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Article / Book Information

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Title(English)	On-site diagnosis of lithium-ion battery degradation using voltage profile and impedance analyses
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種別(和文)	論文要旨
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（博士課程）
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論 文 要 旨

THESIS SUMMARY

系・コース： Department of, Graduate major in	応用化学　系 エネルギー　コース	申請学位（専攻分野）： Academic Degree Requested	博士 Doctor of（　工学　）
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要旨（英文800語程度）
Thesis Summary（approx.800 English Words ）

Lithium-ion batteries (LIBs) are the most common electrochemical energy storage devices in consumer electronics, electric vehicles and stationary storage systems. Despite LIBs having a longer lifetime than other batteries, they still suffer from aging, which reflects in capacity reduction and increase of resistance. Accurate estimation of LIBs degradation is important to understand their economic value and to estimate the remaining useful life. The methods to analyze LIBs degradation are divided into non-invasive and invasive. Non-invasive methods do not leave any reasonable damage to the tested cells, while invasive methods cause permanent damage and require disassembling the cells to evaluate their internal condition.

Most non-invasive methods so far have the demerit of either interfering with the user's operation or not being able to estimate the retained capacity and the internal resistance at the same time. The purpose of this research is to investigate innovative non-invasive methods for the analysis of LIBs degradation that can be performed on-site without interfering with the user's operation. Two methods are proposed and validated with data from cells aged with fast charging and discharging cycles at multiple temperatures (−5 ˚C, 10 ˚C, 25 ˚C). Furthermore, the results of the proposed methods are compared with those of conventional non-invasive and invasive analyses.

Chapter 2 describes the experimental setup, the aging test conditions, and the methods of analysis.

Chapter 3 shows the results of test cell aging. The capacity reduction was more serious at lower temperatures because of the lithium plating phenomenon. On the other hand, the internal resistances increased faster at higher temperatures, suggesting that the film growth is accelerated at high temperatures. Moreover, it is found at all the tested temperatures that the capacity reduction is caused by the loss of lithium inventory (LLI) rather than the loss of active material (LAM).

Chapter 4 describes the diagnosis method based on the pulse power test and analyzes the transient voltage occurring after the application of a discharge current step, starting from the condition of cell completely charged. Differently from the conventional pulse power test, which considers only the initial resistive voltage drop, the method proposed in this thesis also analyzes the diffusion-related transient. The motivation lies in the fact that as the cell reduces its retained capacity due to aging, the electrodes' lithiation condition changes, affecting the diffusion overpotential. A circuit comprising a series resistance (R_s) and a Warburg element (W) is employed to fit the transient voltage, and the circuit parameters are evaluated before and after degradation. The Warburg element, representing the polarization voltage due to diffusion, is modeled as a transmission line, and the transient is simulated in the time domain. R_s increased as the retained capacity decreased, and the relationship between R_s and the retained capacity exhibited a temperature-dependent slope. Specifically, the increase of R_s was greater at higher temperatures. W also increased as the retained capacity decreased, but the slope was the same at all temperatures. This suggests that the change of W can provide important information for estimating the remaining capacity.

Chapter 5 describes the second proposed method. It employs dynamic EIS to measure the impedance while the cell is being charged. Since dynamic EIS is performed in the non-equilibrium condition, the cell changes its state of charge during the measurement causing a voltage drift that creates artifacts. These artifacts produce a measurement error that cannot be neglected, especially at low frequencies. This thesis proposes a method to mathematically model and eliminate the artifacts. Correcting the artifacts allows using the EIS spectra up to low frequencies, obtaining spectra similar to those of static EIS. After correcting the artifacts, the EIS traces are fitted to an equivalent circuit which includes three resistances. The evolution of the parameters of the equivalent circuit is observed as the cell is charged. The estimated parameters are compared before and after aging. The results show that as the cells age, the internal resistances increase, and the change is temperature dependent. Additionally, the resistance associated with the films (R_1), measured at high frequencies, was identified as the one with the highest increase in all aging conditions, suggesting that it can be considered the main indicator of resistive degradation. Moreover, a dependency on SoC was observed for R_1, implying that the measurement of R_1 can also be used for SoC estimation during LIBs operation.

Chapter 6 describes the conclusions. The results of the two proposed methods are coherent to those of the conventional non-invasive and invasive analysis. Moreover, they allow estimating the capacity and the internal resistance as well as cell SoC with reduced interference with the user's operation and are suitable for on-site degradation diagnosis in practical LIBs applications.