

Polychromatic Simultaneous WDXRF for Valence Evaluation of Cathode Active Materials in Lithium-ion Batteries

Tetsuya Yoneda,¹ Takuro Izumi,¹ Satoshi Tokuda,¹ Susumu Adachi,¹ Kenji Sato,¹ Misako Kobayashi,² Takashi Mukai,² Hideaki Tanaka,² and Masahiro Yanagida²

¹ Technology Research Laboratory, Shimadzu Corporation, Kyoto 619-0237, Japan

² Research Institute of Electrochemical Energy, National Institute of Advanced Industrial Science and Technology (AIST), 1-8-31 Midorigaoka, Ikeda, Osaka 563-8577, Japan

E-mail: ttyoneda@shimadzu.co.jp

In the development of lithium-ion batteries (LIBs), cathode materials are being further improved to achieve higher energy capacity. Analyzing the valence of the cathode active material during charge and discharge cycles is a practical method to understand the redox mechanism, which can help in achieving higher energy capacity. Valence has been evaluated using X-ray absorption fine structure (XAFS) measurements with a synchrotron X-ray source. To conduct in-house analyses, we developed a polychromatic simultaneous wavelength dispersive X-ray fluorescence (PS-WDXRF) spectrometer comprising an X-ray tube, a slit, a flat analyzing crystal, and a silicon strip detector (SSD) [1]. The X-ray dispersed by the crystal is simultaneously detected by the SSD, and the detected signals at each channel provide intensity information at different energies. There is no moving part in the optical setup.

The developed PS-WDXRF comprises a 1280-channel SSD and a Ge (220) crystal to detect X-rays in the range 5.38 - 6.52 keV, which is designed for manganese. Manganese-based cathode active materials are attractive as they are inexpensive.

The first step was to obtain and analyze data of pressed powders of manganese oxides. Thus, powders of MnO (II), Mn₂O₃ (III), MnO₂ (IV), and KMnO₄ (VII) were placed in the evacuated chamber of the experimental setup. An X-ray tube voltage of 20 kV and a current of 100 mA was applied, and the target was made from Rh and no filter was used. A 5-min measurement was repeated five times for each sample. The PS-WDXRF analysis showed that the specimens achieved clearly different peak energies at each K β line. This means that the WDXRF has sufficient energy resolution, and the valence information is obtained by the peak energy shift derived from the chemical shift [2, 3]. These results indicate that there is a potential for valence evaluation of cathode materials in a short time with highly precise energy resolution. The recent results of valence evaluation on actual cathode active materials in LIBs will be presented.

[1] K. Sato, A. Nishimura, M. Kaino, S. Adachi, *X-ray Spectrom.* 46, 330–335 (2017).

[2] J. Kawai, M. Takami, C. Satoko, *Phys. Rev. Lett.* 65, 2193–2196 (1990).

[3] K. Sakurai, H. Eba, *Nucl. Instr. Meth. Phys. Res.* B199, 391–395 (2003).