Short Communication

Structural and Properties of LiNi$_{0.5}$Mn$_{1.5}$O$_{4-δ}$ and LiNi$_{0.5}$Mn$_{1.5}$O$_4$ Spinels: A first-Principles Investigation

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The structural and properties of LiNi$_{0.5}$Mn$_{1.5}$O$_{4-Fd-3m}$ and LiNi$_{0.5}$Mn$_{1.5}$O$_4$-$P4_332$ spinels as the high-voltage cathode materials were investigated by the first-principles theory. The calculated results indicate that the crystal structure of the LiNi$_{0.5}$Mn$_{1.5}$O$_{4-Fd-3m}$ is beneficial to the transition of lithium compared with LiNi$_{0.5}$Mn$_{1.5}$O$_4$-$P4_332$. Due to the charge overlap of LiNi$_{0.5}$Mn$_{1.5}$O$_4$-$P4_332$ around Mn, Ni and O atoms significantly increased compared with LiNi$_{0.5}$Mn$_{1.5}$O$_{4-Fd-3m}$, which form a stable bond, therefore their structure is significantly increased. The lengths of the bonds of LiNi$_{0.5}$Mn$_{1.5}$O$_4$-$P4_332$ are shorter than that of the LiNi$_{0.5}$Mn$_{1.5}$O$_{4-Fd-3m}$, indicating that the energy of the bond is smaller, thus the structure of LiNi$_{0.5}$Mn$_{1.5}$O$_4$-$P4_332$ is more stable, but the Mn-Mn bonds hinder the shuttle movement of lithium ions, so the cycle performance of LiNi$_{0.5}$Mn$_{1.5}$O$_{4-Fd-3m}$ may be better than that of LiNi$_{0.5}$Mn$_{1.5}$O$_4$-$P4_332$. The calculated results exhibit the band gap of LiNi$_{0.5}$Mn$_{1.5}$O$_{4-Fd-3m}$ and LiNi$_{0.5}$Mn$_{1.5}$O$_4$-$P4_332$ are 0.487 eV and 0.718 eV, respectively, which indicate that the electro-conductive performance LiNi$_{0.5}$Mn$_{1.5}$O$_{4-Fd-3m}$ is better.

Keywords: first-principles, electrochemical performance, structure, spinel LiNi$_{0.5}$Mn$_{1.5}$O$_4$

1. INTRODUCTION

With many advantages such as no memory effect, the best energy-to-weight ratios, and a slow loss of charge when not in use, Lithium-ion batteries have been favored in consumer electronics for last 30 years [1,2]. 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 [3-7]. Compared with other cathode materials, the charge/discharge voltage platform of LiNi$_{0.5}$Mn$_{1.5}$O$_4$ spinel material
is about 4.7 V, thereby it was a worthwhile study cathode material for new-generation lithium-ion batteries [8,9]. Because of the synthetic temperature, atmospheric conditions and other factors, LiNi$_{0.5}$Mn$_{1.5}$O$_4$ has two different crystal structures, they are P4$_{3}$$\overline{3}$2 and Fd-3m structure [10]. Stoichiometric LiNi$_{0.5}$Mn$_{1.5}$O$_4$ has a cubic, primitive structure (P4$_{3}$$\overline{3}$2), while nonstoichiometric LiNi$_{0.5}$Mn$_{1.5}$O$_{4-\delta}$ has a normal face-centered spinel structure(Fd-3m ). For LiNi$_{0.5}$Mn$_{1.5}$O$_4$, only part of manganese atoms in 16d position is occupied by nickel atoms randomly, while for LiNi$_{0.5}$Mn$_{1.5}$O$_{4-\delta}$, manganese atoms in 4a position were occupied by nickel atoms orderly [11-13]. This paper study mainly on the difference of crystal structure, density of states, bond length, atomic layout and charge density between LiNi$_{0.5}$Mn$_{1.5}$O$_4$ and LiNi$_{0.5}$Mn$_{1.5}$O$_{4-\delta}$ spinels 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) within the generalized gradient approximation (GGA) and following structural models [14]. Li-2s, O-2s2p, Ni-3d4s, Mn-3d4s electrons are chosen as valence electrons, while all the other electrons are chosen as core electrons. The ionic positions and the lattice parameters were fully relaxed before the calculations, and the final force on each atom is less than 0.02 eV/A. A plane-waves cut-off energy of 300 eV and 2×2×2 Monkhorst-Pack k-point over the irreducible Brillouin zone were applied in the calculations [15]. Gaussian smearing method with a smearing width of 0.03 eV was chosen in the calculation of the density of states (DOS). Conventional cell was chosen in the calculations. Here, LiNi$_{0.5}$Mn$_{1.5}$O$_4$ and LiNi$_{0.5}$Mn$_{1.5}$O$_{4-\delta}$ are referred to as LiNi$_{0.5}$Mn$_{1.5}$O$_4$-P4$_{3}$$\overline{3}$2 and LiNi$_{0.5}$Mn$_{1.5}$O$_4$-Fd-3m, respectively. In this paper, we mainly analyzed the crystal structure, density of states, bond length, atomic layout and charge density of LiNi$_{0.5}$Mn$_{1.5}$O$_4$-P4$_{3}$$\overline{3}$2 and LiNi$_{0.5}$Mn$_{1.5}$O$_4$-Fd-3m. LiNi$_{0.5}$Mn$_{1.5}$O$_4$-P4$_{3}$$\overline{3}$2 and LiNi$_{0.5}$Mn$_{1.5}$O$_{4-\delta}$-Fd-3m were prepared by sol gel method as the anode material of battery.

3. RESULTS AND DISCUSSION

3.1 Structures of LiNi$_{0.5}$Mn$_{1.5}$O$_4$-Fd-3m and LiNi$_{0.5}$Mn$_{1.5}$O$_4$-P4$_{3}$$\overline{3}$2

The calculation model was given in Fig. 1. For LiNi$_{0.5}$Mn$_{1.5}$O$_4$-Fd-3m (Fig. 1a), 8a sites are located by Li ions, 16d sites are occupied by Mn and Ni ions and distributed in 32e sites are O ions, which consisting of a normal face-centered spinel array, while for LiNi$_{0.5}$Mn$_{1.5}$O$_4$-P4$_{3}$$\overline{3}$2 (Fig. 1b), 8c sites are located by Li ions, 12d sites and 4a sites are occupied by Mn ions and Ni ions respectively, and distributed in 8c and 24e sites are O ions, which consisting of a primitive, or simple, cubic array. It is consistent with the results in Refs. [16], [17] and [18]. The lattice parameters [19] for LiNi$_{0.5}$Mn$_{1.5}$O$_4$-Fd-3m and LiNi$_{0.5}$Mn$_{1.5}$O$_4$-P4$_{3}$$\overline{3}$2 are 8.166 Å and 8.172 Å. Thence, the fundamental difference is where Ni ions are located. It is well known that the crystal structure of LiNi$_{0.5}$Mn$_{1.5}$O$_4$-
Fd-3m is beneficial to the transition of lithium compared with LiNi0.5Mn1.5O4-P4332. The Mn-Mn bonds of LiNi0.5Mn1.5O4-P4332 make the crystal framework more stable, but which hinder the shuttle movement of lithium ions. It is shown evidence of stability of crystal structure in charge-discharge recycling process, which is consistent with the experimental results in Fig. 2.

![Figure 1](image1.png)

**Figure 1.** Structure cell chart of (a) LiNi0.5Mn1.5O4-Fd-3m (b) LiNi0.5Mn1.5O4-P4332.

3.2 Charge-discharge performance

The first charge-discharge curves and the cycle performances of LiNi0.5Mn1.5O4-Fd-3m and LiNi0.5Mn1.5O4-P4332 at 0.1 C are shown in Fig. 2. The cut-off voltages were 3.5-4.8 V at room temperature. Fig.2a showed that the charge and discharge specific capacity of the LiNi0.5Mn1.5O4-Fd-3m was 119.45 mAhg⁻¹, 112.44 mAhg⁻¹ respectively, while the charge and discharge specific capacity of the LiNi0.5Mn1.5O4-P4332 was 100.26 mAhg⁻¹, 90.23 mAhg⁻¹ respectively. It can be found from Fig. 2b that the cycle property of the LiNi0.5Mn1.5O4-Fd-3m also better than the LiNi0.5Mn1.5O4-P4332, which is consistent with the calculational results in Fig. 1.

![Figure 2](image2.png)

**Figure 2.** (a) First charge-discharge (b) Cycle performances of LiNi0.5Mn1.5O4-Fd-3m and LiNi0.5Mn1.5O4-P4332.
3.3 Density of states

The electron density of states (DOS) and projected electron density of states (PDOS) of LiNi$_{0.5}$Mn$_{1.5}$O$_4$-$Fd$-$3m$ and LiNi$_{0.5}$Mn$_{1.5}$O$_4$-$P4_332$ are shown in Fig. 3, respectively. From the figure, it can be found that the DOS mainly attributed to s, p and d orbits. The calculated band gap of LiNi$_{0.5}$Mn$_{1.5}$O$_4$-$Fd$-$3m$ and LiNi$_{0.5}$Mn$_{1.5}$O$_4$-$P4_332$ is 0.487 eV and 0.718 eV, respectively. The band gap of the LiNi$_{0.5}$Mn$_{1.5}$O$_4$-$Fd$-$3m$ is smaller than that of the LiNi$_{0.5}$Mn$_{1.5}$O$_4$-$P4_332$, thereby the free electrons transitional energy of the LiNi$_{0.5}$Mn$_{1.5}$O$_4$-$Fd$-$3m$ are less than that of the LiNi$_{0.5}$Mn$_{1.5}$O$_4$-$P4_332$, which suggests that the LiNi$_{0.5}$Mn$_{1.5}$O$_4$-$Fd$-$3m$ may exhibit higher electronic conduction compared with LiNi$_{0.5}$Mn$_{1.5}$O$_4$-$P4_332$. The PDOS of different chemical elements of LiNi$_{0.5}$Mn$_{1.5}$O$_4$-$Fd$-$3m$ and LiNi$_{0.5}$Mn$_{1.5}$O$_4$-$P4_332$ are shown in Fig 4. For the LiNi$_{0.5}$Mn$_{1.5}$O$_4$-$P4_332$, the energy provided by O, Mn and Ni was higher than that of the LiNi$_{0.5}$Mn$_{1.5}$O$_4$-$Fd$-$3m$. This may be the reason why the space frame of the LiNi$_{0.5}$Mn$_{1.5}$O$_4$-$Fd$-$3m$ is more stable compared with LiNi$_{0.5}$Mn$_{1.5}$O$_4$-$P4_332$, which is consistent with the charge-discharge and cycling curves in Fig. 2.

![Figure 3](image1)

Figure 3. The density of states of (a) LiNi$_{0.5}$Mn$_{1.5}$O$_4$-$Fd$-$3m$ (b) LiNi$_{0.5}$Mn$_{1.5}$O$_4$-$P4_332$. The Fermi level is set to be zero.

![Figure 4](image2)

Figure 4. The different chemical elements density of states of (a) LiNi$_{0.5}$Mn$_{1.5}$O$_4$-$Fd$-$3m$ (b) LiNi$_{0.5}$Mn$_{1.5}$O$_4$-$P4_332$. 
To further analyze the impact of different chemical elements on the DOS of the LiNi_{0.5}Mn_{1.5}O_{4}·Fd-3m and LiNi_{0.5}Mn_{1.5}O_{4}·P4_{3}32, we have plotted the orbit of different chemical elements, which are shown in Fig. 5. The energy distribution of Li of the LiNi_{0.5}Mn_{1.5}O_{4}·P4_{3}32 is wider compared with LiNi_{0.5}Mn_{1.5}O_{4}·Fd-3m, which suggests that for the LiNi_{0.5}Mn_{1.5}O_{4}·P4_{3}32, Li suffers from more binding force, therefore the number of free ions are relatively small. This may be the reason why the capacity of the LiNi_{0.5}Mn_{1.5}O_{4}·P4_{3}32 is less than the LiNi_{0.5}Mn_{1.5}O_{4}·Fd-3m. From Figs. 5b and c, it is interesting to see that for the LiNi_{0.5}Mn_{1.5}O_{4}·Fd-3m, the concentrations of energy distribution of Ni is increased, which cause better electronic conductivity compared with LiNi_{0.5}Mn_{1.5}O_{4}·P4_{3}32. At the right of Fermi level, the energy of the LiNi_{0.5}Mn_{1.5}O_{4}·P4_{3}32 is wider and sharper, which imply the Ni-O bond is more stable, thus the cycle stability is better.

Figure 5. (a) Li density of states. Ni density of states of (b) LiNi_{0.5}Mn_{1.5}O_{4}·Fd-3m and (c) LiNi_{0.5}Mn_{1.5}O_{4}·P4_{3}32. Mn density of states of (d) LiNi_{0.5}Mn_{1.5}O_{4}·Fd-3m and (e) LiNi_{0.5}Mn_{1.5}O_{4}·P4_{3}32. O density of states of (f) LiNi_{0.5}Mn_{1.5}O_{4}·Fd-3m and (g) LiNi_{0.5}Mn_{1.5}O_{4}·P4_{3}32.
Taking all above diagrams into consideration, we can get the following conclusions. Energy distribution in the range of \(-10 \sim 5\) eV is mainly Ni-O, Mn-O bonds with strong force, which formed through electrons overlap of O-2p, Ni-3d and Mn-3d. The comparison between the intensity degree of Li of LiNi_{0.5}Mn_{1.5}O_{4}-Fd-3m and LiNi_{0.5}Mn_{1.5}O_{4}-P4_{3}32 reveals that for LiNi_{0.5}Mn_{1.5}O_{4}-P4_{3}32 the impact of other orbitals on Li\(^+\) is larger, thereby it is easy to cause the decrease of the capacity of lithium ion batteries.

3.4 Atomic and bond layout analysis

**Table 1.** The atomic layout of the LiNi_{0.5}Mn_{1.5}O_{4}-Fd-3m (e)

<table>
<thead>
<tr>
<th>atom</th>
<th>s</th>
<th>p</th>
<th>d</th>
<th>total charge</th>
<th>net charge</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li</td>
<td>2.00</td>
<td>0.00</td>
<td>0.00</td>
<td>2.00</td>
<td>1.00</td>
</tr>
<tr>
<td>Ni</td>
<td>0.46</td>
<td>0.66</td>
<td>8.12</td>
<td>9.23</td>
<td>0.77</td>
</tr>
<tr>
<td>Mn</td>
<td>0.35</td>
<td>0.45</td>
<td>5.29</td>
<td>6.08</td>
<td>0.92</td>
</tr>
<tr>
<td>O</td>
<td>1.90</td>
<td>4.79</td>
<td>0.00</td>
<td>6.69</td>
<td>-0.69</td>
</tr>
</tbody>
</table>

**Table 2.** The atomic layout of the LiNi_{0.5}Mn_{1.5}O_{4}-P4_{3}32 (e)

<table>
<thead>
<tr>
<th>atom</th>
<th>s</th>
<th>p</th>
<th>d</th>
<th>total charge</th>
<th>net charge</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li</td>
<td>1.97</td>
<td>0.00</td>
<td>0.00</td>
<td>1.97</td>
<td>1.03</td>
</tr>
<tr>
<td>Ni</td>
<td>0.46</td>
<td>0.70</td>
<td>8.12</td>
<td>9.27</td>
<td>0.73</td>
</tr>
<tr>
<td>Mn</td>
<td>0.32</td>
<td>0.43</td>
<td>5.34</td>
<td>6.09</td>
<td>0.91</td>
</tr>
<tr>
<td>O</td>
<td>1.89</td>
<td>4.80</td>
<td>0.00</td>
<td>6.69</td>
<td>-0.69</td>
</tr>
</tbody>
</table>

**Table 3.** The bond length and bond layout of LiNi_{0.5}Mn_{1.5}O_{4}-Fd-3m and LiNi_{0.5}Mn_{1.5}O_{4}-P4_{3}32

<table>
<thead>
<tr>
<th>bond length (Å)</th>
<th>Li-O</th>
<th>Ni-O</th>
<th>Mn-O</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiNi_{0.5}Mn_{1.5}O_{4}-Fd-3m</td>
<td>2.015</td>
<td>2.025</td>
<td>2.101</td>
</tr>
<tr>
<td>LiNi_{0.5}Mn_{1.5}O_{4}-P4_{3}32</td>
<td>1.956</td>
<td>1.981</td>
<td>2.065</td>
</tr>
<tr>
<td>bond layout (e)</td>
<td>LiNi_{0.5}Mn_{1.5}O_{4}-Fd-3m</td>
<td>0.022</td>
<td>0.305</td>
</tr>
<tr>
<td>LiNi_{0.5}Mn_{1.5}O_{4}-P4_{3}32</td>
<td>0.001</td>
<td>0.32</td>
<td>0.235</td>
</tr>
</tbody>
</table>

For the LiNi_{0.5}Mn_{1.5}O_{4}-Fd-3m, the total charge and net charge of Li atoms and the theoretical value are almost identical, which indicate that the ionization degree of Li atoms are higher than that of the LiNi_{0.5}Mn_{1.5}O_{4}-P4_{3}32, thereby it is easy lead to electrons lost and turn into plasma state. This may
be the reason why the charge and discharge capacity of the LiNi$_{0.5}$Mn$_{1.5}$O$_4$-$Fd$-$3m$ is larger than that of the LiNi$_{0.5}$Mn$_{1.5}$O$_4$-$P4_332$. The net charge of the LiNi$_{0.5}$Mn$_{1.5}$O$_4$-$P4_332$ is different from the theoretical net charge, which shows that the ionic and covalent of Ni and Mn of the LiNi$_{0.5}$Mn$_{1.5}$O$_4$-$P4_332$ are relatively strong, thereby it is easy to form Ni-O, Mn-O, and Mn-Mn bonds with atoms surrounding. The lengths of the Ni-O and Mn-O bonds of the LiNi$_{0.5}$Mn$_{1.5}$O$_4$-$Fd$-$3m$ are longer than that of the LiNi$_{0.5}$Mn$_{1.5}$O$_4$-$P4_332$, the difference is 0.044 Å and 0.036 Å, respectively, which demonstrate that the covalent of Ni-O and Mn-O bonds of the LiNi$_{0.5}$Mn$_{1.5}$O$_4$-$P4_332$ with a stable skeleton is stronger and more stable. The stability of the LiNi$_{0.5}$Mn$_{1.5}$O$_4$-$Fd$-$3m$ is not as good as the LiNi$_{0.5}$Mn$_{1.5}$O$_4$-$P4_332$, and easy to occur lattice collapse and cause Jahn-Tener effect in charging and discharging process, which behaviors as the declining of capacity and the deteriorated of cycling performance. The lengths of the Li-O bonds of the LiNi$_{0.5}$Mn$_{1.5}$O$_4$-$Fd$-$3m$ are longer than that of the LiNi$_{0.5}$Mn$_{1.5}$O$_4$-$P4_332$, which reveals that Li-O bonds of the LiNi$_{0.5}$Mn$_{1.5}$O$_4$-$Fd$-$3m$ is quite weak, and the diffusion coefficient of lithium ion is comparatively large and more capacity.

3.5 Analysis of difference of charge density

The charge density of LiNi$_{0.5}$Mn$_{1.5}$O$_4$-$Fd$-$3m$ and LiNi$_{0.5}$Mn$_{1.5}$O$_4$-$P4_332$ are shown in Fig. 6. It is interesting to see that for LiNi$_{0.5}$Mn$_{1.5}$O$_4$-$P4_332$, the charge overlap around Mn, Ni and O atoms significantly increased compared with LiNi$_{0.5}$Mn$_{1.5}$O$_4$-$Fd$-$3m$. Meanwhile, it can be found that the charge of Ni, Mn and O atoms formed Ni-O and Mn-O stable bonds, therefore LiNi$_{0.5}$Mn$_{1.5}$O$_4$-$P4_332$ structural stability is dramatically increased compared with LiNi$_{0.5}$Mn$_{1.5}$O$_4$-$Fd$-$3m$. For LiNi$_{0.5}$Mn$_{1.5}$O$_4$-$Fd$-$3m$, the charge density among Ni, Mn and O atoms decreases simultaneously, so the partial charge from the Ni, Mn and O atoms is centralized near Li-site atoms. Therefore the electronic conductivity of LiNi$_{0.5}$Mn$_{1.5}$O$_4$-$Fd$-$3m$ are improve enormously than that of the LiNi$_{0.5}$Mn$_{1.5}$O$_4$-$P4_332$, which reveals that LiNi$_{0.5}$Mn$_{1.5}$O$_4$-$Fd$-$3m$ has better electronic properties and more capacity.

![Figure 6. Electric charge density difference of (a) LiNi$_{0.5}$Mn$_{1.5}$O$_4$-$Fd$-$3m$ (b) LiNi$_{0.5}$Mn$_{1.5}$O$_4$-$P4_332$.](image)
4. CONCLUSIONS

In conclusion, we have investigated structural and properties of the LiNi0.5Mn1.5O4-Fd-3m and LiNi0.5Mn1.5O4-P432. The calculated results indicate that the crystal structure of the LiNi0.5Mn1.5O4-Fd-3m is benefit to the transition of lithium compared with LiNi0.5Mn1.5O4-P432. Due to the charge overlap of LiNi0.5Mn1.5O4-P432 around Mn, Ni and O atoms significantly increased compared with LiNi0.5Mn1.5O4-Fd-3m, which form a stable bond, therefore their structure is significantly increased. The lengths of the bonds of LiNi0.5Mn1.5O4-P432 are shorter than that of the LiNi0.5Mn1.5O4-Fd-3m, indicating that the energy of the bond is smaller, thus the structure of LiNi0.5Mn1.5O4-P432 is more stable, but the Mn-Mn bonds hinder the shuttle movement of lithium ions, so the cycle performance of LiNi0.5Mn1.5O4-Fd-3m may better than that of LiNi0.5Mn1.5O4-P432.

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References

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