

An Integral Transform for Solving Diffusion Problem of Lithium Cells

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Abstract This paper presents the equations used in the mathematical modeling of lithium cells. The model equations include the material balance equations, the Ohms Law and the flux equation for the porous electrodes in both the electrolyte and the solid phases. These equations are solved analytically, by means of Laplace transform, to give the concentration profile of the lithium ion concentration with respect to the distance and time.

Keywords Laplace transform, diffusion problem, lithium cell

Abstrak Kertas ini memaparkan persamaan-persamaan yang digunakan dalam permodelan sel litium. Persamaan-persamaan yang terlibat dalam model ini termasuk persamaan pengangkutan jirim, hukum Ohm dan persamaan fluks bagi elektrod berongga didalam fasa elektrolit dan fasa pepejal. Persamaan-persamaan ini diselesaikan secara analitik, menggunakan kaedah penjelmaan Laplace, untuk mendapatkan profil kepekatan ion litium terhadap jarak dan masa.

Katakunci Penjelmaan Laplace, masalah serapan, sel litium

1 Introduction

The development of lithium-ion batteries has progressed considerably over the past decade such that they have become a state-of-the-art battery for consumer electronic applications [3,8,9] and electric vehicles [1,13]. Many models have been proposed to predict the behavior and performance of various types of batteries such as lithium-ion [4], nickel-cadmium [14] and nickel-metal hydride [15]. The purpose of such models is to develop an understanding of the specific system so that suggestions can be made towards the improvement and finally the optimization in the battery system. Most of the works in this area were done numerically, such as the thermal analysis [10], energy balance analysis [2] and charge/discharge analysis [5]. The underlying phenomenon of these analyses is to study the diffusion process that occurs inside a battery as the battery is being charge/discharge. However, this work will focus only on solving the diffusion problem using an integral transform technique known as Laplace transform. We began by briefly describing the development of the equations that are used to model the isothermal discharge of lithium ion cell. The cell is divided into three regions as shown in Figure 1. The anode is a carbon base electrode while the cathode is

a closely packed composite electrode employing a $\text{Li}_y\text{Mn}_2\text{O}_4$ active material; separated by a separator. The cathode consists of an inert conducting material, non-aqueous electrolyte and solid active insertion particles.

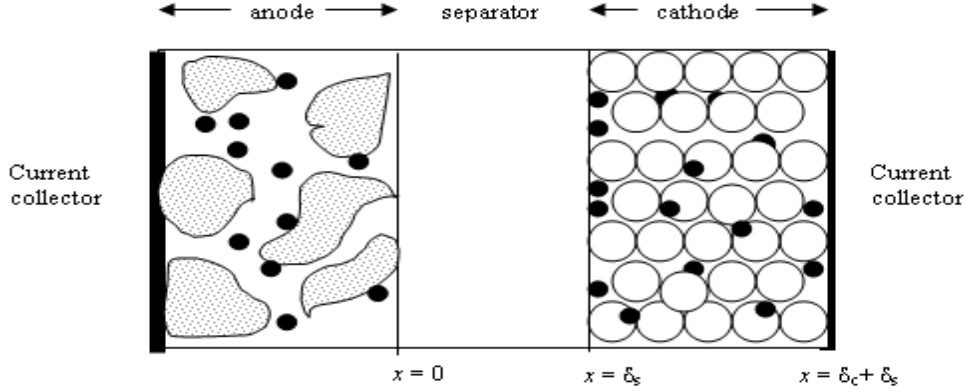


Figure 1. A schematic representation of a lithium-ion cell.
Smaller black spheres represent conducting additives.

2 Model Development of the Diffusion Process

Due to the large salt concentrations used in most lithium batteries, the concentrated solution theory can be used to treat the transport of the electrolyte. According to the concentrated solution theory [11], the driving force for mass transfer at constant temperature and pressure is the gradient of the electrochemical potential for an ionic species; which is related to the binary fluxes of each of the other species given by

$$N_+ = -\nu_+ D \nabla c + \frac{it_+}{z_+ F} \quad (1)$$

and

$$N_- = -\nu_- D \nabla c + \frac{it_-}{z_- F} \quad (2)$$

where c is the concentration of the lithium salt electrolyte ($c = c_j/\nu_j$), D is the salt diffusion coefficient, ν is the velocity of species, z is the charge number of species, F is the Faraday's constant (96487 C/mol), i is the current density and $t_{+,-}$ is the transference number. This flux expression is then substituted into a general material balance for species j is given by

$$\frac{\partial(\varepsilon c_j)}{\partial t} = -\nabla \cdot N_j + P_j; j = 1, 2 \quad (3)$$

where ε is the porosity of the electrode, P_j is the rate of production of species j due to reaction. The subscript 1 stands for the solid phase and 2 for the solution/electrolyte phase. Our model has employed porous electrode due to its large interface area similar the porous

electrode theory described by Newman et al. [11,12]. According to Newman et al. [11,12], the material balance on salt can be written in one-dimensional as

$$\varepsilon \frac{\partial c_2}{\partial t} = \frac{\partial}{\partial x} \left[\varepsilon D_2 \frac{\partial c_2}{\partial x} \right] + a j_n (1 - t_+^0) - \frac{i_2}{F} \frac{\partial t_+}{\partial x} \quad (4)$$

The variation of electrical state in the solution is to be defined with respect to a lithium reference electrode in solution. This leads to the expression for the potential in solution as

$$i_2 = -\kappa \nabla \Phi_2 - \frac{\kappa R T}{F} \left(1 + \frac{d \ln f_{\pm}}{d \ln c} \right) (1 - t_+) \nabla \ln c_2 \quad (5)$$

where Φ_2 is the electric potential, $f_{\pm}$ is the mean molar activity coefficient of the salt, T is temperature, R is the universal gas constant (8.3143 J/mol K) and κ is the conductivity of electrolyte. The term j_n in equation (4) is the pore-wall flux of lithium ions across the interface, which is averaged over the interfacial area between the solid matrix and the electrolyte [5]. For a single electrode reaction, j_n is related to the divergence of the current flowing in the solution phase [5] by

$$a j_n = \frac{1}{F} \frac{\partial i_2}{\partial x} \quad (6)$$

where a is the interfacial area. The constructed model is based on a galvanostatic charge/discharge mode. The boundary condition on the concentration at the lithium electrode is found by setting the anion flux to zero. Hence, at $x = 0$

$$\nabla c_2 = -\frac{I(1 - t_+)}{F D_2} \quad (7)$$

At the positive electrode/current collector boundary, the flux of ions is equal to zero and all currents are carried by electrons. Hence, the boundary conditions on the salt concentration and solution-phase current density at $x = \delta_s + \delta_c$ are

$$\nabla c_2 = 0 \quad \text{and} \quad i_2 = 0. \quad (8)$$

During insertion and de-insertion of the lithium, there is no volume change and the lithium ions diffuse into the solid particles of the active cathode material. The solid insertion particles are taken to be spherical with radius R_s and a known constant solid diffusion coefficient, D_1 . The diffusion in this solid phase is governed by Fick's law, which when written in spherical coordinate gives the governing equation the solid particles diffusion as

$$\frac{\partial c_1}{\partial t} = D_1 \left[\frac{\partial^2 c_1}{\partial r^2} + \frac{2}{r} \frac{\partial c_1}{\partial r} \right] \quad (9)$$

where $c_1(r, t)$ is the concentration of lithium ions inside a spherical electrode particle. This diffusion process is subjected to an interfacial transfer and a symmetrical boundary condition

$$\frac{\partial c_1(0, t)}{\partial r} = 0 \quad (10)$$

and

$$-D_1 \frac{\partial c_1(R_s, t)}{\partial r} = j_n. \quad (11)$$

The initial condition is given by $c_1(r, 0) = c^*$, where c^* is the solid phase initial concentration.

3 Solution and Discussion

The diffusion of lithium ions in the electrolyte phase can now be describe by the material balance in equation (4). Assuming the transference number, t_+ is a constant and using the following dimensionless parameters

$$c = \frac{c_2}{c_0}, \quad y = \frac{x}{\delta_s}, \quad \tau = \frac{D_2 t}{\delta_s^2}, \quad J = \frac{a(1-t_+)\delta_s^2 j_n}{\varepsilon D_2 c_0}, \quad (12)$$

where c_0 is the initial concentration of the solution phase, δ_c is length of the cathode and δ_s length of the separator.

The concentration behavior due to one-dimensional diffusion in the electrolyte phase can now be written as

$$\frac{\partial c}{\partial \tau} = \varepsilon^{1/2} \frac{\partial^2 c}{\partial y^2} + J \quad (13)$$

subjected to the following boundary and initial conditions

$$\frac{\partial c}{\partial y} = 0 \quad \text{at } y = 1 + r \quad (14)$$

$$\frac{\partial c}{\partial y} = \frac{Jr}{\varepsilon^{1/2}} \quad \text{at } y = 1 \quad (15)$$

$$c(y, 0) = 1 \quad \text{for all } y. \quad (16)$$

Applying Laplace transform with respect to dimensionless time τ to equation (13), we get

$$\frac{d^2 \bar{c}_2}{dy^2} - \frac{s \bar{c}_2}{\varepsilon^{1/2}} = -\frac{1}{\varepsilon^{1/2}} \left(1 + \frac{J}{s}\right) \quad (17)$$

where $\bar{c}_2(y, s)$ is the Laplace transform of $c_2(y, \tau)$. Applying boundary conditions (14) and (15) gives

$$\bar{c}_2(y, s) = \frac{1}{s} + \frac{J}{s^2} - \frac{Jr}{\varepsilon^{1/4}} \left(\frac{\cosh q(1+r-y)}{s^{3/2} \sinh(qr)} \right), \quad (18)$$

where $q = s^{1/2}/\varepsilon^{1/4}$. In order to be able to take the inverse of Lapace transform, the last term of equation (18) is expanded in terms of hyperbolic sine and cosine and written as its partial fraction [6,7] given by

$$\begin{aligned} \frac{Jr}{\varepsilon^{0.25}} \frac{\cosh q(1+r-y)}{s^{1.5} \sinh(qr)} &= \frac{J \cosh q(1+r-y)}{s^2 \left(1 + \frac{(qr)^2}{\pi^2}\right) \left(1 + \frac{(qr)^2}{2^2 \pi^2}\right) \dots} \\ &= \frac{A_2}{s^2} + \frac{A_1}{s} + \sum_{m=1}^{\infty} \frac{B_m}{\left(1 + \frac{(qr)^2}{m^2 \pi^2}\right)} \end{aligned} \quad (19)$$

where the numerator and the denominator are polynomials in s which have no common factor and the degree of the numerator is lower than the degree of denominator. Solving

for the partial fraction gives

$$A_1 = \frac{1}{1+r} \left(\frac{(1+r-y)^2}{\varepsilon^{0.25}} - \frac{2r^2}{\varepsilon^{0.5}} \right), \quad (20)$$

$$A_2 = 1, \quad (21)$$

$$B_m = \frac{(-1)^{m+1} 2r^4 \cos \frac{m\pi}{r} (1+r-y)}{\varepsilon m^4 \pi^4}. \quad (22)$$

These values are inserted into equation (19) and the inverse of Laplace transform is applied to the resulting equation. Hence, the solution is

$$\begin{aligned} c(y, \tau) = 1 - J \left(\frac{(1+r-y)^2}{2\varepsilon^{0.5}} - \frac{r^2}{6\varepsilon^{0.5}} \right) \\ + \frac{2J}{\varepsilon^{0.5}} \sum_{m=1}^{\infty} \frac{(-1)^m r^2}{(m\pi)^2} e^{-(m\pi/r)^2 \varepsilon^{0.5} \tau} \cos \left(\frac{m\pi}{r} (1+r-y) \right). \end{aligned} \quad (23)$$

This equation is valid for all time intervals and is related to the discharge/charge coefficient.

Next, for the solid phase analysis, Laplace Transform is applied to equation (9) to get

$$\frac{d^2 \bar{c}_1}{dr^2} - \frac{s}{D_s} \bar{c}_1 = -\frac{c^*}{D_s} r \quad (24)$$

where $\bar{c}_1(y, s)$ is the Laplace transform of $c_1(r, t)$. Equation (24) was integrated twice with respect to r to become

$$\bar{c}_1(r, s) = B(e^{qr} - e^{-qr}) + \frac{c^*}{s} r \quad (25)$$

Here B is one of the two constants of integration obtained upon performing the integration twice on equation (24) and the other constant B . Differentiating equation (25), applying the boundary conditions (10) and (11) and inverting for small time interval, we get

$$\begin{aligned} c_1(\rho, \tau) = \frac{R_s j_n}{D_s \rho} \left[-\exp(-1 + \rho + \tau) \operatorname{erfc} \left(-\sqrt{\tau} + \frac{1-\rho}{2\sqrt{\tau}} \right) + \operatorname{erfc} \left(\frac{1-\rho}{2\sqrt{\tau}} \right) \right. \\ \left. + \exp(-1 - \rho - \tau) \operatorname{erfc} \left(-\sqrt{\tau} + \frac{1+\rho}{2\sqrt{\tau}} \right) - \operatorname{erfc} \left(\frac{1+\rho}{2\sqrt{\tau}} \right) \right] + c^* \end{aligned} \quad (26)$$

where $\rho = r/R_s$ and $\tau = D_s t/R_s^2$ are dimensionless parameters. Equation (26) gives a relationship between the lithium ion concentrations in the solid phase with discharge current only for short time intervals. The long time analysis is quite lengthy and can be found in Hashim Ali et al. [6]. The final solution for the solid diffusion is given by [6] as

$$\begin{aligned} c_1(r, t) = c_0 - \frac{j_n R_s^2}{D_s} \left\{ \frac{3D_s t}{R_s^2} + \frac{1}{2} \left(\frac{r}{R_s} \right)^2 - \frac{3}{10} \right. \\ \left. - 2 \left(\frac{R_s}{r} \right) \sum_{n=1}^{\infty} \frac{\sin(r\alpha_n/R_s)}{\alpha_n^2 \sin \alpha_n} \exp(-\alpha_n^2 D_s t/R_s^2) \right\} \end{aligned} \quad (27)$$

where α_n 's are the positive roots of $\alpha_n \cot \alpha_n = 1$. Equation (27) is valid for all t .

Figure 2 and 3 give the concentration profile of lithium ions during a galvanostatic discharge of 1.39 mA/cm^{-2} in obtained from equation (23) and equation (27), respectively. In Figure 2, the concentration of lithium ions decreases with time since during discharge the front face of the cathode were filled up first as compared to the back at the cathode (at $y = 5$). Figure 3 shows an increase in the lithium ions concentration, from the center of the solid particle ($r = 0$) to the surface of the particle ($r = R_s$), as time increases. These results indicated that the lithium ions inside the solid particle move to the surface of the particle in order to be dispersed into the electrolyte during discharge.

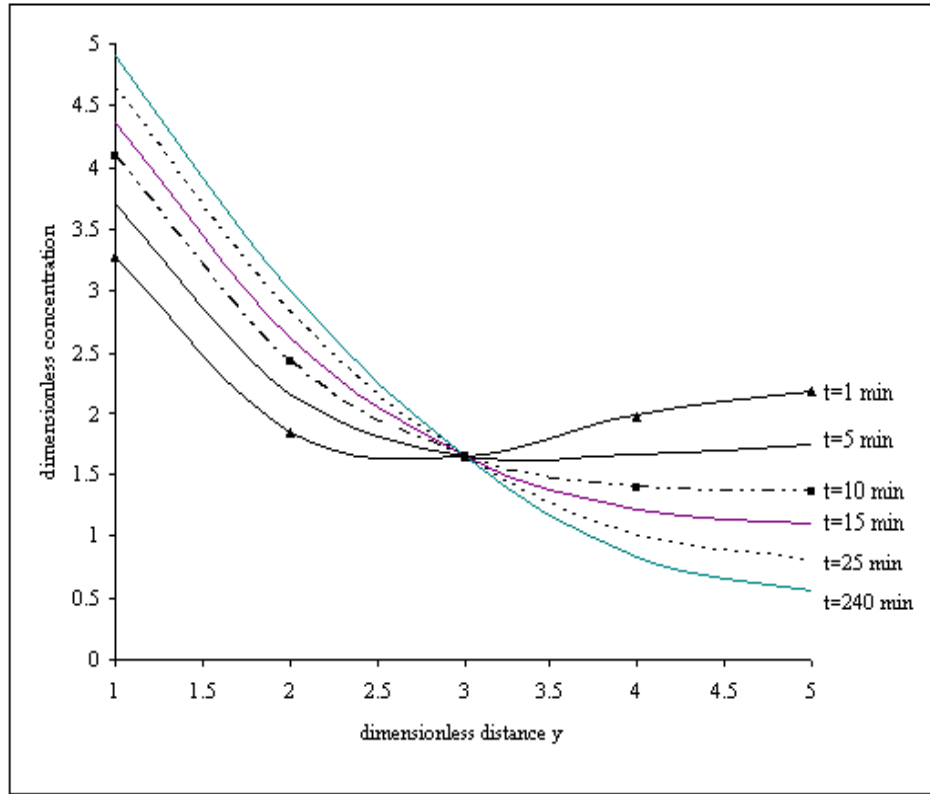


Figure 2. Profile of lithium ion concentration in solution phase.

4 Conclusion

This paper has presented the equations governing the modeling the diffusion process of a lithium ion cell. Two cases have been considered: the electrolyte phase limitation and the solid phase limitation. Both cases contributed to the movement of lithium ion in the three region of a battery. The governing equations for both cases were solved by the well-known transform technique known as the Laplace transform.

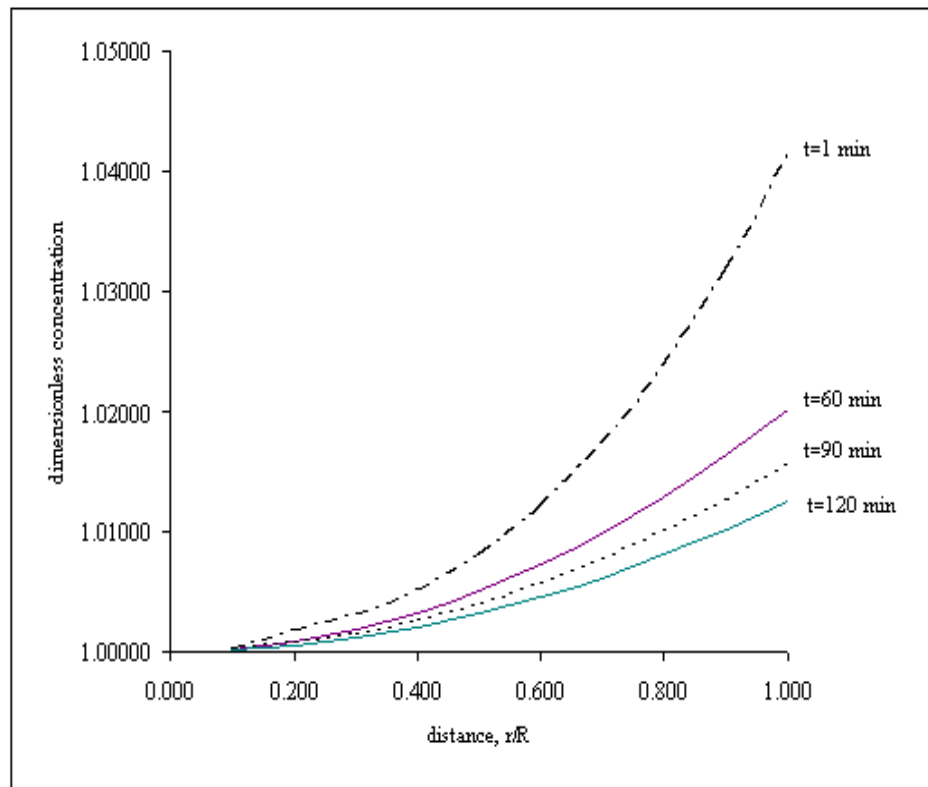


Figure 3. Profile of lithium ion concentration in the solid phase.

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