

Cycling Performance of $\text{LiCr}_{0.1}\text{Mn}_{1.9}\text{O}_4/\text{MPCF}$ at Elevated Temperature

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Spinel LiMn_2O_4 , with economical and environmental advantages, is considered to be a most promising cathode material for lithium-ion batteries. Its main drawback is significant capacity fading upon cycling at elevated temperature, due to several possibilities, e.g. manganese dissolution, electrolyte decomposition, Jahn-Teller distortion etc. Partial replacement of Mn in LiMn_2O_4 by other elements like Li, Co, Cr, Ni, Al can reduce the fading effectively. $\text{LiCr}_{0.1}\text{Mn}_{1.9}\text{O}_4$ has been reported to have better cycling performance at room temperature as well as 55°C compared to spinel LiMn_2O_4 [1-3], however, the cycling performance was studied in cells with lithium metal as anode in these papers. In this work, $\text{LiCr}_{0.1}\text{Mn}_{1.9}\text{O}_4/\text{MPCF}$ (18650 type) cell was assembled, its capacity fading at elevated temperature was studied, and some new results were obtained.

$\text{LiCr}_{0.1}\text{Mn}_{1.9}\text{O}_4$, prepared using the method described in our published paper [4], was used as cathode material, and MPCF (Nikko) as anode for this study. The cells cycled at 25°C , 55°C respectively, and charge-discharged at 0.5C in the $3.0\text{--}4.3\text{V}$ voltage range. In order to analyze the mechanism of capacity fading, the cells were dismantled in the dry box after 100 cycles, and then the structure, electrochemical characteristic and surface chemistry of the electrodes were studied, manganese dissolution in the electrolytes were also analyzed. $\text{Li}/\text{LiCr}_{0.1}\text{Mn}_{1.9}\text{O}_4$ and Li/MPCF cells were also assembled and tested for comparison.

The capacity of $\text{LiCr}_{0.1}\text{Mn}_{1.9}\text{O}_4/\text{MPCF}$ cell was 1.2 Ah . When charge-discharged up to 100 cycles at 25°C , 93% of its initial capacity retained, which was consistent with the cycle performance of $\text{Li}/\text{LiCr}_{0.1}\text{Mn}_{1.9}\text{O}_4$ cell. However, when cycled at 55°C , $\text{LiCr}_{0.1}\text{Mn}_{1.9}\text{O}_4/\text{MPCF}$ showed very faster capacity fading than $\text{Li}/\text{LiCr}_{0.1}\text{Mn}_{1.9}\text{O}_4$, only 64% of its initial capacity maintained at the 100 cycles (Fig.1). After 100 cycles, no new phases were detected from the XRD patterns of electrodes, the position and intensity of all reflection peaks also unchanged (Fig.2). Electrochemical analysis of the electrodes indicated that when $\text{LiCr}_{0.1}\text{Mn}_{1.9}\text{O}_4/\text{MPCF}$ cell discharged to 2.75V , almost all lithium ions were deintercalated from MPCF, but the amounts of lithium ions intercalated into $\text{LiCr}_{0.1}\text{Mn}_{1.9}\text{O}_4$ decreased with cycling, which consisted with the capacity fading of $\text{LiCr}_{0.1}\text{Mn}_{1.9}\text{O}_4/\text{MPCF}$. When the electrodes were reassembled in coin-type cells, but with lithium metal as anode, above 96% of initial capacity of the electrodes could resume. Above results indicated that faster capacity fading of the cell at elevated temperature could be attributed mainly to the severer decrease of active lithium ions transferred between $\text{LiCr}_{0.1}\text{Mn}_{1.9}\text{O}_4$ cathode and MPCF anode. By analyzing the surface of the electrodes, we considered that higher temperature cause severer electrolyte decomposition on the surface of $\text{LiCr}_{0.1}\text{Mn}_{1.9}\text{O}_4$ electrode, and more lithium-contained resultants deplete more active lithium ions, which accelerate the capacity fading of $\text{LiCr}_{0.1}\text{Mn}_{1.9}\text{O}_4/\text{MPCF}$.

At elevated temperature, $\text{LiCr}_{0.1}\text{Mn}_{1.9}\text{O}_4$ exhibited very good effects on reduction of manganese dissolution and stabilization of structure, but the electrolyte decomposition on its surface got severer, which caused faster capacity fading of $\text{LiCr}_{0.1}\text{Mn}_{1.9}\text{O}_4/\text{MPCF}$ cell. Surface treatment of $\text{LiCr}_{0.1}\text{Mn}_{1.9}\text{O}_4$ will be necessary for improving the cycle life of $\text{LiCr}_{0.1}\text{Mn}_{1.9}\text{O}_4/\text{MPCF}$ cell.

References

1. L. Guohua, H. Ikuta, T. Uchida et al., *J. Electrochem. Soc.*, **143**, 178 (1996).
2. D. Zhang, B. N. Popov, R. E. White, *J. Power Sources*, **76**, 81 (1998).
3. M. Yoshio, Y. Xia, N. Kumada et al., *J. Power Sources*, **101**, 79 (2001).
4. Jian-gang Li, Zhi-yuan Tang, Jian-jun Xue et al., *Chinese J. Appl. Chem.*, **18**, 802 (2001).

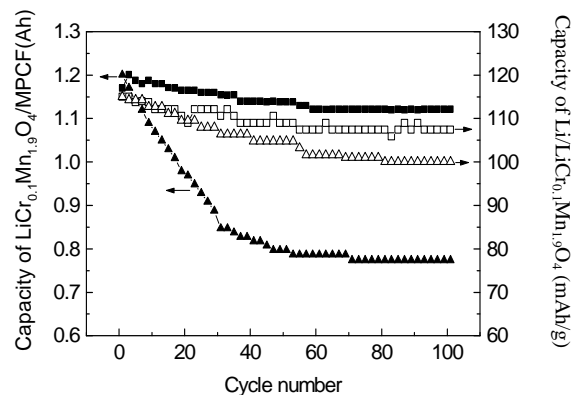


Fig.1 Cycling performance of $\text{LiCr}_{0.1}\text{Mn}_{1.9}\text{O}_4/\text{MPCF}$ at 25°C (■) 55°C (▲) and $\text{Li}/\text{LiCr}_{0.1}\text{Mn}_{1.9}\text{O}_4$ at 25°C (□) 55°C (△) respectively

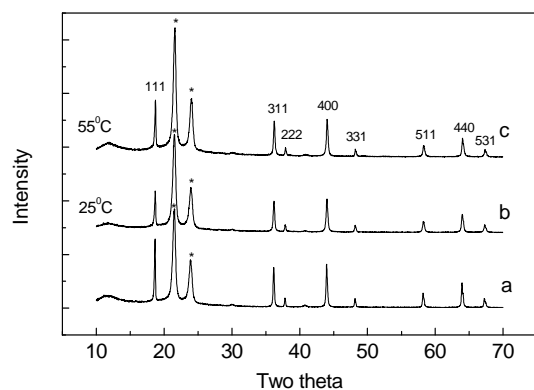


Fig.2 XRD patterns of $\text{LiCr}_{0.1}\text{Mn}_{1.9}\text{O}_4$ electrode a) fresh electrode, b) after 100 cycles at 25°C , c) after 100 cycles at 55°C