

SYNTHESIS AND ELECTROCHEMICAL STUDY OF LiMn_2O_4 COATED BY LiCoO_2

Zhu wei, Yu Shenglun, Pan fusheng,
Zhang shengtao, Huang zongqing

Institute of Chemistry and Chemical Engineering,
Institute of Material Science and Engineering,
Chongqing University, Chongqing, 400044, China

Introduction

Spinel LiMn_2O_4 , because of its low cost, large abundance and low toxicity, is seen as possible alternative to LiCoO_2 which is presently the favourite material. However, the capacity of spinel LiMn_2O_4 fades rapidly on charge-discharge cycling.

The sol-gel method for preparing LiMn_2O_4 has several advantages, such as a low calcination temperature, a short processing time etc. In this study, the sol-gel method has been used to synthesize LiMn_2O_4 and LiCoO_2 -coated LiMn_2O_4 , also the method is improved for more simple. We used cyclic voltammetry(CV) and galvanostatic cycling test to study the effect of the LiCoO_2 -coating on the surface and the electrochemical stability of the LiMn_2O_4 .

Experimental

The LiMn_2O_4 powders were prepared by the sol-gel method using citric acid as a chelating agent. Stoichiometric amount of $\text{Li}_2\text{CO}_3, \text{Mn}(\text{NO}_3)_2$ (50%, solution) (1:1mol ratio) and citric acid were mixed. The mixtures were heating at 80°C for 3h to remove excess water. The resulting precipitate of metal citrate was dried in oven for 3h at 120°C . The precursors were decomposed at 300°C for 1h, ground and then calcined in box furnace at 700°C for 8h. The LiCoO_2 coated LiMn_2O_4 powders were prepared by soaking the prepared LiMn_2O_4 in a stoichiometric mixture of $\text{Li}_2\text{CO}_3, \text{CoCO}_3$ (1:1mol ratio), citric acid and deionized water, and repeated the steps for preparing LiMn_2O_4 . To measure the electrochemical properties, the positive electrode was fabricated by mixing 85% spinel, 10% conductive carbon black and 5% slurry. The sample was then pasted on aluminum foil and dried at 100°C under vacuum for over 8h. Li foil was used as counter and reference electrode. The electrolyte used was 1M LiPF_6 in EC:DEC(1:1), and celgard 2400 used as separator. All electrochemical cell fabrication was performed in a dry-air-filled glove box. Electrochemical characterization was performed on DC-5 battery testing instrument and ZF-10 for three-electrode electrochemical cells at room temperature. Power XRD using Cu K α radiation was used to identify the crystalline phase of the prepared powders.

Results and discussion

XRD Patterns of the prepared and LiCoO_2 -coated LiMn_2O_4 powders show well-defined spinel phases.

Fig.1 shows two pairs of reversible oxidation and reduction current peaks at 4.0 and 4.1V for LiMn_2O_4 (a), two pairs of reversible oxidation and reduction current peak at ≈ 3.95 and ≈ 4.15 for LiCoO_2 -coated LiMn_2O_4 (b: 700°C , c: 750°C , d: 800°C) respectively. The mechanism of the interfacial reaction is not known. More works are continuing.

Fig.2 shows the capacity retention and rate capacity of LiMn_2O_4 are excellent (121.8mAh/g for first cycle, 110.5mAh/g for 30th cycle), so the improved sol-gel method was good for synthesis the LiMn_2O_4 ; the discharge capacity retention of the LiCoO_2 -coated LiMn_2O_4 (b, c, d) is enhanced in comparison with that of LiMn_2O_4 .c(750°C , 8h) is the best of all(131.3mAh/g for first, 120.3mAh/g for 30th). The observed behavior may be due to a reduction in spinel dissolution.

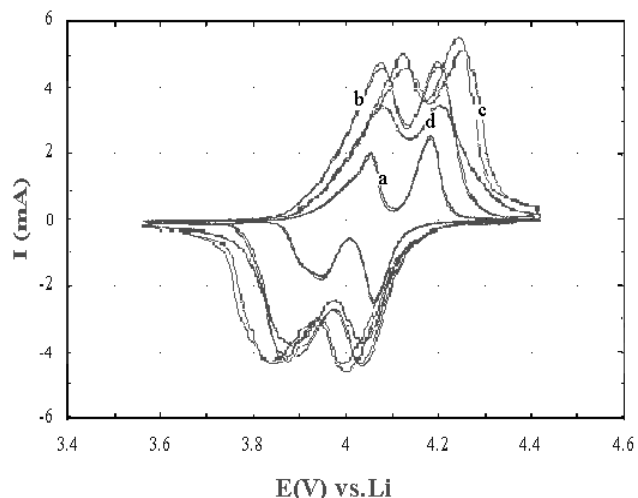


Fig.1. Cyclic voltammogram of LiMn_2O_4 (a: 700°C for 8h) and LiCoO_2 coated LiMn_2O_4 (b: 700°C for 8h; c: 750°C for 8h; d: 800°C for 8h) (scan rate 0.05mV/s)

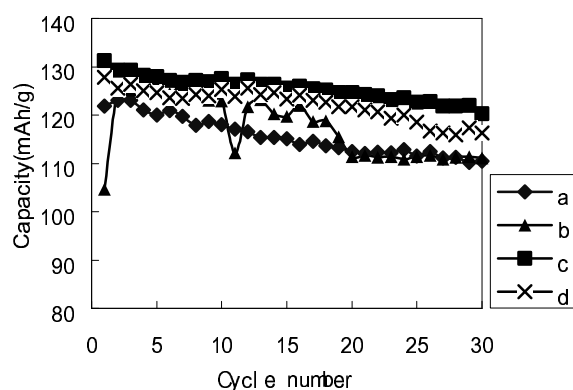


Fig.2. Discharge capacity vs. cycle number for LiMn_2O_4 (a) and LiCoO_2 coated LiMn_2O_4 (b, c, d as same for Fig.1)

Reference

- [1] B J Hwang, R Santhanam, D G Liu, Y W Tsai; J Power Source 102(2001) 326.
- [2] S S Zhang, T R Jow; J Power Source 109(2002) 172.