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# Short- and long-time solutions for material balance equation in lithium-ion batteries by Laplace transform

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**Abstract**

Short- and long-time solutions for material balance equations for porous electrodes in both the solid and the solution phase is presented. These solutions represent the concentration profile of lithium-ions in the solid and solution phases of the positive electrode of a lithium-ion cell, and are obtained using the method of Laplace transform for short- and long-time intervals.
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## 1. Introduction

This paper presents an analytical solution for the material balance equation that governs the concentration distributions in the positive electrode (cathode) of a lithium-ion cell operating under galvanostatic conditions. It is an extension to the work reported by Atlung et al. [1] who have derived analytically a short-time solution for the lithium-ion concentration. These workers [2] have also obtained a short-time analytical expression for the discharge curve in a system using composite insertion electrodes.

Recently, Subramaniam and White [3] presented an extension to the method of separation of variables for solving the equations that control the concentration distributions in solid electrodes. In this work, we have solved the material balance equation by the method of Laplace transform. The material balance equation takes into account the migration term, but for a constant lithium-ion transference number. The solutions obtained are for short- and long-time intervals.

## 2. Description of system

The lithium-ion cell that is being considered in this work has the configuration $LiMn_2O_4$|separator|graphite with a liquid electrolyte. A schematic representation of a closely-packed cathode employing $LiMn_2O_4$ active material is shown in Fig. 1. The particles of active material are considered to be spherical and have high porosity. The electrodes are composites that implies that the active materials are also mixed with carbon black to increase the electronic conductivity. This model uses the porous electrode theory [4] and the concentrated solution theory [5] to treat the composite electrodes. During the discharge process, lithium-ions deintercalate from the negative electrode (anode), diffuse through the separator, and intercalate into the cathode.

## 3. Solution phase of cathode

In order to compare our results with others, we have written the equation in accordance with that of Fuller et al. [6], where the governing equation for the electrolyte concentration is given as:

$$\frac{\partial}{\partial t}\Theta(x,t) = \varepsilon^{1/2} D \frac{\partial^2}{\partial x^2}\Theta(x,t) + \frac{a j_n (1-t_+)}{\varepsilon} \tag{1}$$

where $\Theta(x, t)$ is the material balance of salt in the solution phase. Here, $D$ is the diffusion coefficient of the lithium-ion in the electrolyte, $\varepsilon$ the volume fraction of the solid, $t_+$ the transference number, $a$ the specific interfacial area, and $j_n$ is the pore wall flux of lithium-ion. Similar to Doyle and

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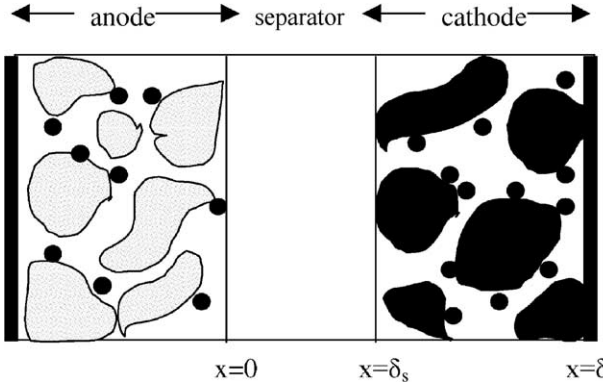


Fig. 1. Schematic representation of lithium-ion battery used in this model.

Newman [7], the following dimensionless parameters are introduced:

$$c = \frac{\Theta}{\Theta_0}, \quad y = \frac{x}{\delta_s}, \quad r = \frac{\delta_c}{\delta_s}, \quad \tau = \frac{Dt}{\delta_s^2}$$

Eq. (1) when written in its dimensionless parameters becomes:

$$\frac{\partial c}{\partial \tau} = \varepsilon^{1/2}\frac{\partial^2 c}{\partial y^2} + J \tag{2}$$

subject to the boundary and initial conditions

$$\frac{\partial c}{\partial y} = 0 \quad \text{at } y = 1 + r \tag{3}$$

$$\frac{\partial c}{\partial y} = \frac{Jr}{\varepsilon^{1/2}} \quad \text{at } y = 1 \tag{4}$$

and

$$c(y, 0) = 1 \tag{5}$$

The term $aj_n$ in Eq. (1) represents the rate of transfer of lithium-ions from the electrolyte solution inside the pores to the solid, and is related to the divergence of the current flow in the electrolyte through Faraday's Law [8], where an average of $j_n$ [7] is taken to be:

$$j_n = \frac{-I}{aFL_+} \quad \text{or} \quad J = \frac{-I(1 - t_0^+)L_s}{FDc_0\varepsilon r} \tag{6}$$

On application of the Laplace transformation with respect to dimensionless time $\tau$, we get:

$$\int_0^\infty \mathrm{e}^{-s\tau}\frac{\partial c}{\partial \tau}\,\mathrm{d}\tau = \varepsilon^{1/2}\int_0^\infty \mathrm{e}^{-s\tau}\frac{\partial^2 c}{\partial y^2}\,\mathrm{d}\tau + J\int_0^\infty \mathrm{e}^{-s\tau}\,\mathrm{d}\tau \tag{7}$$

Integrating both sides of Eq. (7) and interchanging the orders of differentiation and integration of the first term on the right-hand side, we obtain:

$$\frac{\mathrm{d}^2\bar{c}}{\mathrm{d}y^2} - \frac{s}{D}\bar{c} = -\frac{1}{\varepsilon^{1/2}}\left(1 + \frac{J}{s}\right) \tag{8}$$

which gives the solution of:

$$\bar{c}(y, s) = A\cosh(qy) + B\sinh(qy) + \left(1 + \frac{J}{s}\right) \tag{9}$$

where $q = \sqrt{s/\varepsilon^{1/2}}$ and the boundary conditions are:

$$\frac{\mathrm{d}\bar{c}}{\mathrm{d}y} = 0 \quad \text{at } y = 1 + r \tag{10}$$

$$\frac{\mathrm{d}\bar{c}}{\mathrm{d}y} = \frac{Jr}{\varepsilon^{1/2}s} \quad \text{at } y = 1 \tag{11}$$

Applying the boundary conditions (10) and (11) gives:

$$A = -\frac{Jr}{\varepsilon^{1/2}sq}\frac{\cosh q(1 + r)}{\sinh(qr)} \tag{12}$$

and

$$B = \frac{Jr}{\varepsilon^{1/2}sq}\frac{\sinh q(1 + r)}{\sinh(qr)} \tag{13}$$

Eq. (9) now becomes:

$$\bar{c}(y, s) = \frac{1}{s} + \frac{J}{s^2} - \frac{Jr}{\varepsilon^{1/4}}\left(\frac{\cosh q(1 + r - y)}{s^{3/2}\sinh(qr)}\right) \tag{14}$$

Expanding the trigonometric term in Eq. (14) in its exponential form, Eq. (14) can be rewritten as

$$\begin{aligned}\bar{c}(y, s) &= \frac{1}{s} + \frac{J}{s^2} - \frac{Jr}{\varepsilon^{1/4}}\left(\frac{\mathrm{e}^{-q(1-y+2r)} + \mathrm{e}^{-q(y-1)}}{s^{3/2}(1 - \mathrm{e}^{-2qr})}\right) \\ &= \frac{1}{s} + \frac{J}{s^2} - \frac{Jr}{\varepsilon^{1/4}}\frac{1}{s^{3/2}}\sum_{n=0}^{\infty}[\mathrm{e}^{-q(1-y+2r[n+1])} + \mathrm{e}^{-q(y-1+2rn)}]\end{aligned} \tag{15}$$

Using the Laplace transformation Table [9], we get:

$$\begin{aligned}&L^{-1}\left\{\frac{\cosh q(1 + r - y)}{s^{3/2}\sinh(qr)}\right\} \\ &= \sum_{n=0}^{\infty}(4\tau)^{1/2}\left[i\,\mathrm{erfc}\left(\frac{(1 - y + 2r[n + 1])}{2\sqrt{\varepsilon^{1/2}\tau}}\right)\right. \\ &\quad \left. + i\,\mathrm{erfc}\left(\frac{(y - 1 + 2rn)}{2\sqrt{\varepsilon^{1/2}\tau}}\right)\right]\end{aligned} \tag{16}$$

where:

$$i\,\mathrm{erfc}(x) = \frac{1}{\pi^{1/2}}\,\mathrm{e}^{-x^2} - x\,\mathrm{erfc}(x). \tag{17}$$

Hence, the final solution of Eq. (15) is given by:

$$\begin{aligned}c(y, \tau) = 1 + J\tau - \frac{2Jr\tau^{1/2}}{\varepsilon^{1/4}}\sum_{n=0}^{\infty}&\left(i\,\mathrm{erfc}\left(\frac{1 - y + 2r[n + 1]}{2\varepsilon^{1/4}\tau^{1/2}}\right)\right. \\ &\left. + i\,\mathrm{erfc}\left(\frac{(y - 1 + 2rn)}{2\varepsilon^{1/4}\tau^{1/2}}\right)\right)\end{aligned} \tag{18}$$

It can be observed that Eq. (18) is valid only for a short time. In fact, for large values of $s$, Eq. (15) will give the concentration profile as:

$$c(y, \tau) = 1 + J\tau \tag{19}$$

and the concentration increases linearly with time for a particular value of $y$.

In order to obtain the long-time solution, the trigonometric term of Eq. (14) is expanded as follows:

$$\cosh z = \left(1+\frac{4z^2}{\pi^2}\right)\left(1+\frac{4z^2}{3^2\pi^2}\right)\left(1+\frac{4z^2}{5^2\pi^2}\right)\dots \tag{20}$$

$$\sinh z = z\left(1+\frac{z^2}{\pi^2}\right)\left(1+\frac{z^2}{2^2\pi^2}\right)\left(1+\frac{z^2}{3^2\pi^2}\right)\dots \tag{21}$$

Defining:

$$\frac{f(s)}{g(s)} = \frac{\cosh q(1+r-y)}{s^{3/2}\sinh(qr)} = \frac{\cosh q(1+r-y)}{s^2(1+(q^2r^2/\pi^2))(1+(q^2r^2/2^2\pi^2))\dots} \tag{22}$$

where $f(s)$ and $g(s)$ are polynomials in $s$ which have no common factor and the degree of $f(s)$ is lower than the degree of $g(s)$.

Clearly, $s=0$ is a root for Eq. (22) and the other root is given by $q=(n\pi i)/r$ or equivalently $s=(n^2\pi^2\varepsilon^{1/2})/r^2$ where $n=1, 2, 3, \dots$

By partial fraction, Eq. (22) becomes:

$$\frac{\cosh q(1+r-y)}{s^{3/2}\sinh(qr)} = \frac{A_2}{s^2}+\frac{A_1}{s}+\sum_{m=1}^{\infty}\frac{B_m}{(1+(q^2r^2/n^2\pi^2))}, \quad n=1,2,3,\dots \tag{23}$$

This implies that:

$$\cos q(1+r-y) = A_1 s\prod_{n=1}^{\infty}\left(1+\frac{q^2r^2}{n^2\pi^2}\right) + A_2\prod_{n=1}^{\infty}\left(1+\frac{q^2r^2}{n^2\pi^2}\right) + s^2\sum_{m=1}^{\infty}B_m\prod_{n=1,n\neq m}^{\infty}\left(1+\frac{q^2r^2}{n^2\pi^2}\right) \tag{24}$$

Taking the limit as $s\to 0$, we get $A_2=1$.

Eq. (24) can now be rewritten as:

$$\cosh q(1+r-y) = \frac{\sinh(qr)}{s^{1/2}} + A_1 s^{1/2}\sinh(qr) + s^2\sum_{m=1}^{\infty}B_m\prod_{n=1,n\neq m}^{\infty}\left(1+\frac{q^2r^2}{n^2\pi^2}\right) \tag{25}$$

Differentiating Eq. (25) with respect to $s$, taking the limit as $s$ tends to zero, and applying L'Hopital's rule, we get:

$$A_1 = \frac{1}{1+r}\left(\frac{(1+r-y)^2}{\varepsilon^{1/4}}-\frac{2r^2}{\varepsilon^{1/2}}\right) \tag{26}$$

Letting $q=(k\pi i)/r$ and substituting it into Eq. (25) gives:

$$\cosh\left((1+r-y)\frac{k\pi i}{r}\right) = \left(-\frac{\varepsilon^{1/2}k^2\pi^2}{r^2}\right)^2 B_m\prod_{n=1,n\neq k}^{\infty}\left[1-\left(\frac{k}{n}\right)^2\right]$$

or

$$\cos\frac{k\pi}{r}(1+r-y) = \frac{\varepsilon k^4\pi^4}{r^4}B_m\frac{(-1)^{k+1}}{2} \tag{27}$$

Eq. (27) implies that the values for $B_m$ are:

$$B_m = \frac{(-1)^{k+1}2r^4\cos(k\pi/r)(1+r-y)}{\varepsilon k^4\pi^4} \tag{28}$$

Hence, the partial fraction in Eq. (23) becomes:

$$\frac{\cosh q(1+r-y)}{s^{3/2}\sinh(qr)} = \frac{1}{s^2}+\frac{1}{s}\left[\frac{2\varepsilon^{1/4}}{1+r}\left(\frac{(1+r-y)^2}{2\varepsilon^{1/2}}-\frac{r^4}{\varepsilon^{3/4}}\right)\right] + \sum_{n=1}^{\infty}\frac{(-1)^{n+1}2r^4\cos(n\pi/r)(1+r-y)}{\varepsilon n^4\pi^4(1+(q^2r^2/n^2\pi^2))} \tag{29}$$

Eq. (29) is then inserted into Eq. (14). Upon taking the inverse of the Laplace transform of the substituted Eq. (14), we get:

$$c(y,\tau) = 1+J\tau\left(1-\frac{r}{\varepsilon^{1/4}}\right)-\frac{2Jr}{1+r}\left(\frac{(1+r-y)^2}{2\varepsilon^{1/2}}-\frac{r^2}{\varepsilon^{3/4}}\right) - \frac{Jr}{\pi^2\varepsilon^{3/4}}\sum_{n=1}^{\infty}\frac{(-1)^2 2r^2}{n^2}\exp(-\lambda_m^2\varepsilon^{1/2}\tau)\cos(\lambda_m^2(1+r-y)) \tag{30}$$

where $\lambda_m=(m\pi)/r$. This equation is valid for a long-time interval and is related to the discharge/charge coefficient.

## 4. Solid phase of electrode

In the solid phase, the porous electrode solid particles are considered to be spherical with a radius $R$. The concentration of lithium-ions inside a solid sphere of active material, $c_s$, for a definite radius $r$ and time $t$ is given by:

$$\frac{\partial c_s}{\partial t} = D_s\left[\frac{\partial^2 c_s}{\partial r^2}+\frac{2}{r}\frac{\partial c_s}{\partial r}\right] \tag{31}$$

As in [10], Eq. (31) is subjected to the following initial and boundary conditions:

$$c_s(r,0) = c_0 \tag{32}$$

$$\frac{\partial c_s(0,t)}{\partial r} = 0 \tag{33}$$

$$-D_s\frac{\partial c_s(R,t)}{\partial r} = j_n \tag{34}$$

where $c_0$ is the initial concentration of lithium-ion in the solid particle, $j_n$ the average pore wall flux of lithium at the surface of the particle [11], and $D_s$ the diffusion coefficient of the lithium-ion inside the particle. The negative sign indicates that the pore wall flux across the solidlliquid interface is in the opposite direction to the lithium-ion

diffusion into the surface of the insertion material. The radius of the particle is traversed by the lithium-ion when $r = R$. Atlung et al. [1] and Subramaniam and White [3] have set a zero initial condition in their work.

Let $y = r \cdot c$, then the Laplace transform of the linearized Eq. (31) is given by:

$$\frac{\mathrm{d}^2\bar{y}}{\mathrm{d}r^2} - \frac{s}{D_s}\bar{y} = -\frac{c_0}{D_s}r \tag{35}$$

Eq. (35) was integrated with respect to $r$ twice, which is why Eq. (35) becomes

$$\bar{y}(r,s) = B(\mathrm{e}^{qr} - \mathrm{e}^{-qr}) + \frac{c_0}{s}r \tag{36}$$

or

$$r\bar{c}(r,s) = 2B\sinh(qr) + \frac{c_0}{s}r \tag{37}$$

where $q = \sqrt{s/D_s}$.

Here, $B$ is one of the two constants of integration obtained upon performing the integration twice on Eq. (35). It can be easily shown that the other constant of integration is $-B$.

On differentiating Eq. (36) and applying the boundary condition (34), we have:

$$2B = \frac{2j_nR^2}{sD_s\mathrm{e}^{qr}[(1-qr) - (1+qR)\,\mathrm{e}^{-2qR}]} \tag{38}$$

Hence, Eq. (37) now becomes:

$$\bar{c}(r,s) = \frac{c_0}{s} + \frac{j_nR^2}{rsD_s(1-qR)}(\mathrm{e}^{-q(R-r)} - \mathrm{e}^{-q(R+r)}) \times \left[1 - \frac{1+qR}{1-qR}\,\mathrm{e}^{-2qR}\right]^{-1} \tag{39}$$

$$\bar{c}(r,s) = \frac{c_0}{s} + \frac{j_nR^2}{rsD_s(1-qR)}(\mathrm{e}^{-q(R-r)} - \mathrm{e}^{-q(R+r)}) \times \sum_{n=0}^{\infty}\left(\frac{1+qR}{1+qR}\right)^n \mathrm{e}^{-2nqR} \tag{40}$$

$$\bar{c}(r,s) = \frac{c_0}{s} + \frac{j_nR^2}{rD_s}(\mathrm{e}^{-q(R-r)} - \mathrm{e}^{-q(R+r)}) \times \sum_{n=0}^{\infty}\sum_{k=0}^{n}\binom{n}{k}\frac{(-1)^k 2^{n-k}\,\mathrm{e}^{-2nqR}}{s(1-qR)^{n+1-k}} \tag{41}$$

$$\bar{c}(r,s) = \frac{c_0}{s} + \frac{j_nR^2}{rD_s}\left[\frac{(\mathrm{e}^{-q(R-r)} - \mathrm{e}^{-q(R+r)})}{s(1-qR)} + \left(\frac{2}{s(1-qR)^2} - \frac{1}{s(1-qR)}\right)(\mathrm{e}^{-q(3R-r)} - \mathrm{e}^{-q(3R+r)}) + \left(\frac{4}{s(1-qR)^3} - \frac{4}{s(1-qR)^2} + \frac{1}{s(1-qR)}\right) \times (\mathrm{e}^{-q(5R-r)} - \mathrm{e}^{-q(5R+r)}) + \cdots\right] \tag{42}$$

From Eq. (42), it can be observed that the Laplace transform can only be inverted for small time intervals. Upon inversion [9] for $n = 1$ and $k = 1$, we get:

$$c_s(\rho,\tau) = c_0 + \frac{Rj_n}{D_s\rho}\left[-\exp(-1+\rho+\tau)\,\mathrm{erfc}\left(-\sqrt{\tau} + \frac{1+\rho}{2\sqrt{\tau}}\right) + \mathrm{erfc}\left(\frac{1-\rho}{2\sqrt{\tau}}\right) + \exp(-1-\rho+\tau)\,\mathrm{erfc}\left(-\sqrt{\tau} + \frac{1+\rho}{2\sqrt{\tau}}\right) - \mathrm{erfc}\left(\frac{1+\rho}{2\sqrt{\tau}}\right)\right] \tag{43}$$

where the two dimensionless variables are defined as:

$$\rho = \frac{r}{R} \quad \text{and} \quad \tau = \frac{D_s t}{R^2}$$

Eq. (43) gives a relationship between the lithium-ion concentrations in the solid phase with discharge current only for short-time intervals.

On taking the Laplace transform to Eq. (31), we have arrived at Eq. (37). Upon applying the boundary condition (34), we obtained Eq. (38), which we now rewrite as

$$2B = \frac{j_nR^2}{sD_s}\frac{1}{\sinh(qR) - qR\cosh(qR)} \tag{44}$$

Hence, Eq. (37) becomes:

$$\bar{c}(r,s) = \frac{c_0}{s} + \frac{j_nR^2}{rD_s}\frac{\sinh(qr)}{s[\sinh(qR) - qR\cosh(qR)]} \tag{45}$$

We must now consider the inverse transform of the second term on the right-hand side of Eq. (45). Making use of Maclaurin series, we have:

$$\sinh(qR) - qR\cosh(qR) - \frac{-2R^3}{D_s}qs\sum_{n=0}^{\infty}\frac{(n+1)R^{2n}}{(2n+3)!}\frac{s^n}{D_s^n} \tag{46}$$

Hence, the partial fraction of this second term is given by:

$$\frac{\sinh(qr)}{s[\sinh(qR) - qR\cosh(qR)]} = \frac{qr[1 + ((qr)^2/3!) + ((qr)^4/5!) + \cdots]}{(-2R^3/D_s)qs^2\sum((n+1)R^{2n})/((2n+3)!D_s^n s^n)}$$

$$\frac{\sinh(qr)}{s[\sinh(qR) - qR\cosh(qR)]} = \frac{A_0}{s^2} + \frac{A_1}{s} + \frac{F(s)}{G(s)} \tag{48}$$

where:

$$\frac{\sinh(qr)}{q} = A_0\,G(s) + A_1 s\,G(s) + s^2\,F(s) \tag{49}$$

and

$$G(s) = \frac{-2R^3}{D_s}\sum_{n=0}^{\infty}\frac{(n+1)R^{2n}}{(2n+3)!D_s^n}s^n = \frac{\sinh(qR) - qR\cosh(qR)}{sq} \tag{50}$$

If $\lambda_n$ are the roots of $G(s) = 0$, then $\lambda_n = -D_s\alpha_n^2/R^2$, where $\alpha_n$ are the non-zero roots of $\tan\theta = 0$. From Eqs. (49) and (50), we have:

$$A_0 = \frac{-3D_s}{R^3} \tag{51}$$

$$A_1 = \frac{3r}{R^3}\left(\frac{R^2}{10} - \frac{r^2}{6}\right) \tag{52}$$

and

$$\frac{F(s)}{G(s)} = 2\sum_{n=1}^{\infty} \frac{\sin((\alpha_n/r)/R)}{\alpha_n^2 \sin\alpha_n} \frac{1}{s-\lambda_n} \tag{53}$$

where $\lambda_n$ values are simple zeros of an $n$th order polynomial $G(s)$.

Hence, the Laplace transform of Eq. (45) can be written as:

$$c_s(r,t) = c_0 - \frac{j_n R^2}{D_s}\left\{\frac{3D_s t}{R^2} + \frac{1}{2}\left(\frac{r}{R}\right)^2 - \frac{3}{10} - 2\left(\frac{R}{r}\right) \times \sum_{n=1}^{\infty} \frac{\sin(r\alpha_n/R)}{\alpha_n^2 \sin\alpha_n} \exp(-\alpha_n^2 D_s t/R^2)\right\} \tag{54}$$

where the $\alpha_n$ values are the positive roots of $\alpha_n \cot\alpha_n = 1$. Eq. (54) is valid for all $t$. As $t$ tends to infinity, the summation tends to zero and Eq. (54) is simplified to:

$$c_s(r,t) = c_0 - \frac{j_n R^2}{D_s}\left\{\frac{3D_s t}{R^2} + \frac{1}{2}\left(\frac{r}{R}\right)^2 - \frac{3}{10}\right\} \tag{55}$$

## 5. Results and discussion

The profiles of the concentration of lithium-ions during a galvanostatic discharge in the solution phase of the cathode are plotted in Figs. 2–4. Fig. 2 is plotted using Eq. (18), and Figs. 3 and 4 using Eq. (30). The solid volume fraction $\varepsilon$ is taken to be 0.524 [7] with a total thickness of cathode of $x = 0.174 \times 10^{-4}$ cm [7], and the initial concentration is $c_0 = 3.9$ mol cm$^{-2}$. From Fig. 2, the concentration of lithium-ions in the solution phase is lowest at the back of the cathode. This is reasonable because during full charge, it is expected that the lithium-ions concentration in the cathode will be almost zero, and during discharge the lithium-ions fill up the back portion of the cathode last. The concentration of lithium-ions at every point in the cathode increases with the increase in discharge current for a particular time.

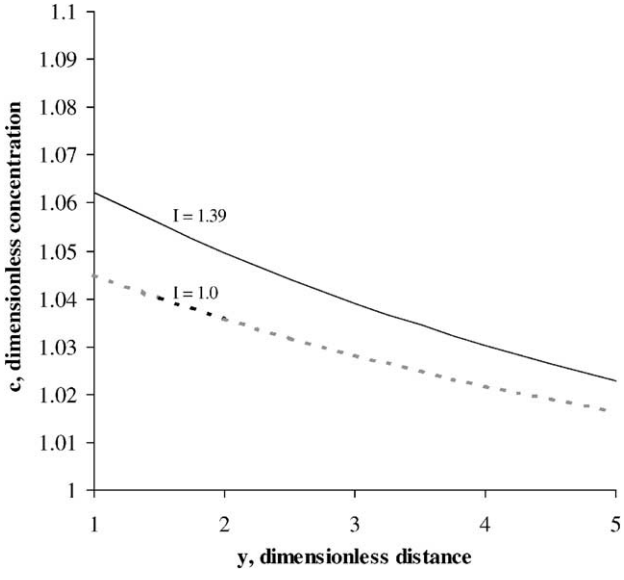


Fig. 2. Concentration profile for short-time interval in solution phase across the cathode during galvanostatic discharge of $I = 1.0$ and 1.39 mA cm$^{-2}$.

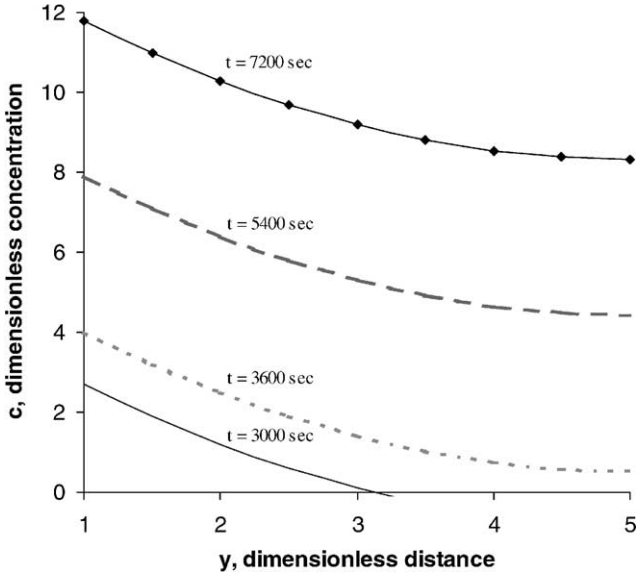


Fig. 3. Concentration profile, for long-time interval in solution phase across cathode during galvanostatic discharge of 1.39 mA cm$^{-2}$.

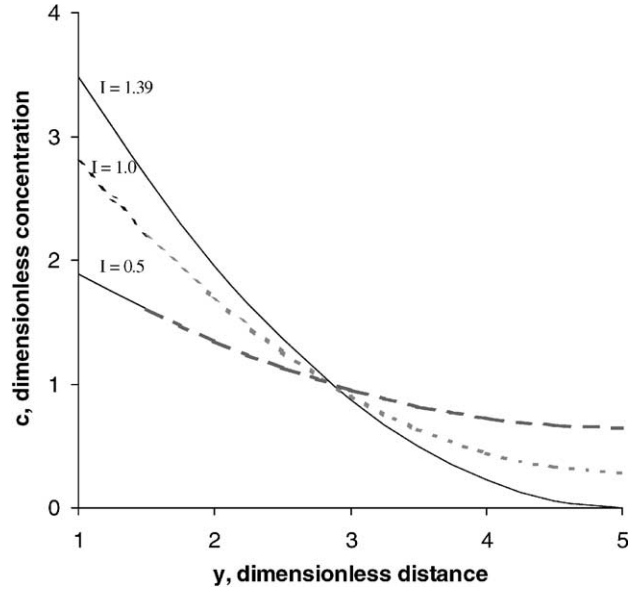


Fig. 4. Concentration profile for solution phase across cathode during discharge of $I = 0.5$, 1.0 and 1.39 mA cm$^{-2}$.

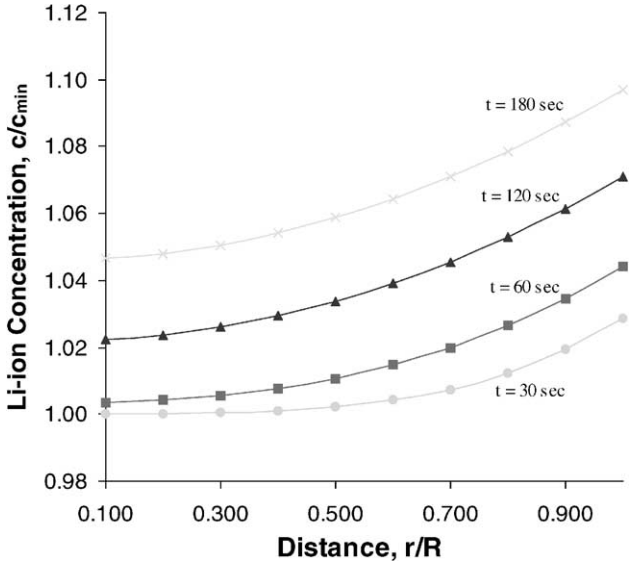


Fig. 5. Concentration profile in solid phase across cathode during galvanostatic discharge for short-time interval.

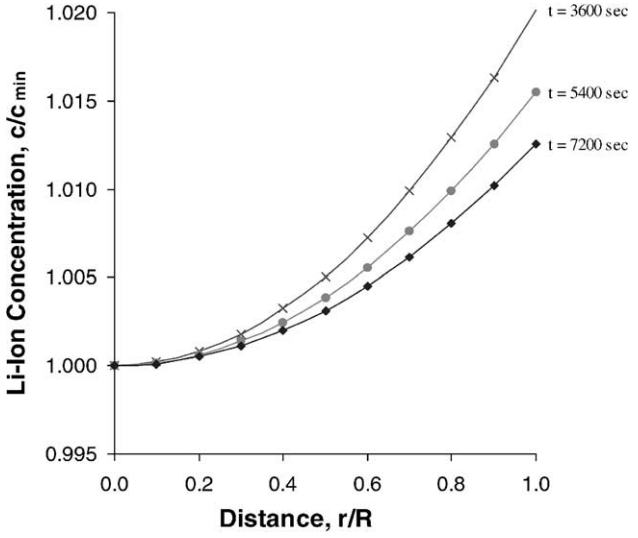


Fig. 6. Concentration profile in solid phase across cathode during galvanostatic discharge for long-time interval.

The filing up of the cathode for a constant discharge current at various times is shown in Fig. 3. For $t = 3000$ s, the cell is not fully charge since the discharge current ($I = 1.39$ mA cm$^{-2}$) sends the lithium-ions until $y = 3.12$ into the bulk of the cathode. As time increases, more and more lithium-ions enter the cathode and reach the back of the cathode. As time increases further to 5400 and 7200 s, the concentration of lithium-ions increases.

Plots of the discharge curves in the solution phase for various discharge currents at fixed time are given in Fig. 4. Again, the concentration is minimum at the back of the cathode, that is at $y = 1 + r$. The profile agrees with the results obtained by Doyle and Newman [7], but the intersection point of the graph occurs near $y = 3$ compared with that of Doyle and Newman, where the intersection point occurs at $y = 2$. This is the effect of taking the boundary condition at the separator|cathode interface as $Jr/\epsilon^{1/3}$, where $J$ is the dimensionless migration term. Doyle and Newman have assumed a steady-state situation when plotting this graph.

Figs. 5 and 6 are obtained by plotting Eqs. (43) and (54). Fig. 5 gives the plot of concentration versus distance for a short-time interval in the solid phase of the cathode at a constant discharge current of 1.39 mA cm$^{-2}$. This plot shows a hyperbolical increase in concentration as the lithium-ions move from the center to the surface of the electrode particle. The concentration profiles inside solid particles for a large time interval at a constant discharge current of 1.39 mA cm$^{-2}$ are given in Fig. 6. Similar to Fig. 5, the plot suggests that, during discharge, lithium-ions inside a solid particle move away from the center of the spherical particle. This is due to the fact that lithium-ions are moving towards the surface of the particle in order to be dispersed into the electrolyte in the cathode region. The concentration of lithium-ions increases in a consistent rate and becomes more rapid as time increases. For a very small time interval, the rise in lithium-ion concentration is rather slow, as shown in Fig. 5 as compared with the increase during a longer time interval. This is due to the fact that a very small amount of lithium-ions have been dispersed in this short period.

Even though there has been a lot of work on mathematical modeling of lithium-ion batteries, most of the work has been done numerically [5,6,8,11–15]. Very few analytical studies are available in the literature. Only recently was the material balance equation for the solution phase solved by involving the migration term analytically, but this was achieved by the method of separation of variables [3,7] and not by Laplace transform as in the present work. Also, the solid phase has been solved by Laplace transform for the initial condition where the lithium-ion concentration in the sphere is zero. The present work considers a constant lithium-ion concentration in the solid particle.

The following table differentiates the work done by other authors with that performed in the present work.

| | |
|---|---|
| Atlung, West and Jacobsen [1] | Solved analytically the following equation for the solid phase: $\frac{\partial c}{\partial t} = D\left(\frac{\partial^2 c}{\partial x^2} + \frac{2}{x}\frac{\partial c}{\partial x}\right), \quad 0 < x \leq r$ The initial and boundary conditions were: |

(i) for $t = 0$, $c = 0$,

(ii) $x \to 0$, $4\pi x^2 \dfrac{\partial c}{\partial x} = 0$,

(iii) $x = r$, $\dfrac{\partial c}{\partial x} = -\dfrac{j_0}{D}$.

Method of solving: Laplace transform solution obtained for short-time only.

Doyle and Newman [7]

Solved analytically the following equation for solution phase:

$$\frac{\partial \theta_2}{\partial \tau} = \varepsilon^{1/2} \frac{\partial^2 \theta}{\partial y^2} + J$$

The initial and boundary conditions were:

(i) $\theta_2 = 0$ at $\tau = 0$,

(ii) $\dfrac{\partial \theta_2}{\partial y} = 0$ at $y = 1 + r$,

(iii) $\varepsilon^{3/2} \dfrac{\partial \theta_2}{\partial y} = \dfrac{\partial \theta_1}{\partial y}$ at $y = 1$,

(iv) $\theta_2 = \theta_1$ at $y = 1$,

Method of solving: separation of variables Solution obtained for long-time only.

Doyle and Newman [7]

Solved the following equation for solid phase:

$$\frac{\partial c_s}{\partial t} = D_s \left[ \frac{\partial^2 c_s}{\partial r^2} + \frac{2}{r} \frac{\partial c_s}{\partial r} \right]$$

Subjected to initial and boundary conditions:

(i) $c_s = c_s^0$ at $t = 0$,

(ii) $\dfrac{\partial c_s}{\partial r} = 0$ at $r = 0$,

(iii) $-D_s \dfrac{\partial c_s}{\partial r} = \dfrac{I}{aFL_+}$ at $r = R_s$.

Method of solving: separation of variables Solution obtained for short- and long-time intervals.

Subramaniam and White [3]

Solved analytically the equation in the solution phase given by:

$$\frac{\partial \theta_2}{\partial \tau} = \varepsilon^{1/2} \frac{\partial^2 \theta_2}{\partial y^2} + J$$

The initial and boundary conditions were:

(i) $\theta_2 = 1$ at $\tau = 0$,

(ii) $\dfrac{\partial \theta_2}{\partial y} = 0$ at $y = 1 + r$,

(iii) $\varepsilon^{3/2} \dfrac{\partial \theta_2}{\partial y} = \dfrac{\partial \theta_1}{\partial y}$ at $y = 1$,

(iv) $\theta_2 = \theta_1$ at $y = 1$.

Method of solving: separation of variables solution obtained for short- and long-time intervals.

Subramaniam and White [3]

Solved diffusion in spherical electrode particle given by equation:

$$\frac{\partial c}{\partial t} = D \left( \frac{\partial^2 c}{\partial r^2} + \frac{2}{r} \frac{\partial c}{\partial r} \right)$$

Subjected to initial and boundary conditions:

(i) $c(r, 0) = 0$,

(ii) $\dfrac{\partial c}{\partial r}(0, t) = 0$,

(iii) $\dfrac{\partial c}{\partial r}(1, t) = \delta$.

Method of solving: separation of variables solution obtained for short- and long-time intervals.

Present authors

Solved analytically concentration of lithium-ions in solution phase of a cathode given by equation:

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

| | |
|---|---|
| | Subjected to the boundary and initial conditions:<br>(i) at $\frac{\partial c}{\partial y} = 0$ at $y = 1 + r$,<br>(ii) $\frac{\partial c}{\partial y} = \frac{Jr}{\varepsilon^{1/2}}$ at $y = 1$,<br>(iii) $c(y, 0) = 1$<br>Method of solving: Laplace transform Solution obtained for short- and long-time intervals. |
| Present authors | Solved equation for concentration of lithium-ions in solid phase of cathode is given by<br>$\frac{\partial c_s}{\partial t} = D_s\left(\frac{\partial^2 c_s}{\partial r^2} + \frac{2}{r}\frac{\partial c_s}{\partial r}\right)$<br>Subjected to the initial and boundary conditions:<br>(i) $c_s(r, 0) = c_0$,<br>(ii) $\frac{\partial c_s}{\partial r}(0, t) = 0$,<br>(iii) $-D_s\frac{\partial c_s}{\partial r}(R, t) = j$<br>Method of solving: Laplace transform solution obtained for short- and long-time intervals. |

## 6. Conclusions

This paper presents the analytical solution for the concentration profile of lithium-ions in the solid and the solution phases of the positive electrode of a lithium-ion cell. The method of Laplace transform has been used extensively in solving the material balance equation in both phases of the cathode for both short- and long-time intervals, and thus, extends the work of Atlung et al. [1]. In solving for the concentration profile in the spherical particle, the initial condition is taken to be $c_0$ instead of a zero initial condition as used by both Carslaw and Jaeger [16] and Atlung et al. [1]. Again, we have extended the work of Atlung et al. [1,2] by deriving the analytical solution for both short- and long-time intervals. The explicit solutions for short- and long-time intervals of both phases are presented together with their graphs.

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