Analysis of Local Structure and Charge/Discharge Mechanism of Mn-based Oxide Electrode Material by Soft X-ray Absorption Fine Structure

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Nowadays, lithium ion batteries are important energy storage system that are widely developed for several applications such as electric vehicles. With the requirements for improving the battery performance, research on battery component, particularly cathode active material, has been widely carried out. Mn-based oxide material, Li_2MnO_3, is one of the most promising next-generation cathode active materials that have high theoretical capacity (*ca.* 460 mAh/g) and has an advantage of rare-metal free [1]. Li_2MnO_3 usually shows layered structure (space group *C*2/*m*) and converts to cation-disordered NaCl-type structure (*Fm*-3*m*) (hereafter denoted as *c*-Li_2MnO_3) after mechanical milling process [2]. We have recently developed a simple synthesis route to prepare *c*-Li_2MnO_3 by mechanochemical milling of Li_2O with MnO_2 and found that it showed an initial discharge capacity of *ca.* 330 mAh/g after forming composite with acetylene black (AB), namely *c*-Li_2MnO_3-AB [3]. In the present work, we have carried out O K-edge XAFS measurements to examine the redox reactions of oxygen atoms during charge/discharge cycling.

c-Li_2MnO_3 was prepared by mechanochemical milling of Li_2O and MnO_2, and the obtained *c*-Li_2MnO_3 was mixed with AB (2 wt%), followed by the SPS (Spark-Plasma-Sintering) treatment at 400°C to form *c*-Li_2MnO_3-AB. Electrochemical charge/discharge tests were carried out using lithium coin-type cells. A solution of 1M $LiPF_6$/(EC+DMC) was used as the electrolyte, and the electrochemical measurements were carried out at a current density of 22.9 mA/g between 1.0 and 4.8 V. O K-edge XAFS measurements were carried out at BL-11 of SR-center in Ritsumeikan University. Varied-line-spacing plane grating with 1200 lines/mm was used as monochromator, and the peak at lower energy of α-Fe_2O_3 (529.4 eV) was used for energy calibration.

The obtained *c*-Li_2MnO_3-AB was black in appearance, and its XRD pattern was assigned as low-crystalline cation-disordered NaCl-type structure. Figure 1 shows the O K-edge XAFS spectra for the *c*-Li_2MnO_3-AB sample cells before electrochemical test and after the first charge (1c) and discharge (1d). Spectra of some reference materials are also shown for comparison. The spectrum of *c*-Li_2MnO_3-AB sample showed several peaks; the one at 534 eV could be assigned as Li_2CO_3 and other three at 528, 532, and 540 eV could be originated from Li_2MnO_3. During charging, the peak at 528 eV increased in its intensity, and that at 540 eV shifted to higher energy, while roughly the reverse changes occurred during discharging, as was reported previously for Li_2MnO_3 with *C*2/*m* space group [4], suggesting the redox reaction of oxygen atom. We are now examining the spectral changes in detail, and further analyses will be reported elsewhere in the near future.

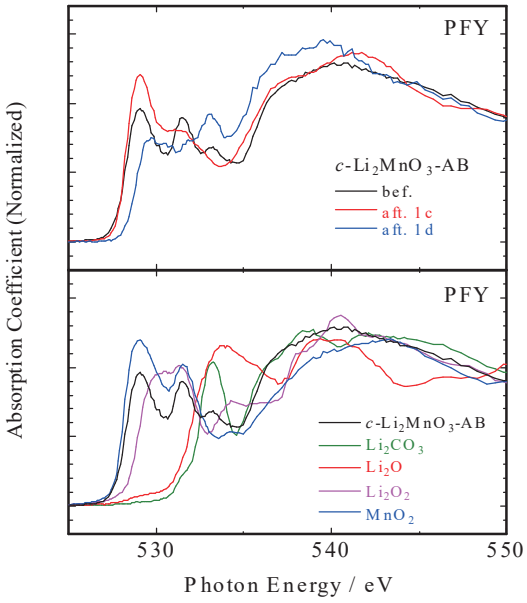

Fig. 1 O K-edge XAFS spectra for the *c*-Li_2MnO_3-AB sample cells before electrochemical test and after the first charge and discharge. Spectra of some reference materials are also shown for comparison.

References

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