New Analysis of Electrochemical Impedance Spectroscopy for Lithium-ion Batteries

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ABSTRACT:

First of all, we express our deepest sympathies for the passing of Professor Su-Moon Park. In the present paper, an electrochemical impedance spectroscopy (EIS), which Professor Su-Moon Park also used frequently for the investigation of electroconducting polymer, is introduced as a recent evaluation tool for a commercially available lithium-ion battery (LIB). The paper surveys how to design equivalent circuits while explaining physical and chemical phenomena in the LIB and how to get more accurate impedance spectra with varying the measuring temperatures. Additionally, a square current EIS (SC-EIS) technique, which we have suggested, is introduced for the larger LIB system as a promising technique for the future.

Keywords: Electrochemical impedance spectroscopy, Lithium-ion battery, Equivalent circuit

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1. Introduction

Today, the economic growth in China and India leads motorization in the countries. The motorization accelerates the crises of fossil fuel shortage and environmental destruction. Therefore, the widespread use of green vehicles in the future is a necessity. In addition, renewable energies such as solar power and wind power, whose energy generation depends on weather of the area, have been introduced to reduce CO₂ emission. In Japan, unfortunately, the FUKUSHIMA atomic power plant disaster occurred on March 11, 2011 due to an earthquake and tsunami. Consequently, the industries were dealt a serious blow by a lack of electric power. Because of this, the introduction of the renewable energies has been accelerated.

Under the circumstances, energy efficient devices have become one of the most important devices because green vehicles, such as hybrid electric vehicles (HEV), plug-in hybrid vehicles (PHEV), battery

electric vehicles (BEV), and even fuel cell electric vehicle (FCEV), mount batteries. Also, solar power and wind power plants require batteries, in which the power leveling are demanded to stabilize electrical power systems. In order to operate the batteries in those systems, an understanding of the state of batteries, such as the state of charge (SOC) of batteries and state of health (SOH), is very important for effective and safe operation of the batteries. Therefore, a non-destructive analysis of the condition is in high demand for the premonitory diagnosis of the on-board batteries of electric vehicles, and of installed batteries in load leveling systems.

Electrochemical impedance spectroscopy (EIS), in which a small-amplitude sinusoidal potential perturbation is applied to a cell, is one of the most powerful tools for the non-destructive analysis of energy devices such as lithium-ion batteries (LIB)¹⁻⁴ and fuel cells.^{5,6} We investigated electrochemical reactions by means of the EIS. The first stage of our work on the EIS focused on electrochemical reactions of electroconducting polymers.⁷⁻¹⁰ At the same time, Professor Su-Moon Park also investigated electroconducting

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polymers by means of the EIS.^{11,12} In addition, Professor Su-Moon Park¹³⁻¹⁵ and our team^{9,16,17} worked in the same field of electroconducting polymers prior to working on the EIS. Thus, Prof. Su-Moon Park and our team encouraged each other in the same field, contributing to the progress of electroconducting polymers and EIS. It is extremely unfortunate that Prof. Su-Moon Park has passed away. We introduce the recent impedance analysis on LIB while expressing our deepest sympathies for his passing.

2. Impedance analysis for lithium-ion batteries

2.1 Equivalent circuit design for EIS on LIB

In order to understand and to analyze the impedance response of the LIB, it is essential to use a proper equivalent circuit (EC) designed with the understanding of each step of the overall battery reaction. By considering the interfaces and layers in the battery, an EC having a large number of elements can be assembled, while using the EC with a large number of elements makes it difficult to obtain meaningful information by the numerical fitting method. It is important to select an EC which represents features and changes in important physical phenomena or in the state of battery components with the minimum number of elements.

Firstly, EC 1 was designed according to the literature.¹⁸⁻²⁰ The electrochemical reactions of both the cathode and anode were expressed with a parallel connection of interfacial capacitance and connected charge transfer resistance with Warburg impedance in series. The EC also contains a resistance of electrolyte and an inductive component, which consists of inductors and resistors (L and R_l) related to the wiring between the paste of electrodes attached to the current collector and the measuring equipment, including the wounded current collector.

Secondly, EC 2 was designed with a basic idea of variation in diffusion length of Li^+ in the active material in the cathode. For simplicity, two typical diffusion elements were considered to represent a model having two types of active materials with two different radii. Two sets of series connection of diffusion elements and charge transfer resistances should be connected in parallel with a capacitance between the electrolyte and the electrical connection between particles. The variation of the capacitance in the particles is

represented as the constant phase element (CPE).²¹ The capacitors for the particles with both radii are connected in parallel and simplified as one CPE.

In order to consider the component of SEI, Li^+ was assumed to move in SEI by migration. The impedance component representing the SEI was made as a parallel connection of resistance and the capacitance of the SEI layer. In the EC 3, the component of SEI was introduced in addition to the EC 2.

In all the spectra obtained in the work, three domains were visually separated into a region of loci in the 1st quadrant, regions of superposition of arcs or semicircles, and loci of increase in the imaginary components, with frequency regions of 100-10 kHz, 10 kHz to 100 mHz, 100-0.1 mHz, respectively. Fig. 1 shows plots of impedance values calculated with ECs 1-3 after the data fitting for the impedance data obtained at SOC = 50%.

Using the EC 1, data fitting was examined and the result was shown in Fig. 1(a). Without the idea of variation in diffusion parameters in the cathode, the 45° inclined loci and the rise in the vertical direction could be expressed in the complex plane in the frequency region lower than 100 mHz. This is possible due to the existence of diffusion components in both the cathode and the anode; although, the feature of the arc in the low frequency region was absent in the calculated impedance shown in Fig. 1(a).

Using both ECs 2 and 3, all the calculated values of impedance were plotted closed to the experimental results, while using EC 1, a small neck-like feature could be observed in the loci of the calculated value in the center of the middle frequency region. Using the EC 3 the data fitting was successfully done with high accuracy.

The fitting errors, i.e., the absolute value of the difference between the fitting complex impedance and the experimental complex impedance, are illustrated in Fig. 2. By the introduction of the idea of variety of cathode particle size, the errors in the fitting decreased in the frequency region below 1 Hz. In the frequency region between 100 Hz and 1 Hz, the errors decreased by the contribution of the SEI component in the EC. In the frequency region below 0.1 Hz corresponding to the impedance response for the diffusion step, the error range increased even using the EC 3, which may be due to the scattered experimental data caused by the small signal input to the analyzer. The EC 3 enables to maintain the fitting error below 0.5 mΩ, which is

Fig. 1. Equivalent circuits used in this study and data fitting results using the circuits. Impedance of the LIB was measured at an SOC of 50%, a frequency range of 100 kHz–0.1 mHz, and a signal amplitude of 10 mV. Symbols of the equivalent circuit are expressed as follows: L represents the inductance of the current collector and battery case; R_i , the resistance of the current collector; R_s and R_F , the resistance of an electrolyte and the SEI, respectively; R_A and R_C , the charge transfer resistance of an anode and cathode, respectively; CPE_F , the constant phase element of SEI; CPE_A and CPE_C , the constant phase element of an electrode surface layer on an anode and cathode, respectively; and W_A and W_C , which represent the Warburg impedance for finite diffusion. The cathode component, including components of two particle size, is composed of R_{C1} and R_{C2} , the interfacial resistance, and W_{C1} and W_{C2} , the Warburg impedance for finite diffusion. This data was reproduced from the data published in ref.¹

almost two orders of magnitude lower than the radius of the semicircles. From the discussion on the fitting error, the data analysis using EC 3 is expected to be a tool to investigate the failure mechanism and/or the state of health of the LIBs.

2.2 Evaluation technique for EIS

In order to accurately analyze LIBs with low impedance, enlargement of the small impedances and shifting of the overlapping frequency domains are considered to be a solution. The values of resistance and interfacial capacitance are the main electrochemical parameters discussed in the EIS. As the mass transfer of charged carrier has a strong negative correlation with temperature, increases in the resistance of LIB at

low temperatures have been reported in the literature.^{22,23} Thus, in order to distinguish each response of elemental steps in an LIB reaction, an expansion of the impedance of LIB was examined by lowering the temperature. Ac impedance spectra acquired under the temperature range between -20°C and 20°C were compared and analyzed.

The Nyquist plots obtained from the LIB with an SOC value of 50% at various temperatures are shown in Fig. 3. All the impedance loci were revealed to have plots in the fourth quadrant in the high frequency region, which had minus values in “ $-Z'$ ”, indicating the existence of an inductive component of the outer lead,¹ and overlapping semicircles in the lower frequency region. At 20°C , two semicircles, one relatively small

Fig. 2. Residual errors for the impedance data shown in Fig. 1. The error was calculated as the distance between the experimental data and the calculated value in a complex plane for each frequency. This data was reproduced from the data published in ref.¹

Fig. 3. Nyquist plots obtained by electrochemical ac impedance for a lithium-ion battery at 20, 0, -5, -10, -15, and -20°C. Each parallel line shows 0 Ω of $-Z''$ at each temperature. The inset is the magnified Nyquist plots at 20°C. This data was reproduced from the data published in ref.²

and the other relatively large, were observed at the higher and the middle frequency region, respectively, as in other reports.^{1,3,19,24,25} However, remarkably, another semicircle appeared at the higher frequency region below 0°C by focusing carefully on the plots, and the size of the new semicircle was observed to increase with the two others by decreasing the temperature of the LIB, T . Namely, the semicircle at the higher frequency, which was not visibly detected at T of the room temperature, is considered to be apparently detectable by setting T at low temperatures. This is one of the techniques to analyze impedance precisely.

2.3 Square current electrochemical impedance spectroscopy

As mentioned above, we have investigated EIS and verified effectiveness of EIS in electrochemical reactions.^{1-12,17,25-28} The conventional EIS measured by a frequency response analyzer (FRA) and potentiostat system is a powerful tool to check the state of LIBs (i.e. SOC and SOH). Meanwhile, the internal resistance of an LIB cell has been decreasing with an increase in the capacity of LIB for vehicles and grids. Fig. 4 shows the relationship between the internal resistance and capacity of LIB cells. As can be seen, the internal resistance of LIB cells reached about 1 mΩ, which is roughly equal to the value of a contact resistance between golds. The low internal resistance of an LIB cell makes it difficult to measure the impedance of the LIB cell through the conventional EIS measuring system. This is because a very low internal resistance makes it difficult to create a fine waveform for not only the input but also the output due to the limitations of the FRA and potentiostat system. For

Fig. 4. Impedance of the real part of LIBs with various capacities, measured between 1000 and 1 Hz.

Fig. 5. Schematic illustration of the difference between a conventional EIS system and the SC-EIS system on a grid.

that reason, we focused on the power controller of the LIB system, which includes a battery management system (BMS), to create a signal for analyzing the state of the batteries. Furthermore, this system can operate without the FRA, which is too expensive of a system to be widespread in society (Fig. 5(a)). Therefore, the system without the FRA should be suitable for widespread use because of its simplicity and cost effectiveness (Fig. 5(b)).

For verification of the system without the FRA, a square wave potential/current for input signals of impedance spectroscopy was applied in the simple electrochemical reaction and LIB cell.²⁹⁻³³ As an example, an application of square current EIS (SC-EIS) was introduced to evaluate a degradation of commercial LIB with the charge-discharge cycling.

A commercially-available laminated LIB was used in the work. Using the technique of Fourier transform in ref,^{26,27} SC-EIS was carried out using the square current input. Optimization of the measuring condition (i.e. frequency of square current), DC-offset, amplitude from 0 to the peak, and sampling frequency, enabled the measurement of the impedance of the LIB cell by SC-EIS as well as by EIS using a conventional FRA and potentiostat system. Specifically, there was a good accordance between Nyquist plots obtained by SC-EIS on an LIB cell and those obtained by EIS

using a conventional FRA and potentiostat system with the error of each plot being less than 3% in the range of 1 kHz - 1 Hz. Therefore, the SC-EIS must be a method of great promise for widespread use in society.

3. Summary

We have investigated electrochemical impedance spectroscopy (EIS) for a long time, and our main epoch was the development of the FFT impedance method for an electrochemical system in 1982.²⁷ We have also verified the effectiveness of EIS for electrochemical reactions.^{1-12,17,25-28} The EIS measured by a frequency response analyzer (FRA) and potentiostat system is a powerful tool to check the state of LIBs. Additionally, a new EIS must necessarily be simple and cost effective for widespread use in society. Here, we have suggested a square current EIS (SC-EIS) technique in which the power controller of an LIB system creates a signal input and analyzes the state of batteries from the input and output. The SC-EIS was revealed to be able to operate as an impedance analyzing system for LIB equally as well as the conventional EIS system.²⁹⁻³³ Moreover, it proved even more effective for LIBs with a high capacity (i.e., the battery with a lower internal resistance, such less than mΩ order).

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