Performance and Structure of LiNi$_{0.5}$Mn$_{1.5}$O$_4$ Prepared from Various Ni Precursors for Lithium Ion Batteries

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ABSTRACT

LiNi$_{1/3}$Mn$_{2/3}$O$_4$ compounds were prepared through a solid-state reaction using various Ni precursors. The effect of the precursors on the electrochemical performance of LiNi$_{1/3}$Mn$_{2/3}$O$_4$ was investigated. LiNi$_{1/3}$Mn$_{2/3}$O$_4$ made from Ni(NO$_3$)$_2$•6H$_2$O shows the best charge-discharge performance. The reversible capacity of LiNi$_{1/3}$Mn$_{2/3}$O$_4$ is about 145 mA h g$^{-1}$ and remained at 143 mA h g$^{-1}$ after 10 cycles at 3.0 to 5.0 V. The XRD results showed that the precursors and dispersion method had significant effects on their structures. Pure spinel phase can be obtained with a high energy ball-milling method and Ni(NO$_3$)$_2$•6H$_2$O as precursor. A trace amount of the NiO phase was detected in LiNi$_{1/3}$Mn$_{2/3}$O$_4$ with the manual grinding method when Ni(CH$_3$COO)$_2$•6H$_2$O, NiO and Ni$_2$O$_3$ were used as precursors.

KEYWORDS

LiNi$_{1/3}$Mn$_{2/3}$O$_4$ spinel, cathode materials, lithium ion battery.

1. Introduction

LiNi$_{1/3}$Mn$_{2/3}$O$_4$ is considered as one of the most promising cathode materials for substituting LiCoO$_2$ because of its high specific capacity, low cost, low toxicity, high stability, and highly reversible discharge capacity at 5 V. Although spinel LiMn$_2$O$_4$ as cathode for Li ion batteries has the advantage of low cost and safety, the Mn$^{4+}$ in this compound decreases the stability of charge/discharge cycles due to deformation of the crystal structure. Also, the stability of LiMn$_2$O$_4$ would further drop due to the dissolution of manganese in the electrolyte, especially at high temperature.

In LiNi$_{1/3}$Mn$_{2/3}$O$_4$, Mn$^{4+}$ forms the lattice frame of the crystal and Ni$^{2+}$ is responsible for redox, which could stabilize this compound and facilitate intercalation/de-intercalation and diffusion of Li ions during cycling. However, the solid-state reaction used commonly to prepare LiNi$_{1/3}$Mn$_{2/3}$O$_4$ is not adequate to control the composition of Ni and Mn, and produces an impurity in the form of NiO. The capacity of LiNi$_{1/3}$Mn$_{2/3}$O$_4$ prepared through solid-state reaction is only 120 mA h g$^{-1}$. In order to obtain a high purity spinel phase, various synthetic methods have been developed. Pure LiNi$_{1/3}$Mn$_{2/3}$O$_4$ spinel, with high electrochemical performance was prepared via a co-precipitation and sol-gel method by Liquan and co-workers, but was limited to small-scale production. The effects of substituting manganese ions with other metal ions and the partial pressure of oxygen on the structural stability of the spinel were documented.

2. Experimental

2.1. Materials

Separator Celgard 2400 was purchased from Celgard, Inc., Charlotte, NC, USA. All the other materials supplied by Aldrich, St Louis, MO, USA, were used without further purification.

2.2. Preparation of LiNi$_{1/3}$Mn$_{2/3}$O$_4$

The stoichiometric amounts of the precursors were weighed accurately, i.e. 37.10 g of Ni(NO$_3$)$_2$•6H$_2$O, 34.67 g of MnO$_2$ and 9.43 g of Li$_2$CO$_3$, and mixed with anhydrous ethanol as the dispersion medium. The mixture was allowed to ball-mill in a planetary micro-mill or was manually ground for 6 h at room temperature. The milled mixture was dried and calcined at 750 °C for 20 h. Ni(CH$_3$COO)$_2$•6H$_2$O, NiO and Ni$_2$O$_3$ were also used as Ni precursors to prepare LiNi$_{1/3}$Mn$_{2/3}$O$_4$. The samples made from different Ni precursors are listed in Table 1.

2.3. Characterization

X-ray phase analysis was carried out on a Rigaku/Max-RA X-ray powder diffractometer (Salem, NC, USA) with CuK$_\alpha$ radiation. The scan range was 10 < 2θ < 70 °, and a step of 0.02 ° was used. The voltage and current were 30 kV and 100 mA, respectively.

2.4. Charge/Discharge Test

The resulting LiNi$_{1/3}$Mn$_{2/3}$O$_4$ was mixed with acetylene black, polyvinylidene difluoride (PVDF) (mass ratio of LiNi$_{1/3}$Mn$_{2/3}$O$_4$).

Table 1 Samples prepared from different Ni precursors and mixing methods.

<table>
<thead>
<tr>
<th>Sample label</th>
<th>Ni source</th>
<th>Mixing methods</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>Ni(NO$_3$)$_2$•6H$_2$O</td>
<td>Ball-milling</td>
</tr>
<tr>
<td>A1</td>
<td>Ni(NO$_3$)$_2$•6H$_2$O</td>
<td>Manual grinding</td>
</tr>
<tr>
<td>B</td>
<td>Ni(CH$_3$COO)$_2$•6H$_2$O</td>
<td>Ball-milling</td>
</tr>
<tr>
<td>C</td>
<td>NiO</td>
<td>Ball-milling</td>
</tr>
<tr>
<td>D</td>
<td>Ni$_2$O$_3$</td>
<td>Ball-milling</td>
</tr>
</tbody>
</table>

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<http://journals.sabinet.co.za/sajchem/>.
acetylene black and PVDF was 80:10:10) in 1-methyl-2-pyrrolidinone (NMP) onto an Al foil (as current collector). The electrodes were dried and pressed with a hydraulic press. Li ion secondary cells were assembled by using lithium sheet as the anode and the above prepared electrodes as cathodes. Celgard 2400 was used as separator which was soaked in electrolyte, i.e. 1 mol L–1 LiPF6 solution in an ethylene carbonate (EC) and dimethyl carbonate (DMC) mixed solvent (1:1 v/v ratio). The cells were assembled in an argon-protected glove box. The charge/discharge studies were carried out by using a Land-BTL10 (Wuhan, China) automatic battery test system.

3. Results and Discussion

3.1. XRD Analysis of LiNi0.5Mn1.5O4

During calcinations of milled mixtures, the partial pressure of oxygen must be controlled very carefully; otherwise, Li2MnO3 or LiMnO2 would be formed in the sample. This prevents a part of the Ni from entering the lattice of LiNi0.5Mn1.5O4 spinel and thereby forms NiO. In our preparations, all the samples were calcined in air. LiNi0.5Mn1.5O4 spinel with only traces of NiO was obtained without any control of partial pressure of oxygen but by using electrolytic MnO2 instead of chemical MnO2. The XRD patterns of LiNi0.5Mn1.5O4 made from Ni(NO3)2•6H2O, Ni(CH3COO)2•6H2O, NiO and Ni2O3, which were ball-milled and calcined at the same temperature, are compared in Fig. 1. Among them, only the LiNi0.5Mn1.5O4 made from Ni(NO3)2•6H2O shows the pure spinel structure compared with the standard pattern (JCPDS: 35-0782). Weak impurity peaks of NiO at 2θ = 37.5°, 68.2° and 80.0° were detected in the XRD patterns of all the other LiNi0.5Mn1.5O4 samples. Although there is a trace of NiO, their XRD patterns show the standard spinel structure. The amounts of NiO are lower than those reported by Kim8 using a solid-state reaction and very close to the sample prepared via a co-precipitation method. We presume that there are two reasons why high purity LiNi0.5Mn1.5O4 can be prepared by ball-milling from Ni(NO3)2•6H2O as a Ni precursor. Firstly, the ball-milling could decrease activation energy, which would facilitate the formation of spinel; secondly, the oxygen formed by decomposition of Ni(NO3)2•6H2O would restrain impurities formed in LiNi0.5Mn1.5O4.

![Figure 1 XRD patterns of LiNi0.5Mn1.5O4: (a) sample A; (b) sample B; (c) sample C; (d) sample D.](image1)

![Figure 2 XRD patterns of LiNi0.5Mn1.5O4: (a) sample A; (b) sample A1.](image2)
The XRD patterns of LiNi_{0.5}Mn_{1.5}O_{4}, prepared by ball-milling and manual grinding, are shown in Fig. 2. LiNi_{0.5}Mn_{1.5}O_{4} prepared by ball-milling shows the pure spinel structure without any impurity peaks in the XRD pattern. However, obvious impurity peaks of NiO are noted in the LiNi_{0.5}Mn_{1.5}O_{4} ground manually. Moreover, the intensities of the peaks of sample A are much stronger than those of sample A1, which indicates that ball-milling could facilitate the crystallization of LiNi_{0.5}Mn_{1.5}O_{4}. It is concluded that milling methods have a significant effect on the structure of LiNi_{0.5}Mn_{1.5}O_{4}.

3.2. Electrochemical Performances of LiNi_{0.5}Mn_{1.5}O_{4}

The LiNi_{0.5}Mn_{1.5}O_{4} cathode has two charge/discharge voltage plateaus, i.e. at 4 V and 5 V. The plateau at 4 V was caused by the Mn^{3+}/Mn^{4+} redox couple and that at 5 V by Ni^{2+}/Ni^{4+}. When there are more Mn^{4+} ions than Ni^{2+} in LiNi_{0.5}Mn_{1.5}O_{4}, then the corresponding capacity at 4 V will be smaller and that at 5 V will be larger, and vice versa. Figures 3a and 3b show the charge/discharge voltage profiles of LiNi_{0.5}Mn_{1.5}O_{4} in the voltage ranges of 3.0 to 5.0 V and 3.0 to 4.9 V, respectively. In Fig. 3a, there is a rapid voltage drop at 4.9 V and then the voltage increases slowly.

![Figure 3 Voltage versus initial capacity](image)
during the course of charge. This could be caused by oxidation of the electrolyte, which will result in an abrupt increase of current similar to the shortcut of a battery. With this electrolyte, it is better to charge/discharge in the voltage range of 3.0 to 4.9 V. During the charge, two voltage plateaus were observed at 4.3 and 4.8 V. The ratio of the corresponding capacities of 4.3 and 4.8 V is 1:2 during charging and 1:1 during discharge.

Compared with sample A, the initial capacity of LiNi0.5Mn1.5O4 made from Ni(CH3COO)2·6H2O (sample B) dropped to 120 mA h g⁻¹ (Fig. 3c). There are three voltage plateaus (at 4.0, 4.4 and 4.6 V) in the voltage profile of sample B, but only two plateaus in that of sample A. The ratio of the corresponding capacities at 4.0, 4.4 and 4.6 V is 1:2:3. The voltage profiles of LiNi0.5Mn1.5O4 made from NiO and Ni2O3 are similar. The plateau at 4.4 V is much smaller and almost disappears in comparison with that of sample A. The capacities at the 4.6 V and 4 V plateaus are 95 and 15 mA h g⁻¹, respectively. It is obvious that the amounts of Mn³⁺ and Ni²⁺ decrease, and Mn and Ni tend to form Mn⁴⁺ and Ni³⁺ in LiNi0.5Mn1.5O4 when metal oxides were used as Ni precursors.

The effect of milling methods on cycle life and coulomb efficiency of LiNi0.5Mn1.5O4 made from Ni(NO3)2·6H2O is shown in Figure 5. LiNi0.5Mn1.5O4 made from various Ni precursors also shows excellent stability. The capacity retention rates of samples A, B, C and D were 97.40 %, 90.50 %, 89.71 % and 97.43 %, respectively (Fig. 5). This showed that LiNi0.5Mn1.5O4 made from Ni(NO3)2·6H2O and Ni2O3 has a good capacity retention rate. The capacity retention rate of LiNi0.5Mn1.5O4 made from NiO is the lowest.

Figure 4 shows the variation in the discharge capacity of samples A and B, as a function of the number of cycles at different voltage ranges. The reversible discharge capacity of sample A at 3.0 to 5.0 V is 11 mA h g⁻¹ higher than that at 3.0 to 4.9 V. The discharge capacity is up to 145 mA h g⁻¹ when the cut-off voltage is 5.0 V. The discharge capacity is up to 133 mA h g⁻¹ when the cut-off voltage is 4.9 V. At 3.0 to 5.0 V, sample A shows high stability with the discharge capacity dropping marginally to 142 mA h g⁻¹ after 10 cycles. However, at 3.0 to 4.9 V, the discharge capacity drops to 124 mA h g⁻¹ after 40 cycles. Also, for sample A, similar discharge capacity fading was observed at different voltage ranges.

LiNi0.5Mn1.5O4 made from various Ni precursors also shows excellent stability. The capacity retention rates of samples A, B, C and D were 97.40 %, 90.50 %, 89.71 % and 97.43 %, respectively (Fig. 5). This showed that LiNi0.5Mn1.5O4 made from Ni(NO3)2·6H2O and Ni2O3 has a good capacity retention rate. The capacity retention rate of LiNi0.5Mn1.5O4 made from NiO is the lowest.
The initial capacity of the ball-milled sample is 12 mA h g\(^{-1}\) higher than that of manually ground sample. The coulomb efficiency of the ball-milled sample is 10\% higher than that of the manually ground sample. The charge capacities of both samples are very close, but there is an obvious difference between discharge capacities. This suggests that the Li ion intercalation/de-intercalation is faster in the ball-milled sample. The capacity retention rate and stability of the ball-milled sample are better than those of the manually ground sample in the first 20 cycles.

4. Conclusion

LiNi\(_{0.5}\)Mn\(_{1.5}\)O\(_4\) spinel, a promising cathode material with high reversible capacity and stability, has been prepared by solid-state reaction. The crystal structure was characterized by XRD. Among the LiNi\(_{0.5}\)Mn\(_{1.5}\)O\(_4\) cathode materials made from various Ni precursors, LiNi\(_{0.5}\)Mn\(_{1.5}\)O\(_4\) made from Ni(NO\(_3\))\(_2\)6H\(_2\)O has the best electrochemical performance. With Ni(NO\(_3\))\(_2\)6H\(_2\)O as the Ni precursor and ball-milling, high purity spinel LiNi\(_{0.5}\)Mn\(_{1.5}\)O\(_4\) can be prepared via a solid-state reaction. Therefore, it has the potential to substitute currently applied complicated preparation methods like co-precipitation, sol-gel and spray pyrolysis methods for producing high purity LiNi\(_{0.5}\)Mn\(_{1.5}\)O\(_4\). The LiNi\(_{0.5}\)Mn\(_{1.5}\)O\(_4\) electrode shows a high initial discharge capacity of 145 mA h g\(^{-1}\) and a very stable cycling performance. The discharge capacity still remained at 142 mA h g\(^{-1}\) after 10 cycles.

Acknowledgements

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References