Journal of Alloys and Compounds 518 (2012) 68–73

Contents lists available at SciVerse ScienceDirect

Journal of Alloys and Compounds

journal homepage: www.elsevier.com/locate/jallcom

Microwave synthesis of spherical spinel $LiNi_{0.5}Mn_{1.5}O_4$ as cathode material for lithium-ion batteries

Minghao Zhang, Jun Wang, Yonggao Xia*, Zhaoping Liu*

Ningbo Institute of Material Technology & Engineering, Chinese Academy of Sciences, Ningbo 315201, PR China

ARTICLE INFO

Article history:
Received 18 September 2011
Received in revised form
19 December 2011
Accepted 25 December 2011
Available online 31 December 2011

Keywords:
Spinel $LiNi_{0.5}Mn_{1.5}O_4$
Microwave synthesis
Oxygen loss
Crystallinity
Improving cycling performance

ABSTRACT

Spinel $LiNi_{0.5}Mn_{1.5}O_4$ cathode material with excellent electrochemical performance was synthesized through microwave heat treatment using spherical $(Ni_{0.25}Mn_{0.75})_3O_4$ precursor which was prepared by a co-precipitation method. Compared with the conventional heat treatment in a muffle furnace, the microwave approach not only diminished the impurity level but also reduced the sizes of primary particles. These characters led to increase in discharge capacity and rate capability of $LiNi_{0.5}Mn_{1.5}O_4$. In this study, it was found that the microwave co-precipitation method was fairly effective for further solving the problem of cycling performance, when the microwave irradiation was introduced in. The $LiNi_{0.5}Mn_{1.5}O_4$ cathode material synthesized by this method delivered a discharge capacity of 142 mAh g^{-1} at 0.1 C rate (corresponding to 97% of the theoretical capacity), and had a capacity retention of 97% after the 50th cycle at room temperature, showing an improved electrochemical performance.

1. Introduction

Lithium-ion batteries (LIBs) have met the increasing needs for various personal electronic devices since their commercialization in the early 1990s [1]. Recently, the possible applications of large-volume LIBs for electric vehicles (EVs) and hybrid electric vehicles (HEVs) have been extensively explored [2,3]. Although $LiCoO_2$ has been dominatingly used as cathode material for small size LIBs, it is difficult to be used in large-volume, high-power LIBs due to its safety problem and high cost. Many studies have focused on the development of other alternative cathode materials in view of cost, safety and environment [4,5].

Spinel $LiNi_{0.5}Mn_{1.5}O_4$ is one of the most promising cathode materials due to its good cycling performance, acceptable thermal stability and low cost [6–8]. It exhibits a theoretical capacity of 147 mAh g^{-1} with one dominant plateau at around 4.7 V [9–11]. The high voltage can supply the battery with a high energy density, which can meet the requirements of EVs and HEVs.

Spinel $LiNi_{0.5}Mn_{1.5}O_4$ is usually synthesized through conventional solid state reaction of stoichiometric amounts of starting materials, under heating at 650–1000 °C for 6–24 h [12]. Since the formation of well-developed crystals are difficult at firing temperature of lower than 800 °C, sintering of the precursor at higher temperatures (>800 °C) for long reaction time is necessary to produce spinel $LiNi_{0.5}Mn_{1.5}O_4$ with excellent cycling performance [13]. However, secondary phases such as NiO and $Li_xNi_{1-x}O$ usually generate at the mean time due to the oxygen loss, and these would deteriorate the electrochemical performance of spinel $LiNi_{0.5}Mn_{1.5}O_4$ material [14]. Therefore, some researchers suggested that the oxygen loss of $LiNi_{0.5}Mn_{1.5}O_4$ material occurring at high sintering temperature for long reaction time could be covered by post-reaction annealing [15,16]. Despite the success of preparing pure spinel $LiNi_{0.5}Mn_{1.5}O_4$, the excessive grain growth due to the conventional calcination way has an adverse influence on the rate capability of the material. To further improve the rate performance of $LiNi_{0.5}Mn_{1.5}O_4$, some researchers took the strategy of synthesizing nanosized spinel $LiNi_{0.5}Mn_{1.5}O_4$ material to reduce the overall transport length for both electrons and ions [17–19]. In addition, various dopants have been proposed to obtain the spinel $LiNi_{0.5}Mn_{1.5}O_4$ material with faster lithium diffusion and better rate capability [20–22].

Due to the experience that the microwave synthesis could reduce the oxygen loss and the excessive grain growth during the sample preparation, it is supposed that the demerits mentioned above could be easily avoided if adopting the microwave irradiation way. Further, the microwave synthesis is simpler and more energy efficient comparing with the conventional calcination way; and recently, several efforts have been made to apply microwave synthesis for preparing electrode materials for LIBs, such as $Li_4Ti_5O_{12}$ [23], $LiMn_2O_4$ [24], and $Li[Ni_{0.4}Co_{0.2}Mn_{0.4}]O_2$ [25]. However, in most cases, the electrochemical performance was not so satisfactory due to low crystallinity. Many researchers have proposed a

---

* Corresponding authors. Tel.: +86 574 86685096; fax: +86 574 86685096.
E-mail addresses: xiayg@nimte.ac.cn (Y. Xia), liuzp@nimte.ac.cn (Z. Liu).

0925-8388/$ – see front matter © 2012 Elsevier B.V. All rights reserved.
doi:10.1016/j.jallcom.2011.12.128

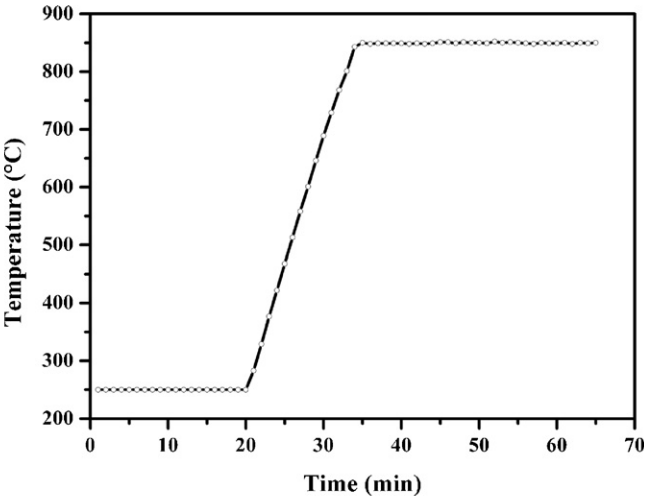

Fig. 1. Heating curve of the microwave irradiation.

two-step synthesis for improving their crystallinity, and they suppose that further heat treatments at higher temperature for long time after microwave treatment are necessary [24–26].

In this study, the electrochemical performance of $LiNi_{0.5}Mn_{1.5}O_4$ cathode material using microwave irradiation has been investigated. The sample synthesized by microwave irradiation using spherical $(Ni_{0.25}Mn_{0.75})_3O_4$ precursor exhibited better electrochemical properties than that of the sample synthesized by conventional heat treatment; moreover, we found that the microwave co-precipitation was a fairly effective method to solve the problem of poor cycling performance when using microwave irradiation to synthesize $LiNi_{0.5}Mn_{1.5}O_4$ compounds. It is concluded that a one-step synthesis of highly crystalline spinel $LiNi_{0.5}Mn_{1.5}O_4$ with excellent electrochemical performance using microwaves irradiation is possible with the help of homogeneous carbonate.

2. Experimental

2.1. Synthesis

In order to prepare the spherical $LiNi_{0.5}Mn_{1.5}O_4$ powders, spherical $(Ni_{0.25}Mn_{0.75})CO_3$ precursor were firstly prepared through co-precipitation method in a continuously stirred tank reactor. 100 ml of a 2 M mixed acid solution of $NiSO_4$ and $MnSO_4$ (Ni:Mn = 1:3 molar ratio) was pumped into a stirred tank reactor. At the same time, a 2 M Na_2CO_3 solution with 0.3 M NH_4OH added in as a chelating agent was also fed into the reactor drop by drop. The co-precipitation temperature was set at 60 °C, and the pH value was fixed to 7.8. After vigorously stirred for 10 h in the reactor, the spherical $(Ni_{0.25}Mn_{0.75})CO_3$ precursor was washed and dried. And then the obtained spherical $(Ni_{0.25}Mn_{0.75})CO_3$ particles were calcined at 500 °C for 3 h for decomposing the carbonate into an oxide compound. Thereafter, the collected spherical $(Ni_{0.25}Mn_{0.75})_3O_4$ powder was mixed with a stoichiometric amount of Li_2CO_3 and placed in a 50 ml porcelain crucible. The precursor was irradiated at 850 °C for 30 min with the 915 MHz microwave under a maximum power of 1300 W, as illustrated in Fig. 1. And one sample was calcined 850 °C for 18 h in a muffle furnace (optimal calcination conditions for electrochemical performances of $LiNi_{0.5}Mn_{1.5}O_4$ synthesized by the conventional solid state reaction [27]) for comparing with the conventional calcination way.

For comparison, direct microwave solid state synthesis was carried out. The stoichiometric amount of $CH_3COOLi{\cdot}2H_2O$, $(CH_3COO)_2Ni{\cdot}4H_2O$ and $(CH_3COO)_2Mn{\cdot}4H_2O$ was mixed in a ball milling machine with 40% (mass fraction) excess of $C_2H_2O_4{\cdot}2H_2O$ as reaction media. Then the mixture was milled in a planetary milling machine for 10 h. The obtained mixture was dried in air at 120 °C for 6 h to form a precursor. The precursor then was irradiated at 850 °C for 30 min as the same way mentioned before.

2.2. Characterizations

The samples were characterized by X-ray powder diffraction (XRD) using an AXS D8 Advance diffractometer in the range of 10–90° (2θ). The morphology and microstructure of the samples were taken by using scanning electron microscopy (SEM, Hitachi, Japan) and transmission electron microscopy (TEM, Tecnai F_{20}). The Li, Ni, and Mn contents in the samples were confirmed by induce coupled plasma spectroscopy (ICP) using an emission spectrometer (Optima 2100 DV, Perkin-Elmer).

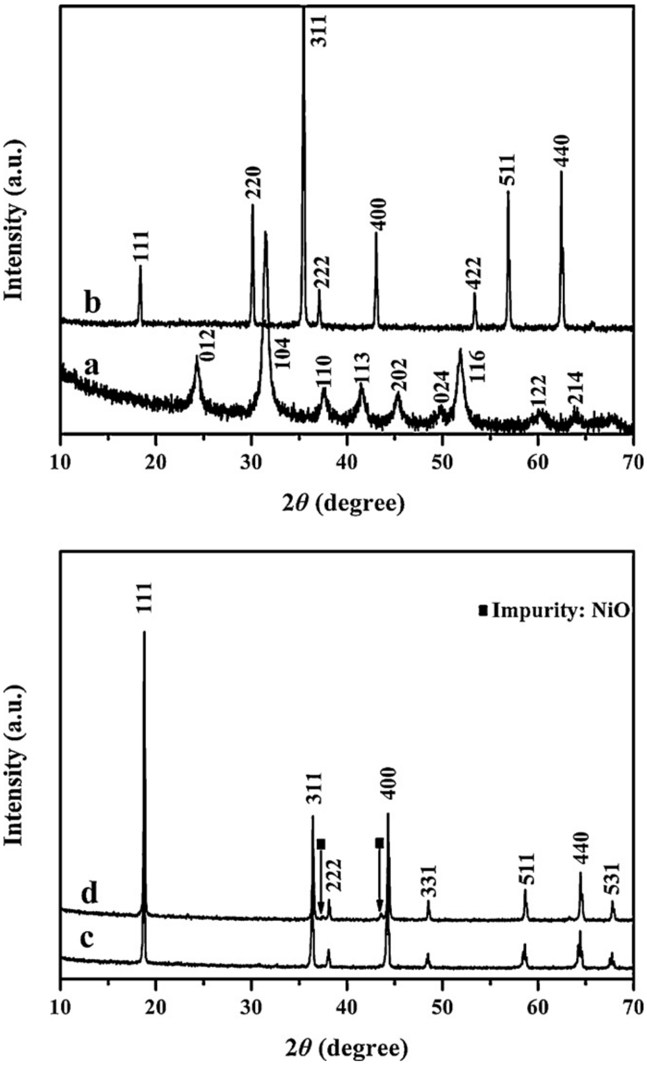

Fig. 2. XRD patterns of the samples: (a) $(Ni_{0.25}Mn_{0.75})CO_3$, (b) $(Ni_{0.25}Mn_{0.75})_3O_4$, (c) $LiNi_{0.5}Mn_{1.5}O_4$ irradiated in the microwave oven, and (d) $LiNi_{0.5}Mn_{1.5}O_4$ calcined in the muffle furnace.

2.3. Electrochemical tests

All of the electrochemical measurements were performed in the form of CR2032-type coin cells with metallic lithium as the counter and reference anode. The cathode consisted of 80 wt.% synthesized active materials, 10 wt.% acetylene black, 10 wt.% polyvinylidence fluoride (PVDF) and tiny amount of 1-methyl-2-pyrrolidone (NMP) solvent to form a slurry, and the slurry was coated on an Al foil and then dried in a vacuum oven at 120 °C for 12 h. The electrode foils had a surface area of 1.3 cm^2 and the areal density of the active material was around 4 mg cm^{-2}. 1 M $LiPF_6$ solution in a mixture of ethylene carbonate (EC)/dimethyl carbonate (DMC) (EC/DMC, volume ratio 1:1) was used as the electrolyte and the Celgard 2502 membrane as separator. Galvanstatic charge/discharge tests were carried out in the voltage range of 3.0–5.0 V with a LAND-CT2001A battery test system. In the rate test, the cell was charged and discharged at different *C* rates from 0.1 to 2 C, where 1 C corresponds to 147 mAh g^{-1}. In the cycling performance test, the cell was charged and discharged at 1 C for 50 cycles. Electrochemical impedance spectroscopy (EIS) measurements were performed on Auto-lab 83710 electrochemical workstation system, with the frequency range of 0.001 Hz–100 KHz.

3. Results and discussion

The XRD pattern of the precursor powder $(Ni_{0.25}Mn_{0.75})CO_3$ is shown in Fig. 2a. The reflections of precursor $(Ni_{0.25}Mn_{0.75})CO_3$ can be indexed to a hexagonal structure with a space group of

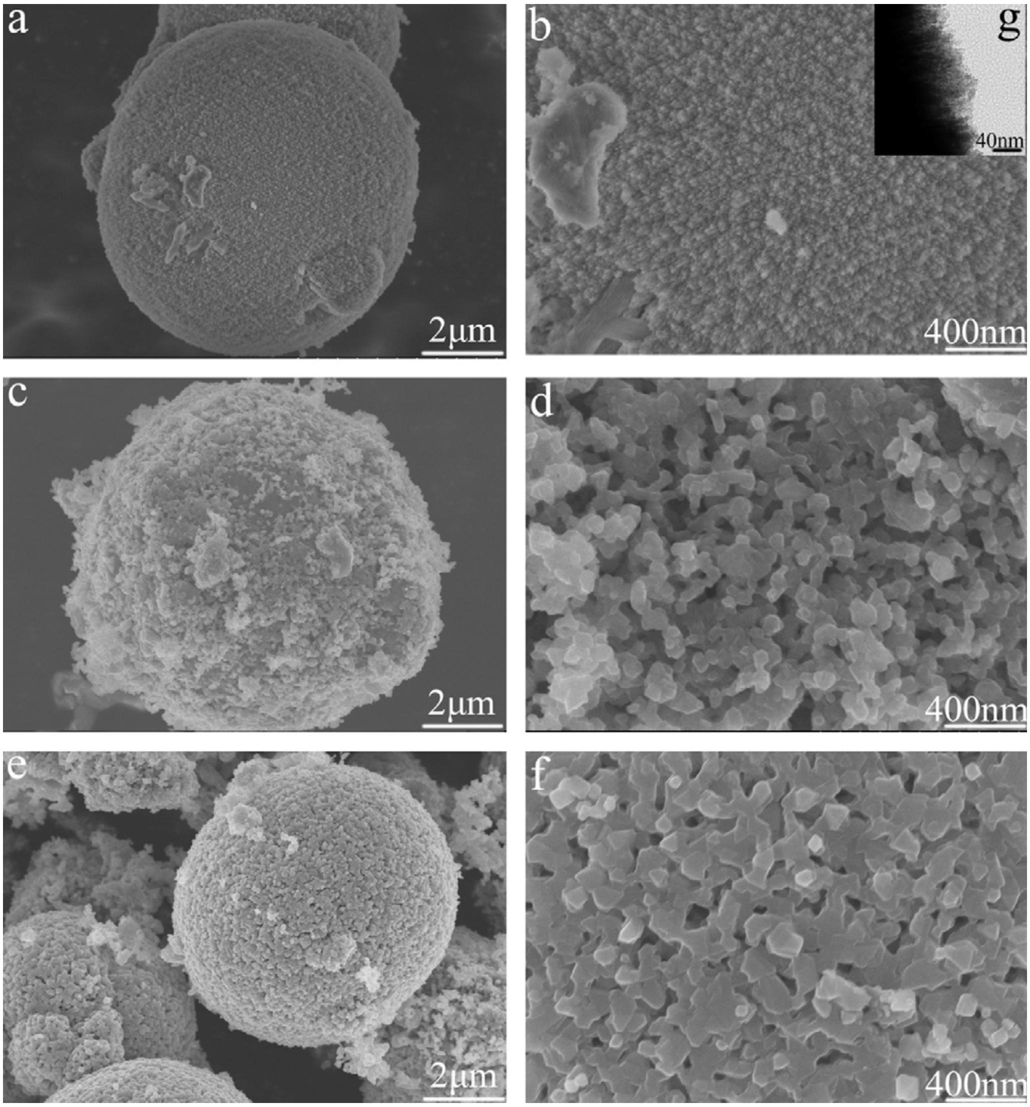

Fig. 3. SEM images of the samples: (a and b) $(Ni_{0.25}Mn_{0.75})CO_3$, (c and d) $LiNi_{0.5}Mn_{1.5}O_4$ irradiated in the microwave oven, and (e and f) $LiNi_{0.5}Mn_{1.5}O_4$ calcined in the muffle furnace. TEM images of the sample: (g) $(Ni_{0.25}Mn_{0.75})CO_3$.

$R\bar{3}c$ corresponding to $MnCO_3$ (JCPDS no. 44-1472) or $NiCO_3$ (JCPDS no. 12-0771), which have divalent transition metals. Due to the homogenous mixed nano-scale particles, the diffraction peaks are quite broad. However, after firing the carbonate precursor at 500 °C for 3 h, the hexagonal carbonate powder transformed to $(Mn)_3O_4$ (JCPDS no. 12-0269) with a cubic spinel structure, as can be seen from Fig. 2b. From the ICP results, the molar ratio of Ni and Mn was 1–3. Therefore, the formulate of the carbonate and oxide powders can be expressed as $(Ni_{0.25}Mn_{0.75})CO_3$ and $(Ni_{0.25}Mn_{0.75})_3O_4$.

Fig. 2c and d shows the XRD patterns of spherical $LiNi_{0.5}Mn_{1.5}O_4$ irradiated in the microwave oven and calcined in the muffle furnace. The samples irradiated in the microwave oven and calcined in the muffle furnace show similar XRD patterns, which can be indexed to the cubic spinel structure. It is worth noting that the weak NiO impurity peaks close to the lines of (2 2 2) and (4 0 0) were observed for the sample calcined in the muffle furnace, which could be attributed to the high calcination temperature and long reaction time [9]. The presence of secondary NiO could be harmful to the electrochemical performance of the spinel $LiNi_{0.5}Mn_{1.5}O_4$ material. And to our surprised, in the case of the co-precipitation precursor, the sample irradiated in the microwave oven for the short time of 30 min has almost the same crystallinity with the sample calcined in the muffle furnace for the long time of 18 h (see Fig. 2c and d), which is very different from the case of the precursor synthesized by the solid state method [28,29]. The higher crystallinity of the sample synthesized by a microwave co-precipitation method indicates a better developed crystalline, and it is beneficial to the cycling performance of the sample.

Fig. 3a and b illustrates SEM images for the precursor $(Ni_{0.25}Mn_{0.75})CO_3$ which has a spherical morphology with an average diameter of approximately 8 μm. It can be seen that these secondary spherical particles consist of primary nanoparticles with particles in the range of 10–20 nm (see Fig. 3g). Although low magnification images of the spherical $(Ni_{0.25}Mn_{0.75})CO_3$ are not shown in this paper, the particle size distribution of the material is depicted in Fig. 4a. As seen from the figure, the precursor $(Ni_{0.25}Mn_{0.75})CO_3$ has a log-normal distribution with the particle mean size of 8 μm, which is in accordance with the result of SEM images.

Fig. 3c and d shows SEM images for the $LiNi_{0.5}Mn_{1.5}O_4$ powder irradiated in the microwave oven. Even though the size of the primary particles increased to 100 nm due to the lithiation reaction and crystal growth [30], the spherical morphology of the precursor was preserved at high irradiation temperature. Similarly, the sample of $LiNi_{0.5}Mn_{1.5}O_4$ calcined in the muffle furnace also

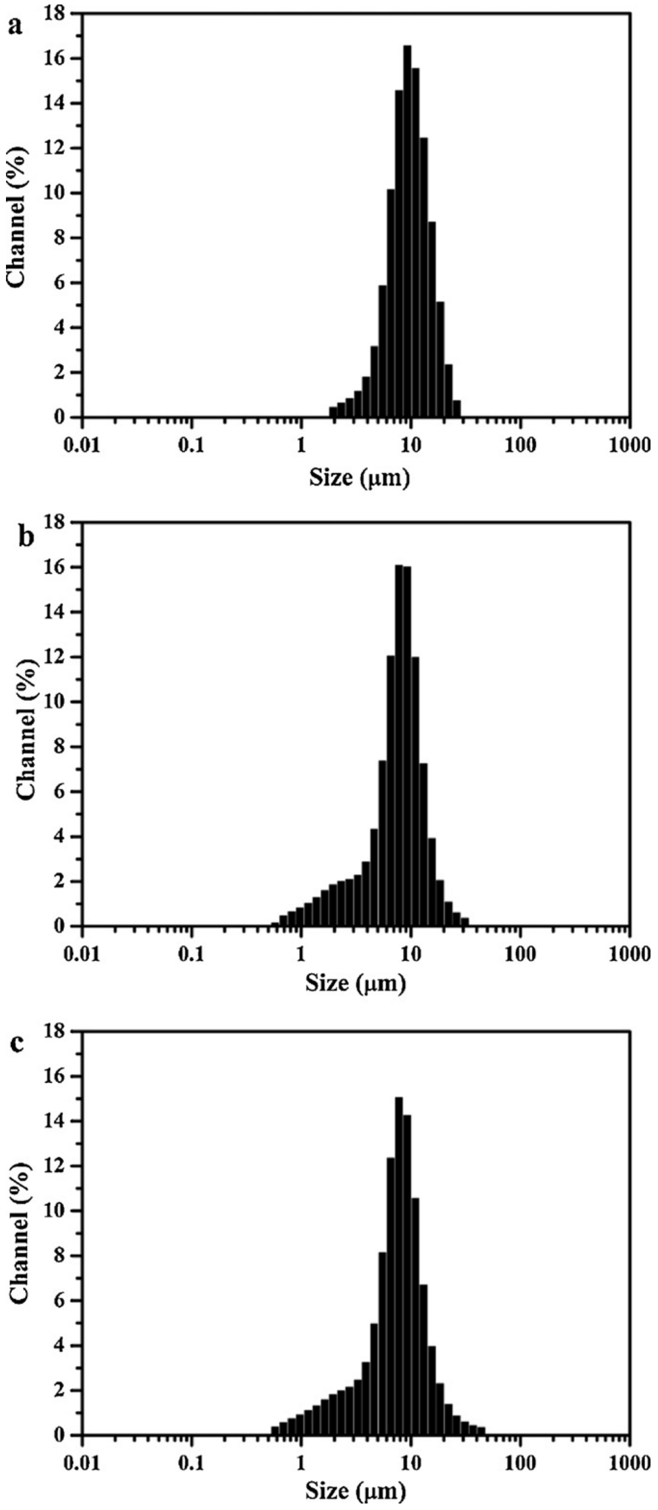

Fig. 4. Particle size distribution of the samples: (a) $(Ni_{0.25}Mn_{0.75})CO_3$ precursor synthesized via co-precipitation method, (b) $LiNi_{0.5}Mn_{1.5}O_4$ irradiated in the microwave oven, and (c) $LiNi_{0.5}Mn_{1.5}O_4$ calcined in the muffle furnace.

maintained the original spherical appearance as the precursor $(Ni_{0.25}Mn_{0.75})CO_3$ (see Fig. 3e and f). However, the micrograph clearly indicates that comparing with the conventional calcination way, microwave irradiation produce the particles with a smaller size. And the particle size and the analysis from XRD can give an important impact on the electrochemical performances of the samples, which will be discussed in detail in the passage below.

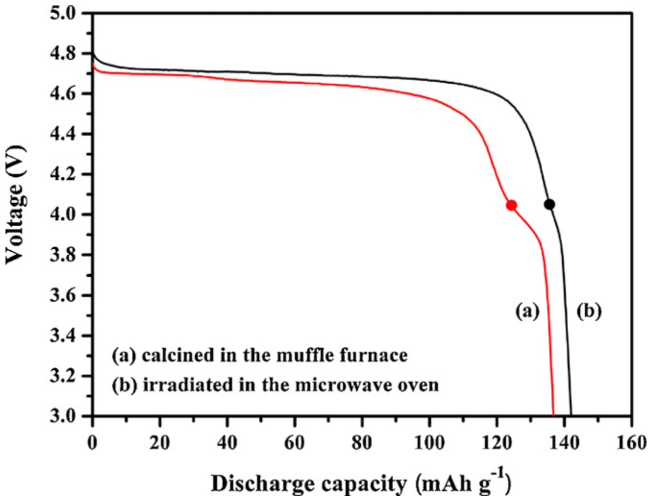

Fig. 5. Discharge curves of $LiNi_{0.5}Mn_{1.5}O_4$ synthesized by a co-precipitation method using two different heat treatment ways.

Additionally, $LiNi_{0.5}Mn_{1.5}O_4$ synthesized by the two different ways shows a similar particle size distribution as the precursor $(Ni_{0.25}Mn_{0.75})CO_3$ (see Fig. 4b and c). The slight difference of the particle size between the precursor and products could be attributed to the particles breakage and agglomeration during the mixing and sintering process of the precursors.

Fig. 5 shows the discharge voltage profiles of the samples calcined in the muffle furnace and irradiated in the microwave oven after 5 charge–discharge cycles. The cell was charged and discharged at 0.1 C with a cut-off voltage range of 3.0–5.0 V versus Li/Li^+ at room temperature. It can be seen from Fig. 5, the samples both have a similar discharge voltage profile with two main capacity regions which are around 4.7 V due to the redox couples Ni^{2+}/Ni^{3+}, Ni^{3+}/Ni^{4+}. However, the discharge curves of the sample calcined in the muffle furnace present a much more obvious plateau in the potential region around 4.0 V (from the redox couples Mn^{3+}/Mn^{4+}), which means that the oxygen deficiency is more severe due to the oxygen loss at high calcination temperature for long reaction time. Therefore, the discharge capacity of the sample synthesized by a microwave co-precipitation method visibly increases compared with the sample synthesized using conventional heat treatment. When the cell discharged at rate of 0.1 C, the discharge capacity of the sample irradiated in the microwave oven delivers a discharge capacity of 142 mAh g^{-1} which is about 97% of the theoretical capacity.

The discharge capacities of samples synthesized by a co-precipitation method at various rates are given in Fig. 6. The cell was charged and discharged at different *C* rates from 0.1 to 2 C. It can be seen from Fig. 6a, the rate capability of the sample synthesized by the conventional calcination way is obviously superior to that of the sample synthesized by the microwave irradiation. The sample irradiated in the microwave has a 130 mAh g^{-1} discharge capacity at 1 C rate, while that of the sample synthesized calcined in the muffle furnace is only 122 mAh g^{-1} at the same rate. Moreover, the sample synthesized by microwave irradiation can deliver a discharge capacity of about 127 mAh g^{-1} even at a high rate of 2 C, which is close to 96% of the discharge capacity at a low rate of 0.5 C. While the retention of the sample synthesized via conventional calcination method is only 89% in the same condition. The results above indicate that the material synthesized by the microwave irradiation show a better rate capability, which could be attributed to the smaller particle size (see Fig. 3). Many researchers [31] have shown that the reduced particle size can improve the rate capability due to the short diffusion path of lithium in $LiNi_{0.5}Mn_{1.5}O_4$

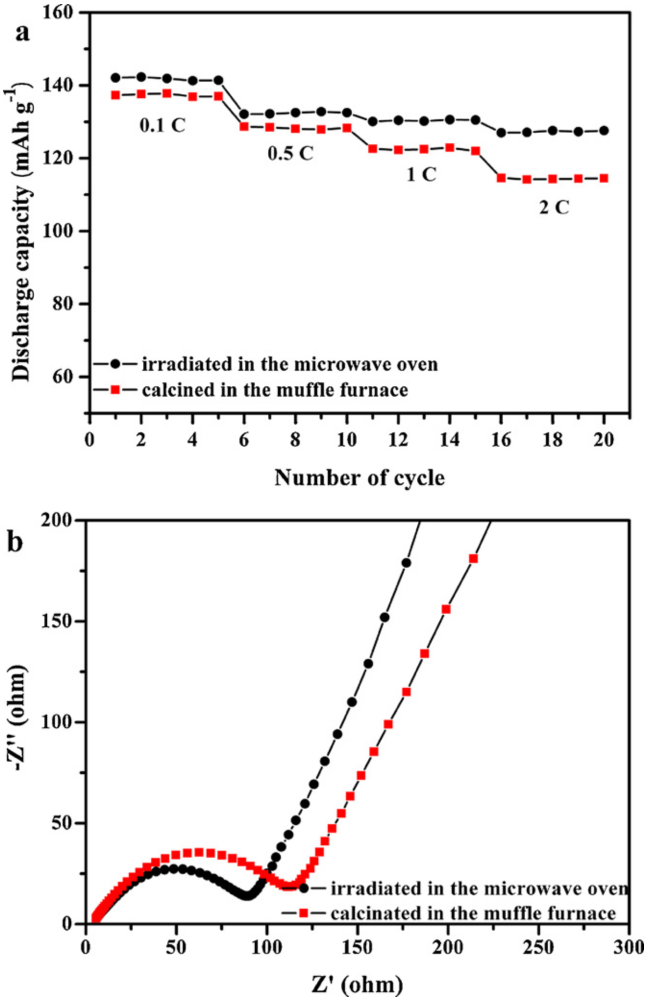

Fig. 6. (a) Rate performances and (b) EIS spectra of $LiNi_{0.5}Mn_{1.5}O_4$ samples.

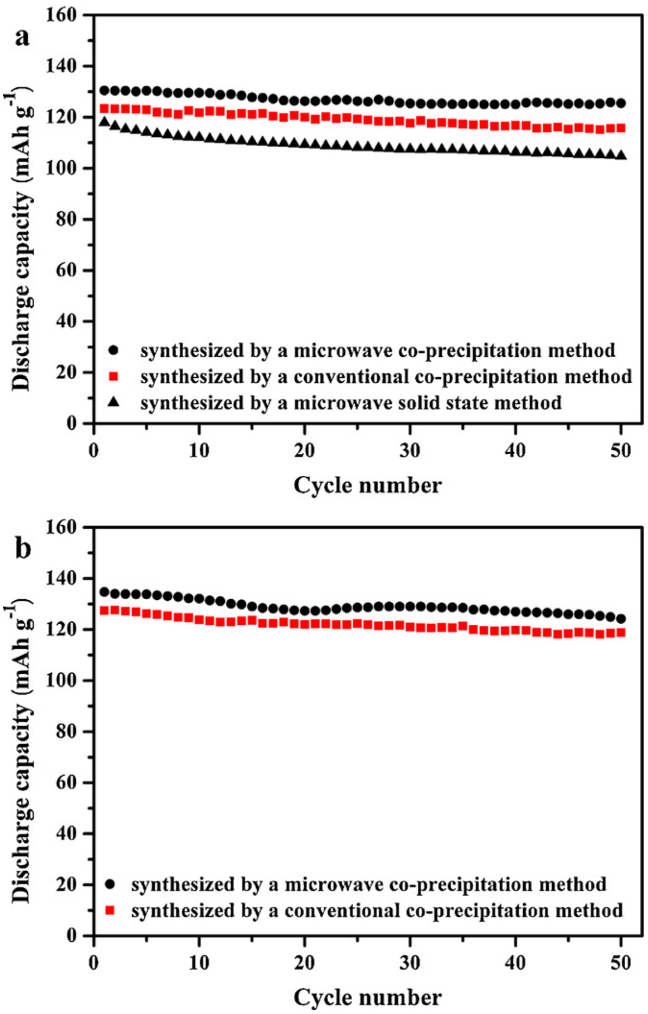

Fig. 7. Cycling performances of $LiNi_{0.5}Mn_{1.5}O_4$ samples operated at (a) room temperature and (b) 55 °C.

particles. The explanation above is in accordance with the EIS results given in Fig. 6b. As can be seen in the figure, both of the two plots consist of a depressed semicircle and a Warburg region, which represent for ionically conducting and charge transfer progress. Clearly, $LiNi_{0.5}Mn_{1.5}O_4$ synthesized by microwave irradiation has a smaller conductivity of electrons and lithium ions than the sample synthesized via traditional calcination way.

As mentioned above, the cycling performance of the sample is the big challenge of microwave synthesis method. Fig. 7 shows the cycling performances of the samples prepared by different methods. Cell cycling (charged and discharged at 1 C rate) was carried out at 25 °C and 55 °C for 50 cycles. It can be seen that the cycling performance of the sample synthesized by a microwave solid state method is not so satisfactory, which is a common issue when using microwave irradiation to synthesize other materials. However, the cycling retention of the sample synthesized through spherical $(Ni_{0.25}Mn_{0.75})_3O_4$ precursor after 50 cycles is close to 97%, which is a little higher than the sample synthesized via conventional calcination way at 25 °C. And moreover, the sample synthesized by microwave irradiation also shows the good cycling performance with a higher discharge capacity even at elevated temperature of 55 °C. The result implies that using the spherical homogeneous $(Ni_{0.25}Mn_{0.75})CO_3$ as the starting material is significantly effective for producing the highly crystalline spinel $LiNi_{0.5}Mn_{1.5}O_4$. We suggest that the contact between particles and particles become much more compact in the spherical material, which minimized the energy required for the formation of highly crystalline $LiNi_{0.5}Mn_{1.5}O_4$. In addition, the micro-nano structure of the spherical particles decreases the contact area between the electrode and the electrolyte, which could reduce the possibility of the manganese dissolution. Therefore, a pure phase, well-developed crystalline and small particle size of spinel $LiNi_{0.5}Mn_{1.5}O_4$ could be synthesized within a short irradiation time.

4. Conclusions

The spinel $LiNi_{0.5}Mn_{1.5}O_4$ powder was successfully synthesized using microwave heat treatment following a co-precipitation method. The sample synthesized by microwave co-precipitation method exhibited higher capacity and better rate capability than that of the sample synthesized by conventional heat treatment; we also found that the microwave co-precipitation was a fairly effective method to solve the problem of poor cycling performance when using microwave irradiation to synthesize $LiNi_{0.5}Mn_{1.5}O_4$ compounds. With the help of co-precipitation using spherical $(Ni_{0.25}Mn_{0.75})CO_3$ as a precursor, a pure phase, small particle size, well-developed crystalline of spinel $LiNi_{0.5}Mn_{1.5}O_4$ could be obtained using microwave irradiation synthesis. Our synthesized sample showed the excellent electrochemical performance. It delivered a discharge capacity of 142 mAh g^{-1} at 0.1 C, and remained a capacity retention of 97% after the 50th cycle at room temperature. And moreover the sample also had an excellent cycling performance even at high temperature. Our experimental results have shown that the microwave co-precipitation synthesis would be a promising way for the synthesis of spinel $LiNi_{0.5}Mn_{1.5}O_4$ material.

Acknowledgements

We are grateful for financial support from the Chinese Academy of Sciences (Program of Knowledge Innovation), the Natural Science Foundation of Ningbo (Grant nos. 2011A610201 and 2010A610150). Zhejiang Provincial Natural Science Foundation of China (Grant nos. R4100194 and Y4100499).

References

[1] C.M. Shen, X.G. Zhang, Y.K. Zhou, Li, Mater. Chem. Phys. 78 (2002) 437.
[2] A.M. Andersson, D.P. Abraham, R. Haasch, S. Maclaren, J. Liu, K. Amine, J. Electrochem. Soc. 149 (2002) A1358.
[3] Y. Inui, Y. Kobayashi, Y. Watanabe, Y. Watase, Y. Kitamura, Energy Convers. Manage. 48 (2007) 2109.
[4] R.V. Chebiam, F. Prado, A. Manthiram, Chem. Mater. 13 (2001) 2951.
[5] S. Venkatraman, Y. Shin, A. Manthiram, Electrochem. Solid-State Lett. 6 (2003) A9.
[6] J.G. Li, X.M. He, R.S. Zhao, C.R. Wan, C.Y. Jiang, D.G. Xia, S.C. Zhang, J. Power Sources 158 (2006) 524.
[7] Y.G. Liang, X.Y. Han, X.W. Zhou, J.T. Sun, Y.H. Zhou, Electrochem. Commun. 9 (2007) 965.
[8] J. Cabana, T. Valdés-Solís, M.R. Palacín, J. Oró-Solé, A. Fuertes, G. Marbán, A.B. Fuertes, J. Power Sources 166 (2007) 492.
[9] Q. Zhong, A. Bonakdarpour, M. Zhang, Y. Gao, J.R. Dahn, J. Electrochem. Soc. 144 (1997) 205.
[10] T. Ohzuku, S. Takeda, M. Iwanaga, J. Power Sources 81–82 (1999) 90.
[11] K. Kanamura, W. Hoshikawa, T. Umegaki, J. Electrochem. Soc. 149 (2002) A339.
[12] R. Santhanam, B. Rambabu, J. Power Sources 195 (2010) 5442.
[13] Y.Y. Sun, Y.F. Yang, H. Zhan, H.X. Shao, Y.H. Zhou, J. Power Sources 195 (2010) 4322.
[14] Q. Sun, X.H. Li, Z.X. Wang, Y. Ji, Trans. Nonferr. Met. Soc. China 19 (2009) 176.
[15] X.L. Wu, S.B. Kim, J. Power Sources 109 (2002) 53.
[16] H.S. Fang, Z.X. Wang, B. Zhang, X.H. Li, G.S. Li, Electrochem. Commun. 9 (2007) 1077.
[17] M. Kunduraci, J.F. Al-Sharab, G.G. Amatucci, Chem. Mater. 18 (2006) 3585.
[18] S.T. Myung, S. Komaba, N. kumagai, H. Yashiro, H.-T. Chung, T.-H. Cho, Electrochim. Acta 47 (2002) 2543.
[19] Y.S. Lee, Y.K. Sun, S. Ota, T. Miyashita, M. Yoshiro, Electrochem. Commun. 4 (2002) 989.
[20] J.H. Kim, S.T. Myung, C.S. Yoon, I.-H. Oh, Y.K. Sun, J. Electrochem. Soc. 151 (2004) A1911.
[21] R. Alcantara, M. Jaraba, P. Lavela, J.L. Tirado, Ph. Biensan, A. de Guibert, C. Jordy, J.P. Peres, Chem. Mater. 15 (2003) 2376.
[22] B. Leon, J.M. Lloris, C.P. Vicente, J.L. Tirado, Electrochem. Solid State Lett. 9 (2006) A96.
[23] J. Li, Y.L. Jin, X.G. Zhang, H. Yang, Solid State Ionics 178 (2007) 1590.
[24] M. Nakayama, K. Watanabe, H. Ikuta, Y. Uchimoto, M. Wakihara, Solid State Ionics 164 (2003) 352.
[25] K.S. Lee, S.T. Myung, Y.K. Sun, Chem. Mater. 19 (2007) 2727.
[26] S.J. Bao, Y.Y. Liang, W.J. Zhou, B.L. He, H.L. Li, J. Power Sources 154 (2006) 239.
[27] T.Y. Yang, K.N. Sun, Z.Y. Lei, N.Q. Zhang, Y. Lang, J. Alloys Compd. 502 (2010) 215.
[28] H. Yan, X. Huang, Z. Lu, H. Huang, R. Xue, L. Chen, J. Power Sources 68 (1997) 530.
[29] P. Kalyani, N. Kalaiselvi, N.G. Renganathan, J. Power Sources 123 (2003) 53.
[30] H.X. Deng, I. Belharouak, Y.K. Sun, K. Amine, J. Mater. Chem. 19 (2009) 4510.
[31] M. Kunduraci, G.G. Amatucci, Electrochim. Acta 53 (2008) 4193.