Preparation and Characterization of Layered $LiMn_{0.5}Ni_{0.5}O_2$ Cathode Materials for Lithium Ion Batteries by Sol-gel Method

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Abstract: Layered $LiMn_{0.5}Ni_{0.5}O_2$ cathode materials were prepared by a sol-gel method using aqueous solutions of corresponding metal acetates and glycolic acid as the chelating agent. The obtained powders have the typical α-$NaFeO_2$ structure, and the particles are between 300~400 nm in sizes. The initial discharge capacity of the $LiMn_{0.5}Ni_{0.5}O_2$ obtained at 900℃ was about 161.2 mAh g^{-1} by cycling the cell between 2.5 V and 4.3 V. After 20 cycles, the discharge capacity of the layered compound remained over 88% of the initial discharge capacity at a current density of 0.1 mA cm^{-2}.

Key words: $LiMn_{0.5}Ni_{0.5}O_2$; sol-gel; lithium ion batteries; layered structure
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As a new generation cathode material for lithium ion batteries, layered $LiMnO_2$ has good characteristics such as low cost, nontoxicity, safety and high capacity. However, the structure is unstable while cycling, and the synthesis of layered $LiMnO_2$ is a bit difficult.

Many groups have reported that transition metal substitution ($LiMn_{1-x}M_xO_2$, M = Ni, Co, Cr, Fe) can improve the stability[1-3]. Kang[4] identified $LiMn_{0.5}Ni_{0.5}O_2$ is a higher rate as lithium battery electrode by using ab into computational modeling. In previous literatures, $LiMn_{0.5}Ni_{0.5}O_2$ were developed by ion-exchange method, which is complex process and expensive cost. In this work, a sol-gel method was attempted to synthesize $LiMn_{0.5}Ni_{0.5}O_2$, and the structure and electrochemical characterization were discussed.

1 Experimental

$CH_3COOLi \cdot 2H_2O$, $Ni(CH_3COO)_2 \cdot 4H_2O$ and $Mn(CH_3COO)_2 \cdot 4H_2O$ were dissolved in distilled water as the stoichiometric amounts of $LiMn_{0.5}Ni_{0.5}O_2$. The pH value of the solution was maintained between 9 and 10 using citric acid and ammonia. The glycolic acid was dripped into the solution as chelating agent and stirred continuously until a transparent sol was obtained. Evaporate the sol at 120℃ for 20 h, then annealed the gel precursor at 500℃ for 6 h, the resulted powder was grounded and calcined at 750~950℃ for 24 h.

2 Rusults and discussion

Fig. 1 shows XRD patterns of as-synthesized $LiMn_{0.5}Ni_{0.5}O_2$ powders. The $LiMn_{0.5}Ni_{0.5}O_2$ powders have well-defined layered R-3m structure, besides some little NiO peaks as impurities appeared. As the temperature increased, the separation between (018) and (110) become obvious, that means the higher the temperature, the better the layered structure[5]. The SEM images of the layered $LiMn_{0.5}Ni_{0.5}O_2$ synthesized at 750~950℃ are shown in Fig. 2. The particles obtained at 900℃ have fine morphology and are between 300~400 nm in sizes.

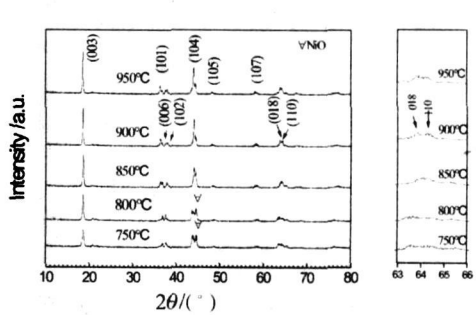

Fig. 1 X-ray diffraction patterns for $LiMn_{0.5}Ni_{0.5}O_2$ synthesized at different temperatures

Fig. 3 presents the initial charge and discharge curves for the $LiMn_{0.5}Ni_{0.5}O_2$ electrode between 2.5~4.3 V at a current density of 0.1 mA cm^{-2}. It shows

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that the initial charge and discharge specific capacities of layered $LiMn_{0.5}Ni_{0.5}O_2$ obtained at 900℃ are determined to be 180.3 and 161.2 mAh g^{-1}, indicating that the coulombic efficiency reaches 89.4%.

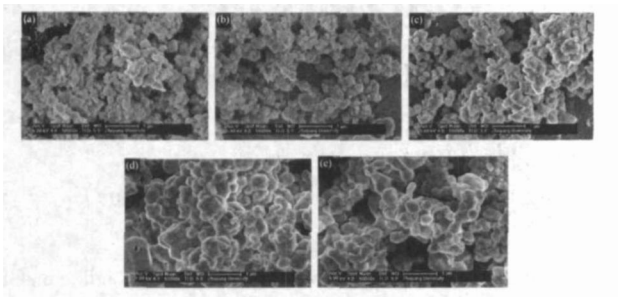

Fig.2 SEM images of Layered $LiMn_{0.5}Ni_{0.5}O_2$ synthesized at (a) 750℃, (b) 800℃, (c) 850℃, (d) 900℃, (e) 950℃

Fig.4 shows the cycling performances of the $LiMn_{0.5}Ni_{0.5}O_2$. After 20 cycles, the discharge capacity of the sample obtained at 850℃ was 140.2 mAh g^{-1}, still remaining 87.0% of the initial discharge capacity. And the samples obtained at 900℃ and 950℃ remained 75.9% and 78.5%, respectively. The fading in capacity should be due to the change from layer structure to spinel structure during charge and discharge process.

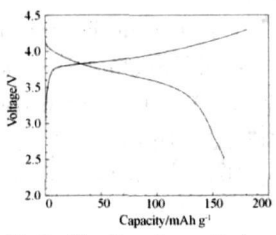

Fig.3 The first charge-discharge curves for $LiMn_{0.5}Ni_{0.5}O_2$

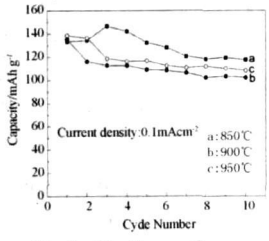

Fig.4 Cycling performances of layered $LiMn_{0.5}Ni_{0.5}O_2$

3 Conclusions

The layered $LiMn_{0.5}Ni_{0.5}O_2$ prepared by sol-gel method shows the typical R-3m structure, and higher the calcined temperature, better the layered crystallization. The particles obtained at 900℃ have fine morphology, are between 300~400 nm in sizes and delivered a capacity of 161.2 mAh g^{-1} on the first cycle and sustained 140.2 mAh g^{-1} after 20 cycles at the charge/discharge voltage range of 2.5~4.3 V.

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溶胶—凝胶法制备层状 $LiMn_{0.5}Ni_{0.5}O_2$ 锂离子电池正极材料及其电化学性能

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摘 要: 以醋酸锂、醋酸锰和醋酸镍为原料, 羟基乙二酸为螯合剂, 通过溶胶—凝胶法制备层状 $LiMn_{0.5}Ni_{0.5}O_2$ 正极材料, 得到的产物具有典型的 $\alpha-NaFeO_2$ 层状结构, 颗粒尺寸在 300~400 nm之间。对 900℃下制得的层状 $LiMn_{0.5}Ni_{0.5}O_2$ 在 2.5~4.3 V之间进行充放电测试, 电流密度为 0.1 mA cm^{-2}, 其首次放电容量达到了 161.2 mAh g^{-1}。经过 20次循环后, 仍然保留了初始容量的 88%。

关键词: $LiMn_{0.5}Ni_{0.5}O_2$; 溶胶—凝胶; 锂离子电池; 层状结构
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