Observation of Li in graphite by muonic x-rays

I. Umegaki,[*1] Y. Higuchi,[*1] K. Ninomiya,[*2] M. K. Kubo,[*3] Y. Kondo,[*1] H. Nozaki,[*1] K. Ishida,[*4] and J. Sugiyama[*1]

In a Li-ion battery, Li reversely intercalates (deinterrcalates) into (from) electrodes as follows:

$$\begin{cases} \text{cathode} : \mathrm{Li}M\mathrm{O}_2 \Leftrightarrow M\mathrm{O}_2 + \mathrm{Li}^+ + e^- & (1) \\ \text{anode} : 6\mathrm{C} + \mathrm{Li}^+ + e^- \Leftrightarrow \mathrm{C}_6\mathrm{Li}, & (2) \end{cases}$$

where M is a transition metal ion, such as Co, Ni, and/or Mn. For safety and high efficiency, these reactions should proceed homogeneously in both electrodes. An inhomogeneous distribution or the segregation of Li may cause overcharged states or a short circuit in a battery. Therefore, it is important to know how these reactions proceed in a Li-ion battery.

However, in order to study the distribution of Li during the reactions, we need a non-destructive compositional analysis technique. Elemental analysis with muonic x-rays (μXEA)[1,2] is a suitable technique for such a purpose. We succeeded in obtaining muonic x-ray spectra of a cathode in J-PARC,[3] where an intense negative muon beam with low momentum is available.[4,5] In order to trace the movement of Li between electrodes in a Li-ion battery in the near future, we attempted to observe Li in the anode of a Li-ion battery as the next step by using a graphite anode sheet.

The graphite anode sheet consists of a mixture of graphite and a binder on a Cu foil. A Li-intercalated graphite sheet was prepared by discharging a pouch cell with an electrochemical analyzer. The composition of the anode was confirmed as $\mathrm{C}_6\mathrm{Li}$ by inductively coupled plasma optical emission spectrometry (ICP-OES). The $\mathrm{C}_6\mathrm{Li}$ sheet was retrieved from the pouch cell and was covered by Al laminate in an Al holder. The sample was set against the incident beam, and a detector was arranged at an angle of 45° to the beam on port 4 at RIKEN RAL.

The muonic x-rays were detected by a Ge semiconductor detector (Canberra), synchronizing with muon pulses at a frequency of 50 Hz in ISIS. As a reference, we also measured a graphite plate with 1 mm thickness.

All signals observed as peaks for the $\mathrm{C}_6\mathrm{Li}$ sheet were assigned to the muonic x-rays of Li, C, Cu, and Al [Fig. 1(b)]. Since energy difference between C-Lβ and Li-Kα is only 300 eV, it was difficult to distinguish these two signals. It is found that the intensity of the signal C-Lβ (18.4 keV) is (19.4±1.4)% of that of the signal C-Lα (14 keV) in the spectra obtained from the graphite plate [Fig. 1(a)]. Assuming the same ratio in $\mathrm{C}_6\mathrm{Li}$, we subtracted the contribution from C-Lβ in the peak observed around 18 keV. The intensity of the signal Li-Kα is deduced as (8.6 ± 0.8)% of that of the signal C-Lα.

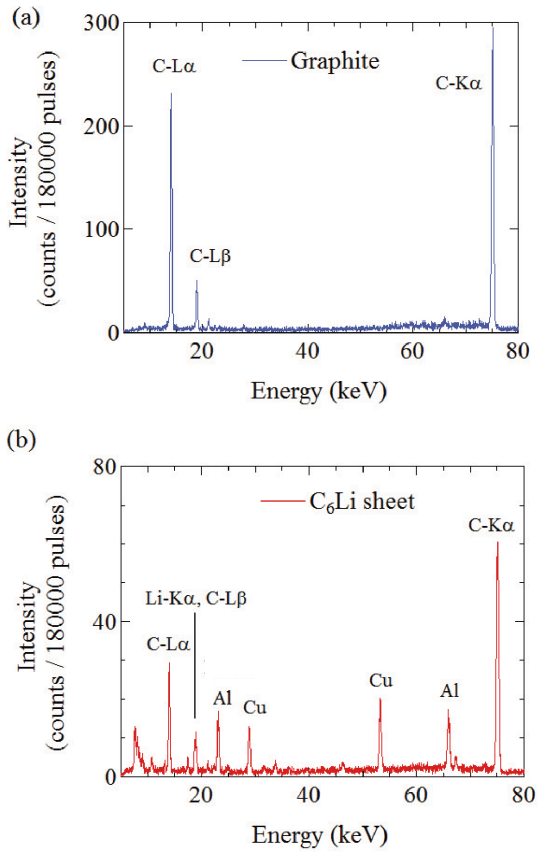

Fig. 1. Muonic x-ray spectra for (a) a graphite plate and (b) a $\mathrm{C}_6\mathrm{Li}$ sheet. Intensity is represented as the number of counts per 180,000 pulses, corresponding to an hour.

We concluded that μXEA can also detect Li in the Li-intercalated graphite anode of a Li-ion battery. This result may lead to further development of μXEA as a non-destructive compositional analysis technique for Li-ion batteries.

*1 Toyota Central Research & Development Labs., Inc.
*2 Department of Chemistry, Graduate School of Science, Osaka University
*3 Division of Arts & Science, College of Liberal Arts, International Christian University
*4 RIKEN Nishina Center

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