

Investigations on the Mechanisms of Extra Anodic Peak Evolution near 3.8V in Cyclic Voltammogram of LiMn_2O_4

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Manganese is approximately 1% of the cost of cobalt and significantly more environmentally benign than either cobalt or nickel. When compared with LiCoO_2 and LiNiO_2 , LiMn_2O_4 offers low cost and non-toxicity, characteristics that are becoming increasingly important in development for the next generation of high energy power sources.

In cyclic voltammogram, LiMn_2O_4 shows two pairs of peaks in 4V range and one pair of peaks in 3V range. But, in some occasions, the extra peak near 3.8V in anodic scan is observed. Its cathodic counterpart that corresponds to this extra peak near 3.8V does not appear at any occasions. And this extra peak does not appear during the first cycle at an initial anodic scan direction.

The observation of this extra peak is reported by many authors.¹⁻⁴ But, to the best of our knowledge, the mechanism of the evolution of this extra peak near 3.8V is not fully understood, yet.

In this study, we report the mechanism of the evolution of the extra 3.8V peak in cyclic voltammogram. LiMn_2O_4 electrodes are prepared in two different forms, which are thin film electrode and composite electrode prepared from powdered LiMn_2O_4 .

The thin film electrode is prepared by electrostatic spray deposition (ESD) technique and characterized by thin-film X-ray diffraction, SEM and *in situ* bending beam method (BBM). BBM is an *in situ* technique that can measure strain of the thin film electrode simultaneously with electrochemical signals. There are many factors that influence the strain of thin film electrode, which are surface film variation, lattice parameter change during lithium insertion/extraction, phase transformation, etc. Fig. 1 shows the differential strain curves of LiMn_2O_4 thin film electrode. In this figure, there are a tensile differential strain peaks in anodic scan, and compressive differential strain peaks in cathodic scan, and every peak is correlated to current peaks in cyclic voltammograms. Near 3.8V in anodic scan, the extra current peak is observed in cyclic voltammogram, and the corresponding tensile differential strain peak is observed. The tensile differential strain peak indicates that there is sudden volume contraction, and this can be analyzed to the phase transformation from tetragonal to cubic phase.

The LiMn_2O_4 powder is prepared by two different synthesis routes. The one is solid state method and the other is sol-gel method. The composite electrode is composed of LiMn_2O_4 powder, conducting material (acetylene black), and binder (PVDF). To investigate the mechanism of the evolution of an extra peak near 3.8V, the composite electrode is cycled between various cutoff voltages with cyclic voltammetry and characterized by X-ray diffraction, *in situ* X-ray absorption spectroscopy (XAS)⁵⁻⁶. Regardless of the synthesis route, every sample showed an extra 3.8V peak when the LiMn_2O_4 electrode is cycled between 2.0~3.5V. Fig. 2 shows the cyclic voltammogram of LiMn_2O_4 . In this figure, marked numbers indicate a position where X-ray diffraction pattern are collected. More details will be discussed in the meeting.

References

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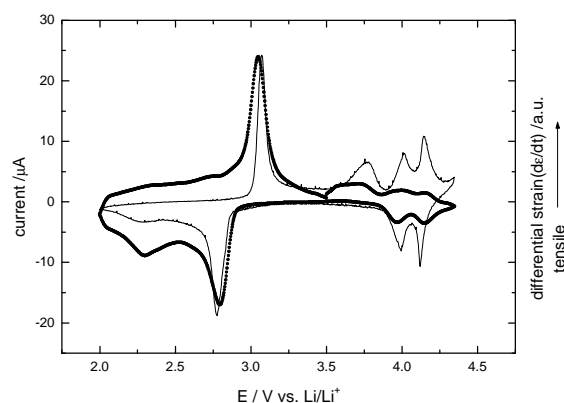


Fig. 1. Differential strain curve (thick line) superimposed on the cyclic voltammogram (thin line) of LiMn_2O_4 thin film electrode. Cutoff voltage: 3.5~4.35V, Scan rate: 0.1mV/s, Electrolyte: LiClO_4/PC

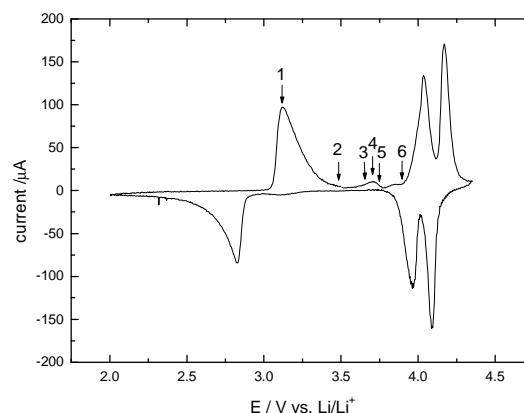


Fig. 2. The cyclic voltammogram of LiMn_2O_4 Scan rate: 50μV/s, Electrolyte: $\text{LiPF}_6/\text{EC-DMC}$ (1:2)