



# Quantitative lithium mapping of lithium-ion battery cathode using laser-induced breakdown spectroscopy

Susumu Imashuku<sup>a,\*</sup>, Hiroyuki Taguchi<sup>a</sup>, Toru Kawamata<sup>b</sup>, Shun Fujieda<sup>b</sup>, Shunsuke Kashiwakura<sup>a</sup>, Shigeru Suzuki<sup>b</sup>, Kazuaki Wagatsuma<sup>a</sup>

<sup>a</sup> Institute for Materials Research, Tohoku University, 2-1-1 Katahira, Aoba-ku, Sendai, 980-8577, Japan

<sup>b</sup> Institute of Multidisciplinary Research for Advanced Materials, Tohoku University, Katahira, Aoba-ku, Sendai, 980-8577, Japan

## HIGHLIGHTS

- Quantitative lithium distribution of Li-ion battery cathode by LIBS.
- Calibration curve is improved by performing LIBS measurements in 1000 Pa argon.
- LIBS measurement can detect a decomposition product of electrolyte, LiF.
- Lithium distribution of the cathode is acquired by laboratory-scale measurement.

## ARTICLE INFO

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## ABSTRACT

A method to obtain the quantitative lithium distribution of a lithium-ion battery cathode using laser-induced breakdown spectroscopy (LIBS) measurements is proposed. We perform LIBS measurements in a reduced argon atmosphere of 1000 Pa and use a calibration curve obtained by measuring the emission intensities at 610.4 nm of standard samples, whose atomic ratios of lithium to cobalt are 0, 0.10, 0.30, 0.51, 0.62, 0.80, and 0.99. The lithium distributions of cycled cathodes, which contain LiCoO<sub>2</sub> as an active material, obtained by this method are relatively consistent with the Co(III) distributions obtained by X-ray absorption spectroscopy (XAS). XAS is the conventional method to quantitatively display the reaction distribution of a cathode material used in a lithium-ion battery. Additionally, LIBS can detect the precipitating decomposition products of the electrolyte, LiF, on the cathode. However, the precision of the lithium ratio using LIBS is not as good as that achieved for the Co(III) ratio obtained using XAS. Therefore, LIBS is suitable to obtain a semi-quantitative lithium distribution in a cathode of a lithium-ion battery through a much simpler procedure than XAS. Furthermore, LIBS has an advantage to detect the decomposition product of the electrolyte using laboratory-scale measurements.

## 1. Introduction

Lithium-ion batteries are used worldwide in portable devices such as laptop computers, cell-phones, and digital cameras. They have also recently been applied to large-scale devices like electric vehicles and stationary electric energy storage systems. A higher charge–discharge rate capacity is demanded for lithium-ion batteries to be more widely applicable in large-scale devices [1–4] because they require a high power output and a rapid charge–discharge cycle. However, a non-uniform reaction distribution on the cathodes hinders this demand from being satisfied [4–12]. Thus, a major challenge is to prevent the non-uniform reaction distribution of the cathodes at high charge–discharge rates. The establishment of an analytical method to quantitatively

visualize the reaction distribution of the cathode has played an important role in overcoming this challenge. Several techniques have been proposed for the visualization of the reaction distribution of the cathode: Raman spectroscopy [13,14], X-ray absorption spectroscopy (XAS) [4,6–9,15–23], X-ray diffraction (XRD) [5,24], laser-induced breakdown spectrometry (LIBS) [10,25–29], X-ray tomography [30], atomic force microscopy (AFM) [31], particle induced  $\gamma$ -ray emission (PIGE) [32], neutron depth profiling [33], and electron forward scattering diffraction (EFSD) [34]. Among these techniques, LIBS is one of the most straightforward analytical methods to visualize the reaction distribution of the cathode. LIBS is an analytical technique to acquire an optical spectrum emitted from atoms evaporated from a sample as a result of the irradiation of a pulsed laser with a high power density. The

\* Corresponding author.

E-mail address: [susumu.imashuku@imr.tohoku.ac.jp](mailto:susumu.imashuku@imr.tohoku.ac.jp) (S. Imashuku).

light emission occurs during the deexcitation of the evaporated atoms in a plasma formed by the pulsed laser irradiation. LIBS can be performed in a laboratory (does not require large-scale facilities such as a synchrotron radiation facility) without any pretreatment of the sample; however, LIBS is a destructive analysis and is difficult to carry out *in situ*. Additionally, LIBS measurements are not restricted by the shape and thickness of the sample. LIBS can directly detect signals from lithium, that is, light associated with the deexcitation of lithium atoms, unlike XAS, Raman spectroscopy, XRD, X-ray tomography, AFM, and EFS. D.

Previously reported lithium distributions of cathodes measured by LIBS were qualitative [5,25–29] because the measurement samples were exposed to ambient pressure. Under the measurement conditions, light emitted from lithium atoms suffers a strong self-absorption effect, that is, the reabsorption of the emitted luminescence by atoms in their fundamental electronic levels in the plasma and located in the colder external part of the plasma [35]. As a result, the intensity of the light emitted from lithium atoms is reduced and does not linearly correspond to the lithium concentration in the cathodes, especially at high lithium concentrations [5]. Thus, it is difficult to obtain the quantitative lithium distribution by ambient pressure LIBS measurements even though standard samples are used [26–28]. Therefore, the reduction of the self-absorption effect is essential to obtain quantitative lithium distributions of the cathode by LIBS. One way to solve this problem is to carry out LIBS measurements in an argon atmosphere. Fabre et al. reported that sweeping samples with an argon flow improved the intensity of the emission lines of lithium in the LIBS measurement of geological materials containing lithium [35]. It has also been reported that the self-absorption effect was buffered under a reduced pressure [36,37].

In this paper, we establish a method to quantitatively acquire the lithium distribution of the cathode of a lithium-ion battery by performing LIBS measurements in a reduced argon atmosphere. Subsequently, we examine the advantages of this method by comparing it with XAS, which is a widely-used technique for visualizing the reaction distribution of the cathode of a lithium-ion battery. We select  $\text{LiCoO}_2$  as an active material in the cathode because it is one of the most widely-used active materials in lithium-ion batteries.

## 2. Experimental

The experimental set-up of the LIBS system is shown in Fig. 1. The laser used in the present study was a Q-switched Nd: YAG laser (LOTIS TII, LS-2137) with a wavelength of 532 nm. The energy and duration of the pulsed laser irradiated on the samples were 20 mJ/pulse and 16–18 ns, respectively. A single pulse from the laser was shot onto the samples for each measurement point. The laser was focused on the sample surface using a plano-convex lens with a focal length of 150 mm. The light emitted from the plasma was collected, using a plano-convex lens with a focal length of 100 mm, through an optical fiber to a spectrometer system consisting of a spectrograph and an ICCD detector. We

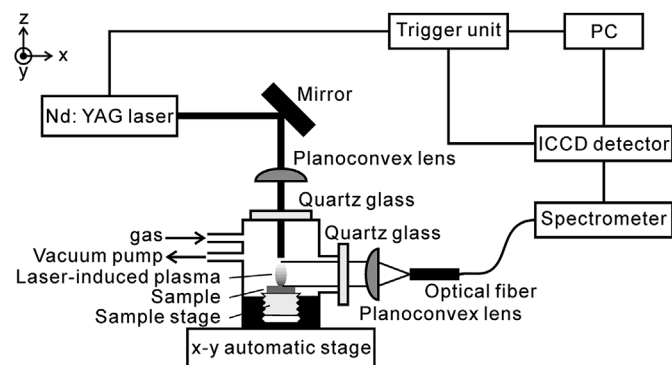


Fig. 1. Schematic illustration of the LIBS system.

used two types of spectrometer systems for the LIBS measurement. A spectrometer system consisting of an Echelle-type spectrograph (ME5000, Andor Technology Ltd., Belfast, UK) and an ICCD detector (DH734-18F, Andor Technology Ltd., Belfast, UK) was used to determine the analytical line of lithium because the spectrometer system could collect spectra over a wide wavelength range (200–895 nm). After determining the analytical line of lithium, a spectrometer system consisting of a Czerny-Turner spectrograph (MS 7504i, SOL instruments Ltd., Minsk, Belarus) and an ICCD detector (DH334T-18F-03, Andor Technology Ltd., Belfast, UK) was used because of its high sensitivity but narrow wavelength range (13.3 nm). The gate of the ICCD detectors was triggered by the laser and the relative delay was controlled by the digital delay generator integrated in the ICCD detectors. The gate width and the relative delay were set to 20  $\mu\text{s}$  and 800 ns, respectively. The samples were placed in a chamber, which enabled the atmosphere to be controlled by introducing gas and the connection of a rotary pump. The pressure inside the chamber was monitored using a Pirani gauge. The analyzed positions of the sample in the x and y directions were controlled by placing the chamber on linear transition automatic stages. The height of the samples was adjusted by rotating the sample stage connected to the chamber with a screw.

We chose  $\text{LiCoO}_2$  as the active material in the cathode. Before LIBS analysis of the cathode, we first measured the emission intensities of standard samples, whose atomic ratios of lithium to cobalt ( $X$ ) were 0, 0.01, 0.10, 0.30, 0.51, 0.62, 0.80, and 0.99, by LIBS to determine the analytical line of lithium and obtain a calibration curve for the quantitative analysis of lithium. The standard samples apart from  $X = 0$  were prepared by a solid state reaction of lithium carbonate ( $\text{Li}_2\text{CO}_3$ ) (purity: 98.0%, Nacalai Tesque, Inc., Kyoto, Japan) and cobalt oxide ( $\text{Co}_3\text{O}_4$ ) (purity: 99.9%, Kojundo Chemical Laboratory Co., Ltd., Saitama, Japan) powders. The raw materials were mixed at various mix ratios with an agate mortar and then heated at 1173 K for 20 h in air. The obtained powders were pressed into pellets at 500 MPa. The standard sample with  $X = 0.99$  was confirmed to be a single phase of  $\text{LiCoO}_2$ , while the standard samples with  $X = 0.01, 0.10, 0.30, 0.51, 0.60,$  and  $0.80$  were shown to be a mixture of  $\text{LiCoO}_2$  and  $\text{Co}_3\text{O}_4$  by X-ray diffraction using the  $\text{Cu-K}\alpha$  line (Ultima IV, Rigaku Corporation, Tokyo, Japan). We used  $\text{Co}_3\text{O}_4$  as the standard sample with  $X = 0$ . The compositions of the standard samples apart from  $X = 0$  were measured by inductively coupled plasma atomic emission spectroscopy (ICP-AES) (IRIS Advantage DUO, Thermo Fisher Scientific, Inc., Waltham, Massachusetts, USA).

The cathode material was prepared by mixing  $\text{LiCoO}_2$  powder (purity: 99.8%, Sigma-Aldrich Co. LLC, Missouri, USA), acetylene black, and polytetrafluoroethylene at a weight ratio of 14:5:1. The mixture was stretched into a sheet with a thickness of approximately 100  $\mu\text{m}$  using an agate mortar. The cathode was cut into a disk with a diameter of 10 mm from the sheet and dried at 353 K. A lithium-ion battery cell was assembled using the cathode, Li foil with a diameter of 15 mm (Honjo Metal Co., Ltd., Osaka, Japan) as the anode, polyethylene film as the separator, and 1 mol  $\text{dm}^{-3}$   $\text{LiPF}_6$  dissolved in a mixed solution of 50 vol% ethylene carbonate and 50 vol% dimethyl carbonate (KISHIDA CHEMICAL Co., Ltd., Osaka, Japan) as electrolyte (Fig. 2). The assembly process was carried out in an argon-filled glove box, where the dew point of water and the concentrations of were controlled at less

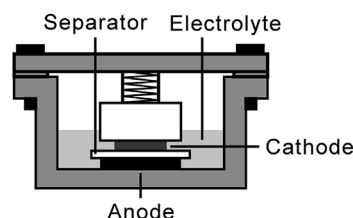


Fig. 2. Schematic illustration of the assembled lithium-ion battery cell.

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