Local Structure and Chemical Bonding of Protonated $Li_xMn_2O_4$ Spinels from First Principles

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Local symmetry and structure of protonated $Li_xMn_2O_4$ ($0 \le x \le 1$) spinels were systematically investigated using a first-principles method. Introduction of protons into $Li_xMn_2O_4$ ($0 \le x \le 1$) spinels does not change the basic Mn−O framework, whereas the local symmetry is broken. Every proton, which prefers to reside in one tetrahedral 8a cavity, moves to one of its four neighboring oxygen ions, forming one OH cluster, while the Li ions are still in the 8a sites. The corresponding O(H) atom relaxes about 0.1 Å away from the ideal position in the original Mn−O network, toward the proton, which enables the H−O bonds to keep a length of 0.99 Å. The calculated results not only are in good agreement with the experiments in the literature but also explain the apparent long H−O bonds obtained from the recent structural refinements.

Introduction

As one of the most promising materials for rechargeable Li batteries with a high energy density and long lifetime, lithium manganese dioxide ($Li_xMn_2O_4$, $0 \le x \le 1$) spinels have been intensively studied for decades.[1−4] The spinels are also capable of absorbing Li ions from liquids with high selectivity[5−7] and might be used to extract Li from natural waters, for example, seawater. To understand the mechanism of insertion/extraction of Li/H ions into the $Li_xMn_2O_4$ spinels, it is important to have some knowledge about the local structure and chemical bonding of Li/H ions in those crystals. Different experimental techniques have been applied to protonated $Li_xMn_2O_4$ spinels.[8−10] Feng et al. studied proton/Li extraction/insertion in the $Li_xMn_2O_4$ spinels using far-IR spectroscopy. They classified Li/H extraction/insertion into redox-type and ion-exchange-type, depending on the amount of trivalent Mn and defects.[8] Koyanaka et al. showed that the lithium absorption capacity for hydrated Mn_2O_4 spinels is dependent on the content of H ions.[9] Recently, using neutron diffraction techniques, Ammundsen et al.[10,11] found that for acid treated samples protons are predominately incorporated into the crystal as OH clusters without any other major changes in the structure of $Li_xMn_2O_4$ spinels. The OH clusters are directed into the interstitial space of the 8a tetrahedral sites. Refinements on neutron diffraction data gave apparently long H−O bonds of about 1.10−1.13 Å in the protonated $Li_xMn_2O_4$ spinels.[11] No detailed knowledge about the local symmetry and structure was present until now. In this respect, theoretical methods, especially first-principles methods, can be very helpful. There are many reports of theoretical calculations on the stability and electronic properties of the $Li_xMn_2O_4$ spinels, for example, refs 12 and 13. However, until now we have found no reports on the first-principles calculations on the protonated $Li_xMn_2O_4$ spinels. Here we present results of theoretical investigation of the symmetry and structure of the local environment of protons in the $Li_xMn_2O_4$ spinels from first-principles. The results obtained here can be helpful to understand the stability, local structure, and chemical bonding of the protonated spinels, as well as to understand the mechanism of Li/H insertion/extraction for related materials. Furthermore, the obtained knowledge about the local bonding in the hydrated spinels can also be useful to explain the apparently long O−H bonds obtained experimentally in many hydrated transition metal oxides.[11,14−18]

Details of the Theoretical Methods

We started from the two end compositions of the $Li_xMn_2O_4$ spinels, $LiMn_2O_4$ ($x = 1$) and Mn_2O_4 spinel ($x = 0$ or

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γ-Mn_2O_4[19]). Then we gradually add protons into the Mn_2O_4 spinel to form a $H_xMn_2O_4$ series or replace the Li ions by protons in the $LiMn_2O_4$ spinel, forming a $(H_xLi_{1-x})Mn_2O_4$ series. At last a fully protonated spinel with chemical composition HMn_2O_4 is obtained. For each spinel, we employed a conventional cell containing eight formula units. Calculations employing a primitive cell of two formula units were also carried out for the spinels with chemical compositions $H_{1/2}Mn_2O_4$, $(Li_{1/2}H_{1/2})Mn_2O_4$, and HMn_2O_4. Structural optimizations were performed for both cell shape and atomic positions.

Theoretical calculations were carried out using the first-principles molecular-dynamics computer code VASP (Vienna ab initio simulation program).[20,21] The calculations were carried out in the spin-polarized generalized gradient approximation (SP-GGA),[22] using the projector-augmented wave method.[23,24] Calculations are limited to ferromagnetic ordering for the ease of computation. As shown later, the influence of protons on the crystal is very local. Therefore, the bonding properties of the protons are expected not to be very dependent on the magnetic ordering. The electronic wave functions were sampled on a $(4 \times 4 \times 4)$ and $(2 \times 2 \times 2)$ mesh in the Brillouin zone (BZ) for a primitive cell and a convention cell, respectively. For structural optimizations the Γ point of the BZ was employed for the conventional cells. The kinetic energy cutoff on the wave functions was 500 eV. The augmentation cutoff energy was 604 eV. Convergence of the total energy with the number of k points and the plane-wave cutoff has been checked.

Calculated Results

A. Crystal Structure of $Li_xMn_2O_4$ ($x = 0$, 1) Spinels. First we discuss the results for the cubic $LiMn_2O_4$ and Mn_2O_4 spinels with space group $Fd\bar{3}m$ (No. 227).[1,19,25] There are eight formula units per conventional unit cell. The schematic structures of the Mn_2O_4 and $LiMn_2O_4$ spinels are shown in Figure 1. The O anions occupy the 32e sites (local symmetry $3m$), forming an approximately face-centered close packed structure with 96 interstitial sites (tetrahedral 8a, 8b, and 48f sites and octahedral 16c and 16d sites). The Li ions are at the 8a sites (local symmetry $\bar{4}3m$; for $LiMn_2O_4$), while the Mn ions occupy the 16d sites (local symmetry $\bar{3}m$). The crystal structure of a cubic spinel can be completely defined by the lattice parameter a and the anion's positional parameter x.

The calculated results ($a = 8.156$ Å and $x = 0.389$ for $LiMn_2O_4$; $a = 8.148$ Å and $x = 0.390$ for Mn_2O_4 spinel) are close to the experimental values[1,19,25] as well as to other theoretical data (density functional theory GGA).[12,13] The calculated lattice parameter for the Mn_2O_4 spinel is slightly smaller than that of $LiMn_2O_4$, in line with the experimental trend.[1,19,25,26]

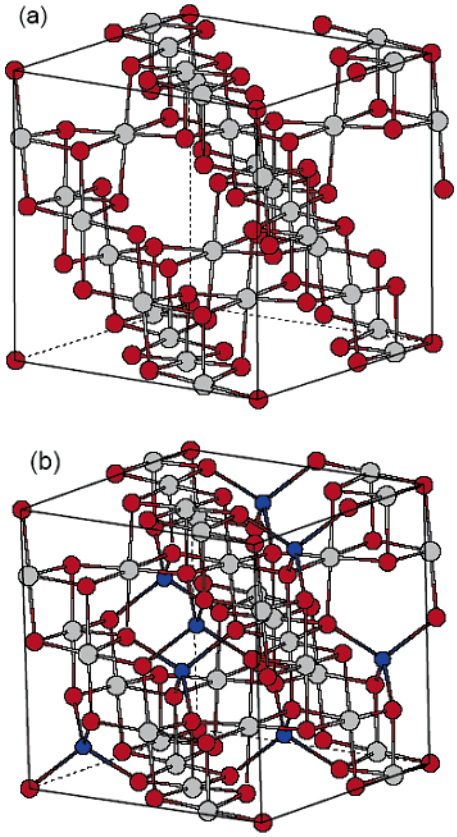

Figure 1. Schematic structures for Mn_2O_4 (a) and $LiMn_2O_4$ (b). The small filled circles in part b represent Li ions. For both part a and part b the filled large circles represent Mn and the open large circles represent O ions.

As shown in Figure 1, in $LiMn_2O_4$ each Li ion at 8a is tetrahedrally coordinated by oxygen atoms with a Li−O bond length of about 1.92 Å and every Mn ion is octahedrally coordinated (six Mn−O bonds of 1.96 Å). In the Mn_2O_4 spinel the Mn−O distance is slightly shorter (1.92 Å). Every O is coordinated by three Mn ions and one Li ion in $LiMn_2O_4$, while every O has only three neighboring Mn ions in Mn_2O_4.

For the protonated $Li_xMn_2O_4$ spinels, the symmetry is broken (see below), but throughout this paper we still call those protonated systems "spinels".

B. $H_xMn_2O_4$ Series. As shown in Figure 1a, the structure of the Mn_2O_4 spinel is composed of MnO_6 octahedra which form a three-dimensional cubic array, imparting stability to the framework. There are 96 interstitial sites (cavities) available for small ions such as protons, as mentioned in the previous section.

First we discuss the most stable configuration for one proton in a conventional cell of the Mn_2O_4 spinel. Figure 2a shows the relaxed structure of the $H_{1/8}Mn_2O_4$ spinel with the relaxed coordinates of the H ion, in one of the tetrahedral 8a cavities. The relaxation showed that the H ion moves from the center of the 8a site to one of the neighboring oxygen ions and forms one OH cluster with an O−H bond of 0.99 Å (Table 1). The Mn−O network is kept basically unchanged, except for the O ion bonded to the proton (O(H), in short), which shows notable relaxation and moves (about

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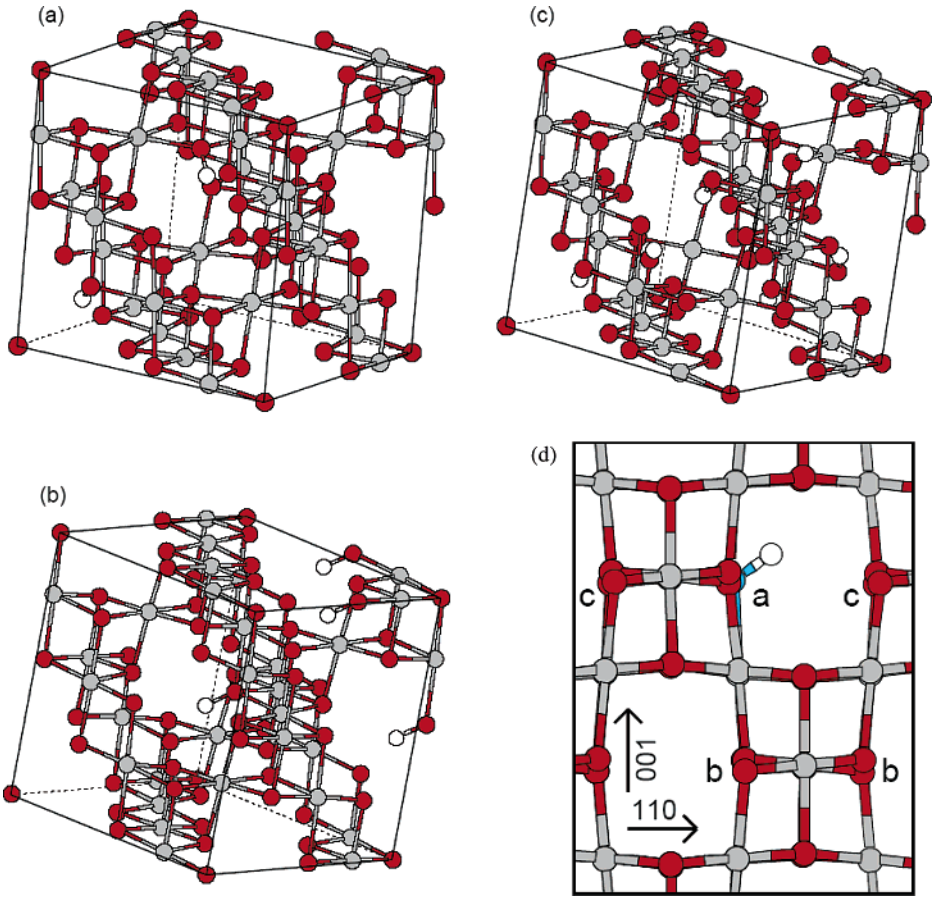

Figure 2. Schematic relaxed structures of the $H_xMn_2O_4$ series, (a) $x = 1/8$, (b) $x = 1/4$, and (c) $x = 1/2$. The open small circles represent H ions, the rest are the same as in Figure 1. Part d shows the details of the local relaxation of one O(H): note the subtle differences between the O atoms bonded to a proton (site a) and others (sites b and c).

Table 1. Calculated Results for the $(H,Li)_xMn_2O_4$ Spinels[a]

	d_{H-O} (Å)	$d_{O(H)-Mn}$ (Å)	$d_{O(H)shift}$ (Å)
C-$H_{1/8}Mn_2O_4$	0.99	2.03, 2.04(×2)	0.08
C-($Li_{7/8}H_{1/8}$)Mn_2O_4	0.99	2.02(×3)	0.07
C-($H_{1/4}$)Mn_2O_4	0.99	2.02, 2.03(×2)	0.13
C-($Li_{3/4}H_{1/4}$)Mn_2O_4	0.99	2.02(×2), 2.03	0.09
P-$H_{1/2}Mn_2O_4$	0.99	2.00, 2.05(×2)	0.14
C-$H_{1/2}Mn_2O_4$	0.99	2.02(×2), 2.03	0.15
P-($Li_{1/2}H_{1/2}$)Mn_2O_4	0.99	2.02(×3)	0.13
C-($Li_{1/2}H_{1/2}$)Mn_2O_4	0.99	2.01, 2.02(×2)	0.13
P-HMn_2O_4	0.99	2.00(×2), 2.02	0.15
C-HMn_2O_4	0.99	2.00(×2), 2.02	0.14

[a] C indicates a conventional cell, and P indicates a primitive cell.

0.08 Å) away from the Mn−O network toward the proton. As a consequence, the O(H) has three longer Mn−O bonds (about 2.04 Å). In the second case we put a proton at one of the 8b cavities of the Mn_2O_4 spinel. The structural optimizations resulted that the proton moves to one of its neighboring oxygen atoms with an O−H distance of 1.00 Å, similar to the case with a proton in an 8a cavity. However, the proton has also three Mn neighbors with a H−Mn distance of 1.80 Å, which causes it to be about 3.0 eV less stable than that of the proton in the 8a cavity. We also investigated the configurations with one proton in one of the tetrahedral 48f cavities or one of the octahedral 16c cavities. The proton kept moving during the relaxation, until it had reached a nearby 8a cavity and had formed a bond with one of the neighboring oxygen atoms as in the stable form.

Table 2. Calculated Results for the Different Configurations for the $H_{1/4}Mn_2O_4$ Spinel[a]

case	two H atoms in Mn_2O_4 spinel	energy (eV)
a	one H_2 in one 8a cavity	3.50
b	two O−H in one 8a cavity	0.50
c	two O−H in two close 8a cavities	0.01
d	two O−H in two far 8a cavities	0.00

[a] We set the calculated energy of the stable configuration to zero.

For the $H_2Mn_{16}O_{32}$ spinel we studied the distribution of protons in the spinel. The calculated results are shown in Table 2. We started with the two H atoms in one tetrahedral 8a cavity. We tried this in various ways yielding two different results. In case a, the structural relaxation produced one H_2 molecule with a H−H bond of 0.78 Å. The H_2 molecule remained during our calculations in the Mn_2O_4 spinel, although the total energy of the hydrated spinel is about 3.5 eV higher than the stable configuration (see Table 2). In case b, we obtained results with the relaxed coordinates for the two H ions being (0.9141, 0.9148, 0.9717) and (0.0789, 0.0785, 0.9559); each of them is bonded to an O ion. There is no H−H bond, but the two protons remain in the same 8a cavity. The O−H bonds have a length of 0.99 Å. The calculated total energy is just about 0.50 eV higher than the stable configuration (Table 2). The stable configurations were obtained for the two H atoms occupying different 8a cavities. One stable configuration is shown in Figure 2b. The energy differences between different configurations of the two H atoms in different 8a cavities are not significant (of the order

of 0.01 eV, as shown in Table 2), which indicates random distribution of the H atoms at the 8a cavities. This is due to the fact that in the spinel structure the tetrahedral cavities are well-separated [see, e.g., Figures 1 and 2d]. Moreover, as the environment is metallic, the partial charge of the protons is screened. One might object that the H could interact indirectly via the oxygen and manganese ions: Strong lattice distortions may be caused by a charge redistribution on the manganese resulting in Mn^{3+} and Mn^{4+} ions, and such a redistribution is typically underestimated in the GGA. To estimate this effect we carried out a test calculation on one H in a large box ($HMn_{16}O_{32}$) using a "GGA + U" approach[27] with a relatively large $U-J$ of 5 eV. The magnetic moments on Mn are affected, where the three Mn ions close to the hydrogen are larger by 0.2−0.3 μ_B. Only the Mn−O bonds in the first and second coordination shell of the O(H) are affected and are slightly longer (up to 0.04 Å). The O−H bond length is not affected. This indicates a rather local effect, suggesting that protons in different 8a cavities would not strongly influence one another. However, as this "GGA + U" calculation provides only a rough estimate, this conclusion needs to be taken with care.

We also have optimized the structure for the $H_4Mn_{16}O_{32}$ spinel with each proton in one of the tetrahedral 8a cavities. The calculated results are listed in Table 1. All protons move to a neighboring O ion and form OH clusters (O−H bond 0.99 Å) (Figure 2c). All the O(H) ions also shift about 0.14 Å away from the Mn−O network without further distortion of the Mn−O bonds.

As shown above, insertion of protons in the Mn_2O_4 spinel does not change the basic Mn−O framework, though the local symmetry is broken. The H ions prefer the 8a cavities. Each proton moves to one of the neighboring O ions, forming one OH cluster with an O−H bond of 0.99 Å. The O(H) ions relax away from the Mn−O network toward the proton, as shown in Figure 2d in detail.

C. $(H_xLi_{1-x})Mn_2O_4$ Spinels. Replacement of one Li ion by a proton in a convention cell of the $LiMn_2O_4$ spinel gives $(Li_{7/8}H_{1/8})Mn_2O_4$. As shown in Figure 3a, for the relaxed structure the Li/Mn−O network basically remains unchanged. The Li ions are still at the centers of the tetrahedral sites. The H ion has shifted to one of the four neighboring O ions. Correspondingly the relaxation shows that the O(H) shifts about 0.08 Å to the proton from the Mn−O network, which keeps the O−H bond length of 0.99 Å. The O(H) ion has three long Mn−O bonds (2.02 Å), as shown in Table 1.

For the $(H_{1/4}Li_{3/4})Mn_2O_4$ spinel, the calculations show that the protons are situated in different 8a cavities and the energy differences for different configurations are not significant (of the order of 0.01 eV), which indicates again a random distribution of the H/Li ions over the 8a sites/cavities (see section B). The Li/Mn−O network is basically kept. The O−H distance is 0.99 Å. Again the two O atoms in the O−H bonds show a shift (about 0.09 Å) away from the original Mn−O network.

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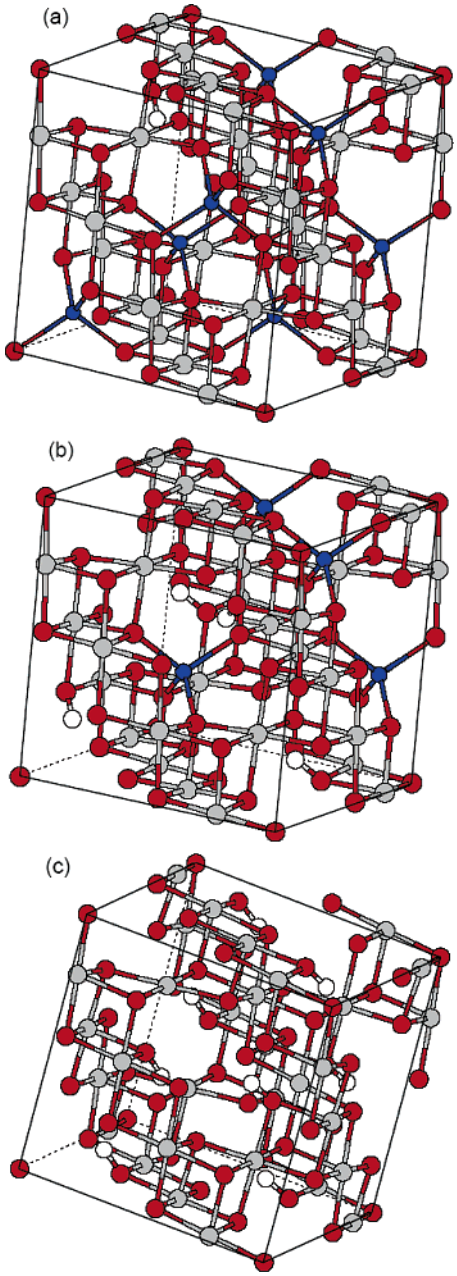

Figure 3. Schematic relaxed structures of the $(Li_{1-x}H_x)Mn_2O_4$ series: (a) $x = 1/8$, (b) $x = 1/2$, and (c) $x = 1$.

The relaxed structure of $(H_{1/2}Li_{1/2})Mn_2O_4$ spinel is shown in Figure 3b. We have calculated the structures within both a convention cell and a primitive cell. The obtained results are the same for both calculations as shown in Table 1. Clearly, the Li ions are still at the tetrahedral sites, while every H ion moves to one of its neighboring O ions (Figure 3b). The H−O interatomic distance is 0.99 Å. The four O(H) ions deviate about 0.13 Å from the Mn−O network toward the H ions. Those O ions have larger Mn−O distances of about 2.02 Å (Table 1). The 12 O ions only bonded to 3 Mn ions have slightly shorter Mn−O distances.

Full replacement of Li by H results in the protonated spinel, HMn_2O_4, the end composition. Structural optimizations were performed for both a primitive cell and a conventional cell, which gave the same results. The Mn−O network frame is basically the same as that of the $Li_xMn_2O_4$ spinel, as shown in Figure 3c. As shown in Table 1 the O−H

bond length is again 0.99 Å and the O(H) ions relax about 0.15 Å from the Mn−O network to the H ions. Also those O ions have rather long Mn−O bonds (about 2.01 Å).

D. Discussion and Conclusion. First-principles calculations showed that the protons in the $(Li,H)_xMn_2O_4$ spinels prefer the tetrahedral 8a cavities and that each proton moves to one of its four oxygen neighbors to form one OH cluster, in agreement with the recent neutron diffraction refinements by Ammundsen.[10,11] They used the space group *Fd*3*m* of a cubic spinel in their refinements. The Li/Mn and O ions were at the regular sites of a cubic spinel, while the protons were found to be at 96g sites. They obtained an apparently unusually long O−H bond of about 1.10−1.12 Å, much longer than that (0.99 Å) from our calculations.

In a first-principles study of H insertion in the pyrolusite and ramsdellite forms of MnO_2, Balachandran et al. found that hydrogen bonds to an oxygen species and tries to maximize its distance from the Mn ions.[28] Note that in the $(Li,H)_xMn_2O_4$ spinels the protons are also farthest away from the Mn ions in the tetrahedral 8a cavities.

Our calculations showed that relaxation is very important to understand the local structure. The local symmetry of the $(H,Li)_xMn_2O_4$ spinels has been broken due to the protonation effects. It is notable that every O(H) ion relaxes about 0.08−0.15 Å away from the Mn−O network toward the nearby proton, as shown in Figure 2d. The local relaxation of the O(H) ions (not accounted so far in the refinement of the neutron data) is the main cause of the apparent discrepancy between the experimental refinements and the theoretical calculations. The calculations also show that only one proton resides in a tetrahedral 8a cavity, which indicates that it is not a random distribution of protons at the 96 g sites, as used in the structural refinements. From the comparison between our calculations and the neutron refinements, it is concluded that for such cases a rigid model for structure refinements may not give correct information about local structures. Furthermore, relaxation effects could also be useful to understand the local structure of the other protonated transition metal compounds with apparently long O−H bonds obtained experimentally.[11,14−18,26]

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