Int. J. Electrochem. Sci., 1(**2006)**12-16

International Journal of ELECTROCHEMICAL SCIENCE
www.electrochemsci.org

Synthesis of Spinel $LiMn_2O_4$ for Li-Ion Batteries via Sol-gel Process

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Received: 21 February 2006 / *Accepted:* 28 March / *Published:* 7 April 2006

Spinel $LiMn_2O_4$ was synthesized from $CH_3COOLi{\cdot}2H_2O$, $Mn(CH_3COO)_2$ and adipic acid via sol-gel process. The crystallinity of as-prepared sample increased and its capacity also increased, while the sintering temperature increased. However, its cycleability reached a maximum value at the sintering temperature of 750 °C, over which it decreased again. The sintering duration had also influence on the capacity. The optimized performance was obtained when the sintering was carried out at 750 °C for 20 hours, where as-prepared spinel $LiMn_2O_4$ presented the initial capacity of 130 mAh g^{-1} and capacity retention of 96.2% at 15th cycle.

Keywords: Sol-gel process; Spinel $LiMn_2O_4$; Synthesis; Li-ion batteries

1. INTRODUCTION

The past decades have witnessed the rapid development of lithium-ion battery in response to growing needs of electronic and information industries. Exploration of new cathode material that is cost effective and environmentally benign, as compared to $LiCoO_2$, has been extensively attempted. The non-toxic property and low cost make spinel $LiMn_2O_4$ an attractive alternative to $LiCoO_2$. Solid phase reaction was first adopted to prepare spinel $LiMn_2O_4$ by Hunter J. C. [1], and was improved by Tarascon J M, Tarascon J M, M.M. Thackeray, N.V. Kosova and S. Soiron [2~6]. Solid phase reaction combined with milling has been widely used to prepare spinel $LiMn_2O_4$ materials today. Another conventional preparation is co-precipitation [7, 8]. The controlled crystallization process is also attempted to prepare spinel $LiMn_2O_4$ [9-16].

In this study, spinel $LiMn_2O_4$ was synthesized from $CH_3COOLi{\cdot}2H_2O$, $Mn(CH_3COO)_2$ and adipic acid via sol-gel process, followed by a solid state reaction. The sintering condition was optimized. The electrochemical performance of as-prepared sample was tested.

2. EXPERIMENTAL PART

$CH_3COOLi{\cdot}2H_2O$, $Mn(CH_3COO)_2{\cdot}4H_2O$ and adipic acid were dissolved in deionized water, respectively, according to their molar ratio of 1:2:3, forming 3 solutions. The solutions were added together under agitation at 80 °C for 10 hours, forming sol solution containing manganese and lithium adipic. The sol solution was vaporized at 100 °C till the dry gel was formed, followed by the heat-treatment at 400 °C for 8 hours. The product was smashed. Finally, spinel $LiMn_2O_4$ was obtained by sintering of the smashed powders at 600-800 °C for 10-30 hours.

The phase composition of powders was characterized by powder X-ray diffraction (XRD, D/max-rB) using CuKα, 40kV, 120mA, with step of 0.02 degree at 6 degree min^{-1}. The particle morphology of the powders was observed using a scanning electron microscopy (SEM, JSM6301F).

The electrode formulation consisted of 80 wt.% $LiMn_2O_4$, 10 wt.% carbon black, and 10 wt.% binder. The load of $LiMn_2O_4$ was about 10mg cm^{-2}. The prepared electrode pellets were dried at 120 °C under vacuum for 48 hours. The test coin cells were assembled in a dry glove box filled with argon. The separator was a Celguard 2400 microporous polypropylene membrane. The electrolyte was 1M $LiPF_6$ in EC + DEC (1:1, v/v). A lithium metal anode was used in this study. The charge–discharge cycling was galvanostatically performed at a current of 0.5 mA cm^{-2} (about 0.4C) with cut-off voltages of 3.35~4.35V at room temperature.

3. RESULTS AND DISCUSSION

Fig. 1 shows the XRD patterns of as-prepared spinel $LiMn_2O_4$ sintered at 700, 750 and 800 °C for 20 hours, indicating that all the samples present cubic spinel crystal structure. The intensities of the reflection lines increase while the sintering temperature increases from 700 °C to 800 °C. Their lattice parameters are calculated to be 0.82422 nm (700 °C), 0.82456 nm (750 °C) and 0.82504 nm (800 °C), respectively. It indicates that both of the crystallinity and the lattice parameter increase while the sintering temperature increases.

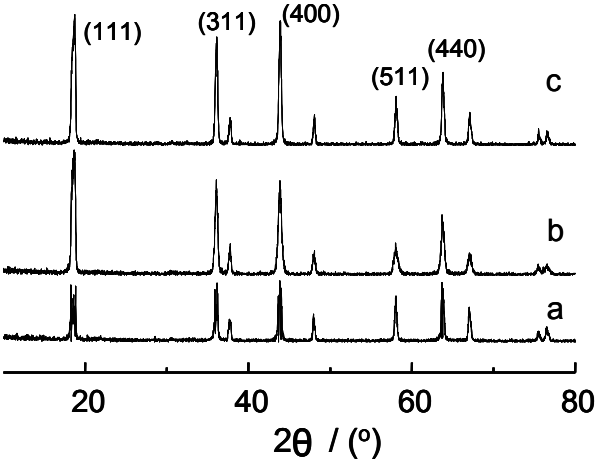

Fig. 1 XRD patterns of as-prepared $LiMn_2O_4$ sintered at 700 °C (a), 750 °C (b) and 800 °C (c) for 20 hours.

Fig. 2 shows the SEM images of as-prepared spinel $LiMn_2O_4$ sintered at 700, 750 and 800 °C for 20 hours, indicating that the grains pile irregularly, and the size of crystal grain increases while the sintering temperature increases.

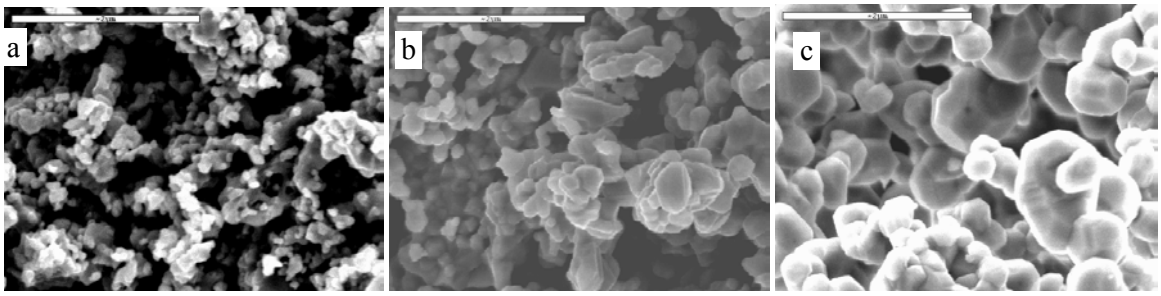

Fig. 2. SEM images of as-prepared $LiMn_2O_4$ sintered at 700 °C (a), 750 °C (b) and 800 °C (c) for 10 hours.

Fig. 3 shows that the electrochemical performance of 3 as-prepared spinel $LiMn_2O_4$ samples sintered at 700, 750 and 800 °C for 20 hours, indicating that the initial capacity increases while the sintering temperature increases. The initial capacity increases from 122 $mAh \cdot g^{-1}$ to 133 mAh g^{-1} when sintering temperature increases from 700 °C to 800 °C. However, the capacity retentions at 15^{th} cycle are 95%, 96.2% and 91.7% for the samples sintered at 700, 750 and 800 °C, respectively. The sample sintered at 750 °C presents the best cycleability. Therefore, sintering temperature for this process is optimized to be 750 °C, at which the spinel $LiMn_2O_4$ can be synthesized to present the initial capacity of 130 mAh g^{-1} and capacity retention of 96.2% at 15^{th} cycle. Its discharge capacity keeps to be 125 mAh g^{-1} after 15 cycles.

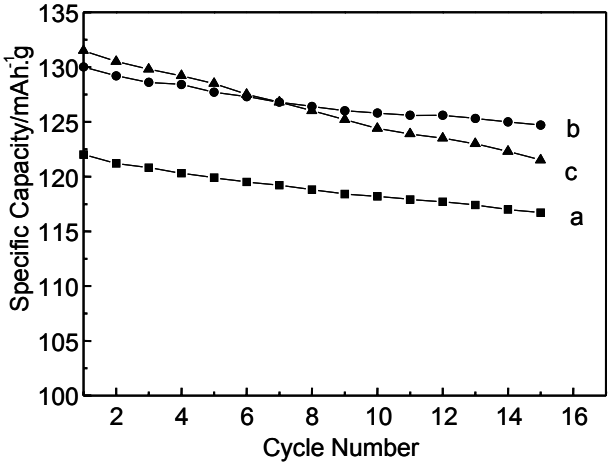

Fig. 3. Cycleabilities of as-prepared $LiMn_2O_4$ sintered at 700 °C (a), 750 °C (b) and 800 °C (c) for 10 hours.

The above results show that the sintering temperature is an important factor for the synthesis of spinel $LiMn_2O_4$. The structure and electrochemical performance are influenced by the sintering temperature. The increase of sintering temperature causes the increase of the lattice parameter, leading to the increase of crystal cell. This increase makes the intercalation and de-intercalation of lithium easier in the spinel crystal, leading to the increase of initial capacity. On the other hand, the increase of lattice parameter leads to an unstable structure of the spinel during cycling, resulting in the decrease of its cycleability.

The sintering duration is an another important factor for the electrochemical performance of spinel $LiMn_2O_4$. Fig. 4 shows the Initial capacities of as-prepared spinel $LiMn_2O_4$ sintered at 750 °C under different heating duration, indicating that the maximum initial capacity is reached at about 20 hours. Therefore, the sintering duration of 20 hours is an optimized value for the synthesis of spinel $LiMn_2O_4$.

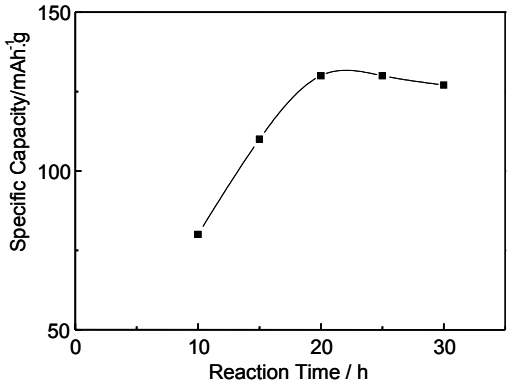

Fig. 4. Initial capacities of as-prepared spinel $LiMn_2O_4$ sintered at 750 °C under different heating duration.

This study is a first attempt for the preparation of spinel $LiMn_2O_4$ via sol-gel process. It shows an effective and promising way to synthesize spinel $LiMn_2O_4$. However, the more detailed investigation needs to be carried out for this process.

4. CONCLUSIONS

Spinel $LiMn_2O_4$ can be synthesized from $CH_3COOLi{\cdot}2H_2O$, $Mn(CH_3COO)_2$ and adipic acid via sol-gel process, followed by a solid state reaction. The sintering temperature and duration are optimized to be 750 °C and 20 hours, respectively, at which the sample presents the initial capacity of 130 mAh g^{-1} and capacity retention of 96.2% at 15^{th} cycle. Its discharge capacity keeps being 125 mAh g^{-1} after 15 cycles.

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