

Application of Polychromatic Simultaneous WDXRF using Laboratory X-ray Source for Development of LIB Cathode Materials

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Lithium-ion batteries (LIBs) have been widely used in electric vehicles and wearable electronic devices. As a result, improvement of cell lifetime have taken an important position at R&D of LIBs. *In situ* X-ray absorption spectroscopy (XAS) is a powerful technique to investigate the degradation mechanism of active materials from the viewpoint of the chemical state (valence state) changes [1]. However, *in situ* XAS requires a special facility such as synchrotron X-ray radiation facility, so that it is hard to perform *in situ* XAS of LIBs at industrial applications. Recently, wavelength-dispersive X-ray fluorescence (WDXRF) spectroscopy has been developed for analysis of chemical shift with sufficient energy resolution detector, called polychromatic simultaneous WDXRF (PS-WDXRF) [2].

In this study, we tried to estimate the chemical state of active materials using the PS-WDXRF spectroscopy. Sample electrodes were prepared in following procedure. LiMn₂O₄ based cathodes were sealed in Al-laminated pouch cells to fabricate half cells. Li metal was used as counter electrodes. The prepared cells were activated with one cycle of charging and discharging step with 0.1 C rate. Subsequently, the cell operated to the state of charge 0, 50, 100% and the depth of discharge 50, 100 %. Each electrode was taken out from the Al-laminated pouch cell, rinsed with dimethyl carbonate, dried and then sealed in new Al-laminated film, under dry atmosphere (at less -60°C dew point). PS-WDXRF measurements were performed to the above mentioned LiMn₂O₄ based cathodes through Al-laminated film (110 μm in thickness). Fig. 1 shows peak energy of Mn Kβ at the various SOC or DOD of the cathodes. A significant decrease of peak energy was observed at the point of SOC100 and almost same energy was observed at SOC0 and DOD100. So that, we conclude these change of the peak energy should reflect the chemical state of the LiMn₂O₄ active material.

References:

- [1] M. Nishijima, M. Hamana, T. Saito, Y. Nitta, M. Hirayama, R. Kanno, J. Electrochem. Soc. 163 (2016) A1841–1845.
[2] K. Sato, A. Nishimura, M. Kaino, S. Adachi, *X-Ray Spectrometry* 46 (2017) 330–335.

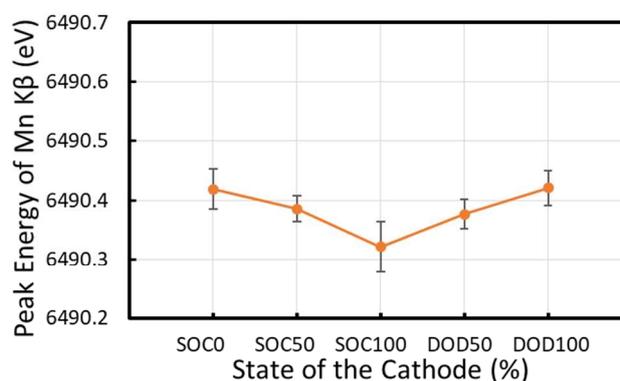


Fig. 1 Change of Peak Energy of Mn Kβ for the State of the Cathodes.

Cathode: LiMn₂O₄:AB:PVdF=90:5:5 (wt%)

Counter electrode: Li metal

Electrolyte: 1M LiPF₆ EC/DEC(1:1 in volume)+VC 1wt%.

CC 0.1C, Cut-off voltage: 3-4.5 V, Operated at 30°C.