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In-Situ TEM Observation of Rechargeable $LiMn_2O_4$ Nanowire-Battery

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For development of rechargeable lithium ion batteries, one of issues is long lifetime. Charge-discharge cycles change the interface structure between electrode materials and electrolyte irreversibly [1], which has been thought to deteriorate the battery lifetime. For detecting such structural change, transmission electron microscopy (TEM) is one of powerful methods [2]. Especially, *in-situ* TEM observation of the electrode materials during the charge-discharge cycles attracts much interest.

We developed a new 'nanowire-battery', consisting of $LiMn_2O_4$ nanowire, ionic liquid electrolyte (ILE) and $Li_4Ti_5O_{12}$ crystal as shown in Fig.1, and observed charge/discharge behavior in-situ in an aberration-corrected TEM, R005 [3]. The nanowire-battery was loaded in our home-made electric biasing double tilting TEM holder. Figure 2 shows a typical cyclic voltammetry (CV) of the nanowire battery without electron beam. Symmetric cathodic and anodic double-pair current peaks are shown at around 1V. The cathodic and anodic peaks correspond to the delitiation/lithiation reaction, respectively, of $LiMn_2O_4$ crystal at 4V verses lithium. They were not shifted more than 0.2V after more than 10 cycles.

Figure 3(a) shows TEM image of a part of nanowire-battery, and Fig. 3(b), a high resolution TEM image of $LiMn_2O_4$ nanowire in contact with ILE. Atomic structure of $LiMn_2O_4$ crystal was observed from the [001] direction as shown in Fig. 3(b). It showed cubic lattice patterns, which was in agreement with the electron diffraction patterns in Fig. 3(c). The charge/discharge cycles of nanowire-battery was performed during *in-situ* TEM observation. We observed structure change of the $LiMn_2O_4$ nanowire during the charge/discharge cycles.

In conclusion, we successfully performed the charge/discharge cycles of our developed nanowire-battery in TEM. The typical cathodic and anodic current peaks of $LiMn_2O_4$ crystal were detected in cyclic voltammetry. We obtained high resolution TEM images of the $LiMn_2O_4$ nanowire in the vicinity of interface between the nanowire and ILE using home-made electric biasing double tilting TEM holder.

References

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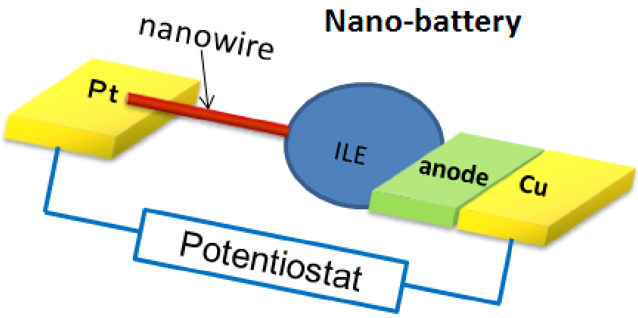

Figure 1: (a) Developed 'nanowire-battery'. $LiMn_2O_4$ nanowire (red) is bridged between Pt and ionic liquid electrolyte.

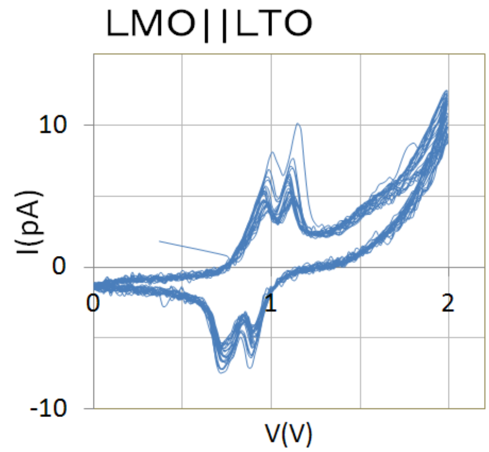

Figure 2: (a) Typical cyclic voltammogram of the nanowire-battery. (b) Illustration of reaction voltage of $LiMn_2O_4$ crystal and $Li_4Ti_5O_{12}$ crystal versus SLE. Red arrow indicates the full-cell voltage of the

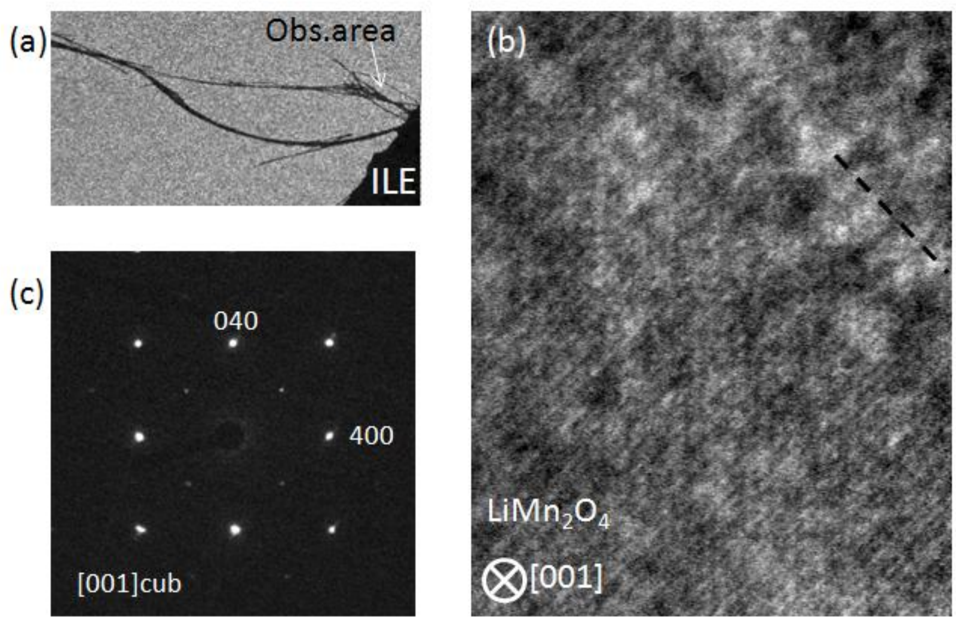

Figure 3: (a) The low-magnified TEM image of a part of the $LiMn_2O_4$ nanowire-battery. $LiMn_2O_4$ nanowires appear as dark contrast. (b) The high resolution TEM image of $LiMn_2O_4$ nanowire viewed from the [001] direction. The dashed line indicates the surface of the nanowire. (c) Transmission electron diffraction pattern of $LiMn_2O_4$ nanowire.