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ABSTRACT

A quantitative understanding of the Li distribution inside all-solid-state Li-ion batteries is important for improving the performance of batteries. We constructed a time-of-flight (TOF) elastic recoil detection analysis (ERDA) system for operando measurements of thin-film Li-ion batteries. The TOF-ERDA measurement provides elementally resolved spectra with a depth resolution much higher than that of conventional stopper-foil ERDA. The Li depth profiles in a cathode film and solid electrolyte were obtained quantitatively to a depth of 100 nm using a 9-MeV Cu ion beam with reflection geometry. In this study, we conducted TOF-ERDA for a thin-film battery having a cathode made from LiCoO₂, an oxide-based solid electrolyte [lithium aluminum titanium phosphate (LATP)], and an anode made from Fe₂(MoO₄)₃ to demonstrate the ability of the measurement system and reveal the Li distribution near the interface with improved resolution. The depth resolution at the interface (30 nm from the surface) was estimated to be 12–14 nm. We quantitatively obtained the Li density in the LiCoO₂ cathode and the variation in the Li distribution around the LiCoO₂/LATP interface and inside the LATP electrolyte upon charging/discharging. TOF-ERDA is thus a powerful tool for the high-resolution quantitative depth analysis of Li in thin-film batteries in operando.

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All-solid-state lithium-ion batteries are promising candidates for the next generation of rechargeable batteries. The use of solid electrolytes instead of organic liquid electrolytes is expected to improve various aspects of performance, such as safety, lifetimes, charging times, and energy density. A key issue in realizing practical applications is optimizing the electrode/solid electrolyte interface. It is necessary to stabilize the material at the interface and reduce the ion transport resistance. To understand the ion transport mechanism and to design a superior interface condition, the interface properties should be characterized at the nanometer level during charging and discharging. In particular, it is important to know the distribution and behavior of lithium (Li) ions at the interface.

Although detecting Li is more challenging than detecting heavier elements, observations of Li distributions using sophisticated

techniques have been reported. For example, electron energy-loss spectroscopy with scanning transmission electron microscopy (STEM-EELS) has been adopted to map cross sections of thin-film batteries with high spatial resolution after the sample has been thinned to a thickness of several hundred nanometers. Nomura *et al.* visualized dynamic changes in the Li-ion distribution in cathode polycrystalline particles.^{1,2} Tian *et al.* reported variations in the Li concentration in a solid electrolyte approximately 10 nm from the electrode interface.³ In addition, nuclear reactions have been used to detect Li inside solid-state batteries. Oudenhoven *et al.* showed that the thermal-neutron-induced reaction of ⁶Li(n, α)³He is useful for observing changes in the overall Li depth distribution inside a thin-film battery by preparing a ⁶Li-enriched LiCoO₂ cathode.⁴ Kobayashi *et al.* achieved a fast trace of the distribution change using a strong thermal-neutron beam.⁵ In

addition, a nuclear reaction analysis based on the ${}^7\text{Li}(p, \alpha){}^4\text{He}$ reaction using a fast proton beam was demonstrated by Mathayan *et al.*⁶

ERDA using mega-electron volt-energy ion beams is another method of directly detecting Li inside thin-film batteries. ERDA has unique advantages in the quantitative and highly sensitive depth profiling of thin-film samples. In addition, it is beneficial to the actual measurement that no special pretreatment is required for the measurement. Tsuchiya and Morita *et al.* succeeded in obtaining variations in Li intensity in thin-film batteries.^{7–9} In some cases, however, H signals interfere with the precise evaluation of the Li profile. In addition, the depth resolution of conventional ERDA is limited to a few tens of nanometers or worse, as it requires a stopper foil in front of the detector to eliminate scattered ions. Penetration of the stopper foil reduces the depth resolution through increased energy straggling. Mathayan *et al.* recently obtained Li depth profiles separately from H, adopting coincidence ERDA.¹⁰ They also performed TOF-ERDA with 8-MeV He.¹⁰ This technique provides elementally resolved depth profiles through the measurement of the TOF and energy of recoil ions.^{11–16} TOF-ERDA does not require stopper foil because scattered ions can be distinguished by their TOF. The adoption of this analysis thus has the potential to greatly increase the depth resolution in general. However, in the previous work, there was little improvement in the resolution because the measurements were performed in a transmission geometry.⁶

Taking full advantage of the high resolution of TOF-ERDA, we recently constructed a TOF-ERDA system for operando measurements of thin-film batteries in a reflection geometry using MeV-energy heavy ions.¹⁷ By focusing on the depth region less than 100 nm from the surface, variations in the Li depth profile upon charging/discharging were observed with high depth resolution. In the present study, we applied this analysis to the LiCoO_2 electrode and its interface with a Li^+ -conducting crystalline glass solid electrolyte (LATP) in a thin-film battery. LATP is an oxide-based solid electrolyte with high Li conductivity. It has the advantage of being stable in air and commercially available in large, flat substrates. Thin-film batteries having LATP electrolytes have thus been widely adopted in precise investigations of interfacial behaviors.^{3,7–9,18} For instance, the possible formation of a Li-deficient region inside an LATP electrolyte was suggested in a depth region approximately 100 nm or less from an interface with LiCoO_2 .^{3,8} We demonstrate the high-depth resolution achieved by the constructed system and reveal the Li distribution around the interface with improved resolution.

The TOF-ERDA system was constructed at a 1.7-MV Tandemron accelerator at the Quantum Science and Engineering Center, Kyoto University. An incident beam of 9-MeV Cu^{5+} ions irradiated the sample at an angle of 15° to the surface. The spot size on the irradiated surface was approximately $3 \times 5 \text{ mm}^2$. The beam current was approximately 10 pA, and the measurement duration for each applied voltage was 150 min. This amounted to a fluence of approximately $6 \times 10^{12} \text{ cm}^{-2}$.

A TOF-energy spectrometer was placed at an angle of 30° to the beam axis, as shown in Fig. 1. The spectrometer had two time detectors (T1 and T2) and an energy detector. Each of the time detectors comprised a microchannel plate detector (Hamamatsu, F4655-12 and F9890-12), carbon foil (ACF-Metals, 3 and $10 \mu\text{g}/\text{cm}^2$ for T1 and T2), and electrostatic grids.¹⁹ The diameters of the carbon foils were 10 and 15 mm for T1 and T2, respectively. The distance between the two

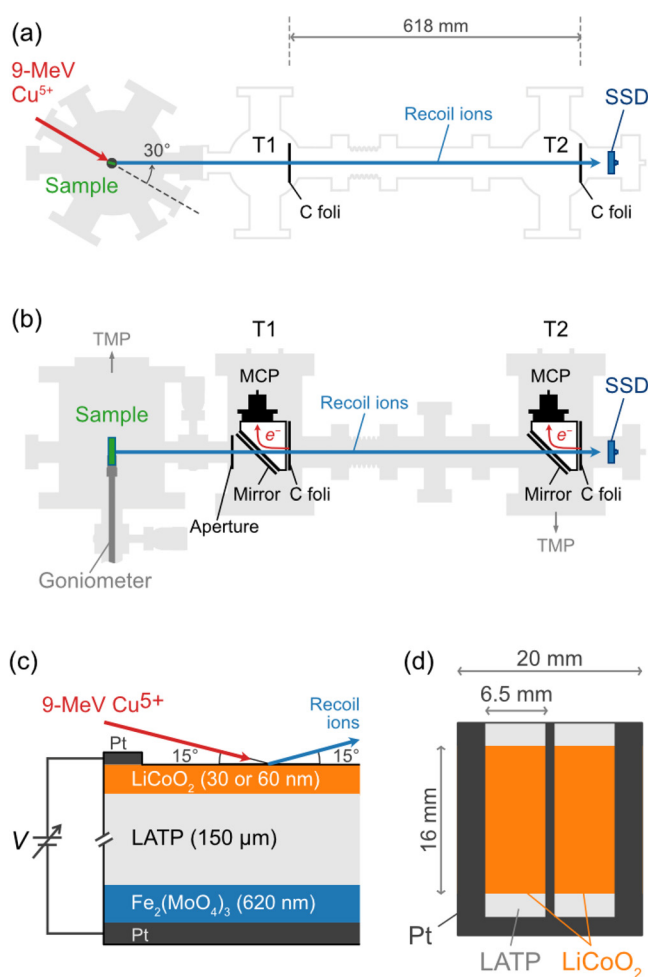


FIG. 1. (a) Top and (b) side views of a schematic of the experimental setup. (c) Cross-sectional and (d) top schematic views of the thin-film, all-solid-state Li-ion battery sample.

carbon foils was 618 mm. The solid angle of the detection system was limited to 0.17 msr by the sensitive area of T2 and the open area ratios of the grid meshes. The T2 foil can be enlarged to 25 mm in diameter, realizing a solid angle of 0.44 msr, in the future. In front of T1, an additional aperture with a 15-mm diameter was placed to reduce the number of the background secondary electrons coming from the sample. The time resolution of the spectrometer was evaluated from the scattering of 4.5-MeV ${}^7\text{Li}^{2+}$ and 6.0-MeV ${}^7\text{Li}^{3+}$ by a Au thin film with a density of $12 \mu\text{g}/\text{cm}^2$ on a silicon wafer. The scattered Li ions formed Gaussian peaks in the TOF spectra with full widths at half maximum (FWHMs) of 422 and 333 ps at 4.5 and 6.0 MeV, respectively. By subtracting the calculated broadening due to the finite thickness of the Au film, the resolution of the spectrometer itself was determined to be 248 ps. To compensate for uncertainty in the thickness of the Au film, the film thickness was also treated as a fitting parameter. This value is comparable to values in the range of 154–540 ps reported by other institutes.^{11–16,20} The detection efficiencies of the time detectors were

evaluated as 0.04–0.26 for H, ~ 0.53 for Li, 0.80–0.90 for O, 0.80–0.92 for Si, and 0.78–0.95 for Cu ions (see the [supplementary material](#)).

A silicon semiconductor detector with an area of 900 mm² (Canberra, PD900-27-100AM) was used as the energy detector. A relatively large detector was used to ensure that the solid angle was not reduced. There are concerns about irradiation damage with heavy ions because thin-film batteries are likely to be fragile. Measurements should be made with high detection sensitivity and low irradiation. Although a larger solid angle reduces depth resolution through kinematic broadening, this effect was limited in the present study because we mostly focused on the buried interface rather than on the topmost surface.

The thin-film battery sample used in this study had a cathode made from LiCoO₂, a solid electrolyte made from LATP, and an anode made from Fe₂(MoO₄)₃. The composition of the LATP electrolyte used in the present experiment (LICGC AG-01: Ohara Inc.) is expressed as Li_{1+x+y}Al_x(Ti,Ge)_{2-x}Si_yP_{3-y}O₁₂. The sample comprised Pt (10 nm)/LiCoO₂ (30 or 60 nm)/LATP (150 μ m)/Fe₂(MoO₄)₃ (20 nm)/Pt (50 nm), including current collector electrodes, as shown in [Fig. 1\(c\)](#). The thin films of the cathodes were formed on a mirror-polished LATP electrolyte sheet through pulsed laser deposition. The Pt films were prepared through RF magnetron sputtering. To improve the depth resolution, the Pt film on the cathode was formed only at the periphery so that the ion beam was directly injected into the LiCoO₂ layer. The configuration of the sample was the same as that in previous studies,⁸ except for the anode, to specify the voltage against Li/Li⁺. Fe₂(MoO₄)₃ operates at 3.0 V vs Li/Li⁺ and works as a reference counter electrode without decomposing the LATP electrolyte.¹⁸ Thus, the voltage at the cathode vs Li/Li⁺ is determined by adding 3.0 V to the applied voltage between the electrodes.

First, measurements were performed at a fixed voltage of 2.8 V vs Li/Li⁺, which corresponded to the initial open-circuit voltage. The measurements for the sample with a 30-nm-thick LiCoO₂ cathode were then repeated at different voltages in the order of 4.2, 3.0, 4.2, 4.4, 4.6, 4.8, and 3.0 V. The measurements for the sample with a 60-nm-thick cathode were performed only at 2.8 and 4.2 V for comparison. All voltages were applied at a constant current of 1 μ A/cm². The measurements commenced 30 min after the target voltages were reached and were performed for a fresh surface at each voltage by changing the irradiation position to avoid the accumulation of irradiation damage.⁸ The Li distribution at the interface was of particular interest. To distinguish between the actual broadening of the Li distribution and the spectral broadening limited by the resolution, we also performed TOF-ERDA measurements for a sample with a Pt blocking layer approximately 40 nm thick inserted between the LiCoO₂ and LATP electrolyte because there was little Li penetration into the Pt blocking layer.

[Figure 2](#) shows a two-dimensional coincidence map of the TOF and energy of recoil and scattered ions obtained at 2.8 V. Distributions of different elements and isotopes, including ⁶Li, ⁷Li, O, Al, P, and Ti, in LiCoO₂ and LATP were observed separately. Note that the distributions of Co and Ge overlapped with the intense distribution of scattered Cu ions. To also examine Co and Ge, it might be beneficial to use heavier incident ions in the future. In addition, surface impurity atoms of H and C, possibly originating from atmospheric water and hydrocarbons, were observed. Cu ions scattered by the Pt electrode on the periphery were detected in low amounts from a small portion of the spread incident beam.

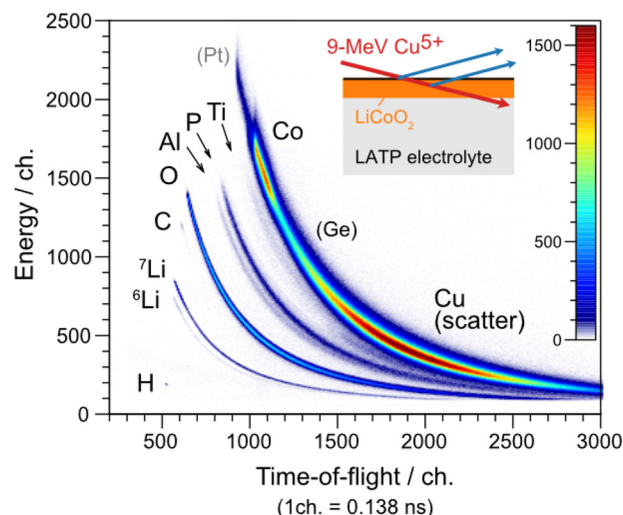


FIG. 2. Two-dimensional coincidence map of the time-of-flight and energy of recoil and scattered ions from the thin-film battery at 2.8 V vs Li/Li⁺ obtained using a 9-MeV Cu⁵⁺ beam. The data are merged for each of the eight channels and plotted as an image map.

The energy spectrum obtained by extracting the ⁷Li signals is shown in [Fig. 3\(a\)](#). To illustrate the advantage of TOF-ERDA, we present results obtained through conventional stopper-foil ERDA in [Fig. S2](#). Relative to the stopper-foil ERDA results, there is a drastic improvement in depth resolution in the TOF-ERDA. In addition, the H peak is separated. The corresponding TOF spectrum of ⁷Li is shown in [Fig. 3\(b\)](#). As the TOF is proportional to the inverse of velocity, the information obtained from the TOF spectrum is essentially the same as that obtained from the energy spectrum, except for the depth resolution. To compare the depth resolutions, the energy spectrum was reproduced from the TOF spectrum by transforming the horizontal and vertical axes, as superimposed in [Fig. 3\(a\)](#). The two spectra are almost identical, indicating that there is little difference in depth resolution between the energy and TOF spectra for the ⁷Li measurements under the present conditions.

The results for the sample with the Pt blocking layer are also plotted in [Figs. 3\(a\)](#) and [3\(b\)](#). The energy broadening at the topmost surface and at the LiCoO₂/Pt interface was evaluated using an error function.²¹ The FWHMs were obtained as 121 and 142 keV in the energy spectrum in [Fig. 3\(a\)](#). The energy broadenings correspond to thicknesses of approximately 12 and 14 nm, assuming a composition of LiCoO₂ having a density of 5.05 g/cm³. In addition, the energy broadening at the LiCoO₂/LATP interface was evaluated to be 12 nm, adopting the same procedure. The LiCoO₂/LATP interface thus had energy broadening roughly equivalent to that of the LiCoO₂/Pt interface, although the channel position at the interface slightly deviated, probably owing to a small difference in the LiCoO₂ thickness.

[Figure 4\(a\)](#) depicts the variation in the TOF spectra of ⁷Li with the applied voltage for the sample having a cathode thickness of 30 nm. The yields are normalized by the total counts from 900 to 1800 channels (129 to 253 ns) and plotted so that the initial height at the LiCoO₂ cathode is approximately unity. We confirm that this

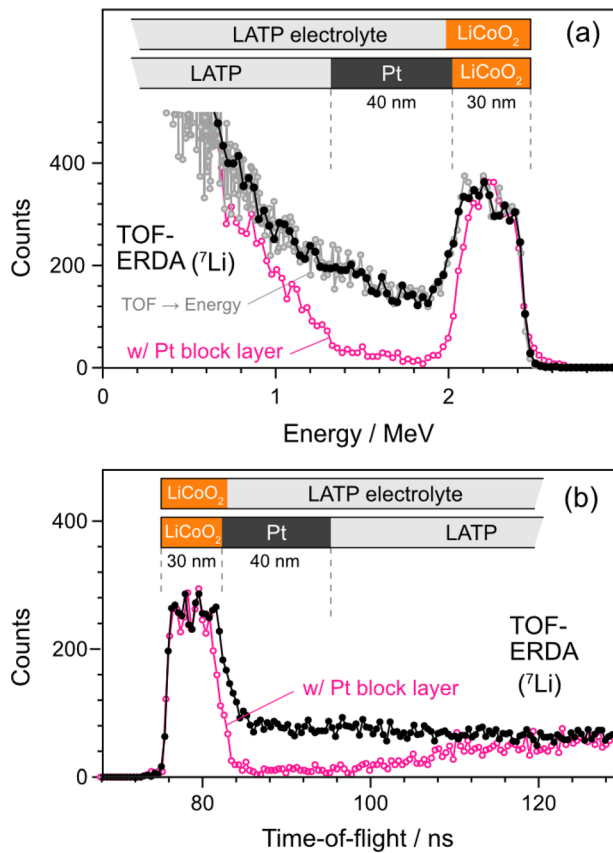


FIG. 3. (a) Energy and (b) time-of-flight spectra of ^7Li obtained by TOF-ERDA. The gray plots are the energy spectrum reproduced from the TOF spectrum. The magenta plots show the spectra obtained with the Pt-blocking layer. The energy scale was calibrated at the surface edge of the ^7Li .

normalization correctly aligns each height of the O, Al, and P spectra measured at different voltages. Note that there was no appreciable change due to the irradiation in the spectra during the measurement (see Fig. S3). It is clearly observed that the amount of ^7Li in the LiCoO_2 cathode changed upon charging/discharging. With charging at 4.2 V, the ^7Li intensity in the LiCoO_2 cathode decreased to approximately 30% of the initial intensity. At 4.2 and 4.4 V, there are small humps at the interface. A similar trend is observed in the results for the sample having the 60-nm-thick cathode, as shown in Fig. 4(b). This suggests that Li ions accumulate at the interface owing to the high resistance. In addition, a dip-like structure appears in the center of the cathode for the 30-nm cathode sample. While the underlying mechanism is unclear, the absence of this structure in the 60-nm cathode sample suggests that this phenomenon may be due to the use of an extremely thin film. The Li yield further decreased as the battery was overcharged to 4.8 V. Finally, when the battery was discharged to 3.0 V, the yield returned almost to the initial state. Meanwhile, no change in the distribution was observed inside the LATP electrolyte. Note that the lower yields in the higher channels were due to the non-linearity of the horizontal scale against the depth length; the Li density inside the LATP electrolyte was constant, regardless of the depth.

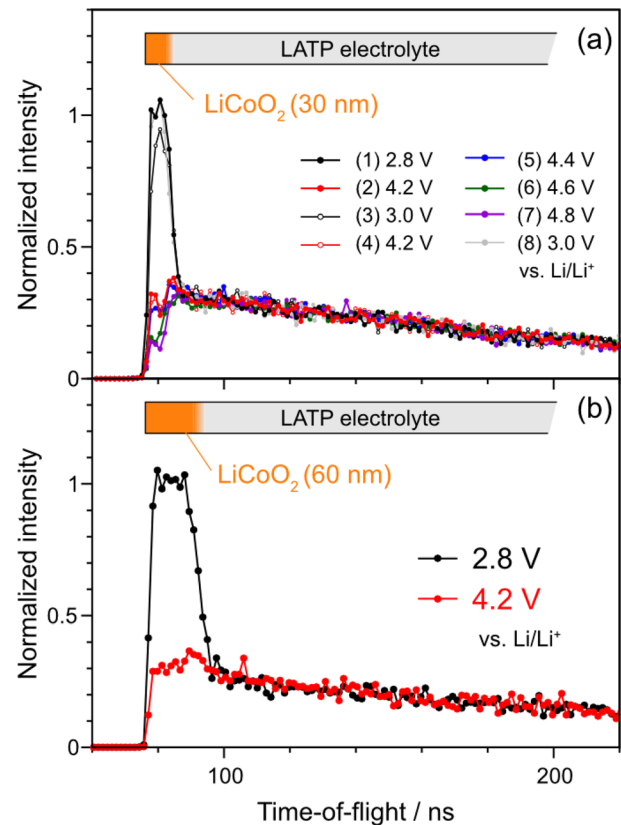


FIG. 4. TOF spectra of ^7Li obtained for different voltages of the batteries with a LiCoO_2 cathode thickness of (a) 30 and (b) 60 nm.

To examine the change in the Li depth profile more precisely, we analyzed the spectra using SIMNRA simulation software.²² Because SIMNRA reproduces energy spectra, the TOF spectra were first converted to energy spectra for fitting, as seen in Fig. 3(a). The composition of the LATP electrolyte was determined in advance by separately adopting Rutherford backscattering spectrometry (RBS) with 2-MeV He^+ and RBS/ERDA with 9-MeV O^{5+} for the LATP sheet itself. This gave a composition of $\text{Li}_{1.2}\text{Al}_{1.0}\text{Ge}_{0.8}\text{Ti}_{0.6}\text{P}_{2.6}\text{O}_{12}$. Note that the value for Al could have been lower because Al signals overlapped with the signals of other heavy elements in the RBS spectrum, and its accurate evaluation was therefore difficult. The Li density inside the LATP electrolyte thus determined was used as the reference for fitting the results of the battery sample. In the simulations, the compositions of elements excluding Li were fixed. The Li density was evaluated as a function of the depth by virtually slicing the sample into multilayers, each with a thickness of 60×10^{15} atoms/cm², excluding Li atoms. The thickness of LiCoO_2 was fixed at 300×10^{15} Co and O atoms/cm², corresponding to 32 nm.

The fitting results and the thus obtained Li density distribution are shown in Fig. 5. According to the stoichiometric ratio of LiCoO_2 , the Li density in each virtual layer of the cathode should be 20×10^{15} atoms/cm². However, the initial Li density at 2.8 V was found to be 0.8–0.85 times that value. This discrepancy might be due to the formation of Co_3O_4 in the cathode film. It has been reported that Li in

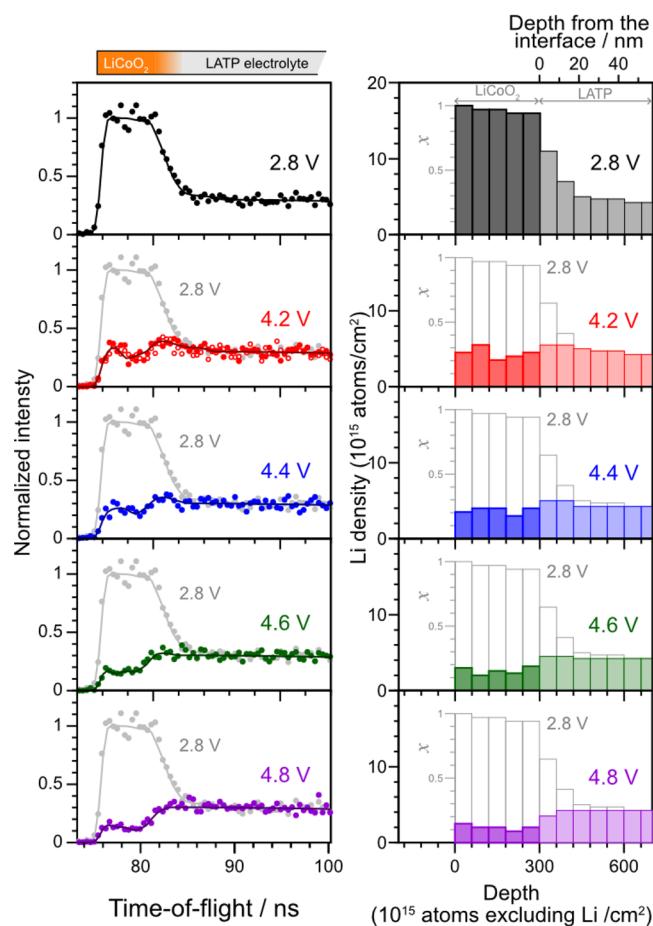


FIG. 5. (a) Fitting results of the ^7Li TOF spectra obtained using SIMNRA software. Experimental data were normalized using the same procedure as in Fig. 4. (b) Li density distribution evaluated by the fitting. The depth is expressed by the atomic density, excluding Li.

LiCoO_2 moves to the LATP electrolyte upon contact,³ which seems consistent with the present results. The Li concentration x in the Li_xCoO_2 ranged from 0.21 to 0.33 at 4.2 V when we assume $x=1$ at the initial state (2.8 V) in each virtual layer. Although there is a large scatter in the intensity of the raw spectra, on average this range seems slightly lower than the value of ~ 0.45 obtained from electrochemical measurements for bulk samples.^{23,24} Although we do not currently understand the cause of this difference, the difference itself suggests that nano-thin films behave differently. The Li density does not change in the LATP electrolyte deeper than 20 nm from the interface. Therefore, it is reasonable to say that the Li-deficient region, if it exists, is within 20 nm from the interface as estimated in the calculations.^{3,25}

In summary, we recently constructed a TOF-ERDA system optimized for quantitative operando measurements of Li depth profiles in thin-film all-solid-state Li-ion batteries with high-depth resolution. Variations in Li depth profiles in the LiCoO_2 cathode and the $\text{LiCoO}_2/\text{LATP}$ electrolyte interface with charging/discharging were obtained. Relative to conventional stopper-foil ERDA, an appreciable improvement in depth resolution was achieved. Quantitative evaluation of the

Li composition showed that approximately 15%–20% of the Li was initially depleted from the LiCoO_2 cathode. It was shown that a slight Li accumulation may have occurred at the interface after charging. It was confirmed that there was no change in Li density during charging and discharging inside the LATP electrolyte deeper than 20 nm from the interface. We expect that TOF-ERDA will be a fundamental technique for quantitatively investigating the nanoscale Li behavior inside electrodes and around the interfaces of thin-film batteries.

See the [supplementary material](#) for the detection efficiencies of the time detectors of the TOF-ERDA system, the results of the stopper-foil ERD, and the variation in the TOF spectra during the measurement.

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AUTHOR DECLARATIONS

Conflict of Interest

The authors have no conflicts to disclose.

Author Contributions

T. Majima: Conceptualization (lead); Data curation (lead); Formal analysis (lead); Funding acquisition (lead); Investigation (lead); Methodology (equal); Project administration (lead); Resources (equal); Visualization (lead); Writing – original draft (lead); Writing – review & editing (lead). **Y. Ogura:** Data curation (supporting); Formal analysis (supporting); Investigation (supporting). **C. Hasegawa:** Data curation (supporting); Formal analysis (supporting); Investigation (supporting). **S. Nakamizo:** Data curation (supporting); Formal analysis (supporting); Investigation (supporting). **B. Tsuchiya:** Funding acquisition (supporting); Methodology (supporting). **K. Amezawa:** Conceptualization (supporting); Funding acquisition (supporting); Methodology (supporting); Resources (supporting). **Y. Iriyama:** Conceptualization (supporting); Funding acquisition (supporting); Investigation (supporting); Methodology (supporting); Project administration (supporting); Resources (equal); Writing – review & editing (supporting). **K. Yasuda:** Conceptualization (supporting); Data curation (supporting); Formal analysis (supporting); Funding acquisition (supporting); Investigation (supporting); Methodology (equal); Project administration (supporting); Resources (supporting); Writing – review & editing (supporting).

DATA AVAILABILITY

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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