Crystal Study of "Nano Inclusion" in $LiMn_2O_4$ Cathode Material of Lithium Ion Battery

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Introduction

$LiMn_2O_4$ with cubic spinel structure has been attracting attention as a cathode for 4V lithium ion batteries, 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. Previously, we reported that we prepared very thin plate-shaped material 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”, that the cycle performance of $LiMn_2O_4$ with “Nano Inclusion” was superior to that of normal $LiMn_2O_4$[1], and that we controlled the size of “Nano Inclusion” and investigated the effect on the cycle performance[2]. In this study, we investigated the crystal structure in detail.

Experiment

We mixed ZnO and SnO_2 in a molar ratio of Zn:Sn=2:1, fired at 1000°C for 12h, then synthesized Zn_2SnO_4 with spinel structure. We mixed Li_2CO_3, MnO_2 and thus obtained Zn_2SnO_4 with a molar ratio of Li : Mn : Zn_2SnO_4=1-x:2(1-x):x (x=0.02, 0.05). We calcinated the mixture at 550°C for 12h in air and then heat-treated at 800°C for 12h in air. We denoted the obtained sample by the value of x for (1-x)$LiMn_2O_4$-$x$$Zn_2SnO_4$ hereafter. We carried out X-ray diffraction measurement, HAADF-STEM observation of the cross section, and electron diffraction measurement of the samples. We investigated the cycle performance with a two-electrode cell. We fabricated the cathode by mixing powder of the samples as the active material, acetylene black as a conducting additive and PVDF as binder at the ratio of 80:15:5 by weight, and coating the mixture onto Al foil by using *N*-methylpyrrolidone as solvent. We used lithium metal as counter electrode. The electrolyte was 1 M solution of $LiPF_6$ in mixture of EC and DMC (2:1, v/v). Cycle tests were carried out at 1C rate between 3.2 and 4.3 V under the constant temperature at 25°C.

Results and discussion

In the XRD patterns of the samples, peaks of SnO_2 and $ZnMn_2O_4$ as well as $LiMn_2O_4$ were observed and the peak intensities of SnO_2 and $ZnMn_2O_4$ increased as x increased.

Fig. 1 shows discharge capacity as a function of cycle number for the samples. The discharge capacity at 1st cycle for $LiMn_2O_4$ was larger than that of all the samples. However, the discharge capacity retention rate of $LiMn_2O_4$ was lower than that of all the samples. As x increased, the discharge capacity decreased, however, the discharge capacity retention rate after 100 cycles increased.

Fig. 2 shows a HAADF-STEM image of the cross section for the x=0.02 sample. “Nano Inclusion”, a white line with nano-order scale, is observed in $LiMn_2O_4$ single crystal as indicated by an arrow. Fig. 3 shows electron diffraction patterns at point a, b and c of Fig.2, respectively. Point a and c belong to the gray area which was identified as $LiMn_2O_4$ by EDX measurement [1]. The electron diffraction pattern of either point a or c is very similar to each other and it is indicated that both the atomic arrangement and the orientation at the either point is the same. This means that the either point belongs to the same single crystal. Point b belongs to the white line, “Nano Inclusion”. The electron diffraction pattern of point b is very similar to those of point a and c. This means that “Nano Inclusion” has both similar atomic arrangement and orientation to the matrix $LiMn_2O_4$ single crystal, and it is concluded that “Nano Inclusion” is connected to the matrix without grain boundary.

“ Nano Inclusion” suppressed the crack formation caused by the deformation of $LiMn_2O_4$ during charge and discharge cycles, and made the discharge capacity retention rate increase.

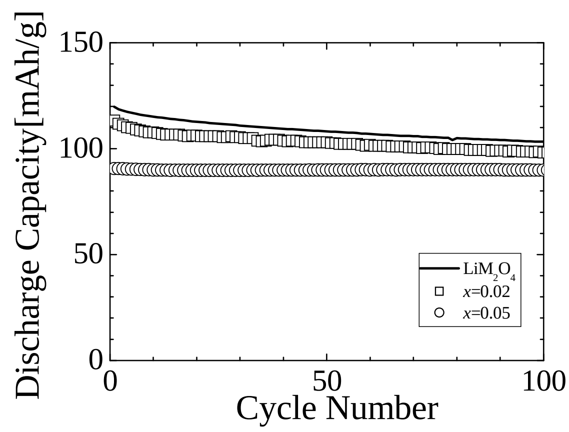


Fig. 1 Discharge capacity as a function of cycle number for (1-x)$LiMn_2O_4$-$x$$Zn_2SnO_4$

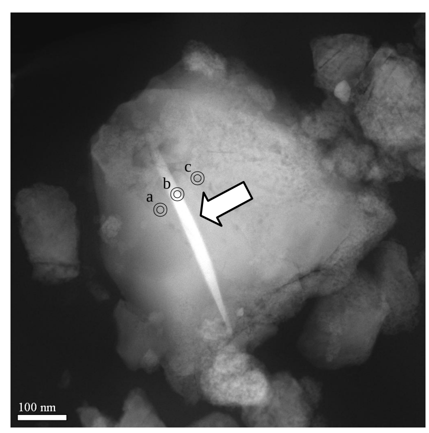
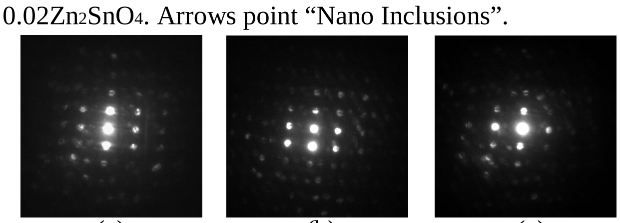


Fig. 2 HAADF-STEM image of $0.98LiMn_2O_4$-$0.02Zn_2SnO_4$. Arrows point “Nano Inclusions”.



(a) (b) (c)

Fig. 3 Electron diffraction patters of $0.98LiMn_2O_4$-$0.02Zn_2SnO_4$ at point a, b and c of Fig.2.

[1] S. Esaki, T. Yao, M. Nishijima, K. Hiroe, and H. Tsubouchi, 219th Meeting of the Electrochemical Society CD Abst. 0205(2011).

[2] S. Esaki, T. Yao, M. Nishijima, K. Hiroe, and H. Tsubouchi, 220th Meeting of the Electrochemical Society CD Abst. 1306(2011).