SYNTHESIS AND ELECTROCHEMICAL STUDY OF LiMn$_2$O$_4$ COATED BY LiCoO$_2$

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Introduction

Spinel LiMn$_2$O$_4$, because of its low cost, large abundance and low toxicity, is seem as possible alternative to LiCoO$_2$ which is presently the favourite material. However, the capacity of spinel LiMn$_2$O$_4$ fades rapidly on charge-discharge cycling.

The sol-gel method for preparing LiMn$_2$O$_4$ 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 synthesise LiMn$_2$O$_4$ and LiCoO$_2$-coated LiMn$_2$O$_4$, 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$_2$O$_4$.

Experimental

The LiMn$_2$O$_4$ powders were prepared by the sol-gel method using citric acid as a chelating agent. Stoichiometric amount of Li$_2$CO$_3$, Mn(NO$_3$)$_2$·6H$_2$O (50%, solution) (1:1mol ratio) and citric acid were mixed. The mixtures were heated 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$_2$O$_4$ powders were prepared by soaking the prepared LiMn$_2$O$_4$ in a stoichiometric mixture of Li$_2$CO$_3$, CoCO$_3$·H$_2$O (1:1mol ratio), citric acid and deionized water, and repeated the steps for preparing LiMn$_2$O$_4$. 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 Ka 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$_2$O$_4$ 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$_2$O$_4$ (a), two pairs of reversible oxidation and reduction current peak at $\approx$3.95 and $\approx$4.15 for LiCoO$_2$-coated LiMn$_2$O$_4$ (b, c, d) 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$_2$O$_4$ 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$_2$O$_4$; the discharge capacity retention of the LiCoO$_2$-coated LiMn$_2$O$_4$ (b, c, d) is enhanced in comparison with that of LiMn$_2$O$_4$ (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.

References