

Na K-edge XAFS measurements of NaCl aqueous solutions

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We have developed electrochemical cells for *in situ* soft X-ray XAFS measurements of second battery system with a liquid electrolyte. The cells need to keep a liquid sample sealed in a high vacuum chamber. In the previous study, we performed Mg K-edge XAFS measurements in aqueous solutions and succeeded to obtain EXAFS oscillations extended to $k = 10 \text{ \AA}^{-1}$ [1]. In this study, we tried to observe Na K-edge XAFS spectra of sodium aqueous solutions, whose energy is less than 1800 eV.

The samples were NaCl aqueous solutions with two kinds of concentrations; 1 M and 6 M. 6 M-NaCl aq. solution is nearly saturated. The windows of the cell used were silicon nitride membranes (size: 4 mm x 4 mm, thickness: 500 nm) [1]. Na K-edge XAFS measurements were performed by using a soft X-ray XAFS beamline (BL-10). Beryl (10 $\bar{1}$ 0) crystals were used for double crystal monochromator. Photon energy was calibrated by using the white line peak of NaCl powder sample located at 1076.6 eV. The XAFS spectra were collected by partial fluorescence yield (PFY) mode with a silicon drift detector (SDD) and a reference spectrum of NaCl powder was collected by the total electron yield (TEY) mode. The region of photon energy was scanned from 1000 to 1500 eV and the acquisition time per spectrum was approximately 90 minutes.

Fig. 1 (a) shows a XAFS spectrum of 6M-NaCl aq. solution. The spectrum has two features at 1077 eV and 1081.6 eV and is significantly different from that of NaCl powder (Fig. 1 (c)). This is because Na⁺ ions are hydrated with water molecules [2]. On the other hand, in 1M-NaCl aq. solution (Fig. 1(b)), the first feature is the same as that of 6M-NaCl aq. solution but the position of the second peak is shifted to 0.5 eV higher. This result suggested that coordination structure of Na⁺ ions in 1M-NaCl aq. solution can be different from that of 6M-NaCl aq. solution. It was reported that the peak shift is attributed to six-coordinated Na, while the main peak in 6M-NaCl aq. solution is to four-coordinated Na from theoretical calculation [2].

The extracted EXAFS oscillation of 6M-NaCl aq. solution was obtained by $k = 7$ at the most. It was worse than that of Mg aq. solutions [1] because the photon flux of the energy region around Na K-edge is lower than that around Mg K-edge and the fluorescence of Ni La line from the jig fixing the X-ray window of the cell overlaps the Na K α line. It will be necessary to change the materials of the jig.

In summary, we succeeded to measure Na K-edge

XAFS spectra of Na ion in solutions, although some problems remain to be solved to increase the intensity of the EXAFS oscillation.

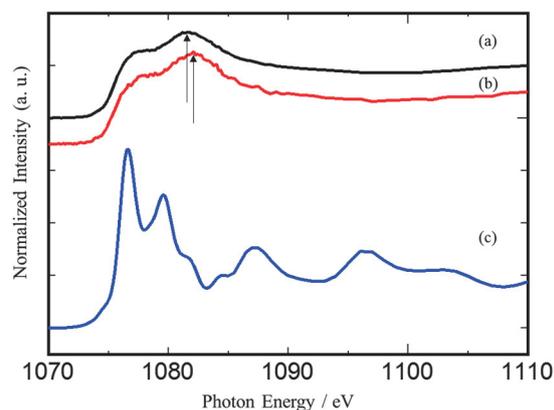


Fig. 1 Na K-edge XAFS spectra of 6M-NaCl aq. solution (a), 1M-NaCl aq. solution (b), and NaCl powder (c).

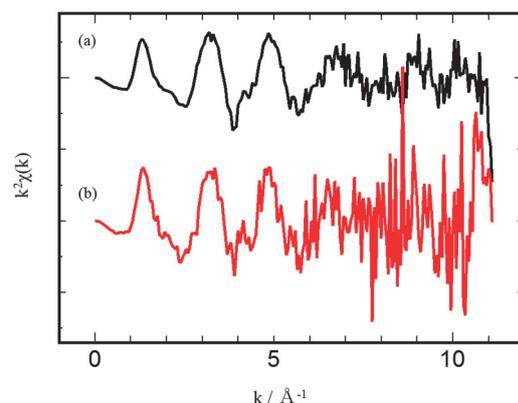


Fig. 2 EXAFS oscillations of 6M-NaCl aq. solution (a), 1M-NaCl aq. solution (b).

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References

- [1] T. Yaji, K. Nakanishi, T. Ohta, *Adv. X-ray Chem. Anal. Japan*, **48** (2017) 452-458 (in Japanese).
- [2] T. Kurisaki, Y. Miki, K. Minami, S. Yokoyama, S. Kokubu, M. Iwase, H. Wakita, *Fukuoka Univ. Sci. Rep.*, **42** (2012) 29-35 (in Japanese).