

## Effect of ball milling and electrolyte on properties of high voltage $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ spinel<sup>①</sup>

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**Abstract:** Effect of ball milling and electrolyte on the properties of high-voltage  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$  was investigated. Ball milling has significant effect on the synthesis and property of  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ . The X-ray diffraction (XRD) patterns indicate that  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$  can't be synthesized without ball milling even calcined at 900 °C. When synthesized with ball milling,  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$  almost exhibits only one plateau at around 4.7 V. With the increase of ball milling time, the capacity of  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$  increases, but the cycling performance is not highly affected. The electrochemical property of  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$  highly depends on the electrolyte. The stable and high-voltage-resistant electrolyte is much beneficial to enhancement of electrochemical property of  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ , such as coulombic efficiency and cycling performance.

**Key words:**  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ ; cathode; lithium ion batteries; ball milling; electrolyte

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### 1 INTRODUCTION

Recently, several research groups have reported transition-metal-substituted spinel materials ( $\text{LiM}_x\text{Mn}_{2-x}\text{O}_4$ , M: Cr, Co, Fe, Ni, Cu) with high-voltage plateaus above 4.5 V<sup>[1-5]</sup>. Among these materials,  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$  is the most promising and attractive one because of its good cyclic property and relatively high capacity with a plateau at around 4.7 V<sup>[3, 6]</sup>.

Now, a variety of methods were used for preparation of  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ , such as solid-state reaction<sup>[4, 7, 8]</sup>, sol-gel<sup>[4, 6]</sup>, coprecipitation<sup>[9]</sup>, emulsion drying<sup>[10]</sup>, composite carbonate process<sup>[11]</sup>, molten salt<sup>[12]</sup>, combustion<sup>[13]</sup> and ultrasonic spray pyrolysis method<sup>[14]</sup>. When the solid-state method is employed to synthesize transition metal oxides for the lithium-ion battery, ball milling as a useful technique is often introduced into the synthetic process in order to get homogeneous precursors<sup>[15, 16]</sup>, which is very favorable for the process of solid-state reaction. The same technique is also an important aid in synthesis of  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ . In addition,  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$  is charged and discharged at high voltage, which requires the electrolyte is of good high voltage resistance. From the previous literatures<sup>[4, 7, 9, 10]</sup>, severe electrolyte decomposition at high voltage and poor coulombic efficiency for  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$  were

often obtained, which indicated that the property of  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$  highly depends on the electrolyte.

So far, however, there is no literature about the influence of ball milling and electrolyte on the property of  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$  spinel. In the present paper, therefore, the effect of ball milling on the synthesis and property of  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$  was studied. The impact of electrolyte on the electrochemical performance was also investigated.

### 2 EXPERIMENTAL

Appropriate amounts of  $\text{Li}_2\text{CO}_3$ , NiO and electrolytic  $\text{MnO}_2$  were initially ground in mortar and then were thoroughly mixed by ball milling for 0, 3 and 6 h, respectively. Subsequently all mixed precursors were calcined at 900 °C for 12 h followed by an annealing treatment at 600 °C for 24 h in air. The powder X-ray diffraction (XRD, Rint-2000, Rigaku) measurement using  $\text{Cu K}\alpha$  radiation was employed to identify the crystalline phase of the synthesized material.

The electrochemical characterizations were performed using CR2025 coin-type cell. For cathode fabrication, the prepared powders were mixed with 20% of carbon black and 10% of polyvinylidene fluoride in N-methyl pyrrolidinone until slurry was obtained. And then, the blended slurries

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were pasted onto an aluminum current collector, and the electrode was dried at 80 °C for 1 d in vacuum. The test cell consisted of the cathode and lithium foil anode separated by a porous polypropylene film, and 1 mol/L LiPF<sub>6</sub> in EC: EMC: DMC (1: 1: 1 in volume) or 1 mol/L LiPF<sub>6</sub> in PC: DMC (1: 1 in volume) as electrolyte. The assembly of the cells was carried out in a dry Ar-filled glove box. The cells were charged and discharged over a voltage range of 3.5 V to 4.9 V versus Li/Li<sup>+</sup> electrode at room temperature.

### 3 RESULTS AND DISCUSSION

#### 3.1 Effect of ball milling on synthesis and electrochemical performance of LiNi<sub>0.5</sub>Mn<sub>1.5</sub>O<sub>4</sub>

Fig. 1 shows the XRD patterns of LiNi<sub>0.5</sub>Mn<sub>1.5</sub>O<sub>4</sub> powders prepared under the different conditions. It's evident that all fundamental peaks can be indexed to the cubic spinel structure. However, clear impurity (NiO) peaks denoted by asterisk are observed for LiNi<sub>0.5</sub>Mn<sub>1.5</sub>O<sub>4</sub> powders prepared without ball milling, which indicates that the amount of Ni in the spinel phase is smaller than that in LiNi<sub>0.5</sub>Mn<sub>1.5</sub>O<sub>4</sub>, and Mn<sup>3+</sup> reduced from Mn<sup>4+</sup> exists in the spinel phase. With the increase of ball milling time, the impurity peaks are greatly suppressed and almost not observed for 6 h, which suggests that the prepared powders with ball milling assistance are almost pure LiNi<sub>0.5</sub>Mn<sub>1.5</sub>O<sub>4</sub> phase. Comparing the patterns, it can be concluded that the impurity in the sample without ball milling would be mainly ascribed to unreacted NiO. The above results could be explained below: although the precursors, in the case of no ball milling process, are ground in mortar, they can't be thoroughly mixed, so the contact area of the precursors particles is limited, which makes the process of the solid-state reaction more difficult. Therefore, the solid-state reaction of the precursors without ball milling assistance is hard to proceed completely even at high temperature, and some unreacted NiO still exists in the prepared powders. When ball milling processing was employed into the synthesis route, fine and homogeneous precursors particles can be obtained, and their contact area and reactivity can be greatly enhanced, which highly facilitated the completeness of solid-state reaction. Thus, the prepared powders are almost pure LiNi<sub>0.5</sub>Mn<sub>1.5</sub>O<sub>4</sub> phase. Here, we should also point out that faint impurity peaks were still observed in the pattern of LiNi<sub>0.5</sub>Mn<sub>1.5</sub>O<sub>4</sub> ball-milled for 3 h and 6 h. However, these peaks may not be completely ascribed to unreacted NiO, especially for 6 h, since they also can be attributed to Li<sub>x</sub>Ni<sub>1-x</sub>O caused by oxygen loss of LiNi<sub>0.5</sub>Mn<sub>1.5</sub>O<sub>4</sub> at high temperature<sup>[4]</sup>. Of course, it's in

all possibility that the impurity in the sample without ball milling also contain Li<sub>x</sub>Ni<sub>1-x</sub>O. In addition, sharp and intensive peaks of samples with ball milling process indicate well crystallization of LiNi<sub>0.5</sub>Mn<sub>1.5</sub>O<sub>4</sub> powders. Hence, the results demonstrate that ball milling is a very effective and necessary process.

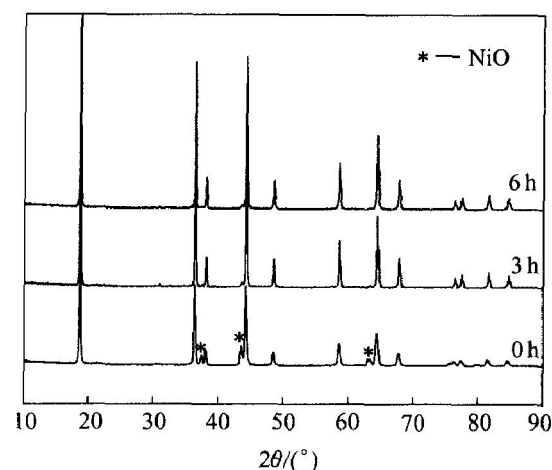
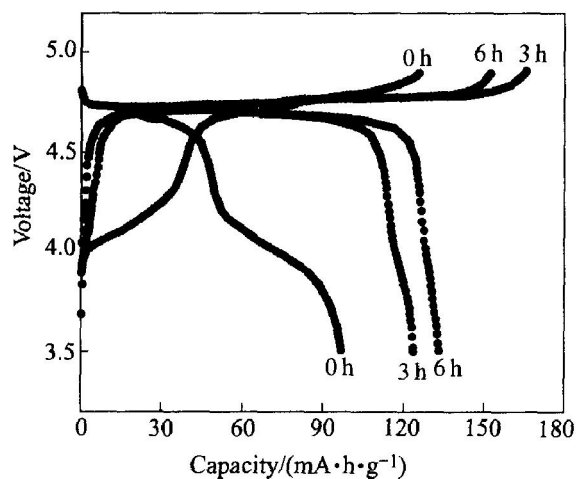


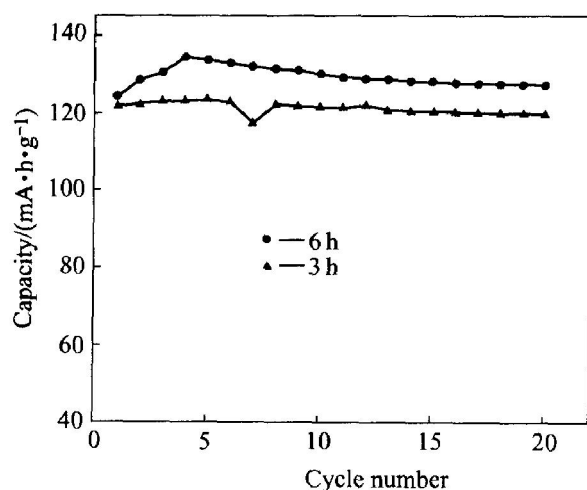
Fig. 1 XRD patterns of LiNi<sub>0.5</sub>Mn<sub>1.5</sub>O<sub>4</sub> processed with different ball milling times

1 mol/L LiPF<sub>6</sub> in EC: EMC: DMC (1: 1: 1 in volume) was used as electrolyte to study the effect of ball milling on the electrochemical performance of LiNi<sub>0.5</sub>Mn<sub>1.5</sub>O<sub>4</sub>. The charge—discharge curves of LiNi<sub>0.5</sub>Mn<sub>1.5</sub>O<sub>4</sub> cycled between 3.5 V and 4.9 V at the rate of 1/7 C are shown in Fig. 2. It's clear that the ball milling processing has significant effect on the charge—discharge profile and capacity of LiNi<sub>0.5</sub>Mn<sub>1.5</sub>O<sub>4</sub> powders. The charge—discharge profiles of samples with different ball milling time are completely different. In the case of no ball milling process, the sample shows a large plateau at around 4.1 V based on Mn<sup>3+</sup>/Mn<sup>4+</sup> redox couple in addition to the 4.7 V plateau based on Ni<sup>2+</sup>/Ni<sup>4+</sup> redox couple<sup>[4]</sup>, and delivers much smaller capacity. The existence of Mn<sup>3+</sup> was reduced from Mn<sup>4+</sup> caused by Ni deficiency in the spinel phase, and the existence of inactive impurity NiO diminished the amount of active material in the powders and resulted in low capacity. This result is in good agreement with the XRD pattern. On the other hand, a large 4.7 V plateau with a faint 4.1 V plateau is observed for the sample ball-milled for 3 h, and the sample ball-milled for 6 h almost exhibits only one plateau at around 4.7 V. As for capacity, it increases quickly with the introduction of ball milling process, as clearly seen in Fig. 2. From the XRD results, inactive impurity amount in the samples drastically decreases when the ball milling process is employed, and hence, the amount of active material in the powders increases. This is a possible expla-

nation why the capacity is higher for the ball-milled materials. Fig. 3 shows the electrochemical cycling performance of  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$  processed with different ball milling time, at the rate of  $1/3C$ . With the increase of ball milling time, the capacity of  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$  is slightly enhanced which is also due to the decrease of inactive impurity amount in the prolonged ball-milled sample and reaches up to  $133 \text{ mA} \cdot \text{h} \cdot \text{g}^{-1}$  in the case of 6 h, but the cycling performances are similar.



**Fig. 2** Charge—discharge curves of  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$  processed with different ball milling time (Charge—discharge rate is  $1/7C$ )

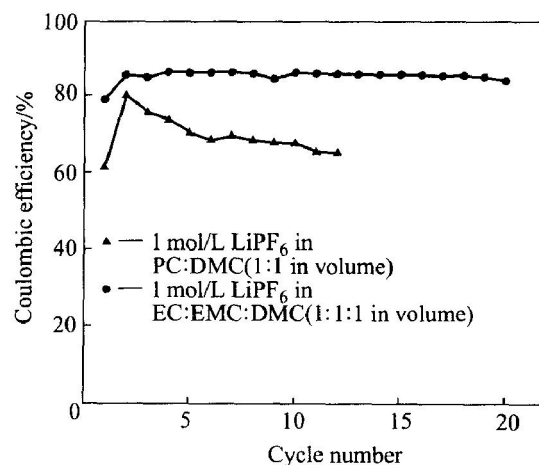


**Fig. 3** Electrochemical cycling performance of  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$  processed with different ball-milling time (Charge—discharge rate is  $1/3C$ )

### 3.2 Effect of electrolyte on electrochemical performance of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$

As for high voltage cathode materials, electrolyte is an essential factor for the electrochemical performance of  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ . Here, two kinds of electrolyte were selected to show the effect of electrolyte on the electrochemical performance of

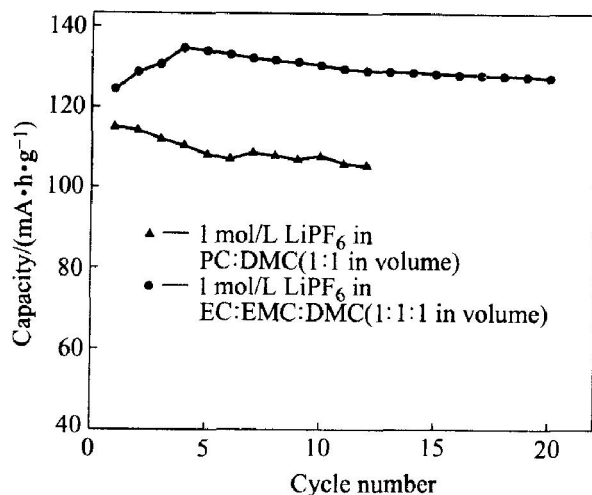
$\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ : one is 1 mol/L  $\text{LiPF}_6$  in EC:EMC:DMC (1:1:1 in volume), the other is 1 mol/L  $\text{LiPF}_6$  in PC:DMC (1:1 in volume). Fig. 4 shows the coulombic efficiency of  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$  ball-milled for 6 h in both electrolyte at the rate of  $1/3C$ . In general, poor coulombic efficiency is observed for both kinds of electrolyte, which is mainly due to the electrolyte decomposition taken place by irreversible reaction with active materials at high voltage<sup>[4]</sup>. When 1 mol/L  $\text{LiPF}_6$  in EC:EMC:DMC (1:1:1 in volume) is selected as electrolyte, the coulombic efficiency is around 85% and almost keeps invariable upon cycling which indicates the electrolyte is relatively stable. On the other hand, in the case of 1 mol/L  $\text{LiPF}_6$  in PC:DMC (1:1 in volume) as electrolyte, the coulombic efficiency is much poor and quickly decreases from the second cycle, which indicates that the electrolyte is very unstable at high voltage and very easy to react continuously with the active materials during the cyclic process.



**Fig. 4** Comparison of coulombic efficiency of electrolytic dependence of  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$  ball-milled for 6 h (Charge—discharge rate is  $1/3C$ )

Fig. 5 shows comparison of cycling performance of electrolytic dependence of  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$  ball-milled for 6 h, at the rate of  $1/3C$ . When 1 mol/L  $\text{LiPF}_6$  in EC:EMC:DMC (1:1:1 in volume) is selected as electrolyte, it exhibits high capacity as well as good cycling performance, whereas the capacity is reduced and faded quickly from the second cycle upon cycling, in the case of 1 mol/L  $\text{LiPF}_6$  in PC:DMC (1:1 in volume) as electrolyte, as clearly seen in Fig. 5. Comparing Fig. 4 with Fig. 5, it's obvious that poor coulombic efficiency is corresponding to poor cycling performance. The instability of electrolyte and continuous side reaction between electrolyte and active materials result in the amount decrease and structural degradation of the  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$  spinel. These effects lead to a quick capacity fade on cycling in

the case of 1 mol/L  $\text{LiPF}_6$  in PC: DMC (1: 1 in volume) as electrolyte.



**Fig. 5** Comparison of cycling performance of electrolytic dependence of  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$  ball-milled for 6 h  
(Charge—discharge rate is 1/3 C)

Therefore, the electrochemical performance depends strongly on the electrolyte, and the development of suitable electrolyte is a key factor for the effective use of  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$  spinel. In order to solve the problem on electrolyte decomposition at high voltage, we think that three approaches must be taken: 1) searching for suitable electrolyte that is highly resistant against oxidation at high voltage, 2) optimizing the  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$  powders, 3) modifying the  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ /electrolyte interface.

#### 4 CONCLUSIONS

Ball milling has great effect on the synthesis and property of  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ . X-ray diffraction (XRD) patterns indicate that  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$  can't be synthesized without ball milling even calcined at 900 °C. When synthesized with ball milling,  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$  almost exhibits only one plateau at 4.7 V. With the increase of ball milling time, the capacity of  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$  increases, but the cycling performance is not highly affected. The electrochemical property of  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$  highly depends on the electrolyte. The stable and high-voltage-resistant electrolyte is very beneficial to enhancement of electrochemical performance of  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ .

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