

# QUASI-STEADY STATE SOLUTION OF LITHIUM ION CONCENTRATION OF HALF-CELL CATHODE IN DILUTE ELECTROLYTE

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## Abstract

This paper focuses on a mathematical model of a Lithium ion battery in dilute electrolyte. The macroscopic model takes into account the conservation of ions in the electrolyte, diffusion within particles, and transfer of Lithium at the electrolyte/electrode particles interface. The asymptotic analysis for the dimensionless model has led to Tafel reaction rate of Lithium intercalation at the electrolyte/electrode particles interface and a quasi-steady state model. Analytic solutions for the Lithium ion concentration and the cell voltage are derived, specifically for electrode materials that have a flat discharge curve characteristic. The analytic solutions give rational results of the concentration profile in the electrolyte across the cell at various currents. The results show that the rate of lithium intercalation into particles is high in the region near the separator. At high discharge rate, the concentration in the electrolyte is depleted, hence limit the discharge.

**Keywords:** Lithium ion battery; Half-cell; Dilute electrolyte;

## 1.0 INTRODUCTION

Nowadays, the lithium ion battery (LIB) is one of the most successful rechargeable batteries because they provide high volumetric energy densities [1]. The study of battery behaviour is necessary in order to increase their efficiency and storage performance. A typical Lithium ion battery consists of two electrodes (cathode and anode), contained of small electrode particles and a separator that lies between the electrodes and an electrolyte which transports ions between the electrodes [2]. During discharge, Lithium diffuses in the anodic particle to the particle surface and undergoes a reaction to release a

Lithium ion into the electrolyte and an electron into particle. The Lithium ion diffuses through the electrolyte across the separator into the cathode where it undergoes a similar reaction with an electron at the particle surface (by an intercalation process). While, the electron travels from anode to the cathode current collector via external circuit to produce electricity. When the cell is charging, the process is reversed: an external power source (the charging circuit) supplies a higher voltage than that produced by the battery, driving the current to pass in the reverse direction from the positive to the

negative electrode, where they become embedded in the electrode material. In order to test the behavior of a specific electrode material, the experiment is usually performed on a half-cell which consists of a working electrode (either anode or cathode) and a reference electrode as the other electrode [14]. A schematic diagram of the half-cell is shown in Figure 1.

In particular, battery modelling must account for conservation of ions in the electrolyte, charge reaction at the electrolyte/electrode particle interface and transport of Lithium within the electrode particles [3], [4]. The typical size of a particle is about  $1 \mu\text{m}$  [5], [7] or even much less than that for nanostructured particles [2], and for the thickness of the cell is about  $10 \mu\text{m}$  [4], [11]. Therefore, the modelling of LIB involves a multiscale system measuring from the microscopic system (electrode particles) to that of the macroscopic system (the length of the cell). Richardson et.al. [3] has derived the macroscopic LIB model in dilute electrolyte. The model is written in the form developed by Newman [4] who has derived the model based on phenomenological physical intuition. This paper discusses on the transport of a LIB in the dilute electrolyte model to obtain analytical solutions for half-cell cathode which has a flat discharge curve characteristic. This material offers cell potential that is almost constant until the particle is almost entirely discharge [9].

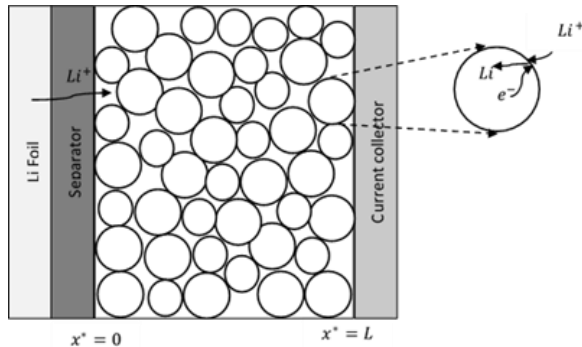


Fig. 1. A schematic diagram for a typical half-cell cathode in which a lithium-foil as the reference electrode (anode). Here  $x^* = 0$  is the separator and  $x^* = L$  is at cathode current collector collector.

The electrolyte model in [3], [4] describes conservation equations for the ions that diffuse by ionic concentration gradient and advect by an electric field. The charge transfer kinetics at the electrolyte/electrode particle interface is described by Butler Volmer equation [4], [6]. The electrolyte model couples with the diffusion of intercalated lithium in the electrode particle. The model discussed

in [5], [7], [8] describes the concentrated solution theory in the electrolyte.

## 2.0 THE DIMENSIONAL MODEL

The model used here is under approximation of charge neutrality in the dilute electrolyte except in a Debye layer near the electrolyte/electrode particle interface. The homogenisation technique has been used by Richardson et.al. [3] to account the microscale effects into the macro-scale problem. The resulting 1-dimensional advective-diffusion model is in the form used by Newman et.al. [4], [5]. The conservation equation of Lithium ion concentration and charge density are given by

$$\epsilon_v \frac{\partial c^*}{\partial t^*} - \frac{\partial}{\partial x^*} \left( BD(c^*) \frac{\partial c^*}{\partial x^*} \right) = (1 - t_+) b_{et} G^* \quad (1)$$

$$\frac{\partial j^*}{\partial x^*} = F b_{et} G^* \quad (2)$$

$$j^* = -\kappa^*(c^*) \left( \frac{\partial \phi^*}{\partial x^*} - 2 \frac{RT}{F} (1 - t_+) \frac{\partial \ln c^*}{\partial x^*} \right) \quad (3)$$

Note that the descriptions of the symbols appear in the equations are listed in Table 1. Here we require  $t_+ < 1$ . The last term in (1) represents the effect of Lithium ions entering the electrolyte via charge transfer of the chemical reaction at the electrolyte/electrode particles interface. Conservation of charge is given by the gradient of the average current density in the electrolyte,  $j^*$  (2) which is determined by where charge enters and leaves the electrolyte phase via surface reaction. We note that in the dilute electrolyte theory, the ion conductivity  $\kappa^*(c^*)$  in (3) is linearly proportional to the concentration of ion.

### Charge reaction at the electrolyte/electrode particles interface

The charge transfer,  $G^*$  is described by Butler Volmer equation which depends upon the concentration of intercalated Lithium, concentration of Lithium ions and the overpotential,  $(\phi^* - V^*)$  (between two phases (electrolyte and electrode particles). Here  $U_{eq}^*(c_s^*)$  is the open circuit potentials and is dependant on the intercalated lithium concentration  $c_s^*$ .

### The electrode particles

At the particle surface, the lithium is intercalated by the surface electrode reaction. Here, we assume that

the diffusion of intercalated lithium within the particle is fast due to sufficiently small electrode particles [2]. Furthermore, in nano-structured electrodes the intercalation reaction occurs predominantly at the surface of a particle [9, 10]. Hence, the conservation of lithium equation within a particle is

$$(1 - \epsilon_v) \frac{\partial c_s^*}{\partial t^*} = -b_{et} G^* \quad (5)$$

### Initial and boundary conditions

The boundary conditions for half-cell cathode during discharge are

$$\phi^*|_{x^*=0} = 0, \quad c^*|_{x^*=0} = C_0, \quad j^*|_{x^*=0} = -\frac{I^*}{A} \quad (6)$$

$$\frac{\partial c^*}{\partial x^*} \Big|_{x^*=L} = 0, \quad j^*|_{x^*=L} = 0 \quad (7)$$

We assume that the battery is initially in an equilibrium state with particles in the cathode are fully charged where

$$c^*|_{t^*=0} = C_0, \quad c_s^*|_{t^*=0} = 0 \quad (8)$$

We shall specify  $I^*$  as a constant input parameter in the discussed model (1)-(8) and determine the resulting time variation of the voltage across the battery,  $V^*$ , as the output (galvanostatic discharge).

Table 1. List of Symbols.

Parameter	Description	Parameter	Description
$D(c^*)$ ( $m^2 s^{-1}$ )	diffusivity of ions	$j^*(C s^{-1} m^{-2})$	Current density
$\epsilon_v$	volume fraction	$T$ (K)	Temperature
$c^*$ ( $mol m^{-3}$ )	concentration of Lithium ions	$A$ ( $m^2$ )	Cross-sectional area
$t_+$	transference number	$G^*$ ( $mol m^{-2} s^{-1}$ )	reaction kinetic at the interface
$t^*$ (s)	Time	$i_0(c^*, c_s^*)$ ( $Am^{-2}$ )	exchange current density
$F$ ( $C mol^{-1}$ )	Faraday's constant	$b_{et}$ ( $m^{-1}$ )	BET surface area
$R$ ( $J mol^{-1} K^{-1}$ )	universal gas constant	$c_s^*$ ( $mol m^{-3}$ )	intercalated lithium concentration
$V^*(JC^{-1})$	voltage of the cell	$U_{eq}^*(c_s^*)$ ( $JC^{-1}$ )	equilibrium potentials
$x^*$ (m)	length	$B$	Diffusion tensor
$\phi^*(JC^{-1})$	Electric potential in the electrolyte	$I^*(C s^{-1})$	The total charge

### 3.0 NONDIMENSIONALISATION

Here we assume that the diffusivity,  $D(c^*)$  and exchange current density,  $i_0$  are constant (see e.g. work by [5,11]). The non-dimensionalisation of (1) – (8) follows

$$\begin{aligned} x^* &= Lx, & c^* &= C_0 c, & c_s^* &= C_{s0} c_s, & t^* &= \tau t, \\ j^* &= \bar{j} j, & I^* &= \bar{I} \bar{I}, & & & & \\ \phi^* &= \bar{\Phi} \phi, & U_{eq}^* &= \bar{\Phi} U_c, & G^* &= \frac{\bar{J}}{L b_{et} F}, & V^* &= \bar{\Phi} V \end{aligned} \quad (9)$$

where  $L$  is the length of the half-cell,  $C_0$  is the initial concentration of ions,  $C_{s0}$  is the maximum concentration of intercalated lithium in the electrode,  $\bar{j}$  represents the typical current density,  $\bar{\Phi} = \frac{RT}{F}$  is the thermal voltage at room temperature and  $\bar{I}A$  represents the magnitude of the typical current. The discharge timescale,  $\tau$  is given by

$$\tau = \frac{L F C_{s0}}{\bar{J}} \quad (10)$$

where lithium is consumed at a rate of  $\frac{\bar{I}A}{F}$ . The dimensionless system is in the form

$$\Gamma \epsilon_v \frac{\partial c}{\partial t} - \frac{\partial^2 c}{\partial x^2} = \frac{1}{\gamma} G(c_s, \phi) \quad (11)$$

$$\frac{\partial j}{\partial x} = G(c_s, \phi),$$

$$\text{where } j = -\frac{\gamma c}{2t_+} \left( \frac{\partial \phi}{\partial x} - 2(1-t_+) \frac{\partial \ln c}{\partial x} \right) \quad (12)$$

$$(1 - \epsilon_v) \frac{\partial c_s}{\partial t} = -G(c_s, \phi) \quad (13)$$

$$G(c_s, \phi) = \Omega \left( e^{-\frac{1}{2}(\phi - V + U_c(c_s))} - e^{\frac{1}{2}(\phi - V + U_c(c_s))} \right) \quad (14)$$

$$\phi|_{x=0} = 0, \quad c|_{x=0} = 1, \quad j|_{x=0} = -\bar{I} \quad (15)$$

$$\frac{\partial c}{\partial x} \Big|_{x=1} = 0, \quad j|_{x=1} = 0 \quad (16)$$

$$c|_{t=0} = 1, \quad c_s|_{t=0} = 0 \quad (17)$$

where the dimensionless parameters are defined by

$$\gamma = \frac{DBFC_0}{\bar{J}L(1-t_+)}, \quad \Omega = \frac{Lb_{et}i_0}{\bar{J}}, \quad \Gamma = \frac{L\bar{J}}{DB_1F C_{s0}} \quad (18)$$

Here,  $\gamma$  is the maximum sustainable flux of ions in the electrolyte to the actual ion flux and  $\Omega$  is the dimensionless reaction rates. The BET surface area  $b_{et}$  and permeability tensor  $B$  are calculated by

$$b_{et} = \frac{\pi}{2a_0} [12], \quad B = \epsilon^{1.5} [7] \quad (19)$$

The size of the key dimensionless parameters if we take  $\bar{J} = 264m^{-2}$  (the dimensional parameters are listed in Table 2) are as follows

$$\gamma \approx 25, \quad \Omega \approx 10^{-3}, \quad \Gamma = 10^{-4} \quad (20)$$

Note that if the cell is discharged at a very slow rate, then  $\Gamma$  is estimated to be extremely small, therefore by neglecting the time derivative in (11) allows us to solve a quasi-steady state for the model.

### The Tafel approximation, $\Omega \ll 1$

During discharge  $\bar{I}(t) > 0$  and  $G < 0$  and of  $O(1)$ . At slow discharge rate,  $\Omega$  is small and hence, we the Butler Volmer equations is approximated by the Tafel equation

$$G(c_s, \phi) = -e^{\frac{1}{2}(\phi - v + u_c(c_s))} \quad (21)$$

provided that  $\log\left(\frac{1}{\Omega}\right) \gg 1$ . This approximation allows us to obtain analytical solution.

### The Quasi steady approximation, $\Gamma \rightarrow 0$

At slow discharge rate,  $\Gamma$  is significantly small, hence (11) – (12) become

$$\frac{\partial^2 c}{\partial x^2} = -\frac{1}{\gamma} G(c_s, \phi) \quad (22)$$

$$\frac{1}{2t_+} \frac{\partial}{\partial x} \left( c \frac{\partial \phi}{\partial x} - 2(1 - t_+) \frac{\partial c}{\partial x} \right) = -\frac{1}{\gamma} G(c_s, \phi), \quad (23)$$

By equating these two equations, integrating the resulting equations in  $x$  and applying boundary conditions (15b) - (16) we obtain

$$c = e^{\phi(x)} \quad (24)$$

Substituting (24) into (11) – (13) and (21), we obtain an ODE system as follows

$$\frac{\partial^2 c}{\partial x^2} = -\frac{1}{\gamma} G(c_s, c), \quad G(c_s, c) = -\sqrt{c} e^{-\frac{1}{2}(v - u_c(c_s))} \quad (25)$$

$$c|_{x=0} = 1, \quad \frac{\partial c}{\partial x}|_{x=0} = -\frac{\bar{I}}{\gamma}, \quad \frac{\partial c}{\partial x}|_{x=1} = 0 \quad (26)$$

$$(1 - \epsilon_v) \frac{\partial c_s}{\partial t} = -G(c_s, c), \quad c_s|_{t=0} = 0 \quad (27)$$

### Flat discharge curve approximation

Under assumption of a flat discharge curve cathode material (e.g. LiFePO<sub>4</sub>) so that  $U_c(c_s) = U_0$  when  $c_s < 1$  and it drops to infinity if  $c_s \geq 1$ . We expect that the Lithium intercalation into particles in the region near separator is faster than in other parts of electrode. This leads to a free boundary problem, where the boundary  $x = s(t)$  is the front between a fully intercalated region ( $c_s = 1$ ) and partially intercalated region ( $c_s < 1$ ). Thus, the reaction equation  $G$  for the free boundary problem

Table 2. Parameter values used in the model.

Parameter	Value	Parameter	Value
$D$ ( $m^2 s^{-1}$ )	$5.34 \times 10^{-10}$ [8]	$T$ (K)	298 [8]
$\epsilon_v$	0.4764	$A$ ( $m^2$ )	$10^{-4}$ [8]
$C_0$ ( $mol m^{-3}$ )	1000 [11]	$a$ (m)	$5.2 \times 10^{-8}$ [14]
$t_+$	0.38 [13]	$i_0$ ( $Am^{-2}$ )	$5.4 \times 10^{-5}$ [8]
$L$ (m)	$6.25 \times 10^{-5}$ [8]	$b_{et}$ ( $m^{-1}$ )	$5 \times 10^7$
$F$ ( $C mol^{-1}$ )	96487 [8]	$C_{s0}$ ( $mol m^{-3}$ )	20950 [8]
$R$ ( $J mol^{-1} K^{-1}$ )	8.3144 [8]		

### 3.1 ANALYTIC SOLUTIONS

We obtain analytic solutions for ODE system (25) – (26) where the solutions are divided into two regimes; before and after free boundary develop. The analytic solutions are in the form of hypergeometric functions,  $H(x)$  which are given by

Solution before free boundary develop;

$$x = -\frac{i}{2} \sqrt{\frac{3\gamma}{K}} c(1)^{-\frac{3}{4}} [c(x)H(c(x)) - H(1)] \quad (28)$$

Solution after free boundary develop;

$$x = \begin{cases} -\frac{\gamma}{\bar{I}}(c(x) - 1), & \text{for } x \leq s(t) \\ -\frac{i}{2} \sqrt{\frac{3\gamma}{K}} c(1)^{-\frac{3}{4}} \sqrt{c(s(t))^{\frac{3}{2}} - c(1)^{\frac{3}{2}}} [c(x)H(c(x)) - c(s(t))H(c(s(t)))] & \text{for } x > s(t) \end{cases} \quad (29)$$

where  $H$  is hypergeometric function and  $K$  and  $V$  are given by

$$K = e^{\left(-\frac{1}{2}(v - u_0)\right)}, \quad (30)$$

$$H(x) = H_2F_1\left(\frac{2}{3}, \frac{1}{2}, \frac{5}{3}, \left(\frac{x}{c(1)}\right)^{\frac{3}{2}}\right) \quad (31)$$

The resulting analytic solution describes that for fixed  $\bar{I}$ , the cell potential decreases with time as  $s(t)$  increases with time and  $c(x, t)$  decreases with  $x$ .

### Numerical procedure

The half-cell model for  $c$  is solved using Matlab 'bvp4c'. Newton method is used for the accuracy of the approximations as we specify  $\bar{I}$  and the electrode particles equation,  $c_s$  is solved using Forward Euler Method.

## 4.0 RESULTS AND DISCUSSION

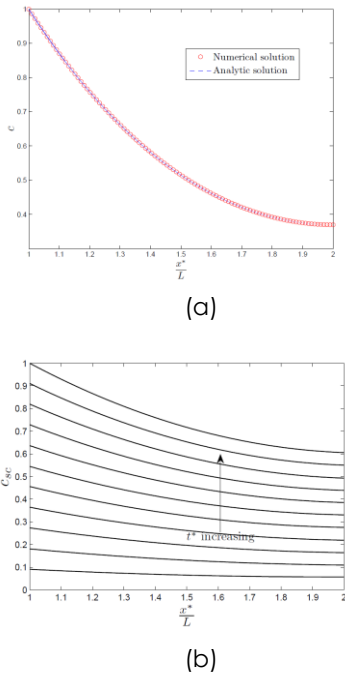


Fig. 1. (a) Dimensionless electrolyte concentration profiles before the free boundary develops by analytical solution (31) and numerical simulation at  $\bar{I} = 1$  across the cell. (b) Dimensionless Lithium concentration distribution in the electrode particles at  $\bar{I} = 1$  across the cell before the free boundary develops. Here  $\hat{t} = 0.55$ .

Before we discuss the results further, we first validate the analytical solution (31) against the numerical simulation in Figure 2(a). The results are presented as a function of the dimensionless thickness of the cell,  $x^*/L$ , where  $x = 0$  is the separator and  $x = 1$  is the cathode current collector. It is observed that the numerical procedure predicts the concentration profiles accurately.

Initially, the concentration of electrolyte is uniform as time increases, until the free boundary develops at time,  $t = \hat{t} \approx 0.05$ . Figure 2(b) shows the concentration in the electrode particles  $c_s$  before the development of free boundary. The figure shows that the rate of lithium intercalation into particles is higher in the region near the separator as compared in other parts of the electrode.

Figure 3. shows that the free boundary for  $t > \hat{t}$  propagates in from the separator. In the region  $x < s(t)$ ,  $c(x)$  (refer to (29)) has a linear concentration profile while for  $x > s(t)$  the particles are still intercalating lithium ions (see Figure 3(a)). As the discharge proceeds, the movement of the free boundary across the electrode is clearly seen in this figure. At higher discharge rate, the intercalation rate is much faster in the region near the separator (see Figure 4).

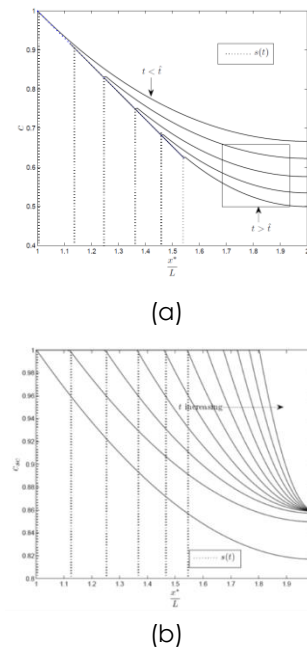


Fig. 3. (a) The dimensionless electrolyte concentration profiles across the cell in comparison to the time before ( $t < \hat{t}$ ) (31) and after ( $t > \hat{t}$ ) (37) formation of free boundary. (b) The dimensionless concentration of lithium in the electrode particles that reaches maximum capacity at  $x = s(t)$ . The profiles are discharged at  $\bar{I} = 0.5$ . The arrow shows the direction of increasing time and  $\hat{t} = 0.64$ .

At large discharge rates, a further boundary develops near to the current collector ( $x = 1$ ) where the electrolyte is driven to zero as shown in Figure 4, hence limit the cell from discharging further.

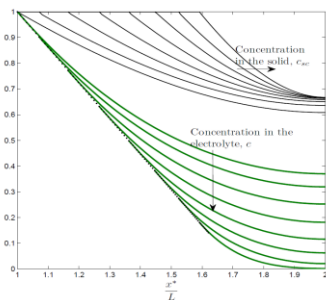


Fig. 4. The dimensionless concentration of Lithium in the electrode particles and Lithium ions in the electrolyte at  $\bar{I} = 1$  discharge rate. The time increase in the direction shown by the arrows.

## 5.0 CONCLUSION

A detailed model for a lithium ion battery based on dilute electrolyte theory has been discussed. The model took into account the intercalation reactions at the electrolyte/electrode particles surface. The macroscopic model was solved in a half cell cathode material with flat discharge curves characteristic. Asymptotic approximations allow us to obtain the quasi-steady state equations and to approximate the Butler Volmer reaction kinetics with simple Tafel kinetics as the reaction rate at the particle surface. The half-cell cathode system develops a free boundary problem dividing the system into two regions, the region where the particles are fully discharged and the region where the particles are partially discharged. We obtained analytic solutions for the electrolyte concentration,  $c$ ; before and after the development of free boundary in a quasistatic regime. The concentration of electrolyte is uniform before the free boundary develops and is decreasing as the time increases after the free boundary develops. Lithium intercalates into particles near the separator faster than in other parts of the electrode. At high discharge currents, the rate of Lithium ion depletion faster compare to low current. The electrolyte concentration was found to zero near the current collector, thereby preventing the solid particles to further discharge. This study can be extended to a moderately dilute solution.

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