

## Chapter 3

### MODEL DEVELOPMENT

#### 3.1 MATHEMATICAL MODELING

Many researchers and batteries developers need to study, understand and improve the action-reaction behavior in the components of batteries in order to manufacture better batteries. Mathematical modeling gives this group of people much information to understand the reaction and performance behavior inside the electrodes of batteries. Once the materials selection and preparation procedures have been selected, it is essential to proceed with detailed designing of a mathematical model for the battery system in order to produce the optimum battery design and configuration for a specific application. The specification of the dependent variables of interest, the governing equations of these variables included with the initial and boundary condition for these variables is needed to start mathematical modeling of batteries. Besides that, variables can be changed for different battery systems and the parameters can be changed to get the optimization for the best output. Hence, mathematical model and simulations allow various battery systems to be repeatedly and simultaneously tested. This in turn allows great saving of materials, cost and time.

To build a battery model, we must consider several aspects. First, the type of electrode use to fabricate the battery. Newman et al. (2003) stated that since electrodes are generally porous, therefore the distribution of the reaction through the depth of the

---

electrode must be considered. Secondly, the active material is an insertion compound, in which the chemical potential and other thermodynamic properties may vary continuously with inserted lithium concentration. In short, the solid-state diffusion of lithium through the active material must be considered. Finally, as in most batteries, the electrolyte is a concentrated, non-ideal solution, and mass transport across the electrolyte has a significant effect on battery performance. Hence, the basic modeling framework must consist of porous electrode theory, concentrated solution theory, Ohm's law, kinetic relationships, and charge and material balances (Newman et al. 2003).

Several researchers (Newman and Tobias 1962; Newman and Tiedemann 1975; Newman et al. 2003) defined the porous electrode theory as a superposition of active material, electrolyte, and filler, with each phase having its own volume fraction. The material balances are averaged about a volume small with respect to the overall dimensions of the electrode but large with respect to the pore dimensions. This allows one to treat electrochemical reaction as a homogeneous term, without having to worry about the exact shape of the electrode–electrolyte interface.

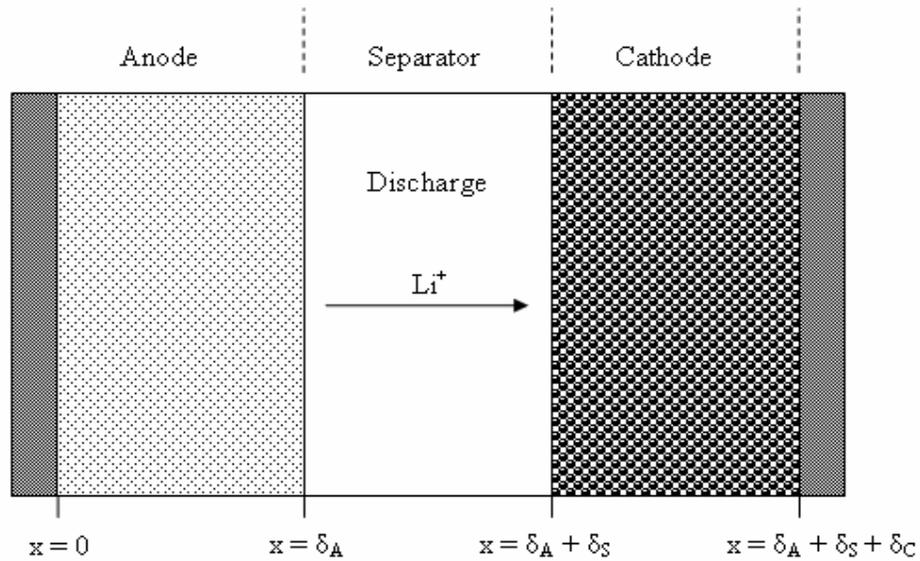
Another important theory is the concentrated solution theory. This theory provides the relationship between driving forces (such as gradients in chemical potential) and mass flux (Newman 1991; Newman et al. 2003; Newman and Thomas 2004). The flux equation is then used in a standard material balance equation to account for the transient change of concentration due to mass flux and reaction. A charge balance is also needed to keep track of how much current has passed from the electrode into the electrolyte.

Next, Newman et al. (2003) and Newman and Thomas (2004) stated that Ohm's law describes the potential drop across the electrode and also in the electrolyte. In the electrolyte, Ohm's law is modified to include the diffusion potential. Finally, the Butler–Volmer equation generally is used to relate the rate of electrochemical reaction to the difference in potential between the electrode and solution, using a constant rate (exchange current density) that depends on the composition of the electrode and the electrolyte. Due to all of theory and law above, most of the governing equations in battery modeling consist of dependent variables in concentration, potential, reaction rate and current density.

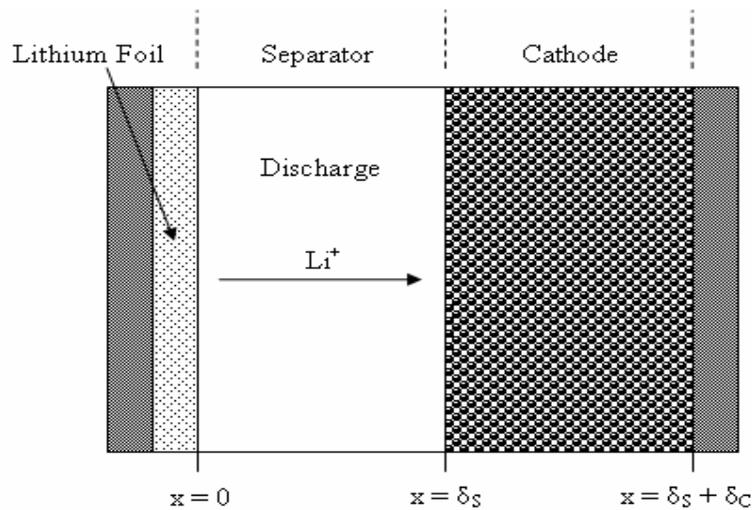
As mentioned in chapter 2, there are 3 major cases in developing mathematical battery model. These three cases are solution-phase diffusion limitations, solid-phase diffusion limitations and ohmically-dominated reaction zone (Doyle and Newman 1997). According to Arora et al. (2000), the solution-phase diffusion limitations are the major limiting factor for the lithium-ion battery model during high-rate discharge. Hence, this work focuses on solution-phase diffusion limitations. According to Subramanian et al. (2005), this solution-phase diffusion limitation is known as macro-scale diffusion model.

The study of lithium-ion battery is normally based on two types of physical configurations. Some researchers (Fuller et al. 1994; Doyle and Newman 1996; Valøena and Reimers 2005; Santhanagopalan et al. 2006; Ning et al. 2006; Norzihani et al. 2010) divide the configurations of lithium-ion battery into three regions, that is anode ( $0 \leq x \leq \delta_A$ ), separator ( $\delta_A \leq x \leq \delta_A + \delta_S$ ) and cathode ( $\delta_A + \delta_S \leq x \leq \delta_A + \delta_S + \delta_C$ ). While other researchers (Doyle et al. 1993; Doyle and Newman 1997; Botte and White

2001; Subramanian et al. 2004; Subramanian et al. 2005) prefer the anode as lithium foil, that is, they did not consider anode as one of the region. So the second configuration has only two regions, that is separator ( $0 \leq x \leq \delta_s$ ) and cathode ( $\delta_s \leq x \leq \delta_s + \delta_c$ ). Figure 3.1 depicts the two configurations lithium-ion battery.



(a)



(b)

**Figure 3.1: Schematic diagram for (a) the “rocking-chair” type battery with an insertion-type cathode and (b) the lithium ion battery with a lithium foil as anode**

According to Doyle and Newman (1997), the macroscopic transport through the cell sandwich as shown in figure 3.1(a) is normally treated as one-dimensional model. The geometry of the lithium-ion cell that is being modeled in this work is divided into two regions, a separator ( $0 < x < \delta_s$ ) and a porous electrode ( $\delta_s < x < \delta_s + \delta_c$ ). In Subramanian et al. (2004), they have made the assumptions for the model of lithium-ion batteries. The assumptions are:

- (a) discharge behavior is dominated by solution-phase diffusion limitations
- (b) kinetic and diffusion-phase limitations are negligible
- (c) diffusion coefficient and transfer number are independent of the electrolyte concentration.

All these assumptions are being considered in this study.

## 3.2 GOVERNING EQUATIONS

In developing the model of the intercalation of lithium ion battery, it is important to know how the concentration of materials varies as a function of time. This can be obtained by looking at the rate of change of the concentration as a function of time in relation to the rate of change in concentration gradient. The rate of change of the concentration as a function of time or in engineering parlance is called as accumulation and can be written as

$$\frac{\partial c_i}{\partial t} = -\nabla \cdot N_i + P_i \quad (3.1)$$

Equation (3.1) is also called as material balance for a minor component. Here  $\frac{\partial c_i}{\partial t}$  is the accumulation,  $-\nabla \cdot N_i$  is the net input and  $P_i$  is the production. Accumulation is simply the rate of change concentration in relation to time. For the net input,  $N_i$  is the diffusive flux of the species  $i$ . Hence, the net amount of material brought in by the different fluxes is the rate of change in fluxes as the ions move from the initial point to the terminal point as shown below

$$\lim_{\Delta x \rightarrow 0} \frac{N_i|_x - N_i|_{x+\Delta x}}{\Delta x} = -\frac{\partial N_i}{\partial x} \quad (3.2)$$

The production per unit volume  $P_i$  involves homogeneous chemical reactions in the bulk of the solution, but not in any electrode reactions at the boundaries of the solution. The reaction is frequently restricted to the electrode surface when in electrochemical systems, where in which case  $P_i$  is zero. Therefore, the equation (3.1) has now become

$$\frac{\partial c_i}{\partial t} = -\nabla \cdot N_i \quad (3.3)$$

According to Doyle (1995), the salt concentration used in lithium batteries are generally large, which is the concentration mostly above one mol. Thus the transport of the electrolyte should be treated rigorously using concentrated solution theory. In concentrated solution theory, the gradient of the electrochemical potential for an ionic species is used to describe the driving force for mass transfer at constant temperature and pressure. Hence, the driving force for the  $i^{\text{th}}$  species is related to the fluxes of each

of the other species through the multicomponent diffusion equation. Newman (1991, 2004) stated that the multicomponent diffusion equation as

$$c_i \nabla \mu_i = \sum_j K_{ij} (v_j - v_i) \quad (3.4)$$

or

$$c_i \nabla \mu_i = RT \sum_j \frac{c_i c_j}{c_T \phi_{ij}} (v_j - v_i) \quad (3.5)$$

where  $c$  is the concentration,  $\mu$  is the electrochemical potential,  $K_{ij}$  are friction coefficients (or interaction coefficients),  $v$  is the velocity (an average velocity),  $R$  is the universal gas constant,  $T$  is the temperature,  $c_T$  is the total concentration and  $\phi_{ij}$  is the diffusion coefficient describing the interaction of species  $i$  and  $j$ . In addition, subscript  $i$  and  $j$  in this equation denote the species  $i$  and species  $j$ , respectively.

In order to find the diffusive flux in term of the driving forces used in equation (3.3), we must invert equation (3.5). For the binary electrolytic solution composed of anions, cations and solvent, equation (3.5) yields two independent equations

$$c_+ \nabla \mu_+ = K_{0+} (v_0 - v_+) + K_{+-} (v_- - v_+) \quad (3.6)$$

$$c_- \nabla \mu_- = K_{0-} (v_0 - v_-) + K_{-+} (v_+ - v_-) \quad (3.7)$$

Then we introduced current density in an electrolytic solution as

$$i = F \sum_i z_i N_i \quad (3.8)$$

where  $F$  is the Faraday's constant and  $z_i$  is the ionic valence of the  $i^{\text{th}}$  species charged. According to Newman (1991) and Newman (2004), with equation (3.8) we can rearrange equation (3.6) and (3.7) to get the following flux expressions as

$$N_+ = c_+ v_+ = -\frac{v_+ \wp}{vRT} \frac{c_T}{c_0} c \nabla \mu_e + \frac{it_+^0}{z_+ F} + c_+ v_0 \quad (3.9)$$

$$N_- = c_- v_- = -\frac{v_- \wp}{vRT} \frac{c_T}{c_0} c \nabla \mu_e + \frac{it_-^0}{z_- F} + c_- v_0 \quad (3.10)$$

and

$$N_0 = c_0 v_0 \quad (3.11)$$

where

$$v = v_+ + v_- \quad (3.12)$$

$$\mu_e = v_+ \mu_+ + v_- \mu_- = vRT \ln(c f_{+-} a_{+-}^\theta) \quad (3.13)$$

$$D = \frac{\wp_{0+} \wp_{0-} (z_+ - z_-)}{z_+ \wp_{0+} - z_- \wp_{0-}} \quad (3.14)$$

$$t_+^0 = 1 - t_-^0 = \frac{z_+ \wp_{0+}}{z_+ \wp_{0+} - z_- \wp_{0-}} \quad (3.15)$$

Here  $f_{+-}$  is the mean molar activity coefficient of the electrolyte,  $\wp$  is the diffusion coefficient of the electrolyte based on a thermodynamic driving force and  $t_+^0$  is a transference number of lithium-ions with respect to the solvent velocity.

The diffusion coefficient  $D$  of the salt that commonly measured is based on a gradient of the concentration and is related to  $\wp$  by

$$D = \wp \frac{c_T}{c_0} \left( 1 + \frac{d \ln \gamma_{\pm}}{d \ln m} \right) \quad (3.16)$$

where  $\gamma_{\pm}$  is the mean molal activity coefficient and  $m$  is the molality (moles of electrolyte per kilogram of solvent). Beside that, the gradient of the chemical potential  $\mu_e$  of electrolyte in the solution is the driving force for diffusion used in equations (3.9) and (3.10). Hence we can expressed the gradient of chemical potential in terms of the gradient of concentration

$$\frac{\wp}{vRT} \frac{c_T}{c_0} c \nabla \mu_e = D \left( 1 - \frac{d \ln c_0}{d \ln c} \right) \nabla c \quad (3.17)$$

Then substitute equation (3.9) into equation (3.3) we get

$$\frac{\partial c}{\partial t} + \nabla \cdot (c v_0) = -\nabla \cdot \left( -\frac{v_+ \wp}{vRT} \frac{c_T}{c_0} c \nabla \mu_e + \frac{i t_+^0}{z_+ F} + c_+ v_0 \right) \quad (3.18)$$

Substitute equation (3.17) into equation (3.18), rearranging and using electroneutrality

$$\sum_i z_i c_i = 0 \quad (3.19)$$

Equation has (3.18) now became

$$\frac{\partial c}{\partial t} + \nabla \cdot (c v_0) = \nabla \cdot \left[ D \left[ 1 - \frac{d \ln c_0}{d \ln c} \right] \nabla c \right] - \frac{i \nabla t_+^0}{z_+ v_+ F} - \nabla \cdot (c_+ v_0) \quad (3.20)$$

and

$$\frac{\partial c_0}{\partial t} = -\nabla \cdot (c_0 v_0) \quad (3.21)$$

Here, equation (3.20) is known as material balance on the salt and equation (3.21) as continuity equation for the solvent velocity. To convert equation (3.20) into one-dimensional form we assumed that the solvent velocity is sufficiently small, which is solvent velocity can be neglected ( $v_0 = 0$ ). Hence, the equation (3.20) became

$$\frac{\partial c}{\partial t} = \frac{\partial}{\partial x} \left[ D \left[ 1 - \frac{d \ln c_0}{d \ln c} \right] \frac{\partial c}{\partial x} \right] - \frac{i_2}{z_+ v_+ F} \frac{\partial t_+^0}{\partial t} \quad (3.22)$$

where  $i_2$  is the current density in solution phase. Equation (3.22) is the one-dimensional material balance on salt with consideration of nonporous electrode ( $\varepsilon = 1$ ). The porous electrode is the preferred configuration for battery application because of the large interfacial area that it provides for the electrode reaction as well as the reduction in the distance between reactants and the surface. Newman and Tiedemann (1975) and Newman and Thomas (2004) stated that the surface area per unit volume,  $a$  and porosity,  $\varepsilon$  are two properties that are necessary to describe the porous solid. Porosity,  $\varepsilon$  is the ratio of volume of the pores in the solid to the total volume of the solid and the specific interface area per unit volume,  $a$  is ratio of the interfacial area between the

solution and the matrix or solid to the total volume of the matrix. From equation (3.20), by using porous electrode theory and taking the reference velocity to be the solvent velocity, in the absence of homogeneous chemical reaction, a material balance for solution-phase on the salt in the pores of the electrode according to Doyle (1995) can be written as

$$\varepsilon \frac{\partial c}{\partial t} + v_0 \cdot \nabla c = \nabla \cdot \left[ \varepsilon D \left[ 1 - \frac{d \ln c_0}{d \ln c} \right] \nabla c \right] + (1 - t_+^0) \frac{aj_{+n}}{v_+} + (1 - t_+^0) \frac{aj_{-n}}{v_-} - \frac{i \nabla t_+^0}{z_+ v_+ F} - c \left( \frac{\partial \varepsilon}{\partial t} + \nabla \cdot v_0 \right) \quad (3.23)$$

where  $t_+^0$  is the lithium-ion transference number,  $j_n$  is the pore-wall flux density of species  $i$  across the interface and the rate of transfer of the species  $i$  from the solid phase to the solution per unit volume of the total electrode is represented by  $aj_n$ . In this study, we assumed that  $\varepsilon$  is constant, only the lithium-ion participates in the electrochemical reaction and thus  $j_{-n} = 0$ . Once again in order to convert equation (3.23) into one-dimensional form we assumed that the solvent velocity is sufficiently small, which is solvent velocity can be neglected ( $v_0 = 0$ ). Hence, the equation (3.23) became

$$\varepsilon \frac{\partial c}{\partial t} = \frac{\partial}{\partial x} \left[ D_{eff} \left[ 1 - \frac{d \ln c_0}{d \ln c} \right] \frac{\partial c}{\partial x} \right] + (1 - t_+^0) \frac{aj_{+n}}{v_+} - \frac{i \nabla t_+^0}{z_+ v_+ F} \quad (3.24)$$

Following the model equations (3.22) and (3.24), material balance equation for lithium-ion concentration in solution/electrolyte phase in separator can be written as

$$\frac{\partial(c)}{\partial t} = \nabla \cdot (D\nabla c) - \frac{i_2 \cdot \nabla t_+^0}{z_+ v_+ F} \quad (3.25)$$

and for the cathode as

$$\varepsilon \frac{\partial(c)}{\partial t} = \nabla \cdot (\varepsilon D_{eff} \nabla c) - \frac{i_2 \cdot \nabla t_+^0}{z_+ v_+ F} + \frac{aj_n (1 - t_+^0)}{v_+} \quad (3.26)$$

This governing equation is an extension of the work reported earlier by Atlung and his co-workers (Atlung et al. 1979). A few researchers (Doyle et al. 1993; Doyle and Newman 1997; Botte and White 2001; Subramanian and White 2001; Hashim Ali et al. 2002; Subramanian et al. 2004; Johan and Arof 2007) used equation (3.25) and (3.26) as above but differ in the variables and the boundary conditions. Besides that, Doyle and Newman (1997) and Subramanian and White (2001) simplified the equations (3.25) and (3.26) by assuming diffusion coefficient and transference number to be a constant. Hence, in one dimension, equation (3.25) and equation (3.26) become

$$\frac{\partial}{\partial t} c_1(x, t) = D \frac{\partial^2}{\partial x^2} c_1(x, t) \quad \text{at} \quad (0 < x < \delta_s) \quad (3.27)$$

$$\varepsilon \frac{\partial}{\partial t} c_2(x, t) = \varepsilon D_{eff} \frac{\partial^2}{\partial x^2} c_2(x, t) + aj_n (1 - t_+^0) \quad \text{at} \quad (\delta_s < x < \delta_c) \quad (3.28)$$

where  $c_1$  (mol/m<sup>3</sup>) is the material balance that governs the concentration of electrolyte in the separator,  $c_2$  (mol/m<sup>3</sup>) is the material balance which governs the concentration of electrolyte in the porous electrode. In this equation,  $D$  is the diffusion coefficient

(m<sup>2</sup>/s),  $\varepsilon$  is the porosity of the solid,  $t_+^0$  is the transference number,  $a$  the specific interfacial area (m<sup>-1</sup>) and  $j_n$  is the pore wall flux of lithium-ion (mol/m<sup>2</sup>/s). According to Bruggeman expression

$$D_{eff} = \varepsilon^{1/2} D \quad (3.29)$$

This deduces the material balance governing the concentration of electrolyte in the porous electrode (3.28) to

$$\frac{\partial}{\partial t} c_2(x,t) = \varepsilon^{1/2} D \frac{\partial^2}{\partial x^2} c_2(x,t) + \frac{aj_n(1-t_+^0)}{\varepsilon} \quad \text{at} \quad (\delta_s < x < \delta_s + \delta_c) \quad (3.30)$$

Subramanian et al. (2004) in their paper assumed initial conditions throughout the cell sandwich (figure 3.1) are uniformed as

$$c_1 = c_2 = 1 \quad \text{at} \quad t = 0 \quad (3.31)$$

The rate of discharge governs the mass flux at  $x = 0$  (lithium foil) for galvanostatic discharge is given as

$$\frac{\partial c_1}{\partial x} = -\frac{I(1+t_+^0)}{nDF} \quad \text{at} \quad x = 0 \quad (3.32)$$

where  $I$  is the current density (A/m<sup>2</sup>),  $n$  is the number of electrons transferred in the electrochemical reaction ( $n = 1$ ) and  $F$  is the Faraday constant.

Then the mass flux at the current collector ( $x = \delta_s + \delta_c$ ) is

$$\frac{\partial c_2}{\partial x} = 0 \quad \text{at} \quad x = \delta_s + \delta_c \quad (3.33)$$

Concentration and mass flux are continuous at the separator/cathode interface ( $x = \delta_s$ )

and are given as

$$c_1 = c_2 \quad \text{at} \quad (x = \delta_s) \quad (3.34)$$

and

$$\frac{\partial c_1}{\partial x} = \varepsilon^{3/2} \frac{\partial c_2}{\partial x} \quad \text{at} \quad (x = \delta_s) \quad (3.35)$$

They also assumed that  $j_n$  is given by its average value everywhere in the porous electrode because when the open-circuit potential depends strongly on the state of charge of the system or when kinetic resistances dominate ohmic resistances.

$$j_n = -\frac{I}{aF\delta_c} \quad (3.36)$$

By substitution equation (3.36) into (3.30) we get

$$\frac{\partial}{\partial t} c_2(x, t) = \varepsilon^{1/2} D \frac{\partial^2}{\partial x^2} c_2(x, t) - \frac{I(1-t_+^0)}{nF\varepsilon\delta_c} \quad \text{at} \quad (\delta_s < x < \delta_s + \delta_c) \quad (3.37)$$

where  $n = 1$ .

Now the equation (3.27) and (3.37) must be converted to dimensionless form in order to avoid dealing with dimensions,  $t$ . Hence the following dimensionless parameters are introduced as

$$\mathcal{G} = \frac{c}{c_0} \quad (3.38)$$

$$y = \frac{x}{\delta_s} \quad (3.39)$$

$$r = \frac{\delta_c}{\delta_s} \quad (3.40)$$

$$\tau = \frac{Dt}{\delta_s^2} \quad (3.41)$$

The following steps below illustrated the conversion of equation (3.27) and (3.37) to the dimensionless form. From equation (3.38), by taking the derivatives of  $\mathcal{G}$  with respect to  $t$  and  $\tau$  shown as

$$\frac{\partial \mathcal{G}}{\partial t} = \frac{1}{c_0} \frac{\partial c}{\partial t} \quad (3.42)$$

$$\frac{\partial \mathcal{G}}{\partial \tau} = \frac{\partial \mathcal{G}}{\partial t} \frac{\partial t}{\partial \tau} \quad (3.43)$$

From equation (3.38) also shown as

$$c = \mathcal{G}c_0 \quad (3.44)$$

Then from equation (3.44) taking the derivatives of  $c$  with respect to  $\mathcal{G}$  and  $t$  is shown as

$$\frac{\partial c}{\partial \mathcal{G}} = c_0 \quad (3.45)$$

$$\frac{\partial c}{\partial t} = c_0 \frac{\partial \mathcal{G}}{\partial t} \quad (3.46)$$

Now substituting equation (3.42) into equation (3.43) to get the equation below as

$$\frac{\partial \mathcal{G}}{\partial \tau} = \frac{1}{c_0} \frac{\partial c}{\partial \tau} \quad (3.47)$$

By rewriting equation (3.47), we get as shown below

$$\frac{\partial c}{\partial \tau} = c_0 \frac{\partial \mathcal{G}}{\partial \tau} \quad (3.48)$$

Then taking derivatives of  $\tau$  with respect to  $t$  from equation (3.41) will be as

$$\frac{\partial \tau}{\partial t} = \frac{D}{\delta_s^2} \quad (3.49)$$

Substitute equation (3.45) into equation (3.46) to get the equation below as

$$\frac{\partial c}{\partial t} = \frac{\partial c}{\partial \mathcal{G}} \frac{\partial \mathcal{G}}{\partial t} \quad (3.50)$$

By using chain rule, equation (3.50) can be written as

$$\frac{\partial c}{\partial t} = \frac{\partial c}{\partial \mathcal{G}} \frac{\partial \mathcal{G}}{\partial \tau} \frac{\partial \tau}{\partial t} \quad (3.51)$$

Substituting equation (3.45), (3.47) and (3.49) into equation (3.51) is shown as

$$\frac{\partial c}{\partial t} = \frac{\partial c}{\partial \tau} \frac{D}{\delta_s^2} \quad (3.52)$$

Then substituting equation (3.48) into equation (3.52), we get as shown below

$$\frac{\partial c}{\partial t} = c_0 \frac{\partial \mathcal{G}}{\partial \tau} \frac{D}{\delta_s^2} \quad (3.53)$$

From equation (3.53) it can be defined that the equation are

$$\frac{\partial c_1}{\partial t} = c_0 \frac{\partial \mathcal{G}_1}{\partial \tau} \frac{D}{\delta_s^2} \quad (3.54)$$

and

$$\frac{\partial c_2}{\partial t} = c_0 \frac{\partial \mathcal{G}_2}{\partial \tau} \frac{D}{\delta_s^2} \quad (3.55)$$

Thus equation (3.54) is substituted into equation (3.27) and equation (3.55) is substituted into equation (3.37) to get

$$\frac{\partial \mathcal{G}_1}{\partial \tau} = \frac{\delta_s^2}{c_0} \left( \frac{\partial^2 c_1}{\partial x^2} \right) \quad (3.56)$$

and

$$\frac{\partial \mathcal{G}_2}{\partial \tau} = \frac{\delta_s^2}{c_0} \left( \varepsilon^{1/2} \frac{\partial^2 c_2}{\partial x^2} + K \right) \quad (3.57)$$

where

$$K = \frac{a j_n (1 - t_+^0)}{\varepsilon} \quad (3.58)$$

From the term  $J$  above,  $a$  is the specific interfacial area ( $\text{m}^{-1}$ ),  $t_+^0$  is the transference number,  $\varepsilon$  is the volume fraction of the solid and  $j_n$  is the pore wall flux of lithium ions ( $\text{mol}/\text{m}^2/\text{s}$ ). The Bruggeman expression has been used for obtaining the effective diffusivity in the electrolyte (Subramanian and White 2001). However, equation (3.56) and (3.57) are not the complete equations that we are going to use. For the term  $\frac{\partial^2 c}{\partial x^2}$ , it

has to be converted to the dimensionless form as follows

$$\frac{\partial^2 c}{\partial x^2} = \frac{\partial}{\partial x} \left( \frac{\partial c}{\partial x} \right) \quad (3.59)$$

Then expand equation (3.59) to get as follows

$$\frac{\partial^2 c}{\partial x^2} = \frac{\partial}{\partial x} \left( \frac{\partial \mathcal{G}}{\partial y} \frac{\partial y}{\partial x} \frac{\partial c}{\partial \mathcal{G}} \right) \quad (3.60)$$

From equation (3.38), by taking the derivatives of  $\mathcal{G}$  with respect to  $y$  is shown as

$$\frac{\partial \mathcal{G}}{\partial y} = \frac{1}{c_0} \frac{\partial c}{\partial y} \quad (3.61)$$

Taking the derivative of  $y$  with respect to  $x$  from equation (3.39), we get as shown below as

$$\frac{\partial y}{\partial x} = \frac{1}{\delta_s} \quad (3.62)$$

Then from equation (3.44), taking the derivative  $c$  with respect to  $\mathcal{G}$  as follows

$$\frac{\partial c}{\partial \mathcal{G}} = c_0 \quad (3.63)$$

After that, substitute equation (3.61), (3.62) and (3.63) into equation (3.60) as shown below as

$$\frac{\partial^2 c}{\partial x^2} = \frac{\partial}{\partial x} \left( \frac{1}{c_0} \frac{\partial c}{\partial y} \frac{1}{\delta_s} c_0 \right) \quad (3.64)$$

Then, from equation (3.38), by taking the derivatives of  $\mathcal{G}$  with respect to  $y$  and shown as

$$\frac{\partial \mathcal{G}}{\partial y} = \frac{\partial \mathcal{G}}{\partial t} \frac{\partial t}{\partial y} \quad (3.65)$$

Now substituting equation (3.42) into equation (3.65) to get as shown below

$$\frac{\partial \mathcal{G}}{\partial y} = \frac{1}{c_0} \frac{\partial c}{\partial y} \quad (3.66)$$

From equation (3.66), deduce it to the equation below

$$\frac{\partial c}{\partial y} = c_0 \frac{\partial \mathcal{G}}{\partial y} \quad (3.67)$$

Take equation (3.67) and substitute into equation (3.64) as follows

$$\frac{\partial^2 c}{\partial x^2} = \frac{c_0}{\delta_s} \left[ \frac{\partial}{\partial x} \left( \frac{\partial \mathcal{G}}{\partial y} \right) \right] \quad (3.68)$$

Expand equation (3.68) as follows

$$\frac{\partial^2 c}{\partial x^2} = \frac{c_0}{\delta_s} \left[ \frac{\partial}{\partial y} \frac{\partial y}{\partial x} \left( \frac{\partial \mathcal{G}}{\partial y} \right) \right] \quad (3.69)$$

Now, substitute equation (3.62) into Equation (3.69) to get the equation shown below

$$\frac{\partial^2 c}{\partial x^2} = \frac{c_0}{\delta_s^2} \left[ \frac{\partial^2 g}{\partial y^2} \right] \quad (3.70)$$

From equation (3.70), it is defined as shown below

$$\frac{\partial^2 c_1}{\partial x^2} = \frac{c_0}{\delta_s^2} \left[ \frac{\partial^2 g_1}{\partial y^2} \right] \quad (3.71)$$

and

$$\frac{\partial^2 c_2}{\partial x^2} = \frac{c_0}{\delta_s^2} \left[ \frac{\partial^2 g_2}{\partial y^2} \right] \quad (3.72)$$

Finally equation (3.71) is substituted into equation (3.56) and equation (3.72) is substituted into equation (3.57) to get complete governing equation in dimensionless form for the region in the separator for  $(0 < y < 1)$

$$\frac{\partial g_1}{\partial \tau} = \frac{\partial^2 g_1}{\partial y^2} \quad (3.73)$$

and for the region in the porous electrode for  $(1 < y < 1+r)$

$$\frac{\partial g_2}{\partial \tau} = \varepsilon^{1/2} \frac{\partial^2 g_2}{\partial y^2} + J \quad (3.74)$$

where

$$J = -\frac{I(1-t_+^0)\delta_s^2}{FD\delta_c c_0 \varepsilon} \quad (3.75)$$

Furthermore, we also need to convert initial condition (3.31) and boundary conditions (3.32) to (3.35) to dimensionless form. The following steps illustrate the conversion of equation (3.31) to (3.35) to the dimensionless form. From equation (3.44), we can define that

$$c_1 = \mathcal{G}_1 c_0 \quad (3.76)$$

and

$$c_2 = \mathcal{G}_2 c_0 \quad (3.77)$$

If

$$c_1 = c_2 \quad (3.78)$$

then from equation (3.76) and equation (3.77), equation (3.78) became

$$\mathcal{G}_1 = \mathcal{G}_2 \quad (3.79)$$

Hence, from equation (3.79), we can deduce that equation (3.31) will result as

$$\mathcal{G}_1 = \mathcal{G}_2 = 1 \quad \text{at} \quad \tau = 0 \quad (3.80)$$

and equation (3.34) is as shown below

$$\mathcal{G}_1 = \mathcal{G}_2 \quad \text{at} \quad y = 1 \quad (3.81)$$

Then, from equation (3.38), by taking the derivatives of  $\mathcal{G}$  with respect to  $x$  and  $y$  is as shown as below

$$\frac{\partial \mathcal{G}}{\partial x} = \frac{1}{c_0} \frac{\partial c}{\partial x} \quad (3.82)$$

$$\frac{\partial \mathcal{G}}{\partial y} = \frac{\partial \mathcal{G}}{\partial x} \frac{\partial x}{\partial y} \quad (3.83)$$

From equation (3.44) taking the derivatives of  $c$  with respect to  $x$  is as shown as

$$\frac{\partial c}{\partial x} = c_0 \frac{\partial \mathcal{G}}{\partial x} \quad (3.84)$$

Substituting equation (3.82) into equation (3.83) to get the equation below

$$\frac{\partial \mathcal{G}}{\partial y} = \frac{1}{c_0} \frac{\partial c}{\partial y} \quad (3.85)$$

Then, by rewriting the equation (3.85), we get as follows

$$\frac{\partial c}{\partial y} = c_0 \frac{\partial \mathcal{G}}{\partial y} \quad (3.86)$$

Now taking derivatives of  $y$  with respect to  $x$  from equation (3.39), will be as follows

$$\frac{\partial y}{\partial x} = \frac{1}{\delta_s} \quad (3.87)$$

Substitute equation (3.45) into equation (3.84) to get the equation as follow

$$\frac{\partial c}{\partial x} = \frac{\partial c}{\partial \mathcal{G}} \frac{\partial \mathcal{G}}{\partial x} \quad (3.88)$$

By using chain rule, equation (3.88) can be written as

$$\frac{\partial c}{\partial x} = \frac{\partial c}{\partial \mathcal{G}} \frac{\partial \mathcal{G}}{\partial y} \frac{\partial y}{\partial x} \quad (3.89)$$

Substituting equation (3.45), (3.85) and (3.87) into equation (3.89) will be shown as

$$\frac{\partial c}{\partial x} = \frac{\partial c}{\partial y} \frac{1}{\delta_s} \quad (3.90)$$

Then substituting equation (3.86) into equation (3.90), we get as follows

$$\frac{\partial c}{\partial x} = c_0 \frac{\partial \mathcal{G}}{\partial y} \frac{1}{\delta_s} \quad (3.91)$$

From equation (3.91) it is defined that the equation becomes

$$\frac{\partial c_1}{\partial x} = c_0 \frac{\partial \mathcal{G}_1}{\partial y} \frac{1}{\delta_s} \quad (3.92)$$

and equation becomes

$$\frac{\partial c_2}{\partial x} = c_0 \frac{\partial \mathcal{G}_2}{\partial y} \frac{1}{\delta_s} \quad (3.93)$$

Then, substitute back equation (3.92) and equation (3.93) into equations (3.32), (3.33) and (3.35) to get as follows

$$\frac{\partial \mathcal{G}_1}{\partial y} = J\varepsilon r \quad \text{at} \quad y = 0 \quad (3.94)$$

$$\frac{\partial \mathcal{G}_2}{\partial y} = 0 \quad \text{at} \quad y = 1 + r \quad (3.95)$$

$$\frac{\partial \mathcal{G}_1}{\partial y} = \varepsilon^{3/2} \frac{\partial \mathcal{G}_2}{\partial y} \quad \text{at} \quad y = 1 \quad (3.96)$$

Now the dimensionless form for governing equation in the separator and cathode with its initial and boundary conditions are summarized in table 3.1

**Table 3.1: Summary of model equations in dimensionless form.**

	Dimensionless Form	Region	From
Governing equation for separator	$\frac{\partial \mathcal{G}_1}{\partial \tau} = \frac{\partial^2 \mathcal{G}_1}{\partial y^2}$	$(0 < y < 1)$	Equation (3.73)
Governing equation for separator	$\frac{\partial \mathcal{G}_2}{\partial \tau} = \varepsilon^{1/2} \frac{\partial^2 \mathcal{G}_2}{\partial y^2} + J$	$(1 < y < 1 + r)$	Equation (3.74)
Initial condition	$\mathcal{G}_1 = \mathcal{G}_2 = 1$	$\tau = 0$	Equation (3.80)
Boundary conditions	$\frac{\partial \mathcal{G}_1}{\partial y} = J\varepsilon r$	$y = 0$	Equation (3.94)
	$\frac{\partial \mathcal{G}_2}{\partial y} = 0$	$y = 1 + r$	Equation (3.95)
	$\mathcal{G}_1 = \mathcal{G}_2$	$y = 1$	Equation (3.81)
	$\frac{\partial \mathcal{G}_1}{\partial y} = \varepsilon^{3/2} \frac{\partial \mathcal{G}_2}{\partial y}$	$y = 1$	Equation (3.96)
where $J = -\frac{I(1-t_+^0)\delta_s^2}{FD\delta_c c_0 \varepsilon}$			Equation (3.75)

---

Ali, S. A. H. (2004). An Analytical Study Of The Galvanostatic Discharge In Secondary Lithium Cells. Institute Of Mathematical Sciences. Kuala Lumpur, University Of Malaya. **Phd thesis**: 142.

Ali, S. A. H., A. Hussin, et al. (2002). "Short- and Long-time solutions for material balance equation in lithium-ion battery by laplace transform." Journal of Power Sources **112**(2): 435-442.

Atlung, S., K. West, et al. (1979). "Dynamic Aspects of Solid Solution Cathodes for Electrochemical Power Sources." Journal of Electrochemical Society **126**(8): 1311-1321.

Botte, G. G. and R. E. White (2001). "Modeling Lithium Intercalation in a Porous Carbon Electrode " Journal of the Electrochemical Society **148**(1): 54-66.

Doyle, M., T. F. Fuller, et al. (1993). "Modeling of Galvanostatic Charge and Discharge of the Lithium/Polymer/Insertion Cell." Journal of Electrochemistry Society **140**(6): 1526-1533.

Doyle, M. and J. Newman (1997). "Analysis of capacity-rate data for lithium batteries using simplified models of the discharge process " Journal of Electrochemistry **27**: 846-856.

Johan, M. R. and A. K. Arof (2007). "Modeling of electrochemical intercalation of lithium into a LiMn<sub>2</sub>O<sub>4</sub> electrode using Green function." Journal of Power Sources **170**: 490-494.

Newman, J. (1991). Electrochemical Systems, 2nd edn. Englewood Cliffs, New Jersey, Prentice-Hall, Inc.

Newman, J. and K. E. Thomas (2004). Electrochemical systems. New Jersey,US, John Wiley & Sons.

Newman, J., K. E. Thomas, et al. (2003). "Modeling of lithium-ion batteries." Journal of Power Sources **119-121**: 838-843.

Newman, J. and W. Tiedemann (1975). "Porous-Electrode Theory with Battery Applications." AIChE Journal **21**(1): 25-41.

Newman, J. S. and C. W. Tobias (1962). "Theoretical Analysis of Current Distribution in Porous Electrodes." Journal of Electrochemical Society **109**(12): 1183-1191.

Onsager, L. (1945). "Theories and Problem of Liquid Diffusion " Annals of New York Aca. Sci. **46**: 241-265.

Subramanian, V. R., D. Tapriyal, et al. (2004). "A Boundary Condition for Porous Electrodes." Electrochemical and Solid-State Letters **7**(9): 259-263.

---

Subramanian, V. R. and R. E. White (2001). "New separation of variables method for composite electrodes with galvanostatic boundary conditions." Journal of Power Sources **96**: 385-395.