Short communication

Modeling of electrochemical intercalation of lithium into a LiMn$_2$O$_4$ electrode using Green function

Mohd Rafie Johan [a,*], Abdul Kariem Arof [b]

[a] *Department of Mechanical Engineering, University of Malaya, Kuala Lumpur 50603, Malaysia*
[b] *Department of Physics, University of Malaya, Kuala Lumpur 50603, Malaysia*

Abstract

A mathematical model is presented for a lithium ion cell under galvanostatic discharge. The non-homogeneous material balance equation for the solution phase of a lithium cell was solved analytically using Green's function. We determined the elementary solutions, the norms and the eigen values of the problems for galvanostatic boundary conditions and systematically tabulate the resulting expressions. The solution has been obtained in a closed form expression.
© 2007 Elsevier B.V. All rights reserved.

1. Introduction

The use of mathematical modeling in the design of battery systems has a long history. Macroscopic models of the current and potential distribution in porous battery electrodes were first developed in the late 1950s [1,2]. Major strides towards understanding the behaviour of porous electrodes were made in the early sixties with the development of porous electrode theory [3] which generalized earlier modeling efforts into a macro-homogeneous modeling framework that is still used in most present day models. In the early seventies, the scope of battery modeling increased from treating a single electrode to modeling the full-cell sandwich including two electrodes and the separator by numerical computation [4,5]. This modeling approach allowed the treatment of complicated interactions between a wide variety of phenomena that had previously been studied separately under limiting conditions.

The earliest model for lithium-ion processes in the composite insertion electrode was developed in the 1980s [6–8]. The model covers only a single porous electrode. It does not have the advantages of a full-cell sandwich model for the treatment of complex interacting phenomena between the cell layers and utility for design purposes. Doyle et al. [9,10] have developed a very general one-dimensional model applicable to almost any of the existing Li/Li$^+$ systems. Their model uses the porous electro theory developed by Newman [5] to describe the potential variations in the solid and solution phases. The material balance in the solution phase is described using the concentrated solution theory and in the solid phase using a Fickian diffusion equation in spherical coordinates. Confining only to thermal conditions, the authors validated their model by demonstrating good agreement with experimental data. Later, this model has been extended to include an energy balance in order to predict cell temperature [11–13]. The problems encountered with Li-ion systems like poor rate capability, thermal runaway, occurrence of undesired side reactions and capacity fade have been addressed in 2002 using the new model [14].

Numerical techniques such as the finite element method and finite difference method allow results of a high accuracy but they demand extensive computing time. Analytical solutions are the best if available due to the solutions being continuous in the independent variables and show explicitly how the parameters of the system are involved. The solutions give much insight into a system, which is one of the primary objectives of modeling. Unfortunately, analytical solutions are not available for most of cases of interest. It is specific to the system, geometry and boundary conditions. Usually, analytical solu-

* Corresponding author. Tel.: +60 379676873; fax: +60 379675317.
  E-mail addresses: mrafiej@um.edu.my (M.R. Johan), akarof@um.edu.my (A.K. Arof).

Nomenclature

a	specific interfacial area ($m^2 m^{-3}$)
c	dimensionless concentration
c_i	concentration of species i ($mol\, m^{-3}$)
$D_{i,\text{eff}}$	effective coefficient diffusion of species i ($m^2\, s^{-1}$)
F	Faraday's constant (996,487 C cq^{-1})
I	superficial current density (A m^{-2})
j_n	pore-wall flux of lithium ion ($mol\, m^{-2}\, s^{-1}$)
J	dimensionless flux
L	thickness of the cell (m)
L_c	thickness of the cathode (m)
L_s	thickness of the separator (m)
N_i	molar flux of species i ($mol\, m^{-2}\, s^{-1}$)
r	dimensionless thickness of the cell/separator
t	time (s)
t_i	transference number of species i
x	distance from the separator/positive electrode boundary (m)
y	dimensionless distance along x-axis
z_i	charge per mole

Greek letters

ε	porosity of electrode
λ_n	eigen value
τ	dimensionless time
Ψ	dimensionless concentration (for homogeneous equation)

Subscripts

I	1, 2, . . .
n	0, 1, 2, . . .
eff	effective
+	positive electrode
Li	lithium
c	cathode
s	separator or solid phase

tion process of Li/Li$^+$ into a spherical particle of graphite/cobalt oxide immersed in a conductive electrolyte using finite integral transform method. In his work, Liu applied pseudo-steady-state condition in order to guarantee a uniform convergence of the solution.

The objective of this paper is to demonstrate a method of Green's function in solving material balance equation in solution phase of electrochemical system. The Green's function approach is a powerful technique for finding solutions to linear, homogeneous and non-homogeneous partial differential equations [21–27]. To our best knowledge, Green's function approach has not been used for the lithium battery systems.

2. Specific capacity of lithium ion cell

In this work, a model has been developed for a galvanostatic discharge behaviour of a Li/LiMn$_2$O$_4$ as shown in Fig. 1. During the discharge process, lithium ions de-intercalate from the anode diffuse through the separator and intercalate into the cathode. For this work, the cathode is closely packed electrode employing a LiMn$_2$O$_4$ active material. For one-dimensional transport of lithium ions in a porous composite cathode with active materials, the material balance equation for species i an be written as

$$\frac{\partial(\varepsilon c_i)}{\partial t} = -\nabla N_i + a j_n (1 - t_i) \tag{1}$$

where ε is the porosity and is considered to be constant, c_i the concentration of the species i, N_i the species flux, a the species interfacial area, j_n the pore wall flux across the electrolyte active material interface and t_i is the transference number of species i. From the concentrated solution theory [5], the series flux is

$$N_i = -\varepsilon D_{i,\text{eff}} \nabla c_i + \frac{t_i I}{z_i F} \tag{2}$$

where I is the electrical current density and $z_i F$ is the charge per mole. The term $D_{i,\text{eff}}$ is the effective diffusion coefficient of
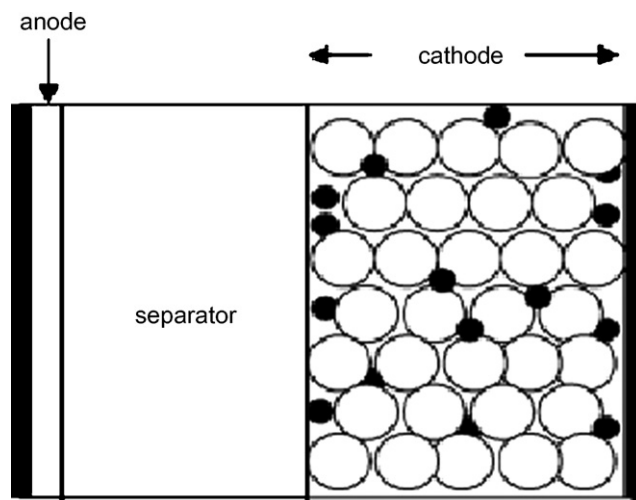
tions are restricted to linear equations with linear boundary conditions. In 1979, Atlung et al. [6] solved the diffusion equation for solid solution cathodes with zero initial concentration using Laplace transformation technique. In 1997, Doyle and Newman [10] solved a similar model for the discharge lithium batteries under steady-state condition using the method of separation of variables. In 2001, Subramaniam and White [15] used an extended method of separation of variables for different electrode geometries with galvanostatic boundary conditions at zero initial concentration. This was followed by the work of Hashim et al. [16,17] who solved the material balance equation in lithium-ion batteries with non-zero initial concentration by using Laplace transform. In 2004, Johan and Arof [18,19] presented analytical solutions for lithium intercalation in different cathode geometries using integral transform technique. Recently, Liu [20] presented an analytical result of the intercala-

Fig. 1. Schematic representation of lithium-ion battery.

species i defined by $D_{i,\text{eff}} = D_i \varepsilon^{3/2}$ [17], where D_i is the diffusion coefficient of species i in the electrolyte. Substituting Eq. (2) into Eq. (1) gives

$$\varepsilon \frac{\partial c_{\text{Li}}}{\partial t} = -\nabla(-\varepsilon D_{i,\text{eff}} \nabla c_i) - \nabla \left(\frac{It_i}{z_i F} \right) + aj_n(1 - t_i) \quad (3)$$

Since i is a lithium ion species, then $t_i = t_{\text{Li}} = t_+ = 0.2$ [10]. We can further simplify Eq. (3) as

$$\frac{\partial c_{\text{Li}}}{\partial t} = \varepsilon^{1/2} D_{\text{Li}} \frac{\partial^2 c_{\text{Li}}}{\partial x^2} + \frac{aj_n(0.8)}{\varepsilon} \quad (4)$$

The distribution of reaction rate in the porous electrode is a complex process. It reflects the solution-phase concentration variations as well as the trade-off between ohmic and kinetic resistances. When using an insertion material having an open circuit potential that depends strongly on the state of charge of the system, a uniform current distribution results [28]. Other than that, a uniform current distribution can be expected when kinetic resistances dominate ohmic resistances [5]. According to [10], for a uniform current distribution, it is possible to assume that the pore wall flux across the electrolyte–intercalation material interface is given by its average value at any point in the porous electrode. Hence

$$j_n = -\frac{I}{aFL_c} \quad (5)$$

where L_c is the thickness of the cathode and I is the discharge current. Introducing the dimensionless parameters

$$c = \frac{c_{\text{Li}}}{c_{\text{Li,O}}}, \qquad y = \frac{x}{L_s}, \qquad r = \frac{L}{L_s}, \qquad \tau = \frac{D_{\text{Li}}t}{L_s^2} \quad (6)$$

Substituting Eq. (6) into Eq. (4) gives

$$\frac{\partial c}{\partial \tau} = \varepsilon^{1/2} \frac{\partial^2 c}{\partial y^2} + J, \quad \tau > 0, \; 1 \le y \le 1 + r \quad (7a)$$

Subjected to the boundary and initial conditions

$$\frac{\partial c}{\partial y} = 0, \quad \tau > 0, \; 1 \le y \le 1 + r \quad (7b)$$

$$\frac{\partial c}{\partial y} = \frac{Jr}{\varepsilon^{1/2}}, \quad \tau > 0, \; y = 1 \quad (7c)$$

$$c(y, 0) = 1 \quad (7d)$$

where dimensionless flux is

$$J = \frac{a(0.8)L_s^2 j}{\varepsilon Dc_{\text{Li,O}}} \quad (8)$$

We solved Eq. (7) by using Green function. The homogeneous version of Eqs. (7a)–(7d) are:

$$\frac{\partial^2 \psi}{\partial y^2} = \frac{1}{\varepsilon^{1/2}} \frac{\partial \psi}{\partial \tau}, \quad \tau > 0, \; 1 \le y \le 1 + r \quad (9a)$$

subject to the boundary and initial conditions

$$\frac{\partial \psi}{\partial y} = 0, \quad \tau >, \; y = 1 + r \quad (9b)$$

$$\frac{\partial \psi}{\partial y} = 0, \quad \tau > 0, \; y = 1 \quad (9c)$$

$$\psi(y, 0) = F(y) = 1 \quad (9d)$$

The solution for the homogeneous Eqs. (9a)–(9d) is

$$\psi(y, \tau) = \sum_{n=0}^{\infty} A_n X(\lambda_n, y) e^{-\lambda_n^2 \tau} \quad (10)$$

where the unknown constant given as

$$A_n = \frac{1}{N(\lambda_n)} \int_1^{1+r} X(\lambda_n, y') F(y') \, dy' \quad (11)$$

and the norm is

$$N(\lambda_n) = \int_1^{1+r} [X(\lambda_n, y')]^2 \, dy \quad (12)$$

Hence, Eq. (10) becomes

$$\psi(y, \tau) = \sum_{n=0}^{\infty} \frac{e^{-\lambda_n^2 \tau}}{N(\lambda_n)} X(\lambda_n, y) \int_1^{1+r} X(\lambda_n, y') F(y') \, dy' \quad (13)$$

Rearrange Eq. (13)

$$\psi(y, \tau) = \int_1^{1+r} \left[\sum_{n=0}^{\infty} \frac{e^{-\lambda_n^2 \tau}}{N(\lambda_n)} X(\lambda_n, y) X(\lambda_n, y') \right] F(y') \, dy' \quad (14)$$

where eigen functions given as

$$X(\lambda_n, y) = \cos \left(\frac{\lambda_n(1 + r - y)}{\varepsilon^{1/4}} \right) \quad (15a)$$

$$X(\lambda_0, y) = 1 \quad (15b)$$

and the norms are

$$N(\lambda_n) = \frac{r}{2} \quad (16a)$$

$$N(\lambda_0) = r \quad (16b)$$

From Eq. (14), we an determine for the homogeneous Green's function as

$$G(y, \tau | y', 0) = \frac{1}{r} + \frac{2}{r} \sum_{n=1}^{\infty} \cos \left(\frac{\lambda_n(1 + r - y)}{\varepsilon^{1/4}} \right) e^{-\lambda_n^2 \tau}$$
$$\times \cos \left(\frac{\lambda_n(1 + r - y')}{\varepsilon^{1/4}} \right) \quad (17)$$

Hence, non-homogeneous Green's function given as:

$$G(y, \tau | y', t') = \frac{1}{r} + \frac{2}{r} \sum_{n=1}^{\infty} \cos \left(\frac{\lambda_n(1 + r - y)}{\varepsilon^{1/4}} \right) e^{-\lambda_n^2(t' - \tau)}$$
$$\times \cos \left(\frac{\lambda_n(1 + r - y')}{\varepsilon^{1/4}} \right) \quad (18)$$

The general solution for Eq. (7) is

$$c(y, t) = \int_1^{1+r} G(y, \tau | y', 0) F(y')$$

$$+ Jr\varepsilon^{1/2} \int_0^{t'} d\tau \int_1^{1+r} G(y, \tau | y', t) \, dy'$$

$$+ \varepsilon^{1/2} Jr \int_0^{t'} d\tau \int_1^{1+r} G(y, \tau | y', t)_{y'=1} \quad (19)$$

Substituting Green's functions Eqs. (17) and (18) into Eq. (19) and perform the integration, finally we obtain

$$c(y, \tau) = 1 + Jr\tau\varepsilon^{1/2} + J\tau\varepsilon^{1/2} + \frac{Jr}{2}\left(y^2 - r^2 + r - \frac{1}{3r}\right)$$

$$- 2J\varepsilon^{1/2} \sum_{n=1}^{\infty} \frac{1}{\lambda_n^2} \cos\left(\frac{\lambda_n r}{\varepsilon^{1/4}}\right)$$

$$\times \cos\left(\frac{\lambda_n(1 + r - y')}{\varepsilon^{1/4}}\right) e^{-\lambda_n^2 \tau} \quad (20)$$

where $\lambda_n = n\pi/r$. The term in the summation is only significant for $n = 1$.

3. Results and discussion

The profile of the concentration of lithium ion during a galvanostatic discharge in the solution phase of the cathode is plotted in Fig. 2 using Eq. (20). Fig. 2 shows that the lithium ion concentration is minimum at the back of the cathode, that is at $y = 1 + r$. This is reasonable because during full charge, it is expected that the lithium ion concentration in the cathode will be almost zero. During discharge, the lithium ion will fill up the back portion of the cathode last. The result displayed in Fig. 1 shows a similar trend to that obtained by Doyle and Newman [10], Hashim et al. [16,17] and Subramaniam and White [15] as shown in Fig. 3. The intersection point of Fig. 2 occurs near $y = 3$ while in the graph displayed in reference [10] show intersection at $y = 2$ and in Ref. [15] show intersection at $y = 1.5$. This is due to the effect of taking the boundary condition at the separator/cathode interface as $Jr/\varepsilon^{1/3}$ while Doyle and Newman

Fig. 3. Concentration profiles in solution phase across cathode compared with published results.

have assumed a steady-state situation when plotting this graph. The result displayed in Refs. [16,17] show a similar intersection point ($y = 3$) with ours.

4. Conclusion

This paper presents the analytical solution for the concentration profile of lithium ion in the solution phase of the positive electrode of a lithium ion cell. The model is justified for solution phase diffusion limitations in the discharge systems. The differential and algebraic equations that describe the concentration, potential and current density in the solution phase of the porous electrode are in general nonlinear and coupled [9]. To find an analytical solution we must first decouple these equations by assuming a form for the reaction rate distribution through the porous electrode. We made an assumption that j_n is a constant at any point in the porous electrode. The concentration profiles will be determined using the boundary and initial conditions. The method Green's function presented here is useful for solving boundary value problems that include the flux boundary conditions. This method yields an unambiguous, straightforward way to obtain analytical solutions for lithium ion diffusion. In solving for the concentration profile, the initial concentration is taken to be c_0 instead of a zero initial condition as used by both Carslaw and Jaeger [27] and Atlung et al. [6]. The method applied can be easily extended to spherical and cylindrical coordinates for concentration profile in solid phase. The method appears to be more general, systematic and straightforward and should be useful for solving the similar problems. However, a more detailed mathematical model is generally required for the final optimization of the battery design.
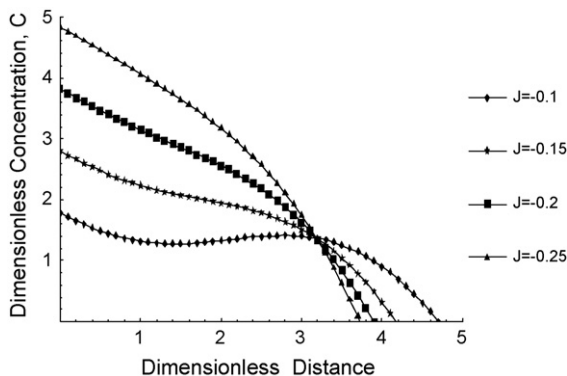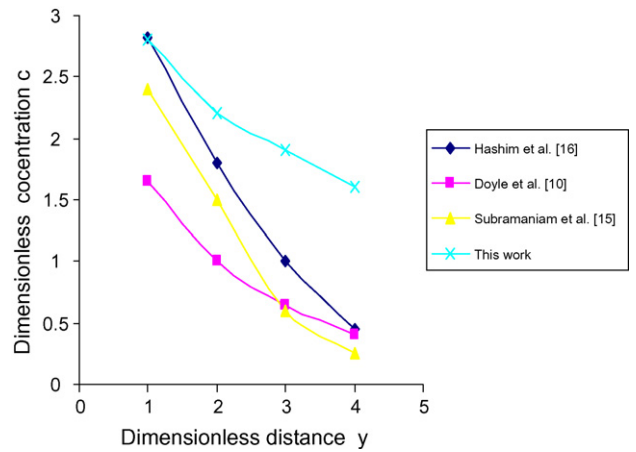
Fig. 2. Concentration profile in solution phase across cathode during galvanostatic discharge as a function of applied current at a particular time ($\tau = 1$).

References

[1] O.S. Ksenzhek, V.V. Stender, Doklady Akademyi Nauk SSSR 106 (1950) 487.
[2] J. Euler, W. Nonnenmaher, Electrochim. Acta 2 (1960) 268.
[3] J. Newman, C.W. Tobias, J. Electrochem. Soc. 109 (1962) 1183.
[4] J. Newman, W. Tiedemann, AIChE 21 (1975) 25.
[5] J. Newman, Electrochemical Systems, Englewood Cliffs, New Jersey, 1971.
[6] S. Atlung, K. West, T. Jacobson, J. Electrochem. Soc. 126 (1979) 1311.
[7] K. West, T. Jacobson, S. Atlung, J. Electrochem. Soc. 129 (1982) 1480.
[8] S. Atlung, B.Z. Christiansen, K. West, T. Jacobson, J. Electrochem. Soc. 131 (1984) 1200.
[9] M. Doyle, T.F. Fuller, J. Newman, J. Electrochem. Soc. 140 (1993) 1526.
[10] M. Doyle, J. Newman, J. Appl. Electrochem. 27 (1997) 846.
[11] C.R. Pals, J. Newman, J. Electrochem. Soc. 142 (1995) 3274.
[12] Z.H. Wang, W.B. Gu, C.Y. Wang, Proceedings of the 196th ECS Fall Meeting, Honolulu, Hawaii, The Electrochemical Society Inc., Pennington, NJ, 1999.
[13] L. Song, J.W. Evans, J. Electrochem. Soc. 147 (1995) 2086.
[14] P.M. Gomadam, J.W. Weidner, R.A. Dongal, R.E. White, J. Power Sources 110 (2002) 267.
[15] V.R. Subramaniam, R.E. White, J. Power Sources 96 (2001) 385.
[16] S.A. Hashim Ali, A. Hussin, A.K. Arof, J. Power Sources 114 (2002) 435.
[17] S.A. Hashim Ali, A.K. Arof, Ionics 9 (2003) 432.
[18] M.R. Johan, A.K. Arof, Ionics 10 (2004) 343.
[19] M.R. Johan, A.K. Arof, Ionics 10 (2004) 405.
[20] S. Liu, Solid State Ionics 177 (2006) 53.
[21] G.F. Roach, Green's Function, Cambridge University Press, Cambridge, 1982.
[22] B. Kusse, E. Westwig, Mathematical Physics, John Wiley and Sons, New York, 1988.
[23] P.M. Morse, H. Feshbach, Methods of Theoretical Physics, McGraw-Hill Book Company, New York, 1953.
[24] I.N. Sneddon, Partial Differential Equations, McGraw-Hill Book Company, New York, 1957.
[25] M.N. Ozisik, Heat Conduction, John Wiley and Sons, New York, 1980.
[26] M.N. Ozisik, Boundary Value Problems of Heat Conduction, International Textbook Company, Scranton, 1968.
[27] H.S. Carslaw, J.C. Jaeger, Conduction of Heat in Solids, Clarendon Press, London, 1959.
[28] T.F. Fuller, M. Doyle, J. Newman, J. Electrochem. Soc. 141 (1994) 1.