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Charge-discharge Behavior of Surface-coated $LiMn_2O_{3.95}F_{0.05}$ Cathode Materials at High Temperature

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Abstract: With inorganic salts such as $LiNO_3$, Li_2CO_3, surface-coated $LiMn_2O_{3.95}F_{0.05}$ were prepared by melt-impregnation method. When these surface-coated $LiMn_2O_{3.95}F_{0.05}$ were used as cathode materials, their charge-discharge characters were carefully compared. As a result, they exhibited good charge-discharge properties at 50°C high temperature. Especially, $LiNO_3$ surface-coated $LiMn_2O_{3.95}F_{0.05}$ retained nearly 80% initial reversible capacity after 130 cycles at 50°C.

Keywords: Inorganic salts, surface-coated $LiMn_2O_{3.95}F_{0.05}$.

Spinel type lithium manganese oxide $LiMn_2O_4$ and related materials have been studied extensively as one of the most attractive cathode materials in lithium ion rechargeable batteries and electric vehicles[1~3]. Especially Li-rich and quaternary spinel oxides $LiMn_{2-y}M_yO_4$ (M=Li or 3d transition metals) showed prospective applications in room temperature[4~6]. However, unfortunately they all exhibited rapid capacity fade at high temperature, *e.g.*, at 50°C, and could not meet the necessary in real applications. Nevertheless, many efforts have been made to investigate the mechanism of capacity fade at high temperature[7~9]. Mainly there are three types possible explanations: the dissolution of manganese caused by H^+ generated during the course of charge-discharge cycles, which is a temperature-control reaction; the increase of inner resistance, which results from the dissolution of manganese; the oxidation of electrolyte. According to above mechanism, many methods[10~12] have been adopted to improve the performances of spinel type lithium manganese oxide at high temperature. Amatucci modified the surface of the $LiMn_2O_4$ by means of acetylacetone and borate, and S. Masaru [13] mixed polyaniline and $LiMn_2O_4$, and N. Matsuhiko[14] coated the surface of $LiMn_2O_4$ with polypyrrole. All the efforts have improved the properties of spinel type lithium manganese oxide. However, the results of long charge-discharge cycle at high temperature have not been provided.

It was well known that a SEI (solid electrochemical interface) film was formed on

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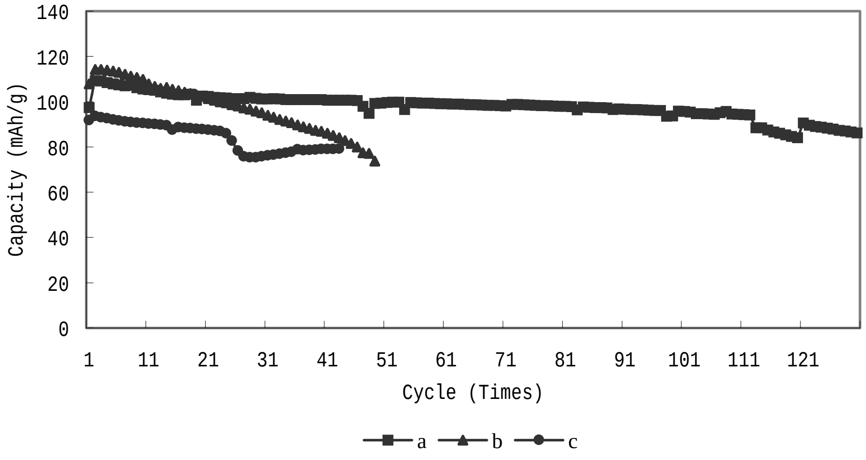
the surface of anode electrode[15]. It could be stable in organic electrolyte, and the constituents of the SEI film were mainly Li_2CO_3 and $ROCO_2Li$ characterized by FTIR[16] and *ab* initial molecular orbital calculations[17]. In this paper, we employed these constituents of SEI coat the surface of $LiMn_2O_{3.95}F_{0.05}$, expecting that these constituents of SEI could be stable between the cathode electrode and electrolyte at high temperature, because the SEI film was the original reaction product of electrolyte and anode electrode, which was stable in the electrolyte. Moreover, lithium ion can move off through the SEI film.

Experimental

Li_2CO_3 was one of the main constituents in SEI. So it was the valuable surface modification agent. For comparison, $LiNO_3$ was adopted. The preparation proceeded as follows: 10 weight percent of Li_2CO_3 or $LiNO_3$ was mixed with $LiMn_2O_{3.95}F_{0.05}$, and then the precursor was ball milled for 6 hours, with alcohol as a dispersing agent. After that the mixture was placed in infrared lamp to evaporate alcohol. Finally, it was calcined for 6 hours in 260°C.

The positive electrode consisted of 80wt% surface-coated $LiMn_2O_{3.95}F_{0.05}$ or $LiMn_2O_{3.95}F_{0.05}$ and 15wt% acetylene black and 5wt% polytetrafluoroethylene (PTFE) as a binder, and metal Al was used as collector. The electrolyte solution was EC+DEC (1:1)+1 mol/L $LiClO_4$. Lithium metal foil was used as the counter electrode during charge-discharge measurements. All cell assemblies were completed in a dry box filled with argon gas. All charge-discharge tests were carried out in a DC-5 fully automatic program test instrument at 50°C, with 0.25 mA constant current in the voltage range of 3.5～4.35 V.

Figure 1 Curves of capacity against charge-discharge cycle



a, b and c were respectively the reversible capacity curves of $LiNO_3$-coated $LiMn_2O_{3.95}F_{0.05}$, $LiMn_2O_{3.95}F_{0.05}$ and Li_2CO_3-coated $LiMn_2O_{3.95}F_{0.05}$.

Electrochemical charge-discharge results

The charge-discharge results were shown in **Figure 1**. In **Figure 1**, it could be found that non-surface-coated $LiMn_2O_{3.95}F_{0.05}$ exhibited poor charge-discharge behavior. After 50 cycles, the cell suddenly deteriorated and did not have the capability of charge-discharge any more. It was mainly because the inner resistance of cell was too high. The Li_2CO_3 and $LiNO_3$ surface-coated $LiMn_2O_{3.95}F_{0.05}$ exhibited about 110 mAh/g and 93 mAh/g reversible capacity respectively. Furthermore, we can find that surface-modified product showed good cycle performance at 50^{o}C. But the result was just opposed to our original purpose. The $LiNO_3$-coated sample exhibited better behavior than the Li_2CO_3- coated sample. The former retained nearly 80% initial reversible capacity at 50°C after 130 cycles. According to the above results, it was obvious that the $LiNO_3$ surface- coated $LiMn_2O_{3.95}F_{0.05}$ exhibited good charge-discharge performance and the surface coat could efficiently suppress the capacity loss at 50°C. We are continuing the investin- gation on the reasonable explanation for this result.

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