Enhanced Electrochemical Performance of Si-doped LiMn$_2$O$_4$ Cathode Material for LiBs Prepared using Mn$_3$O$_4$ Octahedrons

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We proposed a co-modification strategy of Si-doping and octahedral morphology to improve the electrochemical performance of LiMn$_2$O$_4$. The Si-doped LiMn$_2$O$_4$ sample (LiSi$_{0.05}$Mn$_{1.95}$O$_4$ octahedrons) was prepared by high-temperature solid-state method with Mn$_3$O$_4$ octahedrons as manganese precursor and SiO$_2$ nanoparticles as silicon dopant. XRD and SEM characterization results indicated that the introduction of Si$^{4+}$ ions does not produce the substantive impact on the inherent spinel structure of LiMn$_2$O$_4$ and LiSi$_{0.05}$Mn$_{1.95}$O$_4$ octahedrons present relatively uniform particle size distribution. When cycled at 1.0 C, LiSi$_{0.05}$Mn$_{1.95}$O$_4$ octahedrons exhibited higher initial reversible capacity than that of the undoped LiMn$_2$O$_4$. After 100 cycles, LiSi$_{0.05}$Mn$_{1.95}$O$_4$ octahedrons showed better cycling stability with higher capacity retention rate of 94.7%. Moreover, LiSi$_{0.05}$Mn$_{1.95}$O$_4$ octahedrons presented good rate capability and high-temperature cycling performance. Such good electrochemical performance has much to do with the synergistic modification of Si-doping and octahedral morphology.

**Keywords:** LiMn$_2$O$_4$; Silicon doping; Octahedral morphology; Mn$_3$O$_4$ octahedrons; Electrochemical performance

1. INTRODUCTION

Lithium manganate oxide (LiMn$_2$O$_4$) is very important cathode material for lithium-ion batteries (LiBs). Compared with other commercial cathode materials, LiMn$_2$O$_4$ possesses several advantages such as high voltage platform, abundant manganese resource, and low production cost, which promote the widespread use of LiMn$_2$O$_4$ in the field of energy storage and low-speed electric vehicles [1-6]. However, the poor cycling performance of LiMn$_2$O$_4$ seriously affects the large-scale application of this cathode material to some extent.

To enhance the cycling performance, many scientific researchers optimized the electrochemical performance of LiMn$_2$O$_4$ by using several modification strategies such as doping modification [7-15],...
surface coating, controlling nanoparticles granularity, and so on. Among these strategies, the doping modification performs an important role in enhancing the electrochemical performance of LiMn$_2$O$_4$. The doping ions mainly involve the low valent cations (Cu$^{2+}$, Mg$^{2+}$, Al$^{3+}$)[3, 11, 16], high valent cations (Si$^{4+}$, Ti$^{4+}$)[17-19]. Among them, the high valent cations mainly replace the tetravalent manganese ions, which can avoid the decrease of reversible capacity [5, 18]. It has been reported that the Si-doping strategy can contribute to the increase of reversible capacity and improvement of cycling stability [17, 20]. LiMn$_2$O$_4$ nanoparticles, and Mn$^{2+}$ nanoparticles, and LiSi$^{4+}$ nanoparticles were obtained mixture was sintered at 780 °C for 10 h in muffle furnace. First of all, the undoped spinel, the Si-doped LiMn$_2$O$_4$ sample presented a higher initial discharge capacity with better cycling stability. Zhao prepared the LiSi$_3$Mn$_{2-x}$O$_4$ samples by using electrolytic manganese dioxide (EMD) as manganese precursor and tetraethylorthosilicate as silicon dopant [20]. These research works indicate that a certain amount of silicon ions can effectively enhance the electrochemical performance of LiMn$_2$O$_4$.

In this work, the LiSi$_{0.05}$Mn$_{1.95}$O$_4$ octahedrons were prepared by high-temperature solid-state method with Mn$_3$O$_4$ octahedrons as manganese precursor and SiO$_2$ nanoparticles as silicon dopant. Compared with the undoped LiMn$_2$O$_4$, the introduction of Si$^{4+}$ ions does not produce the substantive impact on the inherent spinel structure of LiMn$_2$O$_4$. Electrochemical testing shows that the LiSi$_{0.05}$Mn$_{1.95}$O$_4$ octahedrons showed good electrochemical performance.

2. EXPERIMENTAL

To prepare the Si-doped LiMn$_2$O$_4$ sample, Mn$_3$O$_4$ octahedrons and SiO$_2$ nanoparticles were applied as manganese precursor and silicon dopant. The LiSi$_{0.05}$Mn$_{1.95}$O$_4$ octahedrons were prepared by high-temperature solid-state method. First of all, Mn$_3$O$_4$ octahedrons were prepared by hydrothermal method according to the previous work [21]. A certain amount of potassium permanganate (KMnO$_4$, 4.5 g) and ethylene glycol (C$_2$H$_4$O$_2$, 7.5 ml) were dissolved successively in deionized water (100 ml). The obtained suspension was sealed in 150 ml Teflon-lined stainless steel autoclave and then maintained at 150 °C for 20 h. Based on the hydrothermal reaction process, Mn$_3$O$_4$ octahedrons was obtained by suction filtration and dried at 80 °C for 15 h. And then, the stoichiometric mixture of LiOH·H$_2$O, SiO$_2$ nanoparticles, and Mn$_3$O$_4$ octahedrons were thoroughly mixed with the help of ethanol. Finally, the obtained mixture was sintered at 780 °C for 10 h in muffle furnace. By contrast, both the undoped LiMn$_2$O$_4$ and LiSi$_{0.05}$Mn$_{1.95}$O$_4$ particles were prepared through the similar solid state reaction process with electrolytic MnO$_2$ as manganese precursor.

The microstructures and surface morphologies of the undoped LiMn$_2$O$_4$ particles, LiSi$_{0.05}$Mn$_{1.95}$O$_4$ particles, and LiSi$_{0.05}$Mn$_{1.95}$O$_4$ octahedrons were characterized by X-ray diffraction (XRD) and scanning electron microscope (SEM). XRD pattern was used to confirm the influence of Si-doping on the microstructure of LiMn$_2$O$_4$, and SEM image was applied to study the influence of Si-doping on the surface morphology of LiMn$_2$O$_4$. The electrochemical performance of the undoped LiMn$_2$O$_4$ particles, LiSi$_{0.05}$Mn$_{1.95}$O$_4$ particles, and LiSi$_{0.05}$Mn$_{1.95}$O$_4$ octahedrons were tested by LANHE CT2001A battery tester.
3. RESULTS AND DISCUSSION

Figure 1. XRD patterns of (a) LiMn$_2$O$_4$ particles, (b) LiSi$_{0.05}$Mn$_{1.95}$O$_4$ particles, and (c) LiSi$_{0.05}$Mn$_{1.95}$O$_4$ octahedrons.

Figure 1 shows the XRD patterns of the undoped LiMn$_2$O$_4$ particles, LiSi$_{0.05}$Mn$_{1.95}$O$_4$ particles, and LiSi$_{0.05}$Mn$_{1.95}$O$_4$ octahedrons. As shown here, both LiMn$_2$O$_4$ particles and LiSi$_{0.05}$Mn$_{1.95}$O$_4$ particles present obvious characteristic diffraction peaks of LiMn$_2$O$_4$ (JCPDS No. 35-0782) [12, 22].

Figure 2. SEM images of (a, b) LiMn$_2$O$_4$ particles, (c, d) LiSi$_{0.05}$Mn$_{1.95}$O$_4$ particles, and (e, f) LiSi$_{0.05}$Mn$_{1.95}$O$_4$ octahedrons.

No other impurity peaks of MnO$_2$ or SiO$_2$ can be observed in the above XRD patterns, which suggests the successful transformation of electrolytic MnO$_2$ to LiMn$_2$O$_4$ and integration of Si$^{4+}$ ions in the crystal structure of LiMn$_2$O$_4$ [20]. For the LiSi$_{0.05}$Mn$_{1.95}$O$_4$ octahedrons, the corresponding XRD
pattern shows similar characteristic diffraction peaks of LiMn$_2$O$_4$ without any other impurity peaks of Mn$_3$O$_4$ and SiO$_2$, which indicates that Mn$_3$O$_4$ octahedrons were completely converted to the LiSi$_{0.05}$Mn$_{1.95}$O$_4$ sample [21, 23]. Furthermore, there is no (220) peak in the above XRD patterns of LiSi$_{0.05}$Mn$_{1.95}$O$_4$ particles and LiSi$_{0.05}$Mn$_{1.95}$O$_4$ octahedrons. It has been reported that the emergence of (220) peak means the colonization of doped cations at tetrahedral (8a) sites [13, 24]. Thus, it can be inferred that Si$^{4+}$ ions only replace Mn$^{4+}$ ions at octahedral (16d) sites, which can enhance the spinel structural stability.

Figure 2 shows the SEM images of the undoped LiMn$_2$O$_4$ particles, LiSi$_{0.05}$Mn$_{1.95}$O$_4$ particles, and LiSi$_{0.05}$Mn$_{1.95}$O$_4$ octahedrons. It can be seen from Figure 2(a, b) that the undoped LiMn$_2$O$_4$ particles show uneven particle size distribution. Some large agglomerated particles can be observed in the above SEM images. By contrast, the LiSi$_{0.05}$Mn$_{1.95}$O$_4$ particles shown in Figure 2(c, d) present relatively uniform particle size distribution, which has much to do with the introduction of Si$^{4+}$ ions [17, 20]. The introduction of Si$^{4+}$ ions contributes to the inhibition of large agglomerated particles, and the Si-doped LiMn$_2$O$_4$ sample can present uniform particle size distribution compared to the undoped LiMn$_2$O$_4$ particles. It should be noted that the LiSi$_{0.05}$Mn$_{1.95}$O$_4$ particles shown in Figure 2(c, d) also possess octahedral morphology. However, the corresponding particle size range is larger than that of LiSi$_{0.05}$Mn$_{1.95}$O$_4$ octahedrons shown in Figure 2(e, f). For the LiSi$_{0.05}$Mn$_{1.95}$O$_4$ octahedrons, the particle size distribution is completely different from that of the undoped LiMn$_2$O$_4$ particles and LiSi$_{0.05}$Mn$_{1.95}$O$_4$ particles. The obtained LiSi$_{0.05}$Mn$_{1.95}$O$_4$ octahedrons present uniform particle size distribution with smaller particle size, which may enhance the electrochemical performance of LiMn$_2$O$_4$.

![Figure 3. Initial charge-discharge curves of the undoped LiMn$_2$O$_4$ particles, LiSi$_{0.05}$Mn$_{1.95}$O$_4$ particles, and LiSi$_{0.05}$Mn$_{1.95}$O$_4$ octahedrons.](image)
Figure 3 shows the initial charge-discharge curves of the undoped LiMn$_2$O$_4$ particles, LiSi$_{0.05}$Mn$_{1.95}$O$_4$ particles, and LiSi$_{0.05}$Mn$_{1.95}$O$_4$ octahedrons. These three samples were cycled at 0.5 C under the room temperature environment. It can be clearly observed that there are two obvious voltage platforms in the initial discharge curves of the undoped LiMn$_2$O$_4$ particles. For the LiSi$_{0.05}$Mn$_{1.95}$O$_4$ particles and LiSi$_{0.05}$Mn$_{1.95}$O$_4$ octahedrons, the corresponding voltage platforms coincide quite well with that of the undoped LiMn$_2$O$_4$ particles, which suggests that the introduction of Si$^{4+}$ ions does not change the lithium intercalation process of electrochemical cycling [17, 20].

![Figure 3](image1.png)

**Figure 4.** Cycling performance of the undoped LiMn$_2$O$_4$ particles, LiSi$_{0.05}$Mn$_{1.95}$O$_4$ particles, LiSi$_{0.05}$Mn$_{1.95}$O$_4$ octahedrons at 0.5 C.

![Figure 4](image2.png)

**Figure 5.** Histogram comparsion of initial discharge capacity and capacity retention of the undoped LiMn$_2$O$_4$ particles, LiSi$_{0.05}$Mn$_{1.95}$O$_4$ particles, LiSi$_{0.05}$Mn$_{1.95}$O$_4$ octahedrons at 0.5 C.
Figure 4 presents the cycling performance of the undoped LiMn$_2$O$_4$ particles, LiSi$_{0.05}$Mn$_{1.95}$O$_4$ particles, LiSi$_{0.05}$Mn$_{1.95}$O$_4$ octahedrons at 0.5 C. It can be seen that the undoped LiMn$_2$O$_4$ particles exhibit poor cycling stability with low capacity retention rate of 78.4%. For the Si-doped LiMn$_2$O$_4$ samples, both LiSi$_{0.05}$Mn$_{1.95}$O$_4$ particles and LiSi$_{0.05}$Mn$_{1.95}$O$_4$ octahedrons show relatively better cycling stability (91.7% and 95.9%) compared to the undoped LiMn$_2$O$_4$ particles. Especially, the LiSi$_{0.05}$Mn$_{1.95}$O$_4$ octahedrons exhibit the best cycling stability with highest initial discharge capacity of 123.2 mAh g$^{-1}$ and capacity retention. The change trend of initial discharge capacity and capacity retention of these three samples can be intuitively observed by Figure 5. Compared with the undoped LiMn$_2$O$_4$ particles, the good electrochemical performance is intimately connected to the co-modification of Si-doping and octahedral morphology of LiSi$_{0.05}$Mn$_{1.95}$O$_4$ octahedrons with uniform particle size distribution [17, 23, 25].

![Graph](image_url)

**Figure 6.** Long cycling performance of the undoped LiMn$_2$O$_4$ particles and LiSi$_{0.05}$Mn$_{1.95}$O$_4$ octahedrons at 1.0 C.

Figure 6 shows the long cycling performance of the undoped LiMn$_2$O$_4$ particles and LiSi$_{0.05}$Mn$_{1.95}$O$_4$ octahedrons at 1.0 C. The undoped LiMn$_2$O$_4$ particles show an initial discharge capacity of 113.1 mAh g$^{-1}$. With the increasing of cycling number, the discharge capacity presents a severe attenuation with relatively low retention rate of 75.3% after 100 cycles. For the Si-doped LiMn$_2$O$_4$ sample, LiSi$_{0.05}$Mn$_{1.95}$O$_4$ octahedrons show relatively good electrochemical performance due to the co-modification of Si-doping and octahedral morphology [17, 21, 23]. The initial discharge capacity of LiSi$_{0.05}$Mn$_{1.95}$O$_4$ octahedrons reach up to 118.7 mAh g$^{-1}$. After 100 cycles, the corresponding capacity retention increases to 94.7%. Such good electrochemical performance has much to do with the synergistic effect of Si-doping and octahedral morphology. Table 1 Comparison of LiSi$_{0.05}$Mn$_{1.95}$O$_4$ octahedrons and LiMn$_2$O$_4$-based cathode materials reported by other works. The comparison result can further confirm the positive role of Si-doping and octahedral morphology. Compared with the undoped LiMn$_2$O$_4$ nanoparticles, the Si-doped LiMn$_2$O$_4$ sample can show higher initial discharge capacity, and
the octahedral morphology can enhance the cycling stability of LiMn$_2$O$_4$. The Si-doping can provide the more expanded and regular MnO$_6$ octahedra, which achieves the better accommodation of Mn(III)–Mn(IV) interconversion during the electrochemical cycling process [17, 20]. Moreover, the octahedral morphology enhances the structure stability by suppressing the manganese dissolution [22, 26, 27]. The above positive function contributes to the good electrochemical performance of LiSi$_{0.05}$Mn$_{1.95}$O$_4$ octahedrons.

**Table 1** Comparison of LiSi$_{0.05}$Mn$_{1.95}$O$_4$ octahedrons and LiMn$_2$O$_4$-based cathode materials reported by other works [17, 20, 22].

<table>
<thead>
<tr>
<th>Sample</th>
<th>Cycling condition</th>
<th>Initial capacity (mAh g$^{-1}$)</th>
<th>Capacity retention (%)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiMn$_2$O$_4$ nanoparticles</td>
<td>1.0 C, 100 cycles</td>
<td>114.0</td>
<td>87.8</td>
<td>[22]</td>
</tr>
<tr>
<td>Si-doped LiMn$_2$O$_4$ particles</td>
<td>0.5 C, 100 cycles</td>
<td>134.6</td>
<td>85.1</td>
<td>[20]</td>
</tr>
<tr>
<td>LiSi$<em>{0.05}$Mn$</em>{1.95}$O$_4$ particles</td>
<td>1.0 C, 300 cycles</td>
<td>139</td>
<td>75</td>
<td>[17]</td>
</tr>
<tr>
<td>LiSi$<em>{0.05}$Mn$</em>{1.95}$O$_4$ octahedrons</td>
<td>1.0 C, 100 cycles</td>
<td>118.7</td>
<td>94.7%</td>
<td>This work</td>
</tr>
</tbody>
</table>

**Figure 7.** Rate stability of the undoped LiMn$_2$O$_4$ particles and LiSi$_{0.05}$Mn$_{1.95}$O$_4$ octahedrons.

Figure 7 presents the rate performance of the undoped LiMn$_2$O$_4$ particles and LiSi$_{0.05}$Mn$_{1.95}$O$_4$ octahedrons. It can be found that the discharge capacity is intimately connected to the cycling rate. When cycled at the low rate of 0.5 C, the discharge capacities of the undoped LiMn$_2$O$_4$ particles and LiSi$_{0.05}$Mn$_{1.95}$O$_4$ octahedrons have no obvious difference.
Figure 8. Cycling performance of the undoped LiMn$_2$O$_4$ particles and LiSi$_{0.05}$Mn$_{1.95}$O$_4$ octahedrons at 55 °C.

Figure 9. Rate capability of the undoped LiMn$_2$O$_4$ particles and LiSi$_{0.05}$Mn$_{1.95}$O$_4$ octahedrons at 55 °C.

However, as the cycling rate increases, the corresponding discharge capacity gradually show obvious change. When the cycling rate increases to 5.0 C, the undoped LiMn$_2$O$_4$ particles exhibit fairly small discharge capacity of 52.3 mAh g$^{-1}$, which is 45.2% of the initial discharge capacity of the undoped LiMn$_2$O$_4$ at 0.5 C. For the LiSi$_{0.05}$Mn$_{1.95}$O$_4$ octahedrons, the corresponding discharge capacity can reach up to 92.5 mAh g$^{-1}$, which is 75.1% of the initial discharge capacity of this Si-doped spinel at 0.5 C. Such good performance has much to do with the synergistic effect of Si-doping and octahedral morphology of the LiSi$_{0.05}$Mn$_{1.95}$O$_4$ octahedrons [17, 23, 27].
Figure 8 presents the cycling performance of the undoped LiMn$_2$O$_4$ particles and LiSi$_{0.05}$Mn$_{1.95}$O$_4$ octahedrons at 55 °C, and the cycling rate is set to be 1.0 C. It can be found that the combination of Si-doping and octahedral morphology performs an important role in the improvement of high-temperature electrochemical performance. The undoped LiMn$_2$O$_4$ particles exhibit poor cycling stability with lower capacity retention rate of 58.9%. For the LiSi$_{0.05}$Mn$_{1.95}$O$_4$ octahedrons, the cycling stability was significantly improved with higher discharge capacity of 113.5 mAh g$^{-1}$, and the corresponding capacity retention rate reaches up to 95.3%. Figure 9 shows the high-temperature rate performance of the undoped LiMn$_2$O$_4$ particles and LiSi$_{0.05}$Mn$_{1.95}$O$_4$ octahedrons at 55 °C. It can be found that the discharge capacity is intimately connected to the cycling rate. When cycled at the low rate of 0.5 C, both LiMn$_2$O$_4$ particles and LiSi$_{0.05}$Mn$_{1.95}$O$_4$ octahedrons present similar discharge capacities (115.9 mAh g$^{-1}$ and 123.4 mAh g$^{-1}$). When the cycling rate increases to 5.0 C, the discharge capacity of the undoped LiMn$_2$O$_4$ particles rapidly decreases to 56.9 mAh g$^{-1}$. For the LiSi$_{0.05}$Mn$_{1.95}$O$_4$ octahedrons, the corresponding discharge capacity can reach up to 98.2 mAh g$^{-1}$. The above result further confirms the positive function of Si-doping and octahedral morphology on the electrochemical performance LiMn$_2$O$_4$.

4. CONCLUSIONS

The LiSi$_{0.05}$Mn$_{1.95}$O$_4$ octahedrons were prepared by high-temperature solid-state method with Mn$_3$O$_4$ octahedrons as manganese precursor and SiO$_2$ nanoparticles as silicon dopant. The co-modification strategy of Si-doping and octahedral morphology effectively enhances the electrochemical performance of LiMn$_2$O$_4$. The research result indicated that the Si-doping could provide more expanded and regular MnO$_6$ octahedrons, which achieved the good accommodation of Mn(III)–Mn(IV) interconversion during the electrochemical cycling process. Moreover, the octahedral morphology enhanced the structure stability by suppressing the manganese dissolution. The LiSi$_{0.05}$Mn$_{1.95}$O$_4$ octahedrons exhibited good cycling stability and rate performance, which may promote the widespread use of LiMn$_2$O$_4$.

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