

Sensitivity analysis and evolution patterns of key electrochemical parameters to temperature and SOC for lithium-ion batteries[#]

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ABSTRACT

Battery modeling is a crucial method for battery design and management, in which understanding the variations in key electrochemical parameters is essential for lithium-ion battery(LIB) modeling. To analyze the sensitivity of electrochemical parameters under different conditions, this study investigates electrochemical parameters under different temperatures and states of charge (SOC) in a NCM vs. graphite lithium-ion battery. Half cells were designed and utilized to systematically acquire electrochemical parameters for the cathode. To delineate the correlation between working conditions (temperature, and SOC) and key electrochemical parameters, the evolution patterns of the electrochemical parameter matrix under different temperatures and SOC levels are quantified experimentally. Subsequently, through battery model simulation, the impacts of parameter adjustments on the external characteristics of the battery are assessed, revealing the mapping relationships among conditions, electrochemical parameters, and external battery attributes. The results indicate a high sensitivity of the solid-phase diffusion coefficient (D_s) to temperature. Within the temperature range of 10°C to 55°C, these parameters generally exhibit an increasing trend with rising temperature. Furthermore, as the temperature increases, both the peak values and their corresponding SOC values show a noticeable shift. Simulation results reveal that variations in these parameters significantly impact the impedance and voltage of the battery. This investigation furnishes insights for precise modeling and simulation.

Keywords: lithium-ion battery, solid-phase diffusion coefficient, sensitivity analysis, parameter evolution pattern

NONMENCLATURE

Abbreviations

LIB	Lithium-ion Battery
P2D	Pseudo-Two-Dimensional
D_s	Solid-Phase Diffusion Coefficient
GITT	Galvanostatic Intermittent Titration Technique
EIS	Electrochemical Impedance Spectroscopy
SOC	State of charge
RMSE	Root-Mean-Square Error

1. INTRODUCTION

The advancement of electric vehicles has imposed increased demands on battery technology[1-3]. In the realms of battery design and management, mechanism model simulations offer a robust approximation to the actual state of batteries[4]. The pseudo-two-dimensional (P2D) model, proposed by Newman and Doyle[5], is among the most extensively utilized mechanism models. A wide range of electrochemical parameters is required by both the P2D model and its derivatives[6-8]. However, the transferability of these parameters between models is often hindered by factors such as battery geometry, electrolyte and electrode compositions, separator properties, and manufacturing inconsistencies. As a result, the accuracy of simulations is determined not only by the precision of the model itself but also by the accurate measurement of these electrochemical parameters[9]. The difficulty in obtaining precise parameters, coupled with uncertainties in adjusting them under varying conditions, restricts the application of numerous methods in battery research.

Electrochemical parameters are typically determined through physical, chemical, and electrochemical measurement techniques. Parameters

of significant interest, such as solid-phase diffusion coefficient (D_s) and reaction rate constant, have been shown to substantially influence simulation outcomes[10-12]. Techniques including Galvanostatic Intermittent Titration Technique (GITT)[13, 14], Potentiostatic Intermittent Titration Technique[15, 16], and Electrochemical Impedance Spectroscopy(EIS) are employed to measure solid-phase diffusion coefficients[17], while EIS and Linear Sweep Voltammetry are used to determine reaction rate constants[18-20]. These methods are widely regarded as accurate and are commonly used as reference techniques. The precise measurement of electrochemical parameters is essential for advancing battery research.

A significant challenge in lithium-ion battery research is the establishment of clear correlations between battery parameters and their influencing factors. Research indicates that electrochemical impedance, measured at specific frequency ranges, is correlated with temperature. Therefore, relationships between external factors and internal parameters such as impedance can be established through a combination of experimental measurements and theoretical calculations. However, the experimental determination of these parameters often requires extensive and repetitive testing, and this area of research remains underexplored. The relationships between temperature, state of charge (SOC), and key electrochemical parameters are not yet fully understood, necessitating further investigation.

This study aims to elucidate the sensitivity of electrochemical parameters to various influencing factors. Experimental methods are utilized to measure parameters at different temperatures and SOC levels, and the sensitivity of the solid-phase diffusion coefficient is analyzed. A P2D model corresponding to the measured battery is developed, and simulations are conducted to evaluate the impact of parameter variations on battery performance. The paper is organized as follows: Section 2 describes the experimental methods employed, Section 3 examines the patterns of variation in electrochemical parameters, and employs the P2D model to analyze the effects of parameter changes on battery performance.

2. EXPERIMENTS

This study involves the preparation of coin cells and electrochemical testing. Half-cell fabrication is conducted using a glove box, cutting machine, and pellet

press. The testing setup includes a host computer, a coin cell charge-discharge system (NEWARE CT-4008Tn-5V10mA-164), and a temperature chamber (Binder KB115).

2.1 Half-cell fabrication

The coin cells prepared are graphite vs. lithium half-cells, with the coin cell type being CR2016. The electrodes are sourced from fresh battery samples (NCM vs. graphite). The nominal capacity of the LIB samples is approximately 1 Ah, and the operating voltage is 3~4.2 V.

The full cells were discharged to 0% SOC and then dismantled in an argon-filled glove box. The positive and negative electrode foils, as well as the separator, are then immersed in dimethyl carbonate and subsequently dried in a vacuum oven. The electrodes with a single-side coating are punched into 12 mm diameter discs using a precision disc cutter. The coin cell assembly is carried out within the glove box. The assembly sequence is as follows: negative electrode shell, 16 mm diameter nickel foam, 15.6 mm diameter thin lithium disc, 19 mm diameter separator, 12 mm diameter electrode disc, and positive electrode shell. After assembly, the cells are allowed to rest for 12 hours to ensure complete formation. Following this, activation is performed by setting a small current of 0.2 mA for charge-discharge cycles on the coin cell charge-discharge system. The working voltage for the negative half-cell is 0.01~2 V[21].

2.2 Parameter acquisition

This study primarily investigates the solid-phase diffusion coefficient as a key electrochemical parameter. To ensure the validity of parameter acquisition, measurements and calculations are performed experimentally.

The intrinsic rate behavior of electrodes is highly dependent on the diffusion rate of active ions within the electrode material. As an indicator of ion diffusion kinetics, D_s plays a crucial role in evaluating materials and predicting electrochemical performance. GITT is a conventional method for measuring the solid-phase diffusion coefficient.

In recent years, the application of GITT has extended beyond single materials, and it has increasingly been adopted by researchers as a standardized testing method[22]. The testing procedure for electrode materials in this study is as follows: First, a short current pulse is applied to the battery for 30 minutes. Next, the current is interrupted, allowing the battery to relax for a sufficient period until the voltage stabilizes, thereby

achieving equilibrium before the next pulse. This cycle is repeated until the cutoff charge voltage is reached, with a similar procedure applied during the discharge phase.

3. RESULTS AND DISCUSSION

3.1 Analysis of the solid-phase diffusion coefficient

The solid-phase diffusion coefficient of electrode materials was determined using GITT for half-cells at various states of lithiation. This diffusion coefficient describes the transport of intercalated lithium within the electrode particles, modeled by Fickian diffusion processes. The GITT was performed by applying a 0.05 C current for 30 minutes to alter the SOC, followed by a relaxation period to reach open-circuit voltage (OCV). The equation for calculating D_s is derived from the combination of Fick's first and second laws and the Butler–Volmer equation[23]:

$$D_s = \frac{4}{\pi\tau} \left(\frac{iV_m}{Z_A F S} \right)^2 \left(\frac{dE/d\delta}{d\sqrt{t}} \right)^2 \quad (1)$$

where δ denotes the stoichiometric ratio, V_m represents the molar volume of the electrode material, $dE/d\delta$ signifies the gradient of the system's voltage change relative to composition (i.e., the gradient of the Coulomb titration curve), and $dE/d\sqrt{t}$ illustrates the dependence of potential on the square root of time.

$$D_s = \frac{4}{\pi\tau} \left(\frac{n_A V_m}{S} \right)^2 \left(\frac{\Delta E_s}{\Delta E_t} \right)^2 \quad (2)$$

where n_A is the amount of moles of the electrode Material, ΔE_s is the change in steady-state voltage, and ΔE_t is the voltage change in a single-step GITT experiment.

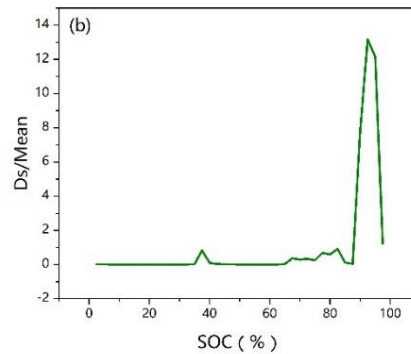
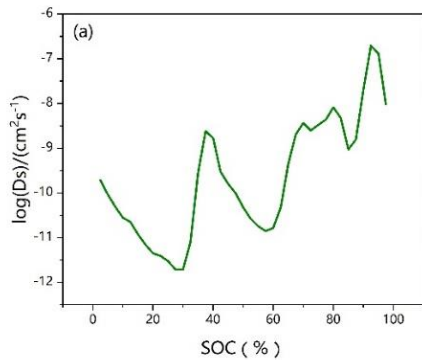


Fig. 1 The logarithm of the solid-phase diffusion coefficient(a) and the ratio of the solid-phase diffusion coefficient to its mean value(b) of graphite half-cells corresponding to SOC

Several assumptions were made in applying the above equation:

- The particle surface area is considered equivalent to the effective surface area for electrochemical reactions.
- A single particle radius is assumed, ignoring any particle size distribution.
- Lithium-ion diffusion is assumed to be purely Fickian.
- The electrode is assumed to contain only one active material component.

These assumptions are routinely applied in P2D

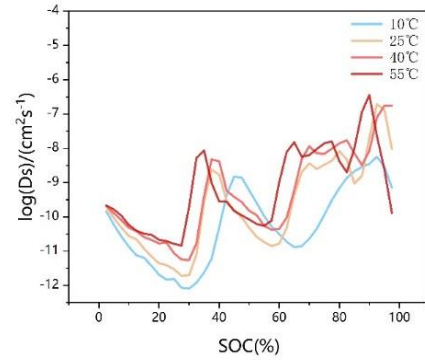


Fig. 2 The logarithm of the solid-phase diffusion coefficient at different temperatures corresponding to SOC

models and their simplified variants. The variations in the solid-phase diffusion coefficient of the graphite negative electrode material with respect to different states of charge (SOC) and temperatures were analyzed, as illustrated in Figs. 1 and 2.

Gaussian peak analysis of the curve indicates that the weighted average center of the W-shaped region is at a

state of charge (SOC) of 0.37. The weighted centers of the troughs are at SOC values of 0.29 and 0.57. At 25°C, the solid-phase diffusion coefficient ranges from 2.43×10^{-12} to $1.30 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$, with a mean

value of $9.05 \times 10^{-9} \text{cm}^2 \text{s}^{-1}$. The relationship between SOC and the solid-phase diffusion coefficient is shown in Fig. 1a. A normalization analysis of the solid-phase diffusion coefficient across the entire state of charge (SOC) range was conducted, using the mean value as the baseline. The deviations of different SOC points from the mean value are illustrated in Fig. 1b. The maximum deviation percentages are 0.02% and 1316.08%, highlighting a significant disparity from the mean value.

Therefore, employing an average solid-phase diffusion coefficient is considered a significant simplification. It is recommended that a variable solid-phase diffusion coefficient, which varies with the state of charge (SOC), be utilized in the P2D model rather than a constant value.

A comparative analysis of the solid-phase diffusion coefficient for the graphite negative electrode at different temperatures was performed, and the resulting curves were smoothed as shown in Fig. 2. Although the shape of the curve remains consistent with temperature variations, a leftward and upward shift of the W-shaped region is observed. Gaussian peak analysis was

T (°C)	Mean Value ($\text{cm}^2 \text{s}^{-1}$)	SOC at Trough1 (%)	SOC at Peak(%)	SOC at Trough2 (%)
10	5.91×10^{-11}	30.77	46.02	69.13
25	9.15×10^{-9}	29.06	37.42	57.41
40	4.85×10^{-10}	28.54	37.86	58.70
55	6.42×10^{-10}	26.18	33.58	54.11

Therefore, it is recommended that when developing coupled thermal models, a variable solid-phase diffusion coefficient that accounts for both temperature and SOC should be used, rather than a constant or an interpolation function considering a single influencing factor.

3.2 Modeling and simulation

A P2D model corresponding to the tested battery was established, and the parameters were obtained from experimental measurements, parameter identification, or literature sources. The simulation results were compared with the measured data to validate the model's accuracy. Notably, the model utilizes a solid-phase diffusion coefficient that varies with SOC. The comparison of the terminal voltage curves

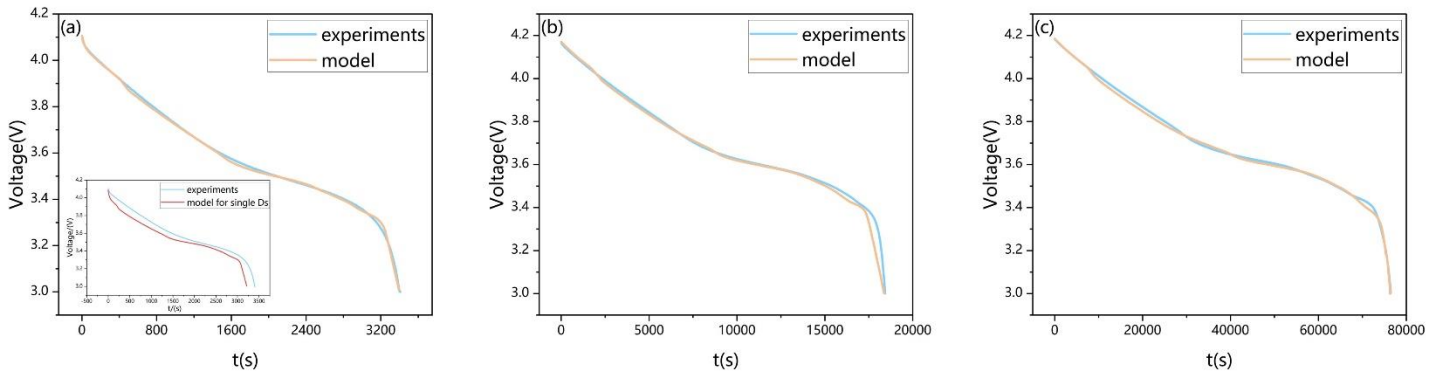


Fig. 3 Comparison of experimental and simulation voltage data at different C-rates (a)1C; (b)0.2C; (c)0.05C

performed on the two troughs and one peak of the W-shaped region, and the mean values are reported in Table 1. Within the temperature range of 10 to 55°C, as the temperature increases, the mean value of the solid-phase diffusion coefficient increases, the W-shaped region narrows, and the SOC values corresponding to the peak and troughs decrease. The peaks and troughs both increase as the temperature rises.

Table 1. Mean values and peak-trough analysis of the solid-Phase diffusion coefficient at different temperatures

under different C-rates is shown in Fig. 3. The simulation curves align well with the experimental curves, and the model accuracy was evaluated using Root-Mean-Square Error (RMSE), as listed in Table 2. This indicates that the model is well-calibrated to the experimental battery data. Fig. 1a additionally demonstrates a comparison between the single-diffusion coefficient (D_s) model and experimental data under a 1C rate. It is evident that the performance of the model with a single D_s is inferior to that of the model utilising a variable D_s . Therefore, this P2D model with a variable D_s will be used to investigate the impact of changes in electrochemical parameters on

battery performance, with a particular focus on the influence of the solid-phase diffusion coefficient.

Table 2. Root-Mean-Squared Error(RMSE) for the output voltage between the P2D simulations and the experimental data at various C-rates

C-rates	RMSE(mV)
1C	8.86
0.2C	29.10
0.05C	12.43

By altering the solid-phase diffusion coefficient, the changes in battery voltage were observed, as shown in Fig. 4. Modifications to D_s were made while preserving the experimentally observed trends by proportionally scaling the parameters to adjust their magnitude. As shown in Fig. 4, within a certain range, an increased D_s in the negative electrode results in a longer discharge duration and a more complete discharge of the battery. Conversely, a reduction in the solid-phase diffusion coefficient of the negative electrode has minimal impact on the initial phase of discharge. However, in the latter phase, the voltage decreases more rapidly.

It is crucial to recognize that other highly sensitive parameters, which were not addressed in this study, represent a substantial and necessary focus for future research.

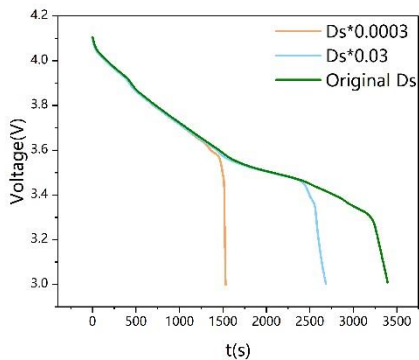


Fig. 4 The impact of solid-phase diffusion coefficients of different orders of magnitude on voltage

4. CONCLUSIONS

Solid-phase diffusion coefficients at different SOC levels and temperatures were determined through GITT testing, and the effects of temperature and SOC on the diffusion coefficient were analyzed. Additionally, the impact of D_s on the battery's external characteristics was assessed using a P2D model.

Experimental results indicate that the solid-phase diffusion coefficient exhibits a W-shaped variation with SOC, differing by up to five orders of magnitude at a given

temperature. Within the 10°C to 55°C range, the coefficient increases with temperature, with the W-shaped region shifting leftward. As temperature rises, both peaks and troughs increase, while corresponding SOC values decrease. These findings highlight the significant impact of temperature and SOC on the diffusion coefficient, suggesting that modeling should avoid using constant values or single-factor adjustments. In the battery model utilized in this study, a reduction in the solid-phase diffusion coefficient of the negative electrode within a specific magnitude range showed negligible effect on the initial discharge voltage. However, during the latter phase of discharge, the voltage drop accelerated, resulting in reduced discharge time and incomplete battery discharge.

These results elucidate the interplay between influencing factors, electrochemical parameters, and battery voltage. They also contribute significantly to refining the precision of modeling and simulation methodologies.

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DECLARATION OF INTEREST STATEMENT

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper. All authors read and approved the final manuscript.

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