

High-Precision Polychromatic XRF system for Valence Evaluation of Cathode Materials in Lithium-ion batteries

Tetsuya Yoneda,¹ Takashi Omori,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

¹Shimadzu Corporation, 1, Nishinokyo Kuwabara-cho, Nakagyo-ku, Kyoto 604-8511, Japan

²Research 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

A detailed chemical-state analysis of 3d transition metals is important to improve the characteristics of lithium-ion batteries (LIBs). With LIBs, some cathode-active materials consist of 3d transition metals, including manganese, nickel, and cobalt. The main challenges in LIB development are their high energy density, quick charge, long life cycle, safety, and cost. In particular, the energy density is closely related to the chemical changes of cathode materials involved with changes in the valence. To achieve higher-energy density, we need to understand in detail the chemical state during charge and discharge. The synchrotron light source is a powerful tool for analyzing these chemical states. The beam has a sufficient intensity, even after being monochromatized with double crystals; thus, it provides detailed chemical-state information using X-ray Absorption Spectroscopy (XAS). However, LIB development requires a faster time to market; therefore, in-house systems should acquire equivalent information easily compared with synchrotron facilities. We develop a high-precision X-ray fluorescence system using a laboratory-type X-ray tube called "polychromatic simultaneous wavelength dispersive X-ray fluorescence (PS-WDXRF)"[1]. The proposed system precisely identifies fluorescent X-ray lines to detect chemical shifts related to the valence information.

The PS-WDXRF system consists of an X-ray tube, slit, flat analyzing crystal, and silicon strip detector (SSD). The system simultaneously acquires the X-ray spectrum in a certain energy range without scanning the optical parts. The X-ray passes through the slit before being dispersed by the Ge (220) crystal. Subsequently, the 1280-channel SSD detects the X-ray signals at each channel corresponding to each energy.

We designed a spectrometer for nickel and cobalt in cathode materials, and obtained data of pressed powders of nickel oxides and lithium nickel oxide. These samples were placed in the evacuated chamber of the system. An X-ray tube voltage of 20 kV and a current of 100 mA were applied, and their target was tungsten. The 5-min measurement was repeated five times for each sample. The PS-WDXRF analysis showed that the spectra obtained from these two samples had clearly different peak energies at each Ni $K\alpha$ line, and the precision obtained was around 20 meV. This means that the system can obtain the valence information from the peak energy shift derived from the chemical shift [2, 3]. Actual cathode materials in LIBs after repeated charges and discharges were applied to the PS-WDXRF system. The results will be presented.

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

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

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