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Two-dimensional electrochemical—thermal coupled modeling of cylindrical LiFePO₄ batteries



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HIGHLIGHTS

• A two-dimensional electrochemical-thermal model for a cylindrical LiFePO₄ battery.

• The effects of the battery current collecting tabs.

• The distributions of potential and reaction rates during discharge process.

• The distribution of the heat generation rates and the temperature within the battery.

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ABSTRACT

The distributions of potential and reaction rates in a lithium ion battery during discharge process have great influences on the battery thermal characteristics. A two-dimensional electrochemical—thermal model has been developed for a cylindrical LiFePO₄ battery by coupling the mass, charge, and energy conservations as well as the cell electrochemical kinetics. The model also includes battery current collecting tabs. The modeling results are validated for both the electrochemical performance and thermal behavior during galvanostatic discharge process. The modeling results agree well with the experimental data. The placement of the positive and the negative current collecting tabs on the cylindrical battery was found to have a significant effect on the distributions of its potential and local reaction rates, which therefore affect heat generation rates, and thus the distribution of the temperature within the battery. © 2014 Elsevier B.V. All rights reserved.

1. Introduction

Large capacity or large size lithium ion power batteries are widely used in the hybrid electrical vehicles (HEV) and electrical vehicles (EV). The performance of a high capacity lithium ion power battery is influenced by the geometrical characteristics, the placing of the current collecting tabs, and the local reaction rates [1]. Larger geometry sizes, higher heat generation rate and extreme operating conditions could lead to quite non-uniform thermal and electrical behaviors [1,2]. Therefore large capacity lithium ion power batteries require a more comprehensive understanding of their electrochemical fundamentals and the thermal behavior.

Modeling and simulation of lithium power batteries is becoming increasingly important in developing the fundamental understanding of electrochemical performances and thermal

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characteristic for improving battery thermal management systems. In recent published works, several one dimensional (1D) electrochemical-thermal coupled models for lithium ion batteries have been used. These models comprising conservation of mass, charge, energy, and electrochemical reaction are developed based on the kinetics models [3-12]. They usually couple the 1D kinetic model of local cell unit to the 2D or 3D thermal model of the whole battery cell by adding heat source terms and temperature dependent parameters, without considering the current collecting tabs [7–10]. However, little attention is paid to the modeling and simulating of the whole battery including both the current collecting tabs and the sandwich structures of cell units, which are closer to the real battery and more suitable for the large capacity or large size lithium ion power batteries [12–15]. In addition, for batteries with LiFePO₄ electrodes, only a handful of kinetic modeling studies have been published so far [8,12,11,16].

In this work, a two-dimensional electrochemical—thermal model has been developed for a commercial Type 38120 cylindrical LiFePO₄ power battery by coupling mass, charge, and energy





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conservations as well as electrochemical kinetics. The current collecting tabs of the cylindrical battery are considered in this model. Effects of the current collecting tabs placing on the cell performance are also investigated.

2. Coupled electrochemical-thermal model

2.1. Computational domain and model assumptions

The two-dimensional electrochemical—thermal model for a commercial Type 38120 cylindrical LiFePO₄/Carbon power battery is developed based on the principles of the mass, charge, and energy conservations as well as the electrochemical kinetics. Table 1 lists the application of these conservation equations in each respective domain. The details of these equations will be given in the later sections.

The nominal voltage and capacity of Type 38120 are 3.2 V and 10 Ah. Fig. 1 illustrates the two-dimensional computational domain of the cylindrical battery in the axial cross-sectional direction. The domain includes several different regions: the cell core part (battery jelly-roll) with the structure of spiral-wound cell unit; the positive and negative terminals as well as the tab groups; the battery outer can made of stainless steel. The spirally coiled cell unit is wound up in the form of a jelly-roll, so it appears as layered structure in the two-dimensional rectangular axial-section as shown in Fig. 1(a), (b).

As shown in Fig. 1, the basic cell unit is assumed to be a sandwich structure that is composed of the negative electrode (ne), the separator (sp), the positive electrode (pe), and the two current collectors (cc) including the tabs. Each positive/negative tab is welded to the corresponding current collector and terminal of each basic cell unit. The electrodes are porous solid matrix that consists of active particles with spherical shapes of uniform sizes and additives (Fig. 1(c)). The positive electrode contains active material particles of iron phosphate (LiFePO₄) and the negative electrode contains the active material particles of amorphous carbon (LiC_6). The separator is a porous polymer membrane that constitutes a physical barrier between the two electrodes. Both electrodes and separator porous matrix are impregnated with electrolyte ensuring the transfer of lithium ions between two electrodes. The electrolyte is a mixture of cyclic and linear carbon solvents in which a lithium salt, lithium hexafluorophosphate LiPF₆ (1.5 mol L^{-1}), is dissolved in a nonaqueous 1:2 liquid mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC). The electrochemical reactions that occur at the interface of the electrode and electrolyte both in the negative and positive during discharge/charge are then,

Negative Electrode :
$$\text{Li}_x \text{C}_6 \underset{\text{charge}}{\overset{\text{discharge}}{\rightleftharpoons}} \text{Li}_{x-z} \text{C}_6 + z \text{Li}^+ + z \text{e}^-$$

Positive Electrode :
$$\text{Li}_{y}\text{FePO}_{4} \underset{\text{discharge}}{\overset{\text{charge}}{\rightleftharpoons}} \text{Li}_{y-z}\text{FePO}_{4} + z\text{Li}^{+} + z\text{e}^{-1}$$

where *x* is the stoichiometric coefficient or the number of moles of lithium present in the graphite structure (C_6), *y* is the stoichiometric coefficient or the number of moles of lithium in the olivine structure

Table 1

Governing equations of different subdomains.

Governing equations	сс	pe/ne	sp	Terminal/tab	Outer can
Electrochemical kinetics Charge conservation Mass conservation Energy balance	- √ -	\checkmark	- - - - - - - - - - - - - -		- √ -

of iron phosphate (FePO₄), Li^+ is the lithium ion, *z* is the number of moles of lithium taking part in the electrochemical reaction.

2.2. Electrochemical kinetics at the interface

The local charge transfer current density is given by the Butler– Volmer equation for electrode kinetics

$$j_{n} = j_{0} \left\{ \exp\left(\frac{\alpha_{a}F}{RT}\eta\right) - \exp\left(-\frac{\alpha_{c}F}{RT}\eta\right) \right\}$$
(1)

where j_0 is the exchange current density, α_a and α_c are the anodic and cathodic charge transfer coefficients, η is the local surface overpotential and F is the Faraday constant. The exchange current density is given by

$$j_0 = Fk_0 c_2^{\alpha_a} \left(c_{1,\max} - c_{1,\text{surf}} \right)^{\alpha_a} c_{1,\text{surf}}^{\alpha_c}$$
(2)

where k_0 is the reaction rate constant, $c_{1,max}$ is the maximum lithium concentration in the active electrodes and c_1 is the lithium concentration on the surface of the active particles. The subscripts 1 and 2 represents the solid phase and electrolyte phase respectively. The overpotential is defined as

$$\eta = \phi_1 - \phi_2 - U_{\text{eq}} \tag{3}$$

where U_{eq} is the open circuit potential of the electrode, ϕ_1 is the solid phase potential and ϕ_2 is the liquid phase potential.

2.3. Charge conservation

The governing equation for charge conservation in the positive/ negative electrode is expressed as

$$\nabla \cdot i_1 + \nabla \cdot i_2 = 0 \tag{4}$$

$$\nabla \cdot i_1 = -S_a j_n \tag{5}$$

$$\nabla \cdot i_2 = S_a j_n \tag{6}$$

where i_1 refers to the electronic current density in the solid phase, i_2 is the ionic current density in the liquid phase, and S_a is the specific surface area.

2.3.1. Electron transport in solid phase

The transport of electrons in the solid phase follows Ohm's law which can be expressed as follows

$$i_1 = -\sigma_1^{\text{eff}} \nabla \phi_1 \tag{7}$$

where σ_1^{eff} refers to the effective electrical conductivity of solid phase.

2.3.2. Lithium ion transport in solution phase

The transport of lithium ions in electrolyte can be expressed as follows [3,17]:

$$\dot{i}_{2} = -\sigma_{2}^{\text{eff}} \nabla \phi_{2} + \frac{2RT\sigma_{2}^{\text{eff}}}{F} \left(1 + \frac{\partial \ln f_{\pm}}{\partial \ln c_{2}}\right) (1 - t_{+}) \nabla (\ln c_{2})$$
(8)

where i_2 consists of two terms, the first term following Ohm's law and the second accounting for the ionic concentration gradient, f_{\pm} is the average molar activity coefficient, t_+ is the transferring number of lithium ions in the liquid phase, and c_2 is the lithium ion



Fig. 1. Schematic graph of (a) axial cross-section of Type 38120 battery (b) partial enlarged detail of two-dimensional computational domain showing various functional layers in the jelly roll (c) diffusion of lithium (Li⁺) in active material particles and electrolyte in the electrodes.

concentration in the liquid phase, R is the universal gas constant, and T is the temperature of electrolyte.

2.4. Mass conservation

2.4.1. Lithium in active particles

The mass conservation of lithium in the spherical active material particle can be described by Fick's law

$$\frac{\partial c_1}{\partial t} + \frac{1}{r^2} \frac{\partial}{\partial r} \left(-r^2 D_1 \frac{\partial c_1}{\partial r} \right) = 0$$
(9)

where c_1 is the concentration of lithium in the active material particles of the electrode, t is the time, D_1 represents the diffusion coefficient of lithium in the solid phase, and r is the radial coordinate inside a spherical particle, which is no larger than the particle radius R.

2.4.2. Lithium ions in the electrolyte

The mass conservation of lithium ions in the electrolyte can be stated as

$$\varepsilon_2 \frac{\partial c_2}{\partial t} + \nabla \cdot J_2 = \frac{S_a j_n}{F} \tag{10}$$

with

$$J_2 = -D_2^{\text{eff}} \nabla c_2 + \frac{i_2 \cdot t_+}{F} \tag{11}$$

where J_2 is the molar flux of lithium ions that consists of two terms: the first term following Fick's law and the second accounting for the electromigration, D_2^{eff} represents the effective diffusion coefficient of lithium ions in the electrolyte, and ε_2 is the volume fraction of the liquid phase. The term on the right side of the Eq. (10) is zero when applied in the separator.

2.5. Energy balance

The energy balance in the lithium ion battery can be expressed as follows in which there are three parts of heat generation sources: reaction heat q_{rea} , activation polarization heat q_{act} , and ohmic heat q_{ohm} .

$$\rho c_{\rm p} \frac{\partial T}{\partial t} - \lambda \nabla^2 T = q_{\rm rea} + q_{\rm act} + q_{\rm ohm}$$
(12)

The heat generation due to electrochemical reaction is

$$q_{\rm rea} = S_{\rm a} j_{\rm n} T \frac{\partial U_{\rm eq}}{\partial T} = S_{\rm a} j_{\rm n} T \frac{\Delta S}{F}$$
(13)

The active polarization heat is

$$q_{\rm act} = S_{\rm a} j_{\rm n} \eta \tag{14}$$

The heat generation due to ohmic losses consists of electrical ohmic heat in the solid phase and ionic ohmic heat in the liquid phase

$$q_{\rm ohm} = -i_1 \cdot \nabla \phi_1 - i_2 \cdot \nabla \phi_2 \tag{15}$$

2.6. Temperature and concentration dependent parameters

The positive and negative electrode active materials are Li_{y-} FePO₄ and Li_xC_6 respectively. The electrolyte is 1.5 mol L⁻¹ LiPF₆dissolved in a mixture of 2:1 EC/DMC. The model input parameters are listed in Table 2 including battery geometrical and design parameters, kinetic and transport properties and thermal properties.

2.6.1. Electrode kinetics related parameters

2.6.1.1. Reaction rate constant k_0 . The temperature dependence of reaction rate constant k_0 follows the Arrhenius formula [4,8,9,13]:

Table 2	
Model parameters for a 10 Ah LiFePO ₄ power b	oattery.

Parameter	Unit	Al foil	Cathode	Separator	Anode	Cu foil	Outer can	Ref.
e ₁		_	0.435	_	0.56	_	_	Estimation
£2		-	0.306	0.54	0.268	_	-	Estimation
δ_i	μm	20	91	40	142	20		Estimation
<i>r</i> ₀	μm	_	1.15	_	14.75	_	_	[11]
C _{2,0}	mol m ⁻³	_		1500		_	_	[19]
C _{1,0}	mol m ⁻³	-	3900	_	16,361	_	-	[19]
$c_{1,\max}$	mol m ⁻³	_	22,806	_	31,370	_	_	[19]
α _a		_	0.5	_	0.5	_	_	[11]
α _c		_	0.5	_	0.5	_	_	[11]
D_1	$m^2 s^{-1}$	_	1.18×10^{-18}	_	$3.9 imes 10^{-14}$	_	_	[9,19]
D_2	$m^2 s^{-1}$	_		Eq. (21)		_	_	[10]
EaR	kJ mol ⁻¹	_	4	_	4	-	_	[11]
E _{aD}	kJ mol ⁻¹	_	20	_	4	_	_	[11]
σ_1	$\mathrm{S}~\mathrm{m}^{-1}$	3.83×10^7	0.1	_	100	6.33×10^7	_	[1]
σ_2	$\mathrm{S}~\mathrm{m}^{-1}$	_		Eq. (19)		_	_	[1]
k ₀	$m^{2.5} mol^{-0.5} s^{-1}$	_	3.626×10^{-11}	_	$1.764 imes 10^{-11}$	_	_	[9]
t_+		_		0.363		_	_	[9]
k	$W m^{-1} K^{-1}$	160	1.48	1	1.04	400	44.5	[9]
ρ	kg m ⁻³	2700	1500	492	2660	8700	7850	[11]
C _{p,1}	J kg ⁻¹ K ⁻¹	900	1260	700	1437	385	475	[11]
C _{p,2}	J kg ⁻¹ K ⁻¹	_		2055		_	_	[11]
T _{ref}	K			298.15				
F	C mol ⁻¹	-		96,487		-	-	[11]

$$k_0(T) = k_{0,\text{ref}} \exp\left[\frac{E_{aR}}{R} \left(\frac{1}{T_{\text{ref}}} - \frac{1}{T}\right)\right]$$
(16)

where E_{aR} is the reaction activation energy, and $k_{0,ref}$ is the reaction rate constant at reference temperature T_{ref} .

2.6.1.2. Open circuit potential (OCP) U_{eq} . The open circuit potential (OCP) depends on both temperature and concentration, which can be expressed with a Taylor's series expansion [13]:

$$U_{eq} = U_{eq,ref} + \frac{\partial U_{eq}}{\partial T} \left(T - T_{ref} \right)$$

= $U_{eq,ref} \left(\text{SOC}, T_{ref} \right) + \frac{\Delta S(\text{SOC})}{F} \left(T - T_{ref} \right)$ (17)

where the state of charge (SOC) of both positive and negative electrodes can be determined as follows:

$$SOC = \frac{c_1}{c_{1,\max}}$$
(18)

As shown in Eq. (17), both the open circuit potential (OCP) and the entropy change ΔS depend on the state of charge (SOC). The dependence of these two variables on the SOC could be determined by experiments. Fig. 2 represents ΔS and OCP changing curves with the SOC at the reference temperature 25 °C for Li_yFePO₄ and Li_xC₆ electrodes, respectively.

2.6.2. Liquid phase parameters

Eqs. (19) and (20) describe the temperature and concentration dependence of ionic conductivity σ_2 and thermodynamic factor $(1 + \partial \ln f_{\pm}/\partial \ln c_2)(1 - t_+)$ for LiPF₆ in EC/DMC (2:1 by volume) [10,20,21]:

$$\begin{aligned} \sigma_2(c_2,T) &= 10^{-4}c_2 \times 1.2544 \times \left(-8.2488 + 0.053248T \\ &-0.00002987T^2 + 0.26235 \times 0.001c_2 - 0.0093063 \\ &\times 0.001c_2T + 0.000008069 \times 0.001c_2T^2 + 0.22002 \\ &\times 10^{-6}c_2^2 - 0.0001765 \times 10^{-6}c_2^2T\right)^2 \end{aligned}$$

$$\left(1 + \frac{\partial \ln f_{\pm}}{\partial \ln c_2}\right) (1 - t_{+}) = \frac{1 - 0.363}{1 - 0.399} \left(0.601 - 0.24 \times 0.01 c_2^{0.5} + 0.982 \times [1 - 0.0052 (T - 294)] \times (0.001 c_2)^{1.5}\right)$$

$$(20)$$

The Li⁺ diffusion coefficient in the liquid phase D_2 is given in Eq. (21) [10,20–22]:

$$D_2(c_2,T) = 10^{\left(-4.43 - \left(\frac{54}{T-229 - 5 \times 0.001 c_2}\right) - 0.22 \times 0.001 c_2\right) - 4}$$
(21)

2.6.3. Solid phase parameters

2.6.3.1. Li diffusion coefficient D_1 . The temperature dependence of the Li⁺ diffusion coefficient D_1 in the solid phase follows the Arrhenius formula [4,8,9,13]. The constant $D_{1,ref}$ at the reference temperature T_{ref} is listed in Table 2.

$$D_1(T) = D_{1,\text{ref}} \exp\left[\frac{E_{\text{aD}}}{R} \left(\frac{1}{T_{\text{ref}}} - \frac{1}{T}\right)\right]$$
(22)

where E_{aD} is the activation energy for diffusion.

2.7. Boundary and initial conditions

At the electrode/separator interface I, insulation is specified for the electronic current of the solid phase. Continuity is specified for the ionic current, lithium ion flux of liquid phase and heat flux.

$$I: n \cdot i_1 = 0, \ n \cdot i_2|_{I_+} = n \cdot i_2|_{I_-}, \ n \cdot J_2|_{I_+} = n \cdot J_2|_{I_-}, \ n \cdot q|_{I_+} = n \cdot q|_{I_-}$$
(23)

At the electrode/current collector interface II, insulation is specified for the ionic current and lithium ion flux of the liquid phase. Continuity is specified for the electronic current and heat flux.

$$II: n \cdot i_2 = 0, \ n \cdot i_1|_{II+} = n \cdot i_1|_{II-}, \ n \cdot J_2 = 0, \ n \cdot q|_{II+} = n \cdot q|_{II-}$$
(24)

At the battery jelly-roll/can interface V, continuity is specified

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Fig. 2. Thermodynamic properties used in the model as a function of SOC in the electrodes: (a) entropy change [5,18], (b) reference open circuit potential [19].

for the heat flux. Insulation is specified for the lithium ion flux, electronic current and ionic current.

$$V: n \cdot i_2 = n \cdot i_1 = n \cdot J_2 = 0, \ n \cdot q|_{V+} = n \cdot q|_{V-}$$
(25)

At the current collector/tab/terminal interface VI, insulation is specified for the ionic current and lithium ion flux of liquid phase. Continuity is specified for the electronic current and heat flux.

$$VI: n \cdot i_2 = n \cdot J_2 = 0, \ n \cdot i_1|_{VI+} = n \cdot i_1|_{VI-}, \ n \cdot q|_{VI+} = n \cdot q|_{VI-}$$
(26)

At the positive terminal boundary III, the applied current of the battery is defined as follows

 $III: n \cdot i_1 = i_{app} \tag{27}$

The negative terminal boundary IV is grounded, thus

$$IV: \phi_1|_{IV} = 0 \tag{28}$$

The working voltage of the battery can be defined as

$$E_{\text{cell}} = \phi_1|_{\text{III}} - \phi_1|_{\text{IV}} \tag{29}$$

At the outer can surface V, the lumped heat exchange between battery and environment is described in Eq. (30)

$$V: -\lambda \frac{\partial T}{\partial n} = h(T - T_{\rm amb})$$
(30)

where the lumped heat transfer coefficient *h* is determined by comparing experimental data of the battery average surface temperature with simulated results in Fig. 3. A lithium ion battery was placed in a thermostatic chamber at 55° Celsius for 10 h, ensuring that the overall temperature of the battery is uniform. Then the battery was put in the environment with the ambient temperature of 25 °C for temperature relaxation to the environmental temperature. By comparing the experimental data with the simulated results, the lumped heat transfer coefficient *h* is determined to be 2.3 W m⁻² K⁻¹, which represents the synthetic action of convection and radiation heat transfer.

The initial conditions of the model are:

$$c_{1} = c_{1,0}, \ c_{2} = c_{2,0}, \ T = T_{0}, \ \phi_{1,pe} = \phi_{1,term+} = \phi_{1,0}, \phi_{1,ne} = \phi_{1,term-} = 0, \ \phi_{2,ne} = \phi_{2,pe} = \phi_{2,0}$$
(31)

3. Numerical simulation and experimental validation

3.1. Numerical simulation

A finite element based commercial software, COMSOL Multiphysics 4.3, was employed to solve the 2D electrochemical—thermal coupled model presented in this paper. A given battery current i_{app} was applied at the terminal boundary. The outputs of the model are the battery working voltage, electronic and ionic current density distribution, lithium and li-ion concentration distribution and temperature field. The MUMPS time dependent solver was chosen with a relative tolerance of 10^{-3} for all the variables; solutions were tested for mesh independence; and the solution time for this model was within 45 min by the computing platform with quad-core processors (3.2 GHz) and a total of 8 GB random access memory (RAM).

3.2. Experimental validation

A commercial Type 38120 LiFePO₄ power battery (ϕ 38 mm × 120 mm cylindrical battery, capacity 10 Ah, nominal voltage 3.2 V, 1.5 mol L⁻¹ LiPF₆ in EC/DMC solvent) was experimentally tested. A YKLE test system was used to monitor the charge–discharge current and working voltage. As shown in Fig. 4,



Fig. 3. Determination of lumped heat transfer coefficient *h* by comparing experimental data with simulated results.



Fig. 4. Top view of the battery cell with the placement of the thermocouples.

six thermocouples (from negative terminal to positive terminal indexed as #1 through #6) were evenly placed on the side face of the battery within the same axial section to monitor the surface temperature change. According to the manufacturer, the end-of-discharge voltage is 2.6 V at constant current discharge; the stop condition for constant charge process is that being charged to 3.65 V and then with constant voltage at 3.65 V till the charge current declines to 0.2 A. Another stop condition for both charge and discharge is when the total charge/discharge capacity reaches 10 Ah.

The model validation is conducted by comparing simulation results with experimental data of charging and discharging behaviors at different conditions. The focus will be on thermal validation and electrochemical validation.

3.2.1. Thermal validation

Fig. 5 shows the average temperature profile of the battery surface obtained by both simulation and experiment measurement. The operating condition for the battery in Fig. 5 is to discharge the battery under different C-rates (0.3C, 0.5C, 1C, 2C) at constant ambient temperature (25 °C). The average measured surface temperature is an average of temperatures obtained by the six thermocouples. As shown in Fig. 5, the average surface temperature increases by around 1.4 K, 4 K, 8.1 K, and 15.8 K above the ambient temperature for discharge rates of 0.3C, 0.5C, 1C, and 2C, respectively. It also can be seen that the surface temperature have the similar growth trends for the low discharge rates, while the temperature increases very fast at a high discharge rate, in particular



Fig. 5. Comparison of simulated results of average surface temperatures with experimental data during galvanostatic discharge (0.3C, 0.5C, 1C, 2C) under natural convection condition.



Fig. 6. Comparison of simulated results of axial surface temperatures with experimental data during 1C discharge under natural convection condition.

when the discharge rate is above 1C in this study. The variation of temperature profile may be due to the internal heat generation, which will be discussed in Section 4. Fig. 6 shows the axial temperature profiles of the battery surface obtained by both simulation and measurement. The operating condition for the battery in Fig. 6 is to discharge the battery under 1C rate at constant ambient temperature (25 °C). The surface temperature was measured by six thermocouples evenly attached to the surface of the battery as shown in Fig. 4. The simulated results differ slightly from the measured data towards the end of discharge. The simulated temperature appears low in the regions near both terminals, while the experimental data shows that these regions have higher temperature. This is because the electrical contact resistance between the connectors and terminals of the cell would cause temperature rise due to the local ohmic heat generation [12]. The contact resistance, however, is not included in the model.

3.2.2. Electrochemical validation

Fig. 7 shows the battery working voltage during discharge process under different C-rates (0.3C, 1C, 2C) at constant ambient temperature (25 $^{\circ}$ C). The simulation results agree with the



Fig. 7. Comparison of simulated results of working voltage with experimental data during galvanostatic discharge (0.3C, 1C, 2C) under natural convection condition.



Fig. 8. Schematic diagram of current distribution in a local cell unit.

experimental data generally well over the entire discharge process. Yet, there are a few differences in general discharge voltage plateau especially towards the end of discharge cycle. It is important to emphasize that these differences are related to the thermodynamic data and the design of batteries. For example, the half-cell open circuit potentials for both Li_x FePO₄ and Li_xC_6 electrodes used in this model are not measured values for the experimental battery used here but instead from published literature; the actual capacity for a new battery is always lager than that offered by the manufacturer, which has an impact on the initial battery capacity design. If these data were made available for the same battery used here for model validation, the remaining discrepancy between the experimental data and simulation results would have been further reduced.

4. Results and discussion

4.1. Electrochemical performance

Fig. 8 shows the current flow in the local cell unit of the battery. In the discharging process, the current in the *x* direction within the electrodes and separator is so small that the current flow between the two current collectors is assumed to be perpendicular to the electrodes. i_0 represents the current density transferred through the separator from the negative electrode to the positive electrode, which can be calculated by Eqs. (7) and (8) subject to the associated boundary conditions (23)–(24). We know that the current density i_0 transferring through the local cell unit is affected strongly by the potential of both electrodes which can be calculated by the current continuity equation.

Fig. 9 shows the potential distribution on the positive and negative electrodes during the discharge with 1C rate. It can be seen that the values of the potential of Fig. 9(a)-(c) are around 3.23, 3.19, and 2.78 V respectively. By halfway discharge, the potential drops slightly complying with the stable discharge voltage platform of LiFePO₄ battery. However, the values of the potential and the appearance of the potential distribution on the negative current collectors during the discharge has hardly changed, thus only the potential distribution on the negative current collectors at the discharge time of 3 min is shown in Fig. 9(d). This is due to the fact that the potential of the negative terminal is specially defined as 0 V in the model. Besides, the potentials on both positive and negative current collectors have the similar variation trend along the axial direction of the battery. As shown in Fig. 8, all the currents inside the battery flow from the negative terminal to the positive terminal during the discharge, which would suggest that the values of the potential decrease along the current direction as in Fig. 9. Therefore, in a cylindrical battery, the potential difference between positive and negative current collectors in the local region of the battery axial cross-section is relative uniform as compared to that of the prismatic



Fig. 9. Potential distributions on the positive current collector (a, b, c) and the negative current collector (d) during discharge with 1C rate. Discharge time is: (a, d) 3 min, (b) 30 min, and (c) 57 min.



Fig. 10. Distributions of current density transferred through the separator in the axial cross-section of battery during discharge at 1C rate. Discharge time is: (a) 3 min, (b) 30 min, and (c) 57 min.

battery published in the literature [1]. This is because the positive and negative terminals are placed in the same side of the prismatic battery, whereas the directions of the current on the positive and negative current collectors are completely opposite, thus leading to the non-uniform distributions of local potential difference as compared to that of the cylindrical battery here.

Inside the cell unit, the ionic current transferring through the separator is equal to the total current in the electrode layers. Therefore the magnitude of the ionic current transferring through the separator reflects the reaction rate. Fig. 10 shows the nonuniform distributions of current density transferred through the separator in the axial cross-section of battery under 1C rate discharge. At the beginning of discharge (Fig. 10(a)), the current density decreases from the negative tabs to the positive ones in the axial direction y coordinate. Meanwhile, in the radial direction, the current density also decreases in x coordinate. Nevertheless, after halfway through discharge (Fig. 10(b) and (c)), the region with higher current density gradually shifts from near the negative tabs and the battery axis to near the positive tabs and the outer can of the battery. This is because the region with the higher current density at the initial stage becomes more utilized by the halfway discharge and the region less utilized tends to have a higher reaction rate.

4.2. Heat generation and temperature distribution

The rise in temperature within a cell unit originates from the electrochemical reaction, ohmic heat and polarization heat as the



Fig. 11. Time history of the total heat generation rate in the axial cross-section of battery regardless of the current collectors during discharge at 1C rate.



Fig. 12. Ohmic heat distributions on current collectors during discharge at 1C rate. Discharge time: 3 min.



Fig. 13. Distribution of temperature at the end of discharge at (a) 1C, (b) 5C and (c) 10C rate under natural convection condition.

charge—discharge is passed through the battery. Fig. 11 plots the total heat generation rates under 1C discharge within the cell units at three different regions of A_1 , A_2 and A_3 as labeled in Fig. 1. The heat generation rate varies very little from each other among the different regions during the entire discharge cycle. The region A_1 close to the negative tabs seems to have the higher heat generation rate than do the region A_2 in the middle and the region A_3 close to the positive tabs at the beginning of discharge, but this trend reverses after the halfway through discharge. The reason is that the

heat generation at the beginning of discharge is mainly caused by the activation reaction rate (working current density). By comparing Fig. 10 with Fig. 11, we can see that the higher reaction rate the local cell unit has, the more quickly the heat is generated in the local region. The region with the highest working current density shifts from the region A_1 close to the negative tabs to the region A_3 close to the positive tabs during the discharge. This trend agrees with that of the heat generation rate. Fig. 12 plots the ohmic heat distributions on the positive and negative current collectors along the axial direction. It can be seen that the ohmic heat generated on both the positive and the negative current collectors decreases from one end near the tab to the other end, which is consistent with the flow of electron current as shown in Fig. 8. In addition, the conductivity of the positive current collector made by Al foil, is lower than that of the negative current collector made by Cu, which results in more ohmic heat generated on the positive current collectors. However, it is also of interest to see that the summation of the ohmic heat in both current collectors along axial direction is relative uniform as compared to that in the lengthwise direction of the prismatic battery in literature [2]. This corresponds to the fact that the positive and negative tabs are placed at both ends of the cylindrical battery, which has a significant effect on the current density and potential distributions, thus affecting the temperature distribution of the battery.

Fig. 13 shows the temperature distribution of the axial crosssection of battery during discharge at 1C, 5C and 10C rate under natural convection condition. The maximum temperature difference, between the hottest and the coldest spots, at 1C, 5C and 10C rates are 0.5 K, 3.1 K, and 9.3 K, respectively, at the end of discharge; the temperature gradient is higher in the axial (x) direction than that in the radial (y) direction. The reason is that the heat dissipates much faster in the region close to the battery terminal sides than in the battery core region, since the region near both terminal sides has relative large dissipated surface compared to the region close to the battery core. Fig. 13 also shows that the temperature is distributed symmetrically around the cross-section in the middle of the axis at all three discharge rates. This phenomenon can be further explained by the results shown in Figs. 11 and 12. As indicated by Fig. 11, the overall heat generate rates vary very little along the axial direction. Also the total ohmic heat generated on the current collectors are relative uniform in the axial direction as shown in Fig. 12. The positioning of the current collectors is one of the primary causes to have such a symmetric temperature distribution since the current collector determines the potential distribution, which further affects the current distribution and the heat generation.

5. Conclusion

A two-dimensional electrochemical—thermal model has been developed for a commercial Type 38120 LiFePO₄ cylindrical power battery by coupling the mass, charge, and energy conservations as well as the electrochemical kinetics. The effect of the current collecting tabs on the battery has been taken into consideration. The modeling results are further validated for both electrochemical performances and thermal behavior using experimental data. The modeling results indicate that the potentials on both positive and negative current collectors have the similar variation trend along the axial direction of the battery due to the arrangement of the positive and negative current collecting tabs in the cylindrical battery. The distribution of potential difference in the axial cross-section of the cylindrical battery is much more uniform than that in the lengthwise direction of the prismatic battery.

The reaction rate and the total heat generation rate of the electrodes are also evaluated. The higher reaction rate the local cell unit has, the more quickly the heat is generated in the local region. The heat generation rate among the different regions is relative uniform during the entire discharge cycle.

Compared to a prismatic battery in the lengthwise direction, the distribution of the sum of the ohmic heat generated on the positive and negative current collectors is relative uniform along the axial direction of the cylindrical battery.

The positioning of the current collectors is one of the primary causes to have such a symmetric temperature distribution on the cylindrical battery since the current collector determines the potential distribution, which further affects the current distribution and the heat generation.

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Nomenclature

<i>c</i> ₁	concentration of lithium in the active material particles $(mol m^{-3})$
62	electrolyte concentration (mol m^{-3})
C _{1,max}	maximum concentration of lithium in the active material (mol m^{-3})
c _{1,surf}	surface concentration of lithium in the active material (mol m^{-3})
<i>D</i> ₁	diffusion coefficient of lithium in the active material $(m^2 s^{-1})$
D_2	diffusion coefficient of electrolyte $(m^2 s^{-1})$
E_{aD}	diffusion coefficient activation energy (kJ mol ⁻¹)
E_{aR}	reaction activation energy (kJ mol $^{-1}$)
E _{cell}	working voltage of the battery (V)
f_{\pm}	average molar activity coefficient
F	Faraday's constant (C mol ⁻¹)
h	lumped heat transfer coefficient (W m ^{-2} K ^{-1})
i _{app}	applied current density of the battery (A m^{-2})
j_0	exchange current density (A m^{-2})
j _n	local charge transfer current density (A m^{-2})
k_0	reaction rate constant ($m^{2.5} \text{ mol}^{-0.5} \text{ s}^{-1}$)
k	thermal conductivity (W (m K) ^{-1})
q	volumetric heat generation (W m^{-3})
$q_{\rm rea}$	reaction heat generation (W m^{-3})
$q_{\rm act}$	polarization heat generation (W m^{-3})
$q_{ m ohm}$	ohmic heat generation (W m^{-3})
R	gas constant, 8.314 (J mol $^{-2}$ K $^{-1}$)
r	radius distance variable of electrode particles (µm)
r_0	radius of electrode particles (µm)
Sa	specific surface area (m ⁻¹)
SOC	state of charge
t	time (s)
t_+	transferring number of Li ⁺
T	absolute temperature (K)
T _{amb}	ambient temperature (K)
U _{eq}	open circuit potential of the electrode (V)
U _{ref}	open circuit potential under the reference temperature (V)

Greek letters

 α_a anodic transfer coefficient

- α_{c} cathodic transfer coefficient
- ε_1 active material volume fraction
- ε_2 electrolyte volume fraction
- ϕ_1 solid phase potential (V)
- ϕ_2 liquid phase potential (V)
- *γ* Bruggeman tortuosity exponent
- σ_1 electronic conductivity of solid matrix (S m⁻¹)
- σ_2 ionic conductivity of electrolyte (S m⁻¹)
- δ_i thickness of each battery component (µm)
- η local surface overpotential (V)

Subscripts, superscripts and acronyms

0 initial or equilibrated value

1 solid phase

- 2 liquid phase
- amb ambient
- current collector cc
- eff effective value
- el electrolyte
- ne negative electrode positive electrode
- pe reference value
- ref
- sp separator

surf surface of active material particles

term+/- positive/negative terminal

References

- [1] K.-H. Kwon, C.-B. Shin, T.-H. Kang, C.-S. Kim, J. Power Sources 163 (2006) 151-157.
- [2] M. Guo, R.E. White, J. Power Sources 221 (2013) 334-344.
- [3] M. Doyle, T.F. Fuller, J. Newman, J. Electrochem. Soc. 140 (1993) 1526–1533.
- [4] D. Bernardi, E. Pawlikowski, J. Newman, J. Electrochem. Soc. 132 (1985) 5–12.

- [5] P. Arora, M. Doyle, R.E. White, J. Electrochem. Soc. 146 (1999) 3543-3553.
- [6] C.R. Pals, J. Newman, J. Electrochem. Soc. 142 (1995) 3274–3281.
 [7] C.R. Pals, J. Newman, J. Electrochem. Soc. 142 (1995) 3282–3288.
 [8] C. Hellwig, S. Sörgel, W.G. Bessler, ECS Trans. 35 (2011) 215–228.

- [9] Y.H. Ye, Y.X. Shi, N.S. Cai, J.J. Lee, X.M. He, J. Power Sources 199 (2012) 227-238.
- [10] W. Wu, X.R. Xiao, X.S. Huang, Electrochim. Acta 83 (2012) 227–240.
- [11] F.J. Jiang, P. Peng, Y.Q. Sun, J. Power Sources 243 (2013) 181–194.

- F.J. Jiang, P. Peng, Y.Q. Sun, J. Power Sources 243 (2013) 181–194.
 L.H. Saw, Y.H. Ye, A.A.O. Tay, Energy Converse Manag. 75 (2013) 162–174.
 M. Guo, G. Sikha, R.E. White, J. Electrochem. Soc. 158 (2) (2011) A122–A132.
 L.J. Lee, K. Smith, A. Pesaran, G.H. Kim, J. Power Sources 241 (2013) 20–32.
 A.H. David McCleary, J.P. Meyers, B. Kim, J. Electrochem. Soc. 160 (2013) A1931-A1943.

- [16] S. Wang, L.L. Liu, X.J. Liu, J. Power Sources 244 (2013) 101–108.
 [17] J. Newman, T. William, AIChE J. 21 (1) (1975) 25–41.
 [18] V.V. Viswanathan, D. Choi, D.H. Wang, W. Xu, S. Towne, R.E. Williford, [10] v.v. viswalidulal, D. Cho, D.H. Wang, W. Xu, S. Towne, R.E. Williford, J.G. Zhang, J. Liu, Z.G. Yang, J. Power Sources 195 (2010) 3720–3729.
 [19] M. Safari, C. Delacourt, J. Electrochem. Soc. 158 (2011) 562–571.
 [20] M. Doyle, J. Newman, A.S. Gozdz, C.N. Schmutz, J.M. Tarascon, J. Electrochem. Soc. 143 (1996) 1890–1930.

- [21] L.O. Valoen, J.N. Reimers, J. Electrochem. Soc. 152 (2005) A882–A891.
 [22] C. Capiglia, Y. Saito, H. Kagayama, P. Mustarelli, T. Iwamoto, T. Tabuchi, H. Tukamoto, J. Power Sources 859 (1999) 81–82.