In-situ TEM Observation of Boundary Migration between Li-rich and Li poor phases in a Single $LiMn_2O_4$ Nanowire Battery

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Phase transition of electrode materials in lithium ion batteries (LIB) inevitably occurrs during charge-discharge processes because of lithium compositional change. Since understanding of the phase transition is a key to improve the battery performance such capacity, charge rate, etc, the phase transition has been investigated intensively with electrochemical measurement and diffraction measurement.

Recent in-situ XRD study showed that charge rate during the battery cycle affect the phase transition of $LiFePO_4$ cathode materials [1]: At high charge rate, the diffraction spots which correspond to the metastable phase appeared. They said that the metastable phase mediates $LiFePO_4$ (Li-rich) phase and $FePO_4$ (Li-poor) one. To understand the full image of phase transition mechanism, micro scale information should be supported.

We have performed in-situ transmission electron microscope (TEM) study on the phase transition $LiMn_2O_4$ cathode by using our developed nanowire battery. In previous study, we have revealed the local phase transition due to inhomogeneous lithium distribution in $LiMn_2O_4$ crystals at high charge rate [2]: We found that at early discharge stage (3.9 V vs Li/Li^+), Li-excess tetragonal phase appeared at the interface region of $LiMn_2O_4$ nanowires with the electrolyte, even though the tetragonal phase has been reported to appear below 3V vs Li/Li^+. The tetragonal phase was considered to result from lithium accumulation at the interface. However, the phase transition inside the $LiMn_2O_4$ nanowires was still unrevealed.

In this study, we perform in-situ TEM observation of phase transition inside $LiMn_2O_4$ nanowire by using the nanowire battery at high charge rate. The nanowire battery consists of nanowire $LiMn_2O_4$ cathode, ionic liquid electrolyte and $Li_4Ti_5O_{12}$ anode as shown in Fig. 1. The nanowire-battery was loaded in our homemade electrical biasing double-tilt TEM holder. During charge-discharge cycles, the single $LiMn_2O_4$ nanowire in the nanowire-battery was observed by an aberration corrected TEM, R005 at 300 kV. TEM images were obtained by bright field imaging with the high contrast aperture which radius size corresponds to 14 mrad. Simultaneously electrochemical properties were measured by cyclic voltammetry. The voltage was scanned from 2.70 to 5.20 V vs Li/Li^+ at scan rate of 0.55 mV/s. The measurement was performed by source-measurement unit, Keithley 2635A.

During charge-discharge process, the phase boundary between Li-rich and Li-poor phases was observed to move reversibly. Fig. 2 shows the sequent TEM images of the phase boundary during discharge process. The phase boundary moved toward electrolyte during discharge process and vice versa during charge process. The phase boundary did not disappear indicating two phases coexisted during the whole charge-discharge process, in contrast of previous report, in which the phase boundary disappear when half of discharge process is completed under low charge rate. The discrepancy is considered to come from the high charge rate. From the analysis of transmission electron diffraction (TED) patterns, the formation of the phase boundary and the orientation relationship between two phases could be determined .

References:

[1] Y. Orikasa, et al., *J. Am. Chem. Soc.* **135** (2013) 5497.
[2] S. Lee, et al., *J. Phys. Chem. C*, **117** (2013) 24236.

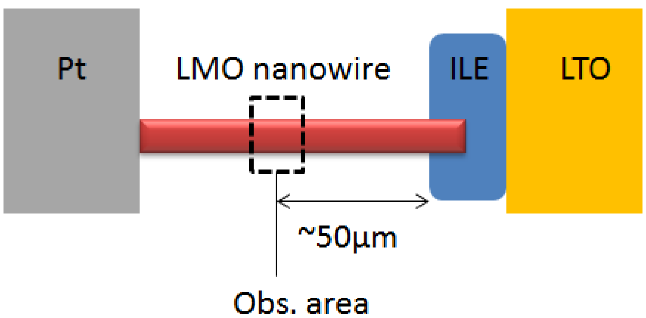

Figure 1. Schematic illustration of $LiMn_2O_4$ nanowire battery. Pt: positive current corrector, ILE, ion liquid electrolyte, LTO, lithium titan oxide ($Li_4Ti_5O_{12}$). The LMO nanowire was observed about 50 µm far from the ILE.

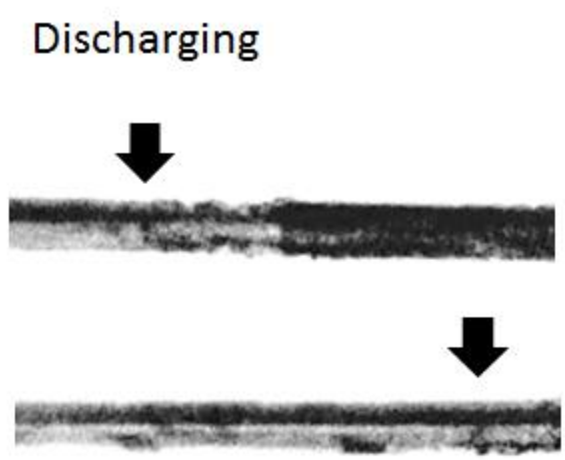

Figure 2. The sequent TEM images of the phase boundary (dark contrast area) during discharge process. The black arrow indicate the most left side of the phase boundary.