

論文 / 著書情報
Article / Book Information

題目(和文)	過渡電圧及び電気化学インピーダンス解析によるリチウムイオン電池のその場劣化診断
Title(English)	On-site diagnosis of lithium-ion battery degradation using voltage profile and impedance analyses
著者(和文)	カヴァリエーレ ダヴィデ
Author(English)	Davide Cavaliere
出典(和文)	学位:博士(工学), 学位授与機関:東京工業大学, 報告番号:甲第12896号, 授与年月日:2024年9月20日, 学位の種別:課程博士, 審査員:荒井 創,平山 雅章,稲木 信介,鈴木 耕太,黒木 秀記
Citation(English)	Degree:Doctor (Engineering), Conferring organization: Tokyo Institute of Technology, Report number:甲第12896号, Conferred date:2024/9/20, Degree Type:Course doctor, Examiner:,,,,
学位種別(和文)	博士論文
Category(English)	Doctoral Thesis
種別(和文)	要約
Type(English)	Outline

Title: On-site diagnosis of lithium-ion battery degradation using voltage profile and impedance analyses

Date: 15th August 2024

Name: Davide Cavaliere

The main purpose of this research is to investigate and propose innovative non-invasive methods for the analysis of LIBs degradation. In fact, most of the non-invasive methods adopted so far have the demerit of either interfering with the user's operation or being difficult to perform on-site because of the expensive equipment involved. In contrast to that, in this thesis I propose two methods that can be performed on-site and do not interfere with the user's operation. They are suitable for practical LIBs applications such as automotive and energy storage. The first method analyzes the transient voltage response at the initial stage of discharge and estimates the total internal resistance and the retained capacity. The second method employs dynamic electrochemical impedance spectroscopy (EIS) during cell charging to observe the variation of the internal resistances before and after aging. To demonstrate the applicability of those methods in properly evaluating LIBs degradation, their results were compared with those of conventional non-invasive and invasive (post-mortem) methods. All methods were applied to experimental data coming from LIBs of market specification aged with fast charge and discharge cycles at multiple temperatures.

Chapter 1 introduces the fundamentals of LIBs technology, and the methods currently adopted for the diagnosis of degradation. 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 the reduction of the retained capacity and the increase of the internal resistance. An accurate estimation of LIBs degradation is important to understand their residual 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 involve disassembling the cells to evaluate their internal condition.

Chapter 2 describes the experimental setup, the aging test conditions, and the methods of analysis. Cells of market specification (NCM523 and graphite) were aged with fast charging and discharging cycles at multiple temperatures (-5°C , 10°C , 25°C). The non-invasive methods consist of discharge voltage and differential voltage (dV/dq) analyses, and static EIS performed at 100% and 0% SoC. The invasive methods consist of the post-mortem analysis of the electrodes extracted from the cells. To clarify the electrode characteristics of the positive and negative electrodes before and after the degradation of the full cells, half-cells were assembled with NCM or graphite electrodes as the working electrode, and metallic lithium as the counter electrode. Moreover, scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS) analyses were carried out to confirm the condition of the surface of the electrodes, and X-ray diffraction (XRD) analysis was performed to evaluate the change of the lithiation condition of the electrodes before and after aging.

Chapter 3 shows the results of the degradation tests according to the methods presented in Chapter 2. The analysis of degradation confirmed that in all cases loss of lithium inventory (LLI) was the main degradation mechanism leading to capacity reduction, and loss of active material (LAM) was negligible. In fact, this result was at first confirmed with non-invasive analysis based on the observation of the dV/dq characteristics. Half-cell capacity measurements demonstrated the absence of LAM, and XRD gave an additional confirmation of LLI happening in the cell degraded at low temperature. The capacity reduced consistently at low temperature. The root cause was identified as the lithium plating phenomenon occurring at the surface of graphite, causing a permanent loss of the cyclable lithium. SEM images confirmed a non-uniform deposition layer at the surface of graphite. In addition, the change of the internal resistance was evaluated with static EIS. For the same capacity

reduction, the increase of resistance was higher at higher temperatures. I hypothesize that the increase of resistance depends mainly on the growth of the films such as the SEI at the surface of graphite and the CEI at the surface of NCM. This growth is caused by side reactions which follow the Arrhenius law, so they proceed faster at higher temperatures.

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 that 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 as long as the cell capacity retention exceeded 80%. I suggest that the proposed method can be adopted to estimate not only the equivalent internal resistance of the cell, but also the retained 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 to use the EIS spectra up to low frequencies, obtaining corrected spectra that are 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 the 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.