이완 시간 분포 분석을 이용한 리튬 이온 배터리의 노화에 관한 연구

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Investigation of the Aging Phenomena in Lithium-Ion Batteries Using Distribution of Relaxation Time Analysis

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ABSTRACT

The aging of Lithium-ion (Li-ion) batteries is a critical issue that impacts their performance and lifespan, with significant implications for applications ranging from portable electronics to electric vehicles and grid energy storage. Electrochemical Impedance Spectroscopy (EIS) is useful for tracking battery performance, understanding its data becomes complex due to the presence of overlapping semicircles in impedance spectra. This article investigates the aging phenomena in Li-ion batteries through the application of Distribution of Relaxation Time (DRT) analysis based on EIS. The aging phenomena is observed using Li-ion cell 18650 and Li-ion coin cell LR2032, and their DRT plots results are compared. Analyzing DRT plots from EIS measurements reveals the mechanisms behind battery aging, including electrode and electrolyte degradation and the behavior of peaks changes with time which is related to battery aging. By identifying distinct electrochemical processes and aging phenomenon at the end-of-life stages, the study contributes to a deeper understanding of battery behavior and performance degradation. Which demonstrate the utility of DRT analysis in estimating battery status and informing real-time monitoring systems, especially in electric vehicle applications. The results of this study will enhance a better understanding of Li-ion battery aging and inform the development of strategies to improve battery performance and extend lifespan for diverse applications.

1. Introduction

The widespread adoption of electric vehicles (EVs) has fueled extensive research into lithium-ion batteries, which serve as their primary power source. Battery degradation is a focal point in this research due to its significant implications. Firstly, as lithium-ion batteries age, capacity degradation and increased internal resistance diminish both the driving range and power capacity of EVs, leading to suboptimal driving experiences [1]. Secondly, various side reactions occur within lithium-ion batteries during aging, causing internal structural damage and raising the risk of thermal runaway, ultimately resulting in potential safety hazards[2].

Typically, the processes of charging and discharging batteries are closely linked to the intercalation and deintercalation of lithium ions within the active materials of the anode and cathode. Consequently, the battery's capacity is directly influenced by the quantity of active materials and the availability of lithium ions[3]. Another important factor contributing to battery aging is the formation of solid-electrolyte interphase (SEI) layers on the electrode surfaces. These layers can hinder ion transport and lead to an increase in internal resistance over time. Moreover, repeated charge and discharge cycles can lead to mechanical stress and structural degradation of electrode materials, further affecting battery performance and longevity. Overall, understanding these various aging mechanisms is crucial for developing strategies to mitigate battery degradation and prolong lifespan.

An Electrochemical Impedance Spectroscopy (EIS) spectrum can provide significant insights into the degradation and aging of Lithium-ion Batteries (LiBs)[4]. Utilizing suitable equivalent circuits, primarily comprising combinations of resistors and constant phase elements with well-defined physical meanings [5], can aid in this analysis. However, finding appropriate equivalent circuits can be challenging, especially for complex electrochemical phenomena. In recent years, the relaxation time distribution (DRT) method has emerged as a valuable tool for extracting characteristic time constants from EIS spectra. This method assists in graphical interpretation of the data [6].

In this paper the distribution of relaxation time method is used to interpret EIS data and to obtain more information about the internal behavior of batteries. One significant advantage of DRTs is their model-free nature, which means they do not rely heavily on detailed information about the system, making them more versatile and easier to apply in various contexts. Specifically, while some research has focused on aspects of battery aging, such as capacity fade and impedance growth, there remains a lack of in-depth investigation into the lower frequency components of DRT, such as charge transfer and diffusion parts. The aging phenomenon of Li-Ion batteries is analyzed using EIS spectrum and DRT peaks analysis towards the lower frequency domain. The results of 18650 Li-Ion cell is compared with Li-Ion coin cell LR2032, and aging phenomena analyzed using DRT plots and peaks analysis.

2. Methodology

2.1 Battery Aging Data

In this section, the aging test of a cylindrical NCM (18650) lithium-ion battery is described. The battery used in the test is a NCM Li-ion model, as specified in Table 1. Initially, the battery underwent aging through charging and discharging cycles to generate EIS AC impedance spectra, measured every 5 cycles. Following this, impedance parameters were extracted using equivalent circuit models, and subsequently, subjected to curve fitting. The aging process was conducted at 25°C using HYSCLAB's B.O.D Incubator, with charge/discharge and EIS tests performed using WonATech's WEIS-500. Cycle tests were conducted at a constant current of 0.5C, with a one-hour rest period after each cycle. EIS tests were performed every 5 cycles, with impedance spectra measured using a 60mV perturbation in the frequency range of 0.1-1kHz, at 100% state of charge (SOC).

The obtained EIS data is verified using Kramer-Kronig (K-K) transformation to ensure accuracy and stability.

$$Z_i(\omega)_{kk} = -\left(\frac{2\omega}{\pi}\right)\int_0^\infty \frac{Z_r(x) - Z_r(\omega)}{x^2 - \omega^2}dx \tag{1}$$

$$Z_r(\omega)_{kk} = Z_r(\infty) + \frac{2}{\pi}\int_0^\infty \frac{XZ_i(x) - \omega Z_i(\omega)}{x^2 - \omega^2}dx \tag{2}$$

Equations (1) and (2) express the K-K relationships between the real and imaginary components of impedance data, providing a mathematical framework for assessing the internal consistency of experimental results.

The NCM battery analysis is compared with a commercially available 45mAh Eunicell LR2032 Li-ion coin cell was utilized. The cell underwent cycling at 25°C, with each cycle comprising a 1C-rate charge up to 4.2 V and a 2C-rate discharge down to 3 V. The specification of LR2032 coin cell is specified in Table 2.

Table 1. Specification of the NCM Battery used for the Aging Test.

Property	Value
Chemistry	Nickel Manganese Cobalt
Type	18650
Capacity. max	2,850 mAh
Nominal voltage	3.65 V

Table 2. Specification of LR2032 coin cell.

Property	Value
Chemistry	LiCoO2/graphite
Type	Eunicell LR2032
Capacity. max	45 mAh
Nominal voltage	3 V

3. Analysis of Distribution of Relaxation Time

Battery research needs both frequency and time analysis together for understanding battery behavior. Using DRT analysis makes it easier to understand each process than only using frequency analysis. The impedance of an electrochemical system can be expressed as

$$Z(\omega) = R_0 + \int_0^{\infty} \frac{g(\tau)}{1 + j\omega\tau} d\tau \qquad (3)$$

Where R_0 is the ohmic resistance and it is the impedance at very high frequencies where the capacitive effects become negligible, $g(\tau)$ is a function that describes the distribution of relaxation times within the system, ω is the angular frequency at which the impedance is being measured, τ = RC is the relaxation time and R & C are the effective resistance and capacitance respectively.

The DRT is obtained by treating the impedance as an infinite sum of time constants

$$Z(\omega) = R_0 + \int_{-\infty}^{+\infty} \frac{\gamma(ln\tau)}{1 + j\omega\tau} d(ln\tau) \qquad (4)$$

Equation (4) represents the relation between impedance data and frequency distribution. Where $\frac{1}{1+j\omega\tau}$ is the DRT kernel and $\gamma(ln\tau) = \tau g(\tau) \geq 0$ is distribution function of relaxation time.

These impedance parameters can be derived by integrating the time constants within each interval of the DRT curve, serving as the basis for regrouping criteria. For each interval, the polarization resistance (Rp) can be calculated using the following formula:

$$R_p = \int_{\tau_L}^{\tau_U} \gamma(\tau) d\tau \qquad (5)$$

where τ_U and τ_L are the upper and lower limits of time constant, respectively.

However, by using DRT analysis, we can break down and understand each process more easily than with frequency domain analysis alone. By looking at a wider range of frequencies it provides more detailed information about what is happening inside the battery. The higher frequencies region reveals faster processes like chemical reactions, while lower frequencies reveal slower processes like ion diffusion inside the battery. Similarly, utilizing time domain analysis offers a clearer picture of each electrochemical process and enhances our understanding of battery behavior.

4. Results and Analysis

4.1 Evolution of Impedance Spectrum

The Nyquist plots of NCM and coin cell are obtained from EIS measurement as shown in Fig. 2 (a) and (b) respectively. Impedance spectra of each cell is measured after a certain number of cycles up to the complete end of life as capacity decay below 80%. Every spectrum of each cell is divided into four sets of frequency ranges. The figures illustrate ultra-high frequency, high frequency, intermediate frequency, and low frequency as depicted in Fig. 1(a). The relationship between the impedance plot and DRT plot is described in Fig. 1 (a) and (b). Additionally, the DRT curve can be segmented into four peaks (R_{Ohm}, R_{SEI}, R_{ct} and R_D), as depicted in Fig. 1(b). The semicircle appears at intermediate frequency related to charge transfer and SEI layer whereas low frequency region is related to diffusion part which are more related to aging with cycling, while the Ultra-frequency and high frequency are related to ohmic resistance and solid electrolyte interface SEI region respectively which is less dependent with cycling as batteries aging.

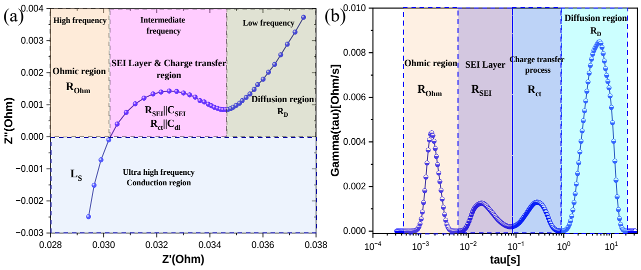

Fig.1. (a) Nyquist plot for NCM cell. (b) Its related DRT plot for NCM cell

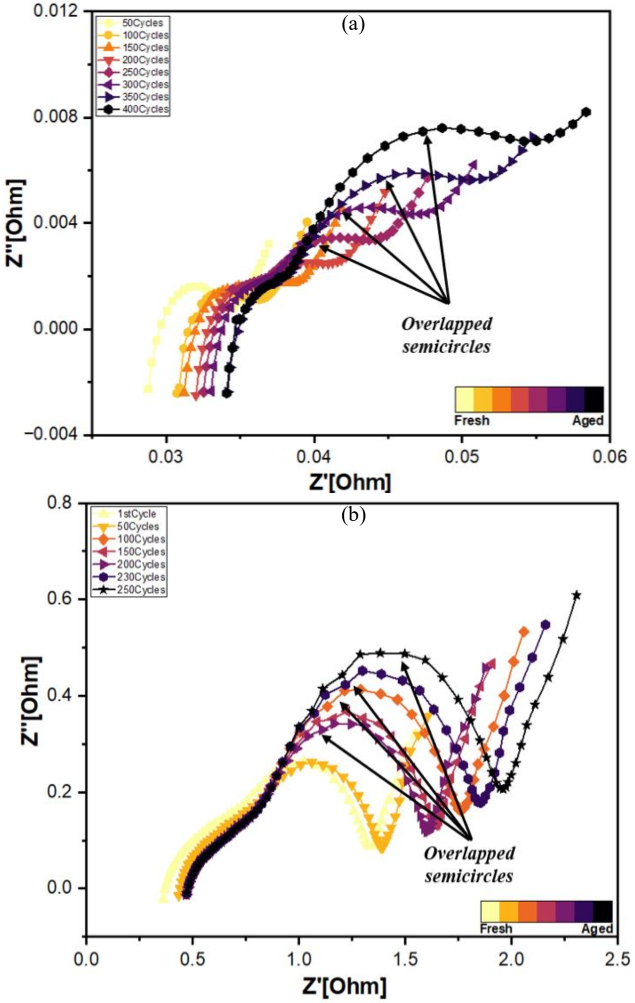

Fig.2. (a) Nyquist plots illustrate the development of NCM cell over its life cycle. (b) Nyquist plots illustrate the development of LR2032 cell over its life cycle.

In Fig. 2 semi-circles are overlapped, which makes it difficult to distinguish them clearly. Each electrochemical process should be represented by a distinct semi-circle, but in practice, they often overlap. As depicted in Fig. 2(a) and (b), both the height and width of these semi-circles increase as the battery undergoes cycling. However, because the reaction time constants for these processes are similar, the semi-circles become superimposed on each other in the impedance spectrum. This overlap makes it challenging to isolate the individual relaxation times and amplitudes associated with each electrochemical process. As a result, accurately interpreting the impedance spectrum and understanding the underlying mechanisms of battery aging becomes more complex.

4.2 Analyzing Battery Aging Using DRT Plots

The EIS impedance data is converted into distribution of relaxation time to elaborate each chemical reaction separately. The DRT plots for the NCM and coin cell are obtained, as depicted in Fig. 3(a) and (b) respectively. In this analysis, we observed a significant phenomenon in the DRT plots for both cells. The peak observed at the extreme right side of each graph, corresponding to the diffusion process, steadily increased in height with the number of cycles. This trend was consistent across all DRT plots, indicating a common behavior as the batteries approached end-of-life conditions. In the same way charge transfer impedance also increases as cells are cycled also the movement of charge transfer process towards higher relaxation time can be observed which means that process is going to slow down with the cycling of battery. The movement of charge transfer impedance towards higher relaxation time indicates that process is becoming slow due to electrode materials degrade, reducing conductivity and increasing charge transfer resistance.

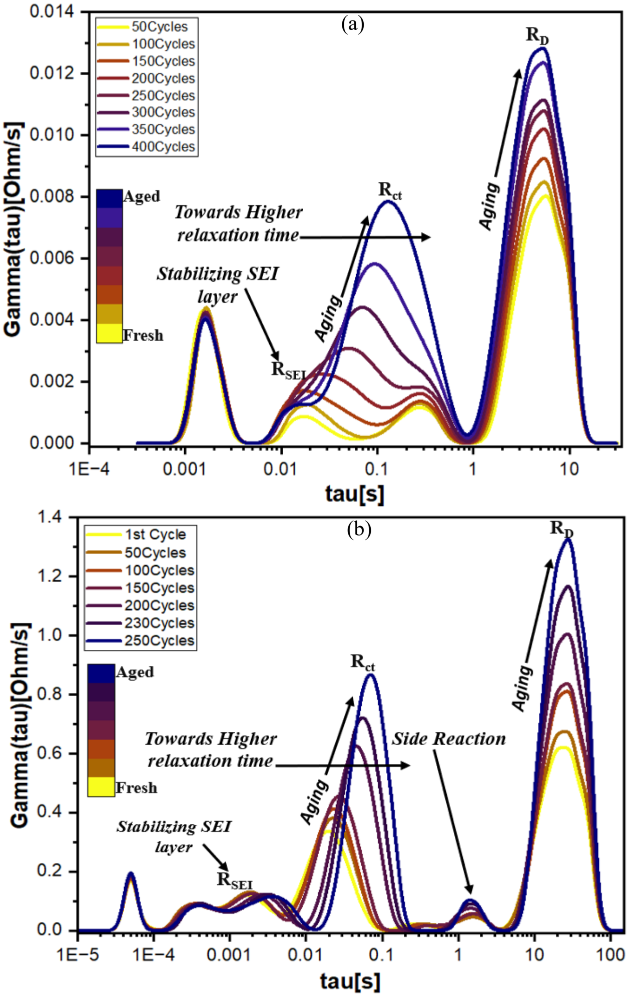

Fig.3. Comparing the development of DRT plots with aging (a) NCM cell DRT plots over the life cycle. (b) Coin cell DRT plots over the life cycle

An increase in charge transfer resistance and diffusion impedance in a lithium-ion battery can indeed indicate a loss of active material in the electrodes, particularly in the negative electrode (anode) and positive electrode (cathode). This impedance increase often signifies degradation processes that lead to reduced electron and ion transport within the electrodes, which can be attributed to particle fractures and structural changes in the active material particles[3]. One of the primary causes of such degradation is the phenomenon of graphite exfoliation and island formation in the negative electrode, which is typically made of graphite. During charging and discharging cycles, the anode undergoes expansion and contraction due to the insertion and extraction of lithium ions.

For both cases i.e. 18650 battery and for LR2032 coin cells the ohmic resistance does not vary as much with cycling, the leftmost peak in DRT is an ohmic part and it can be seen in both cases the variation with aging is minor due to the best and excellent manufacturing process in anode materials. For both cases it is found that impedance of SEI is increases with battery cycling. At the start of the battery's life, the SEI impedance increases more rapidly, but as the battery approaches the end of its life, this growth slows down and stabilizes. Therefore, charge transfer and diffusion impedance are more related to battery aging as these are continuously increasing with cycling which indicates loss of active material in the electrodes of batteries. It is worth noting that the height and area of peaks corresponding to charge transfer and diffusion impedance consistently increase with cycling. This trend indicates that both processes contribute to the internal resistance of the battery, ultimately leading to its failure as they approach the end of life.

5. Conclusion

In this paper, the crucial issue of Lithium-ion (Li-ion) battery aging, which significantly impacts performance and lifespan across various applications, is explored. Despite the complexity of interpreting Electrochemical Impedance Spectroscopy (EIS) data due to overlapping semicircles in impedance spectra, Distribution of Relaxation Time (DRT) analysis is employed to study aging phenomena in Li-ion batteries. Through comparative analysis of DRT plots obtained from Li-ion cell 18650 and Li-ion coin cell LR2032, the mechanisms underlying battery aging, including electrode and electrolyte degradation, are uncovered. Importantly, the findings underscore the significance of lower frequency domain components such as charge transfer and diffusion impedance in understanding battery aging dynamics as it undergoes cycling. The increasing peaks height and area of charge transfer and diffusion impedance during battery cycling indicate battery aging. This research provides valuable insights into battery behavior and degradation, particularly relevant for real-time monitoring systems used in electric vehicles, enhancing our ability to optimize performance and longevity.

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