Study on Electrochemical and Thermal Stability of Modified LiMn Spinel compounds for Lithium Ion Batteries

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Introduction

Lithium manganese oxide spinel (LiMn spinel) compounds have been widely studied as most promising cathode materials for lithium ion batteries because of their low cost, low toxicity and high stability at deep charge-state. One of the important subject matters for commercial use of there is the capacity failure at elevated temperature (1, 2). In this work, we prepared modified LiMn spinel compounds, which changed particle form and substituted a part of Mn, and their electrochemical and thermal stability were investigated.

Experimental

LiMn spinel and substituted LiMn spinel compounds were prepared by calcining a mixture of electrolytic manganese dioxide (EMD), Li_2CO_3 and compounds of substitution element (transition metal and 3B metal) at 800 or 900°C in air or O_2 stream. The prepared samples were characterized by XRD and chemical analysis. The XRD data were analyzed using RETAN94 of the Rietveld program. The charge-discharge cycling tests were carried out at constant current (0.4mA•cm^{-2}) between 3.5V and 4.5V at RT, 50°C and 60°C. The cathodes were consisted of 25mg of sample and 12.5mg of teflonized acetylene black. The CR2032 type coin cells were constructed using the cathode, lithium metal as anode and 1M $LiPF_6$ EC-DMC (1:2 by volume) as electrolyte solution. Thermal stability test were carried out by soaking samples in the above electrolyte solution and keeping for 4 days at room temperature (RT), 50°C, 60°C and 85°C.

Results and Discussion

Figure 1 and Fig.2 show SEM images of $Li_{1.1}Mn_{1.9}O_4$, which a particle form is different, and their cycling performance at elevated temperature, respectively. Sample A is composed by a uniform particles and sample B is composed by non-uniform particles. These samples exhibited different performance for the capacity failure on cycling, and the cycle stability of sample A was more stable. This result means that lithium insertion/extraction reaction into LiMn spinel particles for sample A, which consist by uniform particles, may proceed uniformly in the whole of active material. Figure 3 shows discharge capacity retention of several modified LiMn spinel compounds consists of uniform particles. It was found out that the cycle stability of large grain type or substituted type LiMn spinel compound was good and that the combined type (large grain + substituted type) was showed excellent stability. In order to understand the difference for the cycling performance of these samples, the analysis of crystal structure and Mn dissolution test have been done. From results, it was found that the capacity failure influenced Mn atom migration from 16d site to 8a site during the charge-discharge cycling and the amount of Mn dissolution at elevated temperature. In the viewpoint of the crystal structure and chemical composition, the effect of the characters on the capacity failure will be discussed.

References

[1]Y. Xia,Y. Zhou and M. Yoshio, Electrochemical.Soc, 144 (1997)2593.
[2]A.D. Pasquier, A. Blyr, P. Courjal, G. Amatucci and J.M. Tarascon, J.Electrochemical.Soc.,146(1999)428.

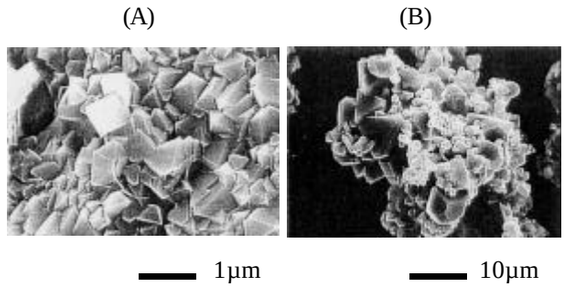

Fig.1 SEM images of LiMn Spinel consist of (A) uniform particles and (B) non-uniform particles, respectively.

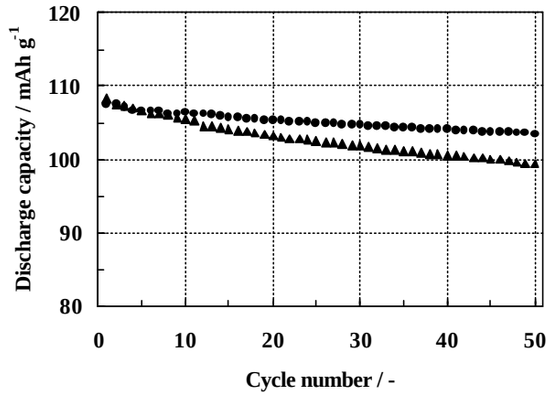

Fig.2 Cycling performance of sample A (circle) and sample B (triangle) (See Fig.1). The cells were cycled 4.5-3.5V at 0.4mA•cm^{-2} (50°C) using 1M $LiPF_6$ EC-DMC (1:2 by volume) as electrolyte solution.

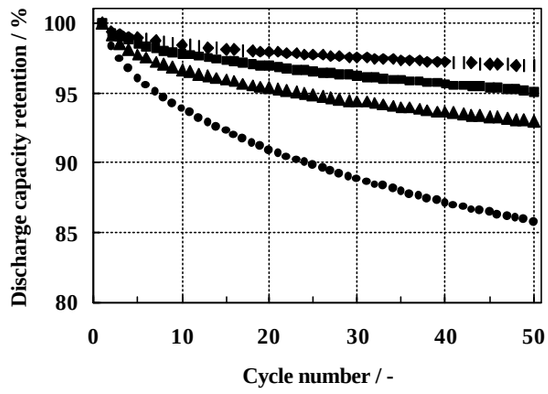

Fig.3 Discharge capacity retention of modified LiMn spinel compounds consist of uniform particles: small grain type (circle), small grain + substituted type (triangle), large grain (square) and large grain + substituted type (diamond), respectively. The cells were cycled 4.5-3.5V at 0.4mA•cm^{-2} (50°C) using 1M $LiPF_6$ EC-DMC (1:2 by volume) as electrolyte solution.