# Structure and Cycling Behavior of $LiCu_{0.05}Mn_{1.95}O_{3.9}F_{0.1}$ Cathode for Lithium-ion Batteries

LIU Chang-jiu, YI Ling-ying, LI Ji-chun, Wu Hua-bin
(Key Laboratory of Nonferrous Materials and New Processing Technology of Ministry of Education, Guilin University of Technology, Guilin 541004, China)

Abstract: The anion-cation multiple doped $LiCu_{0.05}Mn_{1.95}O_{3.9}F_{0.1}$ used as cathode material was synthesized by sol-gel method. X-ray diffraction showed that the sample has perfect spinel structure. Scanning electron microscope showed that the particles of the material are submicron with regular shape. The results of the charge-discharge curves showed that $LiCu_{0.05}Mn_{1.95}O_{3.9}F_{0.1}$ had better performance than undoped $LiMn_2O_4$ material.

Key words: Anion-cation multiple dope; sol-gel method; $LiCu_{0.05}Mn_{1.95}O_{3.9}F_{0.1}$; electrochemical property
CLC number: TM911 Document code: A Article ID: 0529-6579 (2007) S1-0281-02

The spinel $LiMn_2O_4$ has recently attracted much attention as the promising cathode material[1-2]. However, the application of spinel $LiMn_2O_4$ has been restricted because of Mn solubility and Jahn-Teller distortion causing structural instability and capacity attenuation fast[3]. In order to conquer the problems, Cu and F ion doped lithium manganese oxides is prepared by sol-gel method. In this paper we investigated its structural characteristics and electro-chemical properities with satisfactory results.

## 1 Experiments

The spinel $LiMn_2O_4$ and $LiCu_{0.05}-Mn_{1.95}O_{3.9}F_{0.1}$ were prepared using a sol-gel method. The details of the powder synthesis have been reported elsewhere[4].

The structure of the compound was determined by X-ray diffraction. SEM was performed with a JSM-6360 LV scanning electron microscope. The cycling perfor-mance of the cathode materials was eva-luated using LIR2032 coin type-cells. The powers were mixed with acetylene black and polytetrafluoroethylene binder in a weight ratio of 85 ∶10 ∶5. Lithium metal pellet was used for the anode and Cel-gard 2400 membrane as separators. The electrolyte was 1 ∶1 mixture of EC and DMC containing 1 mol LiPF6. The electrochemical properities was analyzed (0.1C) over a potential range of 3.0 ~4.3 V.

## 2 Results and discussion

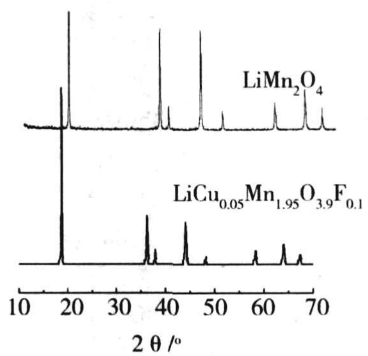


Fig. 1 XRD patterns of $LiMn_2O_4$ and $LiCu_{0.05}Mn_{1.95}O_{3.9}F_{0.1}$

Power XRD patterns for the samples are presented in Fig. 1. The observed peaks of the samples were identifed as a single phase of cubic spinel. The cubic lattice parameter of $LiCu_{0.05}Mn_{1.95}O_{3.9}F_{0.1}$ is 0.824 2 nm. As com-pared with that of $LiMn_2O_4$ (a = 0.824 5 nm), the lattice parameter decreased with the substituted Cu and F ion.

Fig. 2 shows the Scanning electron microscope of the $LiMn_2O_4$ and $LiCu_{0.05}Mn_{1.95}O_{3.9}F_{0.1}$. The particles of the $LiCu_{0.05}Mn_{1.95}O_{3.9}F_{0.1}$ have regular shapes with well defined crystal faces, whereas the particles of the $LiMn_2O_4$ are agglomerate.

①收稿日期: 2007-01-10
基金项目: 广西自然科学基金资助项目 (0342004-2)
作者简介: 刘长久 (1948年生), 男, 教授; E-mail: Liucj1229@163.com

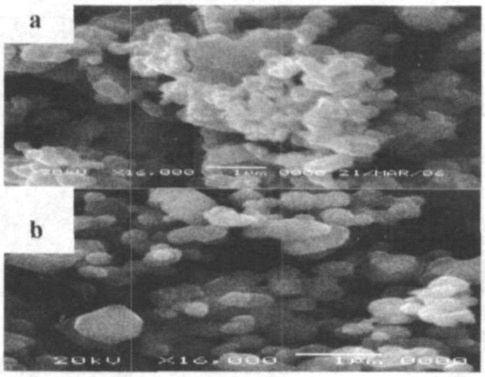


Fig. 2 SEM spectra of $LiMn_2O_4$ (a) and $LiCu_{0.05}Mn_{1.95}O_{3.9}F_{0.1}$ (b)

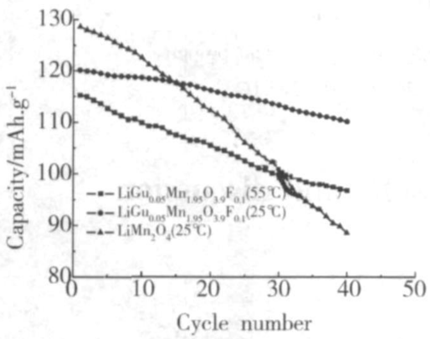


Fig. 3 Cycle life performance of $LiMn_2O_4$ (25 ℃) and $LiCu_{0.05}Mn_{1.95}O_{3.9}F_{0.1}$ (25 ℃ and 55 ℃)

Fig. 3 shows the cycling behavior of $LiMn_2O_4$ at room temperature and $LiCu_{0.05}Mn_{1.95}O_{3.9}F_{0.1}$ at room temperature and elevated temperature. Obviously, the substituted spinel phase is more stable than the $LiMn_2O_4$ spinel phase at room temperature, especially at elevated temperature, the capacity of the cell maintained 83.9% of the initial capacity at the 40 th cycle.

## 3 Conclusion

The spinel material $LiCu_{0.05}Mn_{1.95}O_{3.9}F_{0.1}$ was prepared by sol-gel method. XRD and SEM showed that the sample has a single phase of cubic spinel with regular shape. The charge-discharge test indicate that the material has good structure stability and cycling performance at room temperature and elevated temperature.

## References:

[1] GOODENOUGH J, MANTHIRAM A, WNETRZEWSKI B. Electrodes for lithium batteries [J]. Power Sources, 1981, 43-44: 269-275.

[2] NIETO S, MAJUMDER S B, KATIYAR R S. Improvement of the cycleability of nano-crystalline lithium manganate cathodes by cation Co-doping [J]. J Power Source, 2004, 136: 88-98.

[3] TANG Zhi-yuan, ZHANG Na, LU Xing-he, et al. Influence of doping rare earth on performance of lithium mangan oxide spinels as cathode materials for lithium ion batteries [J]. J Rare Earths, 2005, 1 (23): 120-123.

[4] WU Xiang-lan, KIM Seung-bin. Improvement of electrochemical properties of LiNi0.5Mn1.5O4 spinel [J]. J Power Sources, 2002, 109: 53-57.

# 锂离子电池正极材料 $LiCu_{0.05}Mn_{1.95}O_{3.9}F_{0.1}$的结构与电化学特性

刘长久，易凌英，李继春，吴华斌

(桂林工学院有色金属材料及其加工新技术省部共建教育部重点实验室，广西 桂林 541004)

摘 要：以溶胶－凝胶法合成了阴阳离子复合掺杂尖晶石型锰酸锂正极材料 $LiCu_{0.05}Mn_{1.95}O_{3.9}F_{0.1}$，XRD表征合成产物具有良好的尖晶石结构；SEM测试表明所合成产物的颗粒达到了亚微米级，且分布均匀，形貌较好。以该物质作为锂离子电池的正极材料组装成扣式电池，经充放电循环测试可知：$LiCu_{0.05}Mn_{1.95}O_{3.9}F_{0.1}$材料比 $LiMn_2O_4$ 正极材料能够更好地抑制电池的可逆容量在充放电过程中的衰减，循环性能有了很大改善，表现出很好的电化学可逆特性。

关键词：阴阳离子复合掺杂；溶胶－凝胶法；$LiCu_{0.05}Mn_{1.95}O_{3.9}F_{0.1}$；电化学性能

中图分类号：TM911