

Short Communication

SnO₂ Modification of Spherical Spinel LiMn₂O₄ Cathode Materials for Li-ion Batteries

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Received: 30 June 2006 / *Accepted:* 11 July 2006 / *Published:* 1 August 2006

SnO₂ modification of spherical spinel LiMn₂O₄ was attempted at first time to improve its electrochemical performance. The modification started with the preparation of spherical MnCO₃, followed by pre-heating to produce spherical Mn₂O₃. The SnO₂ modified spherical spinel LiMn₂O₄ was obtained by sintering of the mixture of spherical MnCO₃, SnO₂ and Li₂CO₃. The XRD analysis confirmed the existence of SnO₂ phase and decrease of spinel lattice constant after the modification, indicating the doping of Sn in the spinel. The modified sample presented much better cycleability than that of un-modified sample. This paves a simple way to improve the electrochemical performance of spinel LiMn₂O₄.

Keywords: Spinel LiMn₂O₄; SnO₂; modification; Li-ion battery

1. INTRODUCTION

The past decades have witnessed the rapid development of lithium-ion batteries in response to the growing demands for the lighter, smaller and powerful batteries from electronic and information industries. The layered oxides, LiCoO₂, LiNiO₂, and spinel LiMn₂O₄ have been the most widely studied as the cathode materials for lithium secondary batteries. Among them, spinel LiMn₂O₄ has been extensively investigated because of its low cost, easy preparation and environmental advantages [1-5]. However, LiMn₂O₄ suffers a severe capacity fading problem after long-term cycling, and such a problem limits its practical application. It is deemed that this problem is induced by the dissolution of LiMn₂O₄ electrode into the electrolyte (as Mn²⁺) and a phase transition due to Jahn-Teller distortion [6]. Many works have been focused on improving the cycling behavior of LiMn₂O₄. Among them, surface modification is proved to be an effective route [4, 7].

In this study, spherical spinel LiMn_2O_4 was prepared by controlled crystallization and SnO_2 modification was tried to improve its cycling performance. The result showed the modification is effective for its cycling improvement.

2. EXPERIMENTS

Firstly, spherical MnCO_3 powders were synthesized by controlled crystallization [8, 9] from MnSO_4 , NH_4HCO_3 and $\text{NH}_3\cdot\text{H}_2\text{O}$. NH_3 was used as the complexing agent. The solutions of MnSO_4 , NH_4HCO_3 , and $\text{NH}_3\cdot\text{H}_2\text{O}$ were fed continuously into a crystallization reactor with proper agitation. All particles formed in the reactor gradually adopt a spherical shape after a definite reaction time. The spherical Mn_2O_3 was then obtained by heat-treatment of MnCO_3 at 560°C for 4h. A mixture of Mn_2O_3 , Li_2CO_3 and SnO_2 was calcined at 750°C for 20h to produce SnO_2 modified spherical LiMn_2O_4 . Sample A, B and C are referred to pristine LiMn_2O_4 , 5% SnO_2 modified LiMn_2O_4 and 10% SnO_2 modified LiMn_2O_4 , respectively. The percentage is Sn molar percentage in total molar of Sn and Mn.

The particle morphology of the powders was observed using scanning electron microscopy (SEM; JSM 6301F). Crystal phase of the samples were characterized by powder X-ray diffraction (XRD; D/max-rB) using $\text{CuK}\alpha$, 40 kV \times 120mA radiation with step of 0.02° at $6^\circ\cdot\text{min}^{-1}$. The element composition of particles surface was analyzed by energy dispersive spectroscopy (EDS; Oxford ATW Link Isis300, resolution 128eV).

The cathode consisted of 80% (w/w) LiMn_2O_4 , 10% (w/w) carbon black and 10% (w/w) binder. The net load of the un-modified or SnO_2 modified LiMn_2O_4 was about $10\text{mg}\cdot\text{cm}^{-2}$. The coin cells were assembled in a dry glove box filled with argon, using lithium metal as anode and Celgard 2400 polypropylene membrane as separator. The electrolyte was 1M LiPF_6 in EC+DEC (1:1, v/v). The charge/discharge cycling was galvanostatically tested at a current of $0.5\text{mA}\cdot\text{cm}^{-2}$ with cut-off voltages of 3.35~4.35V at room temperature.

3. RESULTS AND DISCUSSION

3.1. Physical characteristics

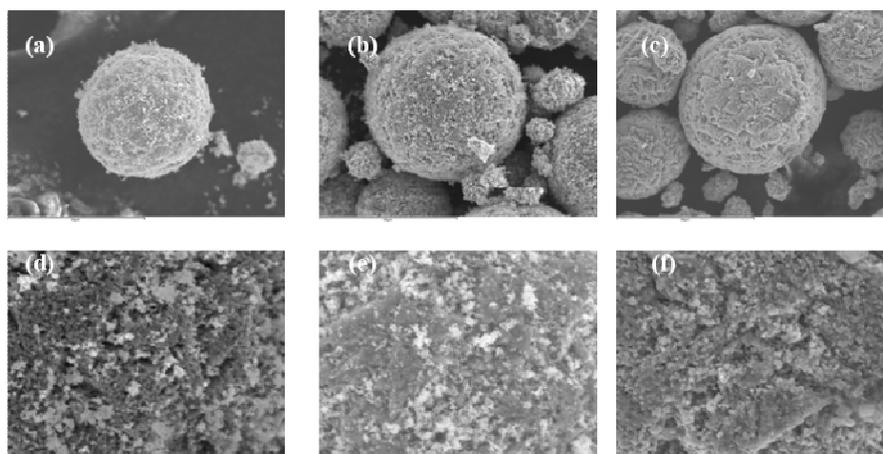


Figure 1. SEM images of (a, d) pristine LiMn_2O_4 , (b, e) 5% SnO_2 modified LiMn_2O_4 and (c, f) 10% SnO_2 modified LiMn_2O_4

The SEM images of samples are shown in Fig. 1. The particles are spherical. Obviously, the particle is compactly made up of a large number of grains, the sizes of which are 100 nm. From images of (a), (b) to (c), the particle surface becomes more and more smooth, indicating that the surface probably covers by more SnO₂. The SnO₂ is uniformly modified on the surface of the particles. The EDS analysis on the surface of sample B and sample C show that the contents of Sn are 11.28% and 14.70%, respectively. They exceed the Sn contents of starting materials (5% and 10%, respectively), indicating that Sn is rich on the surface of the particles. EDS analysis is consistent with the SEM analysis. The XRD patterns are shown in Fig. 2, showing that all LiMn₂O₄ samples are well crystallized and can be identified as spinel cubic phases. In the patterns of sample B and sample C, reflection lines assigned to SnO₂ can be identified, indicating that SnO₂ is coated on the surface of the spherical spinel LiMn₂O₄ particles in the sample B and sample C. The lattice constants are listed in Table 1. It decreases while the amount of Sn increases, indicating that Sn is doped in the spinel. The decrease of lattice constant can make the crystal structure more stable, leading to the stable cycling performance of Sn modified LiMn₂O₄ during charge/discharge process.

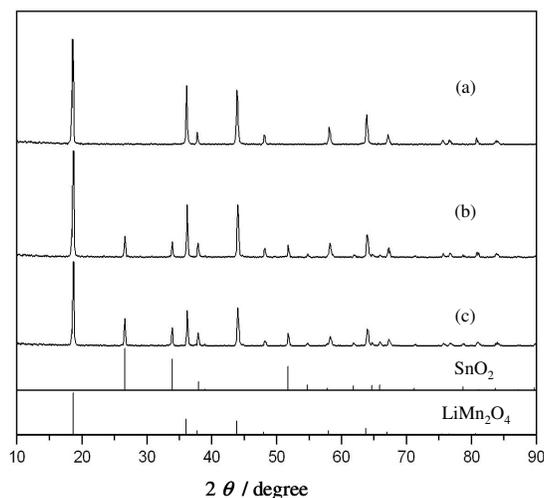


Figure 2. XRD patterns of (a) pristine LiMn₂O₄, (b) 5% SnO₂ modified LiMn₂O₄ and (c) 10% SnO₂ modified LiMn₂O₄

Table 1. The lattice constants of three LiMn₂O₄ samples

Sample	Standard LiMn ₂ O ₄	A	B	C
Lattice constant/Å	8.248	8.2449	8.2288	8.2238

3.2. Electrochemical characteristics

The initial charge/discharge curves are shown in Fig. 3. The initial charge capacities are 128.6, 119.5 and 97.3 mAh g⁻¹ for Sample A, B and C, respectively. They decrease while Sn content increases. This is consistent with previous study, where the doping and coating decrease the capacity. Accordingly, the initial discharge capacities also decrease. They are 118.3, 106.7 and 93.1 mAh g⁻¹ for

Sample A, B and C, respectively. This indicates that the capacity of the spinel decreases by Sn modification.

The cycleabilities are shown in Fig. 4. Sample A presents the discharge capacity of 107.0 mAh g^{-1} at 50th cycle and 99.7 mAh g^{-1} at 100th cycle, where the capacity retentions are 90.4% and 84.3%, respectively. After Sn modification, the discharge capacity decreases, but the capacity retention increases. Sample B presents the capacity retentions of 96.0% at 50th cycle and 92.0% at 100th, where Sample C presents capacity retention of 98.8% and 97.5%, respectively. The capacity retention increases from 84.3% to 97.5% at 100th cycle after Sn modification. The cycleability of spherical spinel LiMn_2O_4 is greatly improved with Sn modification. It is probably due to less surface contact of spherical spinel LiMn_2O_4 with an electrolyte after SnO_2 coating and the more stable structure of the spinel during cycling with Sn doping. However, the mechanism of Sn modification on the spinel should be further study to clarify doping mechanism and coating mechanism. This work is under going.

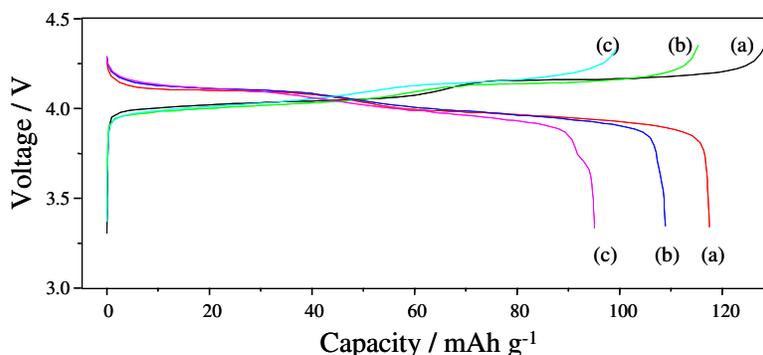


Figure 3. The initial charge/discharge curves of (a) pristine LiMn_2O_4 , (b) 5% SnO_2 modified LiMn_2O_4 and (c) 10% SnO_2 modified LiMn_2O_4

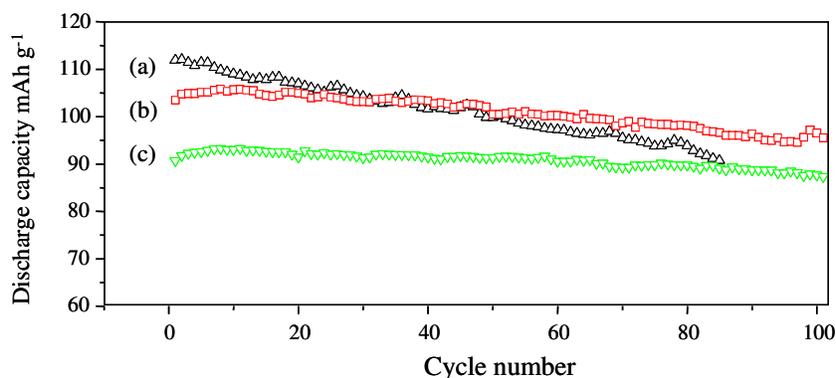


Figure 4. The cycling performance of (a) pure LiMn_2O_4 , (b) 5% SnO_2 modified LiMn_2O_4 and (c) 10% SnO_2 modified LiMn_2O_4

4. CONCLUSIONS

The Sn modified spherical spinel LiMn_2O_4 materials can be prepared based on controlled crystallization from inexpensive materials, MnSO_4 , NH_4HCO_3 , $\text{NH}_3 \cdot \text{H}_2\text{O}$, and Li_2CO_3 and SnO_2 . The XRD analysis confirmed the existence of SnO_2 phase and decrease of spinel lattice constant after the

modification, indicating the doping of Sn in the spinel. The modified sample presented much better cycleability than that of un-modified sample. This paves a simple and cost effective way to improve the electrochemical performance of spinel LiMn_2O_4 .

ACKNOWLEDGEMENT

Authors appreciate the anonymous reviewer for the comment to improve this manuscript.

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