Unveiling Impedance Response of Commercial Coin-type Lithium-ion Batteries Exposed to Overcharge and Over-discharge through Equivalent Circuit Modeling

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Abstract: - This study investigates the impedance spectroscopy response of commercial coin-type lithium-ion cells under overcharge and over-discharge conditions through equivalent circuit modeling. Electrochemical tests were conducted on battery cells, employing impedance spectroscopy to track variations across various charge states, including overcharge and over-discharge conditions. The impedance data highlighted distinct patterns during normal operation, prompting the application of an anomalous diffusion impedance model. Regression analysis of the model parameters offered valuable insights into the cells' electrochemical performance before and after exposure to overcharge and over-discharge.

Key-Words: - Electrochemical impedance spectroscopy, lithium-ion battery, overcharge, over-discharge, equivalent circuit modeling, regression.

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1 Introduction

A Li-ion battery, an electrochemical energy storage device, is a broadly used rechargeable battery. Like other batteries, the Li-ion battery consists of electrochemical reactions on electrodes and a diffusion mechanism to convert this energy to electricity. Due to the electrochemical reactions and the diffusion, the battery model includes nonlinear terms and uncertainties with some additive disturbances (e.g., unmodelled effects), [1].

State of Charge (SoC) could be defined as the available capacity and formulated as a percentage of its fixed capacity. State of Health (SoH) is described as a measure of the battery’s capability to store and release electrical energy, compared with a new one, [2]. These two quantities are key parameters to predict the battery's life and performance; however, the estimation of SoC and SoH is problematic since the battery model includes nonlinearities and uncertainties depending on time, [3]. In recent years, researchers have shown an increased interest in estimating SoC and SoH of Li-ion batteries, [4]. Three primary approaches have provided a basis; i) simple capacity measurement, [5], ii) Voigt elements in series (RC networks), [6], iii) Impedance-based (equivalent circuit) model, [7]. The conventional capacity measurement method is a straightforward technique based on a simple coulomb counting procedure, [5]. RC networks are used to represent battery dynamics [6]. The implementation of these two techniques is not complicated, and they are commonly used, [8]. However, they lack expressing kinetics and mass transfer mechanisms adequately; therefore, they might represent nonrealistic models. On the other hand, the impedance-based model successfully defines electrochemical reactions and diffusion occurring in Li-ion batteries, which is more realistic and physically based, [9].

The objective of this study is to use the impedance-based model to estimate SoC and SoH accurately under non-stationary circumstances. The uncertain terms in the battery dynamics will be estimated by using a novel adaptive-based observer. The estimated terms will be used to determine the SoC and SoH of the battery. Unlike other associated methods, the proposed technique will not assume battery voltage and the current which are persistently excited throughout the estimation of SoC and SoH process. This proposed model is valid for different states of charge and abuse conditions like overcharge and over-discharge. Therefore, it will be a realistic model for engineering applications using batteries, i.e., electric vehicles, and storage-based smart grids.

2 Experimental Method

Electrochemical experiments were conducted on commercially available Li-ion coin cells. Impedance spectroscopy was employed to observe variations linked to diverse SoC, as well as instances of overcharge and over-discharge.

2.1 Battery Cells

Secondary 2032 coin (or button) cells obtained commercially were utilized for the electrochemical experiments. These cells featured lithium cobalt oxide ($LiCoO_2$) cathodes, graphitic carbon (C_6) anodes, and an electrolyte comprising lithium hexafluorophosphate ($LiPF_6$) salt dissolved in a mixture of organic solvents, including ethylene carbonate (EC), propylene carbonate (PC), dimethyl carbonate (DMC), and diethyl carbonate (DEC). The cells exhibited a normal potential range between 3.00 and 4.20 volts. The nominal capacity and nominal potential of the batteries were 30 mAh and 3.6 V, respectively.

2.2 Instrumentation

Experiments were conducted using a Gamry Reference 3000 Potentiostat /Galvanostat connected to a desktop computer. Gamry Framework and Electrochemical (EChem) Analyst software packages were employed for data acquisition and analysis.

2.3 Protocol

The impedance response and capacity of the battery cells were analyzed under various SOC profiles, encompassing different potential ranges. Additionally, the impedance response was studied under overcharge and over-discharge profiles.

The battery cells were initially charged to 4.20 V under galvanostatic control, with a current of 2 mA. Subsequently, each cell underwent discharge to 3 V at a 1C rate, followed by charging back to 4.20 V with the same bias, i.e., at a constant 30 mA current. The cells were then held potentiostatically at a constant cell potential until the current dropped below 20 μA, [10]. Following this constant-potential rest period, impedance measurements were conducted using a 10 mV alternating current perturbation within a frequency range of 10 kHz to 10 mHz. To study the influence of overcharge, the cell was initially charged under a constant current of 4.2 V. Impedance measurements were performed at each 80mV step up to and including 5 V. A similar protocol was followed for the over-discharge. Impedance measurements were performed at each 80 mV step down to and including 2.20 V. After overcharging to a potential of 5 V, the battery was allowed to relax for four days at the open-circuit condition. When held at open-circuit, the overcharged battery rapidly reached a cell potential within the nominal operating range. After over-discharging to a potential of 2.20 V, the battery was allowed to relax for four days in the open-circuit condition. When held at open-circuit, the over-discharged battery also reached a cell potential within the nominal operating range, but this process was slower. The impedance response showed a persistent change to the electrochemical characteristics of a coin cell subjected to overcharge and returned to normal cell potentials; whereas, the electrochemical characteristics returned quickly to normal for a coin cell subject to over-discharge and returned to normal cell potentials.

All experiments were performed at room temperature (around 20 °C), and they were repeated a few times with the same type of battery cells to ensure that the results were both consistent and reproducible.

3 Results

The impedance measurements obtained during normal operating conditions, specifically at 4.2 V, displayed a distinctive pattern: a depressed capacitive loop at high and intermediate frequencies, along with a linear trend at low frequencies characterized by a slope exceeding 45° as shown in Figure 1.

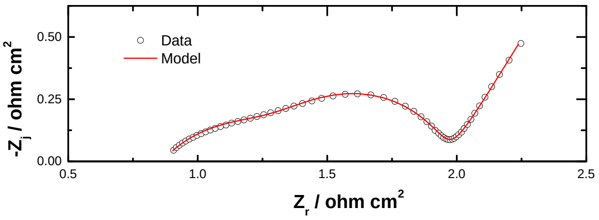


Fig. 1: Impedance response for a battery held at 4.2 V. The line represents the fit of equation (1) to the data

The equivalent circuit model represented in Figure 2 was constructed based on the proposed reactions occurring at both the cathode and anode. This resulting model can be formulated as:

$$Z = R_e + Z_c + Z_a \tag{1}$$

where

$$Z_c = \frac{R_{t,c} + Z_{d,c}}{1 + (j\omega)^{\alpha_c}\left(R_{t,c} + Z_{d,c}\right)Q_c} \tag{2}$$

and

$$Z_{\mathrm{a}} = \frac{R_{\mathrm{t,a}}}{1+\left(\mathrm{j}\omega\right)^{\alpha_{\mathrm{a}}} R_{\mathrm{t,a}} Q_{\mathrm{a}}} \tag{3}$$

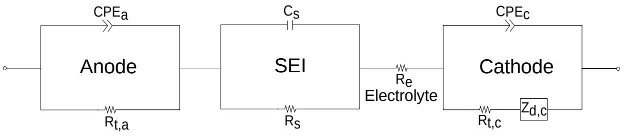
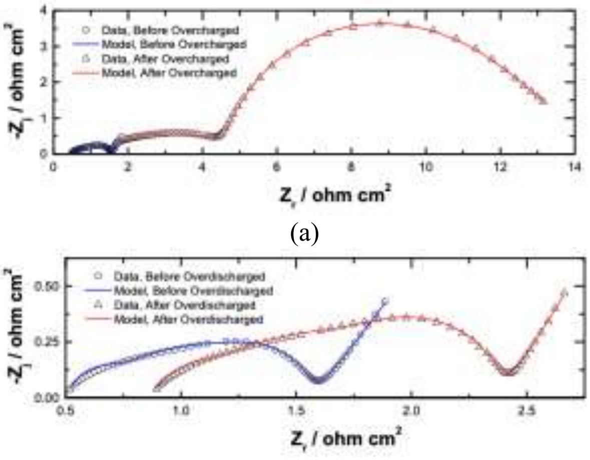


Fig. 2: Equivalent circuit representation of the Li-ion battery cell

The impedance data deviated significantly from what would be expected with a Warburg impedance model, primarily due to the low-frequency impedance slope in a Nyquist plot measuring approximately 56°, well beyond the typical 45° characteristic of a Warburg impedance. Instead, an anomalous diffusion impedance model was adopted, which is applicable to systems experiencing diffusion hindered by intermittent adsorption of diffusing species onto a stationary substrate. This impedance response, incorporating a reflecting boundary condition, was initially elucidated in the literature, [11]. However, since the frequency range in our measurements did not reveal the sharp rise associated with the reflecting boundary condition, we resorted to employing an asymptotic form of their expression. Consequently, the resulting diffusion impedance is expressed as follows:

$$Z_{\mathrm{d,c}}\left(\omega\right) = \left(\frac{Z_{\mathrm{d,c}}\left(0\right)}{\tau^{\gamma/2}}\right)\left(\mathrm{j}\omega\right)^{\gamma/2-1} \tag{4}$$

where $Z_{\mathrm{d,c}}\left(0\right)/\tau^{\gamma/2}$ represents a lumped parameter encompassing both the diffusion time constant (τ) and the zero-frequency asymptote for the real part of the diffusion impedance.



(a)

(b)

Fig. 3: Impedance response and their fit of a coin cell at a potential of 4 V before and after the cell was: (a) overcharged and (b) over-discharged

Figure 3 illustrates the impedance response of a coin cell at a potential of 4 V before and after undergoing specific treatments: overcharging and over-discharging. Panel (a) presents the impedance response before and after overcharging, while panel (b) depicts the response before and after over-discharging. The impedance data is represented graphically along with their respective fits.

Table 1 displays the parameter results obtained through the Levenberg-Marquardt method for regression analysis, [12]. Subsections (a) and (b) of the table respectively present the parameters before and after the cell was subjected to overcharging and over-discharging treatments. These parameters provide valuable insights into the changes occurring within the cell's electrochemical system as a consequence of the applied treatments.

Table 1. Parameter results obtained by Levenberg-Marquardt method for regression: (a) before and after the cell was overcharged and (b) before and after the cell was over-discharged

Parameter	Pristine Cell	Overcharged Cell
R_{e} / Ω cm^2	0.4796 ± 0.0070	1.3053 ± 0.0858
$R_{\mathrm{t,a}}$ / Ω cm^2	0.1586 ± 0.0817	0.7676 ± 0.0317
α_{a}	0.9116 ± 0.0152	0.7826 ± 0.0915
Q_{a} / Ω^{-1} cm^{-2} s$^{\alpha_{\mathrm{a}}}$	0.0112± 0.0009	0.0038 ± 0.0009
R_{s} / Ω cm^2	0.1885 ± 0.0436	1.6471 ± 0.4603
C_{s} / F cm^{-2}	0.0831± 0.0270	0.0963± 0.0011
$R_{\mathrm{t,c}}$ / Ω cm^2	0.5607 ± 0.0299	6.3573± 0.0452
α_{c}	0.6071 ± 0.0717	0.5432 ± 0.0779
Q_{c} / Ω^{-1} cm^{-2} s$^{\alpha_{\mathrm{c}}}$	0.0368 ± 0.0087	0.0014 ± 0.0001
γ	0.6861 ± 0.0529	0.4239 ± 0.0195
$Z_{\mathrm{d}}(0)\,\tau^{-\gamma/2}$ / Ω cm^2 s$^{-\gamma/2}$	0.1406 ± 0.0093	2.2331± 0.1284

(a)

Parameter	Pristine Cell	Overdischarged Cell
R_{e} / Ω cm^2	0.5050 ± 0.0073	0.8726 ± 0.0061
$R_{\mathrm{t,a}}$ / Ω cm^2	0.1468± 0.0700	0.1890 ± 0.0794
α_{a}	0.9890 ± 0.0149	0.8519 ± 0.1108
Q_{a} / Ω^{-1} cm^{-2} s$^{\alpha_{\mathrm{a}}}$	0.0063± 0.0003	0.0023 ± 0.0001
R_{s} / Ω cm^2	0.2053 ± 0.0405	0.4237 ± 0.0338
C_{s} / F cm^{-2}	0.0369± 0.0102	0.0514± 0.0048
$R_{\mathrm{t,c}}$ / Ω cm^2	0.7309 ± 0.0854	0.9237± 0.1081
α_{c}	0.6311 ± 0.0615	0.6120 ± 0.0492
Q_{c} / Ω^{-1} cm^{-2} s$^{\alpha_{\mathrm{c}}}$	0.0185 ± 0.0046	0.0243 ± 0.0043
γ	0.7895 ± 0.0456	0.6644 ± 0.0447
$Z_{\mathrm{d}}(0)\,\tau^{-\gamma/2}$ / Ω cm^2 s$^{-\gamma/2}$	0.1483 ± 0.0087	0.1314± 0.0075

(b)

4 Conclusion

This study conducted a comprehensive investigation into the impedance spectroscopy response of commercial coin-type lithium-ion cells subjected to extreme conditions, including overcharge and over-discharge. Through a combination of electrochemical experiments and equivalent circuit modeling, distinct impedance patterns corresponding to various states of charge conditions were identified. The anomalous diffusion impedance model provided a more accurate representation of the experimental data, indicating that diffusion within the cell was hindered by sporadic adsorption of diffusing species onto a fixed substrate. This insight significantly enhances the understanding of the underlying mechanisms governing lithium-ion battery behavior under such extreme conditions.

The parameter analysis, performed using the Levenberg-Marquardt optimization method, provided crucial information about the changes occurring within the cell's electrochemical system.

The results of this study contribute to an improved understanding of battery degradation mechanisms under overcharge and over-discharge conditions, which can facilitate the development of more effective battery management systems aimed at prolonging battery life and improving performance reliability. This knowledge is essential for various industries, where demand for high-performing and long-lasting lithium-ion batteries continues to rise. As such, the findings presented here are expected to play a significant role in advancing battery diagnostics and maintenance strategies.

Further research is recommended to broaden the scope of this study. Expanding the range of experimental conditions, such as exploring different cell chemistries and cycling profiles, would help generalize the applicability of these findings. Additionally, the validation of the proposed models through practical case studies in real-world applications will be necessary. Continuous efforts in combining electrochemical analysis, impedance modeling, and advanced mathematical methods are expected to lead to further optimization of battery performance and reliability.

Declaration of Generative AI and AI-assisted Technologies in the Writing Process

During the preparation of this work the author used Gemini (Google AI platform) for grammar and language editing reasons. After using this service, the author reviewed and edited the content as needed and take full responsibility for the content of the publication.

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The author performed the experiments, analyzed the results, wrote and reviewed the manuscript.

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Conflict of Interest

The author has no conflicts of interest to declare.

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