Rare earth elements-modified spinel LiMn2O4 for lithium ion battery

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Spinel LiMn2O4 has been studied extensively in order to replace LiCoO2 as a cathode material for secondary lithium batteries since its low cost, abundant and no toxicity [1,2]. The main problem of this material is the rapid loss of capacity, especially at high temperature, due to the dissolution of Mn2+ - the crystal structure change by Jahn-Teller effect and the decomposition of organic electrolytes on its surface during charge process [3].

In order to improve the electrochemical stability of spinel LiMn2O4, many kinds of metals such as Ti, Ge, Fe, Zn, Al, Ga, Cr, Ni and Co have been used as additives for doping spinel LiMn2O4. The purpose of this work is to evaluate the properties of spinel LiMn2O4 doped with rare earth elements at low concentrations by determine their affect on maintaining electrochemical capacity. The doping-metals in this research were rare earth elements La, Pr, Nd, Eu, Y and Sm.

Experimental

Spinel LiMn2O4 and LiM0.02Mn1.98O4 (M= La, Pr, Nd, Eu, Y, Sm) were prepared by intimately mixing stoichiometric amounts of MnO2, LiCO3 with additive materials La(NO3)3H2O, Pr2O3, Nd2O3, Eu2O3,Y2O3 or Sm2O3 respectively in the molar ratio of Li:Mn:M = 1:1.98:0.02 (where M is rare earth element). The mixture were pressed into small flakes, calcined at 750 for 24h and then furnace-cooled slowly to ambient temperature. The final samples were obtained by grinding the products and sieving through 300-400 mesh. The working electrodes were prepared by the mixture with the ratio of LiM0.02Mn1.98O4 : acetylene black : PTFE binder = 85:15:5. The electrochemical behaviors of the resulting compounds were measured in a three-electrode cell. The electrolyte was 1:1 EC (ethylene carbonate) and DMC(dimethyl carbonate) containing 1M LiPF6 (Merck Company). The charge- discharge properties of materials were tested in a R2025 button cell with a lithium anode.

Results and discussion

The XRD results showed that all samples were in Spinel structure.

The spinel LiNd0.02Mn1.98O4 sample presented better reversibility (see Fig.1) than LiMn2O4 by compare their cyclic voltammograms over the potential range of 3.5V to 4.35V(vs. Li/Li+).

Fig.2 presents the first charge-discharge curves of the Li/LiMn2O4 and Li/LiM0.02Mn1.98O4 (M=La, Pr, Nd, Y, Sm) cells. There are two discharge plateaus in all curves, which are, correspond to the two redox peaks on the CV curve, respectively. It can be seen that all the rare earth elements have negative effect to decrease the initial capacity of LiMn2O4 electrode. The additive material with lowest discharge capacity was La, which has largest atom radii among these rare earth elements. It may occupy larger space in spinel structure and hinder the insertion process of lithium ion into spinel crystal lattice.

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The discharge capacities of Li / LiM0.02Mn1.98O4 cells at different cycle number are shown in Fig.5. LiMn2O4 electrode performed the worst electrochemical stability. It lost 20% capacity after 40 cycles, meanwhile LiPr0.02Mn1.98O4 and LiSm0.02Mn1.98O4 only lost the capacity of 4.83.9% respectively. Moreover, their discharge capacity after 40 cycles was much higher than that of LiMn2O4 electrode. All rare earth elements additives in this report performed positive effect in improving the cycling ability.

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References

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Fig.1 Cyclic voltammograms of LiNd0.02Mn1.98O4 electrode

Fig.2 Charge-discharge curves of spinel LiM0.02Mn1.98O4 (M= Y, Pr, Sm, La, Nd) electrodes. I = 2A/cm2.

Fig.3 The capacity of M0.02Mn1.98O4 electrodes vs. Cycle number.