Ion Exchange Method to Synthesis $LiMn_{1-x}Co_xO_2$ and Characterization as Cathode Materials for Lithium-Ion Batteries

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Abstract: Layered structure $LMn_{1-x}Co_xO_2$ ($0.1 \leq x \leq 0.5$) cathode materials were prepared by ion exchange method. The samples have an ordered layered structure and well-crystallized $LMn_{0.5}Co_{0.5}O_2$ delivered the highest discharge capacity of 175 mAh/g and the charge retention was higher than 95% after 20 cycles. By analysis of the results, as more amount of cobalt is introduced into the $LMn_{1-x}Co_xO_2$ system, the more obvious layered structure and better cycle ability are obtained.

Key words: $LMn_{1-x}Co_xO_2$; ion exchange method; lithium ion batteries; layered structure; electrochemical characteristics
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Compared with commercial $LiCoO_2$ cathode material in lithium ion batteries, lithium manganese oxide has great interest due to its low cost and non-toxicity. However, for spinel LMn_2O_4, the capacity fading on cycling is always due to Jahn-Teller lattice distortion[1]. Another kind of lithium manganese oxide, layered structure $LMnO_2$ has a high theoretical capacity (286 mAh/g) and a better cycle ability than LMn_2O_4, but the stoichiometric $LMnO_2$ shows unacceptably drawback as a result of the structure transforms to spinel structure during extended cycling[2-3].

To stabilize the structure instability, partial substitution of manganese with other metal elements to make $LM_xMn_{1-x}O_2$ (M= Co, Al, Ni etc.) has been studied[4-5]. Among these materials, $LMn_{1-x}Co_xO_2$ shows good cycle stability on repeated Li ion insertion and extraction. Moreover, compared with solid-state reaction or hydrothermal synthesis, ion exchange method can prepare more stable materials due to its precursor $NaMnO_2$ has a stable layered structure.

1 Experimental

Abundant Co-doped $LMn_{1-x}Co_xO_2$ ($0.1 \leq x \leq 0.5$) layered structure cathode materials were prepared by ion exchange method. The starting layered $NaMn_{1-x}Co_xO_2$ was prepared by dissolving stoichiometric ratios of CH_3COONa, $Co(CH_3COO)_2 \cdot 4H_2O$ and $Mn(CH_3COO)_2 \cdot 4H_2O$ in distilled water. The solution was mechanically stirred and evaporated under atmospheric pressure in air. The residual gel was calcined at 450℃ to remove gases, and the obtained powder was ground and sintered at 750℃ for 12 h under flowing oxygen. The precursor was mixed with 10 times excess of the eutectic composition of LiNO$_3$ and LiCl, the mol ratio of which was 88∶12. The mixture was heated at 300℃ for 8 h in air, washed with distilled water and ethanol several times, and then, dried the powder at 100℃ for 24 h in air.

2 Results and discussion

Fig. 1 shows the XRD patterns of $LMn_{1-x}Co_xO_2$. The crystal phases of all the samples are identified to be an ordered layered structure and few secondary products are detected. With the increase of the Co substitution amount, the lattice parameters are getting larger, for Co content is 0.1, the lattice parameter is 2.857 Å, but when the Co content reaches 0.5, the lattice parameter is increased to 2.879 Å. This is due to the ionic radius of Co^{3+} (0.754 Å) is larger than that of Mn^{3+} (0.68 Å). From SEM image, it could be seen that the $LMn_{0.7}Co_{0.3}O_2$ powder has regular shape and well-crystallized. The particles have an average size of about 3 μm in length and 0.5 μm in width and show uniform particle distribution.

Typical initial charge-discharge profiles of Li/$LMn_{0.5}Co_{0.5}O_2$ between 3.0 and 4.5 V in different

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current densities are shown in Fig. 2. The charge and discharge capacities faded with the increase of current density, but it can be also observed that almost all of the extracted lithium ions in the charging reaction were inserted at the following discharging reaction.

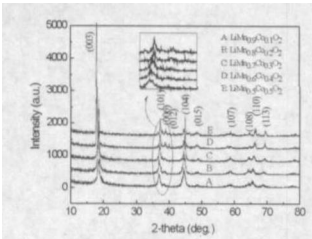

Fig. 1 XRD patterns of $LiMn_{1-x}Co_xO_2$ ($0.1 \le x \le 0.5$)

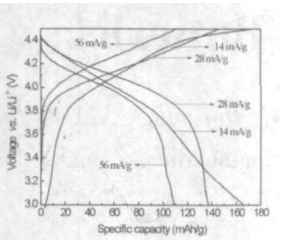

Fig. 2 Influence of the current density on $LiMn_{0.5}Co_{0.5}O_2$

Fig. 3 shows the cycling performance as a function of Co content in the $LiMn_{1-x}Co_xO_2$. As cobalt is introduced into the $LiMn_{1-x}Co_xO_2$ system, the more discharge capacities are obtained. The three samples showed the excellent cycle property, the charge retention was higher than 95% after 20 cycles in the potential range of 3 ~ 4.5 V. The influence of different potential ranges in the cycling is shown in Fig. 4. At 2.0 ~ 4.5 V, the $LiMn_{0.5}Co_{0.5}O_2$ delivered the highest discharge capacity of 175 mAh/g. Good cycle properties are show both at 3.0 ~ 4.5 V and 2.5 ~ 4.5 V.

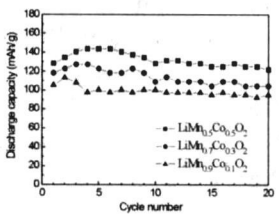

Fig. 3 Discharge capacity as a function of cycle for $LiMn_{1-x}Co_xO_2$

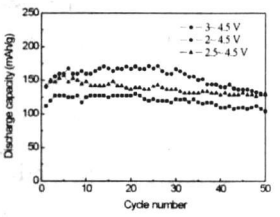

Fig. 4 Discharge capacity vs cycle for $LiMn_{0.5}Co_{0.5}O_2$

3 Conclusions

Layered structure $LiMn_{1-x}Co_xO_2$ ($0.1 \le x \le 0.5$) have been synthesized by ion exchange method. As more amount of cobalt is introduced into the $LiMn_{1-x}Co_xO_2$ system, the more obvious layered structure and better cycle ability are obtained. The $LiMn_{0.5}Co_{0.5}O_2$ delivered the highest discharge capacity of 175 mAh/g and the charge retention was higher than 95% after 20 cycles.

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离子交换法制备 $LiMn_{1-x}Co_xO_2$ 及其电化学性能

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摘 要: 采用离子交换法制备出层状结构锂离子电池正极材料 $LiMn_{1-x}Co_xO_2$ ($0.1 \le x \le 0.5$)。X射线衍射和扫描电镜进行分析表明材料具有明显的层状结构和良好的结晶性。电化学性能研究表明, $LiMn_{0.5}Co_{0.5}O_2$ 的最高放电容量为 175 mAh/g, 并且具有良好的循环性能, 在 3.0 ~ 4.5V的冲放电电压范围内, 经过 20次循环, 可逆容量达 95%。对实验结果的研究表明, 随着 Co含量的增加, 材料具有更明显的层状性能和更优的循环性能。

关键词: $LiMn_{1-x}Co_xO_2$; 离子交换法; 锂离子电池; 层状结构; 电化学性能
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