Hydrothermal Synthesis of Li$_2$MnO$_3$-Stabilized LiMnO$_2$ as a Cathode Material for Li-Ion Battery

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Herein, we reported the composite structure of LiMnO$_2$ and Li$_2$MnO$_3$ as a low-cost and environmentally benign cathode material. This composite with the main phase of LiMnO$_2$ (90%) was synthesized by hydrothermal method at 220°C from LiOH and Mn(CH$_3$COO)$_2$ precursors. The obtained nanosized LiMnO$_2$-LiMnO$_3$ cathode material exhibits a high capacity of 265 mAh g$^{-1}$ at C/10. The incorporation of Li$_2$MnO$_3$ into the LiMnO$_2$ 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 LiMn$_2$O$_4$ and Li$_2$MnO$_3$ as a low-cost and environmentally benign cathode material. This composite with the main phase of LiMnO$_2$ (90%) was synthesized by hydrothermal method at 220°C from LiOH and Mn(CH$_3$COO)$_2$ precursors. The obtained nanosized LiMnO$_2$-LiMnO$_3$ cathode material exhibits a high capacity of 265 mAh g$^{-1}$ at C/10. The incorporation of Li$_2$MnO$_3$ into the LiMnO$_2$ 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.
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 (H2O2, 30% (w/w) in H2O, 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° ≤ 2θ ≤ 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 teflonized acetylene black (binder, 20 wt%) were mixed thoroughly. Then, it was pressed onto a stainless-steel mesh and dried at 120°C for 12 h. For coin-cell (2032 coin-type cell) fabrication, a separator, and Li metal were assembled in an Ar-filled glovebox. The cell was tested of its electrochemical properties by a Neware Battery Tester between 2.0 and 4.8 V vs. Li+/Li.

3. Results and Discussion

3.1. Structural Characterization of Cathode. Figure 1 shows the XRD pattern of the synthesized sample. All peaks can be indexed according to the space group Pmnn of the orthorhombic Li2MnO3 structure. There is a slightly weak peak that appears at ~18.3°, which is assignable to the Li2MnO3 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 LiMnO3 to Li2MnO3 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 Li2MnO3 phase. Rietveld refinement is performed using the model shown in Table 1. The main phase is o-LiMnO2 with space group Pmnn, and the second phase is Li2MnO3 with space group C2/m. In the o-LiMnO2 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 Mn3+. The structure is built up from independent MnO6 and LiO6 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-LiMnO2 is slightly smaller than that in literature [20]. This might be caused by the effect of the Li2MnO3 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-LiMnO2 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 ~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 CO2 from the air onto the sample’s surface.
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_{2}O_{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 1st, 2nd, and 5th 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 ~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 irreversible 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 $\alpha$-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 $\alpha$-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

o-LiMnO₂ was successfully synthesized by the hydrothermal method. The XRD and XPS results show the existence of the Li₁₂MnO₃ phase. SEM and TEM analyses confirmed the presence of a dominant o-LiMnO₂ phase with particle sizes in the range of 100–400 nm. The galvanostatic cycling demonstrates that 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 Li₁₂MnO₃ 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.

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