

A STUDY ON THE STRAIN VARIATIONS DURING LITHIUM IONS INTERCALATION/ DEINTERCALATION INTO/OUT OF CATHODE MATERIALS FOR LITHIUM SECONDARY BATTERIES

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During lithium ions intercalation/deintercalation into/out of cathode materials of lithium secondary batteries, strain is developed. The strain variation of the electrode is induced by several causes, which are volume variation due to lattice parameter change, phase transformation, surface film dissolution/formation, etc. In our previous work, we measured the strain developed in LiMn_2O_4 thin film electrode using *in situ* bending beam method (BBM), and attributed it to a Jahn-Teller distortion and lattice parameter change due to lithium ions insertion and extraction.¹ In the present study, the strain variation due to surface film dissolution/formation is measured using *in situ* BBM and *in situ* electrochemical quartz crystal microbalance (EQCM). Further, we applied BBM to other cathode materials such as LiCoO_2 and $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ and observed strain variations during lithium ions intercalation/deintercalation.

In LiMn_2O_4 systems, several authors previously reported the formation of surface film at the surface of LiMn_2O_4 electrode during cycling at room temperature or storing in the electrolyte at high temperature using *ex situ* techniques.^{2,3} In the present study, dissolution of surface film on thin-film LiMn_2O_4 electrode, which is formed during electrode synthesis, and formation of new surface film during cycling are observed at room temperature using *in situ* BBM and *in situ* EQCM technique with cyclic voltammetry and galvanostatic charge/discharge. The electrolytes used were $\text{LiClO}_4/\text{EC-DEC}$, LiClO_4/PC and $\text{LiPF}_6/\text{EC-DMC}$. The deflectogram (Fig. 1.) and the massogram (Fig. 2.) show the large peaks during anodic scan only in the first cycle, and the peak is not observed from the second cycle forth. These peaks in deflectogram and massogram reveal the appearance of large tensile strain followed by large compressive strain and large mass decrease followed by mass increase, respectively. And, these phenomena are observed regardless of the electrolytes used in this study and scan rate. In the deflectogram, the large peak indicates large tensile strain followed by compressive strain, and in the massogram, it indicates large mass reduction followed by mass increase. The tensile strain and the mass reduction in the early stage of strain peak and mass peak are related to the dissolution of surface film, which is formed during the synthesis of LiMn_2O_4 electrodes. And, the compressive strain and the mass increase are related to the formation of new surface film during cycling. This dissolution of the initial surface film and formation of the new surface film are completed in the first cycle of the cyclic voltammetry, and they are also observed during galvanostatic charge/discharge. The apparent chemical diffusion coefficient (D_{app}) measured at different electrode potentials shows different values at the same electrode potentials below 4.15V during the first anodic and cathodic scans of the cyclic voltammetry, respectively. This difference in the apparent chemical diffusion coefficient can be inferred from the different nature of initial surface film and newly formed surface film.

In LiCoO_2 and $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ systems, the strain

variations due to lattice parameter change induced by lithium ions intercalation/deintercalation and other factors are observed. Details will be discussed at the meeting.

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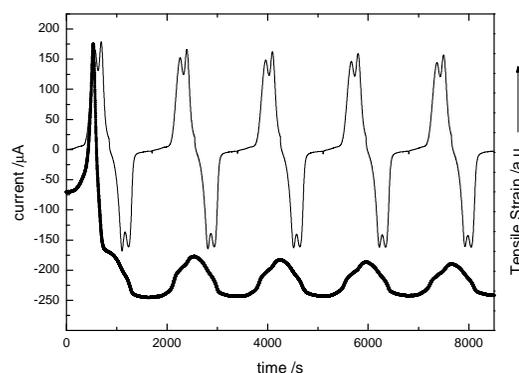


Fig. 1. Expanded view of strain curves (thick line) superimposed on cyclic voltammograms (thin line) to 5 cycles. Cutoff voltage: 3.5~4.35V, scan rate: 1mV/s, electrolyte: 1M LiClO_4/PC

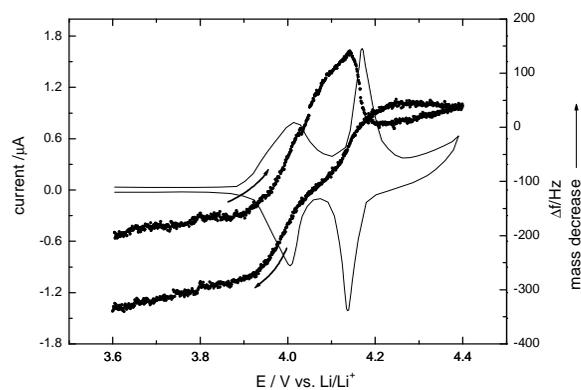


Fig. 2. Frequency (or mass) curves (thick line) of the first cycle superimposed on the cyclic voltammograms. Scan rate : 0.1mV/s, electrolyte : 1M $\text{LiClO}_4/\text{EC-DEC}$