Operando TEM observation of lithium ion battery

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Dynamics of lithium ions is a key issue for improvement of lithium ion battery. However, lithium ions are hardly detected due to light element. Also, change of lithium distribution is necessary to be observed during the battery operation, which has been hardly achieved. Lithiation or delithiation proceses have been observed by in-situ transmission electron the microscope (TEM) observation, but change of lithium distribution should be observed during the cycle of charge and discharge processes, since lithium ion battery is rechargeable. In this study, we fabricated nano-lithium ion battery for TEM observation and observed change of lithium distribution in $LiMn_2O_4$ cathode by electron diffraction (ED) pattern or electro energy loss spectroscopy (EELS) during the battery cycle (operando TEM observation). The nano-lithium ion battery is constructed by $LiMn_2O_4$ nanowires cathode, liquid ion electrolyte and $Li_4Ti_5O_{12}$ crystalline anode (Fig.1). In order to investigate the structural evolution of the cathode, we took the ED patterns of the $LiMn_2O_4$ nanowires sequentially with monitoring the cyclic voltammogram (CV). And also, in order to investigate the compositional evolution of the cathode, we took Li-K edge EELS mapping of the nanowire during the battery operation. TEM observation and EELS measurement was achieved by 50-pm resolved spherical aberration corrected TEM/STEM (R005) [1].

In our developed nanobattery, since several $LiMn_2O_4$ nanowires (around 100 nm in diameter) were bridged between Pt current corrector and $Li_4Ti_5O_{12}$ crystalline anode (Fig. 1(a)), they could be observed by TEM. Simultaneously with TEM observation, CV was obtained as shown in Fig. 1(b). A pair of two cathodic peaks appear in the charge process and a pair of two anodic peaks, in the discharge process. A certain region of the nanowires, which was close to the anode-side, was covered with the ionic liquid electrolyte. The ED patterns were taken at such a region as shown in Fig. 2. We found that the cubic phase of the $LiMn_2O_4$ nanowire changed into two phases of the cubic and orthorhombic phases and finally into the tetragonal phase [2]. It suggests that a lot of lithium ions must be accumulated in the observation area, since the tetragonal phase corresponds to $Li_2Mn_2O_4$ structure. We also observed that the boundary between Li-rich and Li-poor phases moved back and forth inside the nanowire during the operation [3]. It suggests that two phase reaction is occurred during the operation.

Furthermore, we obtained Li-K edge EELS mapping of the nanowire cathode during the battery operation. In this map, the intensity per pixel indicated by color corresponds to the ratio of Li-K edge integrated area to Mn-$M_{2,3}$ edge one for cancelling the thickness dependence. We found that the lithium concentration of the $LiMn_2O_4$ cathode decreased (increased) with time delay with the cathodic (anodic) peaks in the simultaneously measured cyclic voltammogram, and also that the lithium concentration decreased from the side of the current collector to one of the electrolyte during the charge process. It suggests that lithium ions move by electric potential gradient in the cathode (drift model)[4].

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[3] S. Lee, Y. Oshima, et al., ACS Nano 9 (2015) 626-632.

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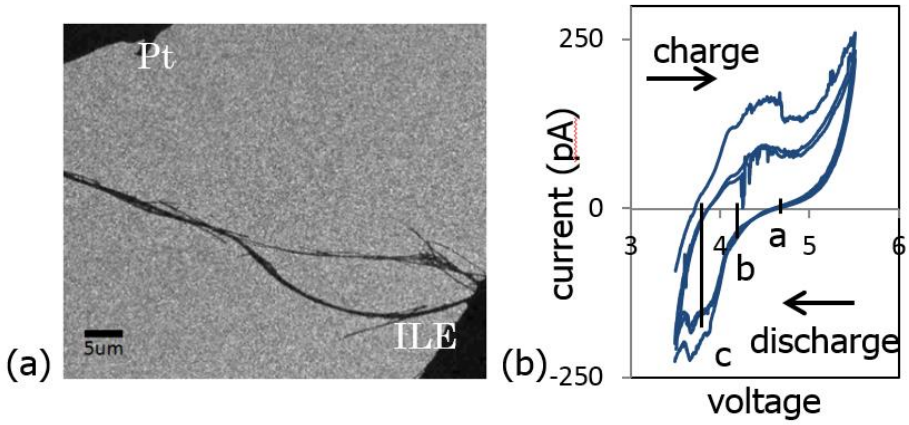

FIG. 1. (a) A typical TEM image of our developed nanobattery. The bundles of several $LiMn_2O_4$ nanowires are observed. The insert is illustration of our developed nanobattery.. (b) Cyclic voltammogram (CV) of our developed nanobattery. The CV curves are reproducibly measured for three cycles of charge and discharge.

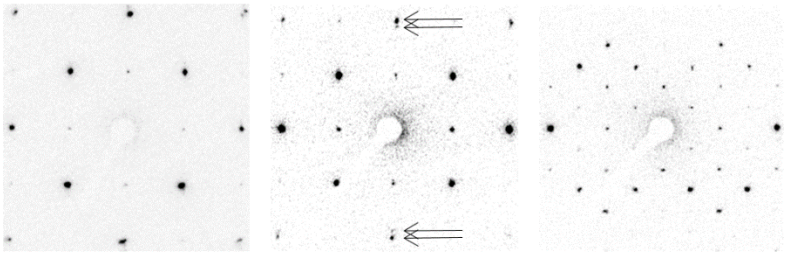

FIG. 2. Electron diffraction patterns obtained at a, b and c in the CV of Fig. 1(b). These patterns were taken sequentially during the discharge process.