## Analysis of K-edge X-ray Absorption Spectra of Early Alkaline Earth Metal Compounds

Atsushi Ikeda-Ohno<sup>1</sup>, Toyonari Yaji<sup>2</sup>, and Akinori Irizawa<sup>2</sup>

1) Advanced Science Research Center, Japan Atomic Energy Agency, 2-4 Shirakata, Tokaimura, Naka-gun, Ibaraki 319-1195, Japan

2) Research Organization of Science & Technology, Ritsumeikan University, 1-1-1 Noji-Higashi, Kusatsu 525-8577, Japan

The utilization of natural energy resources (renewable energy) requires energy storage systems, which are currently dominated by lithium-ion batteries (LIB). In order to minimise the dependence of energy storage systems on LIB, the development of rechargeable batteries that are not based on lithium is indispensable. The battery based on early alkaline earth metals, such as Mg or Ca, is the potential candidate for an alternative to LIB. For the development and realization of such alkaline earth metal-based batteries, the chemical states of charge carriers (i.e. Mg<sup>2+</sup> or Ca<sup>2+</sup>) in the battery system must be understood and described adequately. X-ray absorption spectroscopy (XAS) is a rare but very powerful analytical technique to reveal the chemical states (e.g. oxidation states, speciation, local structure around the atom of interest, etc.) of target elements in a highly element-selective and nondestructive manner. Given this background, the final goal of the present study is to reveal the chemical states of two early alkaline earth elements, Mg and Ca, in the battery systems proposed and developed for Mg- and Ca-based batteries by XAS including both X-ray absorption near edge structure (XANES) and extended X-ray absorption fine structure (EXAFS). To this end, XAS measurements were performed on a series of Mg- and Ca compounds that are potentially formed in the battery systems, and the obtained spectra were analysed in light of the applicability and capability of XAS for the chemical analysis on Mg and Ca in the battery systems.

Mg compounds measured in this study were metallic Mg, MgO, Mg(OH)<sub>2</sub>, MgCO<sub>3</sub>, and MgF<sub>2</sub>, whilst CaO, Ca(OH)<sub>2</sub>, CaO<sub>3</sub>, and CaF<sub>2</sub> were measured for Ca compounds. All the compounds were commercially supplied from Fujifilm-Wako and Thermo Scientific. Sample compounds except metallic Mg were ground with a mortar and pestle, and the ground powder samples were spread thinly on a carbon tape for XAS measurements. X-ray absorption spectra were collected at Mg K-edge (1.305 keV) on the beamline BL-10, Ritsumeikan Univ. SR center, and at Ca K-edge (4.038 keV) on the beamline BL-13, the SR center. The spectra were collected by total electron yield and fluorescence yield modes, and treated/analysed with a dedicated program code WinXAS (Ver. 3.2).[1]



**Fig. 1** (a) Mg K-edge XANES spectra for a series of Mg compounds and (b) Ca K-edge XANES spectra for a series of Ca compounds.

Show in Fig. 1 are the XANES spectra of the Mg compounds (a) and Ca compounds (b). For the Mg K-edge XANES spectra in Fig. 1-(a), the position of absorption edge clearly reflects the oxidation states of Mg (i.e.  $Mg^0$  or  $Mg^{2+}$ ). The spectral shape is very characteristic of speciation and chemical structure. The same applies to the Ca K-edge XANES spectra in Fig. 1-(b). Their corresponding EXAFS spectra (not shown) are also very characteristic of speciation and chemical structure. These results suggest that XAS (XANES and EXAFS) is a powerful tool to investigate the chemical states of Mg/Ca in the battery system in a comprehensive manner.

## Reference

[1] T. Ressler, J. Synchrotron Rad., 1998, 5, 118.