

Research Article

Modeling the Lithium Ion/Electrode Battery Interface Using Fick's Second Law of Diffusion, the Laplace Transform, Charge Transfer Functions, and a [4, 4] Padé Approximant

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This work investigates a one-dimensional model for the solid-state diffusion in a $\text{LiC}_6/\text{LiMnO}_2$ rechargeable cell. This cell is used in hybrid electric vehicles. In this environment the cell experiences low frequency electrical pulses that degrade the electrodes. The model's starting point is Fick's second law of diffusion. The Laplace transform is used to move from time as the independent variable to frequency as the independent variable. To better understand the effect of frequency changes on the cell, a transfer function is constructed. The transfer function is a transcendental function so a Padé approximant is found to better describe the model at the origin. Consider $\partial c(r, t)/\partial t = D[\partial^2 c(r)/\partial^2 r + (2/r)(\partial c(r)/\partial r)]$.

1. Introduction

The Li-ion batteries in hybrid electric vehicles experience electric current pulses during their use. These transient electric pulses stress the crystal structure of the electrodes and cause lithium salt crystal growth, both of which inhibit easy ion diffusion. Also the lithium ion cells are attached in series of 72 cells. This added variable increases the chance of varying pulses. These stressors lead to shortened battery life. In order to build better batteries these pulses need to be better understood. The electric pulses have low frequency, between 0.01 Hz and two Hz [1].

The purpose of this work is to present a relatively simple mathematical model of the Li^+ ions in the electrolyte of a $\text{LiC}_6/\text{LiMnO}_2$ battery diffusing into the electrodes. Lithium ion battery electrolyte conductivity has been explored [2]. Software to help students better understand the chemistry of batteries is available as well [3]. The Li^+ battery electrochemical reactions have also been addressed [4]. Most recently Li^+ ion movement in the electrolyte has been investigated [5].

The model presented here is appropriate for Analytical Chemistry [6], Instrumental Analysis [7], Physical Chemistry [8], or Electrochemistry [9] classes. In Analytical Chemistry

it could be presented as an example of stationary electrode chemistry. In Instrumental Analysis it could be presented as part of the introduction to disk electrode chemistry. In Physical Chemistry it could be presented as a diffusion example. In an Electrochemistry class it could be explored as an example of electrode chemistry or as an aspect of battery systems management. In all courses the model is presented as an in-class lecture. Also it could be extended into an independent study project. This topic will be discussed at the end of the paper.

Transport properties have been known for over a hundred years yet they continue to be relevant [10]. Specifically batteries rely on the movement of ions due to the difference in voltage from electrode to electrode. This motion is termed ion migration. The ions also move from spot to spot in the battery due to differences in their concentrations. This motion is characterized as solid-state diffusion when the ions move in and out of the electrodes.

Mathematical modeling of migration and diffusion within a lithium ion battery is quite involved. The voltages and the solution concentrations must be simulated for the surface of the electrodes and for the electrolyte between them. These equations are made more complex because the kinetics

and transport parameters that describe the surfaces and the highly concentrated electrolyte are nonlinear [11].

Presently four differential equations are used to simulate the ion/electrode diffusion of a typical lithium ion battery that consists of a LiMnO_2 cathode and a LiC_6 anode, separated by the electrolyte, LiPF_6 [12]. There is great interest in moving away from a graphite anode to a better charge carrying semiconductor and replacing the manganese in the cathode with less toxic silicon or sulfur. Both changes are made ultimately to increase electric current [13–16].

This paper relies on one differential equation to model the Li-ion diffusion into the solid-state electrode. The equation is a form of Fick's second law of diffusion [17]. Diffusion is stressed because during the cell's operation a mean electric field is created at the electrode's surface so diffusion plays an important role. Also, simplification of solid-state diffusion as a whole is a current topic [18].

2. Li-Ion/Electrode Model

There are three simple atomic models. The atom can be viewed as a plane, a cylinder, or a sphere. The lithium ion is best described as a sphere. The lithium ion's concentration as a function of time is best described by the Laplacian in spherical coordinates:

$$\begin{aligned} \frac{\partial c(r, \theta, \phi, t)}{\partial t} = & \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial c(r, \theta, \phi, t)}{\partial r} \right) \\ & + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial c(r, \theta, \phi, t)}{\partial \theta} \right) \\ & + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2 c(r, \theta, \phi, t)}{\partial \phi^2}, \end{aligned} \quad (1)$$

where r is the distance from the origin—the center of the lithium ion— θ is the polar angle measured down from the North Pole, and ϕ is the azimuthal angle.

For the case of one-dimensional solid-state diffusion (1) becomes

$$\frac{\partial c(r, t)}{\partial t} = \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial c(r, t)}{\partial r} \right), \quad (2)$$

where D is the solid-state diffusion coefficient. The value of D is $2.0 \times 10^{-12} \text{ cm}^2 \text{ s}^{-1}$ for the LiC_6 electrode and is $3.7 \times 10^{-12} \text{ cm}^2 \text{ s}^{-1}$ for the LiMnO_2 electrode [12].

To simplify, the derivatives on the right side of (2) are solved. This yields

$$\frac{\partial c(r, t)}{\partial t} = D \left[\frac{\partial^2 c(r)}{\partial r^2} + \frac{2}{r} \frac{\partial c(r)}{\partial r} \right]. \quad (3)$$

This partial differential equation has two boundary values. At $r = 0$, the center of the lithium ion, $\partial c(r, t)/\partial r = 0$. At $r = R$, the radius of the lithium ion, $1 \times 10^{-4} \text{ cm}$, $\partial c(r, t)/\partial r = -j(t)/DaF$, where for the negative LiC_6 electrode

$$-j(t) = \frac{i(t)}{AL}. \quad (4)$$

In (4), A is the total electrode plate area, L is the electrode length, and $i(t)$ is the current flowing through the electrode [19]. Returning to the original boundary condition, D is the solid-state diffusion coefficient. The parameter a is the electrode volume fraction, 0.580 for the LiC_6 electrode and 0.500 for the LiMnO_2 electrode. The Faraday constant is F , 96,487 C/mol [12].

3. Laplace Transform

The Laplace transform converts the independent variable of an equation from time to frequency. All other independent variables are unaffected. The Laplace transform is a set of rules that are applied depending on whether the function is a polynomial, exponential derivative, and so forth [20]. For example, consider the boundary condition at $r = R$, $\partial c(r, t)/\partial r = -j(t)/DaF$. The Laplace transform is

$$\frac{\partial C(r, s)}{\partial r} = -\frac{J(s)}{DaF}, \quad (5)$$

where the capital letter indicates that the function has undergone the transform. The independent variable is now s , frequency, rather than time.

Turning to (3), a time derivative is transformed by multiplication by frequency plus a term that includes initial conditions. This change converts $\partial c(r, t)/\partial t$ to $sC(r, s) - c(r, 0)$. The second term is zero since if the frequency is 0 Hz then there is no current pulse and no change in concentration. The transformation of the entire equation can be written as

$$\frac{\partial^2 c(r)}{\partial r^2} + \frac{2}{r} \frac{\partial c(r)}{\partial r} - \frac{s}{D} C(r, s) = 0. \quad (6)$$

The solution to this differential equation is provided in the appendix. The final result at $r = R$ is

$$\begin{aligned} C(R, s) \\ = -\frac{RJ(s) \sinh(R\sqrt{s/D})}{DaF \left[(R\sqrt{s/D}) \cosh(R\sqrt{s/D}) - \sinh(R\sqrt{s/D}) \right]}. \end{aligned} \quad (7)$$

4. Transfer Function

The interest is in the surface concentration of the ions on the electrode so a transfer function from $J(s)$ to $C(R, s)$ is sought. A transfer function is the ratio of output to input for a system. The roots of the numerator of a transfer function are the zeros of the function. Zeros will block the frequency transmission. The roots of the denominator are the singularities. Frequency goes to infinity at these points.

The transfer function shows that the Laplace transform of the output is the product of the transfer function of the system and the transform of the input. In the transform domain the action of a linear system on the input is simply a multiplication with the transfer function. The transfer function is a natural generalization of the concept of gain—the increase in frequencies in the operating frequency range—of a system [21].

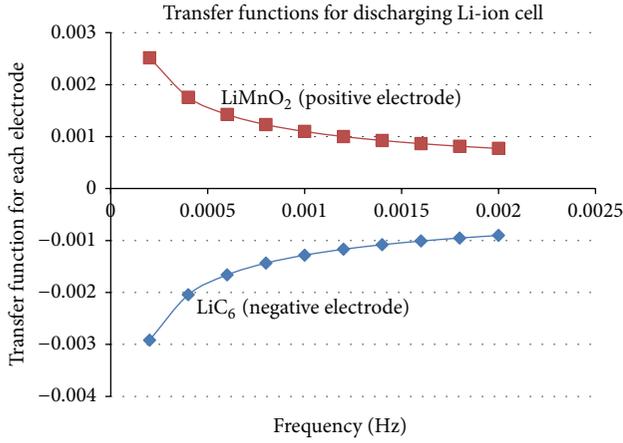


FIGURE 1: Transfer functions for a one-dimensional model of the solid-state diffusion in a typical electric car battery cell. Both transfer functions are moving away from the singularity at $s = 0$. On discharge, as the electron output of the anode moves toward zero, the input into the cathode increases, making its transfer function decrease.

The model yields the transfer function

$$\frac{C(R, s)}{J(s)} = -\frac{R \sinh(R\sqrt{s/D})}{DaF [(R\sqrt{s/D}) \cosh(R\sqrt{s/D}) - \sinh(R\sqrt{s/D})]} \quad (8)$$

This transfer function is shown in Figure 1 for the anode and cathode.

5. Padé Approximation

Polynomials—from a Maclaurin series—are often used in science, rather than a transcendental function, to speed computing time. Nonetheless the polynomials may oscillate which may increase error depending on step size. To help remedy this problem mathematicians have turned to a richer class of functions—the ratio of two polynomials.

This ratio of polynomials is computed as a Padé approximant. The Padé approximation to the model's transfer function is

$$P(s) = \frac{\sum_{m=0}^N b_m s^m}{1 + \sum_{n=1}^N a_n s^n} = \frac{\text{num}(s)}{\text{den}(s)} \quad (9)$$

The denominator begins at one so the solutions are normalized. The coefficients are found from the Maclaurin series. More specifically,

$$\text{den}(s) = \sum_{k=0}^{2(N+1)} c_k s^k - \text{num}(s) = 0, \quad (10)$$

where c_k 's are from the Maclaurin series [22].

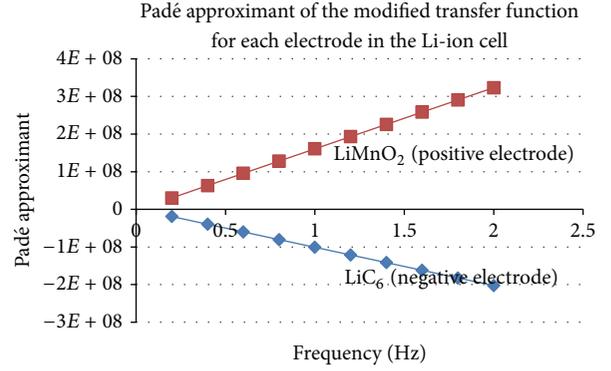


FIGURE 2: The transfer function has been linearized. The singularity at the origin has been removed. Physically, at higher frequency more lithium ions leave the electrodes.

The transfer function has a singularity at $s = 0$ so $q^2 C(R, s)/J(s)$ is expanded, where $q = R\sqrt{s/D}$, to cancel the singularity [23]. The result for the anode is

$$\frac{q^2 C(R, s)}{J(s)} = -\frac{R}{DaF} \left[-3 - \frac{q^2}{5} + \frac{q^4}{175} - \frac{2q^6}{7875} + \frac{37q^8}{3031875} \right]. \quad (11)$$

For $N = 2$, with the variable change, (10) becomes

$$\begin{aligned} & -3 - b_0 + \left(-3a_1 - \frac{1}{5} - b_1 \right) q \\ & + \left(\frac{1}{175} - b_2 - \frac{a_1}{5} - 3a_2 \right) q^2 \\ & + \left(\frac{a_1}{175} - \frac{2}{7875} - \frac{a_2}{5} \right) q^3 \\ & + \left(\frac{37}{3031875} - \frac{2a_1}{7875} + \frac{a_2}{175} \right) q^4 \\ & + \left(\frac{37a_1}{3031875} - \frac{2a_2}{7875} \right) q^5 + \left(\frac{37a_2}{3031875} \right) q^6 = 0. \end{aligned} \quad (12)$$

The q^3 and q^4 terms provide two equations for the two unknowns, a_1 and a_2 . The value of a_1 is $3/55$. The value for a_2 is $1/3465$. With these two values, b_0 , b_1 , and b_2 are found using the first three terms—the constant term, the q coefficient, and the q^2 coefficient. The values are -3 , $-4/11$, and $-1/165$, respectively.

Substituting these values into (9) yields a Padé approximant,

$$\frac{q^2 C(R, s)}{J(s)} = -\frac{R}{DaF} \left[\frac{-3 - 4q^2/11 - q^4/165}{1 + 3q^2/55 + q^4/3465} \right]. \quad (13)$$

As a check, this is the expression returned by *Mathematica*. This function is graphed for each electrode in Figure 2.

This Padé approximant was used because it is the lowest order ratio that provides linearization of the modified charge transfer function. The even powers relate to the powers series for $\sinh(x)$ and $\cosh(x)$.

6. Conclusion

Degradation of Li^+ ion battery electrodes is a current topic. The lithium ions move in and out of the electrodes distorting the electrodes' crystal structure. This leads to a decrease in capacitance and thus cell life. There are also side reactions that form lithium salts on the electrodes and other reactions that dissolve the electrodes. Low frequency electrical pulses also disrupt the electrodes [24].

This work describes a one-dimensional model of the lithium ions' solid-state diffusion. It incorporates the low frequency electrical pulses that occur in the lithium ion cells of hybrid electric vehicles. Simple expressions for solid-state diffusion at low frequencies may provide guidance for models that incorporate the higher frequencies, 500 kHz to 500 MHz, used to charge the cells [1].

In this work a transfer function was determined analytically in terms of hyperbolic functions. These nonpolynomial functions make it difficult to produce a standard transfer function in a simple variable. Instead a Padé approximant was created to produce a linear transfer function.

The same type of analysis can be done for a nickel-metal hydride rechargeable cell. In this cell the ions are more cylindrical than spherical so cylindrical coordinates are relied on. For completeness, a planar molecule would be modeled best using Cartesian coordinates. Both differential equations are in the literature [25].

Appendix

The starting point is (6).

The following notation changes are made: $r \rightarrow x$, $C \rightarrow y$, and $p \rightarrow \sqrt{s/D}$. The rewritten equation is

$$xy'' + 2y' - p^2xy = 0. \quad (\text{A.1})$$

One avenue for this form is a series solution

$$y = \sum_{n=0}^{\infty} a_n x^n. \quad (\text{A.2})$$

Substitution into (A.1) yields

$$\sum_{n=2}^{\infty} n(n-1) a_n x^{n-1} + 2 \sum_{n=1}^{\infty} n a_n x^{n-1} + p^2 \sum_{n=2}^{\infty} a_n x^{n+1} = 0. \quad (\text{A.3})$$

Working on the summations gives

$$2a_1 + \sum_{n=0}^{\infty} \left[(n+2)(n+1) a_{n+2} + 2(n+2) a_{n+2} - p^2 a_n \right] \cdot x^{n+1} = 0, \quad (\text{A.4})$$

$$2a_1 + \sum_{n=0}^{\infty} \left[(n+2)(n+3) a_{n+2} - p^2 a_n \right] x^{n+1} = 0.$$

Solving for the coefficients results in $a_1 = 0$ and

$$a_{n+2} = \left[\frac{p^2}{(n+2)(n+3)} \right] a_n \quad \text{for } n \geq 0. \quad (\text{A.5})$$

Equation (A.5) shows that all odd-numbered terms are zero and the even-numbered terms are given by

$$a_{2m} = \left[\frac{p^{2m}}{(2m+1)!} \right] a_0. \quad (\text{A.6})$$

Substitution into (A.2) provides

$$y = a_0 \sum_{m=0}^{\infty} \left[\frac{p^{2m}}{(2m+1)!} \right] x^{2m}, \quad (\text{A.7})$$

$$y = a_0 \sum_{m=0}^{\infty} \left[\frac{(px)^{2m}}{(2m+1)!} \right].$$

The Maclaurin series for $\sinh z$ is

$$\sinh z = \sum_{m=0}^{\infty} \left[\frac{z^{2m+1}}{(2m+1)!} \right] \quad (\text{A.8})$$

and so

$$\frac{\sinh z}{z} = \sum_{m=0}^{\infty} \left[\frac{z^{2m}}{(2m+1)!} \right]. \quad (\text{A.9})$$

Thus, one solution to the differential equation is

$$y_1 = \frac{\sinh(px)}{px}. \quad (\text{A.10})$$

The second solution is found by solving $y_2 = v y_1$. Differentiating, plugging into the original equation, and using y_1 as one solution give $\sinh(px)v'' + 2p \cosh(px)v' = 0$. Set $u = v'$ so that $\sinh(px)u' + 2p \cosh(px)u = 0$. This equation can be solved by integration:

$$\int \frac{du}{u} = -2p \int \coth(px) dx$$

$$\ln u = -2 \ln [\sinh(px)] + k \quad (\text{A.11})$$

$$u \sinh^2(px) = e^k$$

and so

$$u = \text{Acsch}^2(px). \quad (\text{A.12})$$

Returning to v gives $v = -A/p \coth(px)$, and the second solution is

$$y_2 = \frac{\cosh(px)}{p^2 x}. \quad (\text{A.13})$$

The general solution has the form

$$C(r, s) = \lambda_1 \left[\frac{\sinh(pr)}{pr} \right] + \lambda_2 \left[\frac{\cosh(pr)}{p^2 r} \right]. \quad (\text{A.14})$$

Applying the boundary conditions, at $r = 0$, the second term approaches infinity as r approaches zero, so $\lambda_2 = 0$. At $r = R$,

$$\frac{\partial C(R, s)}{\partial R} = \lambda_1 \left[\frac{pR \cosh(pR) - \sinh(pR)}{pR^2} \right]$$

$$\lambda_1 \left[\frac{pR \cosh(pR) - \sinh(pR)}{pR^2} \right] = - \frac{J(s)}{DaF} \quad (\text{A.15})$$

$$\lambda_1 = - \frac{pRJ(s)}{DaF [pR \cosh(pR) - \sinh(pR)]}$$

Substitution into (A.14) yields (7).

Conflict of Interests

The authors declare no competing financial interests.

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