Effect of "Nano Inclusion" on cycle performance of $LiMn_2O_4$ cathode material at 3V range

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Introduction

$LiMn_2O_4$ which has the cubic spinel structure has been attracting attention as a cathode material because of low toxicity, availability, low cost, and safety. For practical application, it is necessary to solve the capacity fading problem during charge-discharge cycles. $LiMn_2O_4$ works at 4V and 3V ranges. Previously, we reported that, by firing Li_2CO_3 and $MnCO_3$ with Zn_2SnO_4, we formed very thin plate-shaped $ZnMn_2O_4$ inside $LiMn_2O_4$ single crystal having common oxygen arrangement with $LiMn_2O_4$ connected without crystal boundaries, that we named the material "Nano Inclusion" and that the cycle performance of $LiMn_2O_4$ with "Nano Inclusion" was superior to that of $LiMn_2O_4$ at 4V range[1],[2],[3]. We also investigated the effect of the amount of "Nano Inclusion" to the cycle performance at 3V range[4]. In this study, we prepared $LiMn_2O_4$ as previous study and changed heat-treating time. We investigated the effect on the cycle performance.

Experiment

ZnO and SnO_2 were mixed at a molar ratio of Zn:Sn=2:1, fired at 1000°C for 12h, then Zn_2SnO_4 with spinel structure was synthesized. Li_2CO_3, $MnCO_3$ and thus obtained Zn_2SnO_4 were mixed with a molar ratio of Li:Mn:Zn_2SnO_4=0.925:1.85:0.075. The mixture was calcinated at 550°C for 6h in air and then heat-treated at 800°C for z hours in air(z=2,4,8). The obtained sample was denoted by the value of z hereafter. We also synthesized $LiMn_2O_4$. Li_2CO_3 and $MnCO_3$ were mixed and calcinated at 550°C for 6h in air and then heat-treated at 800°C for 4h in air. X-ray diffraction measurements of the samples were carried out. The cycle performance was investigated with a two-electrode cell. The cathode was fabricated by mixing powder of the samples as the active material, acetylene black as a conducting additive and PVDF as a binder at the ratio of 80:15:5 by weight, and coating the mixture onto an Al foil by using N-methylpyrrolidone as a solvent. Lithium metal was used as counter electrode. The electrolyte was a 1 M solution of $LiPF_6$ in a mixture of EC and DMC (2:1, v/v). Cycle tests were carried out at between 2.0 V and 3.5 V under the constant temperature at 25°C. The current density was 120 mAg^{-1}.

Results and Discussion

Fig.1 shows discharge capacity as a function of cycle number for the samples. Discharge capacity of $LiMn_2O_4$ was larger than that of other samples at 1st cycle. But discharge capacity retention of $LiMn_2O_4$ was lower than that of other samples. At the 3V region, it is well known that the large volume change occurs accompanying with charge-discharge cycles and that this property causes not good cycle performance[5]. "Nano Inclusion" does not enter into electrochemical reaction, so it is considered that "Nano Inclusion" suppresses the crack propagation caused by the volume change of $LiMn_2O_4$. HAADF-STEM images for the cross section of the samples are shown in Fig.2. Previously, we reported effect of size of "Nano Inclusion" by heating time[3]. HAADF-STEM images revealed that the particle size of $LiMn_2O_4$ increased as z increased. It is considered that "Nano Inclusion" grew during the heat treatment at 800°C. In this time, the sample of z=8 was the best size of "Nano Inclusion" compared to other samples.

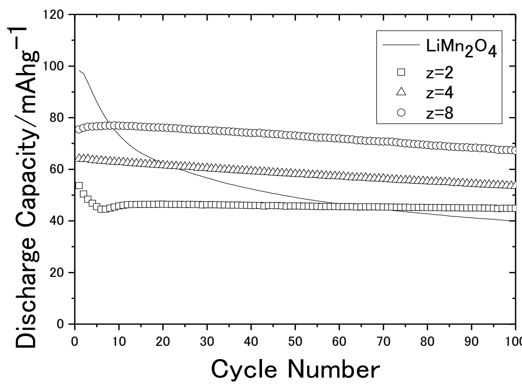
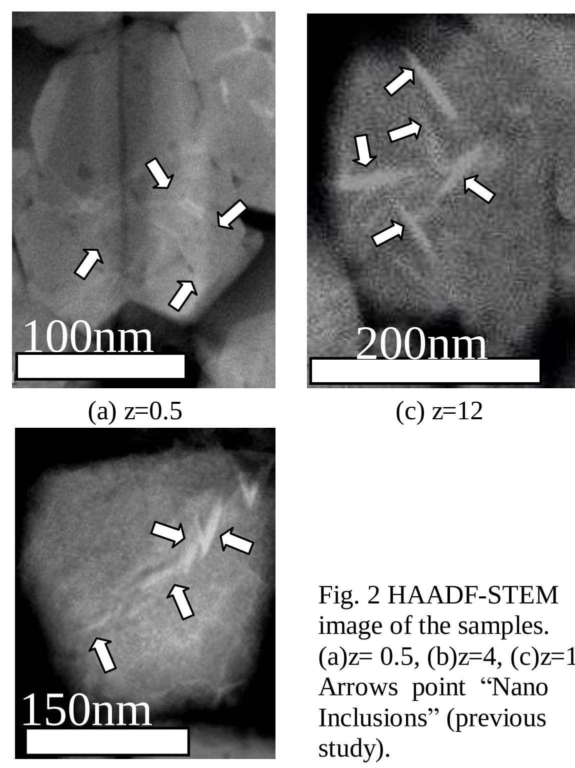


Fig. 1 Discharge capacity as a function of cycle number for $LiMn_2O_4$ and $0.925LiMn_2O_4$-$0.075Zn_2SnO_4$.



(a) z=0.5 (c) z=12 (b) z=4

Fig. 2 HAADF-STEM image of the samples. (a)z= 0.5, (b)z=4, (c)z=12. Arrows point "Nano Inclusions" (previous study).

References

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