**Numerical Analysis on Charge Characteristics in Lithium Ion Batteries by Multiphase Fluids Model**

Satoyuki KAWANO** and Futoshi NISHIMURA**

By improving our previous mathematical model for discharge$^{(1)}$, we developed a simple model of charge characteristics for lithium ion batteries. Through numerical analysis, stable solutions can be obtained for various parameters and operated conditions. From these results, we accumulate understanding of transport phenomena during the charge. Furthermore, a detailed comparison of numerical and experimental results in a commercial battery for PC can be made. Those results concur reasonably well from the viewpoint of engineering applications. Consequently, we confirmed the validity of the simple model proposed here and the numerical method for coupling the equation of transport phenomena with the Poisson equation.

**Key Words:** Lithium Ion Batteries, Electrochemistry, Charge Characteristics, Computational Fluid Dynamics, Multiphase Fluids Model

1. Introduction

From the 1990s, the development of high performance lithium ion batteries for practical use has been strongly desired in wide areas of the engineering field because they offer high energy, safety, and cycle characteristics. For example, in the field of automobiles, lithium ion batteries have been scaled up for electric vehicle (EV) and hybrid electric vehicle (HEV) applications. Large batteries have much higher requirements for energy and safety than small ones. To the present day, lead-acid batteries and nickel-hydrogen batteries are mainly incorporated into commercially produced HEV or EV, but lithium ion batteries can provide higher theoretical capacity that is strongly desired to meet requirements. Environment effects of such batteries have also been reconsidered: LiMn$_2$O$_4$ or LiNiO$_2$ is expected to be applied as electrodes in the very near future although LiCoO$_2$ is used now.

Lithium ion batteries, which are incorporated into various devices, are charged. Overcharging is a serious problem in all rechargeable batteries. Overcharging causes uncontrolled voltage. As voltage continues to increase, it engenders the possibility of thermal runaway or ignition. A Positive Temperature Coefficient (PTC) integrated circuit or shut-down function of a separator should be incorporated as a safety measure against those serious problems. In general, previous approaches to those problems have been mainly experimental, but they present increased risk and cost. Therefore, a more effective method for battery design is desired; computer aided design of lithium ion batteries is anticipated as one such method.

Some simple models for charge characteristics were proposed in previous work. The Newman research group developed a simple mathematical model on galvanostatic discharge and charge characteristics in lithium polymer batteries$^{(2)}$ and lithium ion batteries$^{(3)}$. Battery characteristics were analyzed in these models under the assumption that concentration of lithium ion is equal to that of anion. Furthermore, those results showed reasonable agreement between numerical predictions and experiments from the viewpoint of engineering applications$^{(4)}$. Wang et al. developed a thermal and electrochemical model of battery systems$^{(5)}$ based on their previous model$^{(6),(7)}$. The model contains a unique technique to estimate the potential of liquid phase. In contrast, Kawano and Nishimura developed a novel mathematical model and implicit numerical scheme on discharge characteristics$^{(1)}$. In the model, behavior of lithium ion and anion were analyzed separately, including use of the Poisson equation for an electric field. Our previous results showed that electric charge had a relatively small value, but had a strong effect on transport phenomena and prediction of discharge characteristics for certain physical properties of electrodes. Furthermore, comparisons of numerical and experimental results

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** Center for Interdisciplinary Research, Tohoku University, Aramaki-Aoba, Aoba-ku, Sendai 980–8578, Japan
for discharge characteristics were made for various operating conditions; they showed reasonable agreement from the engineering perspective.

The present study improves our previous mathematical model and numerical code to elucidate transport phenomena and predict charge characteristics in lithium ion batteries. Numerical analyses are made for various physical properties and practical operating conditions. In numerical results, concentration distributions of lithium and ions, electric charge distribution, electric field distribution, and reaction flux distribution are made for better understanding of transport phenomena during the charging. Furthermore, comparisons between the numerical and experimental results for voltage and current in a commercially produced battery for a PC (IBM, ThinkPad) are made to confirm the model validity. Results agree well from the viewpoint of engineering applications.

List of Symbols

\( c_{i,j} \): concentration, mol/m³
\( c_{\text{max},i,j} \): maximum concentration of lithium, mol/m³
\( C \): battery capacity, mAh
\( D_{i,j} \): diffusion coefficient, m²/s
\( F \): Faraday's constant = 9.648 5 × 10⁴, C/mol
\( i_{\text{ex},i,j} \): exchange current density, A/m²
\( i_{i,j} \): current density, A/m²
\( I \): total current density, A/m²
\( I_c \): total current, A
\( J_{j} \): reaction flux, mol/m²s
\( k_{i,j} \): reaction rate constant
\( q_{i,j} \): mass flux based on diffusion and electrophoresis, mol/m²s
\( r \): resistance of components, Ω
\( R \): gas constant = 8.314 4, J/mol·K
\( S \): area of electrode, m²
\( t \): time, s
\( T \): temperature, K
\( U_{j} \): open circuit potential, V
\( x \): coordinate along cell, m
\( \alpha_{i,j} \): ratio of area of solid phase to cross-section
\( \beta_{i,j} \): ratio of area of interface to volume of control volume, 1/m
\( \delta_{i,j} \): thickness, m
\( \Delta t \): temporal grid interval, s
\( \Delta x_{i,j} \): spatio grid interval, m
\( \epsilon_{i,j} \): dielectric constant, F/m
\( \eta_{i,j} \): overpotential, V
\( \rho_{i,j} \): charge density, C/m³
\( \phi_{i,j} \): potential, V
\( \phi_{SB1} \): potential of solid phase at boundary 1, V
\( \phi_{SB4} \): potential of solid phase at boundary 4, V
\( \Phi \): voltage, V
\( \Phi_{OCV} \): open circuit voltage (OCV), V

Subscripts

\( a \): anion
\( e \): electron
\( i \): species \( i = a, e, l, \) or \( s \)
\( j \): region \( j = 1, 2, \) or \( 3 \)
\( l \): lithium ion
\( L \): liquid phase
\( s \): lithium
\( S \): solid phase
\( 1 \): region of negative electrode
\( 2 \): region of separator
\( 3 \): region of positive electrode

Superscripts

0: initial condition

2. Mathematical Model

The lithium ion battery modeled in this work consists of a negative electrode (LiC₆), a separator, and a positive electrode (LiCoO₂). We address one-dimensional transport phenomena in the \( x \) direction from the negative electrode through the separator into the positive electrode, according to the schematics shown in Fig. 1. Basic equations for transport phenomena were recorded in our earlier work. Only remarkable features are described below.

The charging method of constant current and constant voltage is used in this work. This method, developed in the late 1980s, is the most common technique of charging batteries and has been used in various products. In this method, lithium ion batteries are first charged at a constant current until they reach a specified voltage limit; subsequently, they are charged with a constant voltage to a current limit.

The main feature on charge characteristics is that the direction of current \( I_c \) during the charging is opposite to that during the discharge. Furthermore, during the constant voltage charge, we introduce the reasonable model.
that spatial variation of $I$ is zero; that is, $I$ is only a function of time $t$. In this work, $I(t)$ can be estimated from the equation

$$I(t) = (φ_{BA} - φ_{S1} - Φ)/r,$$

(1)

where $Φ$ is the voltage, $φ_{BA}$ is the potential of solid phase at boundary 1, and $φ_{S1}$ is the potential of solid phase at boundary 4, where the number of the boundary is defined in Fig. 1. The resistance of components is $r$. Equation (1) is derived from our previous work(1).

### 3. Results and Discussion

Our own developed numerical code based on implicit SOR scheme(1) is used; details are omitted here. Table 1 shows parameters used in numerical analysis. Temperature $T$ of the laboratory room is set as 293 K. Thickness $δ_j$ of electrodes and the separator are measured values. Diffusion coefficient $D_{j,k}$ is estimated from Refs. (4) and (8), and diffusion coefficients $D_{j,4}$ of lithium ion and anion are estimated from Ref. (9). Permittivity $ε_{L,j}$ of liquid phase is an estimated value based on the present experiment. Ratio $α_j$ of area of solid phase to cross-section is a measured value. Ratio $β_j$ of the interface area to volume of control volume is an estimated value by the use of $1/Δx_j$ and is set as $4.0 \times 10^6$ l/m. The reaction rate constant $k_{1,j}$ of electrochemical reaction is estimated from Refs. (4) and (8). Maximum concentration $c_{max,j}$ of lithium is strongly dependent on the material of electrodes and is set to be a measured value based on present experiment. Electrode area is the measured value and is set as $5.97 \times 10^2$ m$^2$. Initial concentrations $c_{j,0}$ of lithium ion and anion are reference values from Refs. (4) and (8). Initial concentration $c_{j,0}$ of lithium is determined experimentally based on battery capacity $C$, where $C$ is the measured value and set as $1.92 \times 10^3$ mAh. Open circuit voltage (OCV) $φ_a$ and open circuit potentials (OCP) $U_j$ of negative and positive electrodes during the depth of discharge (DOD) are obtained from the present experiment. The DOD is estimated by the use of ratio of discharge capacity to $C$; it can be described as

$$DOD = \frac{1}{C} \int_0^t I(t) dt$$

(2)

where the unit is %. Resistance $r$ of components is based on the present experiment. It is set as $0.119 \Omega$. This work considers the charging method by the use of the constant current and constant voltage; the battery is charged at constant current 1.4 A with the initial voltage 3.0 V until the voltage reaches the limit 4.2 V. After that, it is charged with constant voltage 4.2 V; the charging process ends when current decreases to 0.1 A.

Figure 2 shows the concentration distribution $c_{j,1}$ of lithium in negative electrode during (a) the charge with constant current at $t = 0$, 1, 1000, 2000, 3000, and 3974 s and during (b) the constant voltage charge at $t = 3974$, 4500, 5500, 6000, and 6458 s. The horizontal axis denotes the coordinate $x$ along the cell and the vertical axis denotes $c_{j,1}$ mol/m$^3$. Here, the range is $0 ≤ x ≤ δ_1$. As shown in Fig. 2, $c_{j,1}$ increases as charging proceeds. This result signifies that the direction of electrochemical reaction is obtained accurately. From Fig. 2(a), the increment ratio $Δc_{j,1}/Δt$ of $c_{j,1}$ to unit time is almost constant and is about $5.61$ mol/m$^3$s at boundary 1. A detailed discussion about the value is made later. Spatial variation of $c_{j,1}$ seems to increase over time. This result suggests that the

![Graph](image_url)

**Table 1** Parameters used in numerical analysis

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$δ_j$ [m]</td>
<td>$7.2 \times 10^{-5}$ (*)</td>
</tr>
<tr>
<td>$D_{j,k}$ [m$^2$/s]</td>
<td>$1.0 \times 10^{-9}$ (*)</td>
</tr>
<tr>
<td>$D_{j,4}$ [m$^2$/s]</td>
<td>$1.0 \times 10^{-9}$ (*)</td>
</tr>
<tr>
<td>$ε_{max,j}$ [m$^2$/s]</td>
<td>$1.0 \times 10^{-9}$ (*)</td>
</tr>
<tr>
<td>$α_j$</td>
<td>$0.59$ (*)</td>
</tr>
<tr>
<td>$k_{1,j}$</td>
<td>$1.0 \times 10^{-6}$ (*)</td>
</tr>
<tr>
<td>$β_j$ [1/m]</td>
<td>$4.0 \times 10^{-4}$ (*)</td>
</tr>
<tr>
<td>$c_{max,j}$ [mol/m$^3$]</td>
<td>$3.11 \times 10^{-1}$ (*)</td>
</tr>
<tr>
<td>$c_{j,1}$ [mol/m$^3$]</td>
<td>$3.29 \times 10^{-1}$ (*)</td>
</tr>
<tr>
<td>$c_{j,2}$ [mol/m$^3$]</td>
<td>$1.0 \times 10^{-1}$ (*)</td>
</tr>
<tr>
<td>$c_{j,3}$ [mol/m$^3$]</td>
<td>$1.0 \times 10^{-1}$ (*)</td>
</tr>
</tbody>
</table>

(*) measured value
(1) from ref. 4 and 8
(2) from ref. 9
(3) estimated value based on present experiment

![Fig. 2 Concentration distribution $c_{j,1}$ of lithium in the negative electrode, where the method of charge is changed at $t = 3974$ s.](image_url)
effect of electrochemical reaction is relatively larger than that of diffusion. From Fig. 2 (b), \( \Delta c_{ij}/\Delta t \) decreases as charging proceeds as a result of the decrease of total current. Spatial variation of \( c_{ij} \) seems to decrease. These results must be closely associated with the fact that electrochemical reaction flux \( J_j \) decreases concomitant with decrease of total current and that the effect of diffusion becomes relatively larger than that of electrochemical reaction. It is a specially introduced value to our fluid model. In the present paper, we used a different \( D_{si,j} \) value from previous work(1) because the spatial variation of \( c_{si,j} \) can be well observed. We confirmed that the difference of \( D_{si,j} \) has a negligibly small effect on numerical results of discharge; this concurs with results of our parametric study of \( D_{si,j} \).

Figure 3 shows the concentration distribution \( c_{i,j} \) of lithium ion during (a) the charging with constant current at \( t = 0, 5, 20, 50, 150, \) and 3 974 s and during (b) the constant voltage charging at \( t = 3 974, 4 500, 5 500, \) and 6 458 s. As shown in Fig. 3 (a), \( c_{i,j} \) takes a minimal value at boundary 1 and a maximal value at boundary 4. As charging proceeds, \( c_{i,j} \) becomes small in the negative electrode and becomes large in the positive electrode in comparison with those values at initial concentrations. These results confirm that the qualitative tendency of spatial distribution of \( c_{i,j} \) during the charge is opposite to that during discharge. These results correspond to the fact that the sign of the total current \( I_c \) is opposite. After \( t = 150 \) s, the spatial distribution of \( c_{i,j} \) seems to reach a steady state. From Fig. 3 (b), the spatial distribution of \( c_{i,j} \) becomes small because of the decrease of total current as charging proceeds. The concentration distribution \( c_{a,j} \) of anion can be obtained, where the figure is omitted because the qualitative tendency of spatio-temporal distribution of \( c_{a,j} \) is also quite similar to that of Fig. 3. This result denotes that the electric charge \( \rho_{L,j} \) of liquid phase is small. Our previous work indicated that we must solve Poisson equation in numerical analysis on the discharge characteristics because the previous assumption, \( \rho_{L,j} \approx 0 \), seemed to be valid, but the effect of \( \rho_{L,j} \) has a significant effect at specified conditions. In Fig. 4, the value of \( \rho_{L,j} \) during charging is examined in detail. Figure 4 shows the distribution of \( \rho_{L,j} \) in liquid phase at \( t = 0, 1, 150, 3 974, 4 500, 5 000, 5 500, 6 000, \) and 6 458 s. As shown in Fig. 4, \( \rho_{L,j} \) is not zero for any \( x \) during charging. Rapid temporal variation of \( \rho_{L,j} \) occurs at the beginning of the charging; \( \rho_{L,j} \) is a positive value in the positive electrode and a negative value in the negative electrode. Spatial variation of \( \rho_{L,j} \) in electrodes becomes large with time; after \( t = 150 \) s, the spatial distribution seems to reach a steady state. During charging with constant voltage, \( |\rho_{L,j}| \) decreases; both temporal and spatial variations of \( \rho_{L,j} \) become small as time progresses.

Using these nonzero \( \rho_{L,j} \) models, we conduct a detailed investigation of the effects on the transport phenomena in the lithium ion battery shown in Fig. 4. Figure 5 shows electric field distribution \( \partial \rho_{L,j}/\partial x \) of liquid phase at \( t = 0, 1, 150, 3 974, 4 500, 5 000, 5 500, 6 000, \) and 6 458 s. As shown in Fig. 5, \( \partial \rho_{L,j}/\partial x \) is a positive value at the electrodes and the separator; in addition, the gradi-
ent during charging is opposite to that during discharge as a result of the negative current in charging. These results occur by the fact that $\rho_{L,j}$ is a positive value in the positive electrode and a negative value in the negative electrode, as shown in Fig. 4. As charging proceeds, $\partial \phi_{L,j}/\partial x$ becomes larger than the initial value at boundary 2 and smaller at boundary 3. Spatial variation seems to reach a steady state after $t = 150$ s. In electrodes, $\partial \phi_{L,j}/\partial x$ becomes almost linear at $t = 1$ s; this result corresponds to the fact that spatial variation of $\rho_{L,j}$ at $t = 1$ s in Fig. 4 is small. As charging proceeds, the nonlinearity of $\partial \phi_{L,j}/\partial x$ is recognized along with the nonlinearity of $\rho_{L,j}$, but this effect is not clearly apparent, as shown in Fig. 4, where nonlinearity becomes large as the current in the case of discharge\(^1\).

During charging with constant voltage, $\partial \phi_{L,j}/\partial x$ in electrodes and the separator decreases with time. Furthermore, temporal variation of $\partial \phi_{L,j}/\partial x$ becomes small and spatial distribution must become almost linear. These results correspond to the fact that the both temporal and spatial variations of $\rho_{L,j}$ become small with time, as shown in Fig. 4.

Figure 6 shows the current distribution $i_{L,j}$ of liquid phase at $t = 0, 1, 3974, 4500, 5000, 5500, 6000,$ and $6458$ s. $S$ denotes the electrode area. During charging with constant current, spatial variation of $i_{L,j}$ in electrodes is almost linear and hardly changes. Here, the governing equation of $i_{L,j}$ is simplified as

$$i_{L,j} = -2(1 - \alpha_j)D_j \frac{c_{L,j}F^2}{RT} \frac{\partial \phi_{L,j}}{\partial x}. \quad (3)$$

Equation (3) confirms that $\partial \phi_{L,j}/\partial x$ is a positive value for any $x$ because $i_{L,j}$ is a negative value, as shown in Fig. 6. Furthermore, Fig. 5 shows that the decrement of $c_{L,j}$ increases $\partial \phi_{L,j}/\partial x$ at boundary 2 and the increment of $c_{L,j}$ decreases $\partial \phi_{L,j}/\partial x$ at boundary 3 because $i_{L,j}$ equals to the total current at boundaries 2 and 3. During constant voltage, $i_{L,j}$ decreases in electrodes and the separator. This result corresponds to actual experience: the total current $I_t$ decreases during charging with constant voltage.

Figure 7 shows reaction flux distribution $J_j$ at $t = 0, 1, 3974, 4500, 5000, 5500, 6000,$ and $6458$ s. As shown in Fig. 7, $J_j$ is a positive value in the negative electrode and a negative value in the positive electrode. This result agrees qualitatively with actual phenomena of the direction of electrochemical reaction. During charging with constant current, spatial variation of $J_j$ becomes large over time. It reaches a steady state at about $t = 150$ s. Here, reaction flux $J_j$ can be written as\(^1\)

$$J_j = -\frac{1}{\beta F} \left( \frac{\partial i_{L,j}}{\partial x} + \frac{\partial \rho_{L,j}}{\partial t} \right). \quad (4)$$

At the steady state of $J_j$ at $t = 150$ s, temporal variation of $\rho_{L,j}$ is almost zero, as indicated in Fig. 4. Therefore, only the small nonlinearity of $i_{L,j}$ shown in Fig. 6 affects...
the spatial distribution of $J_j$. Furthermore, the absolute mean value of $J_j$ is about $8.43 \times 10^{-7}$ mol/m² s and $\Delta c_{c,j}/\Delta t$ estimated from the value and the equation $\alpha J_j\partial c_{c,j}/\partial t \approx J_j \beta_j$ obtained from Eq. (5) in previous report$^{(1)}$ and from Fig. 2 (a) is about 5.64 mol/m² s; this agrees very well with the value of 5.61 mol/m² s estimated from Fig. 2 (a) described above. During charging with constant voltage, $J_j$ decreases and the spatial variation becomes small as charging proceeds. This result corresponds to the fact that the both spatial and temporal variations of $c_{c,j}$ in Fig. 2 (b) become small with time.

Here, the basic equation of lithium ion can be described as

$$\frac{\partial c_{c,j}}{\partial t} = D_{i,j} \frac{\partial^2 c_{c,j}}{\partial x^2} + D_{l,j} \frac{F}{RT} \frac{\partial c_{c,j}}{\partial x} \frac{\partial \Phi_{L,j}}{\partial x} - D_{i,j} \frac{1}{\rho} L \frac{\partial \Phi_{L,j}}{\partial x} - J_j \beta_j, \quad (5)$$

where the first term in the right hand side denotes the diffusion. The second term denotes, including $\partial \Phi_{L,j}/\partial x$, and the third term, including $\rho \Phi_{L,j}$ denotes the electrophoresis. The fourth term denotes the electrochemical reaction. Figure 8 shows temporal variation of $\partial q_{i,j}/\partial x$ mol/m² s near the negative electrode during (a) the constant current to the steady state and during (b) the constant voltage. As shown in Fig. 8 (a), the electrochemical reaction term and the term including $\rho \Phi_{L,j}$ are dominant at the beginning of charging. The diffusion term becomes large as charging proceeds; after $t = 150$ s, it seems to reach an almost constant value. This result corresponds to the fact that the spatial variation of $c_{c,j}$ reaches a steady state in Fig. 3 (a).

The term including $\partial \Phi_{L,j}/\partial x$ is not stronger than that of $\rho \Phi_{L,j}$. It is also confirmed that the third term including $\rho \Phi_{L,j}$ can not be neglected. As shown in Fig. 8 (b), all terms decrease as charging proceeds and are theoretically zero as $t$ approaches infinity. These results correspond to the fact that $\partial c_{c,i}/\partial x, \partial c_{c,j}/\partial x, \rho \Phi_{L,j}, \partial \Phi_{L,j}/\partial x,$ and $J_j$ diminish over time, as shown in Figs. 2 – 5, and 7.

Figure 9 shows comparisons of charge characteristics between numerical and experimental results for current $I_c = -1.4$ A. Experiments are made based on so-called the standard test in the industry of batteries. The horizontal axis indicates $t$ and the vertical scales indicate voltage and current. Figure 9 shows numerical results: the charge method of lithium ion battery is changed to the method with constant voltage at $t = 3974$ s and the charge process finishes at $t = 6458$ s. During charging with constant current, numerical and experimental results show good agreement in charge time and predicted voltage. The deviation is 3.40% (135 s) in charge time with constant current; the deviation in predicted voltage is less than 9.33% (0.112 V). During charging with constant voltage, numerical and experimental results show good agreement in charge time and predicted current. The deviation is 15.2% (512 s) in constant voltage charge time; the deviation in predicted current is less than 3.86% (0.054 A). The inaccuracy in charge time becomes higher during charging with constant voltage than that during constant current charging. However, it can be concluded that they agree well from the viewpoint of engineering applications. The
mathematical model and the numerical scheme presented here are thereby validated.

4. Concluding Remarks

A simple mathematical model on charge characteristics was developed for lithium ion batteries by multiphase fluids model. Behaviors of lithium ion and anion were analyzed independently in the present model, including the Poisson equation for an electric field.

Detailed discussions of transport phenomena were made based on numerical and experimental results. Electric charge $\rho_{L,j}$ had a small value, but had a strong effect for prediction of lithium ion battery performance. We made detailed quantitative comparison of numerical and experimental results for charge curves. They showed good agreement from the viewpoint of engineering applications. Consequently, the present numerical analysis of charge characteristics based on multiphase fluids model is confirmed to be sufficiently practical for computational design of lithium ion batteries.

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References