Effect on Storage Characteristics of Mixing Li-Mn Spinel and Li-Ni-Co-Mn Oxide

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Introduction

Recent times have seen rapid growth in the use of small, lightweight, lithium-ion batteries with high energy density. In addition, customer's needs have become diversified with market expansion, resulting in a strong demand for low-cost batteries with excellent performance. Li-Mn spinel is one of the most promising positive electrode materials for Li-ion batteries because of its low cost and thermal stability compared to $LiCoO_2$. However, it suffers some problems in regard to low capacity, and cycle and storage performance at elevated temperatures. Therefore, it is necessary to improve Li-Mn spinel in terms of both capacity and endurance at elevated temperatures. In a previous study, we investigated a mixture of Li-Mn spinel and Li-Ni-Co-Mn oxide, which has a large discharge capacity and good stability at elevated temperature, and found a surprising result: the starage characteristics of a mixture are superior to those of either of Li-Mn spinel or Li-Ni-Co-Mn oxide alone [1)]

In this work, we investigated factors for improving storage characteristics of cells at elevated temperature using a mixture as positive electrode material. We elucidate the effect of mixing by using two separated electrodes, each of which is coated on one side by Li-Ni-Co-Mn oxide or Li-Mn spinel.

Experimental

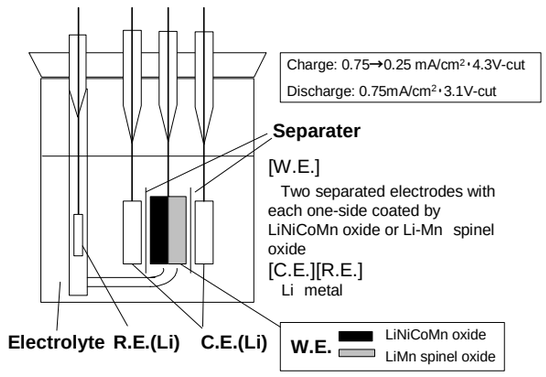
$Li_{1.1}Mn_{1.9}O_4$ (Li-Mn spinel) and $LiNi_{0.4}Co_{0.3}Mn_{0.3}O_2$ (Li-Ni-Co-Mn oxide) were used as positive electrode material. A mixture of positive electrode material were prepared by mixing Li-Mn spinel and Li-Ni-Co-Mn oxide by 4 : 6 weight ratios. In addition, we prepared an imitative mixed electrode that used two separated electrodes, each coated on one side by either Li-Ni-Co-Mn oxide or Li-Mn spinel as shown in Figure 1. The charge/discharge characteristics were measured using three-electrode test cells with lithium metal as a counter and a reference electrode over a potential range of 3.1 V to 4.3 V. As an electrolyte solution, we used EC/DEC (3:7 by volumetric ratio) containing 1.0mol dm^{-3} of $LiPF_6$. The high-temperature storage tests were carried out under a charged state (4.3 V) for 10 days at 45 degree C.

Results and Discussion

Figure 2 shows the capacity recovery ratios of cells using (1) Li-Mn spinel, (2) Li-Ni-Co-Mn oxide, (3)a mixture of Li-Ni-Co-Mn oxide and Li-Mn spinel, and (4) separated electrodes, each coated on one side by either Li-Ni-Co-Mn oxide or Li-Mn spinel (6:4 by weight ratio) as the positive electrodes after storage tests. We found the storage characteristics of a mixture to be better than those of either Li-Mn spinel and Li-Ni-Co-Mn oxide alone. Furthermore, (3) mixture and (4) separated electrodes showed similar storage performances. From these results, we are confident that this effect of mixing derives from the electrochemical interaction with the two active materials. After determining the capacity recovery ratio of the Li -Mn spinel in separated electrodes , we found that performance exceeded 99%, higher than the single material Li-Mn spinel just over 96% as shown in Fig. 3. Moreover, we confirmed that the behavior of change in the lattice constant versus the state of charge (S.O.C.) of the Li-Mn spinel was quite different in each case; that is, the change of the lattice constant in the single material Li-Mn spinel showed step-behavior versus S.O.C., while in a mixture of Li-Ni-Co-Mn oxide and Li-Mn spinel, the step-behavior was gradual. Furthermore, the difference among them was observed at the change in the open-circuit voltage versus the S.O.C. We therefore conclude that the excellent storage performance of a mixture was due to the reduced step-behavior of lattice constants change of Li-Mn spinel in a mixture, which resulted from the electrochemical interaction with the Li-Ni-Co-Mn composite oxide, and the change in the electrochemical characteristics of Li-Mn spinel.

References

1) T. Nohma, H. Kitao, N. Nakanishi and T. Ikemachi, Extended Abstracts of 204th Meeting of The Electrochemical Society, Orlando, 331(2003).



. Fig. 1. Three-electrode test cell using separated electrode with one –side of each coated with either Li-Ni-Co-Mn oxide or Li-Mn spinel.

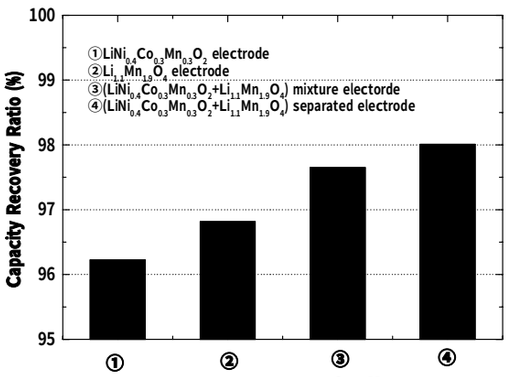


Fig. 2. Capacity recovery ratio of cells using various positive electrodes with an electrode solution after storage at 45degree C for 10 days.

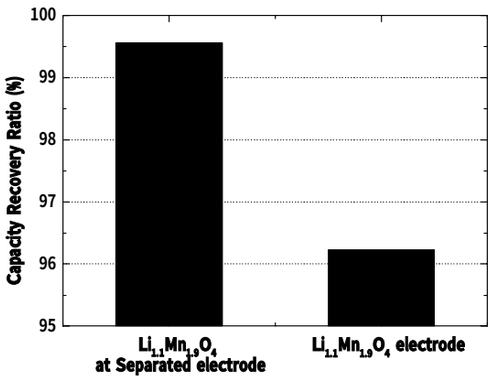


Fig. 3. Capacity recovery ratio of positive electrodes using Li-Mn spinel, or separated of Li-Mn spinel after Storage at 45degree C for 10 days.