



Article

Electrochemical and Thermal Analysis of Lithium-Ion Batteries Based on Variable Solid-State Diffusion Coefficient Concept

Ping Yao and Xuewen Liu *

School of Mechanical and Automotive Engineering, Shanghai University of Engineering Science,
333 Longteng Road, Shanghai 201600, China; m310121484@sues.edu.cn

* Correspondence: xuewen2018@126.com

Abstract: Accurate battery models are of great significance for the optimization design and management of lithium-ion batteries. This study uses a pseudo-two-dimensional electrochemical model combined with a three-dimensional thermal model to describe the electrodynamics and thermodynamics of commercial LIBs and adopts the concept of variable solid-state diffusion in the electrochemical model to improve the fitting ability of the model. Compared with the discharge curve without the VSSD concept, the progressiveness of the model is verified. On the other hand, by comparing the temperature distribution of batteries with different negative electrode thicknesses, it is found that the battery temperature decreases with the increase in battery thickness. At the same time, with the increase in active material volume fraction, the gradient of electrochemical performance is greater, and the heat generation rate is higher. This model can be used for online management of batteries, such as estimating charging status and internal temperature, and further constructing a lithium battery electrochemical capacity degradation model based on the VSSD concept to study the aging behavior of lithium batteries.

Keywords: lithium-ion battery; electrochemical model; thermal model; VSSD; sine approximation



Citation: Yao, P.; Liu, X.

Electrochemical and Thermal Analysis of Lithium-Ion Batteries Based on Variable Solid-State Diffusion Coefficient Concept. *World Electr. Veh. J.* **2024**, *15*, 416. <https://doi.org/10.3390/wevj15090416>

Academic Editors: Rongheng Li and Xuan Zhou

Received: 18 August 2024

Revised: 2 September 2024

Accepted: 7 September 2024

Published: 12 September 2024



Copyright: © 2024 by the authors. Published by MDPI on behalf of the World Electric Vehicle Association. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<https://creativecommons.org/licenses/by/4.0/>).

1. Introduction

With the continuous development of lithium-ion battery technology, and due to its high energy density, long cycle life, and low self-discharge rate, lithium-ion batteries are becoming increasingly widely used in the fields of new-energy electric vehicles and energy storage industry [1,2]. In these novel applications, the batteries in the battery pack are subjected to high currents, dynamically changing loads, and a wide range of operating conditions, such as current and temperature [3]. Therefore, from the perspective of battery usage, it is necessary to study the response and internal state of the battery during its service life. A high-precision battery model is the key to improving the efficiency of battery management systems, and is of great significance for achieving battery system state assessment, life prediction, and healthy operation [4]. The complex interaction between electrochemical reactions and thermal models is the basis for the accurate prediction of LIB's thermal behavior [5]. The experimental research method is not sufficient to study the internal electrochemical process and thermal characteristics of LIBs. At the same time, the experiment of a single-parameter analysis of battery performance has the disadvantages of a high cost and long-time consumption. Therefore, numerical simulation and modeling technology have become indispensable methods in the study of battery performance [6].

The simulation models of lithium-ion batteries are divided into 1D, 2D [7], and 3D [8] models. Among them, 1D models are often used for simple research on basic battery reactions. Two-dimensional models are often based on the symmetrical properties of cylindrical lithium batteries and combined with their radial cross sections and are often used in conjunction with one-dimensional models in practical research. The 3D model is a three-dimensional model of a lithium battery that closely approximates the actual

situation and can objectively present the internal structure of the lithium-ion battery and the temperature conditions of the external environment [9]. The thermal changes inside lithium-ion batteries are affected by parameters such as electrochemical reaction rate, entropy coefficient, diffusion coefficient, and open-circuit voltage. At the same time, many electrochemical parameters in lithium batteries are temperature-sensitive parameters, and temperature changes can lead to changes in the properties of various materials inside the battery, resulting in changes in electrochemical parameters [10]. Therefore, establishing an electrochemical–thermal coupling model is one of the important methods for studying the internal electrochemical and thermal characteristics of lithium batteries. At present, the research on electrochemical and thermal models of lithium-ion batteries focuses on simplifying electrochemical models, including constructing reduced-order models to reduce computational costs while ensuring model accuracy [11–14] and analyzing the applicability of different types of electrochemical models [15,16]. On the other hand, we focus on the specific application of electrochemical thermal coupling models in lithium-ion batteries, including the research and design of battery thermal management systems based on electrochemical thermal coupling models [17–19], the analysis and estimation of the internal state of charge of batteries [20–22], and the analysis of battery aging and capacity degradation behaviors including the side reactions of the SEI film inside lithium-ion batteries [23,24]. In addition, electrochemical thermal coupling models are often used to analyze and study the electrochemical and thermal characteristics of lithium-ion batteries. Huang et al. [25] established an electrochemical–thermal (ECT) coupled model for large lithium batteries and proposed a new method for determining the parameters of the coupled model, which solved the technical problem of difficulty in calibrating model parameters. The experimental results showed that the three-dimensional ECT coupling model had high accuracy, and the non-uniformity of large-sized lithium-ion batteries increased significantly with the increase in discharge rate and battery length. Wang et al. [26] established a precise electrochemical–thermal coupling model, which was validated through charging capacity calibration at different C rates and HPPC testing under different environmental conditions to reflect the electrochemical and heat transfer behavior of lithium-ion batteries exposed to external cold air during electromagnetic induction heating. He et al. [27] developed a three-dimensional model for electrochemical–thermal coupling to analyze the electrochemical and thermal properties of a pouch-type lithium-ion battery in natural convection scenarios. In the thermal model, the rate of heat production, as determined by the electrochemical model, served as the source of heat, while the temperature obtained from the thermal model acted as the starting point for the electrochemical model. Experimental findings at varying discharge rates (1, 3, and 5 C) corroborated the outcomes of the simulations. Computational data indicated that the mean particle size of the electrode at discharge had a direct impact on the battery’s rate of heat production. Jiang et al. [28] developed a model combining one-dimensional (1D) electrochemical and three-dimensional (3D) thermal coupling to examine how a square lithium-ion battery transferred heat while cooling various external surfaces. The parameters for the simulation encompassed the coefficient h for forced convection cooling, the surface area for heat dissipation, and the dimension of battery thickness. Even though the square lithium-ion battery had a smaller side, its orthotropic thermal conductivity enhanced the efficiency of planar heat transfer and the cooling through small-side forced convection. That research revealed a more even temperature spread within a square battery featuring forced convection cooling on its smaller side compared to one with similar cooling on its larger front.

The model of electrochemical–thermal coupling is capable of quantitatively linking battery characteristics with their total performance. Nonetheless, pinpointing the precise electrochemical and thermal factors within the electrochemical–thermal coupling framework continues to be difficult for lithium-ion batteries, leaving the efficacy of the suggested model-oriented battery design or management techniques uncertain. Commonly, in the stages of battery design, production, and manufacturing, factors like diffusion coefficient, conductivity, and electrochemical reaction rate constant in the electrochemical model expe-

rience related alterations due to variations in battery temperature and lithium-ion levels. As a result, it is impossible to accurately measure the performance of commercial lithium-ion batteries that have already been manufactured.

Among the numerous parameters in the electrochemical model of lithium-ion batteries, the solid-state diffusion coefficient can affect the prediction of terminal voltage by influencing the Li^+ concentration on the particle surface. A study investigated the lithium-ion transport inside the battery from the perspective of the electrode material structure [29]. The majority of research views the solid diffusion coefficient as temperature-dependent, with the Arrhenius function extensively applied to account for the temperature's impact on this coefficient [30]. This research introduces the variable solid-state diffusion coefficient (VSSD) idea, calculating the solid-state diffusion coefficient of Li^+ in negative electrode particles based on the temperature and Li^+ concentration. Combined with the electrochemical control equation and the heat generation control equation, a lithium-ion battery electrochemical–thermal coupling model based on the VSSD concept is constructed. Subsequently, the accuracy of the model, as well as the internal electrochemical and thermal characteristics of the battery, is studied and analyzed. To our knowledge, this study is the first attempt to use a specific battery temperature and lithium-ion concentration function formula to describe the solid diffusion coefficient of lithium-ion batteries. The main structure of this article is as follows: First, based on experimental data from the literature, this article uses a sinusoidal approximation method to fit the variation in the diffusion coefficient with the lithium-ion concentration and determines the specific formula for the variable solid diffusion coefficient. Then, an electrochemical–thermal coupling model based on the VSSD concept is constructed, and the model is applied to study and analyze the effects of battery electrode thickness and active material volume fraction on the internal electrochemical and thermal characteristics of the battery, and the corresponding conclusions are obtained.

2. Materials and Methods

2.1. Electrochemical Model

The electrochemical model of lithium-ion batteries mainly consists of the following governing equations: the mass conservation equation for the solid and liquid phases, the charge conservation equation for the solid and liquid phases, and the electrode kinetics' equation at the interface between the solid and liquid phases. The above five governing equations describe the migration and diffusion of active materials inside lithium-ion batteries, and to simplify the model for ease of calculation, the P2D model used the following six assumptions [31]:

- No gas is generated during the operation of the battery;
- The side reactions such as metal lithium deposition and active material loss during the cycling of lithium-ion batteries are not considered;
- The convection of ionic species in the electrolyte is ignored, and only the diffusion and electro-transport processes are analyzed.
- The gas phase reactions inside the lithium-ion battery during charging and discharging are ignored;
- The positive and negative active materials are spherical particles;
- The electrochemical reaction at the solid–liquid interface follows the Butler–Volmer equation.

The electrochemical model usually consists of the following five basic control equations: conservation of charge in the solid phase, conservation of charge in the liquid phase, conservation of the lithium-ion mass in the solid phase, conservation of the lithium-ion mass in the liquid phase, and the electrochemical reaction rate equation at the solid–liquid interface. The modeling principle of its governing equation is:

(1) Conservation of charge in solid state: The charge conservation equation in solid state is usually based on Ohm's law, as shown in Equation (1). In addition, the model usually assumes that the electrode particles are spherical to simplify the calculation, so the

specific area and conductivity of the porous electrode should be corrected, as shown in Equation (3):

$$j_{sum} = -\sigma_s^{eff} \frac{\partial \varphi_s}{\partial x} S_a \quad (1)$$

$$-\sigma_s^{eff} = \varepsilon_s \sigma_s \quad (2)$$

$$S_a = \frac{3\varepsilon_s}{R_p} \quad (3)$$

where σ_s is the solid phase conductivity; σ_s^{eff} is the effective solid phase conductivity; φ_s is the solid electrode potential; j_{sum} is the local current density; S_a is the solid relative surface area; ε_s is the solid phase's volume fraction; and R_p is the radius of the electrode particle.

(2) Conservation of charge in the liquid phase: The liquid phase's charge equation describes the distribution of the liquid-phase potential and also follows Ohm's law. Driven by the concentration difference between the two ends of the electrode, the charge diffuses and transfers in the form of ions, which moves in accordance with Ohm's law. Therefore, the conservation of the charge in the liquid phase is shown in Equation (4):

$$i_l = -\sigma_l^{eff} \frac{\partial \varphi_l}{\partial x} + \frac{2RT\sigma_l^{eff}}{F}(1-t_+) \left(1 + \frac{d \ln f}{d \ln c_l}\right) \frac{\partial \ln c_l}{\partial x} \quad (4)$$

$$\sigma_l^{eff} = \varepsilon_l^{brugg} \sigma_l \quad (5)$$

where σ_l is the liquid-phase conductivity; σ_l^{eff} is the effective liquid-phase conductivity; F is Faraday's constant; R is the gas constant; f is the molar activity coefficient; t_+ is the migration number; φ_l is the volume fraction in the liquid phase; and c_l is the concentration of lithium ions in the liquid phase.

(3) Conservation of mass in the solid phase: Because it is assumed that the diffusion process of lithium ions in the electrode particles occurs in spherical coordinates, only the radial direction of the spherical particles experiences diffusion and follows Fick's second law. The mass conservation of lithium ions in the solid phase can be expressed in spherical coordinates as shown in Equation (6):

$$\frac{\partial c_s}{\partial t} = \frac{1}{r^2} \frac{\partial}{\partial r} \left(D_s r^2 \frac{\partial c_s}{\partial r} \right) \quad (6)$$

In the formula, c_s represents the concentration of lithium ions in the electrode particles; r is the radius of the electrode particles; and D_s is the solid-phase diffusion coefficient.

(4) Liquid-phase mass conservation: The diffusion of lithium ions in the electrolyte, the flow of ions caused by electrochemical migration, and the electrochemical reactions on the surface of the active material all contribute to changes in the lithium concentration in the liquid phase of the electrode and separator. The law of mass conservation for liquid-phase lithium ions is illustrated in Equation (7):

$$\frac{\partial(\varepsilon_l c_l)}{\partial t} = \frac{\partial}{\partial x} \left(D_l^{eff} \frac{\partial c_l}{\partial x} \right) + \frac{S_a j_{sum}}{F} (1-t_+) \quad (7)$$

$$D_l^{eff} = \varepsilon_l^{brugg} D_l \quad (8)$$

In the formula, D_l is the liquid-phase diffusion coefficient and D_l^{eff} is the corrected effective liquid-phase diffusion coefficient

(5) Solid-liquid-phase electrochemical reaction rate equation: The local current density is defined according to the Butler-Volmer equation, where the current density at the equilibrium of the positive and negative reaction rates of the electrode is defined as the exchange current density. Overpotential η is expressed as the potential difference of the electrode when it deviates from the equilibrium potential.

$$j_{sum} = S_a j_0 \left(\exp \left(\frac{\alpha_a F}{RT} \eta \right) - \exp \left(-\frac{\alpha_c F}{RT} \eta \right) \right) \quad (9)$$

$$j_0 = Fk(c_l)^{\alpha_a} (c_{s,max} - c_{s,surf})^{\alpha_a} (c_{s,surf})^{\alpha_c} \quad (10)$$

$$\eta = \phi_s - \phi_l - \frac{j_{sum}}{S_a} R_{film} - U_{j,eq} \quad (11)$$

In the formula, j_0 is the current density; k is the reaction rate constant; α_a and α_c are the cathode/anode transfer coefficients; R_{film} is the membrane resistance; and $U_{j,eq}$ is the equilibrium potential.

2.2. Thermal Model

According to research experience, the temperature distribution of lithium-ion batteries is usually determined by changes in the internal heat flux of the battery, including the heat generated internally and its conduction to the external environment. Therefore, when defining a three-dimensional temperature distribution model for batteries, the following three main processes are usually involved [32]:

- (1) The heat generation process within the battery;
- (2) The process of heat conduction from the inside of the battery to the outer surface;
- (3) The process of heat dissipation from the battery surface to the surrounding environment.

A. Reaction heat: since the electrochemical reaction is reversible, the reaction heat is also reversible heat, represented by Equation (12):

$$q_{rea} = j_{sum} T \frac{\partial U_{eq}}{\partial T} \quad (12)$$

B. Polarization heat: polarization heat is defined as the heat energy required to break this equilibrium, which is irreversible heat and can be expressed by Equation (13):

$$q_{act} = j_{sum} \eta \quad (13)$$

C. Ohmic heat: During the battery cycling process, lithium ions inside the battery undergo electrochemical reactions during migration and diffusion, and inevitably rub against other material particles. At that time, energy is released in the form of heat, defined as Ohmic heat. Like polarization heat, it is irreversible heat, which can be expressed by Equation (14):

$$q_{ohm} = \sigma_s^{eff} \nabla \phi_s \cdot \nabla \phi_s + \nabla \phi_l \cdot (\sigma_l^{eff} \nabla \phi_l) + \frac{2RT\sigma_l^{eff}}{F} \left(1 + \frac{\partial \ln f}{\partial \ln c_l} \right) (t_+ - 1) \nabla(\ln c_l) \quad (14)$$

(1) Thermal conductivity of lithium-ion batteries: The thermal conductivity of lithium-ion batteries exhibits anisotropy because battery cells are assembled from multiple different components. According to Fourier's law, the heat conduction inside lithium-ion batteries can be described according to Equation (15):

$$q_c = -\nabla(\kappa \nabla T) \quad (15)$$

(2) Lithium-ion batteries undergo heat exchange when in contact with the environment. When lithium-ion batteries come into contact with other media, they transfer heat through two pathways: thermal convection and thermal radiation, driven by temperature differences. Convective heat transfer is calculated using Equation (16):

$$q_d = h(T - T_{amb}) \quad (16)$$

(3) The energy conservation equation is:

$$\rho c_p \frac{\partial T}{\partial t} - \lambda \nabla^2 T = q_{rea} + q_{act} + q_{ohm} \quad (17)$$

2.3. Electrochemical–Thermal Coupling Model

Research on lithium batteries must thoroughly account for the intertwined effects of electrochemical and thermal parameters. The P2D model is commonly used to simulate the electrochemical reactions inside batteries and the migration process of lithium ions. By importing the parameters of the P2D model into simulation software, the heat generation of the battery is obtained. The battery heat generation rate is used as the input of the heat transfer model, and the calculation is performed in the thermal model. The output is the average temperature of the battery during the electrochemical reaction. Then, the calculated average temperature is fed back to the electrochemical model, and temperature sensitive parameters such as solid–liquid-phase diffusion coefficient and solid–liquid-phase conductivity are continuously corrected in the electrochemical model [33], so as to more comprehensively and accurately describe the migration dynamics of lithium ions and electrons inside the battery and to deeply explore the electrochemical thermal behavior of lithium ions. The coupling of the electrochemical model and the thermal model is shown in Figure 1.

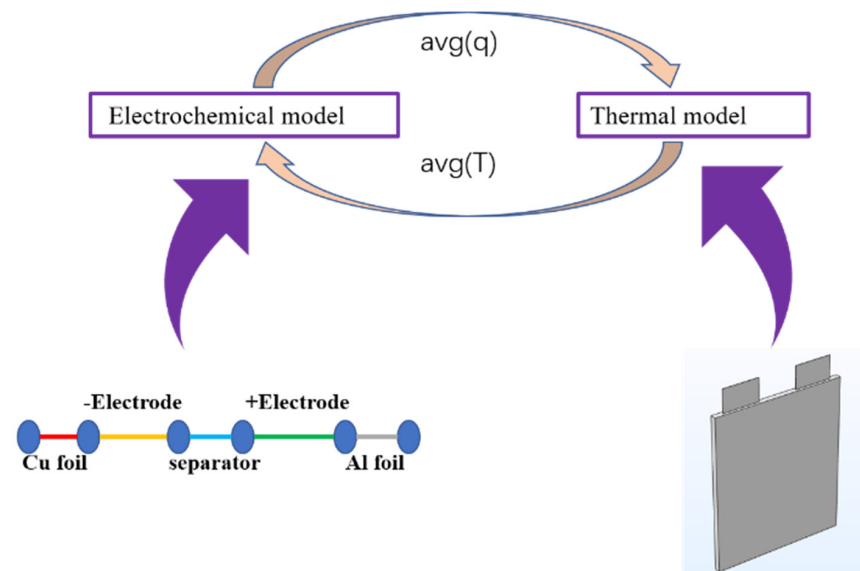


Figure 1. Electrochemical–thermal model coupling.

2.4. Modeling Parameters

(1) We used COMSOL simulation software for the simulation calculations. The parameters in the electrochemical model control equation mainly included the solid–liquid-phase diffusion coefficient, lithium-ion migration number, conductivity, positive and negative electrode thickness, positive and negative electrode particle radius, maximum positive and negative electrode lithium-ion concentration, and average charge discharge current density [34]. The specific modeling parameters for the electrochemical thermal coupling model are listed in Table 1.

This study used the Arrhenius equation to describe temperature-related parameters in the electrochemical model, which was beneficial for improving the electrochemical thermal coupling model of batteries and enhancing its accuracy. The specific expression was as follows:

The expression for the solid-phase diffusion coefficient of the negative electrode was:

$$D_s = 1.4523 \times 10^{-13} e^{\frac{68025.7}{8.314} * (\frac{1}{T_{ref}} - \frac{1}{T})} \quad (18)$$

The expression for the liquid-phase diffusion coefficient was:

$$D_e = 1 \times 10^{-4} * 10^{-4.43 * (54.0 / (T_{ref} - 229.0 - 0.05c_e)) - 2.2 \times 10^{-4} c_e} \quad (19)$$

The expression for liquid-phase conductivity was:

$$\sigma_e = 1 \times 10^{-4} c_2 \left(-10.5 + 0.074 T_{ref} - 6.69 \times 10^{-5} T_{ref}^2 + 6.68 \times 10^{-4} c_e - 1.78 \times 10^{-5} c_e T_{ref} + 2.8 \times 10^{-8} c_e T_{ref}^2 + 4.94 \times 10^{-7} c_e^2 - 8.86 \times 10^{-10} c_e^2 T_{ref}^2 \right) \quad (20)$$

The open-circuit voltage and entropy coefficient of the positive and negative electrodes are shown in Figure 2.

Table 1. Partial parameters of the electrochemical model.

Parameters	Parameter Name	Unit	Cathode	Separator	Anode
L	Length	μm	65	10	55
r_p	Radius	μm	5		3.5
$c_{s,\max}$	Maximum lithium-ion concentration	mol/m^3	25,000		37,420
D_s	Diffusion coefficient of lithium in solid phase	m^2/s	Equation (18)		3×10^{-13}
D_e	Diffusion coefficient of lithium in electrolyte	m^2/s	Equation (19)	Equation (19)	Equation (19)
ε_s	Volume fraction of solid phase	1	0.62		0.43
ε_e	Volume fraction of electrolyte	1	0.26	0.54	0.332
σ_s	Electrical conductivity of solid phase	s/m	100		10
σ_e	Electrical conductivity of electrolyte	s/m	Equation (20)	Equation (20)	Equation (20)
α_a/α_c	Charge transfer coefficients	1	0.5		0.5
c_e	Lithium concentration in electrolyte phase	mol/m^3	1200	1200	1200
k_0	Reaction rate constant	m/s	1×10^{-12}		1×10^{-12}
$\text{SOC}_{\max}$	Maximum state of charge	1	0.975		0.98
$\text{SOC}_{\min}$	Minimum state of charge	1	0		0
t_+	Lithium transference number in electrolyte	1		0.363	
F	Faraday's constant	C/mol		96,485	
T_{ref}	Reference temperature	K		293.15	

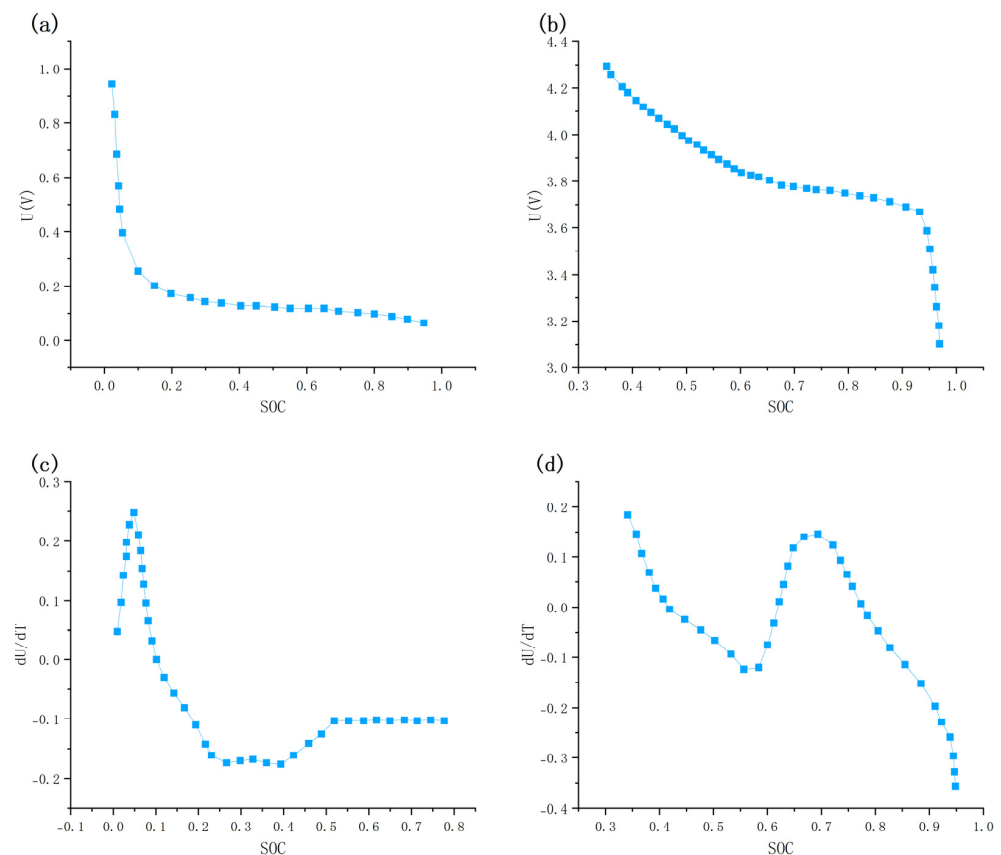


Figure 2. Positive and negative open-circuit voltage and entropy coefficient interpolation function: (a) negative open-circuit voltage; (b) positive open-circuit voltage; (c) negative entropy coefficient; (d) positive electrode entropy coefficient.

(2) We established the geometry of the soft-pack battery in COMSOL Multiphysics 6.0 and obtained the geometric parameters and material properties of the battery based on the literature. The schematic diagram of the thermal model is shown in Figure 3, and the specific parameter values can be seen in Table 2.

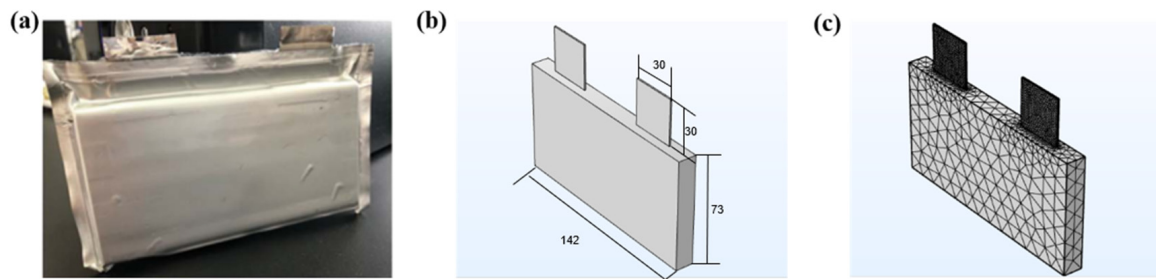


Figure 3. Schematic diagram of lithium-ion battery structure: (a) actual appearance of the battery; (b) Geometric dimensions of three-dimensional thermal models; (c) 3D thermal model grid diagram.

Table 2. Partial parameters of thermal model.

Parameters	Parameter Name	Unit	Values
W-cell	Cell width	mm	142
H-cell	Cell height	mm	73
L-cell	Cell thickness	mm	12
W-tab	Tab width	mm	30
H-tab	Tab height	mm	30
L-tab	Tab thickness	mm	1
ρ	Cell density	Kg/m ³	2560
C_p	Heat capacity	J/kg·K	975
λ_x	Lengthwise thermal conductivity	W/m·K	27.6
λ_y	Thicknesswise thermal conductivity	W/m·K	1.12
λ_z	Heightwise thermal conductivity	W/m·K	27.6
T-amb	Ambient temperature	K	298.15
h	Convective heat transfer coefficient	W/m ² ·K	15

2.5. Simulation Software

At present, the simulation methods for lithium-ion batteries mainly include finite volume method [35,36] and finite element method [37,38]. The finite element method is mainly used to solve partial differential equations and integrals. Its advantage lies in converting complex practical situations into finite element models and using numerical methods for solving calculations. Commonly used simulation software include Ansys (2024 R2) and COMSOL Multiphysics. Due to the significant advantages of COMSOL in conducting multiphysics field-coupling calculations, this study used COMSOL Multiphysics 6.0 to simulate batteries.

3. Results and Discussion

The prediction of battery terminal voltage is affected by the effect of the solid diffusion coefficient on particle-surface lithium-ion concentration. Many studies have shown that there is a correlation between solid diffusion coefficient and temperature, and the Arrhenius function is widely used to describe the effect of temperature on the diffusion coefficient [39,40]. This section proposes the concept of VSSD and establishes an electrochemical thermal coupling model for lithium-ion batteries based on the VSSD to improve the accuracy of model fitting. At the same time, based on model analysis, the internal electrochemical and thermal characteristics of the battery are studied.

3.1. Electrochemical–Thermal Coupling Model Based on VSSD Concept

3.1.1. Variable Solid-State Diffusion Coefficient Concept (VSSD)

Experimental results have shown that introducing the concept of Variable Solid-State Diffusion Coefficient (VSSD) can effectively improve the accuracy of terminal voltage prediction [41]. This article proposes the concept of VSSD, where a function of temperature and concentration of lithium ions is constructed to describe the solid diffusion coefficient of lithium ions in negative particles:

$$D_{s,neg}(c_{s,neg}, T) = D_{s,neg,0}(c_{s,neg}) * \exp\left(\frac{E_{aD_{s,neg}}}{R} \left(\frac{1}{298.15} - \frac{1}{T}\right)\right) \quad (21)$$

where $D_{s,neg}$ is a function of lithium-ion concentration and the solid diffusion coefficient of lithium ion in the negative particle; $E_{aD_{s,neg}}$ is the solid-state diffusion activation energy of lithium ion in the negative particle.

$$D_{s,neg,0} = \lambda_1 * \sin(c_{s,neg} * \kappa_1 + D_{s,neg,avg,1}) + \lambda_2 * \sin(c_{s,neg} * \kappa_2 + D_{s,neg,avg,2}) + \dots + \lambda_n * \sin(c_{s,neg} * \kappa_n + D_{s,neg,avg,n}) \quad (22)$$

Among them, $D_{s,neg,avg}$ is the mean diffusion coefficient, κ_n is the concentration correction factor, and λ_n is the fitting coefficient. According to the MATLAB sine approximation method, when the values of n were taken as four, five, and six, the parameter values of the fitting formula were as shown in Table 3:

Table 3. Numerical parameters of the fitting formula.

n	λ	κ	$D_{s,neg,avg}$
4	$1.04 \times 10^{-12};$	$1.341 \times 10^{-4};$	$-0.126;$
	$3.88 \times 10^{-13};$	$2.682 \times 10^{-4};$	$1.23;$
	$1.3 \times 10^{-13};$	$5.364 \times 10^{-4};$	$2.151;$
	9.943×10^{-14}	8.045×10^{-4}	-1.228
5	$1.05 \times 10^{-12};$	$1.341 \times 10^{-4};$	$-0.05308;$
	$3.87 \times 10^{-13};$	$2.682 \times 10^{-4};$	$1.392;$
	$1.39 \times 10^{-13};$	$5.364 \times 10^{-4};$	$2.148;$
	$7.49 \times 10^{-14};$	$8.045 \times 10^{-4};$	$-1.216;$
6	8.97×10^{-14}	1.073×10^{-3}	1.231
	$1.95 \times 10^{-13};$	$1.331 \times 10^{-4};$	$-0.06272;$
	$1.07 \times 10^{-13};$	$5.324 \times 10^{-4};$	$2.117;$
	$7.81 \times 10^{-14};$	$7.986 \times 10^{-4};$	$-1.387;$
	$3.74 \times 10^{-14};$	$1.597 \times 10^{-3};$	$0.8523;$
	$2.62 \times 10^{-14};$	$1.863 \times 10^{-3};$	$-1.963;$
	$4.81 \times 10^{-14};$	1.331×10^{-3}	-1.904

Based on the measured diffusion coefficient curve with lithium-ion concentration in reference [42], the sine approximation fitting method of MATLAB was used to fit the originally constant diffusion coefficient reference value $D_{s,neg,0}$ into a function of Li^+ concentration; simultaneously, combined with the Arrhenius formula, the solid-state diffusion coefficient of the negative electrode was finally derived as a function of the lithium-ion concentration and temperature, in order to improve the accuracy of the P2D model and the electrochemical–thermal coupling model. The variation in the reference diffusion coefficient with lithium-ion concentration is shown in Figure 4, and the fitting diagram using MATLAB with different terms of sine approximation is shown in Figure 5.

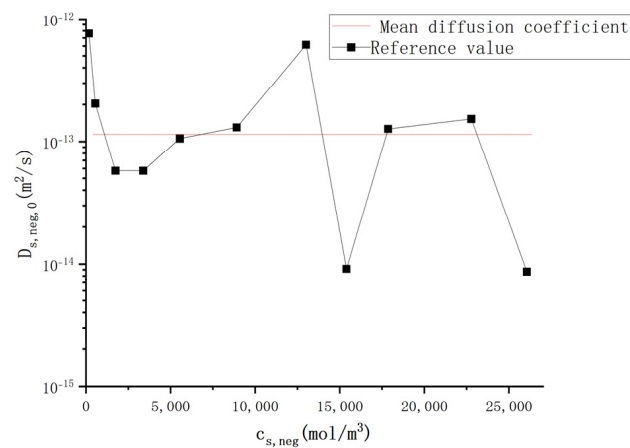


Figure 4. Schematic diagram of the variation in the reference diffusion coefficient with the lithium-ion concentration.

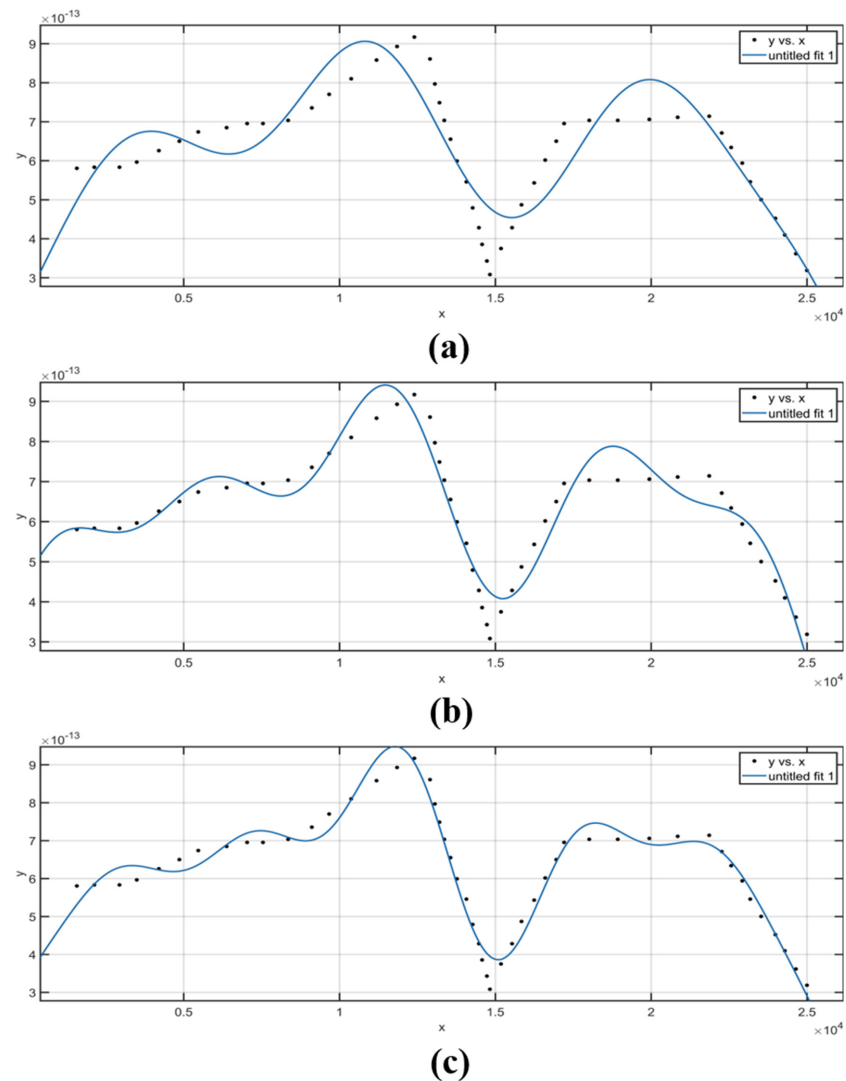


Figure 5. Fitted plots of diffusion coefficients with different numbers of terms as a function of the concentration: (a) four terms; (b) five items; (c) six items.

3.1.2. Sine Approximation's Fitting Results with Different Number of Terms

In order to determine the final formula for the variable solid-state diffusion coefficient, the sine approximation formulas for four, five, and six terms were substituted into the

electrochemical thermal coupling model for the simulation calculation. At the same time, combined with experimental data in the literature, the formula for the variable solid-state diffusion coefficient was determined based on the fitting between simulation data and experimental data. Figures 6–8 show the response curves of the battery discharge voltage fitted by the model and experiment at different discharge rates and ambient temperatures when the number of sine function terms was four, five, and six, respectively. As shown in Figures 6 and 7, when the sine function had four or five terms, the fitting effect was significantly poorer and deviated greatly from the measured data, which could not accurately reflect the internal electrochemical characteristics of the battery. When the number of sine terms was six, the simulation model fitted well with the measured data. Therefore, by comparing the discharge voltage response curves under different sine function terms, it can be seen that the accuracy of the sine approximation formula for the six sine functions was relatively high. The reason may be that the sine approximation of higher terms could better reduce the absolute error.

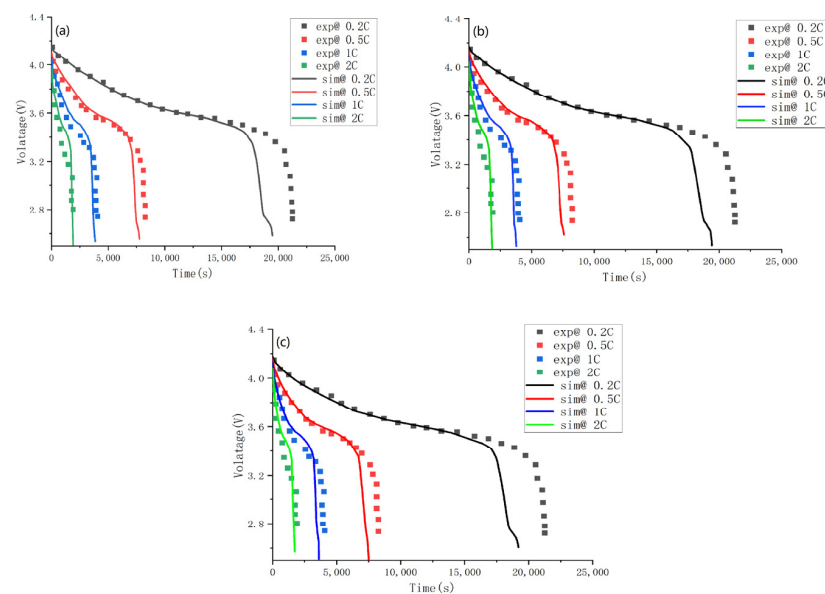


Figure 6. Four-sine formula discharge-voltage fitting curve: (a) 283 K; (b) 293 K; (c) 303 K.

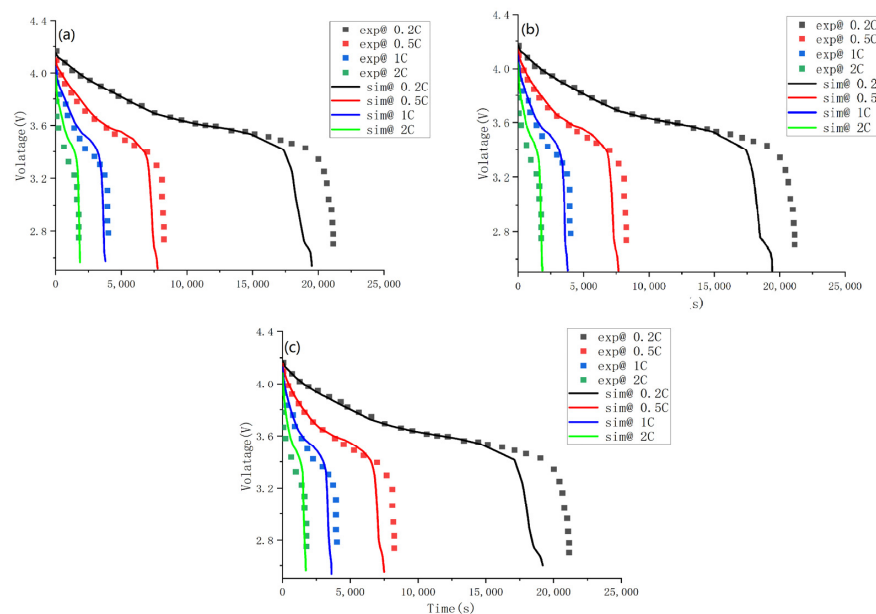


Figure 7. Five-sine formula discharge-voltage fitting curve: (a) 283 K; (b) 293 K; (c) 303 K.

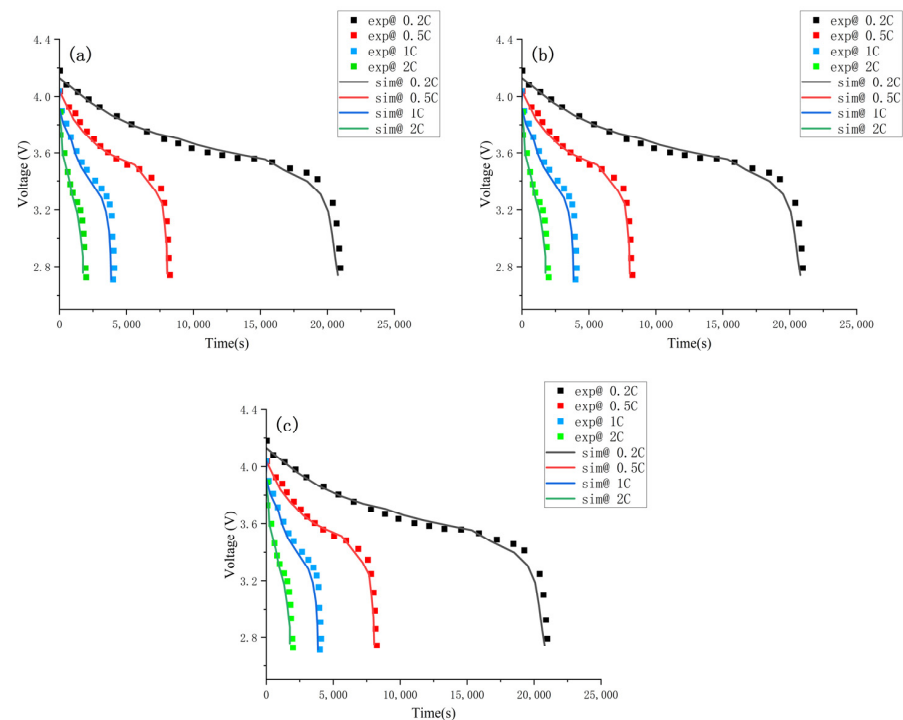


Figure 8. Six-sine formula discharge-voltage fitting curve: (a) 283 K; (b) 293 K; (c) 303 K.

3.2. Verification of Electrochemical–Thermal Coupling Model Based on VSSD Concept

3.2.1. Verification of Electrochemical Model

To compare the fitting ability of electrochemical models without the VSSD concept and those with the VSSD concept with experimental data under different ambient temperatures, the electrochemical parameters were fitted with the test data of constant discharge at different discharge rates. The average temperature of the lithium-ion battery was calculated from the actual measured temperature and used to calculate the values of the temperature-related electrochemical parameters in the electrochemical model.

Figure 9a–c show the fit of the terminal voltage's response curve of the P2D model without the VSSD concept at 283, 293, and 303 K, respectively. As shown in Figure 9a, when the temperature was 283 K and the discharge rate was 0.2 C and 2 C, the fitting results of the terminal voltage response were significantly different from the measured data before and during the discharge period, and the fitting RMSE was 26 and 14 mV. At Figure 9b, it can be seen that the fitting results of the terminal voltage response at different discharge rates at 293 K were in good agreement with the measured data. The root-mean-square values of the discharge fitting at 0.5 C, 1 C, and 2 C were 15, 16, and 12 mV, respectively. From Figure 9c, it can be seen that at 303 K, the voltage response of the fitted terminal was in good agreement with the measured data during 1 C and 2 C discharges, while at the end of 2 C discharge, the voltage response of the fitted terminal deviated significantly from the measured data. For discharges at 0.5 C, 1 C, and 2 C, the fitted effective values were 32, 12, and 5 mV, respectively. These relatively large root-mean-square fits indicated that traditional P2D models could not accurately capture the electrodynamics over a relatively wide operating range. Furthermore, by comparing Figure 9a,c, we can easily observe that at the end of discharge at 0.2 C, the terminal voltage measured at 303 K dropped much faster than at 283 K. Since the OCV curve tends to decline rapidly in low SOC regions, traditional uncorrected P2D models may lack reasonable adjustment capabilities to offset this rapid decline in the OCV curve, and therefore cannot reflect the relatively slow decline trend at lower temperatures. Therefore, the concept of the VSSD was proposed in the electrochemical model, and the solid-state diffusion coefficient was described as a function of lithium-ion concentration and temperature.

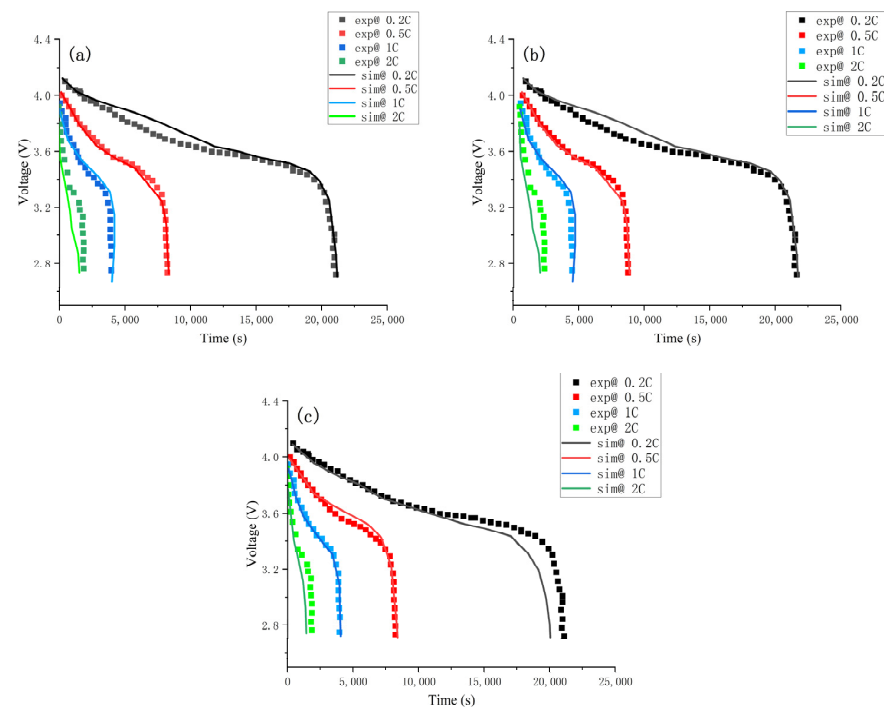


Figure 9. The fitting results of the discharge voltage curve of the P2D model without the VSSD concept under different working conditions: (a) 283 K; (b) 293 K; (c) 303 K.

Figure 10a–c show the discharge voltage's fitting curves of the electrochemical model using the VSSD concept at 283, 293, and 303 K, respectively. Compared with Figure 9a, the fitting performance of the terminal voltage near the end of the 0.2 C discharge in Figure 10a was significantly improved, and the fitting RMSE dropped to 8 mV.

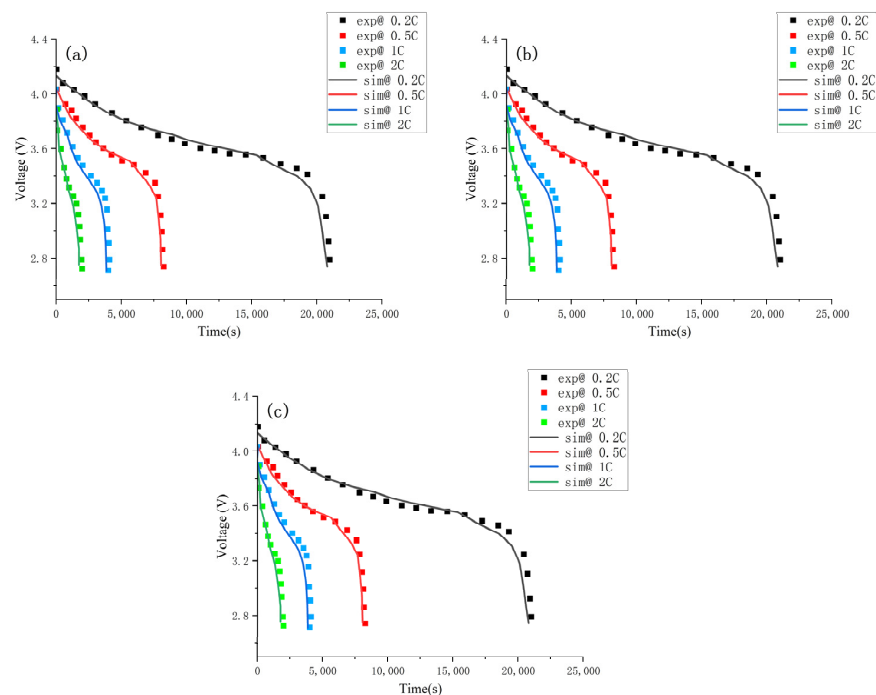


Figure 10. The fitting results of the discharge voltage curve of the electrochemical model based on the concept of VSSD under different working conditions: (a) 283 K; (b) 293 K; (c) 303 K.

As can be seen in Figure 10b,c, under a relatively high ambient temperature, the final discharge voltage curves with different discharge rates fitted the measured data well.

These fitting results demonstrate the necessity of introducing the concept of VSSD into electrochemical models. This may be because the VSSD concept, including the effect of the lithium-ion concentration on solid-state diffusion, can provide greater polarizability adjustment from the perspective of increased degrees of freedom.

3.2.2. Verification of Electrochemical–Thermal Coupling Model

In the case where the P2D model based on the VSSD concept had good fitting accuracy, the VSSD was introduced into a more complex electrochemical–thermal coupling model. Figure 11 shows the discharge voltage curve fitting results of the electrochemical–thermal coupling model based on the concept of VSSD under different working conditions. From Figure 11a–c, it can be seen that due to the influence of thermal parameters in the battery thermal model, there was a certain deviation in the fitting of the model at the end of discharge under high-temperature and low-discharge-rate conditions. However, the fitting of other terminal voltage curves was basically in good agreement with the measured data. Table 4 presents the root-mean-square error of the temperature fitting under different operating conditions. At different ambient temperatures, the average fitted RMSEs of discharge rates at 0.2 C, 0.5 C, 1 C, and 2 C were 0.73, 0.51, 0.29, and 0.58 K, respectively, indicating good fitting results. In summary, these excellent discharge voltage curve fitting performance values show that the electrochemical–thermal coupling model based on the VSSD concept can simulate the internal electrodynamics and thermal dynamics of lithium-ion batteries over a wide operating range and the thermodynamics of large lithium-ion batteries over a wide operating range and can be further used for the optimization design and aging behavior research of lithium-ion batteries.

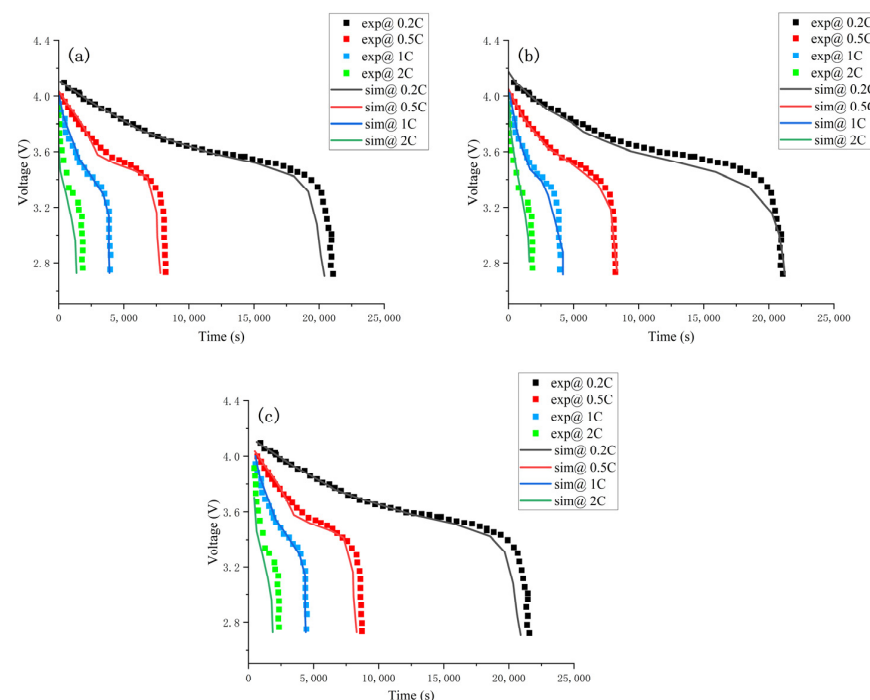


Figure 11. The discharge voltage curve fitting results of the electrochemical–thermal coupling model based on the concept of VSSD under the following working conditions: (a) 283 K; (b) 293 K; (c) 303 K.

Table 4. The fitted RMSEs of voltage curve under different working conditions.

Temperature	0.2 C Rate	0.5 C Rate	1 C Rate	2 C Rate
283 K	0.72	0.45	0.28	0.63
293 K	0.79	0.57	0.34	0.54
303 K	0.68	0.50	0.26	0.58
Average	0.73	0.51	0.29	0.58

3.3. Battery Performance at Different Electrode Thicknesses

From a macro perspective, since the capacity and quality of the battery are greatly affected by the thickness of the battery, the energy density and power density of the battery are also affected by the thickness of the battery. On a microscopic level, the thickness of the electrode affects the length of the diffusion path of lithium ions Li^+ , thereby affecting the mass transfer process and polarization.

Figure 12 shows the effect of the electrode thickness on electrolyte concentration at four different positive thicknesses (45 mm, 55 mm, 65 mm, and 75 mm). The electrolyte concentration of the negative electrode increased with the increase in electrode thickness, while the electrolyte concentration gradient increased with the decrease in positive electrode thickness, which was due to the increase in liquid-phase diffusion polarization due to the extension of the liquid-phase diffusion path. Along with electrochemical characteristics and heat production rate, the temperature distribution is also a key criterion for evaluating battery performance. Based on experience, it was predicted that the temperature at the end of the discharge would be higher and the temperature difference larger. Therefore, the temperature distribution at the end of discharge is shown in Figures 13 and 14, and the temperature difference under different electrode thicknesses is shown in different colors, with a unified temperature legend. From Figure 13, it can be seen that the battery temperature increased with the increase in electrode thickness, with the highest temperature increasing from 303.16 K to 307.36 K, an increase of 4.2 K. This is because at the same discharge rate, polarization and discharge current density increased with the increase in electrode thickness.

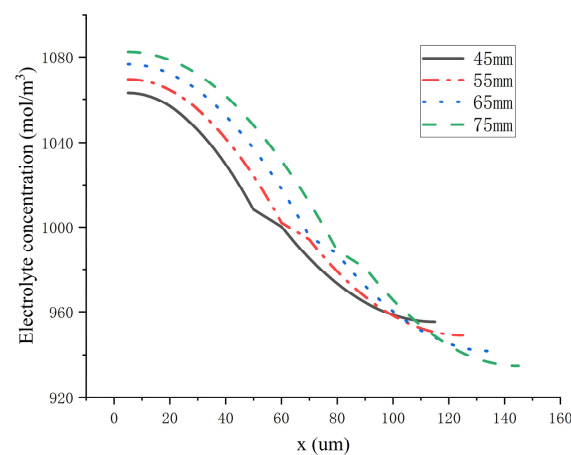


Figure 12. Electrolyte concentration in the direction of the electrode thickness at the end of discharge with different positive electrode thicknesses.

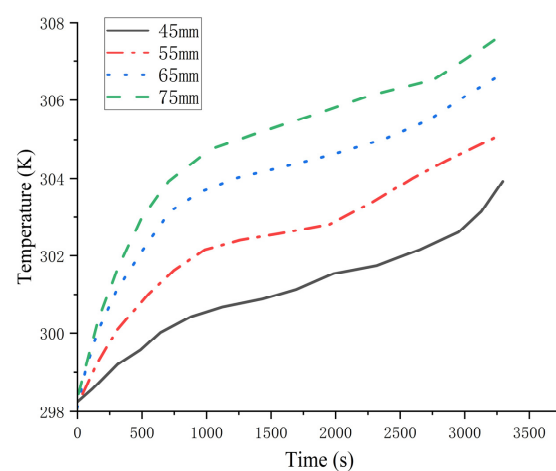


Figure 13. Temperature variation at a 1 C discharge rate at different electrode thicknesses.

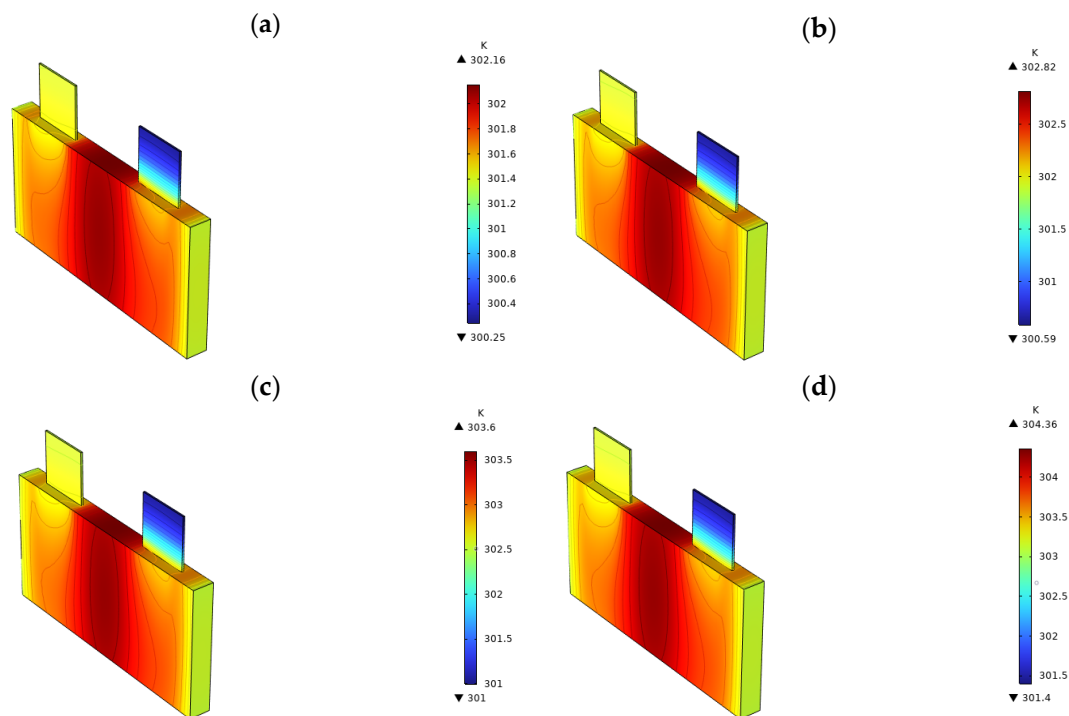


Figure 14. Temperature distribution of the battery at the end of discharge with different electrode thicknesses: (a) 45 mm, (b) 55 mm, (c) 65 mm, (d) 75 mm.

3.4. The Influence of Active-Substance Volume Fraction on Battery Performance

In addition to the thickness of lithium-ion battery electrodes, another important design parameter for battery electrodes is the volume fraction of active material. The active substances in lithium-ion batteries are closely related to their internal electrochemical reactions. This study investigated the effect of the active-substance volume fraction on battery performance by calculating the changes in battery-related parameters under different active-substance volume fractions. This article changed the volume fraction of positive electrode's active material ϵ_{pos} to four values (0.55, 0.6, 0.65, and 0.7) while keeping the volume fraction of negative electrode's active material unchanged, and then analyzed the electrochemical characteristics and thermal behavior. Figures 15 and 16, respectively, depict the changes in electrolyte concentration and temperature at the end of discharge for batteries with different volume fractions of positive electrode materials. Similar to the results in Figures 12 and 14, the change in electrolyte concentration was positively correlated with the active material's volume fraction. This may be due to the increase in the volume fraction of the active material, the increase in battery polarization and internal resistance, especially the increase in the volume fraction of the active substance, which leads to more lithium ions being embedded into the active particle, resulting in an increase in capacity, internal resistance, and polarization, and ultimately leading to an increase in the electrochemical performance gradient and heat generation rate.

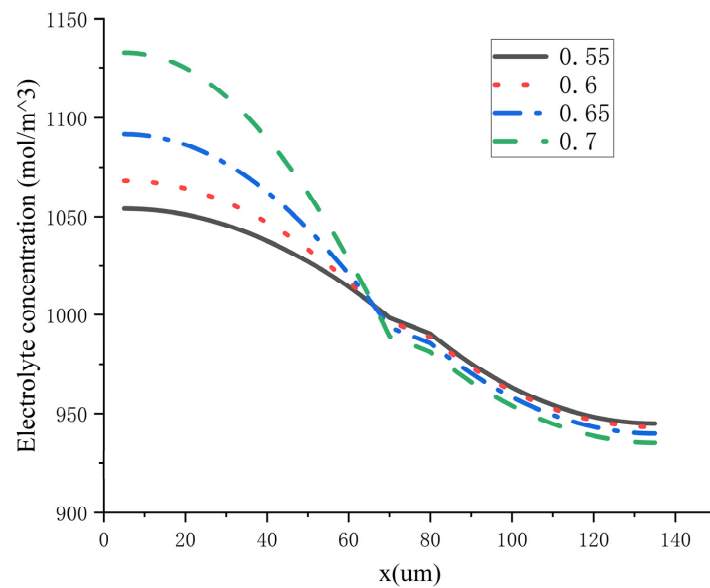


Figure 15. Electrolyte concentrations along the electrode thickness direction under different volume fractions of positive electrode material.

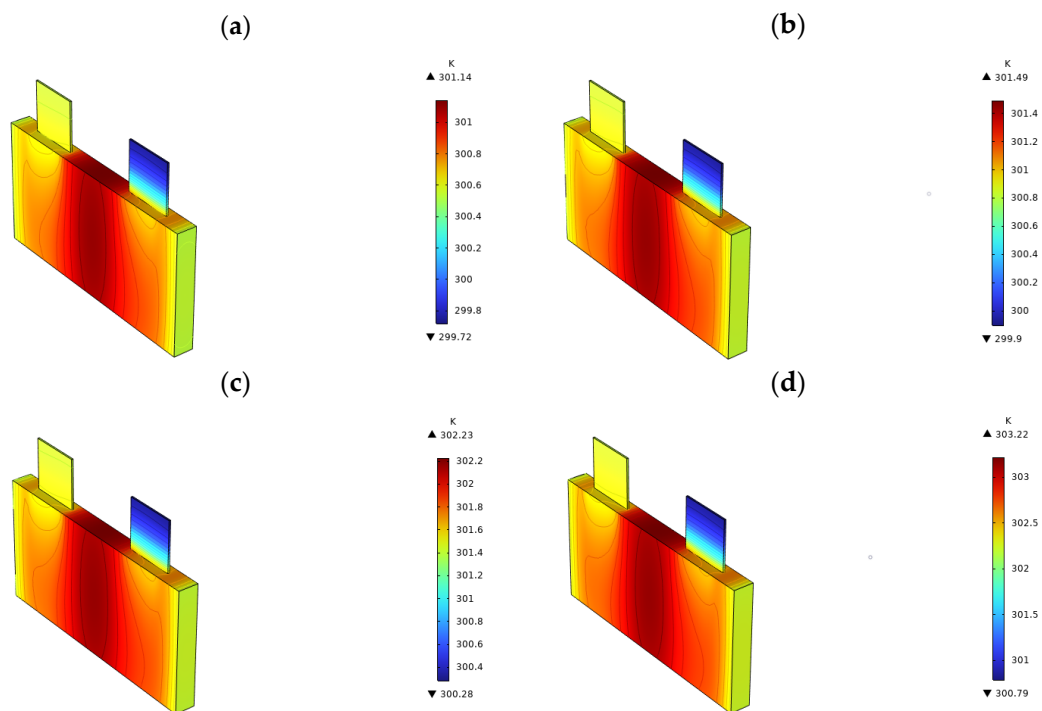


Figure 16. Temperature distribution of the battery at the end of discharge under different volume fractions of positive electrode material: (a) 0.55; (b) 0.6; (c) 0.65; (d) 0.7.

4. Conclusions

In this study, based on the concept of VSSD, a calculation formula for the reference diffusion coefficient as a function of concentration was proposed using the sine approximation method. Combining it with the Arrhenius formula, the diffusion coefficient of lithium batteries was constructed as a function of battery temperature and lithium-ion concentration. Based on the proposed diffusion coefficient function, an electrochemical–thermal coupling model was established. At the same time, the internal electrochemical and thermal characteristics of the battery were analyzed and studied under the electrochemical–thermal coupling model based on the VSSD. The main results were as follows:

- (1) The discharge voltage's response curves with and without the VSSD concept were fitted and compared under different operating conditions of 283/293/303 K and 0.5 C/1 C/1.5 C/2 C, verifying the effectiveness of the proposed function. Meanwhile, by comparing the discharge voltage response curves of the diffusion coefficient function composed of four, five, and six sine functions, it was determined that the diffusion coefficient function composed of six sine functions had the best fitting effect.
- (2) The effect of electrode thickness on battery performance was as follows: with the increase in parameters, the battery capacity increased, resulting in the increase in discharge current, which greatly promoted the polarization of the battery, especially the liquid-phase expansion. Finally, the heat production rate and temperature gradient of the battery were improved.
- (3) The increase in the volume fraction of the active material led to an increase in the polarization and internal resistance of the battery, especially because with the increase in the volume fraction of the active material, more lithium ions were embedded in the active particles, which ultimately led to an increase in the electrochemical performance and heat generation rate.

The excellent terminal voltage fitting performance indicated that the VSSD modeling method composed of six sine functions could effectively capture complex electrodynamics and thermodynamics. This model can be used for online management of batteries, such as estimating charging status and internal temperature, and further constructing a lithium battery electrochemical capacity degradation model based on the VSSD concept to study the capacity degradation behavior of lithium batteries.

Author Contributions: P.Y.: conceptualization, methodology, software, writing—original draft. X.L.: conceptualization, supervision, writing—review and editing. All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Data Availability Statement: The raw data supporting the conclusions of this article will be made available by the authors on request.

Conflicts of Interest: The authors have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

References

1. Etacheri, V.; Marom, R.; Elazari, R.; Salitra, G.; Aurbach, D. Challenges in the development of advanced Li-ion batteries: A review. *Energy Environ. Sci. EES* **2011**, *4*, 3243–3262. [\[CrossRef\]](#)
2. Deng, Y.-P.; Wu, Z.-G.; Liang, R.; Jiang, Y.; Luo, D.; Yu, A.; Chen, Z. Layer-based Heterostructured Cathodes for Lithium-ion and Sodium-ion Batteries. *Adv. Funct. Mater.* **2019**, *29*, 1808522. [\[CrossRef\]](#)
3. Mehta, R.; Gupta, A. Mathematical modelling of electrochemical, thermal and degradation processes in lithium-ion cells—A comprehensive review. *Renew. Sustain. Energy Rev.* **2024**, *192*, 114264. [\[CrossRef\]](#)
4. Wang, M.; Jia, P.; Wei, W.; Xie, Z.; Chen, J.; Dong, H. Research progress on electric thermal coupling model of lithium-ion batteries for energy storage. *Battery Bimon.* **2023**, *53*, 668–672.
5. Alkhedher, M.; Al Tahhan, A.B.; Yousaf, J.; Ghazal, M.; Shahbazian-Yassar, R.; Ramadan, M. Electrochemical and thermal modeling of lithium-ion batteries: A review of coupled approaches for improved thermal performance and safety lithium-ion batteries. *J. Energy Storage* **2024**, *86*, 111172. [\[CrossRef\]](#)
6. Li, H.; Saini, A.; Liu, C.; Yang, J.; Wang, Y.; Yang, T.; Pan, C.; Chen, L.; Jiang, H. Electrochemical and thermal characteristics of prismatic lithium-ion battery based on a three-dimensional electrochemical-thermal coupled model. *J. Energy Storage* **2021**, *42*, 102976. [\[CrossRef\]](#)
7. Yu, Z.; Tian, Y.; Li, B. A simulation study of Li-ion batteries based on a modified P2D model. *J. Power Sources* **2024**, *618*, 234376. [\[CrossRef\]](#)
8. Fang, W.; Ramadass, P.; Zhang, Z. Study of internal short in a Li-ion cell-II. Numerical investigation using a 3D electrochemical-thermal model. *J. Power Sources* **2014**, *248*, 1090–1098. [\[CrossRef\]](#)
9. Zhang, W. Study on Electrochemical Thermal Coupling Simulation of Lithium ion Batteries. Master's Thesis, Hunan University, Changsha, China, 2019.
10. Tian, J. Research on Health Assessment and Fault Diagnosis of Energy Storage Lithium Battery System. Ph.D. Thesis, University of Science and Technology of China, Hefei, China, 2021.

11. Gu, R.; Malysz, P.; Yang, H.; Emadi, A. On the Suitability of Electrochemical-Based Modeling for Lithium-Ion Batteries. *IEEE Trans. Transp. Electr.* **2016**, *2*, 417–431. [\[CrossRef\]](#)
12. Reniers, J.; Mulder, G.; Howey, D. Review and performance comparison of mechanical-chemical degradation models for lithium-ion batteries. *J. Electrochem. Soc.* **2019**, *166*, A3189. [\[CrossRef\]](#)
13. Hashemzadeh, P.; Désilets, M.; Lacroix, M.; Jokar, A. Investigation of the P2D and of the modified single-particle models for predicting the nonlinear behavior of Li-ion batteries. *J. Energy Storage* **2022**, *52 Pt B*, 104909. [\[CrossRef\]](#)
14. Lenzen, M. Life cycle energy and greenhouse gas emissions of nuclear energy: A review. *Energy Convers. Manag.* **2008**, *49*, 2178–2199. [\[CrossRef\]](#)
15. He, T.; Zhang, T.; Wang, Z.; Cai, Q. A comprehensive numerical study on electrochemical-thermal models of a cylindrical lithium-ion battery during discharge process. *Appl. Energy* **2022**, *313*, 118797. [\[CrossRef\]](#)
16. Zhang, X.; Li, P.; Huang, B.; Zhang, H. Numerical investigation on the thermal behavior of cylindrical lithium-ion batteries based on the electrochemical-thermal coupling model. *Int. J. Heat Mass Transf.* **2022**, *199*, 123449. [\[CrossRef\]](#)
17. Zadeh, P.G.; Gholamalizadeh, E.; Wang, Y.; Chung, J.D. Electrochemical modeling of a thermal management system for cylindrical lithium-ion battery pack considering battery capacity fade. *Case Stud. Therm. Eng.* **2022**, *32*, 101878. [\[CrossRef\]](#)
18. Manthiram, A. An Outlook on Lithium Ion Battery Technology. *Acs Cent. Ence* **2017**, *3*, 1063–1069. [\[CrossRef\]](#) [\[PubMed\]](#)
19. Ellabban, O.; Abu-Rub, H.; Blaabjerg, F. Renewable energy resources: Current status, future prospects and their enabling technology. *Renew. Sustain. Energy Rev.* **2014**, *39*, 748–764. [\[CrossRef\]](#)
20. Wang, J.; Meng, J.; Peng, Q.; Liu, T.; Peng, J. An electrochemical-thermal coupling model for lithium-ion battery state-of-charge estimation with improve dual particle filter framework. *J. Energy Storage* **2024**, *87*, 111473. [\[CrossRef\]](#)
21. Dai, H.; Yu, C.; Wei, X.; Sun, Z. State of charge estimation for lithium-ion pouch batteries based on stress measurement. *Energy* **2017**, *129*, 16–27. [\[CrossRef\]](#)
22. Gao, Y.; Liu, K.; Zhu, C.; Zhang, X.; Zhang, D. Co-Estimation of State-of-Charge and State-of-Health for Lithium-Ion Batteries Using an Enhanced Electrochemical Model. *IEEE Trans. Ind. Electron.* **2022**, *69*, 2684–2696. [\[CrossRef\]](#)
23. Chen, S.; Zhang, Q.; Wang, F.; Wang, D.; He, Z. An electrochemical-thermal-aging effects coupled model for lithium-ion batteries performance simulation and state of health estimation. *Appl. Therm. Eng.* **2024**, *239*, 122128. [\[CrossRef\]](#)
24. Yin, L.; Björneklett, A.; Söderlund, E.; Brandell, D. Analyzing and mitigating battery ageing by self-heating through a coupled thermal-electrochemical model of cylindrical Li-ion cells. *J. Energy Storage* **2021**, *39*, 102648. [\[CrossRef\]](#)
25. Huang, Y.; Lai, X.; Ren, D.; Kong, X.; Han, X.; Lu, L.; Zheng, Y. Thermal and stoichiometry inhomogeneity investigation of large-format lithium-ion batteries via a three-dimensional electrochemical-thermal coupling model. *Electrochim. Acta* **2023**, *468*, 143212. [\[CrossRef\]](#)
26. Wang, B.; Yan, M. Research on the heating effect evaluation of the electromagnetic induction heating system at low temperature based on the electrochemical-thermal coupling model. *J. Energy Storage* **2024**, *87*, 111348. [\[CrossRef\]](#)
27. He, C.; Yue, Q.; Wu, M.; Chen, Q.; Zhao, T. A 3D electrochemical-thermal coupled model for electrochemical and thermal analysis of pouch-type lithium-ion batteries. *Int. J. Heat Mass Transf.* **2021**, *181*, 121855. [\[CrossRef\]](#)
28. Jiang, G.; Zhuang, L.; Hu, Q.; Liu, Z.; Huang, J. An investigation of heat transfer and capacity fade in a prismatic Li-ion battery based on an electrochemical-thermal coupling model. *Appl. Therm. Eng.* **2020**, *171*, 115080. [\[CrossRef\]](#)
29. Zhou, Z.; Cazorla, C.; Gao, B.; Luong, H.D.; Momma, T.; Tateyama, Y. First-Principles Study on the Interplay of Strain and State-of-Charge with Li-Ion Diffusion in the Battery Cathode Material LiCoO₂. *ACS Appl. Mater. Interfaces* **2023**, *15*, 53614–53622. [\[CrossRef\]](#)
30. Farag, M.; Sweity, H.; Fleckenstein, M.; Habibi, S. Combined electrochemical, heat generation, and thermal model for large prismatic lithium-ion batteries in real-time applications. *J. Power Sources* **2017**, *360*, 618–633. [\[CrossRef\]](#)
31. Yang, Y. Electrochemical Thermal Coupling Characteristics of Lithium-Ion Batteries and Composite Thermal Management System. Ph.D. Thesis, North China Electric Power University, Beijing, China, 2022.
32. Wang, Q. Research on Liquid Cooling Strategy for Soft Pack Lithium-Ion Battery Module Based on Electrochemical Thermal Coupling Model. Master's Thesis, Hunan University, Changsha, China, 2020.
33. Liu, A.; Gan, X.; He, P. Research Trends on Thermal Models of Lithium ion Batteries. *J. Power Supply* **2019**, *17*, 95–103.
34. Yu, Q. Electrochemical Thermal Coupling Simulation of NCM Ternary Power Battery. Master's Thesis, Chongqing University, Chongqing, China, 2021.
35. Wang, T.; Tseng, K.J.; Zhao, J.; Wei, Z. Thermal investigation of lithium-ion battery module with different cell arrangement structures and forced air-cooling strategies. *Appl. Energy* **2014**, *134*, 229–238. [\[CrossRef\]](#)
36. He, F.; Li, X.; Ma, L. Combined experimental and numerical study of thermal management of battery module consisting of multiple Li-ion cells. *Int. J. Heat Mass Transf.* **2014**, *72*, 622–629. [\[CrossRef\]](#)
37. Baba, N.; Yoshida, H.; Nagaoka, M.; Okuda, C.; Kawauchi, S. Numerical simulation of thermal behavior of lithium-ion secondary batteries using the enhanced single particle model. *J. Power Sources* **2014**, *252*, 214–228. [\[CrossRef\]](#)
38. Xu, M.; Zhang, Z.; Wang, X.; Jia, L.; Yang, L. Two-dimensional electrochemical-thermal coupled modeling of cylindrical LiFePO₄ batteries. *J. Power Sources* **2014**, *256*, 233–243. [\[CrossRef\]](#)
39. Ye, Y.; Saw, L.H.; Shi, Y.; Somasundaram, K.; Tay, A.A. Effect of thermal contact resistances on fast charging of large format lithium ion batteries. *Electrochim. Acta* **2014**, *134*, 327–337. [\[CrossRef\]](#)

40. Zhang, L.; Wang, L.; Hinds, G.; Lyu, C.; Zheng, J.; Li, J. Multi-objective optimization of lithium-ion battery model using genetic algorithm approach. *J. Power Sources* **2014**, *270*, 367–378. [[CrossRef](#)]
41. Mastali, M.; Farkhondeh, M.; Farhad, S.; Fraser, R.A.; Fowler, M. Electrochemical Modeling of Commercial LiFePO₄ and Graphite Electrodes: Kinetic and Transport Properties and Their Temperature Dependence. *J. Electrochem. Soc.* **2016**, *163*, A2803–A2816. [[CrossRef](#)]
42. Wang, Q.-K.; Shen, J.-N.; Ma, Z.-F.; He, Y.-J. Decoupling parameter estimation strategy based electrochemical-thermal coupled modeling method for large format lithium-ion batteries with internal temperature experimental validation. *Chem. Eng. J.* **2021**, *424*, 130308. [[CrossRef](#)]

Disclaimer/Publisher’s Note: The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.