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Improving the elevated temperature performance of Li/$LiMn_2O_4$ cells by coating with ZnO

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Recently, as the most promising candidate cathode material to replace $LiCoO_2$ for lithium secondary batteries, the spinel $LiMn_2O_4$ has been extensively studied and reported to have an excellent cycle life at room temperature with the substitution of mono-, di- or trivalent cations in the 16d sites [1–3]. However, the pure spinel $LiMn_2O_4$ suffers from irreversible capacity loss during cycling and the loss is severe especially at temperatures exceeding 55 °C. After many studies, the major factors responsible for the capacity loss at elevated temperatures have been ascribed to the transformation of crystallinity [4], manganese dissolution [1] and decomposition of the electrolyte [5]. Of these factors, manganese dissolution during cycling is believed to the main one. Based on this, several methods have been employed to improve the performance of $LiMn_2O_4$. For example, Park *et al.* [6] have introduced the encapsulation concept. Guyomard *et al.* have reported an easy way to fabricate $LiMn_2O_4$ with a low surface area [7]. In this paper, improvement in the high-temperature performance of spinel $LiMn_2O_4$ electrodes by coating with ZnO is reported.

The spinel $LiMn_2O_4$ used in this work was prepared using the rheological phase reaction method. The procedure has been detailed previously [8]. Stoichiometric mixtures of $CH_3COOLi{\cdot}2H_2O$, $(CH_3CO_2)_2Mn{\cdot}4H_2O$, and the proper quantity of citric acid were ground for half an hour. The precursor was obtained after keeping the mixture at 80 °C for 8 hr. The spinel $LiMn_2O_4$ was obtained by thermal decomposition of the precursor at 580 °C for 2 hr followed by 10 hr at 750 °C. The modifications with ZnO involved the dispersion of $LiMn_2O_4$ in an ethyl-alcohol solution of $Zn(CH_3CO_2)_2{\cdot}2H_2O$. After evaporation of the solvent at 100 °C, the powder was annealed at 600 °C for 4 hr.

Power X-ray diffraction (XRD) was employed to identify the crystalline phases. The morphology of the powders was observed by Scanning electron microscopy (SEM). The cells were fabricated in an organ-filled glove box using lithium foil as anode, the spinel powders mixed with acetylene black (12 wt%) and polytetrafluoroethylene (PTFE, 8 wt%) as the cathode and 1M $LiClO_4$/PC: DMC (1:1) as the electrolyte. The charge–discharge cycle was performed at a current density of 1 mA/cm^2 in a potential range of 3.0 to 4.4 V.

The surface-treated $LiMn_2O_4$ is shown in Fig. 1. The small zinc oxide particles covering the surface of the spinel powders can be seen clearly. Normally the surface morphology of $LiMn_2O_4$ is extremely smooth [9]. Fig. 2 shows the XRD pattern of the surface-treated spinel powders. The diffraction peaks of ZnO-coated powders were characteristic of the spinel structure of $LiMn_2O_4$ with a cubic lattice parameter of 8.3254 Å. The ZnO content of the composite may be too low to be detected by XRD.

The discharge capacities of ZnO-coated $LiMn_2O_4$ at 55 °C for 60 cycles are shown in Fig. 3. Selected charge-discharge curves of the treated powders are shown in Fig. 4. It can be seen that there are two distinct potential plateaus at about 4.01 and 4.19 V, which are remarkable characteristics of a $LiMn_2O_4$ spinel. The initial discharge capacity of the treated powders was 121 mAh/g. After 60 cycles, the discharge capacity was still 117 mAh/g. There is only a 3% loss in capacity. However, it is reported that the discharge capacity of an unmodified $LiMn_2O_4$ sample was 78 mAh/g after 100 cycles at elevated temperature (41% reduction) [10]. The high-temperature performance of the spinel has been very evidently improved. It is clear that the reduction in capacity loss at elevated temperature is due to coating with ZnO, which may suppress the tendency for Mn dissolution. Liu *et al.* consider that coating prevents contact between the spinel and electrolyte, suppressing Mn dissolution, which is the principal cause of capacity loss [11].

From the results of these experiments, it is concluded that the ZnO-coated $LiMn_2O_4$ compound shows excellent electrochemical properties.

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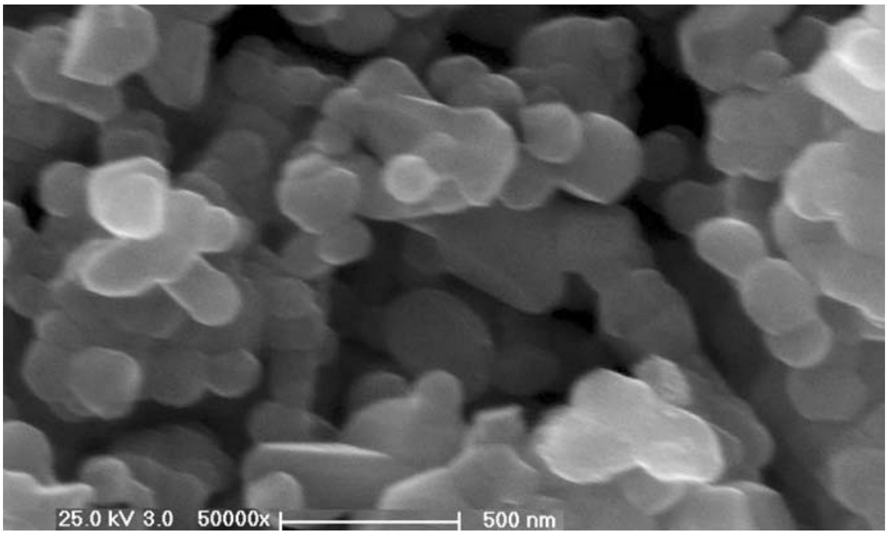

Figure 1 SEM photographs of ZnO-coated $LiMn_2O_4$.

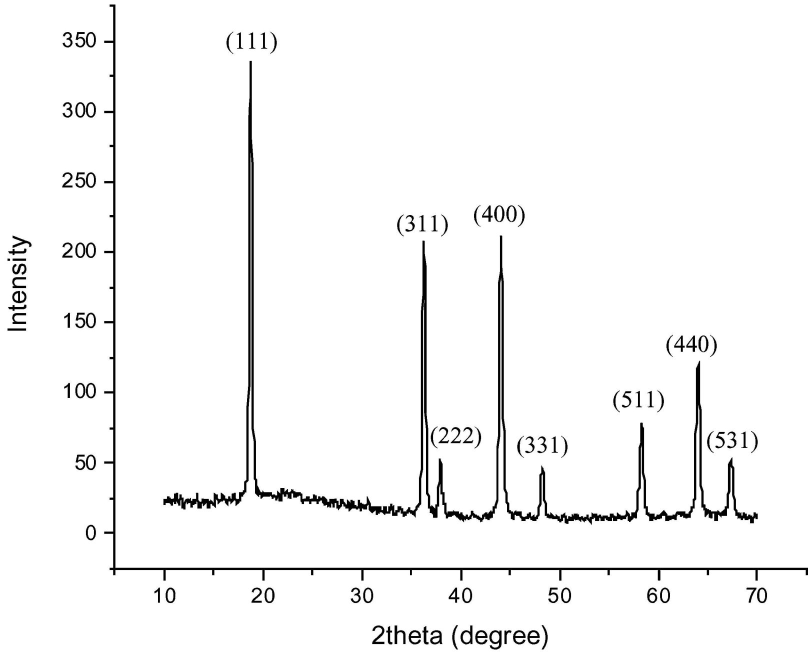

Figure 2 XRD of ZnO-coated $LiMn_2O_4$.

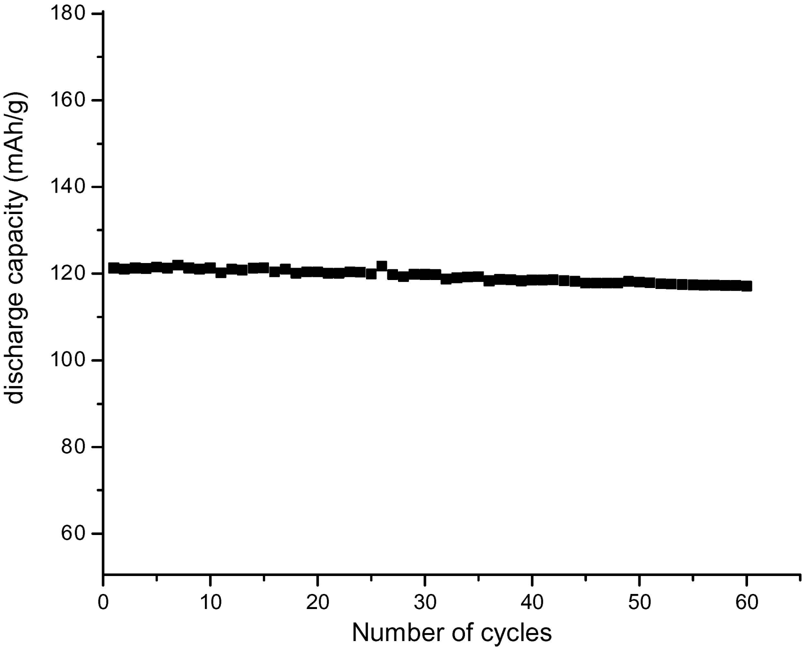

Figure 3 Variation of capacity vs. cycle number for cells with active electrode of ZnO-coated $LiMn._2O_4$ at 55 °C.

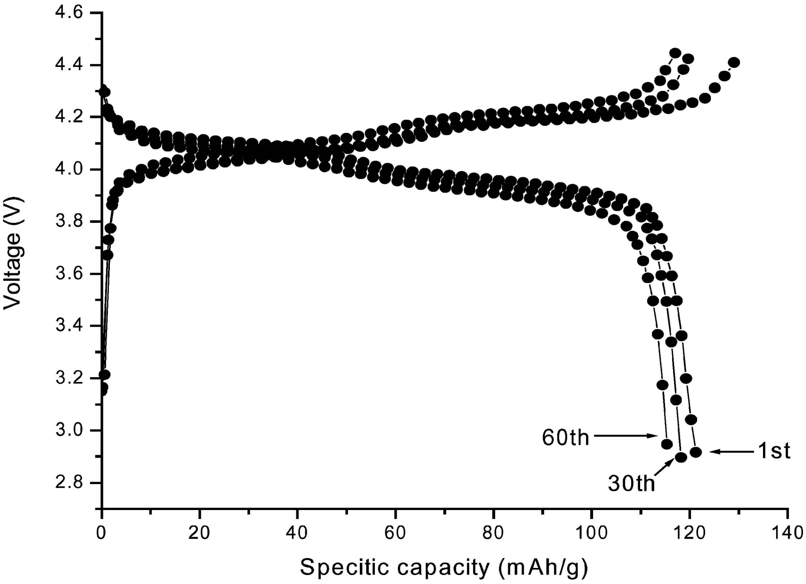

Figure 4 Charge–discharge curves for ZnO-coated $LiMn_2O_4$ at 55 °C.

Acknowledgments

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