In-situ measurement of the lithium distribution in Li-ion batteries using micro-IBA techniques

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Abstract

Direct observation of lithium concentration distribution in lithium-ion battery composite electrodes has been performed for the first time. Lithium-ion battery model cells for particle induced X-ray emission (PIXE) and particle induced gamma ray emission (PIGE) measurements were designed and fabricated. Two dimensional images of lithium concentration in LiFePO₄ composite electrodes were obtained with PIXE and PIGE by scanning the proton microbeam for various charged states of the electrodes. Lithium concentration in LiFePO₄ composite electrodes was decreased from the contact interface between LiFePO₄ electrode and liquid electrolyte during the charge reaction.

Keywords: PIGE, microbeam scanning, lithium-ion battery, lithium distribution, in-situ measurement

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1. Introduction

In recent years research and development (R&D) of lithium-ion batteries (LIBs) are making remarkable progress worldwide. A wide variety of analyzing methods are utilized for diagnosing the performance of LIB. Since the mobility of the lithium ions in the electrodes is critical for improving the performance of LIB, it is useful to diagnose the lithium ion distribution in the electrodes.

Ion beam analysis techniques are powerful tools for quantitatively characterizing the elemental concentrations . Furthermore, microbeam scanning technology allows us to study elemental concentration distributions with high spatial resolution. Particle induced X-ray emission (PIXE) and particle induced gamma-ray emission (PIGE) techniques have been widely used for material study. The microbeam PIXE and PIGE technology (micro-PIXE and micro-PIGE, respectively) have been utilized for measuring the lithium concentration distribution [1, 2, 3, 4].

Microscopic distribution of the lithium ion in working batteries without disassembling (in-situ measurements) have been measured recently with synchrotron radiation, neutron beam, and so on [5]. When a LIB is charged or discharged, concentration of the lithium ions in the electrode changes in time. However, it has not been measured how the spatial distribution of the lithium ions varies in the electrodes in time. Since the movement of the lithium ions is closely related to the performance of the LIB, we are strongly interested in determining the distribution of the lithium ions in working batteries.

For in-situ measurement of the lithium in LIB, it is necessary to irradiate

the ions in an electrode through a metal film which tightly seals a battery. Since the ion beams for PIXE and PIGE measurements lose their energies significantly in the metal film, we have to prepare a special test cell which has an ion beam irradiation window with high transmittance to the ion beam.

Light-ion microbeam line and its scanning system has been developed at the Japan Atomic Energy Agency (JAEA) Takasaki, which is the center-of-excellence for ion beam technology and its application in Japan [6]. By combining the microbeam line with the PIXE and PIGE techniques, we can obtain the two-dimensional maps of various elements over the wide range of atomic numbers [7].

In this study we report on a special test cell for the in-situ measurement and the experiment with this test cell on the ^7Li spatial distribution in a LIB positive electrode using the $^7\text{Li}(\text{p}, \text{p}'\gamma)$ inelastic scattering. Direct observation of the temporal evolution of the lithium ion distribution in the positive electrode is reported for the first time.

2. Experiment

2.1. Sample preparation

A special LIB test cell for the in-situ measurement of the lithium ions has been fabricated. Photograph and schematic illustrations of the test cell are shown in Fig. 1. The case of the cell, made of Teflon, has 40 mm width, 40 mm height, and 20 mm thickness. It has a cylindrical cavity of 5.5 mm in diameter at the center. The cavity, filled by electrolyte (1M $\text{LiPF}_6/\text{EC-EMC}$ 3:7 mol), was sealed by polyether ether ketone (PEEK) of 2 mm thickness on one side and a stainless steel of 3 mm thickness on another side. The PEEK

plate had a circular hole of 1 mm in diameter for ion beam irradiation. This hole was sealed by a 7.5 μm thick Kapton film to prevent the electrolyte from flowing out of the cavity.

The positive electrode was composed of LiFePO_4 as active material, carbon black as conductive material and polyvinylidene fluoride as binder with a ratio of 80:10:10 in weight. This material was deposited on a thin aluminum foil used as a current collector. The thickness of the positive electrode material was approximately 20 μm . The top surface of the electrode material was covered by a 7.5 μm -thick Kapton film to prevent the electrode material surface soaked directly by the electrolyte. This positive electrode assembly was inserted into the cavity and placed just next to the packing Kapton film on the PEEK plate.

As the negative electrode, a thin lithium metal foil was inserted into the cavity and soaked in the electrolyte by placing the foil between the Teflon body and a stainless steel plate current collector. The aluminum foil and the stainless steel plate were connected to a potentiostat for charging the cell. Charging protocol will be described in the next section including the charging conditions and the measuring procedure.

2.2. Experimental Procedure

The measurements were carried out at Takasaki Advanced Radiation Research Institute (TIARA) of JAEA with a 3.0 MeV proton microbeam from a 3 MV single-ended electrostatic accelerator. The diameter and the current of the proton microbeam were typically 1.5 μm and 300 pA, respectively. A schematic illustration of the experimental setup for measurements of the X-rays and the gamma rays is shown in Fig. 2. The proton microbeam was

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9 extracted from the vacuum chamber to the air through a circular window cov-
10 ered with a $7.5\ \mu\text{m}$ -thick Kapton film. The proton microbeam was scanned
11 over the area of $800\ \mu\text{m} \times 800\ \mu\text{m}$ for observing the evolution of the spatial
12 distribution of the lithium ions in the positive electrode material.
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16 The test cell was placed in close contact to the beam extraction window
17 by manipulation of a 3-axes translation stage in the air. The distance from
18 the extraction window to the positive electrode sample was approximately
19 3 mm. By taking into account the propagation through the air and the
20 three $7.5\ \mu\text{m}$ Kapton films as described above, the energy deposition of the
21 proton on the positive electrode was calculated with the simulation code
22 SRIM2008 [8]. The incident proton energy at the surface of the positive
23 electrode was estimated to be 2.6 MeV .
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27 For the characteristic X-ray detection, a Si(Li) detector was installed
28 at an angle of 145° with the beam axis in the vacuum chamber. It has a
29 Si(Li) crystal active area of $30\ \text{mm}^2$, and the distance from the crystal to the
30 sample electrode was 24 mm. The lithium distribution was observed with the
31 478-keV gamma rays from the ${}^7\text{Li}(\text{p}, \text{p}'\gamma)$ inelastic scattering. A high-purity
32 germanium (HPGe) detector was installed just behind the test cell as shown
33 in Fig. 2. The volume of the germanium crystal detector is $100\ \text{cm}^3$. These
34 two detectors were used for the PIXE and PIGE simultaneous measurements.
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38 A schematic illustration of the irradiating window of the test cell is shown
39 in Fig. 3, together with a close-up photograph. In this experiment we have
40 placed the positive electrode at the left-hand side in the beam irradiation
41 window to observe the gradual changes of the lithium distribution at the
42 boundary of the positive electrode and the electrolyte. The scan area of the
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proton microbeam covered this boundary as shown by the dotted square in Fig 3.

The test cell was charged with a power supply HZ-5000 (Hokuto Denko) by connecting the aluminum foil and the stainless steel plate of the test cell with a constant current mode of $20\ \mu\text{A}$. The PIXE and PIGE images were recorded in sequence at the total charging times of 0 (initial condition), 50, 90 and 150 minutes, respectively. The charging was stopped when these images were recorded, which required 20 minutes for each recording. We note that our measurements have shown that the lithium distribution in LiFePO_4 does not change during this measurement time.

3. Results and discussion

Typical X-ray and gamma-ray energy spectra are shown in Figs. 4(a) and 4(b), respectively. These spectra were obtained by irradiating the positive electrode of the in-situ test cell before charging. The characteristics X-rays from iron and the gamma rays from lithium, which are contained in the positive electrode, are prominent in these spectra. In addition, emissions from some other elements are also seen in the X-ray spectrum, in which several peaks are from the elements not contained in the positive electrode. The argon events are from the air, and the phosphorus and the calcium events are from the calcium phosphate small grains contained in the Kapton film. The micro-PIXE images of P and Ca show that these elements are located in the same regions with a few or a few tens of micrometers in diameter, consistent with the distributed calcium phosphate small grains in Kapton. It indicates that most of the X-rays from phosphorus in the positive electrode

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9 active material (LiFePO_4) are absorbed by the three $7.5\ \mu\text{m}$ -Kapton films
10 before reaching the Si(Li) detector.
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13 Concentration maps of the lithium and the iron contained in the positive
14 electrode at the charging times of 0, 50, 90 and 150 minutes are shown in
15 Fig. 5, with the lithium distribution at the left side column (labeled Li)
16 and the iron distribution at the center column (labeled Fe). These maps
17 show that the yield of the lithium events gradually decreases with increasing
18 the total charging time. Since we cannot determine the total amount of the
19 irradiating proton number in this experimental setup, the yield of the lithium
20 event has been normalized by the iron event pixel by pixel because the irons
21 in the positive electrode active material do not move during charging and
22 discharging.
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32 Normalized lithium maps thus determined are shown at the right side
33 column in Fig. 5 (labeled Li/Fe). They show that the lithium concentration
34 near the edge of the electrode gradually decreases with increasing the total
35 charging time. We find that the lithium depression area first appear near the
36 edge and gradually spread to the far side from the edge. These maps provide
37 valuable information on the lithium movement in the positive electrode of the
38 working LIB. This result shows that the in-situ measurement of the lithium
39 concentration distribution is feasible by using the in-situ test cell we have
40 fabricated in this study.
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51 **4. Conclusions**

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54 We have developed a new method for in-situ measurement of the lithium
55 distributions in a lithium-ion battery (LIB) using micro-IBA technique. We
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9 have fabricated a special LIB test cell for the in-situ measurement of ele-
10 mental distributions in a LIB electrode and measured the time dependent
11 lithium ion distribution during charging the LIB. We have obtained the two-
12 dimensional maps of the lithium and iron distributions by PIGE and PIXE
13 method, respectively. Distributions of the lithium concentration have been
14 determined by normalizing the lithium yield by the iron yield pixel by pixel.
15 Decrease in the lithium concentration from the edge of the positive electrode
16 during the charging has been clearly observed. Thus we have demonstrated
17 for the first time the feasibility of the in-situ measurement of LIB using the
18 micro-IBA technology. This new technology is expected to provide a new
19 diagnosing scheme for improving the performance of LIB.
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Figure 1: Photograph (front view, upper left) and schematic illustrations (side view) of a lithium ion battery test cell for the in-situ measurement of the spatial distribution of lithium in LIB positive electrode.

Figure 2: Schematic illustration of the experimental setup for PIXE and PIGE simultaneous measurement at JAEA Takasaki.

Figure 3: Schematic illustration of the irradiating window of the in-situ test cell. Positive electrode is fixed at the left-hand side in the window circle. Beam scanning area is shown by a dotted square.

Figure 4: Typical X-ray (a) and gamma-ray (b) energy spectra observed with Si(Li) and HPGe detector, respectively.

Figure 5: Spatial distributions of Li, Fe, and their ratio (Li/Fe) before charging (0 min) and after total charging times of 50, 90 and 150 minutes, respectively. The size of the scan area is $800\text{ }\mu\text{m} \times 800\text{ }\mu\text{m}$ for each map. Solid lines in the Li/Fe maps are the same as those shown in the maps of Fe distribution and indicate the approximate position of the positive electrode. In these images the gamma rays and the X-rays are not observed in the lower part and lower-left corner, because in these areas incident protons were stopped with the edge of the beam irradiation window.

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