A transfer function type of simplified electrochemical model with modified boundary conditions and Padé approximation for Li-ion battery: Part 1. lithium concentration estimation

Shifei Yuan a, *, Lei Jiang b, **, Chengliang Yin a, Hongjie Wu a, Xi Zhang a

a National Engineering Laboratory for Automotive Electronic Control Technology, Shanghai Jiao Tong University, Shanghai, China
b Automotive Engineering College, Shanghai University of Engineering Science, Shanghai, China

HIGHLIGHTS

● The modified boundary condition and Padé method is used for model simplification.
● A low order transfer function for solid/liquid concentration estimation is derived.
● The pulse charge/discharge and dynamic profiles are used for model verification.
● The simplified model presents high accuracy with extremely less computational cost.

ARTICLE INFO

Article history:
Received 2 December 2016
Received in revised form 27 February 2017
Accepted 15 March 2017
Available online xxx

Keywords:
Lithium-ion battery
Simplified electrochemical model (SEM)
Transfer function
Modified boundary condition
Padé approximation
Concentration estimation

ABSTRACT

To guarantee the safety, high efficiency and long lifetime for lithium-ion battery, an advanced battery management system requires a physics-meaningful yet computationally efficient battery model. The pseudo-two dimensional (P2D) electrochemical model can provide physical information about the lithium concentration and potential distributions across the cell dimension. However, the extensive computation burden caused by the temporal and spatial discretization limits its real-time application. In this research, we propose a new simplified electrochemical model (SEM) by modifying the boundary conditions for electrolyte diffusion equations, which significantly facilitates the analytical solving process. Then to obtain a reduced order transfer function, the Padé approximation method is adopted to simplify the derived transcendental impedance solution. The proposed model with the reduced order transfer function can be briefly computable and preserve physical meanings through the presence of parameters such as the solid/electrolyte diffusion coefficients (Ds&De) and particle radius. The simulation illustrates that the proposed simplified model maintains high accuracy for electrolyte phase concentration (Ce) predictions, saying 0.8% and 0.24% modeling error respectively, when compared to the rigorous model under 1C-rate pulse charge/discharge and urban dynamometer driving schedule (UDDS) profiles. Meanwhile, this simplified model yields significantly reduced computational burden, which benefits its real-time application.

© 2017 Elsevier B.V. All rights reserved.

1. Introduction

The lithium-ion (Li-ion) batteries are widely utilized in multiple applications, ranging from portable electronic devices to vehicle energy sources including hybrid electric vehicles (HEVs) and pure electric vehicles (EVs), due to their higher energy and power density. During the operation, the li-ion batteries will encounter potential safety hazards and degradation mechanism, such as the electrolyte concentration exhausted depletion and solid electrolyte interface (SEI) film generation. To enhance the safety, efficiency and lifespan of the li-ion battery system, an advanced battery management system (BMS) with the physical insight into cell internal degradation and safety conditions should be developed.

In the literature, based on different modeling priorities on external and internal characteristics, the li-ion battery models can
be categorized as equivalent circuit empirical model [1-7] and physics-based electrochemical model [8-18]. Equivalent circuit models (ECMs) are the most widely developed and investigated models for state of charge (SoC), state of health (SoH), state of available power (SoP) and state of energy (SoE) estimation due to their systematic simplicity and facile of implementation. However, the ECMs are weak in providing physical knowledge about the cell internal electrochemical dynamics, which will remarkably limit their applications in advanced control-oriented issues, such as the fast charging optimization, electrochemical physics-based SoH conditioning etc. Alternatively, physics-based electrochemical models (EMs) [8,9] are originally developed to describe the electrochemical dynamics within the cell based on porous electrode and concentrated solution theories. However, the extensive computation burden of the governing partial differential equations (PDEs) limits their real-time application for advanced battery system control. For practical BMS designers, the optimal choice is to obtain a reduced order model (ROM) that can perfectly balance the computational complexity and prediction capabilities with physical significance.

Many techniques on model order reduction (MOR) are proposed to accelerate the computation process for the electrochemical model. The primary contributions focus on simplifying the computational complexity for the solid phase diffusion equations. The finite element method [10] and the residue grouping method [11] are employed by Smith et al. to derive reduced-order models for Li-ion batteries. The finite element method is an effective algorithm used by many commercial software for the spatial discretization of solid phase diffusion equations, and its calculation result is usually taken as the baseline to verify other model's performance. However, the highly extensive computation burden hinders its usage in real-time application. The residue grouping model can provide equivalent performance as the finite element model with significantly reduced computation time. Meanwhile, the parametric connection between the residue grouping model and full order model has been retained. The parabolic approximation [12,13], perturbation techniques, volume averaging, and intuition-based simplifications [14,15] are also adopted to approximate the concentration distribution throughout the solid particle. These volume-average integration methods perform well at low discharge rates rather than highly dynamic current profile. The electrode-average model is proposed by Di Domenico et al. [16] for battery voltage prediction and state of charge estimation with the assumption of fixed electrolyte concentration. The simulation results indicate that the average model can present a good battery voltage prediction during a pulse test procedure with a maximum error of 0.3 mV for mild current rates. To further extend the model effectiveness and reduce the computing time, Prada et al. [17] modified the average model by neglecting the solid concentration distribution along the electrode and considering the mass diffusion inside a representative solid particle. The mass conservation equations in the electrodes and electrolyte phase are coupled together to improve the voltage performance at high current rates.

In addition, the current-dependent spherical particle radius is also used to obtain good agreement with experimental data for low and high charge/discharge rates. Wang et al. [18] takes a sixth-order polynomial profile to approximate the solid diffusion equation. Forman et al. [19] utilizes the Padé approximation to represent the solid diffusion equation. The Padé approximation works well in lower frequencies, but diverges notably in higher frequencies. Cai and White [20-22] use proper orthogonal decomposition to design the electrochemical variables at discrete locations within the solid particle and across the one dimensional (1D) cell. This method accurately simulates the cell behavior at high currents but requires either existing experimental data or simulation results to generate the reduced order model. Plett et al. [23] uses the discrete-time realization algorithm (DRA) to approximate the transcendental transfer function of the spherical solid diffusion equation. The simulation shows that a third-order discrete-time model can closely approximate this infinite-order model behavior at the cost of missing its physical significance.

In the field of simplifying the electrolyte diffusion equations, several attempts are also promising and attractive to the BMS engineers. Smith et al. [24,25] linearizes the coupled electrolyte PDEs of the pseudo-two dimensional model with the finite element method (FEM) and derives analytical transfer function from the linearized model. This procedure is able to capture the lithium electrolyte concentration Ce (x,t) at different spatial locations, resulting in an increased computation burden. Galerkin's approximation [26,27] is used to model the lithium electrolyte concentration under the assumption of a galvanostatic discharge condition. Plett et al. [28] proposed a physics-based one-dimensional discrete-time state-space reduced order model (ROM) using discrete-time realization algorithm (DRA) to approximate the lithium electrolyte concentration. The simulation indicates the ROM can present the electrolyte phase concentration predictions with high accuracy at the cost of missing physical significance. Marcicki et al. [29,30] developed a transfer function type of reduced order model with Padé approximations. Their simplification work has made tremendous advance to promote the reduced order model for model-based control and estimation applications. However, the weakness in their research is that the lengths of the negative electrode, separator and positive electrode are fixed, and the generalization ability to other cells with different geometry dimensions is limited. The integral method analysis (IMA) is used by Tanim et al. [31-33] to solve the lithium-ion diffusion equation in the electrolyte domain. The simulation reveals that the simplified model presents high accuracy performance, acceptable computation cost, and retains physics-meaningful variables and parameters. Greco et al. [34] has obtained the steady-state analytical solution for the electrolyte phase concentration difference at cell's two terminals, by considering the electrolyte diffusion coefficient and current density to be constant and uniform. The simulation results show that the steady-state analytical solution has close agreement with the transient computation result in the one-dimensional electrolyte diffusion model.

The simplification of the electrolyte diffusion equations draws our emphasis in this paper. The reason and significance for model order reduction is listed in the following aspects: 1) the boundary conditions of electrolyte diffusion equations for negative electrode, separator and positive electrode are coupled together, which causes some obstacle to achieve a generalized analytical solution for the electrolyte diffusion equations. 2) to solve the electrolyte diffusion equations numerically, temporal and spatial discretization is a necessary procedure to convert the partial differential equations (PDEs) to ordinary differential equations (ODEs), which will result in an increased computation burden and limited real-time application. In another way, if the readers focus on one specific point within the cell, they should also conduct the spatial discretization and calculation for all points along the cell dimension to achieve the desired result. To simplify the solving process of PDEs, a non-coupled electrolyte diffusion equations with modified boundary conditions are newly proposed in this research.

This paper is organized as follows. In Section 2, the pseudo two dimensional (P2D) battery model is briefly introduced. In Section 3, the simplification work on solid diffusion equation with Padé approximation is presented and validated in frequency and time domain. In Section 4, the modified boundary conditions for electrolyte diffusion equations are proposed, and the simplified transfer
function with Padé approximation is obtained accordingly. The model performance comparisons about two models has been conducted in frequency and time domain. Finally, the concluding remarks and the plans for future work are given.

2. P2D electrochemical model

2.1. Electrochemical mechanism

The pseudo two dimensional (P2D) electrochemical model for lithium-ion battery was firstly established by Doyle, Fuller and Newman [8,9] based on the knowledge of the porous electrode theory, solution diffusion theory and Butler-Volmer kinetics. The lithium-ion cell is composed of five elements (as shown in Fig. 1): negative current collector (x = 0), the negative electrode (width = L_n), separator (width = L_s), the positive electrode (width = L_p) and the positive current collector (x = L_p). Lithium metal oxide (Li_xMO_2) and lithiated carbon (Li_xC_6) are the active materials in the positive and negative electrodes, respectively. The electrolyte in liquid or gel-polymer phase acts as the medium between positive and negative electrodes. The separator prevents the transmission of electrons, yet permits the lithium ion transport.

Take the discharge process for example, the active material in the positive electrode is increased and lithium ions are intercalated as follows

Positive: \( Li_y - z MO_2 + zLi^+ + ze^- \xrightarrow{\text{discharge}} Li_y MO_2 \) (1)

The active material in the negative electrode is reduced and lithium ions are de-intercalated as follows

Negative: \( Li_x C_6 \xrightarrow{\text{charge}} Li_{x-z} C_6 + ze^- + zLi^+ \) (2)

In the electrolyte phase, lithium ions migrate from negative to positive region via diffusion and ionic conduction dynamics.

2.2. Governing equations

To make the presentation more clear and coherent, the pseudo-2D electrochemical model [8,9,28] is briefly reproduced in this section. In general, the P2D model describes the conservation of species and chargers in solid and electrolyte phases \( (c_e, c_r, \phi_e, \phi_r) \). First, the lithium in the solid phase is governed by Fick’s diffusion law:

\[
\frac{\partial c_L(x, r, t)}{\partial t} + \frac{D_L}{r^2} \frac{\partial}{\partial r}(r^2 \frac{\partial c_L(x, r, t)}{\partial r}) = 0
\]

where, \( r \in (0, R_i) \) is the radial coordinate, \( c_L (x, r, t) \) is the Li ions concentration in the particle as a function of space domain \( x \), radial position \( r \) and time, and \( D_L \) is the solid phase diffusion coefficient. Solid particles in the electrodes are modeled as spheres with radius \( R_i \).

The boundary conditions are:

\[
\frac{\partial c_L(x, r, t)}{\partial r} \bigg|_{r=0} = 0
\]

\[
D_L \frac{\partial c_L(x, r, t)}{\partial r} \bigg|_{r=R_i} = -j^{Li}(x, t) \frac{1}{a_i F}
\]

where, \( j^{Li}(x, t) \) is the rate of electrochemical reaction at the particle surface, \( a_i \) is the specific interfacial surface area, and \( F \) is Faraday’s constant (96,487 C/mol).

Charge conservation in the solid phase of each electrode is described by Ohm’s law

\[
\frac{\partial}{\partial x} \left( \sigma^{eff} \frac{\partial \phi_s}{\partial x} (x, t) \right) - j^{Li} = 0
\]

where, \( \phi_s (x, t) \) and \( \sigma^{eff} \) are the potential and effective conductivity of the solid electrode, respectively. \( \sigma^{eff} \) is calculated with \( \sigma^{eff} = \sigma c_e \) and \( \sigma \) is the active material reference conductivity. For the spherical active material particles, the electrode volume fraction \( c_s \) is expressed as \( c_s = a R_i / 3 \). The boundary conditions are expressed as

\[
-\sigma^{eff} \frac{\partial \phi_s}{\partial x} \bigg|_{x=0} = +\sigma^{eff} \frac{\partial \phi_s}{\partial x} \bigg|_{x=L_e} = \frac{I_{app}(t)}{A}
\]

\[
\frac{\partial \phi_s}{\partial x} \bigg|_{x=L_e} = \frac{\partial \phi_s}{\partial x} \bigg|_{x=-L_e} = 0
\]

where, \( A \) is the electrode plate area and \( I_{app}(t) \) is the applied current.

Conservation of lithium ions in the electrolyte phase yields

\[
\frac{\partial (c_e c_r)}{\partial t} = \frac{\partial}{\partial x} \left( D_e^{eff} \frac{\partial c_e}{\partial x} \right) + 1 - t^0_1 f^{Li}
\]

where \( c_e \) is the electrolyte phase Li concentration, \( c_r \) is the electrolyte phase volume fraction, \( D_e \) is the electrolyte phase diffusion coefficient, \( t^0_1 \) is the transference number of Li^+ with respect to the velocity of solvent. The effective diffusion coefficient \( D_e^{eff} \) is calculated with the Bruggman relation \( D_e^{eff} = D_e^{brug} \). The boundary conditions at the current collectors require zero flux,

\[
\frac{\partial c_e}{\partial x} \bigg|_{x=0} = \frac{\partial c_e}{\partial x} \bigg|_{x=L_e} = 0
\]

Electrolyte phase charge conservation is linearized [24] to yield

\[
\frac{\partial}{\partial x} \left( k^{eff} \frac{\partial c_e}{\partial x} \right) + \frac{\partial}{\partial x} \left( \frac{k^{eff}}{c_e} \frac{\partial c_e}{\partial x} \right) + j^{Li} = 0
\]
where $\phi_e$ is the electrolyte phase potential, $\kappa$ is the ionic conductivity, and $\kappa_{\text{eff}}$ is the effective ionic conductivity, with the Bruggman relation $\kappa_{\text{eff}} = \kappa / \rho_{\text{eff}}$. The effective diffusive conductivity $\kappa_D$ is expressed as $\kappa_D = (1 - \rho^2) \left[ 1 + \frac{\ln J}{\rho_0} \right]$. In this work we assume the value of $J$ ln $f_p$ / d ln $c_e$ is zero.

With the boundary conditions at the two current collectors,

$$\frac{\partial \phi_e}{\partial x} \bigg|_{x=0} = \frac{\partial \phi_e}{\partial x} \bigg|_{x=L} = 0$$

(12)

Finally, the Butler-Volmer equation describes the electrochemical reaction kinetic,

$$j^{Li} = k(c_e)^{\alpha_a} (c_{s,max} - c_{s,e})^{\alpha_a} (c_{s,e})^{\alpha_a} \left\{ \exp \left[ \frac{\alpha_aF}{RT} \eta \right] - \exp \left[ - \frac{\alpha_aF}{RT} \eta \right] \right\}$$

(13)

where, $k$ is the kinetic rate constant and $c_{s,max}$, $c_{s,e}$ is the maximum and surface solid phase Li concentration, respectively. $\alpha_a$ and $\alpha_c$ are the anodic and cathodic transfer coefficients. $\eta$ is the overpotential, which is defined as the difference between solid and electrolyte phase potentials minus the thermodynamic equilibrium potential $U$ of the solid phase,

$$\eta = \phi_s - \phi_e - U$$

(14)

Voltage across the cell terminals is calculated from

$$V(t) = \phi_s(L, t) - \phi_s(0, t) - \frac{R_f}{A} j_{\text{app}}(t)$$

(15)

where $R_f$ is an empirical contact resistance.

The most electrochemical model parameters are derived from those publications by Doyle et al. [8,9] and James et al. [28] and listed in Table 1. In the lithium-ion cell, the positive electrode is manganese dioxide (Li$_x$Mn$_2$O$_4$) and the negative electrode is carbon (Li$_x$C$_6$).

### 3. Solid concentration simplification

#### 3.1. Simplified transfer function by Padé approximation

To obtain an analytical solution for the solid phase diffusion equation, the Laplace transform [29,35], can be applied to Eq.(3):

$$D_s \frac{d^2 C_t(x, r, s)}{dr^2} + \frac{2D_s}{r} \frac{dC_t(x, r, s)}{dr} - sC_t(x, r, s) = 0$$

(16)

With boundary conditions in Laplace transformation,

$$\left. \frac{dC_t(x, r, s)}{dr} \right|_{r=0} = 0, \quad \left. \frac{dC_t(x, r, s)}{dr} \right|_{r=R_s} = \frac{-j^{Li}(x, s)}{a_F}$$

(17)

The general solution of Eq.(16) can be expressed as

$$C_t(x, R_s, s) = \frac{R_s}{a_F D_s} \left[ \frac{\sinh \left( \sqrt{\frac{D_s}{R_s}} R_s \right)}{\sqrt{\frac{D_s}{R_s}}} - \sinh \left( \sqrt{\frac{D_s}{R_s}} R_s \right) \right]$$

(18)

The lithium concentration at the surface of the particle $C_t(x, R_s, s)$ is determined by calculating the solution at $r = R_s$.

$$C_t(x, R_s, s) = \frac{R_s}{a_F D_s} \left[ \frac{\sinh \left( \sqrt{\frac{D_s}{R_s}} R_s \right)}{\sqrt{\frac{D_s}{R_s}}} - \sinh \left( \sqrt{\frac{D_s}{R_s}} R_s \right) \right]$$

(19)

To facilitate the engineering application, the Padé approximation method [19,36], is applied to obtained a linearized representation of the model, as shown in Table 2. The strength of the approximated model is capable of preserving its physical meaning, through the presence of parameters such as the solid diffusion coefficient and particle radius.

#### 3.2. Frequency domain simulation

A comparison of various Padé approximations and the transcendental PDE solution is conducted in the frequency domain as shown in Fig. 2(a). It can be seen that the Padé approximations are accurate at low frequency domain ($10^{-3} - 10^{-1}$ Hz), and will diverge at higher frequency domain. The fitting error of the magnitude and phase is gradually minimized as the Padé approximation order increases.
increases. Therefore, there should be a tradeoff between the modeling precision and the computational complexity. In Ref. [29], the research reveals that a 3rd order Padé approximation is sufficient to accurately capture the battery dynamics under driving cycles, such as supplemental federal test procedures (SFTP) and federal urban dynamometer schedule (FUDS) profiles.

The primary advantage of the Padé approximation method lays on its computational simplicity and well preserving electrochemical properties. However, its major drawback is the loss of fitting precisions at the higher frequency. The Nyquist plotting of the PDE solution is shown as Fig. 2(b), and it indicates that the phase angle of the PDE result tends to be 45° in high frequency. This

<table>
<thead>
<tr>
<th>Order</th>
<th>Padé approximated transfer functions for the solid diffusion equation.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Padé – 1st: [0, 1]</td>
<td>$\frac{\alpha}{s + \alpha}$</td>
</tr>
<tr>
<td>Padé – 2nd: [1, 2]</td>
<td>$\frac{\alpha_1}{s + \alpha_0} + \frac{\alpha_2}{s + \alpha_1}$</td>
</tr>
<tr>
<td>Padé – 3rd: [2, 3]</td>
<td>$\frac{\alpha_2}{s + \alpha_1} + \frac{\alpha_3}{s + \alpha_2} + \frac{\alpha_4}{s + \alpha_3}$</td>
</tr>
<tr>
<td>Padé – 4th: [3, 4]</td>
<td>$\frac{\alpha_3}{s + \alpha_2} + \frac{\alpha_4}{s + \alpha_3} + \frac{\alpha_5}{s + \alpha_4} + \frac{\alpha_6}{s + \alpha_5}$</td>
</tr>
</tbody>
</table>

Fig. 2. (a) Bode plotting of the original PDE result and various Padé approximated results; (b) Nyquist plotting for original PDE result (negative electrode).
characteristic belongs to be non-integer order property, to be specific, the fractional order system behavior, which is hardly described with the integer approximation method, such as Padé method, or polynomial approximations. To improve the modeling accuracy in the frequency domain, it can refer to the electrochemistry-based fractional theory [37,38] and the discretization method [39-41] for fractional order modeling.

3.3. Time domain simulation

To numerically solve the solid diffusion equation for the negative electrode, the 20th order finite difference method (20th FDM) is adopted here as the baseline. In this simulation, a negative electrode particle is subject to a −1C pulse discharge and charge cycle, as shown in Fig. 3(a). The current is applied as: 1) 16.148 A, 0.5 h; 2) rest for 1 h; 3) −16.148 A, 0.5 h; 4) ending rest for 1 h. Fig. 3(b) shows the pulse responses of three Padé approximations compared to the numerical solution of the rigorous PDE in the time domain. The results indicate that the 2nd and 3rd order Padé approximations are much more accurate than the 1st order Padé approximation, particularly during the time immediately after the current is applied. While all the approximations converge to the correct steady state concentration at the end of the rest, the 1st order Padé approximation is not able to capture any dynamics and simply reverts back to the bulk concentration value as soon as the current is stopped. It’s analyzed that the maximum errors of 1st, 2nd and 3rd order Padé approximations are about 7.48%, 1.48%, and 0.6%, respectively.

To verify the simplified model performance under more complex driving cycles, the urban dynamometer driving schedule (UDDS) profile with the maximum current of −5C is chosen in the simulation, as shown in Fig. 3(c). Fig. 3(d) compares the dynamic responses of three Padé-approximated models and 20th FDM model. It’s analyzed that the maximum errors of 1st, 2nd and 3rd order Padé approximations are about 4.75%, 2.88%, and 1.69%, and the standard deviations are about 0.95%, 0.57% and 0.33%. The results show that the 3rd order Padé-based model has the strongest capability to trace the 20th FDM baseline model with high precision.

In this research, the FDM model and the Padé approximated models are both programmed and simulated in the MATLAB platform, and the simulations are implemented on a 1.8 GHz Intel quadruple-cores processor with 6 GB DDR3 RAM. The computation cost of the 20th FDM model is about 0.319s and 0.063s for pulse current cycle and UDDES profile separately, while the runtime of the 1st, 2nd and 3rd order Padé approximated models has been significantly reduced to 0.031s, 0.037s, 0.051s for pulse current cycle, and 0.006s, 0.008s, 0.011s for UDDES profile. The runtime comparison indicates clearly that the Padé-based simplified model presents great superiority in the computational complexity (more than six times faster), and this is mostly due to the fact that the 3rd order Padé approximation requires only 3 states in the calculation, which is far

![Fig. 3. Time domain simulation for Padé and PDE result: (a) pulse current; (b) surface concentration (pulse profile); (c) the UDDES current; (d) surface concentration (UDDES profile).](attachment:image.png)
less than the 20th FDM model.

4. Electrolyte concentration simplification

In this section, we will present the main contribution of this paper. Since the electrolyte solution fills across the overall cell region, including negative electrode, separator and positive electrode. The conservation of Li\(^+\) in the electrolyte phase follows the Fick’s diffusion law:

\[
\text{Negative electrode} : \quad \frac{\partial c_{xe}}{\partial t} = \frac{\partial}{\partial x} \left( D_{eff} \frac{\partial c_{xe}}{\partial x} \right) + \frac{1 - t^{0}_L}{F} j^{ei}_L (0 \leq x \leq L_n) \tag{20}
\]

\[
\text{Separator} : \quad \frac{\partial c_{es}}{\partial t} = \frac{\partial}{\partial x} \left( D_{eff} \frac{\partial c_{es}}{\partial x} \right) (L_n \leq x \leq L_n + L_s) \tag{21}
\]

\[
\text{Positive electrode} : \quad \frac{\partial c_{xp}}{\partial t} = \frac{\partial}{\partial x} \left( D_{eff} \frac{\partial c_{xp}}{\partial x} \right) - \frac{1 - t^{0}_L}{F} j^{ei}_L (L_n + L_s \leq x \leq L_c)
\]

The original boundary conditions are listed as:

\[
\left. \frac{\partial c_{xe}}{\partial x} \right|_{x=0} = \left. \frac{\partial c_{es}}{\partial x} \right|_{x=L_n} = 0 \tag{23}
\]

\[
c_{e|x=L_n} = c_{e|x=L_s} = D_{eff} \frac{\partial c_{es}}{\partial x} \bigg|_{x=L_n} = D_{eff} \frac{\partial c_{es}}{\partial x} \bigg|_{x=L_s} \tag{24}
\]

\[
c_{e|x=(L_n+L_s)} = c_{e|x=(L_n+L_s)} = D_{eff} \frac{\partial c_{es}}{\partial x} \bigg|_{x=(L_n+L_s)} \tag{25}
\]

To solve the coupled PDEs of Eqs.(20)–(22), the six boundary conditions should be employed together. This case will bring a series of obstacles: 1) due to the electrochemical parameter variations in each domain, it’s technically difficult to achieve a compact analytical solution of the electrolyte diffusion equations in general form. Therefore, the numerical solving approaches, such as FDM, FEM, become an effective method to obtain a reduced order model. 2) In both FDM and FEM, the spatial discretization is a necessary procedure to convert the PDEs to ODEs, which will result in an enhanced computation burden and limited real-time application. In another way, if the readers focus on one specific point within the cell, they should conduct the spatial discretization including the specific point, and also have to solve a whole sets of ODEs to get the result. To simplify the solving process of PDEs, a non-coupled modified boundary conditions for the electrolyte diffusion equations are newly proposed in this paper.

4.1. Modified boundary conditions

The modified boundary conditions are proposed with the following three assumptions:

a) The electrochemical parameters are lumped and fixed in each domain of the cell;

b) The variables of exchange current density \(j^{ei}_L\) and \(j^{ei}_P\) maintain uniform distribution and spatial-lumped in each domain;

c) The integral ascending concentration in negative electrode equals with the integral descending concentration in positive electrode, vice versa, which follows the mass conservation of lithium ions.

During discharge, the lithium concentration of electrolyte phase will increase in negative electrode and decrease in positive electrode domain under each exchange current density \(j^{ei}_L\) and \(j^{ei}_P\). Considering the lithium ions mass conservation in electrolyte phase, we aims to find the equilibrium point P for the electrolyte phase diffusion process, which will decouple the boundary conditions between the electrodes and separator and greatly simplify the analyzing process. The new modified boundary conditions are given for the negative electrode/separator and separator/positive electrode interfaces. The detailed analysis is conducted as follows:

As shown in Fig. 4, the exchange current density \(j^{ei}_L\) and \(j^{ei}_P\) are applied in the negative and positive electrode with the opposite directions. Here the exchange current density \(j^{ei}_L\) and \(j^{ei}_P\) are assumed to be uniformly distributed in each spatial domain, and the equilibrium point P can be calculated by the Eq.(26)

\[
\begin{align*}
\frac{j^{ei}_L(t)}{L_n} & = \frac{j^{ei}_P (t)}{L_p} = \frac{L_n}{L_p} \times \left( \frac{L_n}{2} + x \right) \\
\frac{j^{ei}_L(t)}{L_n \cdot A} & = \frac{j^{ei}_P (t)}{L_p \cdot A} \\
\end{align*}
\tag{26}
\]

By solving the equation, the variable x can be gained as

\[
x = \frac{L_n}{2} + \frac{L_p}{4}
\tag{27}
\]

By considering the lithium concentration in the separator is quasi-linear behavior, the new modified boundary condition for negative electrode/separator is presented as

\[
\left. \frac{\partial c_{xe}}{\partial x} \right|_{x=0} = 0; \quad \left. \frac{\partial c_{es}}{\partial x} \right|_{x=L_n} = \frac{c_{e}(L_n)}{L_n \cdot A} \frac{L_n}{L_p \cdot A} \tag{28}
\]

Similarly, the new modified boundary condition for separator/
positive electrode can also be expressed as

$$\frac{\partial \psi}{\partial x} \bigg|_{x=L_p} = 0; \quad \frac{\partial \psi}{\partial x} \bigg|_{x=L_n+L_p} = \frac{c_p (L_n + L_p)}{L_n + L_p + 3/4L_p}$$

(29)

4.2. Simplified transfer function by Padé approximation

For the negative electrode region, the transcendent transfer function can be obtained by solving the electrolyte diffusion equation with the modified boundary condition, as Eq.(28). The solution of the transfer function relating $C_p^0(x,s)$ with respect to $j_{01}^p(x,s)$ has the form as:

$$C_p^0(x,s) = \frac{1 - t_0^p}{F} \left( s^{1/2} \frac{1}{2} K \sinh \left( \frac{\sqrt{\gamma} s L_p}{D_p^0} \right) - 4 \cosh \left( \frac{\sqrt{\gamma} s L_p}{D_p^0} \right) \right) \sqrt{D_p^0 s e}$$

(30)

where, $K = -2L_p - L_0 - L_n; \quad \epsilon = \epsilon_{x_p}$

The resulting transcendental transfer functions are obtained by evaluating $x = 0, 1, 4L_n, 1/2L_n, 3/4L_n, L_n$ five even interval points. To simplify the expressions, the reduced order transfer function is obtained with the Padé approximation method, as shown in Table 3.

For the positive electrode region, the transcendental transfer function can be obtained by solving the electrolyte diffusion equation with the modified boundary condition of Eq.(29). The solution of the transfer function relating $C_p^0(x,s)$ with respect to $j_{01}^p(x,s)$ has the form as:

$$C_p^0(x,s) = \frac{1 - t_0^p}{F} \left( s^{1/2} \frac{1}{2} K' \sinh \left( \frac{\sqrt{\gamma} s L_p}{D_p^0} \right) + 4 \cosh \left( \frac{\sqrt{\gamma} s L_p}{D_p^0} \right) \right) \sqrt{D_p^0 s e}$$

(31)

where, $K' = 2L_p + L_n - L_p; \quad \epsilon = \epsilon_{x_p}$

Similarly, the resulting transcendental transfer functions can be obtained by evaluating $x = L_n + L_p, L_n + L_p + 1/4L_p, L_n + L_p + 1/2L_p, L_n + L_p + 3/4L_p, L_n + L_p + 5$ five even interval points. To simplify the expressions, the reduced order transfer function is obtained with the Padé approximation method, as shown in Table 4.

4.3. Frequency domain simulation

In contrast, the finite element method (FEM) with 48 uniform discretized points as shown in Smith et al. [24,25], is referred as the baseline for the model comparison and validation. Among the FEM and approximated PDE model, a comparison of the frequency response is shown in Fig. 5(a)-(b) for the negative electrode end ($x = 0$) and positive electrode end ($x = L_n + L_p + L_0$). The result reveals that the approximated PDE model can match the FEM result over a wide variety of frequency range, and the detailed statistical modeling errors are shown in Table 5.

To further simplify the transcendental transfer function of the PDE model, the approximated Padé result is achieved, and the Nyquist plotting of PDE and Padé results are shown in Fig. 5(c) and (d). Two major features can be drawn as: 1) For the negative electrode, the magnitude of the transfer function reaches its maximum value at the electrode end ($x = 0$), and decreases when moving to the separator. 2) The contour profile of the Nyquist plotting behaves as the semi-circle shape, which presents the electrolyte phase diffusion process. As the frequency rises, the impedance will approach to zero following the semi-circle path. The modeling error statistics of PDE and Padé results are listed in Table 5. The result shows the Padé-based reduced order model can present high accuracy when compared with the rigorous PDE model.

Table 3

<table>
<thead>
<tr>
<th>Position (negative)</th>
<th>$C_p^0(x,s)/j_{app} (s)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$x = 0$</td>
<td>$1 - t_0^p$</td>
</tr>
<tr>
<td>$x = 1/4L_n$</td>
<td>$s^{1/2} \frac{1}{2} K \sinh \left( \frac{\sqrt{\gamma} s L_p}{D_p^0} \right)$</td>
</tr>
<tr>
<td>$x = 1/2L_n$</td>
<td>$1 - t_0^p$</td>
</tr>
<tr>
<td>$x = 3/4L_n$</td>
<td>$s^{1/2} \frac{1}{2} K \sinh \left( \frac{\sqrt{\gamma} s L_p}{D_p^0} \right)$</td>
</tr>
<tr>
<td>$x = L_p$</td>
<td>$1 - t_0^p$</td>
</tr>
</tbody>
</table>

Table 4

<table>
<thead>
<tr>
<th>Position (positive)</th>
<th>$C_p^0(x,s)/j_{app} (s)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$x = L_n + L_p$</td>
<td>$1 - t_0^p$</td>
</tr>
<tr>
<td>$x = L_n + L_p + 1/4L_p$</td>
<td>$s^{1/2} \frac{1}{2} K' \sinh \left( \frac{\sqrt{\gamma} s L_p}{D_p^0} \right)$</td>
</tr>
<tr>
<td>$x = L_n + L_p + 1/2L_p$</td>
<td>$1 - t_0^p$</td>
</tr>
<tr>
<td>$x = L_n + L_p + 3/4L_p$</td>
<td>$s^{1/2} \frac{1}{2} K' \sinh \left( \frac{\sqrt{\gamma} s L_p}{D_p^0} \right)$</td>
</tr>
<tr>
<td>$x = L_n + L_p + 5$</td>
<td>$1 - t_0^p$</td>
</tr>
</tbody>
</table>
4.4. Time domain simulation

The PDE model is numerically discretized by finite element method (FEM) with 48 uniform discretized points, and the Padé approximations is computed according to the formulas in Tables 3 and 4. To validate the proposed model, the pulse charge/discharge cycle and the urban dynamometer driving schedule (UDDS) profiles, as shown in Fig. 6, are selected in this time domain simulation.

To compare the modeling difference, four specific points \( x = 0, x = L_n, x = L_n + L_s, x = L_c \) are chosen here. When the applied pulse current is 19.38 A and 96.90 A, the electrolyte concentration by Padé approximations can be calculated and plotted as Fig. 7(a) and Fig. 7(d). The pulse response of the Padé approximations is compared to PDE result in Fig. 7(b) and (e). It can be found that when charging the lithium ion is transported from positive to negative region, resulting a decreased electrolyte concentration in negative region, and an increased electrolyte concentration in positive region. The comparison of these modeling errors is listed in Table 6. When the applied current is about 19.38 A (~1C), the average root of mean square error (RMSE) of four points is 7.4170 mol.m\(^{-3}\), and the maximum error of four points is 17.3416 mol.m\(^{-3}\). If we assume the initial electrolyte concentration is about 2000 mol.m\(^{-3}\), the maximum error is about 0.867%, which shows sufficient precision for real-time application. As the applied current rises up to 96.90 A (~5C), the maximum modeling error is

![Nyquist plot of Conc / lapp in Negative](image)

![Nyquist plot of Conc / lapp in Positive](image)

![Nyquist plot of Conc / lapp in Negative](image)

![Nyquist plot of Conc / lapp in Positive](image)

Fig. 5. Frequency response and comparisons: FEM vs PDE results (a) at \( x = 0 \); (b) at \( x = L_n + L_s + L_p \); Padé vs PDE results (c) in negative electrode; (d) in positive electrode.

<table>
<thead>
<tr>
<th>Method</th>
<th>Negative electrode (0.001–100 rad/s)</th>
<th>Positive electrode (0.001–100 rad/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Space</td>
<td>RMSE</td>
</tr>
<tr>
<td>Padé vs FEM</td>
<td>( x = 0 )</td>
<td>0.4124</td>
</tr>
<tr>
<td>Padé vs approx. PDE</td>
<td>( x = 0 )</td>
<td>0.0336</td>
</tr>
<tr>
<td></td>
<td>( x = 1/4L_n )</td>
<td>0.0226</td>
</tr>
<tr>
<td></td>
<td>( x = 1/2L_n )</td>
<td>0.0069</td>
</tr>
<tr>
<td></td>
<td>( x = 3/4L_n )</td>
<td>0.0375</td>
</tr>
<tr>
<td></td>
<td>( x = L_n )</td>
<td>0.0441</td>
</tr>
</tbody>
</table>

4.4. Time domain simulation

The PDE model is numerically discretized by finite element method (FEM) with 48 uniform discretized points, and the Padé approximations is computed according to the formulas in Tables 3 and 4. To validate the proposed model, the pulse charge/discharge cycle and the urban dynamometer driving schedule (UDDS) profiles, as shown in Fig. 6, are selected in this time domain simulation.

To compare the modeling difference, four specific points \( x = 0, x = L_n, x = L_n + L_s, x = L_c \) are chosen here. When the applied pulse current is 19.38 A and 96.90 A, the electrolyte concentration by Padé approximations can be calculated and plotted as Fig. 7(a) and Fig. 7(d). The pulse response of the Padé approximations is compared to PDE result in Fig. 7(b) and (e). It can be found that when charging the lithium ion is transported from positive to negative region, resulting a decreased electrolyte concentration in negative region, and an increased electrolyte concentration in positive region. The comparison of these modeling errors is listed in Table 6. When the applied current is about 19.38 A (~1C), the average root of mean square error (RMSE) of four points is 7.4170 mol.m\(^{-3}\), and the maximum error of four points is 17.3416 mol.m\(^{-3}\). If we assume the initial electrolyte concentration is about 2000 mol.m\(^{-3}\), the maximum error is about 0.867%, which shows sufficient precision for real-time application. As the applied current rises up to 96.90 A (~5C), the maximum modeling error is
quasi-linearly increased to 4.336% accordingly. The simulations present clearly the 1st order Padé/C19e approximation can match the PDE with high fidelity. In the rigorous pseudo two dimensional (P2D) model, the current distribution in positive and negative domain is non-uniform, as shown in Fig. 7(c) and (f). The local current density will rise up greatly at the interface between the electrode and separator, and this non-uniform distribution will be enhanced as the current increases. In the simplified model, the current distribution in each domain is assumed to be uniform and can be seen as an averaged current density, which presents the equivalent capability to result in the similar electrolyte concentration distribution. When the high current is initially applied, the current distribution will be highly non-uniform at the interface and it reflects that the overpotential (η) is also non-uniformly distributed. These insightful information about the current spatial distribution cannot be described with the simplified model. However, the superior of the simplified model is to provide the electrolyte concentration prediction with high accuracy at the acceptable computational cost.

To verify the model performance under dynamic conditions, the urban dynamometer driving schedule (UDDS) profile with a maximum magnitude of 19.38 A (~1C) and 96.90 A (~5C) is employed in this simulation. The electrolyte concentration by Padé approximations can be calculated and plotted as Fig. 8(a) and (d) separately. Fig. 8(b)–(c) and (e)–(f) show the concentration response of the Padé approximations compared to PDE result under UDDS profiles. The comparison of these modeling errors is listed in Table 6. It indicates that when the maximum UDDS current is about 19.38 A (~1C), the average RMSE of four points is 0.8323 mol.m$^{-3}$, and the maximum error of four points is 3.8764 mol.m$^{-3}$. If we assume the initial electrolyte concentration is about 2000 mol.m$^{-3}$, the maximum error will be 0.194%, which is nearly four times less than the case of 19.38 A pulse charge/discharge profile. This is mostly due to the maximum current time duration for UDDS is less than the pulse current profile. As the maximum UDDS current rises up to 96.90 A (~5C), the maximum modeling error quasi-linearly increases to 0.969% accordingly. This simulations indicate that the Padé approximation can match the PDE result with higher fidelity in UDDS cycle than the pulse charge/discharge profile. It needs to point out that, in this study the PDE model is executed in the multi-physics software (COMSOL) and the runtime is about 4.26s and 12.98s for the pulse current and UDDS profiles. After model order reduction, the simplified model is performed in MATLAB/Simulink platform, and its runtime has significantly reduced to 0.037s and 0.091s accordingly. In addition, the transfer function type of simplified model can be conveniently applied to predict the cell internal electrolyte concentration across the cell dimension, which will be beneficial to guide the cell’s safety operation and avoid the dangerous hazards, such as lithium plating.

Fig. 6. Two sets of applied current profiles with a magnitude of 19.38 A (~1C) and 96.90 A (~5C): (a) pulse charge/discharge; (b) UDDS profile.

Please cite this article in press as: S. Yuan, et al., Journal of Power Sources (2017), http://dx.doi.org/10.1016/j.jpowsour.2017.03.060
5. Conclusion

To facilitate the lithium ion concentration estimation for solid and electrolyte phase, the traditional P2D model is simplified with Padé approximation and modified boundary conditions. The fruitful results can be summarized as:

First, the analytical solution of the solid diffusion equation is deducted and its reduced order transfer function is acquired with Padé approximation method. The simulation in time and frequency domain indicates that the 3rd order Padé approximation result presents high accuracy (<1.69%) under pulse charge/discharge and dynamic driving cycles.

Table 6
Error statistics of two different models (PDE vs Padé).

<table>
<thead>
<tr>
<th>Space</th>
<th>Pulse current profile:</th>
<th>UDDS profile:</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( I_{\text{app}} = 19.38 , \text{A (1C)} )</td>
<td>( I_{\text{app}} = 96.80 , \text{A (5C)} )</td>
</tr>
<tr>
<td></td>
<td>( I_{\text{app}} = 19.38 , \text{A (1C)} )</td>
<td>( I_{\text{app}} = 96.80 , \text{A (5C)} )</td>
</tr>
<tr>
<td>( x = 0 )</td>
<td>8.7559</td>
<td>15.6488</td>
</tr>
<tr>
<td>( x = L_a )</td>
<td>9.4579</td>
<td>17.3416</td>
</tr>
<tr>
<td>( x = L_a + L_s )</td>
<td>8.0537</td>
<td>14.4036</td>
</tr>
<tr>
<td>( x = L_c )</td>
<td>3.4004</td>
<td>7.2459</td>
</tr>
</tbody>
</table>

Fig. 7. Simulation results of electrolyte concentration under pulse current profiles when \( I_{\text{app}} = 19.38 \, \text{A} \): (a) Padé result in 3D; (b) Padé vs PDE; (c) reaction flux; and when \( I_{\text{app}} = 96.90 \, \text{A} \): (d) Padé result in 3D; (e) Padé vs PDE; (f) reaction flux.

Please cite this article in press as: S. Yuan, et al., Journal of Power Sources (2017), http://dx.doi.org/10.1016/j.jpowsour.2017.03.060
Second, to simplify the lithium ion concentration estimation in electrolyte phase, the electrolyte diffusion equations with modified boundary conditions are proposed. Then its reduced order transfer function is obtained with Padé approximation method to simplify the derived transcendental impedance solution. The simulation illustrates that the proposed simplified model presents high accuracy for electrolyte concentration (Ce) predictions, saying 0.8% and 0.24% modeling error respectively, when compared to P2D model under 1C-rate pulse charge/discharge and UDDS profiles.

In the next paper of this series, the transfer function type of simplified electrochemical battery model will be established to address the current-voltage relationship. To improve the model flexibility, the electrochemical model parameter will be estimated online based on the simplified battery model.

Acknowledgements

This research work is supported by a grant from the National High Technology Research and Development Program of China (863 Program) (2011AA11A229), and the U.S.—China Clean Energy Research Center Clean Vehicles Consortium (CERC-CVC) (No. 2010DFA72760-305).

References

A: surface area of the electrode, m²
学霸图书馆
www.xuebalib.com

本文献由“学霸图书馆-文献云下载”收集自网络，仅供学习交流使用。

学霸图书馆（www.xuebalib.com）是一个“整合众多图书馆数据库资源，提供一站式文献检索和下载服务”的24小时在线不限IP图书馆。

图书馆致力于便利、促进学习与科研，提供最强文献下载服务。

图书馆导航：
图书馆首页 文献云下载 图书馆入口 外文数据库大全 疑难文献辅助工具