Cycle Performance of Nano Inclusion Containing $LiMn_2O_4$ Cathode Material At 3V Range

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Introduction

$LiMn_2O_4$ with 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 $ZnSn_2O_4$, 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 the 4V range[1],[2]. We have investigated the effect of the amount and the size of "Nano Inclusion" to the cycle performance[3],[4]. In this study, we prepared $LiMn_2O_4$ with "Nano Inclusion" as previous study, and investigated the effect on the cycle performance at the 3V range.

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 $Li:Mn:Zn_2SnO_4=1\text{-}x:2(1\text{-}x):x$ (x=0, 0.05, 0.075, 0.10). The mixture was calcinated at 550°C for 6h in air and then heat-treated at 800°C for 4h in air. The obtained sample was denoted as $(1\text{-}x)LiMn_2O_4\text{-}xZn_2SnO_4$ hereafter. In order to analyze the crystal phase of each sample, 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 XRD patterns of $(1\text{-}x)LiMn_2O_4\text{-}xZn_2SnO_4$. It is indicated that the sample of x=0 contained only $LiMn_2O_4$ and that the samples of x>0 contained not only $LiMn_2O_4$ but also SnO_2 and $ZnMn_2O_4$. For the samples of x>0, Zn_2SnO_4, the starting material, was not detected.

Fig. 2 shows discharge capacity as a function of cycle number for the samples. As x increased, the discharge capacity decreased but discharge capacity retention was improved. The discharge capacity retention of x=0 was 56.8 % at 50 cycle and 46.1 % at 100 cycle. For x=0.10, 92.1 % at 50 cycle and 87.3 % at 100 cycle were observed, where the amount of "Nano Inclusion" was maximum among our 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 clack propagation caused by the volume change of $LiMn_2O_4$. Consequently it is considered that "Nano Inclusion" makes the discharge capacity retention rate increase.

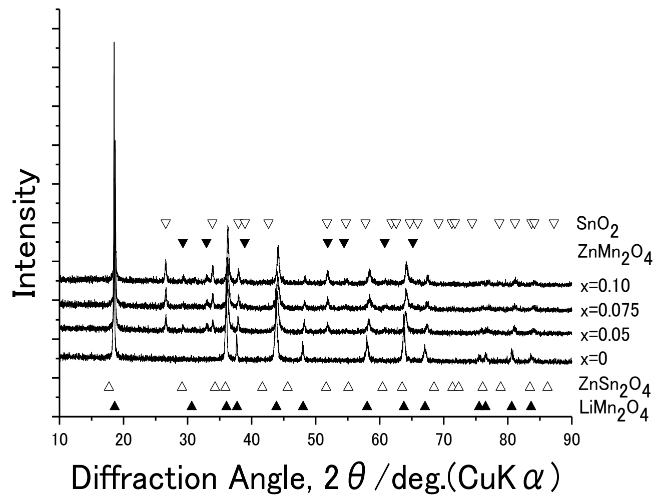

Fig.1 Powder X-ray diffraction patterns (10°-90°) of $(1\text{-}x)LiMn_2O_4\text{-}xZn_2SnO_4$ samples.

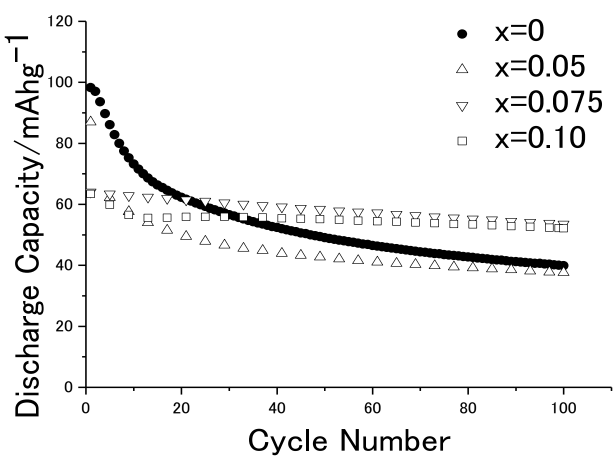

Fig. 2 Discharge capacity as a function of cycle number for $(1\text{-}x)LiMn_2O_4\text{-}xZn_2SnO_4$.

References

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