Hydrothermal Synthesis of Li₂MnO₃-Stabilized LiMnO₂ as a Cathode Material for Li-Ion Battery

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Herein, we reported the composite structure of LiMnO₂ and Li₂MnO₃ as a low-cost and environmentally benign cathode material. This composite with the main phase of LiMnO₂ (90%) was synthesized by hydrothermal method at 220°C from LiOH and Mn(CH₃COO)₂ precursors. The obtained nanosized LiMnO₂-LiMnO₃ cathode material exhibits a high capacity of 265 mAh g⁻¹ at C/10. The incorporation of Li₂MnO₃ into the LiMnO₂ phase could stabilize the structure, leading to the improved cycle stability of the cathode. The capacity retention of the cathode was 93% after 80 cycles at C/2. Our results facilitate a potential strategy for developing high-performance cathode materials based on the Li-Mn-O system.

1. Introduction

Although lithium-ion batteries (LIBs) have a dominant position as the power source in mobile electronics, they still do not meet the growing demand for these power-consuming devices [1]. In addition, the reduction of product costs, including production costs and treatment costs that affect the environment after disposal, is of considerable concern to manufacturers. Accordingly, the use of inexpensive and environmentally friendly commercial cathode materials such as LiMn₂O₄ and Li₂MnO₃ as a low-cost and environmentally benign cathode material. This composite with the main phase of LiMnO₂ (90%) was synthesized by hydrothermal method at 220°C from LiOH and Mn(CH₃COO)₂ precursors. The obtained nanosized LiMnO₂-LiMnO₃ cathode material exhibits a high capacity of 265 mAh g⁻¹ at C/10. The incorporation of Li₂MnO₃ into the LiMnO₂ phase could stabilize the structure, leading to the improved cycle stability of the cathode. The capacity retention of the cathode was 93% after 80 cycles at C/2. Our results facilitate a potential strategy for developing high-performance cathode materials based on the Li-Mn-O system.

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2. Experimental

The integrated structure was synthesized by a hydrothermal method. First, manganese (II) acetate tetrahydrate (4.9 g, Sigma-Aldrich) and lithium hydroxide monohydrate (3.36 g, Sigma-Aldrich) were dissolved in distilled water (40 mL) separately. Then, hydrogen peroxide (H$_2$O$_2$, 30% (w/w) in H$_2$O, 1.6 mL) was added to the Li solution before adding Mn solution slowly. The mixture was mixed with methanol (20 mL) and stirred for 0.5 h. Subsequently, it was located into a Teflon-lined autoclave for the hydrothermal reaction at 220°C for 12 h. Finally, the powder was centrifuged and washed with ethanol and distilled water thoroughly.

The phase of the sample was identified by X-ray diffraction (XRD) measurements using Philips X’Pert with Cu-Kα radiation in a range of $10° \leq 2θ \leq 100°$. The morphology of particles was recorded by scanning electron microscopy (SEM, Nova NanoSEM 450) and high-resolution transmission electron microscopy (HRTEM, JOEL JEM-2100F). The oxidation state of elements was determined by X-ray photon spectroscopy (XPS, K-Alpha+ Thermo Scientific). The chemical composition was analyzed by ICP (Optima 8300 ICP-OES spectrometer).

For cathode fabrication, the active material (70 wt%), Ketjen black (10 wt%), and tefazonated acetylene black (binder, 20 wt%) were mixed thoroughly. Then, it was pressed onto a stainless-steel mesh and dried at 120°C. The main phase is o-LiMnO$_2$ with space group $Pmmn$ of the orthorhombic Li$_2$MnO$_3$ structure. There is a slightly weak peak that is assignable to the Li$_2$MnO$_3$ phase (space group $C2/m$). This second phase originated from the oxidation decomposition reaction [14]. All peaks are sharp, indicating the high crystallinity of particles. Note that the ratio of LiMnO$_2$ to Li$_2$MnO$_3$ phase can be changed by using an oxidizing agent [15] or controlling the synthesis temperature [16]. The ICP result shows that the ratio of Li : Mn = 1.095 : 1 due to the existence of the Li$_2$MnO$_3$ phase. Rietveld refinement is performed using the model shown in Table 1. The main phase is o-LiMnO$_2$ with space group $Pmmn$, and the second phase is Li$_2$MnO$_3$ with space group $C2/m$. In the o-LiMnO$_2$ structure, Mn and Li occupy the 2a Wyckoff site. The oxygen occupies the 2b Wyckoff site. The oxygen array is distorted from idea cubic-close packing due to Jahn-Teller effect on Mn$^{3+}$. The structure is built up from independent MnO$_6$ and LiO$_6$ octahedra that are arranged in corrugated layers. The Rietveld refinement shows that the degree of substitution of Li/Mn in the octahedra is about 5%. The cation disorder can improve the electrochemical performance of the cathode [17–19]. The lattice parameter of o-LiMnO$_2$ is slightly smaller than that in literature [20]. This might be caused by the effect of the Li$_2$MnO$_3$ phase.

SEM and TEM analyses were performed to study the particle’s morphology and are shown in Figure 2. Accordingly, the particles have a well-defined shape (Figure 2(a)). The particles are elongated, parallelogram-shaped grains. The particle size ranges from 100 to 400 nm. The d-spacing is calculated as 0.588 nm, which corresponds to the (010) plane at $2θ = 15°$. These results further confirm the predominance of the o-LiMnO$_2$ phase with good crystallinity of the particles.

To examine the oxidation state of Mn in the compound, XPS measurement was carried out and shown in Figure 3. The survey XPS profiles (Figure 3(a)) contain peaks at $\sim$641, 530, 285, and 55 eV, which are allocated for Mn 2p, O 1s, C 1s, and Li 1s, respectively. This indicates the presence of Li, Mn, C, and O in the sample. The presence of C is due to the absorption of CO$_2$ from the air onto the sample’s surface.

### Table 1: Rietveld refinement and crystal data obtained from the XRD data.

<table>
<thead>
<tr>
<th>Phase</th>
<th>o-LiMnO$_2$</th>
<th>Li$_2$MnO$_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Space group</td>
<td>$Pmmn$</td>
<td>$C2/m$</td>
</tr>
<tr>
<td>Phase fraction</td>
<td>90%</td>
<td>10%</td>
</tr>
<tr>
<td>$a$</td>
<td>4.5758</td>
<td>4.8660</td>
</tr>
<tr>
<td>$b$</td>
<td>5.7482</td>
<td>8.4210</td>
</tr>
<tr>
<td>$c$</td>
<td>2.8100</td>
<td>5.0257</td>
</tr>
<tr>
<td>$β$</td>
<td>108.9202</td>
<td></td>
</tr>
<tr>
<td>Li/Mn substitution</td>
<td>5%</td>
<td></td>
</tr>
<tr>
<td>Fitting quality</td>
<td>$R_p$ (%) = 5.35</td>
<td>$R_w$ (%) = 8.03</td>
</tr>
</tbody>
</table>

Figure 1: XRD pattern of prepared sample indexed against the standard o-LiMnO$_2$ (PDF #35-0749, space group $Pmmn$) and Li$_2$MnO$_3$ phase (PDF #84-1634, space group $C2/m$).
Figure 3(b) shows the Mn 2p core-level spectrum, which exhibits two peaks, namely, Mn 2p_{3/2} and Mn 2p_{1/2}. These peaks locate at 641.88 and 653.58 eV, respectively, with the spin-orbital splitting value of 11.7 eV. The binding energy of Mn 2p_{3/2} of the sample is in between binding energy of those in Mn_2O_3 (641.6 eV) and MnO_2 (642.6 eV) [24]. This result indicates the coexistence of both Mn^{3+} and Mn^{4+} in the sample. Figure 3(c) shows the Mn 3s spectrum to further evaluate the oxidation state of Mn. The splitting in Mn 3s spectrum is caused by the coupling of the nonionized 3s electron with 3d valence-band electrons, and its value indicates the oxidation state of Mn. Here, it is 5.3 eV so the oxidation state of Mn in the compound is +3.

Figure 4 shows the charge-discharge curve and the corresponding dQ/dV plot, measured between 2.0 and 4.8 V at C/10 rate (1C = 280 mA g^{-1}) at the 1^{st}, 2^{nd}, and 5^{th} cycles. The cell exhibits two charging voltage plateaus at 3.45 and 4.3 V. The plateau at 4.5 V which is typical for the activation
of Li$_2$MnO$_3$ does not appear. It might be caused by the small fraction of the Li$_2$MnO$_3$ phase. The plateaus at 3.45 V are irreversible due to the structural change. For the first discharge, there is a plateau at 4 V and a long plateau $\sim$3.0 V. The first charge and discharge capacity is 297 and 216 mAh g$^{-1}$, respectively. The low first Coulombic efficiency (72.7%) is due to the irreversible structural change during the first cycle of the LiMnO$_2$ and Li$_2$MnO$_3$ phase [4, 6, 25–31]. During cycling, the capacity contribution in the 4 V region increases, resulting in an increase in the overall capacity. After 5 cycles, the cathode could deliver a capacity of 265 mAh g$^{-1}$, which is higher than those reported in the literature [20, 32–37]. The $dQ/dV$ plot (Figure 4(b)) shows peaks that correspond to the plateaus observed in Figure 4(a). For the first cycle, the peak at 3.5 V is reversible while the peak at 4.3 V is reversible and there is a strong peak appearing at 2.9 V. For the subsequent cycles, the peak at 4.3 V shifts to lower voltage and induces two peaks at 3.8 and 4.0 V. These are typical peaks of spinel LiMnO$_4$, indicating the transformation of o-LiMnO$_2$ to a spinel-like phase during cycling [38].

A fresh cell was cycled 5 times at each C-rate including C/10, C/5, C/2, 1C, 2C, and 5C between 2.0 and 4.8 V to check its C-rate performance. Figure 5(a) shows the resulting discharge capacities. At C/10 rate, the highest capacity of 265 mAh g$^{-1}$ is obtained after 5 cycles. With increasing C-rate, the capacities decrease as expected. The capacity is 249, 226, 208, 180, and 103 mAh g$^{-1}$ for C/5, C/2, 1C, 2C, and 5C, respectively. The capacity is still as high as 263 mAh g$^{-1}$ at C/10 after a severe test at 5C. Figure 5(b) shows the cycling stability and Coulombic efficiency of the sample at C/2. The capacity increases gradually over the first 12 cycles due to the transition of o-LiMnO$_2$ to a new spinel-like phase [4, 39]. However, the transformation is slow in this compound due to the stabilization of the Li$_2$MnO$_3$ phase. After 80 cycles, the capacity retention is 93%. The Coulombic efficiency is close to 100%, indicating less energy loss during the charge-discharge process.
4. Conclusion

$\text{o-LiMnO}_2$ was successfully synthesized by the hydrothermal method. The XRD and XPS results show the existence of the Li$_3$MnO$_2$ phase. SEM and TEM analyses confirmed the presence of a dominant o-LiMnO$_2$ phase with particle sizes in the range of 100–400 nm. The galvanostatic cycling demonstrates a high capacity of 265 mAh g$^{-1}$ and 93% capacity retention after 80 cycles at C/2 could be achieved with this cathode. The structural change from the initial phase to the spinel-like phase is retarded due to the stabilization of the Li$_3$MnO$_2$ phase. Lastly, this work promotes environmentally friendly, low-cost, and high-capacity cathode materials for LIBs.

Data Availability

The data used to support the findings of this study are available from the corresponding author upon request.

Conflicts of Interest

The authors declare that there is no conflict of interest regarding the publication.

Acknowledgments

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References

[13] N. H. Vu, J. C. Im, S. Unithrattil, and W. B. Im, “Synergic coating and doping effects of Ti-modified integrated layered-spinel Li$_2$MnO$_{0.75}$Ni$_{0.25}$O$_2$ with a high capacity and long lifetime cathode material for Li-ion batteries,” Journal of Materials Chemistry A, vol. 6, no. 5, pp. 2200–2211, 2018.
[18] R. Wang, X. Li, L. Liu et al., “A disordered rock-salt Li-excess cathode material with high capacity and substantial oxygen redox activity: Li$_{1.25}$Ni$_{0.25}$Mn$_{0.5}$O$_{2}$,” Electrochemistry Communications, vol. 60, pp. 70–73, 2015.
Z. Zheng, W.-B. Hua, C. Yu et al., "Heterogeneous intergrowth $x$Li$_{1.5}$Ni$_{0.25}$Mn$_{0.75}$O$_{2.5}$ $(1 - x)$Li$_{0.5}$Ni$_{0.25}$Mn$_{0.75}$O$_2$ $(0 \leq x \leq 1)$ composites: synergistic effect on electrochemical performance," *Dalton Transactions*, vol. 44, no. 32, pp. 14255–14264, 2015.


D. Y. W. Yu, K. Yanagida, Y. Kato, and H. Nakamura, "Electrochemical activities in Li$_{2-x}$Mn$_x$O$_2$ (0 $\leq x \leq 3$):" *Journal of the Electrochemical Society*, vol. 156, no. 6, pp. A417–A424, 2009.

N. H. Vu, V.-D. Dao, H. Tran Huu, and W. B. Im, "Effect of synthesis temperature on structure and electrochemical performance of spinel-layered Li$_{1.33}$MnTiO$_{4+x}$ in Li-ion batteries," *Energies*, vol. 13, no. 11, p. 2962, 2020.


