyang et al. considered the magnetic structures of LiMn$_2$O$_4$ with one ferromagnetic (FM) and two AFM arrangements of Mn ions. According to DFT calculations, they found that the AFM ordering of Mn chains along the [110] direction was more stable than other magnetic structures. Recently, Liu et al. conducted extensive work on LiMn$_2$O$_4$ with different structures and magnetic configurations to find its ground state. They used eight different AFM and two FM orders, including Ouyang’s structures, and found that the most stable structure is a highly symmetrical configuration with alternating AFM (|↑↑↓↓|) layer and FM layer along the [001] direction. Koyama et al. and Huang just assumed a simple high-spin FM configuration of Mn to investigate point defects in LiMn$_2$O$_4$. Different magnetic configurations will affect the ground-state structure of LiMn$_2$O$_4$ and further affect the properties of defects in the system. Therefore, to achieve accurate defect properties in LiMn$_2$O$_4$ computationally, it is better to investigate it based on a reasonable magnetic structure.

In this work, we use the first-principles calculation method based on DFT to comprehensively explore defect-related properties in spinel LiMn$_2$O$_4$. The formation energies of various isolated intrinsic point defects and the binding energies between point defects are calculated based on the lowest energy magnetic configuration proposed by Liu et al. Furthermore, Bader charges are calculated to shed light on charge compensation associated with the creation of defects. Finally, we discuss the effect of defects on the diffusion of lithium ions. It is noteworthy that point defects in semiconductors and insulators may occur in charged states, and the thermodynamics of charged defects in LiMn$_2$O$_4$ have already been investigated by Hoang based on a ferromagnetic spin configuration. Since the magnetic configuration used by Hoang is different from that of our work, we speculate that some conclusions on thermodynamics of charged point defects drawn from calculations based on the present magnetic

Figure 1. (a) Crystal and magnetic configurations of spinel-type LiMn$_2$O$_4$. Green spheres are Li, red spheres are O, yellow and purple spheres are Mn$^{3+}$ and Mn$^{4+}$, respectively. The blue arrows indicate the direction of the magnetic moment of Mn. The Mn ions are with AFM configuration in the Mn$^{3+}$ layer and with FM configuration in the Mn$^{4+}$ layer. (b) The structure of Mn$^{3+}$-O$_6$ and Mn$^{4+}$-O$_6$ octahedrons and two paths for Li migration that consist of different oxidation states of Mn ions. (c) Schematic representation of electron distribution in the 3d orbital of Mn ions.
configuration may be inconsistent with the results of Hoang. Therefore, we will study charged defects in LiMn$_2$O$_4$ in future work, but only neutral defects are considered in the present work.

2. COMPUTATIONAL METHODOLOGY

DFT calculations were performed by the projector augmented wave (PAW) potential method, as implemented in the Vienna ab initio simulation package (VASP). The interactions between electrons are treated by the generalized gradient approximation of Perdew and Wang with the Hubbard parameter correction (GGA+U). The $U$ values for the d-orbitals of Mn were set to 3.9 eV based on previous reports. The electronic configurations of 1s$^2$2s$^1$, 3p$^6$3d$^5$4s$^2$, and 2s$^2$2p$^6$ are employed as valence electrons for Li, Mn, and O, respectively, and all the other electrons are treated as core electrons. The conventional cubic spinel unit cell with the AFM magnetic configuration reported by Liu et al. was taken as the initial structure. The energy cutoff for the plane wave was set as 500 eV. The Brillouin zone was sampled by 2 $\times$ 2 $\times$ 2 special k-points using the Monkhorst–Pack scheme for geometry optimization, and 4 $\times$ 4 $\times$ 4 for the calculations of total energies and electronic structures. Geometry relaxation was complete when the residual forces acting on every atom were less than 0.02 eV Å$^{-1}$. Point defects were considered to have a low concentration in the bulk, so the cell volume and shape were fixed to the optimized crystal of bulk during the relaxation of defective lattice, and only atoms’ coordinates were fully relaxed.

The climbing image nudged elastic band (CINEB) method was used to investigate the minimum energy pathways of ion hopping from one lattice site to the adjacent positions. We insert five images during the CINEB calculation and the residual forces acting on every atom were less than 0.02 eV Å$^{-1}$. To describe the electron charge transfer between ions in the material, this paper adopts the Bader charge analysis method based on the charge density calculation.

3. RESULTS AND DISCUSSION

3.1. Lattice and Magnetic Structure. The ground-state structure of LiMn$_2$O$_4$ is a highly symmetrical configuration with alternating AFM (↑↑↓↓) layer and FM layer along the [001] direction, as predicted by Liu et al. Figure 1a shows the ground structure of LiMn$_2$O$_4$. After structural optimization, the cubic cell transforms into a tetragonally distorted cell with a lattice elongation of 7% along the c direction. The calculated lattice parameters ($a = b = 8.20$ Å and $c = 8.74$ Å) are consistent with the experimental data ($a = b = 8.11$ Å and $c = 8.65$ Å) and previous calculated results ($a = b = 8.20$ Å and $c = 8.76$ Å; $a = b = 8.22$ Å and $c = 8.76$ Å). The spinel LiMn$_2$O$_4$ is thus an orthorhombic lattice instead of a cubic lattice, but Mn$^{4+}$($t_2g$) and Mn$^{4+}$ to be 3.9 $\mu_B$ and 3.2 $\mu_B$, respectively. We further find that the Bader charge around Li is +0.89 e, and the Bader charges for yellow and purple Mn are +1.71 e and +1.84 e, respectively. For oxygen, due to different Mn ions around it, we denote O on the Mn$^{3+}$ layer as OMn$^{3+}$. Similarly, the O on the Mn$^{4+}$ layer is denoted as OMn$^{4+}$. We find that the Bader charges of the two O are almost equal (the Bader charges of OMn$^{3+}$ and OMn$^{4+}$ are −1.09 e and −1.13 e, respectively).

The JT effect originates from the orbital degeneration of transition metal ions. In spinel LiMn$_2$O$_4$, Mn$^{3+}$(t$_2g^1$, $e_g^2$) is a JT ion, which will cause distortion of the surrounding tetragonal lattice, but Mn$^{4+}$(t$_2g^3$, $e_g^1$) is not a JT ion. We can clearly observe in Figure 2 that the $e_g$ orbital of Mn$^{3+}$ atom in the spin-up channel splits into a d$_{xz}$ orbital and d$_{yz}$ orbital, opening a gap of about 0.5 eV between them. The d$_{xz}$ orbital is filled while the d$_{yz}$ orbital is unoccupied. This leads to a larger magnetic moment for Mn$^{3+}$ compared with that of Mn$^{4+}$. By comparing the projected DOS of Mn and O, it is found that the Mn-d and O-p orbitals are hybridized to form covalent bonds between O and Mn. The profiles of p$_x$ and p$_y$ of O in both Mn$^{3+}$ and Mn$^{4+}$ layers are almost identical, and thus, the bond status of trivalent and quadrivalent Mn—O are basically the same in the (001) plane. An additional covalent
bond is formed just below the Fermi level by Mn$^{3+}$-$d_{z^2}$ and O-$p_{z}$, which makes the structure more stable.

### 3.2. Isolated Point Defects

We then focus on single or isolated point defects in LiMn$_2$O$_4$. The following intrinsic defects are considered in this work: Li vacancy (V$_{Li}$), Mn vacancy (V$_{Mn}$), O vacancy (V$_{O}$), Li interstitial (I$_{Li}$), Mn interstitial (I$_{Mn}$), Li antisite (L$_{Li}$), and Mn antisite (M$_{Li}$).

The formation energy of a point defect $E_f$ is defined as

$$ E_f = E_{\text{defect}} - E_{\text{bulk}} - \sum_i n_i \mu_i $$

where $E_{\text{defect}}$ and $E_{\text{bulk}}$ are the total energies of the unit cell with and without the defect, respectively. The generation of defects involves adding atoms into or removing atoms from the unit cell, $\mu_i$ is the atomic chemical potential of species $i$, and $n_i$ is the number of atoms $i$ added to (positive) or removed from (negative) the lattice to produce the defect. The atomic chemical potential can also be written as $\mu_i = \mu^0_i + \Delta \mu_i$, where $\mu^0_i$ is the chemical potential of element $i$ in its standard state.

The standard states for Li and O are bcc Li and gaseous O$_2$, respectively. As for Mn, we choose the structure of I$_{Mn}$, Li antisite (L$_{Li}$), and Mn antisite (M$_{Li}$). The atomic chemical potentials are constrained by thermodynamic equilibrium conditions with various phases. 

In Table S1 and S2, the formation energy of VO under the same condition a, the environment that LiMn$_2$O$_4$, O$_2$, and LiMn$_2$O$_4$ phases that coexist with O$_2$ and LiMn$_2$O$_4$, respectively. The negative values of formation energies indicate that LiMn$_2$O$_4$ would spontaneously form defects, and therefore, the assumption of local equilibrium under those conditions indicates instability.

### Table 1. Calculated Formation Energies $E_f$ of Intrinsic Defects in LiMn$_2$O$_4$ under Some O-Rich Equilibrium Conditions

| defects | a | b | c | d | e |
|---------|---|---|---|---|---|
| V$_{Li}$ | 1.22 | 0.46 | 0.38 | −0.09 | −0.22 |
| V$_{Mn}$ | 0.22 | 0.60 | 0.64 | 0.88 | 0.94 |
| V$_{O}$ | −0.13 | 0.25 | 0.29 | 0.53 | 0.59 |
| V$_{Li}$ | 2.28 | 2.28 | 2.28 | 2.28 | 2.28 |
| V$_{O}$ | 2.30 | 2.30 | 2.30 | 2.30 | 2.30 |
| I$_{Li}$ | −1.43 | −0.29 | −0.17 | 0.54 | 0.73 |
| I$_{Mn}$ | −1.22 | −0.08 | 0.04 | 0.75 | 0.94 |
| M$_{Li}$ | 2.84 | 1.70 | 1.58 | 0.87 | 0.68 |
| L$_{Li}$ | 1.28 | 2.04 | 2.12 | 2.59 | 2.72 |
| L$_{Mn}$ | 1.00 | 1.76 | 1.84 | 2.31 | 2.44 |
| M$_{Li}$ | 4.14 | 3.76 | 3.72 | 3.48 | 3.42 |
| M$_{Mn}$ | 3.98 | 3.60 | 3.56 | 3.32 | 3.26 |

As we choose the O-rich condition, an environment that is more close to the experimental operation condition, to determine the chemical potentials for each of the elements, the formation energy of O vacancies is irrelevant to the equilibrium conditions. As shown in Table 2, the formation energies of V$_{Li}$ and V$_{O}$ are almost equal (2.28 and 2.30 eV), which are higher than that of other metal cation vacancies. Koyama et al. studied oxygen vacancy and metal interstitials in LiMn$_2$O$_4$ through the local spin density approximation (LSDA) and ultrasoft pseudopotentials based on FM configuration. They reported that V$_O$ has a formation energy of 2.17 eV when the chemical potential of oxygen is determined by the equilibrium between Mn$_2$O$_3$ and MnO$_2$. We also calculated the formation energy of V$_O$ under the same conditions and found the value to be 1.81 eV. The difference may originate from the fact that we use different calculation methods and magnetic configurations of LiMn$_2$O$_4$ compared with Koyama’s work.

The formation energy of V$_{Li}$ is in the range of −0.22 to 1.22 eV, depending on the equilibrium conditions. It is found that the formation energy of V$_{Li}$ is negative (−0.09 eV at condition d and −0.22 eV at condition c). A negative formation energy indicates that the system would spontaneously form defects, and therefore, the assumption of local equilibrium under those conditions indicates instability. Strictly speaking, the atomic chemical potentials are limited in a range that avoids the formation of competitive phases containing Li, O, and Mn. As for Mn vacancies, the formation energy of V$_{Mn}$ is relatively low. The formation of V$_{Mn}^{IV}$ is lower by 0.35 eV than that of V$_{Mn}^{III}$, thus, Mn vacancies are more likely to form in the Mn$^{3+}$ layer. Note that the formation energy of V$_{Mn}^{II}$ is negative (−0.13 eV) at condition a, the environment that LiMn$_2$O$_4$, O$_2$, and LiMnO$_2$ are in equilibrium with each other. Again, this
Spinels are Li1-

generally appear in LiMn2O4 and make the spinel more stable. TGA measurement to test the electronic concentration in the synthesis process. Tarascon et al. used the quenching from 920°C, and the time-of-flight (TOF) neutron powder diffraction measurement shows that 3.5% O vacancies indicate that the material would be unstable in the presence of O2 and Li2MnO4.

The formation energies for vacancies are not very much high, and thus, they would appear in LiMn2O4 at a detectable concentration in the synthesis process. Tarascon et al. used the TGA measurement to test the effect of annealing temperatures on the oxygen content. They found that at 1000°C, LiMn2O4 even has a reversible oxygen loss of 5% and forms LiMnO3.25 Kanno et al. synthesized tetragonal spinel LiMnO4 by quenching from 920°C, and the time-of-flight (TOF) neutron powder diffraction measurement shows that 3.5% O vacancies are generated and no significant stoichiometric composition deviation was observed at Li 8a and Mn 16d sites.49

As for cation antisites, namely, Li1+Mn, Li16dMn, and Mn16dLi, we found that the formation energies of Li antisites were lower than that of the Mn antisite under most equilibrium conditions. The formation energy of Mn16dLi is lower than that of Li antisites, just only under condition ε. The calculated formation energies of these cation antisites do not exceed 3.0 eV and thus Mn16dLi and LiMn are likely to appear in LiMn2O4 as revealed by several experiments.22,33,47,50 Paulsen and Dahn have investigated in detail the phase diagram and the stability region of the Li–Mn–O spinel between 400 and 800 °C by various experimental methods.23 They found that the thermodynamic stable phases in the range of 400–800 °C are only the spinel with the composition Li1+nMn2−nO4 (δ < 0.02). If the temperature is above 800°C, the stable Li–Mn–O spinel is Li1+Mn2O4. In other words, LiMn and Mn16dLi antisites generally appear in LiMn2O4 and make the spinel more stable.

Among interstitial defects, i.e., an external Li or Mn atom entering the empty 16c site, the formation energies of Li interstitials are moderate (1.0–2.44 eV for ILi and 1.28–2.72 eV for IMn). Thus, the Li insertion process of LiMn2O4 is feasible and LiMn2O4 has the ability to accommodate extra Li ions. Moreover, the excess Li ions tend to occupy the 16c site of the Mn4+ layer. Yamada et al. found that excess Li would be preferably inserted into the interstitial 16c sites under reducing experimental conditions, forming tetragonal Li16dMn4+O4.51 Gummow et al. also reported that tetragonal lithiumed spinel Li16dMn4+O4 can be synthesized under appropriate reducing conditions.52 As for Mn interstitial, the formation energy of it is so high that it is hard to form at the assumed equilibrium conditions.

The occurrence of defects can result in a local structural change. We show the distance between the defect X with the most stable configuration and its surrounding O atoms in Table 2. The bond length of O–Li in pristine LiMn2O4 is 2.00 Å. We found that VLi had no significant influence on the original Li1−O4 tetrahedron, as the distance of VLi–O is still 2.0 Å. When a Mn substitutes a Li to form Mn16dLi, the length of Mn–O bonds in the Mn4+O4 tetrahedron is 2.04 Å, slightly longer than the bond length of O–Li. VIV shows the original Mn–O4 octahedron to expand. The distance of VIV–Mn4+ is 2.33 Å in the direction of c-axis and 2.21 Å in the a/b plane, while the bond lengths of Mn4+–O are 1.96 and 1.93 Å in defect-free LiMn2O4. The outward relaxation of O is due to the missing of strong covalent bonds between O and Mn. Li16dMn mainly affects the O atoms in the Mn4+O4 plane. The four Mn4+–O bonds in the (001) plane are 1.96–1.97 Å, but the distances of Li16dMn–O are elongated to 2.07 Å. For interstitial defects at the 16c site, the newly formed Mn16dLi octahedron in the Mn4+ layer distorts slightly (two Mn–O bonds with a length of 2.02 Å and four Mn–O bonds with a length of 1.96 Å). In addition to O atoms affected by the 16c Mn, we found that there was a repulsion for the adjacent 8a Li ions due to the Coulomb repulsive interaction between the interstitial Mn and Li cations, which increased the distance of 16c ILi and 8a Li from 1.88 to 2.23 Å. IIIV also affects its neighboring 8a Li, but the Coulomb repulsion effect is less compared with the case of Mn interstitial. The distance between Li (8a) and Li (16c) is 2.13 Å, which is 0.1 Å lower than the distance of Li (8a) and IMn(16c). The occurrence of IIIV causes the Li ion to directly deviate from the oxygen defect, resulting in a distance of VIV– Li to be 2.40 Å. Consequently, the other three Li–O bonds in the formed Li1−O4 unit due to the removal of a O atom are decreased to 1.89 Å.

### 3.3. Electronic Structure Analysis

When defects are generated in the lattice, atom’s charge will rearrange, and charge compensation to the defects occurs. To understand the charge transfer between atoms when a defect exists, the Bader charges are calculated and shown in Table 3. If an exotic Mn is embedded into the 16c octahedral site, the interstitial Mn then bonds with its surrounding six oxygen atoms. The charge transfer in the lattice with an interstitial defect of IMn is mainly realized by changing the oxidation state of the lattice 16d Mn on the opposite side of the new bonding oxygen. That is to say, charge compensation in the case of Mn interstitial is carried out by the six Mn on the 180° Mn–O–Mn chain. By checking the Mn–O6 octahedron in which the Bader charge of Mn decreased by 0.13 e, we found that it shows noticeable distortion. For the embedding of the low valence element of Li in the 16c site to form ILi, the Bader charge of Mn in the direction of b-axis is decreased by 0.15 e. The VO defect at the 32e site causes the reduction of the two Mn4+ bonded with the O atoms.

Table 2. Distance \(d_{X,O}\) between the Center of Defect X and Its Surrounding O Atoms

| defects  | \(d_{V_Li}\) (Å) | \(d_{Mn}\) (Å) | \(d_{V_{IV}}\) (Å) | \(d_{IMn}\) (Å) | \(d_{ILi}\) (Å) | \(d_{V_{III}}\) (Å) | \(d_{V_{IIIV}}\) (Å) |
|----------|-----------------|----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| V_Li     | 2.00(4x)        | 1.96(4x)       | 1.93(2x)        | 2.02(2x)        | 2.14(2x)        | 2.40(2x)        |
| Mn       | 2.04(4x)        | 2.07(4x)       | 2.21(4x)        | 2.33(2x)        | 2.23(2x)        | 2.04(2x)        |

“The values in parentheses indicate the number of X–O “bonds”.

Table 3. Change in Bader Charges \(\Delta Q\) of the Atoms Near Some Isolated Defects

| defects | \(\Delta Q\) (e) | \(V_{Li}\) | \(Mn\) | \(V_{ILi}\) | \(V_{Mn}\) | \(I_{Mn}\) | \(I_{Li}\) | \(V_{O}\) |
|---------|-----------------|----------|-------|------------|------------|----------|----------|-------|
| Mn      | +0.13           | +0.13    | +0.13 | +0.13      | +0.13      | +0.17    | +0.05    | -0.02  |
| O       | +0.14           | -0.05    | +0.05 | +0.17      | -0.13      | +0.15    | +0.07    | -0.02  |
Especially for VLi, the charge of the surrounding O decreased. Charge compensation is carried out by the surrounding Mn3+ also disappears. Mn4+ for charge compensation, as its Bader charge is increased by 0.13 e in the two cases. Thus, V_{Mn} or Li_{Mn} gives rise to an increase in Mn4+ ions and subsequently a decrease in Mn3+ ions. As a result, the JT distortion around the defects is suppressed and the stability of the spinel structure is increased.

The powder neutron-diffraction study, which did not detect any structural phase transition from 4 to 290 K, verified the stability of Li-substituted spinel LiMn$_{1.38}$Li$_{0.62}$O$_4$.

However, if the defect is in the 8a site (V_{Li} and M_{Li}), it affects the Bader charge of the O in the X-O$_4$ tetrahedron directly (again, here, X represents the defect) and has no obvious effects on the charge of the surrounding Mn ions. Especially for V_{Li}, the charge of the surrounding O decreased by 0.14 e.

The charge transfer in the defective lattice is further illustrated by the DOS of the e_g orbital of Mn. As can be seen from Figure 3, in the case of I_{Li} or V_{Li} and V_{O}, the original Mn4+ around defects is reduced to Mn3+, which is manifested by the split of the e_g orbital and the formation of a low-energy d_{z^2} orbital below the Fermi level. For the defects of V_{Mn} and Li_{Mn}, charge compensation is carried out by the surrounding Mn3+ oxidation to Mn4+. These two kinds of defects can reduce the JT distortion around the defects, and the original d_{z^2} orbital also disappears.

**3.4. Defect pairs.** The electrostatic and elastic interactions between point defects may cause the clustering or association of some defects. Thus, in this section, we investigate the interactions between some point defects.

The binding energy $E_b$ between isolated defects A and B is defined as follows:

$$E_b = E_f(AB) - E_f(A) - E_f(B)$$  

(Eg(AB) is the formation energy when defects A and B exist in the nearest-neighbor mode, and $E_f(A)$ and $E_f(B)$ are the formation energies of isolated defects A and B, respectively. The above definition shows that if the binding energy is negative, defects A and B have an attractive interaction; otherwise, defects A and B show a repulsive interaction. We choose the lowest energy configuration of the defect pair to calculate the formation energies of defect pairs and the corresponding binding energies between point defects.

The formation energies of some defect pairs under our considered thermodynamic equilibrium conditions are shown in Table S3. It is found that the formation energies of defect pairs $V_{Li}-V_{Li}$, $V_{Mn}^{III}-V_{Li}$, $Mn_{Li}^{III}-V_{Li}$, $V_{O}^{III}-V_{Li}$, $Li_{Mn}^{III}-V_{Li}$, $Li_{Mn}^{III}-V_{O}^{III}$, $Mn_{Li}^{III}-Mn_{Li}^{III}$, and $Mn_{Li}^{III}-Li_{Mn}^{III}$ are less than 1.0 eV under some equilibrium conditions; thus, these defect pairs may occur in LiMn$_2$O$_4$ with detectable concentrations in the experimental synthesis process. Defect pairs $V_{Li}/V_{O}$ and $V_{Li}/V_{O}$ in some cases have moderate formation energy ($1.0 - 1.6$ eV), indicating the two defect pairs may also appear in the LiMn$_2$O$_4$. However, the pairs of Mn vacancy, O vacancy, and $V_{Li}^{III}-V_{Mn}^{III}$ are hard to form due to their high formation energy, especially for O vacancy. Among these defect pairs, we pay particular attention to the cation exchange defect, i.e., the $Mn_{Li}^{III}-Li_{Mn}^{III}$ defect pair because cation mixing is common in cathode materials. The formation energy of $Mn_{Li}^{III}-Li_{Mn}^{III}$ is 0.81 eV. Therefore, a considerable concentration of Li/Mn exchange defect can be observed in LiMn$_2$O$_4$ samples prepared by various experimental methods. By using the X-ray diffraction technique, Tarascon et al. reported that the amount of Li/Mn mixing can reach 10% in LiMn$_2$O$_4$ powders.

Then, we consider the binding energy between point defects. The binding energy is independent of the atomic chemical potentials and is listed in Table 4.

**Table 4. Binding Energy $E_b$ between Some Isolated Point Defects**

| Defect pair | $V_{Li}-V_{Li}$ | $V_{Mn}^{III}-V_{Li}$ | $V_{O}^{III}-V_{Li}$ | $Li_{Mn}^{III}-V_{Li}$ | $Li_{Mn}^{III}-V_{O}^{III}$ |
|-------------|-----------------|-----------------------|----------------------|-------------------------|---------------------------|
| $E_b$ (eV)  | -0.05           | 0.18                  | -0.60                | 0.07                    | -1.76                     |
| $E_b$ (eV)  | Mn_{Li}^{III}-V_{Li} | Mn_{Mn}^{III}-Mn_{Li}^{III} | V_{Mn}^{III}-V_{O}^{III} | Li_{Mn}^{III}-Li_{Mn}^{III} | Li_{Mn}^{III}-Mn_{Li}^{III} |
| $E_b$ (eV)  | -0.44           | -0.47                 | 1.93                 | 0.85                    | -0.60                     |
| $E_b$ (eV)  | 0.24            |                       |                      |                         |                           |

![Figure 3. DOS of the e_g orbital of Mn around some point defects. The Fermi energy is set at zero.](https://doi.org/10.1021/acsomega.1c01162)
cathode materials, such as in LiFePO$_4$. $^{36}$ $^{36}$ IMn and V$_{Li}$ have an extremely high binding energy ($-1.76$ eV), showing a strong agglomeration phenomenon. So, Li vacancies are prone to be formed near the Mn interstitial. O vacancies tend to be separated, as the binding energy between them is positive ($0.24$ eV). The binding energy of the LiMn antisite is $0.85$ eV, hinting that LiMn would not be clustering. There is a strong repulsion between VMn$_{III}$ and VMn$_{IV}$, as the binding energy between VMn$_{III}$ and VMn$_{IV}$ is a significant positive value ($1.93$ eV). The result is in accordance with the finding that VMn$_{III}$−VMn$_{IV}$ has relatively high formation energy.

The Frenkel defect can be regarded as a kind of defect pair, namely an interstitial in 16c site plus a vacancy near it. Our calculated results show that the Li-Frenkel is unstable. After the structural relaxation for the Li-Frenkel, it was found that the Li atom at the 16c site moves back to its original 8a site, forming the pristine lattice again. This suggests that the generation of Li-Frenkel in LiMn$_2$O$_4$ is impossible. For the Mn-Frenkel defect, i.e., the defect pair IMn$^{IV}$−VMn, the lowest energy configuration is IMn$^{III}$−VMn$^{III}$, with a binding energy of $-2.01$ eV, showing significant attraction between IMn$^{III}$ and VMn$^{III}$. So, the 16c Mn atom tends to approach the lattice 16d site if there is a Mn vacancy around it.

Huang et al. investigated the local structure of Li and O in oxygen-deficient tetragonal LiMn$_2$O$_4$ with a spherical aberration-corrected scanning transmission electron microscope (STEM) and first-principles calculations. $^{36}$ They revealed that Li ions move away from their ideal positions due to the presence of oxygen vacancies, resulting in defect complexes formed by Li and O vacancies. Their finding is consistent with our result that V$_{Li}^{IV}$ and V$_{Li}$ have a strong attractive interaction. Koyama et al. studied O vacancy and interstitials of Li and Mn in the cubic LiMn$_2$O$_4$ by first-principles calculations based on FM configuration. $^{29}$ They revealed that when a Mn interstitial is placed at the 16c site, the configuration that a Li atom near the interstitial moves into the other neighboring 16c site has low energy compared with the simple interstitial lattice structure. That is, Li vacancy is prone to form near the interstitial Mn. The present finding that IMn$^{IV}$ and V$_{Li}$ have a strong attractive interaction is qualitatively in accordance with the conclusion of Koyama et al.

### 3.5. Diffusion of Li in LiMn$_2$O$_4$

Diffusion of Li is an important elementary step in the charge/discharge process in electrode materials. As for LiMn$_2$O$_4$, the diffusion of Li is mediated via the vacancy mechanism, which is composed of a series of jumps of Li ions between two 8a sites through a 16c site. In this section, we discuss the effect of point defects on the migration of Li ions.

After a Li vacancy is generated, the neighboring Li atom is allowed to migrate to the vacancy site through a ‘ring’ consisting of six Mn$^{3+}$/Mn$^{4+}$ ions, that is, the Li ion jumps over the 16c octahedron sharing edges with six Mn−O$_6$ octahedrons. Usually, there are two kinds of Mn$^6$ rings, as depicted in Figure 1b. We named the diffusion path that comprises of four Mn$^{3+}$ and two Mn$^{4+}$ in the Mn$^6$ ring as Path 1. The center of the 16c site in Path 1 is located on the Mn$^{3+}$...
layer. The path involves migration across the Mn6 ring composed of two Mn4+ and four Mn3+ named Path 2 in which the 16c site is located on the Mn4+ layer. We use the CINEB method with five images to study the diffusion behavior of Li going through the two different diffusion paths. We first investigate the diffusion of Li in pristine LiMn2O4. The calculated migration barrier of Li is shown in Figure 4a. Due to the different oxidation states of Mn in Path 1 and Path 2, the volume of the 16c octahedron and the electrostatic interaction between Mn and the migrated Li are different. We clearly observe different Li diffusion barriers for the two paths (0.35 eV for Path 1 and 0.68 eV for Path 2). Our calculated diffusion barriers are generally in agreement with the previous theoretic values based on the same magnetic configuration.21,30 Xiao et al. reported that the migration barrier is 0.38 eV for Path 1,30 and a barrier of 0.23 eV for Path 1 and 0.70 eV for Path 2 were reported by Liu et al.21 We also found that a metastable configuration is reached when Li diffuses via Path 2. This configuration corresponds to the migrated Li at the 16c position in the center of the Mn6 ring. By comparison of the two paths, it is obvious that Li ions can easily diffuse through the path with more Mn4+ ions. The reason for the lower migration barrier of Li in Path 2 can be attributed to the electrostatic interaction between cations. Compared with Mn3+, Mn4+ has a smaller electron cloud range, and thus, Mn4+ ions have a small Coulomb repelling effect on the mobile Li ions. Thus, if the symmetry is consistent, the higher the Mn4+ ratio, the lower the migration barrier of Li. We further speculate that a higher oxidized ion substituting a Mn in the Mn6 ring would increase the Li diffusion kinetics in spinel LiMn2O4.

Then, we consider the effects of point defects on the migration of Li. For this purpose, the defects with the lowest energy in each type are only considered, and Li vacancy is generated in the neighboring of the defect to study the migration process. The interstitials are not considered because they are located in the 16c site and hence block the diffusion of Li. The defects considered here are MnLi, LiMn and VO, which are commonly observed in experiments.

The calculated energy barriers of Li migration in the lattice with defects of MnLi, LiMn, and VO are shown in Figure 4b,c,d, respectively. One should note that in some cases the Mn6 ring in the diffusion path is different from that of pristine LiMn2O4 because of charge transfer. The six-membered rings in the migration paths of the defective cell are also shown in the inset of Figure 4b,c,d. MnLi is the defect that a Mn is in a Li site (8a site), which does not change the oxidation state of Mn of the diffusion ring. The diffusion energy barriers for Li migrating through Paths 1 and 2 are 0.27 and 0.65 eV, respectively. Compared with Li diffusion in defect-free LiMn2O4, it is revealed that MnLi leads to a decrease in the diffusion barrier of Li slightly. As for the antisite LiMn, Li is prone to substitute Mn3+. In this case, the Mn6 ring in the diffusion channel is changed to a Mn5Li ring, that is to say, the ring is composed of five Mn ions and one Li ion. The diffusion barriers of Path 1 and Path 2 are 0.25 and 0.46 eV, respectively. The diffusion barrier of Li is reduced by 0.1 or 0.22 eV in comparison with that of Li diffusion in perfect LiMn2O4. This is because the Coulomb repulsive interaction of Li–Li is much weaker than that of Li–Mn. Xiao et al. have studied Li diffusion in Li-excess LiMn1.5O4 by first-principles calculations.30 They found that when a Mn3+ in the Mn6 ring is replaced by a Li, the diffusion barrier of Li is 0.24 or 0.29 eV, depending on the atomic arrangement of Mn4+, Mn3+, and Li+ in the ring. The presently calculated diffusion barrier of Path 1 is in good agreement with their result.

When an anion defect (i.e., O vacancy) is present in the lattice, Li ions around it have a strong tendency to move outward from the VO defect, and the previous study has shown that two Mn4+ around it are reduced to Mn3+. In this case, the Mn6 ring in the diffusion path is also different from the Mn6 ring of the perfect lattice, as shown in Figure 4d. The energy barriers for Li migrating through Path 1 (0.97 eV) and Path 2 (1.0 eV) are almost equal. The higher diffusion barrier in the case of VO is mainly caused by the charge distribution of the Mn ring in the diffusion path. Both Path 1 and Path 2 in the case of VO are asymmetrically arranged in the Mn ring and have a high ratio of Mn3+ ions, and this causes much more serious JT distortion and coulombic repulsion between Mn and migrated Li.

By studying the influence of point defects on the diffusion energy barrier of Li, we found that both LiMn and MnLi antisites can effectively reduce the diffusion energy barrier, but VO results in an increase of diffusion barrier significantly. One should be aware that the kinetics process for Li migration is not only determined by the migration barrier but also by the concentration of point defects in the lattice. Consequently, if the antisite defects or the cation mixing is at a high concentration, they could promote Li diffusion kinetics. From an experimental point of view, 10% cation mixing could be achieved by adjusting the synthesis conditions.22 Such defect concentration is relatively considerable and it is possible to measure the diffusion kinetics of Li ions in LiMn2O4 samples with cation mixing. Hence, cation mixing is beneficial for improving the charge/discharge rate of LiMn2O4.

4. CONCLUSIONS

In summary, defect properties of spinel LiMn2O4 were studied by means of first-principles calculations based on a reasonable magnetic configuration. The formation energies of intrinsic defects of vacancies, interstitials, and cation antisites were calculated under assumed equilibrium conditions and the binding energies of some defect pairs were calculated to determine the clustering of some point defects. Charge distribution and compensation involving the creation of defects were also investigated. The present work reveals that O, Mn, and Li vacancies, Mn and Li antisites, and Li interstitial may exist in LiMn2O4, but their concentrations are sensitive to experimental conditions and thermal history. The defect pairs \( \text{Mn}^{3+}\text{Li}^{+} - \text{V}^{4+}_{\text{O}}\text{V}^{4+}_{\text{Li}}\text{V}^{4+}_{\text{Li}}\text{Mn}^{3+}\text{Li}^{+} - \text{V}^{4+}_{\text{Li}}\text{V}^{4+}_{\text{Li}}\text{Mn}^{3+}\text{Li}^{+} - \text{Mn}^{3+}\), and \( \text{Li}^{3+}_{\text{Mn}}\text{Mn}^{3+}\text{Li}^{3+}_{\text{Mn}}\text{Mn}^{3+}\text{Li}^{3+}_{\text{Mn}}\text{Mn}^{3+}\text{Li}^{3+}_{\text{Mn}}\) are more stable than corresponding isolated defects. The charge compensation associated with the creation of defects was also determined according to Bader charges. We found that the compensation was mainly achieved through the redox of the surrounding Mn3+/Mn4+, except for the case of defects at the 8a site. Finally, the diffusion of Li ions around defects was studied. It was found that O vacancy significantly increased the diffusion barrier of Li. In contrast, the antisite defects, i.e., LiMn and MnLi, decreased the Li diffusion barrier obviously. Our theoretical studies provide clear information on the defect properties in LiMn2O4 on the atomic scale and could help in adjusting the performance of spinel LiMn2O4 from defect engineering.
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