이완 시간 분포를 이용한 새로운 배터리의 노화 진단 방법

무하마드 소하입, 최우진
숭실대학교 전기공학부

A Novel Aging Diagnosis Method Using Distribution of Relaxation Time

Muhammad Sohaib and Woojin Choi
School of Electrical Engineering, Soongsil University

ABSTRACT

Electrochemical Impedance Spectroscopy (EIS) is a widely recognized tool for investigating the internal processes that drive the aging of lithium-ion batteries. The Distribution of Relaxation Times (DRT) method has emerged as an advanced technique to further examine the electrochemical behavior of lithium-ion batteries using EIS data. Unlike conventional methods, DRT isolates individual relaxation processes, offering deeper insights into the complex electrochemical dynamics underlying battery aging. This study emphasizes the systematic application of DRT analysis to a specific number of cylindrical 18650 and coin cells throughout their life cycles, up to the point of failure. Key parameters extracted from the DRT spectra, such as peak height, full width at half maximum (FWHM), and peak center relaxation time, are closely related to battery aging and highlight the most significant shifts in internal electrochemical processes as the batteries age. These parameters are compared to reveal the evolution of distinct electrochemical processes during aging, providing a comprehensive view of aging pathways. The findings emphasize the effectiveness of the DRT method and its reliability in delivering in-depth insights into lithium-ion battery aging, with the potential to improve predictions of performance and lifespan.

1. Introduction

The rapid increase in the use of electric vehicles (EVs) has sparked significant interest in the advancement of lithium-ion batteries (LIBs), which are essential for powering these vehicles. A key area of focus in current research is the degradation of these batteries, as it has far-reaching implications. As lithium-ion batteries undergo aging, there is a decline in capacity and an increase in internal resistance, leading to reduced driving range and power capacity for EVs. This, in turn, results in suboptimal driving experiences[1]. Furthermore, the aging process in lithium-ion batteries triggers various side reactions, causing internal structural damage and elevating the risk of thermal runaway, thereby posing potential safety hazards[2]. It is imperative to gain a deep understanding of the aging mechanisms and degradation models to effectively estimate battery health using historical data, optimize current operational conditions, and forecast future performance.

The performance and lifespan of batteries are intricately linked to the complex process of charging and discharging, which involves the insertion and removal of lithium ions within the active materials of the battery's anode and cathode. The capacity of the battery is directly influenced by the quantity of active materials and the presence of lithium ions[3]. Another critical factor contributing to battery aging and degradation is the formation of solid-electrolyte interphase (SEI) layers on the electrode surfaces. These layers can impede ion movement, leading to an increase in internal resistance over time. Furthermore, repetitive charge and discharge cycles can subject the electrode materials to mechanical strain, causing their deterioration and further impacting battery performance and longevity. Regarding degradation modes, battery aging mechanisms are often categorized as loss of lithium-ion inventory (LLI) and loss of anode/cathode active materials (LAM) for battery management and online diagnosis[4].

The Electrochemical Impedance Spectroscopy (EIS) spectrum provides valuable insights into the degradation mechanism of Lithium-ion Batteries (LiBs)[5]. However, differentiating each electrochemical process in the EIS spectrum can be challenging due to overlapping semicircles. Additionally, identifying appropriate equivalent circuits can be difficult, especially for complex electrochemical phenomena. This research aims to improve the analysis of Distribution of Relaxation Time (DRT) to effectively distinguish overlapping time scales in Electrochemical Impedance Spectroscopy (EIS) for graphical interpretation. This addresses a significant gap in the current understanding of electric vehicle battery behavior.

In this study, the distribution of relaxation time (DRT) method is employed to interpret Electrochemical Impedance Spectroscopy (EIS) data and to gain comprehensive insights into the internal mechanisms of electric vehicle (EV) batteries. While previous research has predominantly focused on battery aging indicators such as capacity fade and impedance growth, there exists an evident gap in the thorough investigation of higher values of 'tau' components in DRT, encompassing charge transfer and diffusion processes. The degradation mechanism of Li-Ion batteries is examined using EIS spectra and DRT peak analysis within the higher relaxation time tau domain. A comparative analysis of the performance of 18650 Li-Ion cell with Li-Ion coin cell LR2032 is conducted, and the degradation phenomena are evaluated using DRT plots and parameters derived from DRT analyses.

2. Analysis of Battery Aging Data

In this section, the aging test is conducted on a cylindrical NCM 18650 lithium-ion battery. The specific battery 18650 utilized in the test is detailed in Table 1. Initially, the battery underwent repeated charging and discharging cycles to generate impedance spectra, with measurements taken at every 5 cycles. Impedance parameters were extracted through analysis and subsequently subjected to curve fitting. The aging process was carried out at a controlled temperature, with regular charge/discharge and EIS tests. A one-hour rest period followed each cycle.

Table 1. 18650 Battery Aging Test Condition

State	Property	Value
Charging	Constant current	0.5C (1,375 mA)
	Constant voltage	4.2 V
	Cut-off current	0.02C (55mA)
Discharging	Constant current	0.5C (1,375 mA)
	Cut-off voltage	2.5 V
Rest	Rest time	1 hour

The EIS data underwent verification using the Kramer-Kronig (K-K) transformation to ensure the accuracy and stability of the results. Additionally, a commercially available 45mAh Li-ion coin cell was analyzed for comparison. The coin cell underwent cycling, with specifications provided in Table 2, offering a comparative perspective alongside the NCM battery analysis.

Table 2. LR2032 coin cell Aging Test Condition

State	Property	Value
Charging	Constant current	1C(45mA)
	Constant voltage	4.2V
	Cut-off current	-
Discharging	Constant current	2C(90mA)
	Cut-off voltage	3V
Rest	Rest time	1 hour

3. Exploring the Distribution of Relaxation Time (DRT) Method

In the field of electrochemical research, the Distribution of Relaxation Time (DRT) method plays a crucial role in comprehending relaxation processes in intricate systems. When it comes to battery research, a comprehensive understanding of battery behavior necessitates the combined analysis of frequency and time. The application of DRT analysis facilitates a more comprehensive understanding of each process in comparison to solely relying on frequency analysis. This method enables the expression of the impedance of an electrochemical system which can be expressed as

$$Z(\omega) = R_0 + \int_0^\infty \frac{g(\tau)}{1 + j\omega\tau} d\tau \qquad (1)$$

The ohmic resistance (R_0) represents the impedance at very high frequencies where capacitive effects are negligible. The function $g(\tau)$ describes the distribution of relaxation times within the system, while ω represents the angular frequency at which the impedance is measured. The relaxation time (τ) is defined as the product of the effective resistance (R) and capacitance (C).

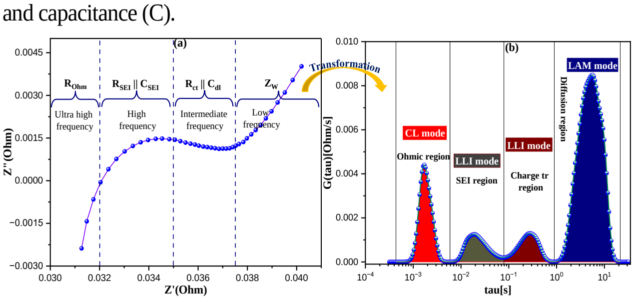

Fig.1. (a) Nyquist plot for 18650 cell. (b) Corresponding DRT plot for 18650 cell.

The impedance parameters are calculated by integrating the time constants in each segment of the DRT curve. This forms the basis for grouping criteria. The polarization resistance (Rp) for each segment can be calculated using the equation (4), where τ_U and τ_L are the upper and lower limits of time constant, respectively.

$$R_p = \int_{\tau_L}^{\tau_U} \gamma(\tau) d\tau \qquad (2)$$

Through the application of DRT analysis, a more comprehensive understanding of each process can be attained compared to relying solely on frequency domain analysis. In EIS Nyquist plots, the challenge of distinguishing overlapping semicircles is addressed by DRT, which offers detailed insights into internal processes and the ability to separate individual electrochemical processes, as depicted in Fig. 1(a) and (b).

4. Results and Analysis

4.1 Analysis of Impedance Spectrum

The Nyquist plots for a specific number of cycles for 18650 and coin cell were obtained from EIS measurements, as illustrated in Fig. 2 and Fig. 3, respectively. The impedance spectra of each cell were measured until the capacity decayed below 75% after a certain number of cycles. Each spectrum was divided into four sets of frequency ranges. The semicircle appears at an intermediate frequency, representing charge transfer and SEI layer, while the low-frequency region is associated with the diffusion part, more closely related to degradation mechanisms with cycling. The ultra-frequency and high frequency are related to ohmic resistance and solid electrolyte interface (SEI) region, respectively, and are less dependent on cycling as batteries age.

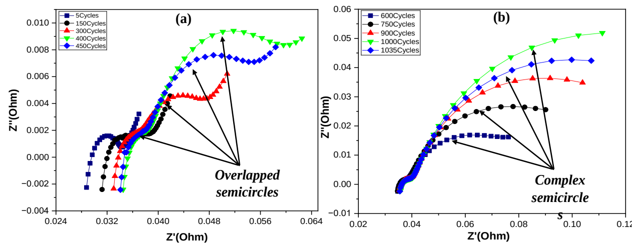

Fig.2. . Nyquist plots reveal increasing semicircle complexity in 18650 cell over its life cycles.

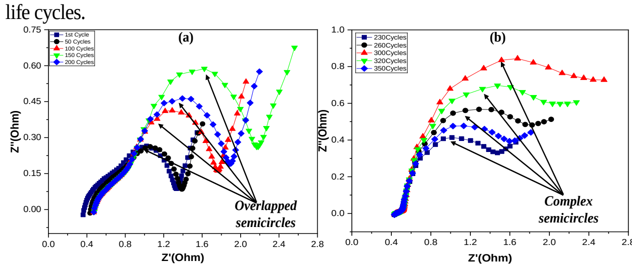

Fig.3. Nyquist plots reveal increasing semicircle complexity in coin cell over its life cycles.

In Fig. 2(a,b) and Fig. 3(a,b), the semicircles overlap, and as the number of cycles increases, these circles become more complex, making it difficult to distinguish them clearly. Ideally, each electrochemical process should be represented by a distinct semicircle, but in practice, they often overlap. As depicted in Fig. 2(a,b) and Fig. 3(a, b), both the height and width of these semicircles increase as the battery undergoes cycling.

The overlapping of these electrochemical processes in batteries presents a challenge in isolating the individual relaxation times and amplitudes associated with each process. This overlapping makes it difficult to accurately interpret the impedance spectrum and understand the underlying degradation mechanisms of the battery. As a result, a comprehensive understanding of the electrochemical behavior and degradation processes of the battery becomes more complex.

4.2 Analyzing Degradation Mechanisms with DRT Plots

The EIS impedance data is used to create a distribution of relaxation time, which helps to analyze each chemical reaction separately. The DRT plots for the 18650 and coin cell are shown in Fig. 4(a) and (b) respectively, over the life cycles. This analysis reveals a significant observation in the DRT plots for both cells. A peak is noticed at the far right side of each graph, corresponding to the diffusion process, and its height steadily increases with the number of cycles. This consistent trend across all DRT plots indicates a common behavior as the batteries approach end-of-life conditions. Similarly, the charge transfer impedance also increases as cells are cycled, and there is a noticeable shift of the charge transfer process towards higher relaxation time, indicating a slowdown in the process as the battery is cycled[2].

In order to identify polarization processes inside lithium-ion batteries (LiBs), it is crucial to perform a multi-peak fitting and analysis of the distribution function, $\gamma(\ln\tau)$. This method helps distinguish different processes by breaking down complex signals into simpler parts. Gaussian functions are commonly used for fitting due to their simplicity and clear physical meanings.

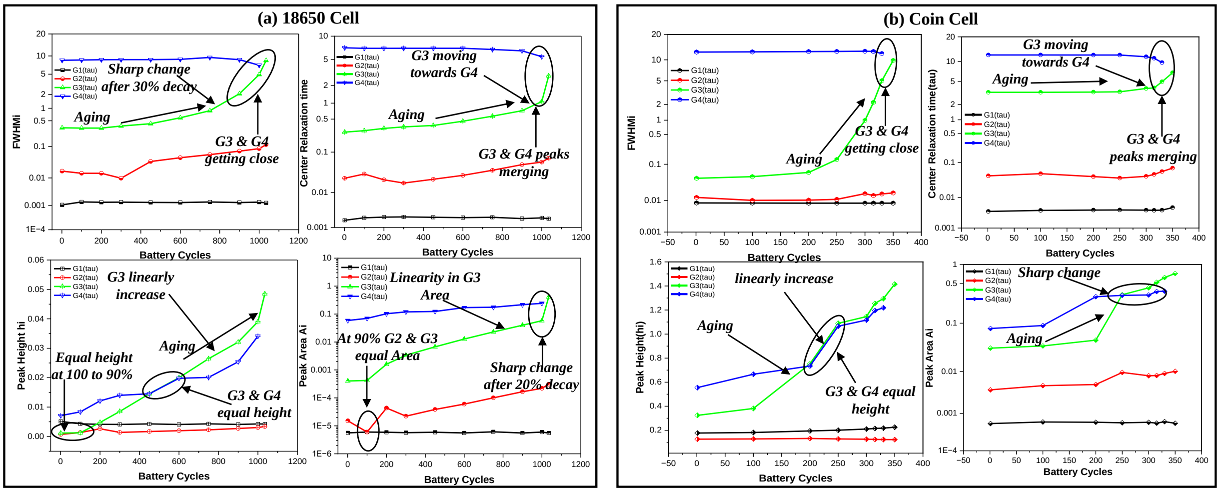

Fig.5. (a) DRT parameters of 18650 cell reveal degradation mechanisms over the life cycles. (b) Extraction of DRT parameters and degradation mechanisms in coin cell over their life cycles.

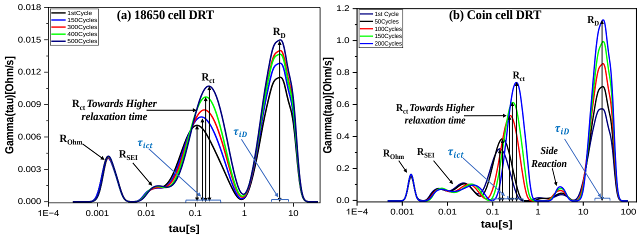

Fig.4. Comparison of DRT Plot Evolution During Degradation (a) DRT plots of 18650 cell over its lifecycle. (b) DRT plots of coin cell over its lifecycle.

$$G_i(\tau) = \frac{A_i}{\sigma_i\sqrt{2\pi}} e^{\frac{-(\tau-\eta_i)^2}{2\sigma_i^2}} \tag{3}$$

In this equation, A_i represents the peak amplitude η_i is the characteristic time indicating the peak's position, and σ_i controls the peak width, also known as the full width at half maximum (FWHM), approximately $2\sigma_i\sqrt{(2ln2)}$.

The height of the peak, h_i, is calculated by

$$h_i = \frac{A_i}{\sigma_i\sqrt{2\pi}} \tag{4}$$

Peak fitting with the Distribution of Relaxation Times (DRT) allows for precise separation of electrochemical processes in batteries. Using Gaussian functions in Origin, key parameters were calculated from DRT plots for an 18650 and coin cell as shown in Fig. 5(a) and (b) respectively.

The performance of battery electrode materials degrades over time due to factors such as structural changes, particle cracking, and the loss of active material. This degradation reduces the ability of the materials to conduct electricity and ions at the interface between the electrode and the electrolyte, leading to increased resistance to the transfer of charge. Additionally, microscopic pores in the electrode materials, particularly caused by the growth of the solid-electrolyte interphase (SEI) layer, further contribute to higher resistance and instability of the SEI layer, which in turn leads to rapid ion movement as the battery nears the end of its life. Loss of conductivity, often due to the breakdown of the electrolyte, leads to an increase in resistance to the flow of current, while an increase in SEI resistance indicates loss of lithium ions, resulting in reduced capacity. Furthermore, repeated cycling of the battery also leads to fractures in the anode, causing further loss of active material, which in turn negatively impacts the processes of charge transfer and diffusion Fig. 1(b).

It is important to understand the processes of charge transfer and diffusion in order to analyze the performance and failure of lithium-ion batteries. These processes are represented as distinct peaks in the Distribution of Relaxation Times (DRT) plot, which can help diagnose battery health and identify points of failure. When the peaks for charge transfer and diffusion merge at a single time constant ('tau'), as shown in Fig. 5 (a) and (b), it indicates a critical state of degradation. This merging suggests that the battery can no longer sustain electrochemical reactions due to the formation of the solid electrolyte interphase (SEI) layer, lithium plating, and the loss of active materials, all of which increase internal resistance. At this stage, the battery has reached its end-of-life (EOL) and can no longer deliver sufficient voltage or current for practical use.

5. Conclusion

This study explores the factors contributing to the aging of lithium-ion batteries, which are closely tied to their electrochemical processes and structural changes over time. Through the use of Electrochemical Impedance Spectroscopy (EIS) and Distribution of Relaxation Times (DRT) analysis, researchers gain a deeper understanding of the complex behavior of batteries. In Nyquist plots, overlapping semicircles reveal intricate interactions, while distinct peaks in DRT plots provide clarity. Key parameters such as peak height, full width at half maximum (FWHM), and peak center relaxation time, extracted from the DRT plots, are closely linked to battery aging, offering valuable insights into the most significant changes in internal processes. SEI layer, particle cracking, and the loss of active material further accelerate aging, leading to increased internal resistance and reduced capacity. This detailed understanding of battery aging enables more accurate diagnosis of battery health, identification of failure points, and improvements in the performance and lifespan of lithium-ion batteries in practical applications.

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