



An electrochemical–thermal model based on dynamic responses for lithium iron phosphate battery



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HIGHLIGHTS

- A model based on dynamic responses for LiFePO₄ battery is developed.
- Effects of current collectors on LiFePO₄ battery are considered in this model.
- Dynamic analysis for pulse behavior and electrochemical rates are conducted.
- Endothermic and exothermic phenomena in different discharge rates are discussed.

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ABSTRACT

An electrochemical–thermal model is developed to predict electrochemical and thermal behaviors of commercial LiFePO₄ battery during a discharging process. A series of temperatures and lithium ion concentrations dependent parameters relevant to the reaction rate and Li⁺ transport are employed in this model. A non-negligible contribution of current collectors to the average heat generation of the battery is considered. Simulation results on rate capability and temperature performance show good agreement with the literature data. The behavior of Li⁺ distribution at pulse-relaxation discharge, the variation of electrochemical reaction rate and thermal behavior at a constant current discharge are studied. Results of pulse-relaxation discharge describe the dynamic change of Li⁺ concentration distribution in liquid and solid phases, which is helpful to analysis the polarization of the battery. In constant current discharge processes, the electrochemical reaction rate of positive electrode has a regular change with the time and the position in the electrode. When discharge finished, there is still a part of the LiFePO₄ material has not been adequately utilized. At low rate, the discharge process accompanies endothermic and exothermic processes. With the rate increasing, the endothermic process disappears gradually, and only exothermic process left at high rate.

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1. Introduction

Lithium ion battery is nowadays one of the most popular energy storage devices due to high energy, power density and cycle life characteristics [1,2]. It has been known that the overall performance of batteries not only depends on electrolyte and electrode materials, but also depends on operation conditions and choice of physical parameters [3]. Designers need an understanding on thermodynamic and kinetic characteristics of batteries that is costly and time-consuming by experimental methods. Conversely, numerical modeling and simulation for batteries are economic, which can provide guidelines for design in a short time [4], and

information during the electrochemical and transport process. For example, the local electric potential and ion concentrations throughout the porous electrodes can be calculated while the data cannot be obtained experimentally [5,6].

The accuracy of numerical modeling and simulation of electrochemical and thermal behavior relies on the model construction and the parameters applied during simulation [7]. The most famous and practical model for lithium ion battery is the porous electrode model [8,9], which was based on the porous electrode theory containing charge transfer kinetics at reaction sites, species and charge conservations. It was combined with an energy conservation equation by Newman and Pals [10,11], and was developed as an electro-thermal model, which made it possibly simulate and predict the interaction between temperature and electrochemical reaction of batteries. Previously, the electrochemical models and

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Nomenclature

List of symbols

A_{cell}	area of the positive electrode (both sides) (m^2)
$c_{1,i}$	lithium in active material (mol m^{-3})
$C_{1,\text{max},i}$	maximum concentration (mol m^{-3})
$C_{1,\text{surf},i}$	Li^+ concentration on the surface of active material particles (mol m^{-3})
$C_{p,i}$	heat capacity (J (kg K)^{-1})
$D_{1,i}$	solid phase diffusivity ($\text{m}^2 \text{s}^{-1}$)
$D_{10,i}$	reference solid phase diffusivity ($\text{m}^2 \text{s}^{-1}$)
$E_{a,D,i}$	diffusion active energy (kJ mol^{-1})
$E_{a,k,i}$	reaction active energy (kJ mol^{-1})
h	heat transfer coefficient ($\text{W m}^{-2} \text{K}^{-1}$)
I	current (A)
I_{app}	cell current density related to A_{cell} (A m^{-2})
$j_{0,i}$	exchange current density (A m^{-2})
$j_{\text{loc},i}$	local current density (A m^{-2})
$k_{0,i}$	reaction rate constant ($\text{m}^{2.5} \text{mol}^{-0.5} \text{s}^{-1}$)
k_i	thermal conductivity (W (m K)^{-1})
L_i	thickness of component (m)
Q_{act}	active heat generation (J m^{-3})
Q_{ohm}	ohmic heat generation (J m^{-3})
Q_{rea}	reaction heat generation (J m^{-3})
r	radius distance variable of particle (m)
R_i	characteristic radius of electrode particles (m)
$S_{a,i}$	specific surface area (m^{-1})
$\text{SOC}_{0,i}$	initial state of charge
t	time (s)

t^+	Li^+ transference number
T	absolute temperature (K)
T_{amb}	ambient temperature (K)
U_i	open circuit voltage (V)
v	thermodynamic factor relating to electrolyte activity
x	distance from half negative foil along negative-positive direction (m)

Greek letters

$\alpha_{a,i}$	transfer coefficient for anodic current
$\alpha_{c,i}$	transfer coefficient for cathodic current
$\epsilon_{1,i}$	active material volume fraction
$\epsilon_{2,i}$	volume fraction
φ_i	electric potential (V)
γ_i	Bruggeman exponent
k	ionic or electronic conductivity (S m^{-1})
ρ_i	density (kg m^{-3})
σ_i	solid phase conductivity (S m^{-1})

Subscripts and superscripts

0	initial or equilibrated state
1	solid phase
2	liquid phase
amb	ambient temperature
n	negative electrode
p	positive electrode
irr	irreversible
re	reversible
s	separator

electrochemical thermal models were built for simulating the cathode materials of lithium ion battery, such as LiCoO_2 , LiMn_2O_4 or $\text{Li}(\text{NiCoMn})\text{O}_2$ [12–18]. Later, based on the observation of a phase change occurred in the LiFePO_4 cathode during the lithiated and unlithiated process [19,20], Srinivasan [21] developed a model that accounted for the phase change with the shrinking core, and investigated the cause for the low power capability of the materials. The other models without special features about the two-phase process were also founded for further qualitative analysis [22–31]. For instance, Wang [22] analyzed the effect of local current density on electrode design for the LiFePO_4 battery. Ye [23] developed an electro-thermal cycle life model by incorporating the dominant capacity fading mechanism to investigate the capacity fading effect on the performance. Gerver [24] and Christian Hellwig [25] gave a multidimensional modeling framework for simulating coupled thermal and electrochemical phenomena that are critical for safety, durability and design optimization studies. These models demonstrated that the porous electrode theory can be used to simulate a LiFePO_4 battery system without considering the phase change.

In the previous work [8–31], the computational domains were divided into three parts, named negative electrode, separator and positive electrode, but the current collectors of a battery were neglected. Because a rate of the heat generation is an average value obtained through dividing the total heat generation by the cell volume, about 10% of the cell volume comes from the current collectors, indicating that the contribution of the collectors to the heat generation rate cannot be neglected.

Besides, the material properties treated as parameters also have an important influence on the accuracy of the simulation [7]. During the discharge process, lithium ions deintercalate from the negative porous electrode, then transfer through separator and

intercalate into the positive electrode, resulting in changes of temperature and lithium ion concentrations in the solid and liquid phases that may affect the diffusion coefficient, ionic conductivity, ion transference number as well as the reaction rate constant [24,32–34]. Therefore, it is necessary to rectify dynamically these parameters during a simulation.

In this study, we develop an electrochemical thermal model for a LiFePO_4 battery by considering the current collectors into the computational domain, dynamic responses in lithium ion concentration, and temperature as parameters during the discharge process. By comparing experimental results with simulation at different operating temperatures and discharge rates, this model can be used to study the dynamic evolution for pulses, relaxation behavior, electrochemical reaction and thermal behavior at a constant discharge rate in lithium iron phosphate battery.

2. Model development

2.1. Model assumption and simulation domain

This electrochemical–thermal model for a LiFePO_4 battery is developed based on the porous electrode model [8,9]. The active materials of solid electrodes are treated as homogenous media, and are comprised with spherical particles. Since the current collectors play an important role in electron and heat transferring, the current collectors are considered as a computing domain.

Fig. 1 shows a schematic computational domain of one-dimensional (1D) battery model [8,9]. Because both positive and negative current collectors have two sides contacting and reacting with electrolyte, we take a half of their thickness into simulation domain in order to accurately calculate the current flow and the

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