The effect of local current density on electrode design for lithium-ion batteries

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ABSTRACT

Local current density is an important parameter in battery modeling, which affects the performance of lithium-ion batteries. In this study, we take $LiFePO_4$ cathode material as an example. A simplified mathematical model has been developed to study the internal mechanism of the electrode. According to the results of the model, the local current density distribution has a regular change at different time in the discharge process. The parameter "critical thickness" as an optimized variable has been presented for battery design. By qualitative analysis to estimate the critical thickness under different condition, we can optimize the design parameter of a battery according to the practical demand.

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1. Introduction

In modern times, lithium-ion batteries are widely used for portable electronic devices, EVs and HEVs. Among various battery materials, $LiFePO_4$ has been considered as one of the most attractive cathode material for lithium-ion batteries due to its low cost, non-toxicity, great thermal stability and flat charge/discharge voltage plateau. Padhi et al. [1] first reported $LiFePO_4$ as a potential cathode material for lithium-ion batteries in 1997. Since then, it has been attracting considerable attention as a cathode material for lithium-ion batteries due to its high theoretical capacity 170 mAh g^{-1}, thermal stability, and low environmental impact [2].

However, these advantages are counteracted by the low electronic conductivity and ion conductivity of the material, which is considered to result in ohmic drops within the electrode. In addition, its poor high-rate capability also limits the commercial utilizations. Various ideas have been proposed to solve these two problems, including the reduction of the particle size to reduce transport length [3] and carbon coating on the particle surface to improve the conductivity of the solid phase [4,5].

Battery modeling is an efficient tool in battery design and test, which is based on basic physical and chemical principles [6–8,11]. It is the mathematical description of the internal structure and the charging and discharging behavior, to find the relationship between the design variables and the electrochemical performance.

By performing a specific mathematical model, one can predict the electrochemical performance, capacity fade and thermal behavior of a battery. Usually, battery modeling is a complex system coupled with several nonlinear differential and algebra equations.

Doyle and Newman firstly developed a general model for lithium-ion batteries [9], which is based on porous electrode theory: the electrode is considered as a compound which consists of two phases: the porous matrices and the electrolyte within the pores. The quantities at any point across the electrode area are assumed to be continuous functions of time and space, and the electrode is treated as a superposition of two continua. The model is developed to simulate the charging and discharging curves of batteries, and predict the parameter distribution inside the battery, as the potential distribution and ion concentration distribution.

The mechanism of $LiFePO_4$ electrode is considered to be unique, because during the charge/discharge process, lithium ions diffuse along a one-dimensional pathway and phase transition. So the mathematical modeling of a $LiFePO_4$ cathode requires describing the behavior of the phase transition between $FePO_4$ and $LiFePO_4$. Srinivasan and Newman [10] first develop a model based on the shrinking-core model presented by Padhi. It is coupled with two particle sizes and fitting based on experimental data.

In this study, to make a qualitative analysis, we use a simplified model based on Doyle's research to estimate the performance of $LiFePO_4$ electrode. We ignore the phase transition process and treat it as solid diffusion. In battery modeling, local current density represents the reaction current density on the surface of the particles, which is directly related to the surface lithium ion diffusion flux. According to the results by solving the model equations, we notice that during the discharging process, the local current

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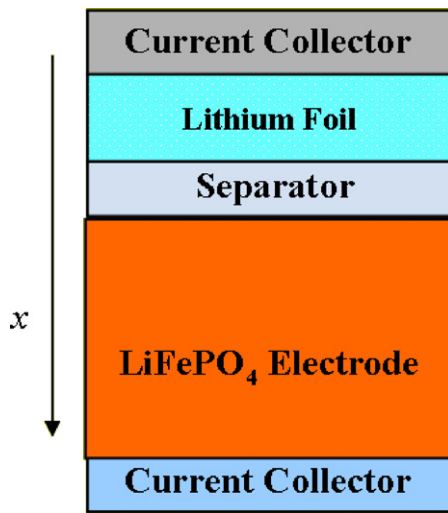
Fig. 1. The schematic of the battery modeled in this study, consisting of a Li-foil electrode, a porous LiFePO$_4$ cathode and a separator between them. The battery is filled with electrolyte. Both electrodes are attached to a current collector.

density distribution across the electrode area presents a peak value. As discharging process goes on, the peak moves from the current collector to the electrode–separator interface. This phenomenon will be helpful to battery design.

2. Model developments

The schematic of the battery modeled in this study is shown in Fig. 1. The battery consists of a Li foil anode and a LiFePO$_4$ cathode with a porous separator between the two electrodes. The cathode consists of a large amount of solid spherical particles. So the porous-electrode theory can be introduced in this model. We developed a one-dimensional model in this study. The mathematical equations that describe the processes are listed below.

In the electrode scale, according to porous electrode theory, the current density in the electrolyte phase is determined by a modified Ohm's Law:

$$i_2 = \nabla \cdot \left\{ -\kappa_2 \nabla \Phi_2 + \frac{2RT\kappa_2}{F} \left[1 + \frac{\partial \ln f}{\partial \ln c_2} \right] [1 - t_+] \nabla (\ln c_2) \right\} \tag{1}$$

Here the subscript '2' refers to the electrolyte phase. Φ_2 is the potential, c_2 is the concentration of lithium ion and κ_2 is the ion conductivity in the electrolyte.

In the solid phase (denoted by subscript '1'), the current density is determined by Ohm's law:

$$i_1 = I - i_2 = -\kappa_1 \nabla \Phi_1 \tag{2}$$

where I is the applied current density. As a consequence of the assumption of electroneutrality that the divergence of the total current density is zero. For a one-dimensional model, it is expressed as

$$i_1 + i_2 = I \tag{3}$$

According to porous-electrode theory, the mass balance in the electrode is

$$\varepsilon \frac{dc_2}{dt} = \nabla \cdot (D \nabla c_2) + \frac{a i_n}{F}(1 - t_+) \tag{4}$$

A rate equation is used to determine the dependence of the local electrochemical reaction rate on concentration and potential. The Butler–Volmer equation is commonly used:

$$i_n = i_0 \left\{ exp \left(\frac{\eta F}{RT} \right) - \exp \left(\frac{-\eta F}{RT} \right) \right\} \tag{5}$$

Here i_n refers to the local current density and $\eta = \Phi_1 - \Phi_2 - E_{ocv}$ refers to the surface overpotential. E_{ocv} is the open-circuit potential of LiFePO$_4$ with respect to a lithium reference electrode, which is a function of the state of discharge (SOD), and can be evaluated by discharging at very low rate. Generally the state of discharge can be represented as an expression of solid phase concentration c_1: c_1/c_{max} [10]. c_{max} is the maximum concentration of lithium ions that can be incorporated into the lattice, which is take to be 22785 mol m^{-3} for LiFePO$_4$. The exchange current density i_0 is given by:

$$i_0 = Fkc_2^{0.5}c_1^{0.5}(c_{max} - c_1)^{0.5} \tag{6}$$

where $(c_{max} - c_1)$ denotes the concentration of unoccupied sites in Li$_x$FePO$_4$ and k is the reaction rate constant.

A charge balance relates the divergence of the current to the surface diffusion flux j_n, or the local current density i_n due to reaction:

$$a i_n = a F j_n = \nabla \cdot i_2 \tag{7}$$

The boundary condition is: at the current collector interface ($x = 0$), $i_2 = 0$; at the electrode–separator interface, $i_2 = I$.

In the solid phase, the phase transition from FePO$_4$ (charged) to LiFePO$_4$ (discharged) during charge/discharge is ignored. The process of lithium ions insertion/extraction is treated as solid diffusion, and follows the second Fick's Law in spherical coordinates:

$$\frac{\partial c_s}{\partial t} = D_1 \frac{\partial^2 c_s}{\partial r^2} + \frac{2D_1}{r} \frac{\partial c_s}{\partial r} \tag{8}$$

The boundary condition is:

$$\frac{\partial c_s}{\partial r} = 0, \quad r = 0$$

$$j_n = \frac{i_n}{F} = -D_1 \frac{\partial c_s}{\partial r}, \quad r = R_s$$

The solid diffusion is based on particle scale, where R_s is the particle radius. c_s denotes to the solid phase concentration of lithium ions in the particles. At the surface of the particles, the solid concentration is corresponding to the solid phase concentration c_1 in the electrode scale. The surface diffusion flux of lithium ions, j_n, is embedded into Eqs. (4) and (5) in the electrode scale.

All equations ((1), (2), (4), (5), (7) and (8)) are simultaneously solved using Newton's iterative method [12]. The electrode domain is discretized using finite difference method. Six unknowns are involved in this model, including the concentration in the solid and electrolyte phase c_1 and c_2, the potential in the two phases Φ_1 and Φ_2, the current density in the electrolyte phase i_2, and the local current density i_n, respectively. At each time step, the iteration commences by providing initial guesses for all unknowns, until the convergence is reached. Time stepping moves on until the cut-off voltage is reached. From the results we can obtain the distribution of all the unknowns across the electrode area at different time. The parameters used in the model are listed in Table 1 and the open-circuit potential curve is shown in Fig. 2, which is obtained by discharging the cell at 0.02 C.

3. Results and discussions

During the discharge process, lithium ions migrate and diffuse from anode to cathode across the separator and insert into the

Table 1
Parameters used in the model.

Parameter	Value
Diffusion coefficient in LiFePO$_4$, D_1	9×10^{-18} m^2 s^{-1}
Solid phase conductivity, κ_1	5×10^{-3} S m^{-1}
Electrolyte conductivity, κ_2	[10]
Particle radius	4 μm
Initial salt concentration	1 M
Reaction rate constant, k	2×10^{-11}
Separator thickness	25 μm
Transfer coefficient, α	0.5
Ion transfer number for lithium ions, t_+	0.39

active material particles. The electrode reaction occurs on the surface of the particles, resulting in a surface diffusion flux of lithium ions j_n into the particles. Based on the Butler–Volmer equation (Eq. (5)), the local current density i_n is produced by the electrode reaction, and in the meantime it is described as a flux boundary condition in the solid diffusion process (Eq. (8)).

In the solid diffusion, what we care about is the relation between the surface diffusion flux j_n/local current density i_n and the surface concentration of lithium ions c_1. By discretizing Eq. (8) using backward differences in the radial coordinates, a following form of matrix equation can be obtained:

$$Ac_s^k = \tau c_s^{k-1} + b^k \tag{9}$$

where A is a tridiagonal coefficient matrix, c_s is the concentration vector inside the particles, b is a vector relative to the local current density i_n and k denotes the present time step while $k-1$ denotes the previous. By solving this equation using Thomas algorithm, an expression related local current density to surface concentration on the particles can be obtained:

$$c_1^k = pc_1^{k-1} + qi_n^k \tag{10}$$

where p and q are coefficients, which vary at different time step and different position in the electrode domain. In the discharge process, as the electrode reaction produces surface flux, lithium ions insert into the particles continuously. As a result, the surface concentration of lithium ions increases and the state of discharge also rises. While the surface concentration rises up to a value closed to c_{max}, namely the local SOD is close to 1, the lithium ions will be difficult to be inserted.
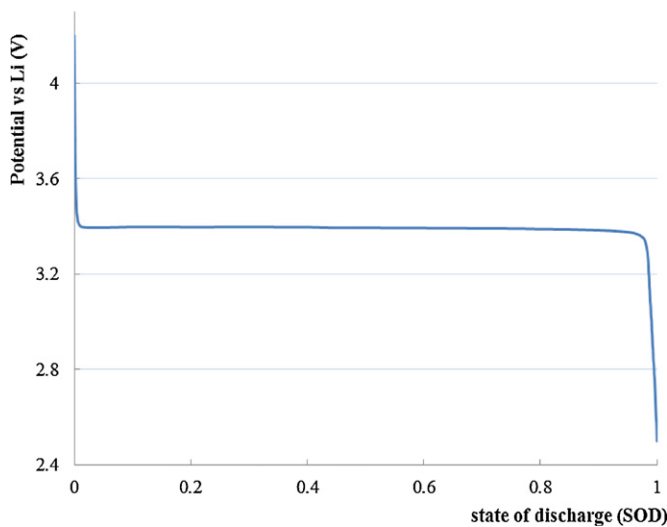
Fig. 2. The equilibrium potential curve for LiFePO$_4$. It is obtained by discharging at 0.02 C.

We simulate the local current density, surface concentration and local state of discharge distribution across the cathode area at 1 C discharge. To make a general discussion, the cathode thickness is set to be 100 μm. The curves at different time in the discharge are shown in Figs. 3–5. In Fig. 3, a peak exists in the local current density curve which moves from current collector to the cathode–separator interface as discharge proceeds. At the beginning of discharge, the peak presents at the current collector interface, namely the local current density at the boundary is much higher than that in the interior, indicating a much faster reaction rate near the current collector region. Therefore, the surface concentration near the current collector increases very fast as shown in Fig. 4. As the reaction proceeds, the surface concentration in this region will rise up to be closed to maximum concentration and the particles will approximately reach the fully discharged state in a short time (Fig. 5).

The battery is discharged under galvanostatic conditions. By charge balance, the amount of lithium ions inserted into particles will be constant per unit time, so the integral of local current density across the cathode area is also a constant relative to the applied current density (Eq. (7)). When the particles close to the current collector approximately reach their fully discharged state, lithium ion can hardly continue to be inserted, resulting in a very low local current density in this region during the later discharge process. To satisfy the charge balance condition, the peak moves to the leftward region until the local state of discharge approximately equals to 1 (as shown in Fig. 3). This process repeats until the end of discharge is reached.

In Figs. 4 and 5, the surface concentration and state of discharge distributions at different time represent the same trend. The particles close to the current collector boundary are firstly approaching the fully discharge state. As a consequence, we can conclude that high local current density means high diffusion flux and reaction rate which results in fast growth rate of surface concentration and state of discharge.

As the curve at $t = 3575$ s shown in Fig. 3, we can find that at the end of discharge, the peak of the local current density has not reached the separator-cathode boundary. Correspondingly, the surface concentration in the region close to separator also has not reached the maximum concentration and the local state of discharge is far less than 1, which indicates that the active material has not been adequately utilized. That is because the stop condition is determined by cut-off voltage in both simulation and practice. When cut-off voltage is reached, the utilization of active material may not be 100%. As a result, to optimize battery design and achieve better performance, it is essential to choose appropriate value for some design parameters.

In electrode design, porosity ε, electrode thickness h, compacted density ρ_c and surface density ρ_s (the mass of active material per unit electrode area) are four important design parameters. For a specific electrode material (the intrinsic density has been fixed), if the component of the slurry is given (including the active material, conductor and polymer binder), the four parameters can be approximately related by the following equations:

$$\varepsilon = 1 - \varepsilon_{act} - \varepsilon_{cond} - \varepsilon_{bind} = 1 - \rho_c \left(\frac{1}{\rho_{act}} + \frac{x_{cond}}{x_{act}\rho_{cond}} + \frac{x_{bind}}{x_{act}\rho_{bind}} \right) \tag{11}$$

$$\rho_s = \frac{\rho_c}{h} \tag{12}$$

where ρ_{act}, ρ_{cond}, ρ_{bind} are the intrinsic density of active material, conductor and binder, x_{act}, x_{cond}, x_{bind} denote the mass fraction of the three, and ε_{act}, ε_{cond}, ε_{bind} denote the volume fraction of them in the electrode, respectively. If the porosity and the electrode thickness are fixed, the other two parameters can also be determined
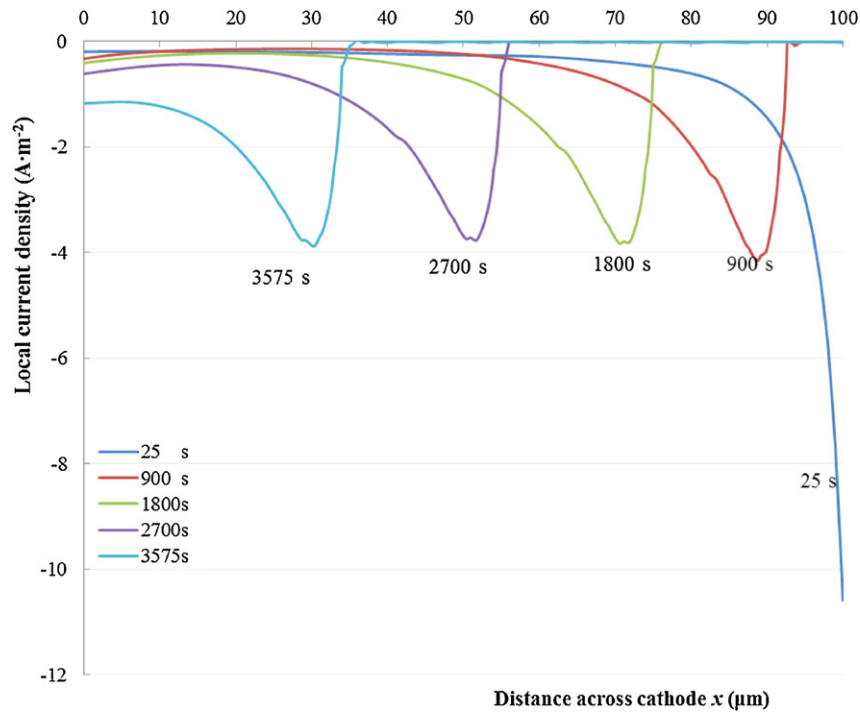
Fig. 3. The local current density distributions at different time during the discharge at 1 C rate. The cathode thickness is set to be 100 μm. The abscissa denotes the cathode thickness: the left side represents the separator–electrode interface and the right side the current collector boundary. The numbers in the legend denote the time of discharge in seconds. The value of local current density is negative which means the charges flow into the particles.

from the equations above. As a consequence, we need to analyze the effect of two parameters: porosity and electrode thickness, which are also introduced as parameters in our model, on the performance of a battery.

To achieve the optimum utilization of the active material, we should select an appropriate electrode thickness. From the

discussion above, we may derive a 'critical thickness' as the optimum thickness. It is determined by the location of the peak in the local current density distribution. When the cut-off voltage is reached, if the peak value of local current density just arrives at the electrode–separator interface, namely, the active material in the whole electrode has been adequately utilized, this thickness
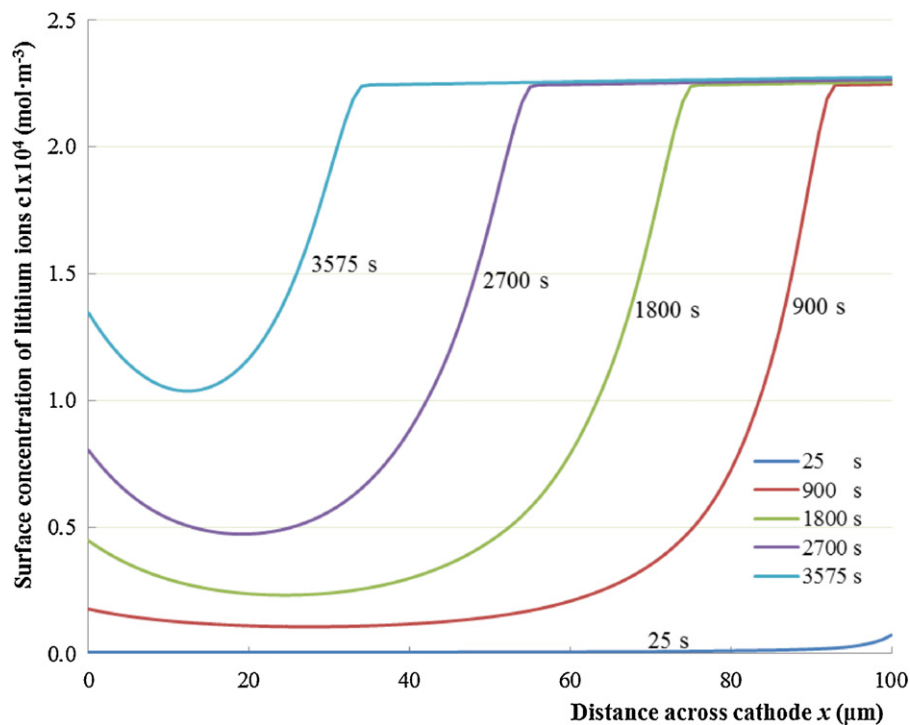
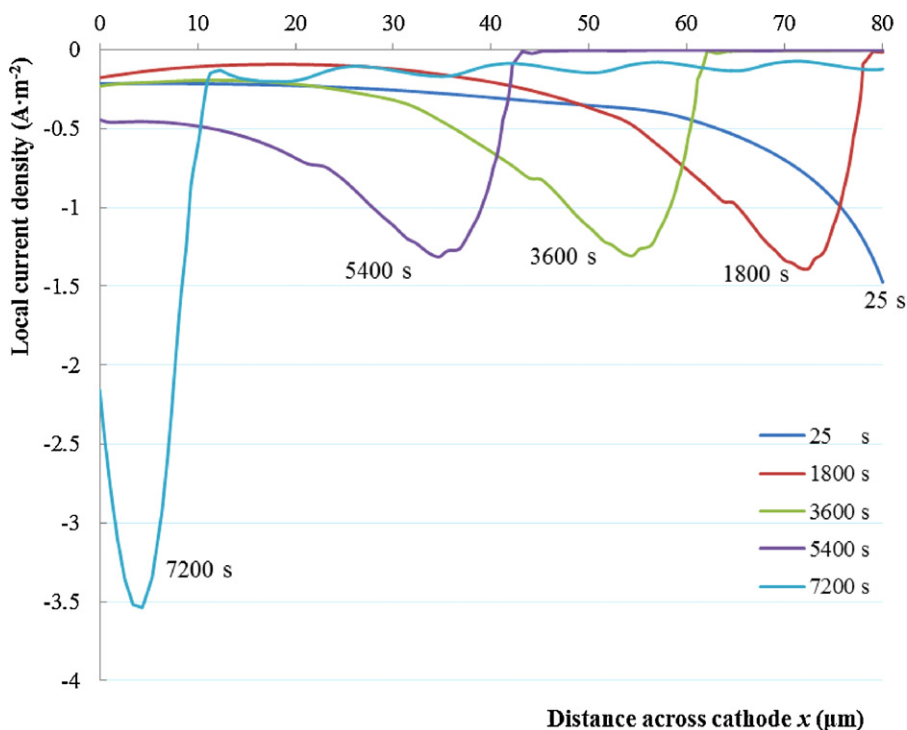**Fig. 4.** The surface concentration distributions at different time during the discharge at 1 C rate.
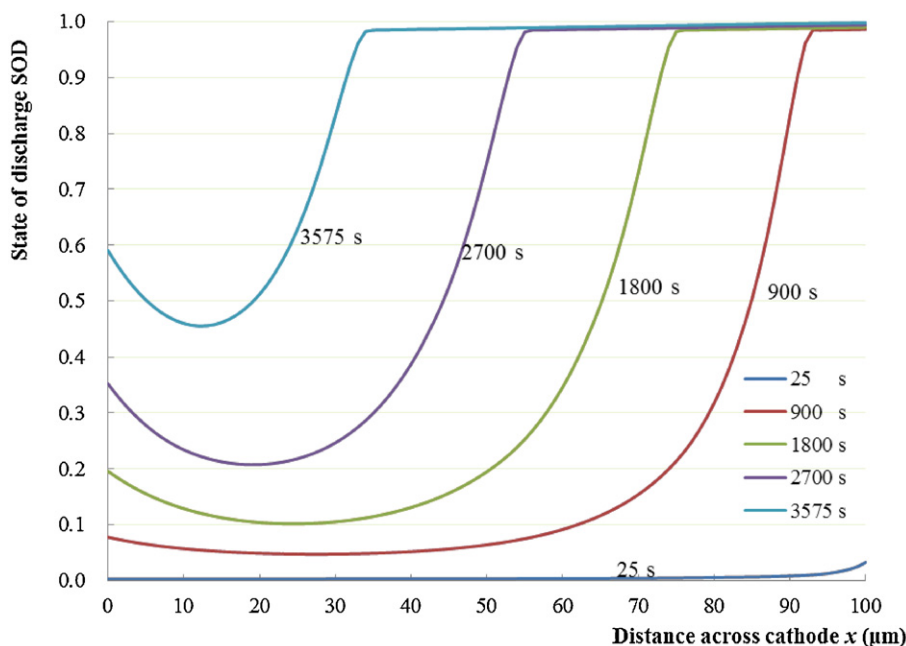
Fig. 5. The state of discharge distributions at different time during the discharge at 1 C rate. The fully discharged state moves from the current collector to the interior as discharge proceeds.

is considered to be the "critical thickness" under the condition. If this electrode thickness is greater than critical thickness, when the cut-off voltage has been reached, the peak has not arrive at the electrode–separator interface yet, indicating there are some redundant active material which has not been utilized. Otherwise, if the thickness is less than critical thickness, before the cut-off voltage is reached, the peak has already reached the boundary, indicating that the active material may be inadequate.

In other words, to calculate the critical thickness, two stop conditions should be satisfied at the same time: the cut-off voltage is reached and the peak of local current density distribution just arrives at the separator–cathode boundary. For a specific electrode component, the critical thickness is related to the porosity of the electrode and the discharge current density/discharge rate.

In the following discussion, we will make a qualitative analysis about the effect of porosity and discharge rate on the critical

Fig. 6. The local current density distributions at different time during the discharge at 0.5 C rate. The cathode thickness and the porosity are set to be 0.45 and 80 μm, respectively. The peak approximately moves to the separator when cut-off voltage is reached, indicating the critical thickness is 80 μm under this condition.
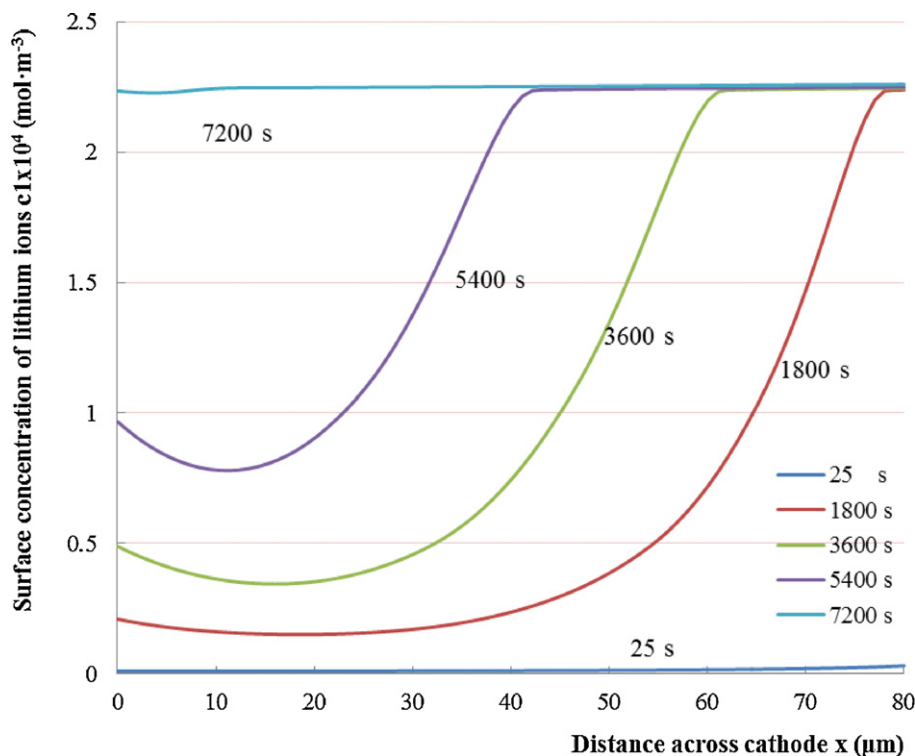
Fig. 7. The surface concentration distributions at different time during the discharge at 0.5 C rate. The porosity and thickness are 0.45 and 80 μm. When the thickness is designed to be the critical thickness, the active materials are adequately utilized at the end of discharge.

thickness. We take three porosity values (0.45, 0.4, 0.35) and four discharge rates (0.5 C, 1 C, 2 C, 5 C), and calculate the local current density distribution at different time of various electrode thickness, in order to find the critical thickness.

When the porosity equals to 0.45, the local current density and surface concentration distributions at 0.5 C are shown below (Figs. 6 and 7). From the figures we can find that the critical thickness is 80 μm at this discharge rate. When cut-off voltage is reached, the peak of the local current density curve approximately reaches the boundary at the same time. The calculation process is repeated then the critical thickness under various conditions is obtained.

All the results are summarized in Table 2. We can infer if the porosity has been fixed, as the discharge rate grows, the critical thickness becomes less; if the discharge rate is fixed, as the porosity reduces, the critical thickness also decrease (Table 2).

It is only a qualitative, not a quantitative analysis, but still has great significance on battery design. There is an experienced rule in the battery industry: to make better battery for higher discharge rates, the electrode thickness should be smaller. Our results provide some theoretical support on this rule. Once demand of design has been confirmed, we can manufacture the corresponding batteries with the optimized thickness which matches compacted density (porosity) and discharge rates.

4. Conclusions

Local current density is an important parameter in battery modeling, which represents the surface ion flux and relates to the electrochemical reaction rates. Based on the solution of the mathematical model we can estimate the local current density distribution across the electrode area. At different time during the discharge process, the curve appears the different trend. A peak is discovered on the curves and it moves on. By qualitative analysis we get a parameter called "critical thickness" which may be important for battery design. In further research we will make quantitative analysis to get accurate results.

Acknowledgements

Appendix.

Table 2
Critical thickness (μm) for LiFePO₄ of different porosity and discharge rates.

Porosity	Discharge rates (C)			
	0.5	1	2	5
0.45	80	70	55	30
0.4	75	60	50	20
0.35	70	55	40	15

List of symbols

a	specific interfacial area per unit volume of electrode (m^{-1})
c_2	salt concentration in the electrolyte ($mol\,m^{-3}$)
c_1	concentration of lithium in solid phase ($mol\,m^{-3}$)
c_{max}	maximum concentration of lithium in solid phase ($mol\,m^{-3}$)
D_1	diffusion coefficient of lithium ion in solid phase ($m^2\,s^{-1}$)

D_2 diffusion coefficient of lithium ion in the electrolyte $(m^2 s^{-1})$

F Faraday's constant $(96{,}487\,C\,mol^{-1})$

h electrode thickness (m)

I applied current density (A)

i_0 exchange-current density, referred to the active surface area $(A\,m^{-2})$

i_n local current density at the particle surface, referred to the active surface area $(A\,m^{-2})$

R_s particle radius (m)

t_+ ion transport number of the electrolyte

R universal gas constant $(8.314\,J\,mol^{-1}\,K^{-1})$

ε porosity, the volume fraction of electrolyte in the electrode

Φ_1 potential of the solid phase (V)

Φ_2 potential of the liquid phase (V)

η surface overpotential (V)

α transfer coefficient

ρ_c compacted density, mass of active materials per unit volume of the electrode $(kg\,m^{-3})$

ρ_s surface density, mass of active materials per unit area of the electrode $(kg\,m^{-3})$

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