

Realtime X-ray fluorescence observation of conducting ions in solid-electrolyte

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Introduction

Direct observation of ions is significant to understanding the conducting process of solid-electrolytes. Element mapping by micro X-ray fluorescence (XRF) is an extremely strong tool in this respect, since the precipitation of metals on the cathode surface can be given as fairly strong experimental proof of ionic migration. The present report describes the first realtime observation of ion conducting by a projection-type XRF microscope [1,2].

Experimental

RbAg_4I_5 and $\text{Rb}_4\text{Cu}_{16}\text{I}_7\text{Cl}_{13}$, which are well-known ion conductors, were prepared by quenching molten salts and by another method using salts described elsewhere [3], respectively. A junction (see Fig.1(a)) was prepared by a conventional procedure to make a pellet (13mm dia, 0.9 mm thick) from 0.22 g RbAg_4I_5 and 0.30 g $\text{Rb}_4\text{Cu}_{16}\text{I}_7\text{Cl}_{13}$ powders. On the both side silver and copper electrode were placed, respectively. XRF imaging was carried out with quasi-monochromatic X-rays at BL-16A1 [2]. The exposure time for one image was 1 sec. Additional XRF and XAFS experiments were performed at BL-4A.

Results and Discussion

As soon as the circuit was switched on, an electric current of ca. 0.3mA was observed. As copper is more electropositive than silver, the copper electrode can reduce silver ions by means of an electric current passed through an external circuit. Figure 1(b) is an XRF image before closure of the circuit and strong XRF from copper was observed in the $\text{Rb}_4\text{Cu}_{16}\text{I}_7\text{Cl}_{13}$ part (right part). About 2 hours after closure of the circuit, the intensity of XRF from copper in the RbAg_4I_5 part (left part) also strengthened and the distribution of the copper became more homogeneous in the pellet (Fig.1(c)). It is assumed that this phenomenon occurs because the copper ions emitted from the electrode move to the RbAg_4I_5 part and replace the silver ions in just proportion. In another piece of pellet prepared in almost the same way, the copper concentration in RbAg_4I_5 part was observed. In the

beginning, the concentration at the point near the junction was higher than that at the point some distance away from it. As time went by, the concentration grew at the point that was further away from the junction. Therefore, copper migration was also observed by conventional XRF analysis. Penetration of copper species into RbAg_4I_5 was also checked. Figure 2 shows XAFS spectra near the Cu-K absorption edge. As shown in the spectra, copper in RbAg_4I_5 has an absorption edge of the same energy as cuprous (Cu^{I}) in CuCl , CuI and $\text{Rb}_4\text{Cu}_{16}\text{I}_7\text{Cl}_{13}$. In addition to this, the spectral shape of copper in RbAg_4I_5 is similar to that of $\text{Rb}_4\text{Cu}_{16}\text{I}_7\text{Cl}_{13}$ above the edge. Therefore, it was confirmed that copper, as cuprous, substitutes the silver ion in RbAg_4I_5 and conducts in it at the same time. The authors gratefully acknowledge the kind assistance of Drs. H. Sawa, Y.Wakabayashi, Y.Uchida during the experiments.

References

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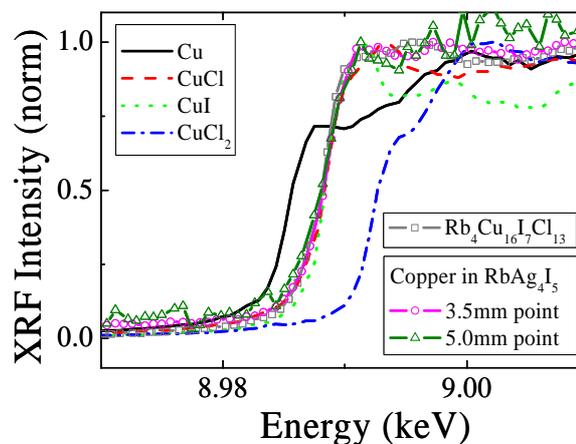


Figure 2. Cu-K fluorescent XAFS of solid electrolytes and reference compounds.

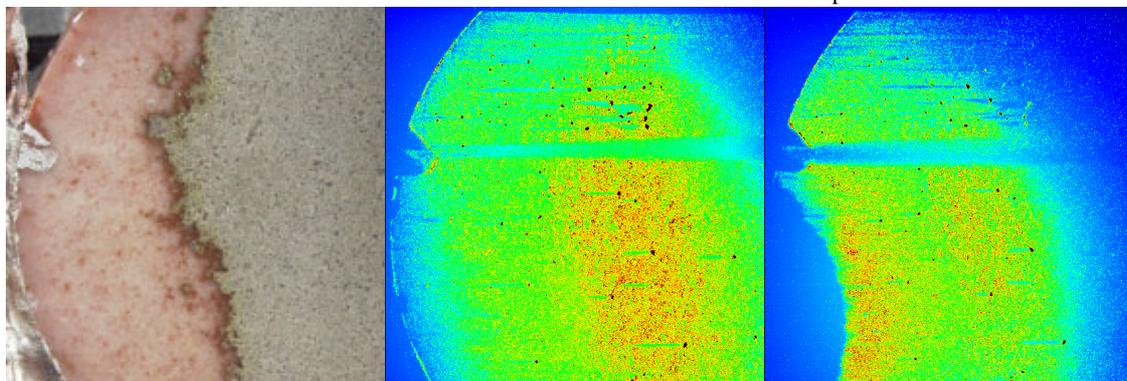


Figure 1. Junction of the ionic conductors RbAg_4I_5 (left part) and $\text{Rb}_4\text{Cu}_{16}\text{I}_7\text{Cl}_{13}$ (right part). (a) Optical photo of a part of the pellet, (b) XRF image of the same part, taken before closure of the circuit, and (c) 2 hours after closure of the circuit. For the images, incident energy is 9.3 keV (quasi-monochromatic, above Cu-K absorption edge), image size is 8 mm \times 8 mm (1000 \times 1000 pixels).