Observation of a LiCoO_2 Cathode Material of a Li-Ion Battery by High Spatial Resolution TOF-SIMS*

Miwa Ohnishi[†]

Kogakuin University, 2665-1 Nakano-machi, Hachioji, Tokyo 192-0015, Japan

Osamu Matsuoka and Hidenobu Nogi

Mitsui Chemicals, Inc., 580-32 Nagaura, Sodegaura, Chiba 299-0265, Japan

Tetsuo Sakamoto

Kogakuin University, 2665-1 Nakano-machi, Hachioji, Tokyo 192-0015, Japan

(Received 31 January 2012; Accepted 2 April 2012; Published 26 May 2012)

Lithium (Li)-ion batteries will be important to future generations for use as clean energy-storage devices. However, the surface chemical reaction mechanism of the electrode has not been revealed to date. In this study, surface observation and chemical species mapping of cathode material for the Li-ion batteries were performed using a laboratory-made time-of-flight secondary ion mass spectrometry (TOF-SIMS) apparatus. The most notable feature of this apparatus is its high-spatial resolution (~ 40 nm), which is achieved by employing a focused ion beam. In order to reveal the spatial distributions of chemical species on the LiCoO_2 cathode material, we applied the new TOF-SIMS measurement. Differences in the distribution of molecular species on the crystal face were observed with this apparatus. [DOI:10.1380/ejsnt.2012.207]

Keywords: Secondary ion mass spectroscopy; Surface chemical reaction; Cobalt oxides

I. INTRODUCTION

Lithium (Li)-ion batteries will be important to future generations for use as clean energy-storage devices in storage systems for natural power sources. In addition, the recent progress in developing pure electric vehicles (EV) and hybrid electric vehicles (HEV) has resulted in a requirement for both high power operation and long battery life. The electric power characteristics of battery systems are related to the nature of electrode reaction. This reaction involves several steps: lithium diffusion in the electrolyte, adsorption of solvated lithium on the cathode surface, desolvation, surface diffusion, charge transfer, intercalation from the surface to the bulk, and the bulk diffusion of lithium in the electrode material. The composition and properties of the solid electrolyte interphase (SEI) layer formed at the negative electrode interface of a Li-ion battery have been characterized [1]. A recent study of the positive electrode, demonstrated that the SEI layer is expected to be present on the positive electrode [2]. Another research reported that the interface reaction of an ideal epitaxial electrode and an electrolyte depends on the orientation of an electrode [3]. The horizontal face of the c -axis of a LiCoO_2 particle is electrically active. However, the details of the mechanism of the chargedischarge system for the actual material are unknown. In order to develop a high-power battery system, it is essential to know details of the interface reaction between an electrolyte and an electrode. To reveal the compositional distributions of chemical species on an actual electrode, high spatial resolution time-of-flight secondary ion mass spectrometry (TOF-SIMS) has been applied to analyze

the crystal surface of cathode materials of the Li-ion batteries.

II. EXPERIMENTAL

The positive electrode mainly consisted of the LiCoO_2 particles. Polyvinylidene-di-fluoride (PVDF) and carbon black were added as a binder and the conductive material, respectively. The sample comprised electrode particles subjected to an aging test in the electrolyte with a sulfur-containing additive (1,3-PropenSulton, synthesized by Mitsui Chemical Inc.) at 0.5 wt%. It is known that, for the negative electrode, a component containing sulfur is a good additive to enhance the conductivity of the electrolytes and the capacity of batteries [4]. The electrolyte consisted of a solvent (a mixture of ethylene carbonate (EC), ethyl methyl carbonate (EMC), and di-methyl carbonate (DMC) with a ratio of 1:1:1 vol%), and 1 M LiPF_6 . The aging test was performed for two days at a constant temperature of 80°C under full state-of-charge (4.2 V). The battery was disassembled and the positive electrode was cleaned with DMC in an inert Ar atmosphere. Powder from the cathode material was stripped from the electrode and embedded on an indium substrate in air atmosphere. Surface observation and chemical species mapping of cathode materials of Li-ion batteries were performed with a TOF-SIMS apparatus [5]. This apparatus features single-particle analysis with high lateral resolution (down to 40 nm) [5]. The apparatus has two beams: a focused ion beam (FIB) and an electron beam (EB). The FIB was used to section a particle, observe the surface, and obtain the chemical mapping. The EB was used for the observation during the FIB sectioning. In this study, the particles of cathode material on the indium substrate were observed with EB- and FIB-induced secondary electron imaging (SEM and SIM, respectively) and elemental maps with a combination of pulsed FIB and TOF-SIMS. A 30-keV Ga^+ focused ion beam was rastered over a sam-

*This paper was presented at the 6th International Symposium on Surface Science –Towards Nano, Bio and Green Innovation–, Tower Hall Funabori, Tokyo, Japan, December 11-15, 2011.

[†]Corresponding author: kt13380@ns.kogakuin.ac.jp

ple area of $20\ \mu\text{m} \times 20\ \mu\text{m}$ to obtain the SIM image. The Ga^+ ion current was approximately 300 pA. Pulsed Ga^+ was used as the primary ion beam for elemental mapping. The pulse width was 300 ns; the sweep numbers were 300 and 150-200 for the negative and the positive analyses modes, respectively. The extractor was at 1.6 keV. The total count/pixel was adjusted to approximately 200-300.

III. RESULTS AND DISCUSSIONS

Figure 1 shows an SEM image of cathode materials. Crystal-like grains ($\sim$ several μm) and nano-sized particles were observed on the surface of the sample. The crystal-like grains are LiCoO_2 . The nano-sized particles are considered to be carbon black. LiCoO_2 grains are subhedral crystals. Figures 2 and 3 show the TOF-SIMS spectra of cathode material of the Li-ion battery. The mass-to-charge ratio (m/z) is shown on the horizontal axes. The m/z of the positive and negative ion analyses modes were calibrated by $^{23}\text{Na}^+$ and $^{69}\text{Ga}^+$, and $^{16}\text{O}^-$ and $^{24}\text{C}_2^-$, respectively. Each peak was identified by the spatial distribution in the elemental map. Figure 4 displays an SIM image, an SEM image, and TOF-SIMS elemental maps of the cathode material of the Li-ion battery. Each elemental map has a field of view (FoV) of $20\ \mu\text{m}$ and pixel number as 256×256 . The size of one pixel in these elemental maps is approximately $80\ \text{nm} \times 80\ \text{nm}$. The $^7\text{Li}^+$,

FIG. 1: SEM image of cathode materials. Crystal-like grains are LiCoO_2 . The nano-sized particles are considered to be carbon black.

FIG. 2: TOF-SIMS spectrum in the positive ion analysis mode of LiCoO_2 cathode material subjected to the aging test in the electrolyte with a sulfur-containing compound.

$^{33}\text{Li}_2\text{F}^+$, and $^{59}\text{Co}^+$ species were analyzed in the positive ion mode. Other species were analyzed in the negative ion mode. The image in which $m/z = 48$ is a combination map of SO^- and C_4^- . Each species showed a characteristic distribution.

Fluorine ions are considered to originate from PVDF and/or LiPF_6 . Lithium fluoride ions are considered to originate from LiPF_6 and/or LiF . LiF is a major salt-

FIG. 3: TOF-SIMS spectrum in the negative ion analysis mode of LiCoO_2 cathode material subjected to the aging test in the electrolyte with a sulfur-containing compound.

FIG. 4: SIM image, SEM image, and TOF-SIMS elemental maps of LiCoO_2 cathode material. The size of each pixel in these maps is approximately $80\ \text{nm} \times 80\ \text{nm}$.

FIG. 5: Overlay of secondary electron image (SEM) of LiCoO₂ cathode material and the TOF-SIMS elemental mapping of phosphate and sulfate ions.

reduction product. The HF contaminant also reacts with semi carbonates to give an LiF byproduct. The amount of LiF increases during storage [1,6]. Using XPS spectra, decomposition products of types Li_xPF_y and Li_xPF_yO_z were observed on the LiNi_{0.8}Co_{0.2}O₂ electrode as reported in [6].

In this study, phosphoric ions were observed on the LiCoO₂ cathode material. The phosphoric ions are considered to be decomposition products of LiPF₆. Differences in the distributions of phosphate ions were found to be dependent on the crystal face (Fig. 5). The sample was prepared under air atmosphere. However, it is improbable that the phosphate moved during sample preparation. These spatial distributions of phosphate ions were considered to originate from the original sample. From the SEM image (Fig. 5), we can identify the *c*-axis. Many phosphoric ions were distributed on the side of the layer. This face is electrically activated [3]. This result corroborates that phosphoric ions formed during charge and discharge cycles. The observation of decomposition products on the electrically-activated face is consistent with the result of

in-situ X-ray observation of epitaxial film of LiCoO₂ [3].

The sulfate ions originated from the additive, 1,3-PropanSulton and were observed at $m/z = 48, 64, 80$, and 96 for SO⁻ and C₄⁻, SO₂⁻, SO₃⁻, and SO₄⁻, respectively. ⁶⁴PO₂H⁻ and ⁸⁰PO₃H⁻ from ⁶⁴SO₂⁻ and ⁸⁰SO₃⁻ could not be eliminated under these analytical conditions. However, the elemental mappings of ⁶³PO₂⁻ and ⁶⁴SO₂⁻, and ⁷⁹PO₃⁻ and ⁸⁰SO₃⁻ had different distributions (Figs. 4 and 5). These results indicate that there were few disturbances of ⁶⁴PO₂H⁻ and ⁸⁰PO₃H⁻. The observation of sulfate ions on LiCoO₂ particles indicates that the sulfur containing additive most probably worked on the cathode material. These sulfate ions exhibit granularity distribution or were observed as spots on the crater of the crystal (Fig. 5). The different distributions of sulfate and phosphoric ions are shown in Fig. 5. It is improbable that sulfate moved during sample preparation; therefore, these spatial distributions of sulfate ions were considered to be inherent to the original sample. The sample was analyzed after the aging test and the sulfate ions were then considered with the residue.

IV. COUCLUSIONS

The spatial distributions of chemical species on LiCoO₂ particles were observed. The results indicated that each species has a characteristic distribution. The distribution of phosphate ion that originated from LiPF₆ was clarified on a scale of approximately 80 nm. Many phosphate ions were detected on the electrically-activated face of the LiCoO₂ crystal. The possibility that electrolyte decomposed during the chargedischarge process was shown on the actual sample. There are different distributions between the electrolyte decomposition and the additive. It is possible that these chemical species were formed during the chargedischarge timing cycle.

Acknowledgments

This study was supported by SENTAN (JST).

- [1] P. Verma, P. Maire, and P. Novák, *Electrochim. Acta* **55**, 6332 (2010).
- [2] K. Edström, T. Gustafsson, and J. O. Thomas, *Electrochim. Acta* **50**, 397 (2004).
- [3] M. Hirayama, N. Sonoyama, T. Abe, M. Minoura, M. Ito, D. Mori, A. Yamada, R. Kanno, T. Terashima, M. Takano, K. Tamura, and J. Mizuki, *J. Power Sources* **168**, 493 (2007).
- [4] B. T. Yu, W. H. Qiu, F. S. Li, and L. Cheng, *J. Power Sources* **158**, 1373 (2006).
- [5] T. Sakamoto, M. Koizumi, J. Kawasaki, and J. Yamaguchi, *Appl. Surf. Sci.* **255**, 1617 (2008).
- [6] A. M. Andersson, D. P. Abraham, R. Haasch, S. MacLaren, J. Liu, and K. Amine, *J. Electrochem. Soc.* **149**, A1358 (2002).