



Distinction of impedance responses of Li-ion batteries for individual electrodes using symmetric cells



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ABSTRACT

Symmetric cells were prepared with a newly designed separable cell module, which enabled ca. 70 mm by 70 mm electrode sheets to be used for a pouch type 5 Ah class Li-ion battery (LIB). Impedance analysis of the LIB as a full cell state was successfully performed with electrochemical parameters obtained by an impedance analysis of symmetric cells of anodes and cathodes obtained from the operated Li-ion batteries. While the charge transfer resistance of the cathode was found to increase after reassembling the cells symmetrically, other electrochemical parameters were found not to change when comparing the values obtained for full cells with symmetric cells. Electrodes degraded by charge/discharge cycling of the battery were also investigated, and the parameter change caused by the degradation was confirmed.

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1. Introduction

The Li-ion battery (LIB) is now produced in large quantities because of its high performance characteristics achieved in 1991. It is used as the energy supply for portable electric equipment (e.g., cellular phones and portable computers), and will be used as an energy source of electric vehicles (EVs). In order to enhance the cruising distance of EVs, battery performance is requested to be improved; thus, new materials have been proposed and examined to increase their power and the capacity as well as the lifespan. To understand the mechanism of electrode reactions and the fading capacity of the cell, efforts have been made by various groups to improve battery performance [1–4]. Electrochemical impedance spectroscopy (EIS), which enables us to classify the elemental steps by the time constant and to evaluate the values of the electrochemical parameters, is one of the useful methods to evaluate the electrochemical reaction without a large disturbance in the electrochemical system. EIS was applied for the fundamental analysis on the reaction of active material for LIB using a half cell [5,6], and for the investigation of an internal impedance change on a full cell of LIB [7,8]. EIS on a full cell of LIB has a merit to its application due to

the negligibly small perturbation to be applied to the cell without change in the charged state of the cell and the opportunity to investigate with or without the interruption of a continuous operation of the LIB. The impedance response from the full LIB cell is composed of responses from each component in the LIB cell. LIBs equip a set of two kinds of electrodes and electrolytes with separator and current collectors, which are sometimes wound in a spiral shape, and current lead tubs. In order to identify the time constant of individual responses other than through the full cell impedance and the adequate equivalent circuit for analysis, it is necessary to discuss the electrochemical parameters for each individual, elemental step in the full cell by analyzing the full cell impedance. We have proposed an equivalent circuit for an analysis of the LIB and reported the change in impedance response with numerically-fitted electrode parameters on degraded LIB with a fading capacity [9,10] based on assumptions about the time constant of impedance responses with a discussion on electrode reaction from previous literature [11]. Also, the technique to enhance the LIB impedance with a shift in the time constant by temperature control was proposed in order to analyze the smaller impedance of a larger scale LIB [12]. Further improvements on LIBs for a high-power output with a high capacity will lead to a decrease in the internal impedance of LIBs. In addition, the value of the impedance of the anode tends to be smaller than that of the cathode, causing a difficulty in distinguishing the impedance response of each electrode whose time constants are not far from each other. In order to understand and analyze the impedance responses of LIBs, half cells of the anode or the cathode with reference electrodes have been investigated [5,6]. On the other hand, the introduction of the reference electrode into a large,

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commercial LIB will be difficult due to the narrow gap between the electrodes, which is important for a high-power output without interruption of the current distribution vertical to the electrode plane. The interrupted current distribution and non-uniformity of the gap between electrodes may lead to a heterogeneous reaction in the electrodes. One of the solutions to obtain the impedance response of each electrode without the introduction of a reference electrode is to use the symmetric cell. Chen et al. examined the symmetric cells with small pieces of anodes and cathodes taken from large sheets of an electrode to fabricate a 18650-sized LIB [13–15]. Two pieces sampled from electrode sheets were placed parallel to each other in an electrochemical two-electrode cell, and EIS was adopted to obtain the impedance of two electrodes connected in series. They examined the impedance change of the electrodes by varying the storage time in the cell. The EIS analysis of the whole electrode sheet was reported in detail by Illing et al. [16] They estimated the time constants of each reaction in full cell by using symmetric cells of anodes and cathodes with DRT method. An EIS study on a whole sheet of an LIB instead of a small, sampled piece of an electrode has more practical information, since a large LIB electrode is considered to contain a non-uniform degradation. Experimental and simulated current distribution in electrochemical cells was reported [17,18]. Such uneven currents led to the heterogeneous state of degradation in an electrode sheet. Although the careful sampling method developed will clarify the degradation state of each section of the electrode sheet, precise studies on whole LIB electrode sheets will reveal information about electrochemical parameters for an entire electrode, even if the information were averaged to represent the whole electrode.

We developed a separable cell, which consisted of two electrode sheets 70 mm x 70 mm in size that were compatible to configure a 5 Ah class pouch type LIB cell, mounted it in electrode holders with 10 mm separation of electrodes, and enabled to change electrodes between electrochemical measurements. In this study, the electrochemical impedance of symmetric cells of cathodes and anodes were analyzed and compared with that of full cells of the anode and the cathode. The obtained fitting data from the symmetric cells were utilized to analyze the impedance response of a full cell. Furthermore, LIB electrode sheets degraded by continuous charge/discharge cycling of full cells were investigated.

2. Theoretical background

The impedance of the electrochemical system with two electrodes soaked in an electrolyte is considered to be expressed the serial connection of each element having individual impedance, with a reasonable assumption of linearity in the system. Thus, the total impedance of the whole cell is shown as a sum of the impedance components for the electrodes and electrolyte with some residual, electrical impedance related to the lead cables connected from the outside of the electrochemical cell to the sites of electrochemical reactions. Here, the impedance of an electrochemical system, (i), equipping electrode, (1), electrode, (2), an electrolyte solution with a separator, and current leads are shown in Eq. (2.1), which represents a connection of each component in the series.

$$Z_{i, \text{whole}} = Z_e + Z_{\text{sol}} + Z_{i,1} + Z_{i,2} \quad (2.1)$$

Where, Z_e equals the residual electric impedance, Z_{sol} equals the impedance of the electrolyte, and $Z_{i,n}$ equals the impedance of the electrode (n) (n = 1, 2).

Thus, the impedance of a whole LIB cell (m), which has an anode and a cathode, is expressed as:

$$Z_{i, \text{whole}} = Z_e + Z_{\text{sol}} + Z_{m, \text{anode}} + Z_{m, \text{cathode}} \quad (2.2)$$

While the three-electrode cell with a reference electrode conventionally used in the electrochemical methods with a

potentiostat/galvanostat is controlling the system, the two-electrode system is considered to be impossible to realize the electrochemical reaction of each electrode. A symmetric cell, which equips a set of two identical electrodes in the two-electrode system with a configuration of electrodes and an electrolyte in a line/plane symmetric location, has a unique feature. The impedance of the symmetric cell (i) fabricated with two identical electrodes is expressed as:

$$Z_{\text{symm-i, whole}} = Z_e + Z_{\text{sol}} + Z_{i, \text{identical-1}} + Z_{i, \text{identical-2}} \quad (2.3)$$

Here, in the case when two identical electrodes were used in the electrochemical cell,

$$Z_{i, \text{identical-1}} = Z_{i, \text{identical-2}} = Z_{i, \text{identical}} \quad (2.4)$$

And the equation (2.3) will be expressed as (2.5)

$$Z_{\text{symm-i, whole}} = 2(1/2 Z_e + 1/2 Z_{\text{sol}} + Z_{i, \text{identical}}) \quad (2.5)$$

In this study, the equivalent circuits for the LIB cell components shown in Fig. 2 were used according to our previous study described below. In this study, the electrolyte impedance is represented by a simple resistor without the capacitance between the two electrodes, which is due to the geometric configuration of two electrodes sandwiching the electrolyte solution, since the space between the electrodes has a negligibly low capacitance. The residual impedance of the electric pathway is represented by an inductor and resistor connected in parallel according to our previous study. For both anodes and cathodes, an equivalent circuit with two components connected in series was considered, in a similar way to previous literature [19,20]. One component of Randles circuit equipped with a Warburg impedance represents the Faradaic reaction site, while another set of capacitors and resistors connected in series was introduced. The Randles impedance for an LIB electrode is considered to appear in the frequency region of 100–1 Hz according to previous literature [9]. In the anode layer, solid electrolyte interphase (SEI) was reported to form after the initial charging process in LIB and to grow during continuous cycling or storage of LIB [21–23]. In SEI, Li^+ is transferred between the electrolyte solution and the surface of graphite particles by migration, and the Li^+ transfer is represented as a simple register. Meanwhile a capacitance of the SEI layer appeared under a gradient of applied voltage. Some researchers also reported a change in the SEI-like layer on the cathode material during the charge/discharge cycling [24,25]. In addition, resistance and capacitance would exist between the current collector and the layer of the anode or cathode [26,27]. Inside the layer of the anode or cathode, despite the addition of conducting particles to the cathode layer, the mixture of active material, the conducting additive, and binder polymer would all have a resistance and capacitance when forming percolation electrical pathways.

3. Experimental

A full pouch-type LIB cell fabricated in a dry room maintained a dew point below -50°C in the laboratory used in this work. The full LIB cell was composed of a carbon anode with a capacity of 1.6 mAh cm^{-2} , and a LiCoO_2 cathode with a capacity of 1.5 mA cm^{-2} with the electrode areas of 49.00 cm^2 and 46.24 cm^2 for anode and cathode, respectively, after being dried in a vacuum at 120°C for 2 hours. The electrolyte used was 1.0 mol dm^{-3} LiPF_6 in a 1:1 mixture of ethylenecarbonate (EC) and diethylecarbonate (DEC) containing less than 20 ppm of H_2O in a separator (Cellgard 2500) without any additives.

The pouch-type cells were charged and discharged in 2 initial cycles between 3.0 and 4.2 V at a rate of 0.1 C (7.0 mA) as the aging process to stabilize the cell performance, and were maintained at

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