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The research progress on layered Li_xMnO_2

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Abstract: The structural characteristics, preparation methods and electrochemical properties of Li_xMnO_2 were introduced in this paper, and many problems of the research status of Li_xMnO_2 at present were pointet out, meanwhile the developmental direction of layered Li_xMnO_2 in the future was put forward.

Key words: layered structure; Li_xMnO_2; progress

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1 Introduction

Since lithium secondary batteries appeared on the market in 1991, extensive attention had been devoted to them because of their well performances such as high voltage, high capacity, memoryless effect *et al.* The properties of cathode materials had influence on lithium batteries properties to a considerable degree. The more pratical interest cathode materials included mainly lithium cobalt oxygen, lithium nickel oxygen, lithium manganates and so on. Lithium cobalt oxygen, presently the most widely used in comerical on account of its simple preparing process, stable performance, high capacity and well cyclability, but its shortcoming was lack of cobalt and over high cost. In additions, it was very difficult in preparing single phase $LiNiO_2$, and its safety need to be investigated further.

Lithium manganates was known as the most developmental potential cathode materials for lithium ion batteries due to their high energy density, low cost, nontoxicity. In which cubic spinel $LiMn_2O_4$ and layered $LiMnO_2$ could be used for cathodes. At present, spinel $LiMn_2O_4$ which was studied extensivly was three-dimensional tunnel structure, its theoretical capacity was 148mAh/g and its structure was thermodynamical stabilization phase and its preparation process was simple, but it wasn't resolved effectivly sucn as poor cyclability and high temperature capacity loss etc. Many scholars pay attention to the preparation of layered $LiMnO_2$ recently since it was the most developmental prospect cathode material, with bigger lithium reversible intercalation ability and theoretical discharge specific capacity (285 mAh/g).

2 Strutural characterization

According to J. M. Paulsen *et al.*[1], alkali metal manganates A_xMnO_y (A=K or Na) had three different

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layered structure distinguished by the stacking of the oxygen. The structures were designated by a letter which refered to the oxygen environment of the alkali ion (octahedral: O, prismatic: P)followed by a number indicating the number of MnO_2 sheets within the unit crystal cell. LixMnOy was easily produced by exchanging between A_xMnO_y and Li^+. O_3-type layered structure $LiMnO_2$ was synthesized by exchanging Na^+ inα-$NaMnO_2$ exchanged with Li^+ using LiBr dissolved in alcohol. Li^+ occupied prioritily octahedral sites because of O_3-structure with octahedral alkali ion sites. Therefore, the O_3-type structure could remain undisturbed during ion exchange. However the P_2 structure, with prismatic sites, transformed to O_2 and P_3 structure transformed to O_3 structure, respectively. These transformations could easily occur since only a gliding MnO_2 layers was required.

O_3-type material initial charge capacity could reach to 250 mAh/g, but this structure converted easily to spinel during cell cycling, which led to rapid capacity loss.

There were very different structure between that of O_2-type and spinel. Thus the transformation of O_2-type to spinel structure could be done only by a rearrangement of oxygen lattice which required the breaking of all Mn-O bonds. This was highly unlikely at room temperature. Consequently, O_2-type lithium manganates which were prepared by ion exchange method from P_2-type sodium manganates synthesized in advance wouldn't be able to transform to spinel structure during the electrochemical process. Their stacking would remain unchanged and they would cycle well.

3 Preparation method

The preparation methods of layered lithium managanese oxygen and doping chemical compounds included mainly ion exchange, hydrothermal, high temperature reduction quenching quickly, sol-gel, intercalation, high temperature solid-state reaction at present.

3.1 Ion-exchange method

Layered struture α-$NaMnO_2$ was firstly synthesized through solid-state reaction, then ion exchange proceeded in lithium salt -organic solvent, which was used to prepare layered $LiMnO_2$ firstly by Rober Armstrong *et al.*[2]. They obtained α-$NaMnO_2$ from Na_2CO_3 and Mn_2O_3 according to stoichionmetric compositions which were mixtured and reacted in arogen at 700-730℃ for 18-72 h, then the amounts of α-$NaMnO_2$ were added into excessive amount of LiCl or LiBr in n-hexanol, heating return flow at 145-150℃ for 6-8 h, after quenching into room temperature, filting followed flushing with n-hexanol and alcohol separately, finally dring. Jeong Y U *et al.*[3] also prepared layered $Na_xMnO_{2.15}$, in which $NaMnO_4$ was reduced in solution and the precipitats obtained were firing in air at 500℃ for 24 h. but tunnel struture $Na_xMnO_2+\delta$ was produced at 600℃, the corresponding struture $Li_xMnO_2+\delta$ was required then according to above-mentioned ion exchange process. Xu Ming-fei *et al.*[4] employed Mn_2O_3 by decomposing MnO_2 at 600-800℃ and Na_2CO_3 to prepare α-$NaMnO_2$ in arogen at 710℃ for 24 h, α-$NaMnO_2$ was put into 4 mol/L of LiBr or LiCl solution in n-hexanol, heating return flow at 145-154℃, after cooling, filted and washed, layered lithium manganese oxygen was prepared.

J. M. Paulsen *et al.*[1] prepared sodium manganese oxide which composition was $Li_xNa_{1-x}MnO_y$ by high temperature solid-state reaction, the different conditions of solid-state reaction decided different x at 800℃. only when $x=0$ and x was between 0.16 and 0.2, yielded single phase material. At $x=0$, $NaMnO_2$ was α-$NaMnO_2$(O_3-type), the latter had the same crystal struture as β-$Na_{0.7}MnO_2$ which was the desired P_2-type. P_2 phase $Na_{23}(Li_{16}Mn_{56})O_2$ was selected at x-0.2 during ion exchanging, after ion exchanging, P_2-type $Na_{23}(Li_{16}Mn_{56})O_2$ was changed to O_2-type $Li_{23}(Li_{16}Mn_{56})O_2$. It was found that this material wouldn't rapidly transformed to spinel structure during charge-discharge cycle . The O_2 phase had a reversible capacity in the range of 150 mAh/g and was cycled between 2 and 4. 8 V.

3. 2 Hydrothermal reaction method

Mit-suharu Tabuchi, *et al.*[5] adopted directly Mn_2O_3 and mixture alkali such as $LiOH \cdot H_2O$-KOH or Li-Cl-KOH to prepare layered substablization $LiMnO_2$ at 220℃ for 1—8 h, hydrothermal reaction during the pressure of 25—30 kg/cm^2, the precipitates were flushed repeatly with methanol for the sake of removing residual alkali solution, then firing at 100℃ for half an hour. Yoshiaki Nitta *et al.*[6] obtained layered lithium managanese oxygen from starting materials of γ-MnOOH and $LiOH \cdot H_2O$ at 130℃, 3×10^5 Pa for 0. 5—4 h in the high pressure reaction. Liu Yu-ge *et al.*[7] investigated layered O_3-type $LiMnO_2$, synthesized through Mn_2O_3 by calcining MnO_2 electrolyzed at 800℃ for 15 h, then led LiOH · H_2O, NaOH put into uydrothermal reactive caldron at 180℃.

3. 3 Melting-soak method

Melting-soak method was twice heating advanced by YoshioMand *et al.*[8]. If $LiNO_3$ was used as the source of Li ion, when $n(LiNO_3) : n(MnO_2) = 1 : 3$,. the first heating temperature was 260℃, and the second temperature was 320—360℃, monoclinic $Li_{0.33}MnO_2$ was producted. Nakamura Hetal[9] reduced largely reaction temperature with LiI replacing $LiNO_3$ and $Li_{0.47}Mn_{0.98}O_2$ was synthesized, when $n(LiI) : n(MnO_2) = 1 : 1$, reaction temperature was at 150—200℃.

3. 4 Sol-gel method

The patent[10] reported that $LiMn_xO_2$ precursor was synthesized through mechanical ball milling accelerating the solid state reaction from raw materials consisting of $LiOH \cdot H_2O$(or Li_2COOH) and MnCOOH (or $MnCO_3$), as well as citric acid(or oxalic acid *et al.* solid polyacide), the pasted mixtures were dried at 100—300℃, and a subsequent heat treatment was carried out at 500—700℃ in air for 4—20 h. The layered LiMnxO2 and doping chemical compound were obtained . LU Zhong-hua *et al.*[11] prepared the precursor with $CH_3CO_2Li_2H_2O$ $Cr(NO_3)_3 \cdot 9H_2O$ and $(CH_3CO_3)_2Mn \cdot 4H_2O$ according to stoichionmetric compositions, the pH of the solution was adjusted to 10 by using ammonium hydroxide, and the precursor obtained was decomposed at 480℃ for 12 h, after cooling, the samples were grinded and pressed, and the blocks were conserved under argon atmothesphere to react at 900℃ for 3 h. There was a O_3-type layered $Li[Cr_xLi_{1/3-x}Mn_{2/3-2x/3}]O_2$ obtained. Layered $LiMn_{1-x}Cr_xO_2$ was synthesized by Z. P. Guo *et al.*[12] with similar method, the test data were also compared from high temperature solid-state reaction to it, the results displayed that layered $LiMn_{1-x}Cr_xO_2$ prepared by this method had higher capacity.

3. 5 Intercalation method

The patent[13] put forward that high purity layered $LiMnO_2$ was prepared by lithium hydroxide inserted to the interlayer space of layered $Mn(OH)_2$ precursor in oxidizer jointed action, with $Mn(OH)_2$ as precursor material and lithium compound as intercalate object material.

3. 6 High temperature solid-state method

Jang Yong-II, *et al.*[14] prepared Al doping monoclinic $LiAl_YMn_{1-y}O_2$ at high temperature, the best technological conditions were 5%—7% Al, temperature at 950℃, oxygen pressure of 1. 0—0. 7 MPa . The mechanism of Al^{3+} stabilized monoclinic $LiMnO_2$ was that there was no distortion when MnO_6 octahedra was substituted for AlO_6 octaghedra because of Al^{3+} as no-JT ion, in addition, the more stable monoclinic structure was due to the ion-radii of Al^{3+} was smaller than Mn^{3+}. Yong-II Jiang *et al.*[15] prepared O_2-type layered $LiMnO_2$ of mixed phase by Mn_3O_4 and LiOH at 950℃, oxygen pressure of 1.0−0.6 MPa. When the electrodes were charged and discharged at 3.33 mA/g, its biggest specific discharge capacity was 272 mAh/g, while at 33.3 mA/g, its specific discharge capacity only was 150 mAh/g after 30 cycles.

It was unsuccessful that layered $LiMnO_2$ was synthesized at high temperature solid-state reaction method since nonlayered $LiMn_2O_4$ (spinel) and $LiMnO_2$ (monoclinic) and Li_2MnO_3 (rock-salt) were very stable compared to layered $LiMnO_2$. These impure phase and layered $LiMnO_2$ were produced together during the reaction, which reduced sharply electrochemical property of the material.

The literature[16] reported that it was feasible that single phase $LiMnO_2$ was prepared quickly in argon atmosphere at high temperature followed by quenching sharply into liquid nitrogen. With the starting materials consisting of Li_2CO_3 and $MnCO_3$, $x(Li):x(Mn)=0.98:1.02$, at 920−960℃ for 6 h, stablation of single phase $LiMnO_2$ only above 700℃ was confirmed from XRD analysis.

4 Conclusions

From environmental protection, performance price ratio to safety, lithium manganates as cathode material for lithium ion batteries had more advantageous than lithium cobalt oxygen or lithium nickel oxygen systems. It had a well prospect for practical use in the near future. A large number of experiments had proved that layered Li_xMnO_2 transformed easily to spinel phase during the cycles, but there were much different opinion about influence on phase transform to cycle performance. The preparation of monoclinic layered Li_xMnO_2 had no more difficulties than avoiding that the transformation of O_2-type layered Li_xMnO_2 to spinel phase. It was stressed on new technique of preparation of stable layered Li_xMnO_2 as cathode materials from now on. Especially chemical compositions of O_2-type layered lithium manganates, and reaserch on technique and electrochemical performance further were also important. There were different crystal struture layered Li_xMnO_2 which were composed by different methods. The former methods were insuitable to be producted on a large scale because of complicated technique and hard control conditions. Although high temperature solid-state method was simple in technique, the pure phase stutrcure layered Li_xMnO_2 was obtained rather difficultly, and it was impossible on a large scale production that pure layered Li_xMnO_2 must be quenching quickly from high temperature into liquid nitrogen. As preparation of single phase $LiMnO_2$ was stable at only above 700℃, the author of this paper pointed out that pure layered Li_xMnO_2 was synthesized by quenching quickly from high temperature solid-state reaction to room temperature, in additions, this method was simple and suitable for mass production.

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