Effect of different MnO₂ precursors on the electrochemical properties of spinel

LiNi_{0.5}Mn_{1.5}O₄ cathode active materials for high-voltage lithium ion batteries

Ye Ma^{a,b,*,1}, Haoqing Tang^{a,1}, Zhiyuan Tang^{a,b,*}, Wenfeng Mao^a, Xinhe Zhang^c

Abstract

$\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ (LNMO) cathode materials with different morphologies are prepared via a facile template method using various MnO_2 precursors. The structures, morphologies and electrochemical properties of the as-prepared $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ samples are tested by various physical and electrochemical methods. The results of characterization show that the spinel LNMO cathode materials have good crystal structure and the MnO_2 precursors have no effect on the final products. Moreover, the specific morphology of LNMO is closely related to that of MnO_2 precursor, and further influence the electrochemical performance. In addition, the LNMO sample using NH_4HCO_3 as precipitant exhibits excellent rate capability and cyclic stability in all as-prepared samples. Cycled at 0.5 C and 1 C, the discharge capacities of LNMO cathode active particles using NH_4HCO_3 as precipitant are 110.6 mAh g^{-1} and 102.2 mAh g^{-1} after 200 charge-discharge cycles, respectively, which are the largest compared with the LNMO using $(\text{NH}_4)_2\text{S}_2\text{O}_8$ and KMnO_4 as oxidants.

Keywords: Lithium-ion battery; lithium nickel manganese oxides; manganese oxides; morphology; electrochemical performance

1. Introduction

Rechargeable lithium-ion batteries (LIBs) have gained increased popularity due to its high energy storage density, long cycle life, fast charging and discharging ability and friendliness to environment, and are considered as one of the most promising power sources for electric vehicle (EV), hybrid electric vehicle (HEV), wearable electronic products and laptops [1-5]. LIBs first commercialization was achieved in 1991, and it has contains cathode and anode electrode active material, membrane and organic electrolyte for Li^+ transportation. Of which, electrode materials, especially the cathode materials, play an important role in achieving the energy demands. However, the available energy density of conventional cathode materials, such as LiCoO_2 , LiMn_2O_4 , and LiFePO_4 , is difficult to meet the demand. Many efforts have been made to search for new cathode materials that could potentially satisfy the market for high demand on portable electronic devices and electric vehicle technology [6-8]. Among the different kinds of cathode materials, spinel structured $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ (LNMO), which exhibits higher energy density, lower cost and better cycling stability, is a promising cathode material for energy density improvement of current LIBs, because it provides higher working voltage at 4.7 V, which is higher than commercial cathodes such as LiFePO_4 (3.4V), LiMn_2O_4 (4.0V) and LiCoO_2 (3.9V) [9-16].

The common methods of synthesizing LNMO mainly include solid state method [17, 18], co-precipitation method [19, 20] and sol-gel method [21, 22]. All above methods have their own drawbacks, for example, particles synthesized via solid state method may have some disadvantages such as large particle size, poor particle size uniformity and so on. In addition, these methods cannot control the morphology of LNMO effectively, which can directly affect the electrochemical properties of the materials. It was reported that using manganese oxides as

precursors can improve the electrochemical performance of LNMO nanoparticles [23-25], and to a certain extent, can control the morphology of LNMO.

In this paper, we synthesized spinel LNMO samples with different morphologies via template method using various MnO_2 precursors. The effects of MnO_2 precursors on the final structures, morphologies and rate capability were investigated. The results show that LNMO are maintained the morphology of MnO_2 precursors. That is to say that we can control the morphology of LNMO through choosing different MnO_2 precursors, which provides a new choice for the development of high performance electrode in lithium-ion batteries.

2. Experimental

2.1 Synthesis of MnO_2 with different morphologies

MnO_2 with different morphologies were synthesized via three different ways, including using NH_4HCO_3 as precipitant, which marked as $\text{MnO}_2\text{-A}$, and using $(\text{NH}_4)_2\text{S}_2\text{O}_8$ and KMnO_4 as oxidants, which marked as $\text{MnO}_2\text{-B}$ and $\text{MnO}_2\text{-C}$, respectively. $\text{MnO}_2\text{-A}$ was synthesized from NH_4HCO_3 and MnSO_4 by using the method of Zhou's [26]. 140 mL ethanol was poured into MnSO_4 solution (15 mmol/L, 1400 mL), followed by the addition of 1.4 L NH_4HCO_3 solution (0.15 mol/L) under continuous stirring in 1.5 h at room temperature, resulting in a pre-product, MnCO_3 after centrifuge. Then the pre-product was oxidized into $\text{MnO}_2\text{-A}$ by calcination for 4h at 400 °C. To prepare $\text{MnO}_2\text{-B}$, $(\text{NH}_4)_2\text{S}_2\text{O}_8$ and MnSO_4 were dispersed into distilled water to get the solution of 0.15 mol/L, respectively. Then $(\text{NH}_4)_2\text{S}_2\text{O}_8$ solution was dropped into the other one under stirring at 80 °C, followed by putting in water bath at 80 °C for 4h. After washing the product with distilled water and drying, $\text{MnO}_2\text{-B}$ was obtained. The synthesis process of $\text{MnO}_2\text{-C}$ is similar to that of $\text{MnO}_2\text{-B}$. While, MnSO_4 solution (0.15 mol/L) was added into KMnO_4 solution (0.2 mol/L) under

stirring at room temperature, followed by washing with distilled water and drying, $\text{MnO}_2\text{-C}$ was prepared. It is necessary to point out that an excess of K^+ is conducive to maintain the structural stability of $\text{MnO}_2\text{-C}$, as reported by Devaraj [27].

The reaction equations of three kinds of MnO_2 can be described as follows:

2.2 Preparation of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$

Stoichiometric amount of LiOH , $\text{Ni}(\text{NO}_3)_2$ and MnO_2 were dispersed in appropriate ethanol to obtain a mixture. Then, the mixture was stirred by slow magnetic stirring until ethanol volatilized completely. After drying and grinding, the powder was converted into $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ (LNMO) by calcination at 850°C for 20 hours. LNMO obtained from $\text{MnO}_2\text{-A}$, $\text{MnO}_2\text{-B}$ and $\text{MnO}_2\text{-C}$ were marked LNMO-A, LNMO-B, LNMO-C, respectively.

2.3 Material characterization

The phase composition and crystalline structure of the MnO_2 and $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ were examined by X-ray diffraction (XRD, Rigaku D/max 2500 v/pc) using Cu-K α radiation. The particle morphology and microstructure of the composite were observed with scanning electron microscopy (SEM, XL30ESEM, Philips) and transmission electron microscopy (TEM, JEM-2100F).

2.4 Electrochemical measurements

The electrochemical tests of LNMO were performed using 2032 coin-type half cells, which were composed of the LNMO electrode, lithium metal, a Celgard 2300 separator, and LiPF_6 in ethylene carbonate/diethyl carbonate/dimethyl carbonate (1:1:1 w/w) as the electrolyte. All cells were assembled in an Argon-filled glove box. The LNMO electrodes were fabricated by mixing the obtained active powder, super P and polyvinylidene (PVDF) in a weight ratio of 80: 10: 10 in N-methyl-2-pyrrolidinone (NMP), and the cathode active materials loading was about 3.0 mg/cm^2 . All the cells were tested using a multichannel battery workstation (Neware Co. China). Cyclic voltammetry (CV) was carried out on a Gamry PCI4-750 electrochemical working station.

3. Results and discussion

3.1 Structural characterization

XRD patterns of MnO_2 with different morphologies are presented in Fig. 1a, in which the majority of diffraction lines of MnO_2 -A and MnO_2 -B match well with α - MnO_2 (JCPDS no. 44-0141), while the diffraction line of MnO_2 -C matches with δ - MnO_2 (JCPDS no. 18-0802)[27]. The structure of α - MnO_2 consists of double chains of edge-sharing MnO_6 octahedra, which are linked at corners to form 1D (2×2) and (1×1) tunnels that extend in a direction parallel to the c axis of the tetragonal unit cell. δ - MnO_2 is a 2D layered structure with an interlayer separation of $\sim 7 \text{ \AA}$ [27]. Fig. 1b shows the XRD patterns of LNMO prepared from three different ways, in which the majority of diffraction lines matched well with the cubic LNMO spinel phase with the space group of $\text{Fd}\bar{3}\text{m}$. These results indicate that the MnO_2 with diverse morphologies does not affect the crystal structure of the resulting product. In addition, it can be seen that all the three LNMO samples have weak diffraction peaks at 37.91° , 43.86° and 63.5° , as marked with asterisks, which can be ascribed to NiO and

$\text{Li}_x\text{Ni}_{1-x}\text{O}$. It is the most common impurity in the preparation of LNMO when sintered over 700 °C [28, 32, 37].

3.2 Morphological analysis

In order to estimate the effect of the morphology of MnO_2 on LNMO, the morphology and the inner microstructure of prepared products were examined by SEM and TEM. For the MnO_2 -A particles (Fig. 2a), irregular cube morphology which composed of uniform thickness lamellas can be clearly seen. Besides, it can be seen that the size of MnO_2 -A particles ranges from 3 μm to 5 μm . Fig. 2b shows that the MnO_2 -B sample has noticeable agglomeration during the precipitation process. The diameter of secondary particles is from 3 to 5 μm . From the SEM image of MnO_2 -C sample (Fig. 2c), it can be clearly seen that the particle size of MnO_2 -C is the smaller than others, which is about 200 nm. What's more, the agglomeration at high temperature calcination process has been decreased significantly. More packed holes come from the primary particle aggregation are appeared, which are in favor of increase specific surface area and improve electrochemical performance.

Fig. 3 shows the morphology of LNMO, in which all LNMO are maintained the morphology of each MnO_2 . In detail, LNMO prepared from MnO_2 -A, marked as LNMO-A, has a morphology of hollow cube, while LNMO-B has structure with a solid sphere, and LNMO-C is aggregated with many nanosheets. More detail structural information could be obtained by lattice fringe images. The lattice fringe images examined by HR-TEM, and the result is shown in Fig. 3d, 3e and 3f. The lattice fringes of three LNMO can be clearly imaged, which indicate that different MnO_2 does not affect the crystal structure of LNMO.

3.3 Electrochemical performance

In order to evaluate the cyclic reversibility performance of three LNMO samples, all cells were charged at 0.5 C, and then discharged at 0.5 C, 1 C, 2 C, 5 C, 8 C, 10 C, respectively, finally recovered to 0.5 C. The obtained results are displayed in Fig. 4. It can be clearly observed that the specific capacity delivered by LNMO-A is larger than those of LNMO-B and LNMO-C at different discharge rates. The reasons can be attributed to the particle morphology and the crystal structure of the as-prepared samples. Specifically speaking, the smaller particle diameter has shorter transport distance for both Li^+ and electron, which could enhance the transmission speed and improve the kinetics performance [29]. What's more, the stack holes between secondary particles could enlarge the contact area between the active material and the electrolyte and increase the active sites for Li^+ insertion/de-insertion. Moreover, when it comes to higher current densities, it is obvious that LNMO-C exhibits a better stability and a larger specific capacity. This phenomenon may be caused by trace K^+ doped in the particle structure when preparing MnO_2 -C. It has been reported that K^+ is benefited on structure stability of $\delta\text{-MnO}_2$ [27].

The spinel structure of the resulting samples was confirmed with galvanostatic charge/discharge experiments. Fig.5 presents the cycling performance and charge/discharge profiles at 0.5 C, 1 C and 5 C rates of the resulting samples, which indicates that all three samples are characteristic of spinel structure. The long and smooth potential plateau at about 4.7 V in the discharge profile (Fig. 5b, d, f) is ascribed to oxidation/reduction of $\text{Ni}^{2+}/\text{Ni}^{3+}$ and $\text{Ni}^{3+}/\text{Ni}^{4+}$, while the short potential plateau at about 4.0 V corresponds to the reaction of $\text{Mn}^{3+}/\text{Mn}^{4+}$ redox couples [10, 30, 31]. This short plateaus become more obvious in LNMO-A and LNMO-B samples, which prove the existence of larger amount of Mn^{3+} , and this plateau was longer in LNMO-B, indicated the amount of Mn^{3+} was larger. In comparison, the shorter plateau in LNMO-C indicates that Mn^{3+} ions are almost absent in this sample, because the existence of K^+ decreased the reduction of Mn^{4+} . Figs. 5a, 5c and 5e

present the discharge variations of LNMO-A, LNMO-B and LNMO-C at 0.5 C, 1 C and 5 C. When discharged at 0.5 C, those three samples deliver a discharge specific capacity of 123.4 mAh g⁻¹, 117.7 mAh g⁻¹ and 114.9 mAh g⁻¹, respectively. After 100 cycles at 1 C, 87.17%、88.41% and 68.94% of specific capacity retention are maintained compared with the highest specific capacity, respectively. It can be clearly seen that the specific capacity of LNMO-A is larger than the other ones, while the difference between LNMO-B and LNMO-C is small at low rates. But obviously, the cycling stability of LNMO-C is poorer. At 5 C, however, the electrochemical performance of LNMO-C becomes better than LNMO-B, which may be caused by K⁺. On the other hand, LNMO-A and LNMO-B exhibit better cycle stability and rate capacity than LNMO-C, which is resulted from the existence of Mn³⁺, for the reason that Mn³⁺ makes the spinel structure become more stable in charge/discharge process [32]. The reaction is a one-step reversible phase-transfer reaction during lithium insertion/extraction process, as a result, the transport of lithium has little influence on spinel structure.

Figure 6 depicts the representative CV response of the synthesized LNMO samples at low scan rate (0.05 mV/s). Two strong redox peaks at about 4.7 V corresponding to the two-step oxidation/reduction of Ni²⁺/Ni³⁺ and Ni³⁺/Ni⁴⁺ are presented, while the small redox peaks at about 4.0 V are attributed to the Mn³⁺/Mn⁴⁺ redox couple. As the scan rate was slow, we can ignore the effect causing by electric double layer capacity. As a consequence, the Mn³⁺ amount can be compared through the peak areas at 4.0 V qualitatively. We can clearly see that the content of Mn³⁺ in LNMO-C was lowest, while LNMO-B's was the highest one. Such results are in agreement with the two charge/discharge plateaus in Fig. 5. In addition, the potential differences between cathodic and anodic peaks are all about 0.12V, suggesting that the electrode polarization of three LNMO samples were similar. Furthermore, the potential differences (ΔV) between those two anodic peaks

calculated and shown in Table 1, from which we can see that ΔV among three samples were little. It has been reported that the voltage gap between the two voltage plateaus depends on the degree of ions ordering [33, 34]. As the three LNMO samples were synthesized via a similar process, except the MnO_2 precursors, we can judge that the ions ordering in three LNMO samples were almost the same. Besides, LNMO-A has a larger curve area and higher redox peak current compared with others, suggesting that LNMO-A has the higher capacity and the faster kinetics for the reversible insertion and de-insertion of lithium ions due to the hollow structure and larger active area [35, 36].

4. Conclusion

In summary, we have developed a facile template method for preparing LNMO with different morphologies, and discussed the difference on structure, morphology and electrochemical performance among the three samples. Based on three different MnO_2 precursors, we have synthesized spinel LNMO cathode materials successfully, which exhibits excellent rate capability and cyclic stability. The specific morphology of LNMO is closely related to that of MnO_2 precursor, and which can further influence the electrochemical performance. Through controlling the formation of MnO_2 precursor, we have firstly realized controlled synthesis of LNMO. The LNMO sample using NH_4HCO_3 as precipitant exhibits superior rate capability and cyclic stability in all as-prepared samples. The reasons of good electrochemical performance can be attributed to the smaller particle diameter and the stack holes between secondary particles.

Acknowledgments

This work was supported by National Science Foundation of China (Grant No. 20973124).

References

- [1] M. Armand, J.M. Tarascon, *Nature* 451 (2008) 652–657.
- [2] B. Dunn, H. Kamath, J.M. Tarascon, *Science* 334 (2011) 928–935.
- [3] H. Li, Z.X. Wang, L.Q. Chen, X.J. Huang, *Adv. Mater.* 21 (2009) 4593–4607.
- [4] B.G. Pollet, I. Staffell, J.L. Shang, *Electrochim. Acta* 84 (2012) 235–249.
- [5] J.B. Goodenough, K.-S. Park, *J. Am. Chem. Soc.* 135 (2013) 1167–1176.
- [6] H. Tao, Z. Feng, H. Liu, X. Kan, P. Chen, *Open Mater. Sci. J.* 5 (2011) 204–214.
- [7] B.G. Pollet, I. Staffell, J.L. Shang, *Electrochim. Acta* 84 (2012) 235–249.
- [8] W.-f Mao, C.-x Ma, Y. Ma, Z.-y Tang, *Ionics* 20 (2014) 897–900.
- [9] A Kraytsberg, Y. Ein-Eli, *Adv. Energy Mater.* 2 (2012) 922–939.
- [10] H.B. Lin, Y.M. Zhang, J.N. Hu , Y.T. Wang , L.D. Xing , M.Q. Xu , X.P. Li ,W.S. Li. *J. Power Sources*, 257 (2014) 37–44.
- [11] M. Kassem, J. Bernard, R. Revel, S. Pélissier, F. Duclaud, C. Delacourt, *J. Power Sources*, 208 (2012) 296–305.
- [12] S. Liu, L. Xiong, C. He, *J. Power Sources*, 261 (2014) 285–291.
- [13] Z. Qiao, O. Sha, Z.Y. Tang, J. Yan, S.L. Wang, H.B. Liu, Q. Xu, Y.J. Su, *Mater. Lett.* 87 (2012) 176–179.
- [14] K. Alexander, E-E. Yair, *Adv. Energy Mater.* 2 (2012) 922–939.
- [15] Jeffrey W. Fergus, *J. Power Sources* 195 (2010) 939–954.
- [16] C. M. Julien, A. Mauger, *Ionics* 19 (2013) 951–988.
- [17] Z Zhu, Y Hui, D Zhang, W Li, L Qi, *J. Power Sources* 224 (2013) 13–19.
- [18] W.W. Wu, H.F. Xiang, G.B. Zhong, W. Su, W. Tang, Y. Zhang, Y. Yu, C.H. Chen, *Electrochim. Acta* 119 (2014) 206–213.
- [19] M. Zhang, Y. Liu, Y. Xia, B. Qiu, J. Wang, Z. Liu, *J. Alloys and Compounds* 598 (2014) 73–78.

[20] D. Liu, J. Han, J. B. Goodenough, J. Power Sources 195 (2010) 2918-2923.

[21] X. -L Cui, Y. -Li Li, S.-Y Li, L.-X Li, J. -L Liu, Ionics 19 (2013) 1489-1494.

[22] B. J. Hwang, Y. W. Wu, M. Venkateswarlu, M. Y. Cheng, R. Santhanam, J. Power Sources 193 (2009) 828-833.

[23] J. Yang, X. Zhang, Z. Zhu, F. Cheng, J. Chen, J. Electroanal. Chemistry 688 (2013) 113-117.

[24] G. Wang, J. Xie, T. Zhu, G. Cao, X. Zhao, S. Zhang, Functional Mater. Lett. 7 (2014) 1450009-1450012.

[25] C. Y. Zhu, T. Akiyama, RSC Adv. 4 (2014) 10151-10156.

[26] L. Zhou, D. Y. Zhao, X. W. Lou, Angew. Chemie 51 (2012) 239-241.

[27] S. Devaraj, N. Munichandraiah, J Phys Chem C 112 (2008) 4406-4417.

[28] X. Zhu, X. Li, Y. Zhu, S. Jin, Y. Wang, Y. Qian, Electrochim. Acta 121 (2014) 253-257.

[29] X. Zhang, F. Cheng, J. Yang, J. Chen, Nano Lett. 13 (2013) 2822-2825.

[30] T.-F. Yi, Y. Xie, Y.-R. Zhu, R.-S. Zhu, M.-F. Ye, J. Power Sources 211 (2012) 59-65.

[31] Y. Talyosef, B. Markovsky, G. Salitra, D. Aurbach, H. J. Kim, S. Choi, J. Power Sources 146 (2005) 664-669.

[32] J.-H. Kim, S.-T. Myung, C. S. Yoon, S. G. Kang, Y.-K. Sun, Chem. Mater. 16 (2004) 906-914.

[33] D. Liu, J. Trottier, P. Charest, J. Fréchette, A. Guerfi, A. Mauger, C. M. Julien, K. Zaghib, J. Power Sources 204 (2012) 127-132.

[34] W. Zhu, D. Liu, J. Trottier, C. Gagnon, A. Guerfi, C. M. Julien, A. Mauger, K. Zaghib, J. Power Sources 264 (2014) 290-298.

[35] L. Mai, S. Li, Y. Dong, Y. Zhao, Y. Luo, H. Xu, Nanoscale 5 (2013) 4864-4869

[36] H. Tang, J. Zhu, Z. Tang, C. Ma, J. Electroanal. Chem. 731 (2014) 60-66.

[37] L. Wang, H. Li, X. Huang, E. Baudrin, Solid State Ionics 193 (2011) 32-38.

1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60
61
62
63
64
65

List of Figures:

Fig. 1. (a) The XRD patterns of MnO_2 : MnO_2 -A synthesized from NH_4HCO_3 ; MnO_2 -B synthesized from $(\text{NH}_4)_2\text{S}_2\text{O}_8$; MnO_2 -C synthesized from KMnO_4 ; (b) XRD patterns of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ (LNMO): LNMO-A synthesized from MnO_2 -A; LNMO-B synthesized from MnO_2 -B; LNMO-C synthesized from MnO_2 -C.

Fig. 2. FE-SEM micrographs of (a) MnO_2 -A synthesized from NH_4HCO_3 ; (b) MnO_2 -B synthesized from $(\text{NH}_4)_2\text{S}_2\text{O}_8$ and (c) MnO_2 -C synthesized from KMnO_4 .

Fig. 3. FE-SEM micrographs of (a) LNMO-A; (b) LNMO-B, and (c) LNMO-C. TEM micrographs of (d) LNMO-A; (e) LNMO-B and (f) LNMO-C.

Fig. 4. Comparison of discharge C-rate capability between pristine LNMO-A, LNMO-B and LNMO-C where charged at 0.5 C and discharged varied from 0.5 C to 10.0 C.

Fig. 5. Cycling performance of LNMO-A, LNMO-B and LNMO-C at charge and discharge rates of 0.5 C, 1 C, 5 C under a voltage range of 3.5 to 5.0 V (a, c, e). The charge and discharge curves of LNMO-A, LNMO-B and LNMO-C at charge and discharge rates of 0.5 C, 1 C, 5 C under a voltage range of 3.5 to 5.0 V (b, d, f).

Fig. 6. Cyclic voltammetry curves of LNMO in the voltage range of 3.5-5.0V with a scan rate of 0.05mV s^{-1} .

Fig. 1

Fig. 2

Fig. 3

Fig. 4

Fig. 5

Fig. 6

Table 1

The voltage difference ΔV , between two anodic peaks in the different LNMO samples

Cathode	LNMO-A	LNMO-B	LNMO-C
V1 (V)	4.7650	4.7500	4.7320
V2 (V)	4.8140	4.8025	4.7830
ΔV (mV)	49	52.5	51