Toward the analytical model of SEI formation and development in lithium-ion battery: The case of solution of the nonlinear transport equation

Gunawan Nugroho\textsuperscript{1}, Nur Laila Hamidah\textsuperscript{1}, Fu-Ming Wang\textsuperscript{2}

\textsuperscript{1} Department of Engineering Physics, Institut Teknologi Sepuluh Nopember, Kampus-ITS-Sukolilo, Surabaya 60111, Indonesia
\textsuperscript{2} National Taiwan University of Science and Technology, No. 43, Section 4, Jilong Rd, Da’an District, Taipei City 10607, Taiwan

E-mail: gunawan@ep.its.ac.id, gunawanf317@gmail.com

Abstract. The nonlinear lithium-ion transport equation with variable diffusion coefficient is considered in this research. The solution is produced by transforming the second order spatial variable into the first order differential in, $\xi$. The method of characteristics is then implemented for covering the initial-boundary conditions. Several interesting results are obtained after the calculating the generated solution. It is found that dendrite formation is detected after 100 s which is considered as steady operation. In this case, the concentration ratio is smaller than boundary value at the top surface and the ratio of tip and surface current is high. Also the development of dendrite length is investigated to support the insight from the analytical model.

1. Introduction

Lithium ion battery (LIB) becomes the most popular types of rechargeable battery for many electronic applications and it gained increasing attention as an important device for electric vehicles and power storage systems. The LIB performance is measured by several important parameters such as high energy density, no memory effect, high stability, rapid charge performance, low cost and life cycle, respectively [1].

The problem of advancing the lithium battery is significantly affected by the formation of dendritic growth during electro disposition – electro dissolution cycles [2]. The SEI (Solid Electrolyte Interphase) formation causes several drawbacks such as density loss due to release of the lithium crystal and even explosion. Hence, an understanding a dendrites evolution is important from the practical point of view. Some experimental and theoretical works were conducted to gain the understanding of the dendrites growth [3,4]. The works conclude that the formation is mainly caused by the current distribution on the lithium surface. Meanwhile, theoretical studies through the solutions of the governing equations often play a special role in the description and prediction of the dendrites growth. They are found able to describe the detailed behavior of the concerning systems and facilitate a proper understanding, paving the way to correct solutions by combining with the experimental data [5].

The main difficulty of the governing equations is the contribution of the variable diffusion which then forms nonlinear terms representing an actual laboratory data and render difficulty to the conventional analysis in general cases. However, it is not surprising that they attract many efforts until
recently, since the simplified solution of this nonlinear problems still supplements the considerable results [6]. Concerning to the simplified solutions, there are some works have already been conducted in the literatures. One of them is the simulation of the three discharge/charge rates until the rated capacity is irreversibly lost in side reactions. It is concluded that the degradation is faster due to SEI accumulation in negative electrode [7]. The potential drop across the SEI layer is also investigated by assuming that the capacity fading is driven by solvent reaction at film interphase [8]. It is found that moderate potential drop will substantially increase capacity fade.

The analysis based on the variable porosity model is also implemented for a lithium battery. The work proposes a novel mass balance model to predict the volume fraction variation due to lithium deposition [9]. The model quantifies the loss of unprotected anode and helps the required pre-lithiation. The procedure for obtaining the solutions is derived in a quite complicated way which is based on the implementation of kinetics equations. The resulting expression is then integrated the current density which then compared with the applied current. However, the results are not considerably differs with the simplified analysis.

Accordingly, this work investigates the transient one-dimensional diffusion equation with variable diffusion coefficient. The method of characteristics is utilized by transforming the coordinate of the second order term. The solution is then supplemented by algebraic reaction models to determine the current density where dendrite tip grow at and the dendrite length.

2. The transport equation and its solution
The mass conservation of the transient one-dimensional lithium transport is,
\[ \frac{\partial C}{\partial t} = \frac{\partial}{\partial x} \left( D \frac{\partial C}{\partial x} \right) - \frac{i \Delta t}{z F} \]
(1a)
where, \( C \) is a time dependent concentration, \( D \) is concentration-dependent diffusion coefficient, \( t \) is the Li\(^+\) transport number, \( z \) is charge number and \( i \) is the current density. In this research the diffusion coefficient is defined by the following equation,
\[ D = ae^{-bc} \]
(1b)
with \( a = 2.582 \times 10^{-5} \text{ cm}^2\text{s}^{-1} \) and \( b = 2.856 \text{ M}^{-1} \) as determined experimentally [2]. Hence, the transport equation becomes,
\[ \frac{\partial C}{\partial t} = \frac{\partial}{\partial x} \left( ae^{-bc} \frac{\partial C}{\partial x} \right) - \frac{i \Delta t}{z F} \]
(1c)
Equation (1c) is supplemented by the following initial and boundary values,
\[ C = C_i \]
\[ t = 0: \]
\[ At \ x = 0: \ D \frac{\partial C}{\partial x} = \frac{i_f(1-t_f)}{n F} \]
(1d)
\[ x = \delta: \ C = C_0 \]
where \( i_f \) is the time-dependent current density on the flat Li surface and \( C_0 \) is the bulk concentration.

The solution of equations (1c) & (1d) is then substituted into,
\[ \frac{i_t}{i_f} = \left( \frac{C_0}{C_i} \right) \frac{ae}{n} \]
(2)
as the ratio of the dendrite tip current density to the current density of flat surface. In this case the parameter value is \( a_c = 0.2 - 0.4 \). Since \( i_t \) is defined, the dendrite length can be calculated as,
\[ h = \frac{M}{nP} \int_0^t i_t dt \]
(3)
The step now is to consider equation (1c), suppose that $B = e^{-bc}$, equation (1c) is then transformed into,

$$\frac{\partial B}{\partial t} = aB \frac{\partial^2 B}{\partial x^2} + b \frac{i\lambda}{z_F} B$$  \hspace{1cm} (4a)

Let, $\frac{\partial^2 B}{\partial x^2} = \frac{\partial B}{\partial \xi}$, the solution is,

$$B = e^{a\xi} \left( a_2 \cosh a_4 x + a_3 \sinh a_4 x \right)$$  \hspace{1cm} (4b)

Equation (4a) is then becomes,

$$\frac{\partial B}{\partial t} = aB \frac{\partial B}{\partial \xi} + b \frac{i\lambda}{z_F} B$$  \hspace{1cm} (4c)

Suppose there is a function $r = r(t, \xi)$ such that, $\frac{dB}{dr} = \frac{\partial t}{\partial r} \frac{\partial B}{\partial \xi} + \frac{\partial \xi}{\partial r} \frac{\partial B}{\partial \xi}$, the characteristics are expressed as,

$$r = t \text{ and } \xi = -abr + \xi_0 \text{ or } \xi = -abr + \xi_0$$  \hspace{1cm} (5a)

The solution of equation (4c) is then,

$$B = B_0 e^{\frac{i\lambda}{z_F} r} \text{ or } B = F(\xi_0) e^{\frac{i\lambda}{z_F} \xi_0}$$  \hspace{1cm} (5b)

Unfortunately the function, $\xi_0$ cannot be extracted explicitly without choosing $F(\xi_0)$, the simplest case is, $F(\xi_0) = \xi_0$ and equation (5b) becomes,

$$\xi = -a\xi_0 e^{\frac{i\lambda}{z_F} t + \xi_0}$$  \hspace{1cm} (5c)

The expression for $\xi_0$ is then,

$$\xi_0 = \xi \left( 1 - ae^{\frac{i\lambda}{z_F} t} \right)^{-1}$$  \hspace{1cm} (5d)

The step now is to determine $\xi$ by substituting (4b) and (5d) into equation (5b) as,

$$B = \xi \left( 1 - ae^{\frac{i\lambda}{z_F} t} \right)^{-1} e^{\frac{i\lambda}{z_F} \xi} = e^{a\xi} \left( a_2 \cosh a_4 x + a_3 \sinh a_4 x \right) \text{ or }$$

$$-a_3 \xi \cosh a_4 x$$

which solution is a Lambert W-function as,

$$\xi = \frac{1}{a_1} \left[ \frac{ae^{\frac{i\lambda}{z_F} \xi}}{at - e^{\frac{i\lambda}{z_F} \xi}} \right] a_1 \left( a_2 \cosh a_4 x + a_3 \sinh a_4 x \right)$$  \hspace{1cm} (6a)

Therefore, the solution of the diffusion equation is,

$$C = \frac{1}{b} \ln \left[ \frac{1}{a_1} \left( 1 - ae^{\frac{i\lambda}{z_F} t} \right)^{-1} e^{\frac{i\lambda}{z_F} \xi} W \left[ \frac{ae^{\frac{i\lambda}{z_F} \xi}}{at - e^{\frac{i\lambda}{z_F} \xi}} \right] a_1 \left( a_2 \cosh a_4 x + a_3 \sinh a_4 x \right) \right]$$  \hspace{1cm} (6c)

Implementing initial condition will produce the following expression,

$$C_i = \frac{1}{b} \ln \left[ \frac{1}{a_1} W \left[ a_1 \left( a_2 \cosh a_4 x + a_3 \sinh a_4 x \right) \right] \right] \text{ or }$$
\[ (a_2 \cosh a_4 x + a_3 \sinh a_4 x) = e^{-bC} \exp (a_0 e^{-bC}) \] (7a)

Thus, by assuming that \( a_4 = \frac{\pi}{\delta} \), the case of boundary conditions is formulated as in the following,

\[ i_f (1-t_z) \frac{1}{b} \left[ \frac{a_3}{a_1 a_2} \left( \frac{b}{z + F} \right)^{-1} \frac{e^{-b \frac{h_2}{z + F} t}}{e^{z + F}} \right] W \left[ \left( \frac{at - e^{-b \frac{h_2}{z + F} t}}{z + F} \right) a_1 a_2 \right] \]

\[ + W \left[ \left( \frac{at - e^{-b \frac{h_2}{z + F} t}}{z + F} \right) a_1 a_2 \right] \]

or

\[ i_f (1-t_z) \frac{1}{b} \left[ \frac{a_3}{a_1 a_2} \left( \frac{b}{z + F} \right)^{-1} \frac{e^{-b \frac{h_2}{z + F} t}}{e^{z + F}} \right] W \left[ \left( \frac{at - e^{-b \frac{h_2}{z + F} t}}{z + F} \right) a_1 a_2 \right] \]

Substituting \( D \) into (7b) we have,

\[ i_f (1-t_z) \frac{1}{b} \left[ \frac{a_3}{a_1 a_2} \left( \frac{b}{z + F} \right)^{-1} \frac{e^{-b \frac{h_2}{z + F} t}}{e^{z + F}} \right] W \left[ \left( \frac{at - e^{-b \frac{h_2}{z + F} t}}{z + F} \right) a_1 a_2 \right] + W \left[ \left( \frac{at - e^{-b \frac{h_2}{z + F} t}}{z + F} \right) a_1 a_2 \right] \]

The third boundary condition will produce,

\[ C_0 = -\frac{1}{b} \ln \left[ \frac{a_3}{a_1} \left( \frac{b}{z + F} \right)^{-1} \frac{e^{-b \frac{h_2}{z + F} t}}{e^{z + F}} \right] W \left[ \left( \frac{at - e^{-b \frac{h_2}{z + F} t}}{z + F} \right) a_1 a_2 \right] \]

The step now is to consider equations (7c) and (7d), perform \( a_2 \) from (7d) as,

\[ a_2 = -0.0866 e^{-bC_0} \exp \left( \frac{a_0 e^{-bC_0}}{e^{z + F} - at} - a_3 \right) \] (8a)

Substituting the result into (7c), the expression for \( a_3 \) is defined in implicit form as,

\[ a_3 = \frac{i_f (t_z - 1) a_0}{b \delta \pi} \left( e^{-b \frac{h_2}{z + F} t} - at \right) \left[ W \left( \left( \frac{at - e^{-b \frac{h_2}{z + F} t}}{z + F} \right) a_1 a_2 \right) \right]^{-1} + 1 \] (8b)

The complete solution of the diffusion equation is then,

\[ C(x,t) = -\frac{1}{b \delta \pi} \left( \frac{\delta}{\pi} \right)^2 \left( \frac{b}{z + F} \right)^{-1} \frac{e^{-b \frac{h_2}{z + F} t}}{e^{z + F}} \left[ \left( \frac{at - e^{-b \frac{h_2}{z + F} t}}{z + F} \right) a_1 \left( a_2 \cosh \frac{\pi}{\delta} x + a_3 \sinh \frac{\pi}{\delta} x \right) \right] \] (8c)

Therefore, the ratio of the current tip density to the current density on the surface is,

\[ \frac{i_t}{i_f} = \left[ \frac{1}{b \delta \pi} \left( \frac{\delta}{\pi} \right)^2 \left( \frac{b}{z + F} \right)^{-1} \frac{e^{-b \frac{h_2}{z + F} t}}{e^{z + F}} \left[ \left( \frac{at - e^{-b \frac{h_2}{z + F} t}}{z + F} \right) a_1 \left( a_2 \cosh \frac{\pi}{\delta} x + a_3 \sinh \frac{\pi}{\delta} x \right) \right] \right]^{-1} \] (9a)

And the dendrite length is,
\[
    h = -\frac{M}{n\rho F} \int_0^t \left[ -\frac{1}{bC_j} \ln\left( \frac{\delta}{\pi} \right)^2 \left( 1 - ae^{-\frac{iN}{zF}} \right)^{-1} e^{\frac{iN}{zF}} W \left[ \left( at - e^{-\frac{iN}{zF}} \right) a_1 \left( a_2 \cosh \frac{\pi}{\delta} x + a_3 \sinh \frac{\pi}{\delta} x \right) \right] \right] \, dt
\]

(9b)

3. The example of dendrite formation and development
SEI is formed on the surface during the first charge and discharge cycle which is the product of solvent molecules decomposition and intercalation into the planes. The presence of SEI will decrease density stability of the LIB. In this study, the SEI formation is influenced by the presence of electrolyte additive, which is parametrized as, \( \alpha_c \). In this section the SEI formation will be evaluated according to the solution of the nonlinear diffusion equation and the parameter values are taken from Alokar [2], except the value of parameter \( b \) is adjusted into 18560 M\(^{-1}\)

![Figure 1](image_url)

**Figure 1.** The behavior of the lithium concentration within the layer, \( \delta \). The result is at the steady battery operation, 100 s.

Figure 1 depicts the evolution of the lithium concentration within the thin layer, revealing the condition that the concentration is approaching the initial value at the steady operation. The figure also indicates that the SEI formation already affects battery performance since the concentration at the top layer is smaller than the initial value.
Figure 2. The behavior of tip current within the layer, $\delta$, at the steady battery operation, 100 s.

On the other hand, the result of current ratio shows that the tip current increase with the presence of dendrite (SEI) formation as described in figure 2. The current result is consistent with the concentration since the current on the surface layer is higher than surface current.

Moreover, in order to realize the thickness of SEI formed within the layer, the thickness is also calculated according to the solution of the transport equation. In this case, the value $\alpha_c = 0.2$ is implemented.

Figure 3. The development of dendrite length for a current density of 0.2 mA cm$^{-2}$ until steady time operation, 100 s.

Figure 3 shows that the SEI formation is higher for higher concentration ratio which indicates the rate of dendrite development is affected by the operating conditions and lower current ratio correspond to faster dendrite formation. However, the experimental data of dendrite length is commonly spread in several values for a single concentration ratio, and the model based on the solution of the nonlinear
transport equation can be a valuable insight about the kinetic mechanism in understanding the dendrite growth.

4. Conclusions
The solution of the one-dimensional time dependent transport equation is produced in this research. The variable diffusion coefficient is considered which the parameters are provided by the experimental data from the literatures. The characteristic method is utilized for generating solution in term of Lambert function. The calculation examples in steady state condition show that the concentration ratio is suppressed at the top layer, $\delta$, which indicate the SEI formation. The result is also supported from the tip to surface current ratio which decreasing toward the top layer.

Acknowledgment
The authors are grateful for financial support from the Institut Teknologi Sepuluh Nopember under contract no: 850/PKS/ITS/2017.

References
[1] Hamidah NL and Wang F-M 2013 *National Taiwan University of Science and Technology* 1–155
[2] Alokar R 2013 Mathematical model of the dendritic growth during lithium electrodeposition *Journal of Power Sources* **232** p 23 – 28
[3] Fan L-Z, Wang X-L and Long F 2009 All-solid-state polymer electrolyte with plastic crystal materials for rechargeable lithium-ion battery *Journal of Power Sources* **189** p 775–778
[4] Zhang SS 2006 A review on electrolyte additives for lithium-ion batteries *Journal of Power Sources* **169** p 1379–1394
[5] Kasavajjula U, Wang C and Appleby AJ 2007 Nano- and bulk-silicon-based insertion anodes for lithium-ion secondary cells *Journal of Power Sources* **163** p 1003–1039
[6] Chada TS, Suthar B, Rife D, Subramanian VR and Biswas P 2017 Model based of one-dimensional oriented lithium-ion battery electrodes *Journal of Electrochemical Society* **164** (11) p 3114 – 3121
[7] Rashid M and Gupta A 2014 Mathematical model of combined effect of SEI formation and gas evolution in li-ion batteries *ECS Electrochemistry Letters* **3** (10) p 95 – 98
[8] Phul S, Deshpande A and Krishnamurthy B 2015 A mathematical model to study the effect of potential drop across the sei layer on the capacity fading of a lithium ion battery *Electrochimica Acta* **164** p 281 – 287
[9] Ashwin TR, McGordon A and Jennings PA 2017 A mass transfer based variable porosity model with particle radius change for a lithium-ion battery *Electrochimica Acta* **232** p 203 – 214