

Shifting in Time Constant of Impedance Response for Analysis of Li-ion Batteries

Toshiyuki Momma,^{1,2} Daikichi Mukoyama,² H. Nara²
Tetsuya Osaka^{1,2}

1. Department of Applied Chemistry, School of Advanced Science and Engineering, Waseda University, 3-4-1 Okubo, Shinjuku, Tokyo 169-8555, Japan.

2. Research Institute for Science and Engineering, Waseda University
3-4-1 Okubo, Shinjuku, Tokyo 169-8555, Japan

Analyzing technique of Li-ion batteries (LIB) 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. Electrochemical impedance spectroscopy (EIS) is one of the most effective methods of investigation of LIB without destruction of the cell. We have proposed an equivalent circuit for analysis of electrochemical reactions, diffusion parameters, and resistivity of solid electrolyte interphase (SEI), and demonstrated analysis of impedance spectra with using the proposed circuit.[1-3] In our previous study [1, 2], the equivalent circuit to express each elemental step in a commercial lithium ion battery (LIB) by EIS was carefully investigated. Also, with the designed equivalent circuit, impedance responses of LIB during capacity fading by continuous charge-discharge cycling was analyzed, and succeeding rises in impedance of cathode reaction and the SEI were illustrated, while the resistance of SEI in fresh LIB was remarkably smaller than those of the charge transfer reactions at the electrodes/electrolyte interfaces [3]. In addition, in these years, the internal resistance of LIB became smaller and smaller for the high power output to be applied to the electric vehicles, as satisfy the demands for high power and high capacity lead to difficulty in assigning each characteristic in impedance spectroscopy to elementary steps correctly or in precise evaluation of each step having close values in time constants, which sets limits on detail characterization of a battery by EIS. Under the situation, to investigate the condition of each elemental step during the operation of LIB precisely, addition to the adequate equivalent circuit, it would be helpful to acquire the impedance raw data in the state being easily distinguished and analyzed. We also tried to solve this issue, and reported the analysis of impedance with controlled temperature.

In this study, an expansion of impedance/resistance and a shifting of time constant of elemental steps of LIB was confirmed and discussed by changing the temperature.

A commercially obtained laminated LIB using a carbon anode with a nominal capacity and voltage of 0.8 Ah and 3.8 V, respectively, was examined in this study. The LIB was characterized by EIS at every 5 °C from -20 °C to 0 °C, and at 20 °C. After changing the environmental temperature of LIB, the LIB was kept for 7200 s before the measurements. The EIS were obtained at the 3.837 V of DC off-set to maintain the SOC value as 50%, with 5 mV of ac signal in the frequency range of 100 kHz to 10 mHz.

Figure 1 and 2 illustrate Bode plots and Nyquist plots of LIB impedance obtained with varying the temperature. In the Bode plots, the shifting of time constant of the impedance components was observed, as shown in Fig. 1. With increasing the whole impedance value by decreasing the measuring temperature, a shifting of time constant

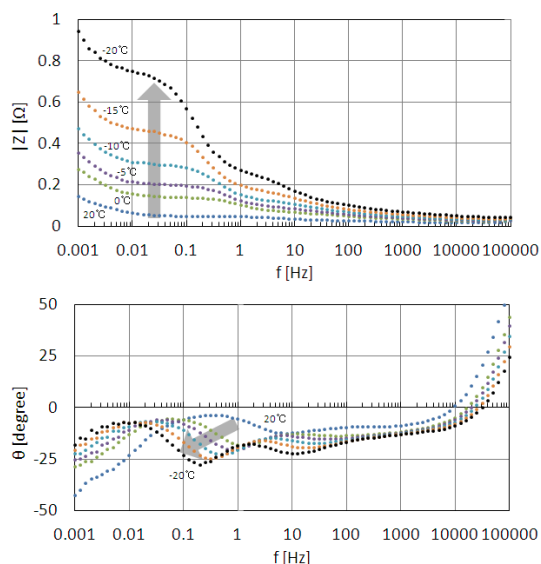


Fig. 1 Bode plots of LIB impedance measured at varied temperature.

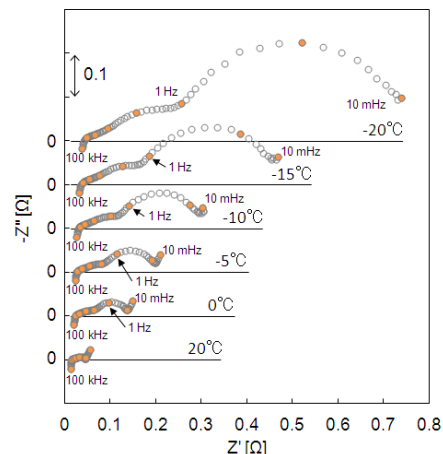


Fig. 2 Nyquist plots of LIB impedance measured at varied temperature.

around $10 - 10^{-1}$ Hz was found, and a slight shift of time constant around 10 Hz was also seen. In the Nyquist plot shown in Fig. 2, the responding frequency domain of SEI at low temperature is clearly separated from the one of interfacial impedance, and at 20 °C the SEI response was found to overlap with that of the inductive component of the outer electric lead. From the analysis shifting the time constant of the impedance response is useful tool to analyze the overlapping response at highest frequency around $10 - 10^2$ Hz.

Increasing the measuring temperature above the ambient temperature illustrated that the electrochemical impedance became smaller than the one at ambient temperature. While the small impedance made difficult to distinguish and analyze, the frequency domain of diffusion impedance was also shifted to higher frequency, as enables to estimate diffusion parameters.

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