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Short communication

Proposal of novel equivalent circuit for electrochemical impedance analysis of commercially available lithium ion battery

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ABSTRACT

To analyze impedance response of an electrochemical system, it is important to model the system with an adequate equivalent circuit. In the present work, an equivalent circuit was designed for the analysis of lithium ion batteries with the contributions of a variety of diffusion parameters resulting from the various particle sizes for the cathode and the solid-electrolyte interphase formed on the anode particles, as well as electrochemical reactions and inductive components. Residual errors resulting from the data fitting was investigated for a variety of equivalent circuits used. The electrochemical impedance of the electrodes in commercial lithium ion batteries at various states of charge was analyzed to evaluate the proposed circuit.

1. Introduction

Analyzing technique of lithium ion batteries (LIBs) is strongly demanded both in the field of developments of LIB having features of safety, long life, and high capacity with high power, and in the field of checking the condition of the installed LIB on duty. In order to improve the rate characteristics of LIB for rapid charge and high power output, estimation of the rate determining step is a shortcut to select the materials of electrodes and electrolyte. For the premonitory diagnosis of the on-board batteries of electric vehicles and of installed batteries in load leveling systems, non-destructive analysis of the condition is strongly demanded.

Electrochemical impedance spectroscopy is one of the most effective methods of investigation of LIB without destruction of the battery [1–4]. In order to understand and to analyze the impedance response of the LIB, it is essential to use a proper equivalent circuit designed with the understanding on each step of the overall battery reaction. Considering the interfaces and layers in the battery, an equivalent circuit having a large number of elements could be assembled, while using such a circuit with a large number of elements makes it difficult to obtain meaningful information by the numerical fitting method. It is important to select an equivalent circuit which represents features and changes in important physical phenomena or in the state of battery components with the minimum number of elements.

Some analyses of LIB have been reported. In Nyquist plot of LIB impedance was reported to have semicircles in high frequency range and middle frequency range. The large semicircle in the middle frequency range was reported to be mainly attributed to the cathode and the small semicircle in the high frequency to the anode [1,2] by the studies on the influences of the charge–discharge cycles and the cell temperature. A series of electrochemical studies on the performance and fading characteristics of LIBs revealed that the cathode was the main contributor to the cell's overall performance [5,6]. To evaluate diffusion impedance, which has another large contribution to the total impedance, some idealized models have been reported, such as spherical Li^+ diffusion in particles and a solid-electrolyte interphase (SEI) [7] as well as a transmission line model [8]. Mechanism of capacity fading in some batteries was proposed to be an increase in the resistance of SEI [9]. In order to improve the analyzing technique of ac impedance spectroscopy to evaluate the battery performance, it is necessary to take into account the growing SEI on the active materials.

We have proposed an equivalent circuit for commercial LIB on the basis of equivalent circuit with the components and interfaces in LIB [10–12]. In order to improve the analyzing technique of ac impedance spectroscopy to evaluate the battery performance, it is necessary to model an equivalent circuit expressing the contributions of Li^+ diffusion and growing SEI.

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In this study, an equivalent circuit representing the LIB with the contribution of variety of particle size of cathode and SEI is proposed, and the fitting results are discussed quantitatively.

2. Experiment

A commercially available prismatic LIB with a nominal capacity of 850 mAh for cellular phones was used in this work, and the LIB was subjected to electrochemical tests at room temperature. It was charged at 1.0 of *C*-rate to 4.1 V, and was then maintained at 4.1 V for 3 h (the state of charge (SOC) = 100%). The battery was then discharged at 1.0 of *C*-rate. During the discharge, the current was stopped to obtain the LIBs with different SOC.

The ac impedance spectra were obtained at the open circuit voltage with 10 mV of ac signal in the frequency range of 100 kHz to 0.1 mHz. All measurements were performed at 25 °C.

Data fitting was carried out with Microsoft Excel Solver to reach the minimum value of the error, i.e., the sum of all the difference between the acquired experimental complex impedance data and the impedances calculated with the equivalent circuit using the parameters obtained by fitting for each frequency.

3. Results and discussion

3.1. Design of equivalent circuit for impedance analysis of LIB

An equivalent circuit 1 was designed according to the literature [1,3,13]. The electrochemical reactions of both of cathode and anode were expressed with a parallel connection of interfacial capacitance and connected charge transfer resistance with Warburg impedance in series. The circuit also contains a solution resistance and an inductive component, which consists of inductor and resistor (L and R_I) related with the wiring between the paste of electrode attached to the current collector and the measuring equipment, including the wounded current collector.

Equivalent circuit 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 element and charge transfer resistance should be connected in parallel with a capacitance between the electrolyte and the electrical connection between particles. The variation of the capacitance in particles is represented as the constant phase element (CPE) [14]. The capacitors for 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 equivalent circuit 3, the component of SEI was introduced in addition to the circuit 2.

3.2. Fitting results of LIB impedance with equivalent circuits

In all the spectra obtained in this study, three domains were visually separated into a region of loci in the 1st quadrant, a region

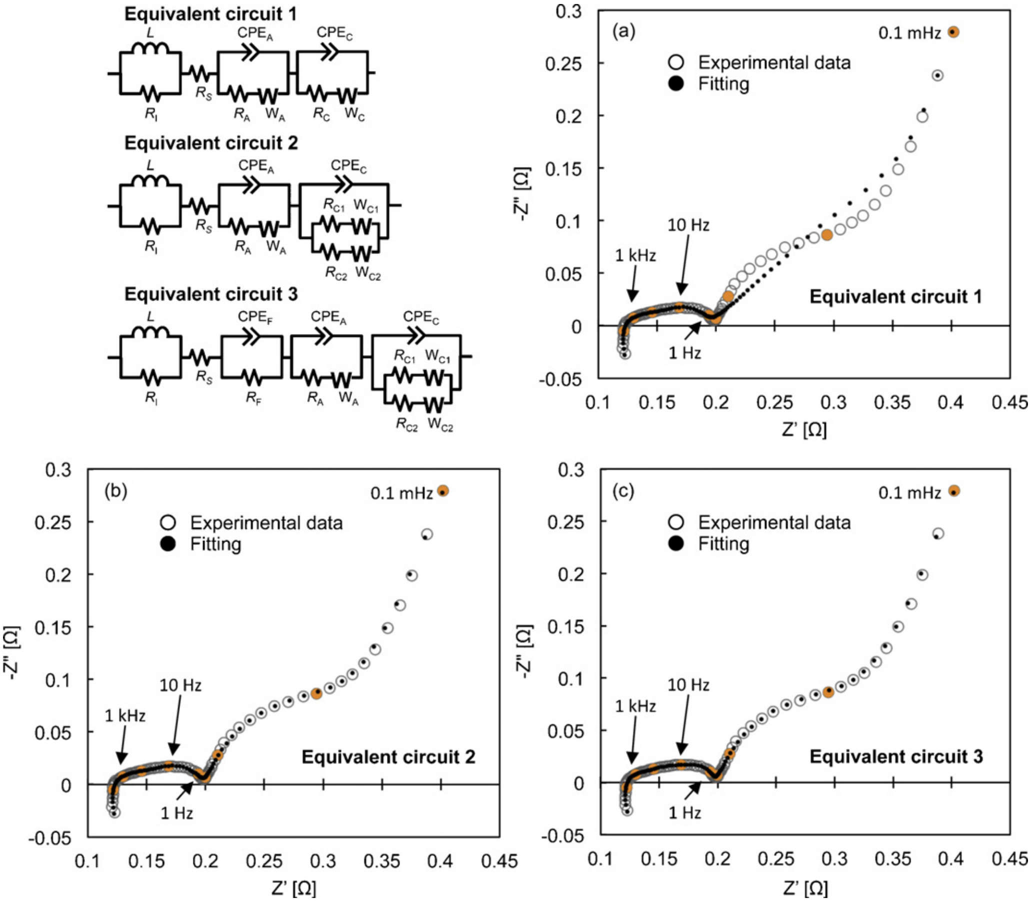

Fig. 1. Equivalent circuits used in this study and data fitting results using the circuits. Impedance of the LIB was measured at an SOC of 50%, a frequency range of 100 kHz–0.1 mHz, and a signal amplitude of 10 mV. Symbols of the equivalent circuit were expressed as follows: L, inductance of current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

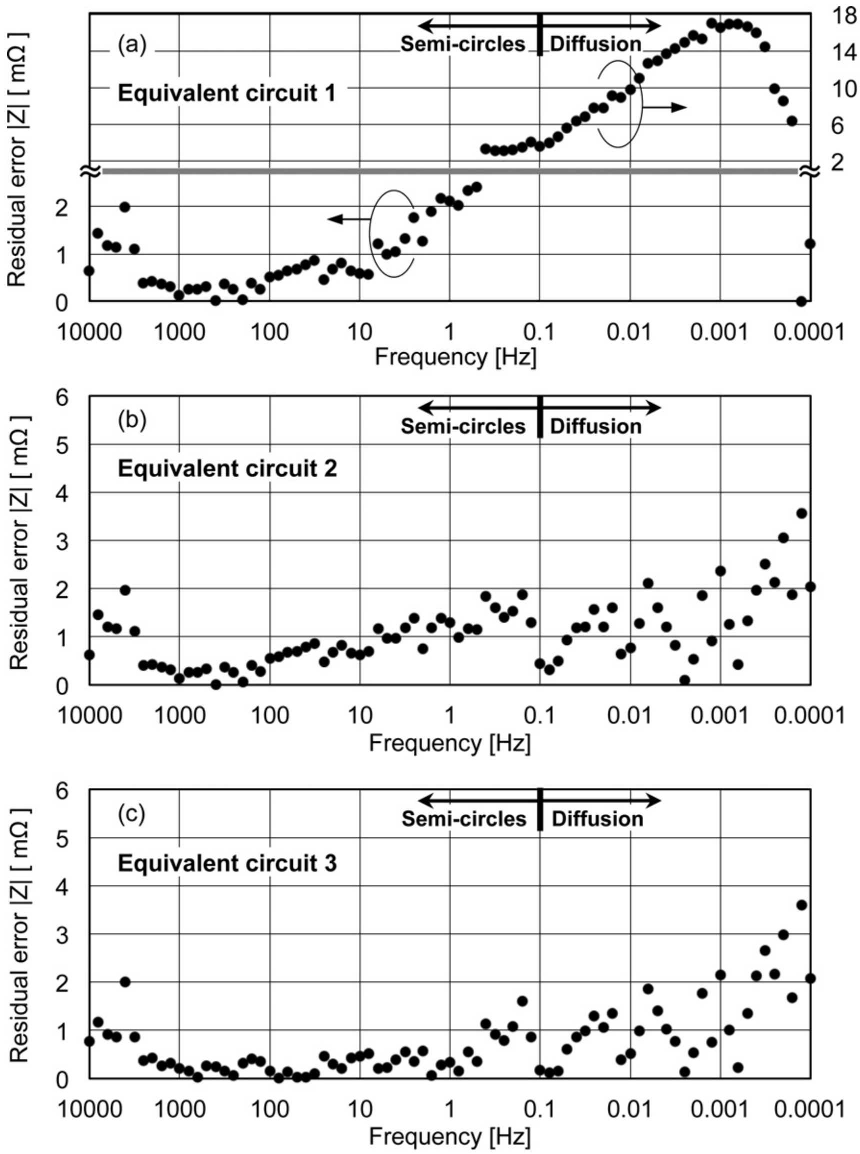

Fig. 2. Residual errors for the impedance data shown in Fig. 1. The error was calculated as the distance between the experimental data and calculated value in complex plane for each frequency.

of superposition of arcs or semicircles, and a loci of increase in the imaginary component, with the frequency region of 100–10 kHz, 10 kHz to 100 mHz, 100–0.1 mHz, respectively. Fig. 1 shows plots of impedance values calculated with equivalent circuits 1–3 after the data fitting for the impedance data obtained at SOC = 50%.

Using the circuit 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 inclined loci with 45° and the rise in the vertical direction could be expressed in the complex plane in the frequency region lower than 100 mHz due to the existence of diffusion components in both cathode and anode, while the feature of the arc in the low frequency region was absent in the calculated impedance shown in Fig. 1(a).

Using both of equivalent circuit 2 and 3, all the calculated values of impedance were plotted closed to the experimental results, while using circuit 1, a small neck-like feature could be observed in the loci of calculated value in the middle of middle frequency region. Using the circuit 3 the data fitting was successfully done with high accuracy, and the parameters obtained are as follows; L: 0.12 μH, R_I: 0.31 Ω, R_S: 0.12 Ω, R_F: 32 mΩ, p of CPE$_F$: 0.59, T of CPE$_F$: 0.30, R_A: 26 mΩ, p of CPE$_A$: 0.82, T of CPE$_A$: 0.66, σ of W_A: 4.5×10^{-3}, C_L of W_A: 26 kF, R_{C1}: 110 mΩ, R_{C2}: 24 mΩ, p of CPE$_C$: 1.0, T of CPE$_C$: 2.6, σ of W_{C1}: 5.0×10^{-5}, C_L of W_{C1}: 7.2 kF, σ of W_{C2}: 3.6×10^{-5}, C_L of W_{C2}: 0.49 kF. CPE parameters can be expressed; $Z_{CPE} = 1/(j\omega)^p T$. When $p = 1$, T has units of a capacitance "F". Parameters of the Warburg impedance represented, σ is the diffusion constant, C_L is the limiting capacitance.

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 were decreased in the frequency region below 1 Hz. In the frequency region between 100 Hz and 1 Hz the errors were decreased by the contribution of SEI component in the equivalent circuit. In the frequency region below 0.1 Hz corresponding to the impedance response for the diffusion step, the error range increased even using the circuit 3, as may be due to the scattered experimental data caused by the small signal input to the analyzer. The circuit 3 enables to maintain the fitting error below 0.5 mΩ, which is almost 2 orders of magnitude lower than the radius of semicircles.

From the discussion on the fitting error, the data analysis using equivalent circuit 3 is expected to be a tool to investigate the failure

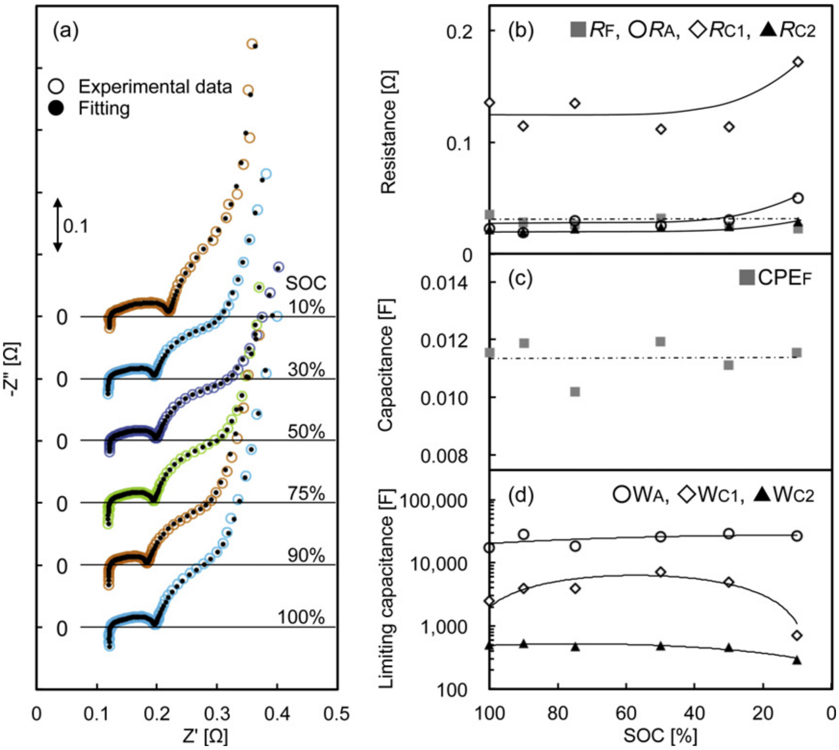

Fig. 3. Impedance spectra and fitting data of the LIB with a variation of SOC (a). Change in the resistance parameters (b), capacitance of SEI (c), and limiting capacitance (d) obtained by data fitting using equivalent circuit 3 with variation of SOC.

mechanism and/or the state of health of LIBs. Further discussion on the relationship between the change in parameters estimated by the impedance fitting and the capacity fading of LIB would be required.

3.3. Impedance analysis of LIB with variety of SOC

Impedance spectra obtained from LIB with various SOC and the resulting fitting data with the circuit 3 were illustrated in Fig. 3. For spectra, the fitting data successfully obtained with high accuracy. The value of R_{C1} was relatively high compared with that of R_{C2} while the total resistance, which calculated as parallel connection of R_{C1} and R_{C2}, was small. R_F value did not show a drastic change by the change in SOC, as would be due to the independency of SEI characteristics from SOC. From the change in limiting capacitance for each electrode, it would be suggested that the capacity of this LIB was dominated by the capacitance of the cathode, whose limiting capacity decreased with decreasing the SOC. Estimation of these values in addition to the impedance for ion diffusion are the demanded parameters to investigate the phenomenon of capacity fading during a continuous charge–discharge cyclings.

4. Conclusion

The impedance of a commercial Li-ion battery for cellular phones was measured. Advanced equivalent circuit 3 is designed to represent the impedance response of LIB consisting of components for anode, SEI, cathode containing particles of two different sizes, and an inductive component. The impedance data were fitted with the equivalent circuits, and the fitting errors were investigated. The advanced circuit 3 enabled to achieve fitting with high accuracy.

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