

# Simplified Multiphysics Model for All-Solid-State Microbatteries

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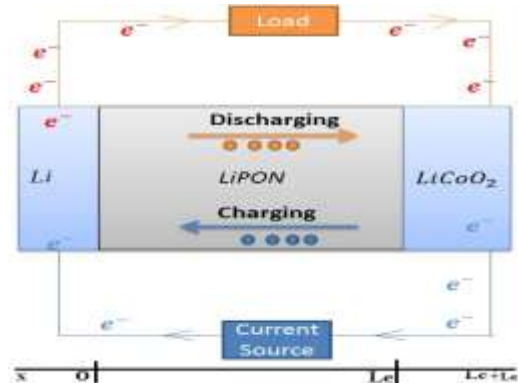
**Abstract:** Lithium microbatteries are replacing conventional power sources in many microsystems areas such as wireless sensors and biomedical monitors. In many of these applications, compact models of micro batteries are needed both at the microsystems design stage and at the real-time power management stage. These compact models are typically derived from physics-based discretized formulations. We have developed a simplified partial-differential equation (PDE) model for an all-solid state Li metal microbattery. The simplified PDE model was analyzed using both COMSOL Multiphysics and a finite-difference scheme implemented in Matlab. Both implementations deviate by at most 2% from a full PDE model.

**Keywords:** Microbatteries, Compact Models, Finite Element, Finite Difference

## 1. Introduction

Many authors have addressed modeling of liquid electrolyte lithium batteries, but only few recent publications exist that address mathematical modeling of all-solid state microbatteries [1-4]. A one-dimensional model was used to simulate the performance of all-solid-state Li-ion batteries [1]. Figure 1 shows the schematic diagram for the one-dimensional battery that was used during the model development process. Like conventional rechargeable batteries, all-solid state lithium microbatteries can be operated in two modes. When the battery is discharged, lithium ions and electrons are released from the anode. The electrons travel through the external circuit while doing some electrical work and lithium ions travel through the solid electrolyte (LiPON) to the cathode. Lithium ions and electrons will recombine at the cathode creating lithium atoms which are hosted inside the layered structure of the cathode until its hosting capacity is reached. When  $\text{LiCoO}_2$  has reached its hosting capacity, the battery is in fully discharged state. The opposite process occurs when the battery is charged which is shown by

electrical loop (blue color) in the lower half of fig. 1.



**Figure 1.** Schematic representation of planar all-solid state Li microbattery

## 1.1 Model Equations

Lithium ion transport through the electrolyte or electrodes can be due to migration, diffusion or both of them [8]. Migration is the transport of charged body due to an electric field and diffusion is the movement of a chemical species due to concentration gradient. The flux ( $\varphi$ ) of lithium ion inside the electrolyte is given by the Nernst-Planck-Poisson (NPP) equation:

$$i = -D_i \frac{\partial}{\partial x} c_i + \frac{zF}{RT} D_i c_i E \quad (1)$$

The terms on the right hand side of the above equation represent the contributions of diffusion and migration, respectively, to the mass transfer. Here  $z$  and  $C$  are the charge (dimensionless) and the concentration  $\frac{\text{mol}}{\text{m}^3}$  of lithium species.  $E$  ( $\frac{\text{V}}{\text{m}}$ ) is the electric field,  $D$  ( $\frac{\text{m}^2}{\text{s}^2}$ ) is diffusion coefficient,  $T$  is the temperature (K),  $R$  is the gas constant ( $8.3145 \frac{\text{J}}{\text{mol K}}$ ), and  $F$  is Faraday's constant ( $96485 \frac{\text{C}}{\text{mol}}$ ). Where in (1)  $i = 1$  &  $z = 1$  is used for lithium ion and  $i = 2$  &  $z = -1$  for the negative ions. The net Lithium flow rate into or out of the electrolyte is given by Fick's second law of diffusion.

$$\frac{\partial c_1}{\partial t} = -D_1 \frac{\partial \varphi_1}{\partial x} = D_1 \frac{\partial^2 c_1}{\partial x^2} - \frac{F}{RT} D_1 \left( \frac{\partial E}{\partial x} \right) \quad (2)$$

$$\frac{\partial c_2}{\partial t} = -D_2 \frac{\partial \varphi_2}{\partial x} = D_2 \frac{\partial^2 c_2}{\partial x^2} + \frac{F}{RT} D_2 \left( \frac{\partial E}{\partial x} \right) \quad (3)$$

Diffusion due to concentration gradient is the main transport mechanism in the electrodes and it is given by Fick's second law of diffusion without migration terms:

$$\frac{\partial c_3}{\partial t} = -D \frac{\partial \varphi_3}{\partial x} = D \frac{\partial^2 c_3}{\partial x^2} \quad (4)$$

The electrolyte is composed of two ionic species. Lithium ions are positively charged and to keep the global electro-neutrality of the electrolyte similar amount of negatively charged ions exist in the electrolyte [1]. Hence, equations (2) & (3) describe the mass conservation rule for lithium and negative ions respectively. The external electronic current and Lithium flux are related by the following equation:

$$= \frac{I}{zFA} \quad (5)$$

Where, A is the surface area of the electrolyte-electrode interface. Boundary and initial conditions should be setup to solve the above equations for the electrolyte and cathode domain. Equations (6) to (13) show the setup for initial and boundary conditions for the model:

$$\frac{I}{nFA} = -D_1 \frac{\partial}{\partial x} c_1(0, t) + \frac{F}{RT} D_1 c_1(0, t) E(0, t) \quad (6)$$

$$-\frac{I}{nFA} = -D_1 \frac{\partial}{\partial x} c_1(L_e, t) + \frac{F}{RT} D_1 c_1(L_e, t) E(0, t) \quad (7)$$

$$-D_2 \frac{\partial}{\partial x} c_2(0, t) - \frac{F}{RT} D_2 c_2(0, t) E(0, t) = 0 \quad (8)$$

$$-D_2 \frac{\partial}{\partial x} c_2(L_c, t) - \frac{F}{RT} D_2 c_2(L_c, t) E(L_c, t) = 0 \quad (9)$$

$$-D_3 \frac{\partial}{\partial x} c_3(0, t) = \frac{I}{nFA} \quad (10)$$

$$-D_3 \frac{\partial}{\partial x} c_3(L_c, t) = 0 \quad (11)$$

$$c_1(x, 0) = c_2(x, 0) = c_{1initial} \quad (12)$$

$$c_3(x, 0) = c_{3initial} \quad (13)$$

The two domains were solved separately and the origin of x coordinate for cathode domain was moved to just at the electrolyte-cathode interface. The all-solid state microbattery model inside COMSOL's model library [9] uses finite element method [7] to solve equations (2) & (3) coupled with equations (6) to (9) as boundary conditions and equation (12) as initial condition for the electrolyte domain. Equation (4) is used to solve for the cathode domain with boundary conditions given by equations (10) & (11) and initial condition by (13). Assuming local electro neutrality, the above model setup in COMSOL library is simplified while keeping the results as accurate as possible.

## 1.2. Model Assumptions

During the reformulation of COMSOL's microbattery model, the following assumptions have been made:

1. Geometry is planar.
2. Reactions occur only at the surface.
3. Initial concentration of Li ion in the electrolyte is uniform.
4. Electrolyte bulk is electro neutral both globally and locally.
5. Electronic resistance and electrode reaction of Li anode are ignored.
6. The electrodes are also current collectors.

## 2. Model Reformulation

By considering the above assumptions, the existing microbattery model in COMSOL library was reformulated and simulated using both COMSOL and a finite-difference scheme implemented in Matlab and solved using its ode45 solver. Multiplying Equation (3) by  $D_1$ , Equation (2)  $D_2$  and adding them will help us to drop the migration term from each equation and get unified mass conservation equation:

$$\frac{\partial c}{\partial t} = \frac{D_1 D_2}{2(D_1 + D_2)} \frac{\partial^2 c}{\partial x^2} \quad (14)$$

Applying the same algebraic manipulation to boundary conditions (6) & (8) new boundary condition is set at the  $x=0$ :

$$\frac{\partial}{\partial x} c(0, t) = -\frac{I}{2 * D_1 zFA} \quad (15)$$

Multiplying Equation (7) by  $D_2$  and Equation (9) by  $D_1$  and adding the two, the boundary condition at  $x=L_e$  is found:

$$\frac{\partial}{\partial x} c(L_e, t) = -\frac{I}{2 * D_1 z F A} \quad (16)$$

The initial condition for the electrolyte concentration and the equations for the cathode domain will remain unchanged. After solving for electrolyte and cathode concentration, approximate algebraic formulas are used to calculate the charge transfer potential at the anode and cathode interface:

$$\eta_{ctn}(t) = \frac{2RT}{F} \operatorname{asinh}\left(\frac{I(t)}{2i_{on}}\right) \quad (17)$$

$$\eta_{ctp}(t) = \frac{2RT}{F} \operatorname{asinh}\left(\frac{I(t)}{2i_{op}}\right) \quad (18)$$

Similarly the electrolyte potential drop and the cathode diffusion over potential are given by the following formulas:

$$\eta_{el} = -\int_0^{L_e} E(x, t) + \frac{RT}{F} \ln\left(\frac{c(L_e, t)}{c(0, t)}\right) \quad (19)$$

$$\eta_{catd} = \frac{RT}{F} \ln\left(\frac{c(L_e + L_c, t)}{c(L_e, t)}\right) \quad (20)$$

### 3. Results

The simplified model uses the same battery parameters as the COMSOL library full nonlinear model. Both models were solved using COMSOL and the simplified model is further verified using Matlab ODE solver. The discrepancy between our model and the nonlinear model is within 2% and runs six times faster than the nonlinear model. Figure 2 shows the steady state Lithium concentration profile in the electrolyte for discharge rate of  $C=1$  as a function of time and electrolyte length. Finer meshing is required at the boundaries to decrease the maximum error due to Neumann boundary conditions imposed at the two ends of the electrolyte. The linear diffusion equation is used for cathode diffusion in both COMSOL and simplified model. Therefore, the same lithium concentration profile was obtained in both cases as shown in figure 3 for discharge rate of  $C=1$ .

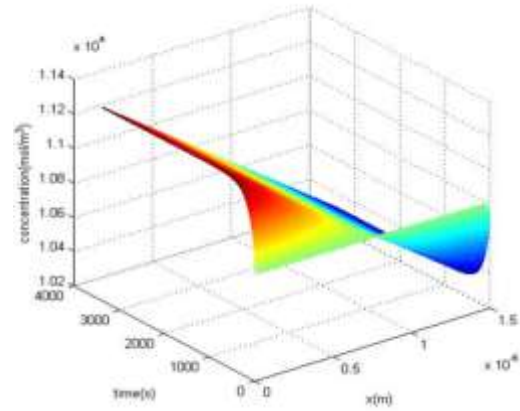


Figure 2. Electrolyte concentration profile for  $C=1$

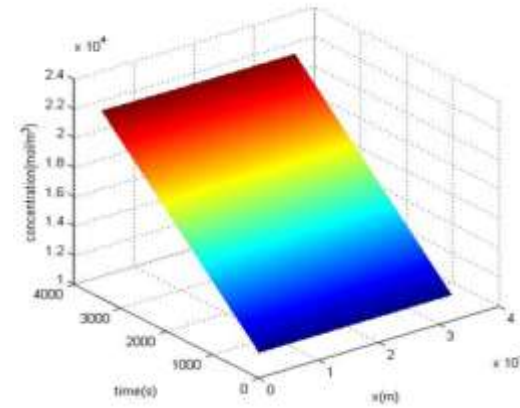
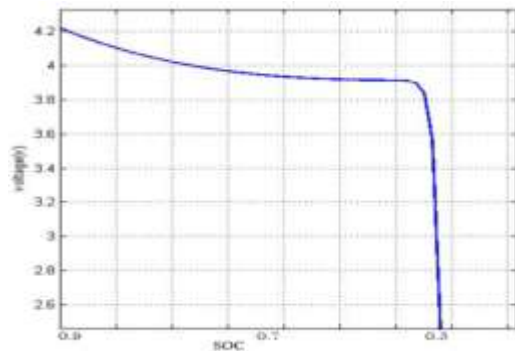
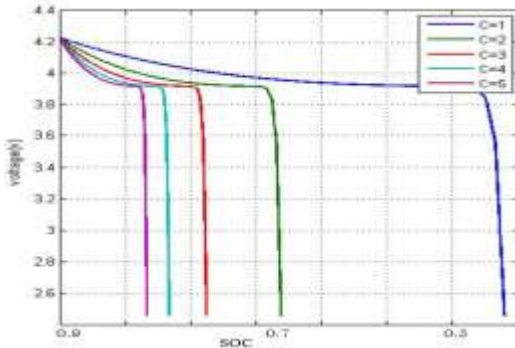


Figure 3. Electrolyte concentration profile for  $C=1$

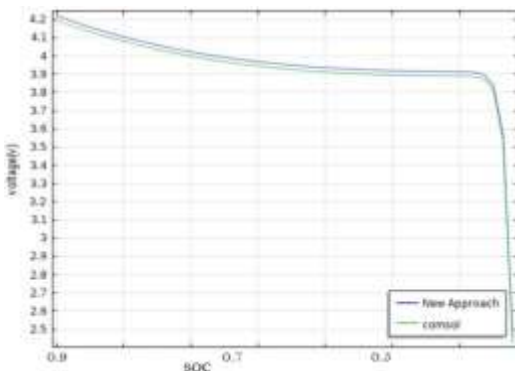
The State of Charge (SOC) interval was found from the discharge time interval by linear interpolation. Even though lithium ion batteries do not have memory effect, they cannot be discharged to full state. SOC of 1 indicates ideal state where the battery is fully charged state and 0 indicates fully discharged state. Figure 4 shows the discharge profile for normal discharging rate. To keep the simulation practical SOC interval of 0.98 to 0.5 was considered. The voltage profile as function of state of charge was also compared for the two approaches (Figure 6). Reasonable agreement between the two methods was found with maximum relative deviation of 2%. Similar agreement was also obtained between the two approaches for higher discharging rates. Figure 5 shows discharge profile for different discharging rates.



**Figure 4.** Voltage vs. state of charge for C=1.



**Figure 5.** Voltage vs. state of charge for different C.



**Figure 6.** Voltage vs. state of charge for full nonlinear COMSOL and simplified models.

#### 4. Conclusions

Based on local electro neutrality assumption for the electrolyte, our simplified model is able to predict the discharge profile of an all-solid-state micro battery within 2% of the full nonlinear model available in the COMSOL library. The model was able to predict the lithium concentration profile in the electrolyte and cathode, the different voltage drops and finally the discharge curve of the battery. Such a simplified finite difference model will be basis of

a compact model that can be used in an embedded battery management subsystem and in the battery-circuit co-design work flow.

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