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 (deintercalates) into (from) electrodes as follows:

\[
\begin{align*}
\text{cathode} & : \text{LiM}_2O_2 \leftrightarrow \text{M}_2O_2 + \text{Li}^+ + e^- \\
\text{anode} & : 6\text{C} + \text{Li}^+ + e^- \leftrightarrow \text{C}_6\text{Li},
\end{align*}
\]

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 (\( \mu \) XEA)\(^1,2\) 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 \( \text{C}_6\text{Li} \) by inductively coupled plasma optical emission spectrometry (ICP-OES). The \( \text{C}_6\text{Li} \) 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 \( \text{C}_6\text{Li} \) sheet were assigned to the muonic x-rays of Li, C, Cu, and Al [Fig. 1(b)]. Since energy difference between C-L\( \beta \) and Li-K\( \alpha \) is only 300 eV, it was difficult to distinguish these two signals. It is found that the intensity of the signal C-L\( \beta \) (18.4 keV) is (19.4 \( \pm \) 1.4)% of that of the signal C-L\( \alpha \) (14 keV) in the spectra obtained from the graphite plate [Fig. 1(a)]. Assuming the same ratio in \( \text{C}_6\text{Li} \), we subtracted the contribution from C-L\( \beta \) in the peak observed around 18 keV. The intensity of the signal Li-K\( \alpha \) is deduced as (8.6 \( \pm \) 0.8)% of that of the signal C-L\( \alpha \).

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

References