A LiNi$_{0.5}$Mn$_{1.5}$O$_4$ material for use as a 5 V spinel cathode for lithium-ion batteries was synthesized for the first time using a hydrothermal approach. The effects of the LiOH concentration and hydrothermal temperature on the hydrothermal products were investigated systematically, where the LiOH concentration (e.g., 1.1 M) was proven critical to successfully synthesize the 5 V spinel. At a LiOH concentration (e.g., 0.8–1.0 M), the obtained products may be MnOOH, α-Mn$_2$O$_3$, and 4 V spinel, while high concentrations (e.g., >1.8 M) favor the Li$_2$MnO$_3$ phase. The particle size of the as-prepared 5 V spinel is ca. 30 nm, and its formation is associated with the dissolution-recrystallization mechanism from an amorphous precursor. Cell tests show that the as-prepared LiNi$_0.5$Mn$_{1.5}$O$_4$ material obtained at 180°C exhibits a capacity of ca. 100 mAh g$^{-1}$ at a current density of 28 mA g$^{-1}$, where ca. 60 mAh g$^{-1}$ above 4.2 V. Such a 5 V material shows an excellent rate capability with a capacity of ca. 73 mA h g$^{-1}$ delivered at 2800 mA g$^{-1}$, 73% of that obtained at 28 mA g$^{-1}$.

**Experimental**

All chemicals in our experiments were of analytical grade and used as purchased without further purification from Sinopharm Chemical Reagent Co. Ltd., Shanghai, China.

The LiNi$_0.5$Mn$_{1.5}$O$_4$ spinel materials were prepared according to the following procedures. An appropriate amount of LiOH·H$_2$O (≧95%) was dissolved in 30 mL deionized water and then added dropwise into a Teflon-lined stainless steel autoclave containing 0.0075 mol MnSO$_4$·H$_2$O (≧99%), 0.0025 mol NiSO$_4$·6H$_2$O (≧98.5%), and 0.0075 mol (NH$_4$)$_2$SO$_4$ (20 mL solution in the 100 mL Teflon container). The autoclave was sealed and heated at 180°C for 48 h. The resulting precipitate was separated from the solvents by filtration and then washed with deionized water. The sample was obtained after drying at 120°C for 24 h. The samples were named as LMNO-1, LMNO-2, LMNO-3, LMNO-4, and LMNO-5 for the usage of 1.843, 2.253, 2.48, 2.662, and 3.686 g of LiOH·H$_2$O, corresponding to the usage of LiOH by 0.9, 1.0, 1.1, 1.3, and 1.8 M (in 50 mL solution), respectively. Note here that it is an excess of the LiOH concentration assuming the target product to be LiNi$_0.5$Mn$_{1.5}$O$_4$; e.g., 0.1 M is an excess to 0.8 M LiOH for sample LMNO-1.

The structures of the as-prepared samples were examined by powder X-ray diffraction (XRD) analysis performed using an X’Pert PRO diffractometer with CuKα radiation (PANalytical, Holland). Scanning electron microscopy (SEM) studies were performed on an LEO1530 to identify the morphologies of the samples (Zeiss, USA). Thermogravimetric analysis (TGA) experiments were carried out by an STA 409 PC analyzer (Netzsch, Germany) at a heating rate of 10°C min$^{-1}$ under Ar flow (25 mL min$^{-1}$). The H contents of the samples were calculated by the mass loss of water between 120 and 400°C from TGA. The Mn, Ni, and Li contents were determined by inductive coupled plasma–atomic emission spectroscopy carried out on IRIS Intrepid II XSP (Thermo Electron, USA). The mean oxidation state of Mn was analyzed by a titration method using oxalate/KMnO$_4$, assuming Ni as +2.

Electrode fabrication and coin cell assembly were carried out as described in our previous report. In brief, the active material was mixed with 10 wt % acetylene black and 10 wt % binder ([poly(vinylidene fluoride)] PVDF) and then ground by ball milling. The cathode was obtained by pressing the mixture onto a piece of aluminum foil and then dried in a vacuum oven at 120°C for 2 h. The coin cells were fabricated with the prepared cathode, lithium...
The effect of LiOH concentration on the hydrothermal products.— The XRD patterns of samples LMNO-1, LMNO-2, LMNO-3, LMNO-4, and LMNO-5 are shown in Fig. 1. It is clear that the hydrothermal product prepared at a low LiOH concentration (e.g., 0.9 M) mainly consists of α-MnO₂ and β-MnOOH (Feitknechtite) (Fig. 1a) and possesses nanowire and nanorod morphologies (Fig. 1a). As can be seen from the XRD patterns shown in Fig. 1a, α-MnO₂ disappeared when the LiOH concentration increased gradually to 1.3 M, accompanied by the appearance of spinel materials (including LiMn₃O₅ and LiNi₀.₅Mn₁.₅O₄) (Figs. 1b–1d). Compared to the morphology of sample LMNO-1, that of sample LMNO-2 still shows a few nanowires and nanorods while only nanosized particles were obtained when the LiOH concentration is higher than 1.0 M (Figs. 2c–2e).

Figures 1b–1e indicate that a further increase of the LiOH concentration to 1.8 M (LMNO-5) led to a structure change which was confirmed different from samples LMNO-2, LMNO-3, and LMNO-4 by their XRD patterns; sample LMNO-5 consists of the Li₂MnO₃ material while the other three samples show the spinel structure. Generally, the most remarkable difference between the XRD patterns of Li₂MnO₃ and a spinel lies in the diffraction intensities at 2θ positions of 36.5° and 44.3°, where the spinel shows almost equal intensities while Li₂MnO₃ exhibits stronger intensity at 44.3°.

It was observed that the XRD peak intensities of sample LMNO-2 were significantly enhanced compared with those of samples LMNO-3 and LMNO-4, which agrees well with their morphology observations. For example, sample LMNO-2 has an average particle size of ca. 250 nm, while the average particle sizes of samples LMNO-3 and LMNO-4 are ca. 30 nm. This change of the particle size was expected to be LiOH concentration dependent in the hydrothermal growth process of crystals because higher alkaline concentration facilitates dissolution of manganese oxide and thus resulted in smaller particle sizes according to the dissolution-recrystallization mechanism. In order to confirm this phenomenon, an extra experiment with the LiOH concentration (1.05 M) was employed for the synthesis. The result indicated that the obtained sample has an average size of ca. 60 nm (Fig. 2c), which falls between the values of samples LMNO-2 and LMNO-3 being 250 and 30 nm, respectively. However, a further increase in the LiOH concentration higher than 1.1 M did not result in a decrease in the particle size due to the balance between crystal dissolution and recrystallization.

The effect of reaction temperature on the hydrothermal products.— In our previous studies on the hydrothermal synthesis of Li₂MnO₃-LiMn₂O₄ composites at 120–180°C, we concluded that the appropriate high temperature facilitated the formation of LiMn₂O₄ and Li₂MnO₃ materials. Here, we attempted to increase the reaction temperature to higher than 180°C in order to investigate the effect of temperature on the hydrothermal products at various LiOH concentrations. The XRD patterns and SEM images of the samples synthesized at 220°C with various LiOH concentrations are shown in Figs. 3 and 4, respectively. The product synthesized with 0.9 M LiOH at 220°C, similar to that obtained at 180°C, consists of α-MnO₂ and β-MnOOH (Feitknechtite) (Fig. 3a) with nanowires, nanorods, and some big particles observed in the SEM images (Fig. 3a). At an intermediate LiOH concentration (1.0–1.1 M LiOH), the product was confirmed as spinel phase composed with nanoparticles, while at a high LiOH concentration (1.8 M LiOH) only nanosized Li₂MnO₃ particles were obtained. A remarkable difference between the products obtained at 180 and 220°C using 1.0 M LiOH was observed; some nanowires and nanorods appeared in the sample prepared under 180°C, which, however, were not found in the sample prepared under 220°C.

Shown in Fig. 5 are the XRD patterns of the samples prepared at 250°C with various LiOH concentrations. The results show that the
hydrothermal products obtained at 250°C are markedly different from those at 180 and 220°C. The product prepared with 0.9 M LiOH at 250°C mainly consists of \( \alpha\)-MnOOH (Groutite) and \( \alpha\)-MnO\(_2\) rather than \( \beta\)-MnOOH and \( \alpha\)-MnO\(_2\). A possible existence of a small amount of \( \beta\)-MnOOH at 250°C, as marked by an arrow in Fig. 5a, could not be excluded. The morphology of the sample obtained at 250°C with 0.9 M LiOH (Fig. 6) was found to possess bigger particles with smooth surface compared to those of samples prepared at 180 and 220°C. From Fig. 5c, it is clear that a small amount of \( \alpha\)-MnOOH still exists when the concentration of LiOH increased to 1.0 M. However, the morphology of \( \alpha\)-MnOOH (possibly nanorods and nanowires as shown in Fig. 6a) was not observed in the sample prepared at 1.0 M LiOH (Fig. 6c). Therefore, an extra experiment with 0.95 M LiOH was carried out in order to observe a transition state between nanorod (or nanowire) and nanoparticle. The result shows that the sample prepared at 0.95 M LiOH presents an XRD pattern similar to that obtained at 0.9 M LiOH (Fig. 5b). However, some very small particles are attached to the big rodlike or spherelike particles in the case of 0.95 M LiOH (Fig. 6b).

Figure 3. (Color online) XRD patterns of the samples synthesized in the presence of (a) 0.9, (b) 1.0, (c) 1.1, (d) 1.3, and (e) 1.8 M LiOH at 220°C.

Figure 4. SEM images of the samples synthesized at 220°C with (a) 0.9, (b) 1.0, (c) 1.1, and (d) 1.8 M LiOH.

Figure 5. (Color online) XRD patterns of the samples synthesized using (a) 0.9, (b) 0.95, (c) 1.0, (d) 1.1, and (e) 1.3 M LiOH at 250°C. (The peak marked by arrow possibly resulted from \( \beta\)-MnOOH.) The JCPDS numbers used for \( \alpha\)-MnOOH, LiMn\(_2\)O\(_4\), Li\(_2\)MnO\(_3\), and LiNi\(_0.5\)Mn\(_1.5\)O\(_4\) are 89-2354, 89-8321, 84-1634, and 32-581, respectively.

Figure 6. SEM images of the samples synthesized at 250°C with (a) 0.9, (b) 0.95, (c) 1.1, and (d) 1.3 M LiOH.
because the 4 V spinel chemical technique such as CV was employed for the identification seems very difficult to identify 4 and 5 V spinels due to their almost phases in our samples using XRD and SEM techniques. However, it continues investigation, for the sake of convenience and safety.

In summary, we can conclude that 1.1 M LiOH is a suitable alkaline concentration to prepare the 5 V spinel material. The LiOH concentrations lower and higher than 1.1 M may lead to the formation of MnOOH, 4 V spinel, and/or Li2MnO3 phases. Note here that because the preparation of the 5 V spinel is very sensitive to the reaction time from 2 to 24 h was found to result in the gradual disappearance of δ-MnO2 and development of the spinel phase as indicated by the variation of the two peaks at 12.3 and 18.6° (Figs. 8b–8e). The phase transformation from δ-MnO2 to spinel was also

![Figure 7](image_url)

**Figure 7.** (Color online) CV curves of samples LMNO-1, LMNO-2, LMNO-3, LMNO-4, and LMNO-5, corresponding to the presence of (a) 0.9, (b) 1.0, (c) 1.1, (d) 1.3, and (e) 1.8 M LiOH (1 mV s⁻¹); (f) a comparison of the initial scanning processes of the five samples.

![Figure 8](image_url)

**Figure 8.** XRD patterns of the samples synthesized in 1.1 M LiOH solution for (a) 0, (b) 2, (c) 6, (d) 12, (e) 24, and (f) 336 h at 180°C.
accompanied by the disappearance of big particles with petallike surface and appearance of nanosized particles (Figs. 9b–9e). This is in good agreement with the dissolution–recrystallization mechanism as discussed before.\textsuperscript{29,32} A further increase in the reaction time did not increase the phase purity but led to a better crystal shape; e.g., at 336 h some well-defined particles could be observed (Fig. 9f).

The composition of the hydrothermal products.— Table I shows the composition of the hydrothermal products synthesized at 180°C, where the H contents in these samples were calculated based on the mass loss between 120 and 400°C from TGA (Fig. 10), which may exist in these samples as the forms of H-substituted phases,\textsuperscript{29,32} hydroxides, and/or crystal water. Sample LMNO-1 had a low Li content but a high H content because the main components were α-MnO\textsubscript{2} and β-MnOOH. The result agrees well with the low current density during the initial anodic CV sweeping (Fig. 7a). The Li content in sample LMNO-5 is higher than the other samples, which was ascribed to the higher Li content in Li\textsubscript{2}MnO\textsubscript{3} than in LiMn\textsubscript{2}O\textsubscript{4}. Assuming Ni ions in the samples as +2, we can obtain the mean Mn oxidation by titration and the result is shown in Table I. The mean oxidation of Mn in sample LMNO-3 is ca. +3.8, lower than +4 in normal 5 V spinels of LiNi\textsubscript{0.5}Mn\textsubscript{1.5}O\textsubscript{4}. This suggests that there are still some impurities and/or oxygen-deficiency phases in the form of Mn\textsuperscript{3+} in sample LMNO-3. An attempt to obtain a pure 5 V spinel phase by increasing usage oxidation was unsuccessful at this stage. The formula of the as-prepared 5 V spinel (sample LMNO-3) can be written accordingly as Li\textsubscript{0.86}Ni\textsubscript{0.47}Mn\textsubscript{1.5}O\textsubscript{3.63}H\textsubscript{1.25} (Table I).

The electrochemical performance of the as-prepared hydrothermal samples.— Figure 11a shows the charge/discharge curves of sample LMNO-1 synthesized with 0.9 M LiOH at 180°C. Upon the initial charging to 4.95 V, the capacity is ca. 29 mAh g\textsuperscript{-1}, which is consistent with its very low Li content (Table I). The subsequent discharge process indicates that it delivered ca. 79 mAh g\textsuperscript{-1}, which mainly originated from α-MnO\textsubscript{2}. For sample LMNO-2, a discharge plateau at ca. 4.6 V was observed, which was followed by another plateau at ca. 4.0 V (Fig. 11b). The discharge capacity was ca. 72 mAh g\textsuperscript{-1}, where, however, the contribution from the 5 V spinel was only 40 mAh g\textsuperscript{-1} above 4.3 V. By contrast, sample LMNO-3 delivered ca. 96 mAh g\textsuperscript{-1} at a current density of 140 mA g\textsuperscript{-1} and ca. 60 mAh g\textsuperscript{-1} above 4.3 V (Fig. 11c).

Sample LMNO-4 exhibits a lower capacity above 4.3 V (Fig. 11d), which was probably ascribed to the existence of the Li\textsubscript{2}MnO\textsubscript{3} phase. We attempted to discharge it till a lower cutoff voltage of 2.0 V because Li\textsubscript{2}MnO\textsubscript{3} can obtain high capacity until that cutoff voltage.\textsuperscript{32} It was observed that it delivered ca. 183 mAh g\textsuperscript{-1} but decayed quickly, e.g., only remaining ca. 115 mAh g\textsuperscript{-1} after ten hours of discharge.

Table I. Compositions and mean oxidation states of Mn of the as-prepared products.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Li</th>
<th>Ni</th>
<th>Mn</th>
<th>H\textsuperscript{a}</th>
<th>Mean oxidation state of Mn\textsuperscript{b}</th>
<th>Composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>LMNO-1</td>
<td>0.22%</td>
<td>15.36%</td>
<td>45.68%</td>
<td>1.29%</td>
<td>3.69</td>
<td>Li\textsubscript{0.06}Ni\textsubscript{0.47}Mn\textsubscript{1.5}O\textsubscript{3.52}H\textsubscript{2.32}</td>
</tr>
<tr>
<td>LMNO-2</td>
<td>2.40%</td>
<td>15.44%</td>
<td>45.64%</td>
<td>0.69%</td>
<td>3.71</td>
<td>Li\textsubscript{0.63}Ni\textsubscript{0.48}Mn\textsubscript{1.5}O\textsubscript{3.42}H\textsubscript{1.24}</td>
</tr>
<tr>
<td>LMNO-3</td>
<td>3.18%</td>
<td>14.77%</td>
<td>44.30%</td>
<td>0.67%</td>
<td>3.80</td>
<td>Li\textsubscript{0.86}Ni\textsubscript{0.47}Mn\textsubscript{1.5}O\textsubscript{3.63}H\textsubscript{1.25}</td>
</tr>
<tr>
<td>LMNO-4</td>
<td>3.22%</td>
<td>15.07%</td>
<td>44.44%</td>
<td>0.48%</td>
<td>3.71</td>
<td>Li\textsubscript{0.86}Ni\textsubscript{0.48}Mn\textsubscript{1.5}O\textsubscript{3.42}H\textsubscript{0.88}</td>
</tr>
<tr>
<td>LMNO-5</td>
<td>5.16%</td>
<td>14.25%</td>
<td>42.00%</td>
<td>0.50%</td>
<td>3.77</td>
<td>Li\textsubscript{1.46}Ni\textsubscript{0.48}Mn\textsubscript{1.5}O\textsubscript{3.95}H\textsubscript{0.98}</td>
</tr>
</tbody>
</table>

\textsuperscript{a}Calculated based on the mass loss between 120 and 400°C from TGA.

\textsuperscript{b}Mean oxidation state of Mn was calculated by assuming Ni possessing +2.
cycles. Although we cannot distinguish how many capacities originated from the Li$_2$MnO$_3$ phase, we can still reach the conclusion that the value would not be high because the charge/discharge curves exhibit the characteristics of a typical spinel. By contrast, at 1.8 M LiOH the obtained sample LMNO-5 exhibits typical charge/discharge plots of the Li$_2$MnO$_3$ phases, i.e., with high capacity (219 mAh g$^{-1}$) and without marked discharge plateau until the cutoff voltage of 2.0 V.$^{29,32}$

Rate capability of the hydrothermally synthesized 5 V spinel.— Because sample LMNO-3 exhibits an average particle size of ca. 30 nm (Fig. 2), it is expected to possess a good rate capability as a cathode for lithium-ion batteries. In fact, the charge/discharge performance of sample LMNO-3 at various current densities shows that the 5 V spinel material delivered ca. 100, 91, 74, and 73 mAh g$^{-1}$ at current densities of 28, 140, 1400, and 2800 mA g$^{-1}$, respectively (Fig. 12). Defining 1C capacity as the value obtained at a low current density, we obtained 73% capacity at the 28C rate, which indicates an excellent rate capability of sample LMNO-3. The rate capability of such a nanosized 5 V spinel is better than those of a submicro LiNi$_{0.5}$Mn$_{1.5}$O$_4$$^{31,33}$ and is comparable with that of nanosized LiNi$_{0.5}$Mn$_{1.5}$O$_4$ prepared by solid-state reaction.$^{17}$ For ex-

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**Figure 11.** (Color online) Charge/discharge curves of samples (a) LMNO-1, (b) LMNO-2, (c) LMNO-3, (d) LMNO-4, and (e) LMNO-5 at a current density of 140 mA g$^{-1}$. 

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samples, a submicro LiNi$_{0.86}$Ni$_{0.47}$Mn$_{1.5}$O$_{3.63}$H$_{1.25}$ was synthesized at 800°C and delivered a capacity of 89 mAh g$^{-1}$ (at 28 mA g$^{-1}$). Shaju and Bruce$^{1}$ prepared the ordered nano-LiNi$_{0.8}$Mn$_{1.2}$O$_{3}$ and disordered nano-LiNi$_{0.8}$Mn$_{1.2}$O$_{3}$ at 700 and 750°C, respectively, and when they discharged at 3000 mA g$^{-1}$, they showed 63 and 88% of the capacities obtained at 135 mA g$^{-1}$, respectively. The good capability of our 5 V spinel is associated with its small particle size of ca. 30 nm. By integrating the discharging curve of sample LMNO-3 at 2800 mA g$^{-1}$, the energy density was calculated as 303 Wh kg$^{-1}$, corresponding to a power density of 11.6 kW kg$^{-1}$, which suggests its promising application in high power lithium-ion batteries.

Conclusion

The LiNi$_{1/2}$Mn$_{1/2}$O$_{2}$ material was hydrothermally synthesized using MnSO$_4$, NiSO$_4$, (NH$_4$)$_2$SO$_4$, and LiOH as the starting materials. The effects of the hydrothermal temperature, reaction time, and LiOH concentration on the hydrothermal products were investigated systematically. The LiOH concentration was confirmed as the crucial factor to form the 5 V spinel LiNi$_{0.5}$Mn$_{1.5}$O$_{4}$. This is evident in the different products, MnOOH, 4 V spinel, 5 V spinel, and Li$_2$MnO$_3$ being the main phases for the LiOH concentrations of 0.9, 1.0, 1.1, and 1.8 M, respectively. The hydrothermal temperature showed a slight effect on the formation of the spinels at 1.1 M LiOH, while it significantly affected those products at or below 0.9 M and at or above 1.3 M. It was observed that at 0.9 M LiOH, the hydrothermal products consist mainly of $\alpha$-MnOOH and $\epsilon$-MnOOH at 180 and 250°C, respectively, while at 1.3 M, the main phases of as-prepared samples at 180 and 250°C are spinel and Li$_2$MnO$_3$ materials, respectively. The changes of phase and morphology with the hydrothermal time confirmed that the hydrothermal products obey the dissolution–recrystallization mechanism of manganese oxides.

The as-obtained 5 V spinel material has a composition of Li$_{1-x}$Ni$_x$Mn$_{1-x}$O$_{3+y}$H$_{2y}$, with the protons existing in the form of substitution Li sites or crystal water. This 5 V spinel delivered ca. 100, 91, 74, and 73 mAh g$^{-1}$ at current densities of 28, 140, 1400, and 2800 mA g$^{-1}$, respectively, indicating an excellent rate capability of the as-prepared 5 V spinel material.

Acknowledgments

Y.Y. gratefully thanks the financial support from the National Basic Research Program of China (973 Program) (grant no. 2007CB809702) and the National Natural Science Foundation of China (grant no. 20873115 and no. 20021002).

Xiamen University assisted in meeting the publication costs of this article.

References