

Degradation Analysis of LiCoO₂ Positive Electrode Material of a Li-Ion Battery Using the Li K-Edge Signal Obtained from STEM-EELS Measurements*

Noboru Taguchi,[†] Hikari Sakaebe, Kuniaki Tatsumi, and Tomoki Akita

Research Institute for Ubiquitous Energy Devices,

National Institute of Advanced Industrial Science and Technology (AIST), Ikeda, Osaka 563-8577, Japan

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The Li distribution in positive electrode material (LiCoO₂) was observed after a charge-discharge cycling test by analytical transmission electron microscopy (TEM). The electron energy-loss spectroscopy (EELS) imaging method revealed an inhomogeneous Li distribution in the LiCoO₂ particles after the charge-discharge cycling test. Using the alternating least-squares (ALS) method for the data matrix of the EELS spectra, we obtained LiCoO₂ and Li-poor LiCoO₂ spectra from the LiCoO₂ particles. Around the degraded LiCoO₂ particles, Co₃O₄ and fluoride components were detected. It is suggested that inhomogeneous electrochemical reactions are one cause of LiCoO₂ and electrolyte degradation.

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Keywords: Scanning transmission electron microscopy (STEM); Electron energy-loss spectroscopy (EELS); Cobalt oxides; Li-ion battery; Li K-edge

I. INTRODUCTION

To study the degradation mechanism of Li-ion battery materials, it is important to understand the atomic structures and chemical states of these materials. Analytical transmission electron microscopy (TEM) is useful for studying these materials because of its high spatial resolution. In particular, direct analysis of Li ions using electron energy-loss spectroscopy (EELS) can be a powerful method of investigating the chemical state of Li in Li-ion battery materials [1–3]. However, M-edge signals from Mn, Co, and Ni appear near the energy region of the Li K-edge signal in EELS images, and the overlap between the Li K-edge and M-edges of these transition metals often reduces the accuracy of the quantitative analysis or interferes with the chemical analysis of the spectrum. The aforementioned transition metals are widely used as electrodes in Li-ion batteries for charge compensation during the Li insertion and extraction reactions. High-energy-resolution EELS is effective in reducing the overlapping problem in Li K-edge analysis.

By using EELS with a monochromator, the Li-ion distributions inside LiCoO₂ particles in positive electrode material with and without surface modification during the charge-discharge cycle have been reported [4, 5]. However, the products generated from the electrochemical reactions in a LiCoO₂ system have not been previously examined by analytical TEM.

In the present study, Li K-edge analysis using monochromated STEM-EELS was performed. In addition, maps of the Li intensity and of the reaction products were also reconstructed from EELS images [4, 6]. To obtain chemical information about the sample, analyses not only of the intensities of the EELS distributions but also of their shapes were conducted as post-analysis. Such a

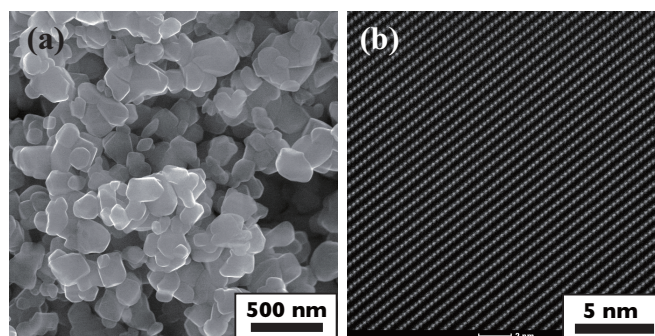


FIG. 1. (a) SEM image of LiCoO₂ particles. (b) ADF-STEM image of LiCoO₂. Incident beam direction is $\langle 100 \rangle$.

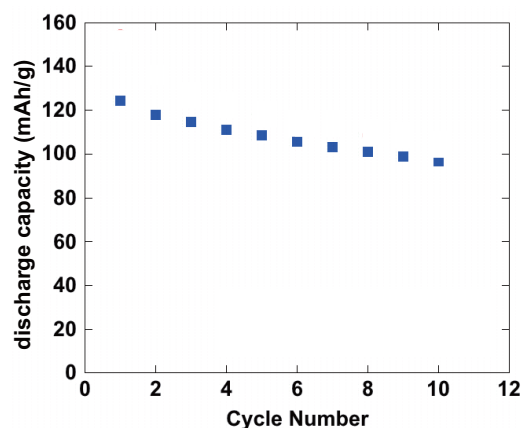


FIG. 2. Cycling test results for cells containing LiCoO₂.

large matrix of spectral data is suitable for analysis via a chemometrics approach. To obtain individual pure spectra from the series of spectra without a reference spectrum, we applied a self-modeling curve-resolution technique (the alternating least-squares (ALS) method) [7–11] to the series of spectra to perform spectral decomposition.

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[†] Corresponding author: n-taguchi@aist.go.jp

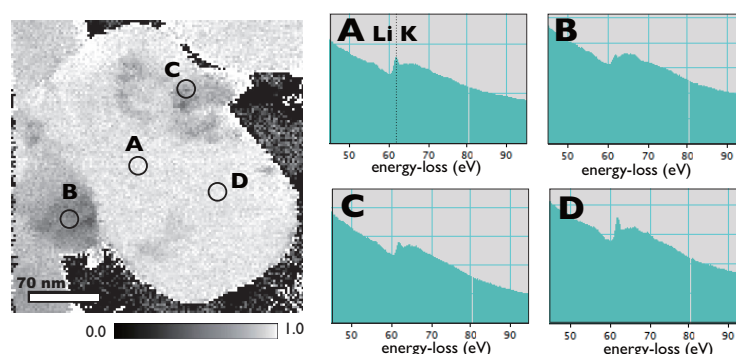


FIG. 3. Li-K/Co-M intensity ratio map for LiCoO_2 after cycling test. Image contrast is normalized to Li K-edge/Co M-edge intensity ratio of as-prepared LiCoO_2 . Intensity scale corresponds to x in Li_xCoO_2 . Raw spectra of Li-K edge are shown for all spots (A-D).

The degradation process of LiCoO_2 was analyzed based on the series of decomposed spectra.

II. EXPERIMENTAL

Small LiCoO_2 particles, which are suitable for TEM and EELS analyses, were synthesized by the Pechini process [12]. $\text{Co}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$, $\text{LiCH}_3\text{COO} \cdot \text{H}_2\text{O}$, and citric acid were mixed at 165°C in an ethylene glycol solution ($\text{Co}/\text{Li} = 1:1$ atomic ratio). The obtained gel was pre-calcined at 400°C in air to decompose the precursor. The precursor was calcined again at 750°C for 1 h in air. The LiCoO_2 particles were about 200 nm in size.

A composite containing 84 wt% active material (LiCoO_2), 8 wt% acetylene black (AB), and 8 wt% polyvinylidene fluoride (PVDF) was used as the positive electrode. A sheet-type two-electrode cell with 16 mm ϕ electrodes sealed in Al-laminated type film was assembled using Li metal as the counter electrode and 1.0 mol $\cdot\text{dm}^{-3}$ LiPF_6/EC (ethylene carbonate+DMC(dimethyl carbonate)) (1:1 in volume) as the electrolyte. The cell was cycled in the voltage range between 3.0 V and 4.2 V with a 0.1 C charge-discharge rate (1 C = 150 mA/g). The temperature around the cell in the charge-discharge tests was 20°C .

For the TEM observations, LiCoO_2 powder was directly dispersed on a carbon film supported by a Cu mesh. A TITAN³ G2 60–300 electron microscope (FEI Company) equipped with a Super X (Bruker Corporation) for energy-dispersive X-ray spectroscopy (EDS) and a GIF Quantum ERS (Gatan Inc.) for EELS was operated at an accelerating voltage of 200 kV. The EDS and EELS measurements were performed on LiCoO_2 after the 10th discharge by a spectrum-imaging scheme based on STEM observations. The process of spectrum imaging refers to the acquisition of three-dimensional data that contain both spectral and spatial information about the specimen. Each EELS image integrates the signal from the whole region along the beam direction at each pixel. In the EELS acquisition for Li-K mapping, a monochromator was applied to achieve a higher energy resolution. The FWHM of the zero-loss peak was less than 0.3 eV

with an energy dispersion of 0.05 eV/channel.

The ALS method was applied to these EELS data [7–11, 13–15]. As an initial ALS estimation, the orthogonal projection approach (OPA) was used [16, 17].

III. RESULTS AND DISCUSSION

Figure 1 (a) shows the SEM image of the synthesized LiCoO_2 particles. The primary particles display a partial agglomerate formation, and the size of primary particles is about 200 nm. Thus, smaller-sized particles, which are suitable for TEM observations, were obtained. The typical layered structure of LiCoO_2 was also confirmed by using X-ray diffraction (XRD) (not shown) and ADF-STEM observations (Fig. 1 (b)).

Figure 2 shows the cycling performance of the cell. The discharge capacity of LiCoO_2 depends on the particle size [18]. Much larger particles (~ 300 nm) generally show much better electrochemical properties [4]. In the present study, we treated the smaller particles as the typical model sample to represent the capacity fading and irreducible capacity in the TEM analyses.

The Li K-edge EELS plots of the LiCoO_2 particles after 10th discharge are shown in Fig. 3 (A-D) along with the Li distribution. We obtained the spectra around the Li K-edge in each pixel of the ADF-STEM image. This information enabled the spatial distribution of Li to be reconstructed from the Li K-edge spectra [4, 5]. We reconstructed the Li/Co intensity-ratio map using the series of spectra in Fig. 3. Inhomogeneous Li distributions in the particles were clearly observed. At spot D, the shape of the spectra is the same as that of bare LiCoO_2 [4, 19]. Compared with the intensity of the Li K-edge at spot D, the corresponding intensity at spot A is slightly decreased. Considerably decreased Li K-edge intensities are observed at spots B and C, and the regions around these spots are believed to have been damaged during the charge-discharge cycling.

In our previous study, the homogeneity of the Li-ion distribution in Al- and Si-oxide-coated LiCoO_2 agreed well with the capacity retention after the cycling test [4]. Specifically, LiCoO_2 with poor cycling had a decidedly

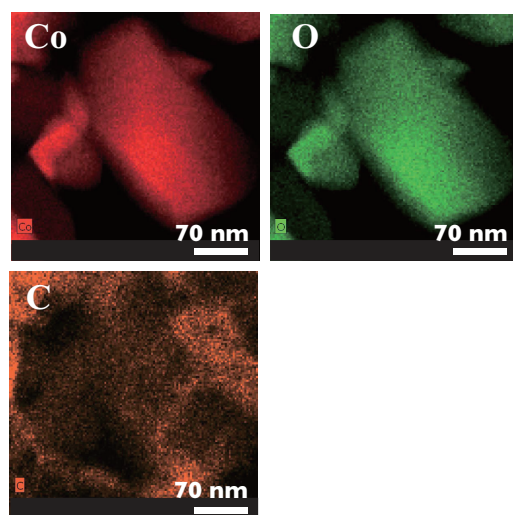


FIG. 4. Co, O, and C EDS mapping results of LiCoO_2 after cycling test.

inhomogeneous Li distribution, while Al-oxide-coated LiCoO_2 with good cycling exhibited a quite homogeneous Li distribution. The present LiCoO_2 with poor cycling is consistent with this trend, showing an inhomogeneous Li distribution.

The results of the EDS mapping of the LiCoO_2 particles after the 10th discharge are shown in Fig. 4. The gross intensity maps in the energy windows of Co, O, and C are indicated. No intensity changes related to the Li-poor regions are observed in the maps of either Co or O. Only

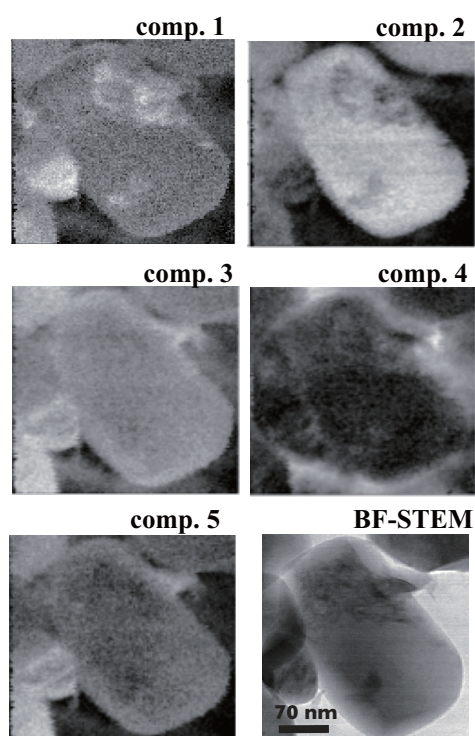


FIG. 5. Component maps obtained from ALS. BF-STEM image is also shown.

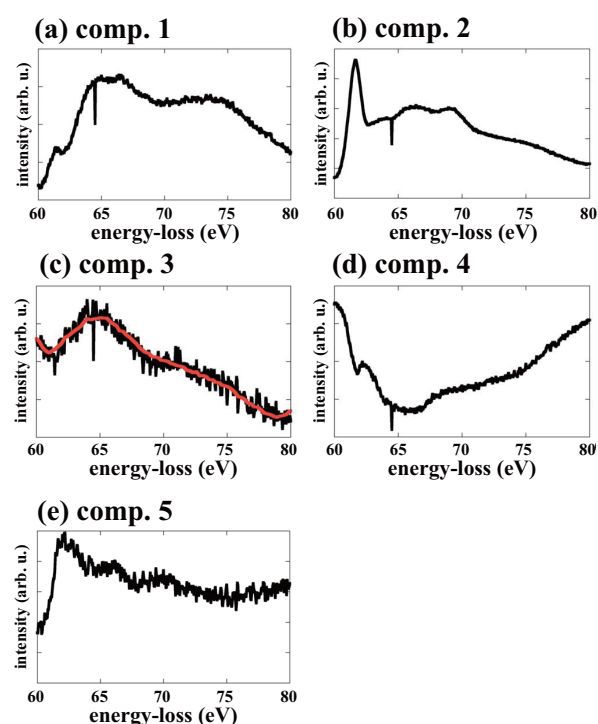


FIG. 6. EELS distributions obtained from ALS analysis of LiCoO_2 after cycling test.

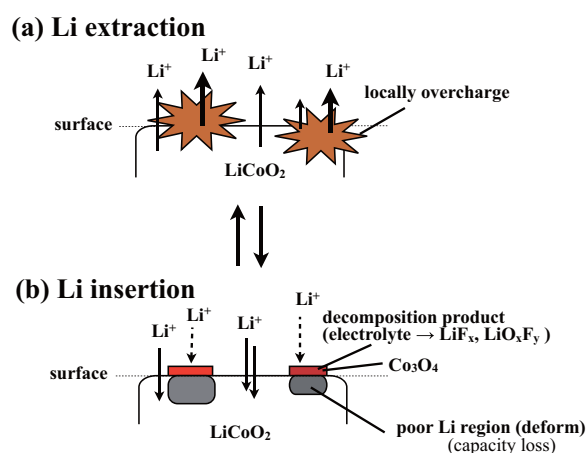


FIG. 7. Schematic image of sample degradation process during cycling test.

intensity changes due to variations in sample thickness can be seen. Thus, the amounts of Co and O do not change drastically during charge-discharge cycling.

In the present sample, the degraded LiCoO_2 area can be clearly seen from the Li K-edge EELS and Li distribution images. The information about the chemical state near the damaged region is quite important in order to investigate the reaction products. In addition to the Li intensity analysis shown in Fig. 3, the fine structures of the EELS distributions also yield chemical information about the sample. On these data, we performed ALS analysis in order to identify the primary spectral compo-

nents, especially in the degraded regions. From the ALS analysis, we identified five types of components from the spectral images, and their intensity maps are shown in Fig. 5. The intensity map of comp. 1 corresponds closely to a Li-poor region. In contrast, comp. 2 corresponds to a bare LiCoO₂ region. In comps. 3 and 5, very similar regions are observed, as these components were mainly obtained around the same particle edge. Similarly, comp. 4 was also obtained from the region surrounding the particle.

The decomposed spectra for all of these components are shown in Fig. 6. In the spectrum of comp. 1 (Fig. 6 (a)), a weak Li K-edge peak can be seen around 62 eV. The Li K-edge spectrum of delithiated LiCoO₂ (Li_{0.5}CoO₂) corresponds closely to the shape of the comp. 1 spectrum [19]. The Co and O intensities did not drastically change from the EDS results after the 10th discharge, which are shown in Fig. 4. This result indicates that the Li-poor region does not transform pure Co-oxide completely as a result of the Li absence but rather creates Li-poor states, such as a charged state in which Li is partially extracted. In the BF-STEM image, the region with greater particle contrast corresponds closely to the region in which comp. 1 is mainly observed. In general, BF-STEM images are sensitive to diffraction contrast, such as that introduced by local strain or dislocation in the crystal. In LiCoO₂, significant Li extraction causes substantial change in the lattice constant. Local states are considered to induce more particle damage than are charged states. Thus, local area deformation is believed to prevent normal diffusion of Li ions in materials.

In comp. 3, the Li K-edge peak completely disappears, as shown in Fig. 6 (c), in which there is no peak near 62 eV. This spectrum corresponds closely to that of Co₃O₄ [19]. Based on the present EELS results, the main product around the LiCoO₂ particle is believed to be Co₃O₄. The spectrum of comp. 2 in Fig. 6 (b) corresponds to that of LiCoO₂ and includes the sharp Li K-edge peak. The intensity distribution of comp. 4 is that of the particles surrounding the LiCoO₂, and the same distribution is obtained from EDS analysis of carbon. Thus, comp. 4 is thought to be a background signal from carbon from AB (conductive additive), electrolytes, or contamination from TEM sample preparation, among other sources (Fig. 6 (d)). Finally, the peak of comp. 5 in Fig. 6 (e) agrees well with the LiF_x and LiO_xF_y peaks previously reported by Muto *et al.* [10]. These F compounds are believed to be decomposition products from the electrolyte LiPF₆. The reaction products around the particle surface were

determined from the results of TEM-EELS analysis of a LiNi_{0.8}Co_{0.15}Al_{0.05}O₂ sample, which was fabricated by a focused ion beam (FIB). Results similar to those observed in the degradation analysis of LiNi_{0.8}Co_{0.15}Al_{0.05}O₂ using STEM-EELS [8–11] were obtained even in the case of LiCoO₂.

Considering these ALS results, we can draw a schematic image of the degradation process around a LiCoO₂ particle, as is shown in Fig. 7. First, LiCoO₂ (positive electrode) is delithiated (charge process), and Li is diffused to Li metal (anode). In this delithiation process, excess Li extraction may occur locally. Crystal deformation is induced in the local area, and thus further Li diffusion is prevented. Then, side reactions occur around the surface of the damaged region, and Co₃O₄ particles or other electrolyte decomposition products are generated (Fig. 7 (a)). In the discharge (Li insertion) process, Li returns to the positive electrode. However, such reaction products and deformed areas are considered unfavorable for the diffusion of Li ions. Finally, a Li-poor region (comp. 1) appears in the LiCoO₂ particle (Fig. 7 (b)).

IV. CONCLUSION

STEM-EELS analysis of the Li K-edge in LiCoO₂ particles was conducted after charge-discharge cycling by using a monochromator. From the resulting spectra, the LiCoO₂ particles were confirmed to have inhomogeneous Li distributions. ALS analysis revealed that the Li-poor region was not Li-free Co oxide and that Co₃O₄ and electrolyte decomposition products were distributed across the surface. Local overcharge states induced side reactions and particle deformation, preventing Li diffusion in the Li insertion and exertion processes during the charge-discharge cycling. STEM-EELS imaging with ALS analysis was successfully applied in the degradation analysis of LiCoO₂ positive electrode material.

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