Effect of High Levels of Impurity Calcium on the Electrochemical Performance of Spinel LiMn$_2$O$_4$

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**Abstract:** Spinel LiMn$_2$O$_4$ was synthesized by solid-state method, using Mn$_2$O$_3$ as manganese source. By X-ray diffraction, scanning electron microscope and electrochemical performance test, effects of impurity calcium from manganese source, i.e., MnCO$_3$ on the electrochemical properties of spinel LiMn$_2$O$_4$ were systematically studied. The results showed that all samples with different contents of impurity calcium were indexed to spinel phase with the cubic space of Fd3m, and no impurity phase was detected; the particle size and morphology of samples were not obviously different; when the contents of impurity were low, the first charge-discharge capacity remained almost unchanged with the increase of calcium; and in contrast, it distinctly decreased. The results also showed that the cycle-stability of LiMn$_2$O$_4$ was improved collaboratively.

With the rapid development of the global economy, it is bound to increase consumption such as the oil and other fossil fuel resources. The lithium-ion secondary battery, called "green power", has attracted much more attention due to the most prominent features such as its small, lightweight, long working hours, long cycle life, no memory effect, fast charge and discharge, low self-discharge and environmental friendly etc.\[1,2\]. Owing to the serious attenuation of charge-discharge reversible capacity, instability and other shortcomings on electrochemical properties of the spinel LiMn$_2$O$_4$, its development is facing with lots of restriction \[3, 4, 5\]. Much work has been done in an effort to improve the electrochemical performance of the spinel LiMn$_2$O$_4$ by suppressing Jahn-Teller distortion. Ma\[6\] studied the influence of different manganese sources on the performance of spinel LiMn$_2$O$_4$, finding that the spinel LiMn$_2$O$_4$ synthesized by Mn$_2$O$_3$ exhibited dense particles, uniform distribution and the most excellent electrochemical performance. The price of high-purity Mn$_2$O$_3$ is significantly higher than electrolytic manganese dioxide (EMD), but the value of the industrial-grade Mn$_2$O$_3$ is lower than EMD. Industrial-grade Mn$_2$O$_3$ contains large amounts of impurities such as Ca$^{2+}$, Mg$^{2+}$, SiO$_3^{2-}$, SO$_4^{2-}$, K$^+$, Na$^+$. Peng\[7\] discussed the electrochemical properties of the spinel LiMn$_2$O$_4$ prepared by Mn$_2$O$_3$ that containing K$^+$, showing that its first charge-discharge capacity drastically decreased and the capacity retention also declined with the increase of K$^+$. Xie[8] researched the electrochemical properties of the spinel LiMn$_2$O$_4$ that containing Ca$^{2+}$ and Mg$^{2+}$, illustrating that morphology of the samples was improved and cycle performance was enhanced with the increase of Ca$^{2+}$ and Mg$^{2+}$. However, no relevant literatures are reported on the effects of Mn$_2$O$_3$ that containing high contents of impurity calcium on the electrochemical properties of the spinel LiMn$_2$O$_4$. In this paper, spinel LiMn$_2$O$_4$ is synthesized by solid-state method, using Mn$_2$O$_3$ that containing high contents of impurity calcium as manganese source, and the electrochemical properties of the batteries and the microscopic appearance of the spinel LiMn$_2$O$_4$ will be studied.

1 Experiment

1.1 Preparation of Spinel LiMn$_2$O$_4$ and Battery

All the manganese sources were prepared in laboratory. LiCO$_3$ is produced by Shanghai Li Industrial Company Limited. Different manganese sources and LiCO$_3$ were weighed in Li/Mn at molar ratios of 1:2 and then completely mixed in an agate mortar for grinding. Then took the
mixture into a corundum crucible and heated to 560 ºC at 3 ºC/min in air, 5h later raised to 780 ºC at
the same heating rate, after 48 hours heat preservation, the raw materials were cooled down to room
temperature, then passed through 200 mesh sieve, finally achieved the spinel LiMn2O4 as cathode
material. The cathode material, the conductive agent (acetylene black) and the
polytetrafluoroethylene (PTFE) emulsion were uniformly mixed according to the mass ratio of
85:10:5 accurately, and dried in an oven for 24h at 110ºC. Subsequently the mixture was pressed
into 5~10mg weight, 0.1mm thick slices, and then it was rushed into a wafer with a φ8 punch, thus
the positive films were obtained. The lithium tablets were used as anode materials and 1.0M
commercial LiPF6 in DMC: EC: DEC (1:1:1 in volume) as the electrolyte. And then they are
assembled the CR2032 button-type batteries in an argon-filled glove-box.

1.2 Characterization and Electrochemical Measurements

The crystal structure of the materials was analyzed by an X-ray diffraction operated at 40KV and
150mA from 10° to 90° (Rigaku, D/Max-RB, Japan) with a wavelength of Cu Kα (λ =0.15406nm).
Scanning electron microscopy (SEM) was obtained through a spectrometer (SEM, Hitachi S-3400N
Japan). Electrical performance test was carried out using a NEWARE tester, Charge-discharge
cycles were carried out at 0.1C in CR2023 coin cells, with a potential range between 3.0 and 4.3V
at room temperature.

2 Results and Discussion

2.1 Effect of Manganese Source with Low Levels of Calcium on the Performance of Spinel
Li1.06Mn2O4

Table 1 The contents of calcium in Mn2O3 and corresponding electrical properties of Li1.06Mn2O4 as
cathode materials

<table>
<thead>
<tr>
<th>Samples</th>
<th>Ca2+ (μg•g−1)</th>
<th>The first charge capacity of Li1.06Mn2O4 (mA•h•g−1)</th>
<th>The first discharge capacity of Li1.06Mn2O4 (mA•h•g−1)</th>
<th>Discharge capacity retention rate after 50 cycles (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>High purity</td>
<td>49</td>
<td>133.910</td>
<td>128.487</td>
<td>89.15</td>
</tr>
<tr>
<td>1-1</td>
<td>492</td>
<td>133.229</td>
<td>127.065</td>
<td>89.95</td>
</tr>
<tr>
<td>1-2</td>
<td>2240</td>
<td>132.483</td>
<td>126.902</td>
<td>90.68</td>
</tr>
<tr>
<td>1-3</td>
<td>4560</td>
<td>131.271</td>
<td>126.191</td>
<td>92.17</td>
</tr>
<tr>
<td>1-4</td>
<td>7747</td>
<td>129.825</td>
<td>125.035</td>
<td>92.93</td>
</tr>
</tbody>
</table>

Samples with low contents of Ca2+ are listed in Table 1.

Figure 1 shows the first charge-discharge curves of Li1.06Mn2O4 containing Ca2+ at lower range.
As shown in the figure, all the curves have two distinct charge-discharge platforms at 4.0V and 4.1V,
ilustrating that all the samples undergo two reversible electrochemical reactions in the vicinity of
the two electrodes, the former corresponds to the escape of lithium-ions from the tetrahedral 8a
position, the latter corresponds to the intercalation of lithium-ions from the empty octahedral 16c
position. The first charge-discharge capacities of Li1.06Mn2O4 remain almost unchanged with the
increase of Ca2+.

Figure 2(a) reveals cycling-curves of discharge-capacity of spinel Li1.06Mn2O4 after 50 cycles. It
can be seen from the figure that cyclic stability of lithium-rich Li1.06Mn2O4 is improved with the
increase of impurity Ca2+, it is the reason that impurity Ca2+ replaces part of Mn3+ (16d) which
results in improvement of morphology and more dispersion of the particles. So the electrolyte keeps
in contact with the active materials more fully.
Figure 1 The initial charge-discharge curves of synthetic Li$_{1.06}$Mn$_2$O$_4$ with low levels of calcium

Figure 2 The discharge-cycle characteristics (a) and XRD patterns (b) of synthetic Li$_{1.06}$Mn$_2$O$_4$ with low levels of calcium

Figure 2(b) is the XRD patterns of synthetic lithium-rich Li$_{1.06}$Mn$_2$O$_4$ with low contents of calcium. All synthetic samples are indexed to spinel phase with the cubic space of Fd3m, which are in agreement with that of standard spinel LiMn$_2$O$_4$. No peaks of calcium compounds are detected in each sample with the increase of calcium, which may be related to the fact that the content of impurity calcium is small. Additionally, the spinel lattice sizes of the as-prepared samples calculated according to the XRD patterns are from 0.8249 nm to 0.8245 nm, their changes are not obvious.

Figure 3 is the SEM of the Li$_{1.06}$Mn$_2$O$_4$ containing low levels of Ca$^{2+}$. It can be seen from the figure that all samples display dense spherical particles. The cathode materials synthesized by MnCO$_3$ also exhibit fine and evenly distributed particles, but there is a certain amount of agglomeration. Particles progressively become much larger, agglomeration is improved with the increase of Ca$^{2+}$. That is especially obvious for sample 1-4, the particles become more dispersed and the agglomeration is improved more distinctly.
Figure 3 The SEM of synthetic Li$_{1.06}$Mn$_2$O$_4$ with low levels of calcium
(a: Li$_{1.06}$Mn$_2$O$_4$, b: 1-1, c: 1-2, d: 1-3, e: 1-4)

2.2 Effect of Manganese Source with High Levels of Calcium on the Performance of Spinel LiMn$_2$O$_4$

Table 2 The contents of calcium in Mn$_2$O$_3$ and corresponding electrical properties of LiMn$_2$O$_4$ as cathode materials

<table>
<thead>
<tr>
<th>Samples</th>
<th>$\text{Ca}^{2+}$ (μg•g$^{-1}$)</th>
<th>The first charge capacity of LiMn$_2$O$_4$(mA•h•g$^{-1}$)</th>
<th>The first discharge capacity of LiMn$_2$O$_4$(mA•h•g$^{-1}$)</th>
<th>Discharge capacity retention rate after 50 cycles (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>High purity</td>
<td>20.85</td>
<td>137.939</td>
<td>126.856</td>
<td>69.47</td>
</tr>
<tr>
<td>2-1</td>
<td>7640.99</td>
<td>122.035</td>
<td>115.900</td>
<td>72.38</td>
</tr>
<tr>
<td>2-2</td>
<td>8659.93</td>
<td>120.805</td>
<td>114.276</td>
<td>82.42</td>
</tr>
<tr>
<td>2-3</td>
<td>11336.00</td>
<td>104.561</td>
<td>101.130</td>
<td>84.64</td>
</tr>
<tr>
<td>2-4</td>
<td>15103.58</td>
<td>98.300</td>
<td>97.179</td>
<td>86.89</td>
</tr>
</tbody>
</table>

Samples with high contents of $\text{Ca}^{2+}$ are listed in Table 2.

Figure 4(a) is the first charge-discharge curves of LiMn$_2$O$_4$ with high contents of $\text{Ca}^{2+}$. It can be seen from the figure that all the charge-discharge curves have two obvious platforms, corresponding to the insertion and prolapse of lithium-ions respectively. With the increase of calcium, it appears seriously damped for the first charge-discharge capacity of LiMn$_2$O$_4$. Especially, first charge-discharge capacity decays obviously for sample 2-4. The severe capacity loss is mainly due to the decrease of active substance Mn$^{3+}$ of the spinel material. Replacement of Mn$^{3+}$-ions by Ca$^{2+}$-ions forms LiMn$_{2-x}$Ca$_x$O$_4$, which results in decrease of active-ions Mn$^{3+}$ and obstacle of Li$^+$ diffusion in the process of charge-discharge. To reach the charge balance, the amount of Mn$^{4+}$-ion inevitably increases in the spinel structure. The increased Li/Mn ratio suggests the Li$^+$-ions would diffuse into the octahedral sites to occupy the Mn sites to form LiMn$_{2-y}$Li$_y$O$_4$ [9]. And the increase of the ratio of Mn$^{4+}$/Mn$^{3+}$ in the spinel LiMn$_2$O$_4$ would reduce the spinel lattice size because the radius of Mn$^{3+}$-ion is larger than that of Mn$^{4+}$-ion. As a result, the charge-discharge capacity decreases...
along with it.

Figure 4(b) is the cyclic performance-curves of LiMn$_2$O$_4$containing high levels of Ca$^{2+}$ at room temperature. It can be obtained from figure that the samples with high levels of Ca$^{2+}$-ion exhibit more excellent cycle stability than the sample without Ca$^{2+}$-ion (high-purity). This is mainly because the discharge capacity can be affected by the relative crystallinity of synthesized samples, while the Ca$^{2+}$-ion will have a large impact on the crystallization quality. The adjunction of Ca$^{2+}$-ion reduces the unit cell volume of the spinel LiMn$_2$O$_4$, and bond length of Ca-O is stronger than Mn-O on the basis of standard Gibbs energies, thereby the crystal structure is enhanced and Jahn-Teller is effectively suppressed. As a result, it is more conducive to deintercalation of the lithium-ions and the improvement of cycling performance of the samples.

Figure 5 is the XRD spectra of LiMn$_2$O$_4$ with high contents of calcium. It can be seen from the figure that all the diffraction peaks completely match with the cubic spinel structure with space group of Fd3m, indicating that the calcium substitution does not change the intrinsic spinel structure of LiMn$_2$O$_4$ (Joint Committee on Powder Diffraction Standards (JCPDS) no. 18-0736), in which lithium ions occupy the tetrahedral 8a sites, manganese ions occupy the octahedral 16d sites, and oxygen ions occupy the 32e sites $^{[11]}$. X-ray diffraction patterns also reveal that the materials are good crystallinity and no diffraction peak of impurity can be discovered. It is believed that Ca$^{2+}$-ion completely occupies the Mn$^{3+}$-ion (16d) site in LiMn$_{2-x}$Ca$_x$O$_4$, which stabilizes the structures of the materials.

![Figure 4](image1.png)  ![Figure 5](image2.png)
Figure 6 is SEM images of the LiMn$_2$O$_4$ containing high levels of Ca$^{2+}$. From the view of microstructure, all cathode materials present irregular-shaped particles and uneven particle size distribution. Furthermore, it is important to note that the substitution of Ca$^{2+}$-ion contributes to improving the crystallization and decrease of the average microscopic particle size of obtained products. That is especially obvious for sample 2-4, the particles with good crystallization have more regular morphology, which leads to shortening the paths of prolapse-embedded of the lithium-ions and decrease of polarization effects of Li$^+$-ions. Simultaneously, agglomeration of the electrode materials is improved and the particles become more small dense with the increase of Ca$^{2+}$-ion. Additionally, the increase of specific surface area results in the more sufficient contact between the cathode material and the electrolyte.

Conclusions

(1) The Li$_{1.06}$Mn$_2$O$_4$ samples containing low contents of calcium are synthesized by solid-state method, using Mn$_2$O$_3$ as manganese source. The samples are indexed to spinel phase with the cubic space of Fd3m, small and distributed particles and no agglomeration. Particles become more dispersed with the increase of calcium. The first charge and discharge capacities of assembled batteries remain almost unchanged, and the efficiency of the first charge-discharge and the retention rate of 50 cycles are improved.

(2) The LiMn$_2$O$_4$ samples containing high contents of calcium are synthesized by solid-state method, using Mn$_2$O$_3$ as manganese source. The samples completely match with the cubic spinel structure with space group of Fd3m, particle size distribution is more discrete and there is a certain amount of agglomeration. The initial charge-discharge capacities emerge seriously attenuated with the increase of calcium, but stability of 50-cycles is significantly improved.

(3) Comprehensive results show that effects of manganese source with low contents of calcium on the electrochemical properties of lithium manganese oxide are beneficial. Only when the content
of calcium is higher, it is obviously adverse to electrochemical properties of lithium manganese oxide.

References


[8] Xing Zou, Haichao Xie, Gui Chen. Effect of Li Doping on Electrochemical Performances of Spinel LiMn2O4 prepared by Mn2O3 [C]. Elecric Technology and Civil Engineering, 2:690-693.

