

Computational Model of solid-state lithium ion batteries

Leta Jule*¹, Francis Dejene¹, Kittessa Roro²

¹Physics Department, University of the Free State, Private Bag X13,
Phuthaditjhaba, South Africa

²CSIR-Energy center, Council for Scientific and Industrial Research
P.O Box 395 Pretoria, South Africa

E-mail: JuleLT@ufs.ac.za

Abstract. It is important to have a simple but accurate model to evaluate the thermal behavior of batteries under a variety of operating conditions and be able to predict discharging currents as well. Theoretical models, which are usually based on a combination of electrochemistry and physics, can give accurate predictions even though they are complicated, need sophisticated measurements, estimation of transport properties and electrochemical reaction constants, to be accurately solved. To achieve this goal, one dimensional tertiary current distribution interface is used to model the electrolyte transport and the electrochemical reactions, solving for the electrolyte potential, the electrolyte concentration of Li ions, and the electric potential of the positive electrolyte-electrode interface boundary. In addition, the model is constructed in COMSOL MultiPhysics 5.2 to use optimization capabilities for validating the model with measured data. It is shown that the model can accurately predict various discharge currents and the different sources of voltage losses. Such models are well-suited for battery design purposes, though not optimal for the low computing-power environment of micro-controllers. Furthermore, it is believed that this modified model was adapted for implementation in battery management systems and can be used for the scale-up of large size batteries and battery packs.

1. Introduction

All-solid-state batteries are a quickly growing multimillion dollar business, which nowadays have a large beneficial impact on many applications, such as autonomous devices for ambient intelligence and medical implants. To describe the performance of these batteries under various conditions, mathematical modeling of the Li-ion system was initiated in the mid-1980s. Simulating discharge voltage curves of Li-ion batteries already dates back to the early 1980s [1]. Interesting reviews dealing with the mathematical modeling of Li-ion batteries can be found in the literature [2-5] These models are mainly based on the porous electrode theory developed by Newman [6]. Alternatively, equivalent electronic network models have been presented for various types of rechargeable batteries [7-11]. All these models are based on the macroscopic descriptions of the fundamental electrochemical and physical processes occurring inside these systems, enabling the quantification of the relevant processes.

The electronic network models were elegantly used to visualize these processes. Good agreement between the simulations and experimental results was reported [7-11]. In addition, the degradation (aging) process of Li-ion batteries has also been addressed [12,13]. However, all these reports did not address thin-film all-solid-state Li-ion batteries. Solid-state Li-ion batteries represent the state-of-the-art in modern battery technology. Further improvement in the solid-state battery technology requires an in-depth understanding of the electrochemical processes involved, and the ability to simulate these processes is therefore a necessity. The ionically conductive solidstate electrolytes play an important role in the solid-state battery design [14,15]. A majority of all-solid-state Li-ion batteries have a flat thin-film design. An example of the cross section of an as-deposited solid-state Li-ion battery. To mitigate this drawback an all-solid-state lithium-ion battery is often fabricated by thin-film methods, with thicknesses in the range of a few micrometers. These thin-film batteries typically do not make use of porous electrodes; all electrochemical reactions instead take place on the interface between the electrolyte and solid electrode domains.

The aim of the current paper is to develop a mathematical model models a thin-film for all-solid-state lithium battery in one dimension batteries using COMSOL Multiphysics 5.2, which includes all important physical and electrochemical characteristics and is capable of describing the basic functionality of these devices under a wide variety of operating conditions calculating various discharge currents and the different sources of voltage losses.

2. Theoretical Model

The solid electrolyte differs from a binary concentrated liquid electrolyte, and hence this model does not use the Lithium-Ion Battery interface. Instead, it uses the Tertiary Current Distribution interface to model the electrolyte transport and the electrochemical reactions, solving for the electrolyte potential, (SI unit: V), the electrolyte concentration of Li ions, c_{Li^+} (SI unit: mol/m³), and the electric potential of the positive electrolyte-electrode interface boundary, ϕ_{bnd} (SI unit: V). In addition, the model uses the Transport of Diluted Species interface to model the transport of lithium in the positive electrode, solving for the concentration of solid lithium, c_{Li} .

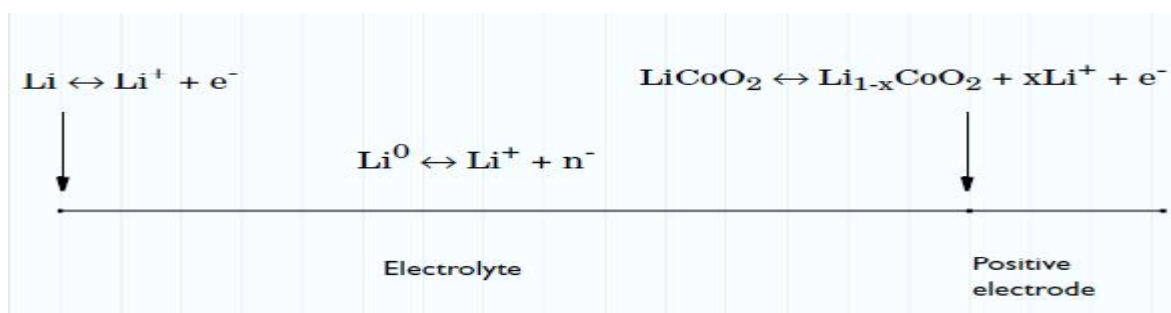
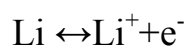


Figure 1. Model geometry – electrolyte and positive electrode domains.

The location of the positive and negative electrode reactions are indicated by arrows. The model geometry, shown in figure 1, is in one dimension and consists of two domains: the electrolyte and the positive electrode, 1500 nm and 320 nm thick, respectively. The negative electrode is assumed to have high electric conductivity and is not included in the model. A conventional solid-state Li-ion battery consists of the following elements. The negative electrode comprises metallic lithium. The positive electrode is based on the conventional LiCoO₂ chemistry [16]. On the negative electrode, lithium metal reacts with lithium ions in the electrolyte according to



where the reaction kinetics for this reaction is described using a Butler-Volmer expression

$$i_{neg} = Fk_{neg} \left(\frac{C_{Li^+}}{C_{Li^+}^0}, 0 \right)^{\alpha_{neg}} \left(e^{F\eta/(RT)} + e^{-(1-\alpha_{neg})F\eta/(RT)} \right) \quad (1)$$

Here F (96485 C/mol) is Faraday's constant, k_{neg} (SI unit: mol/(m²·s)) is the rate constant of the reaction, C_{Li^+} is the total concentration of lithium in the electrolyte, α_{neg} is the charge transfer coefficient for the reaction, R (8.3145 J/(mol·K)) is the molar gas constant, and T (SI unit: K) is the temperature.

On the positive electrode the active electrode material reacts according to



This reaction is also described using Butler-Volmer kinetics

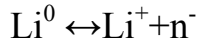
$$i_{pos} = i_{0,pos} \left(e^{F\eta/(RT)} + e^{-(1-\alpha_{pos})F\eta/(RT)} \right) \quad (3)$$

$$i_{0,pos} = Fk_{pos} \left(\frac{(C_{Li,max} - C_{Li})C_{Li^+}}{(C_{Li,max} - C_{Li,min})C_{Li^+}^0} \right)^{\alpha_{pos}} \left(\frac{(C_{Li,max} - C_{Li})C_{Li^+}}{(C_{Li,max} - C_{Li,min})C_{Li^+}^0} \right)^{1-\alpha_{pos}} \quad (4)$$

where $C_{Li,max}$ and $C_{Li,min}$ are the maximum and minimum levels of lithium in the solid electrode, respectively. The overpotential, η (SI unit: V), is generally defined as:

$$\eta = \phi_s - \phi_e - E_{eq} \quad (5)$$

where ϕ_s (SI unit: V) is the potential of the electrode (solid) and E_{eq} (SI unit: V) is the equilibrium potential of the reaction. E_{eq} is set to 0 for negative electrode. For the positive electrode the equilibrium potential depends on the concentration of lithium in the electrode. By Setting the negative electrode to an electric potential of zero volts, and apply a current condition on the positive electrode for the simulation. The electrolyte is a solid-state Li₃PO₄ electrolyte. The chemical reaction



describes the ionization reaction in the electrolyte, where immobile oxygen-bonded lithium (Li^0) is transferred to mobile Li^+ ions and uncompensated negative charges (n^-). The dissociation rate for this reaction is denoted by k_d , and the inverse reaction rate by k_r , so that the overall rate for the electrolyte transfer reaction is written as :

$$r_d = K_d C_{Li^0} - K_r C_{Li^+} C_{n^-} \quad (6)$$

At equilibrium the fraction of the total amount of lithium that is dissociated, δ , is

$$C_{Li^+}^{eq} = C_{n^-}^{eq} = \delta c_0$$

with the result that k_d is related to k_r according to , $k_d = \frac{k_r c_0 \delta^2}{1 - \delta}$

The transport of Li^+ and n^- is described by the Nernst-Planck equation

$$N_i = D_i \nabla c_i + \frac{z_i F}{RT} D c_i \nabla \phi_1 \quad (7)$$

where D_i is the species diffusion coefficient and z_i the species charge. Assume local electroneutrality so that at all times. Couple the flux on the electrolyte boundaries to the electrochemical reactions using Faraday's law. In the positive electrode, solid lithium is transported by Fick's law:

$$N_{Li} = D_{Li} \nabla c_{Li} \quad (8)$$

Coupling the flux of solid lithium on the electrode-electrolyte boundary to the electrochemical reactions using Faraday's law, assuming the flux of solid lithium to zero on the right most boundary.

3. Results and Discussion

Figure 2 shows the electrolyte concentration of Li^+ at the last time-step of the solver for various discharge currents. The concentration deviation from the equilibrium concentration at the electrodes is higher for higher discharge currents. Figure 3 shows the concentration profile of solid lithium in the positive electrode. The concentration gradients get steeper with higher discharge rates.

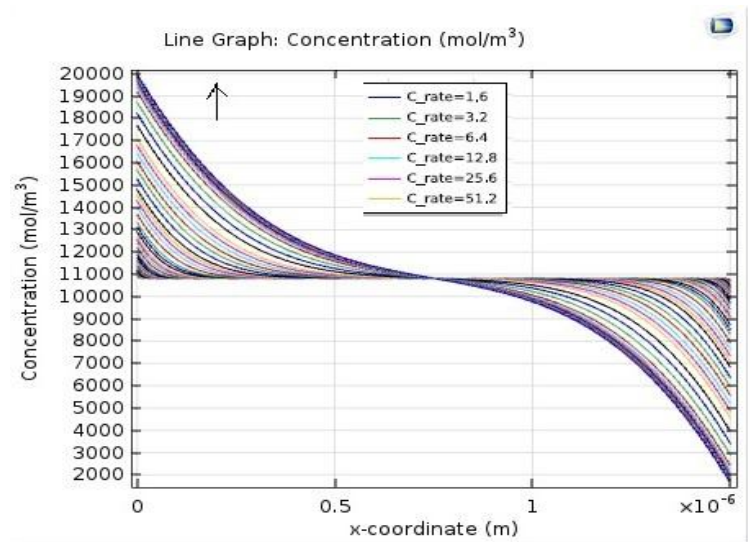


Figure 2. Electrolyte concentration at end of discharge for various discharge rates.

Figure 4. The position (voltage) of the plateau before depletion is shifted downwards for higher discharge rates. The reason for this are the higher internal losses for higher currents.

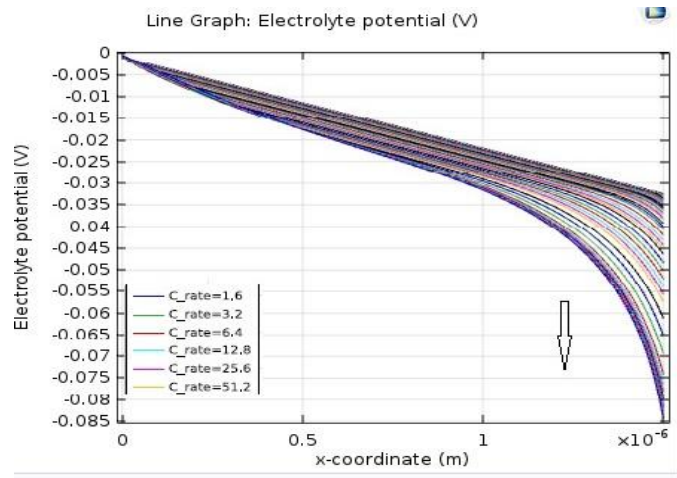


Figure 3. Electrolyte potential for various discharge rates.

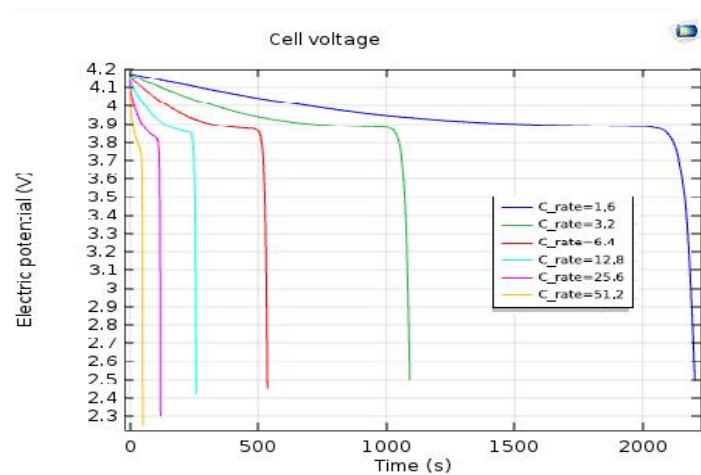


Figure 4. Discharge curves (cell voltage vs. time) for various discharge rates.

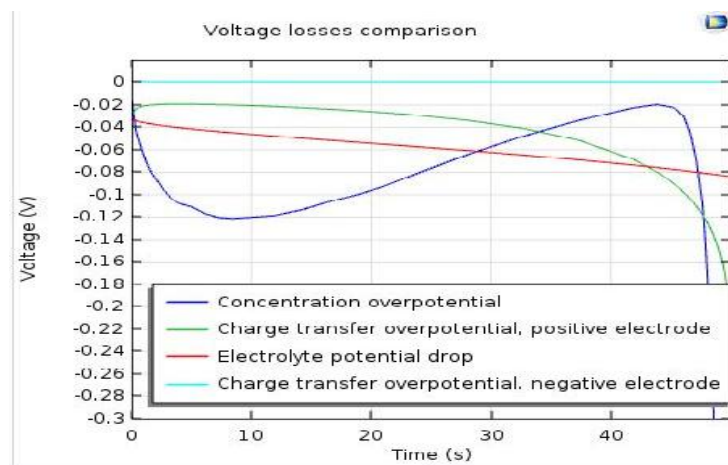


Figure 5. Comparing different sources of voltage loss during a 51.2 C discharge.

Figure 5 compares the different voltage losses; the activation overpotentials of the positive and negative electrode reactions, the electrolyte potential drop and the concentration over potential. The concentration overpotential is calculated as:

$$\eta_{\text{conc}} = E_{\text{eq}}(C_{\text{Li}}) - E_{\text{eq}}(C_{\text{Li}}') \quad (9)$$

where C_{Li}' is the average concentration of solid lithium in the positive electrode.

The largest changes are seen in the concentration overpotential. The reason for this is the voltage plateau of the equilibrium potential towards end of discharge, compared to the large initial equilibrium voltage drop for a fully charged battery. The electrolyte voltage drop and overpotential of the positive electrode reaction also undergo changes during the discharge. This is also due to concentration changes in the electrolyte and the positive electrode.

4. Conclusions

A one-dimensional model has been applied to simulate the performance of all-solid-state Li-ion batteries. The model describes the electrode, electrolyte, and the interface between those elements. The proposed model provides a detailed information about the various diffusion and migration fluxes, concentration profiles, and the corresponding overpotential contributions, occurring across the electrode and electrolyte. The model provides good prediction, including discharge curves with high C-rates.

References

- [1] M. Doyle, T. F. Fuller, and J. Newman, *J. Electrochem. Soc.*, 140, 1526 (1993).
- [2] C. R. Pals and J. Newman, *J. Electrochem. Soc.*, 142, 3274 (1995).
- [3] L. Song and J. W. Evans, *J. Electrochem. Soc.*, 147, 2086 (2000).
- [4] G. G. Botte, V. R. Subramanian, and R. E. White, *Electrochim. Acta*, 45, 2595 (2000).
- [5] P. M. Gomadam, J. W. Weidner, R. A. Dougal, and R. E. White, *J. Power Sources*, 110, 267 (2002).
- [6] J. S. Newman, *Electrochemical Systems*, Prentice-Hall, Englewood Cliffs, NJ (1991).
- [7] W. S. Kruijt, P. H. L. Notten, and H. J. Bergveld, *J. Electrochem. Soc.*, 145, 3764 (1998).
- [8] P. H. L. Notten, W. S. Kruijt, and H. J. Bergveld, *J. Electrochem. Soc.*, 145, 3774 (1998).
- [9] H. J. Bergveld, W. S. Kruijt, and P. H. L. Notten, *J. Power Sources*, 77, 143 (1999).
- [10] D. Danilov, R.A.H. Nielsson, and P.H. Notten, *J. Electrochemical Society*, vol. 158, pp. A215– A222, (2011).
- [11] H. J. Bergveld, W. S. Kruijt, and P. H. L. Notten, *Battery Management Systems Design by Modelling*, Philips Research Book Series, Vol. 1, Kluwer Academic Publishers, Boston (2002).
- [12] D. Danilov and P. H. L. Notten, Abstract 390, in *Proceedings of the 12th IMLB Conference*, Nara, Japan, (2004).
- [13] D. Danilov and P. H. L. Notten, in *Proceedings of the 5th IEEE Vehicle Power and Propulsion Conference*, IEEE, Dearborn, p. 317 (2009).
- [14] J. B. Bates, N. J. Dudney, G. R. Gruzalski, R. A. Zuhr, A. Choudhury, C. F. Luck, and J. D. Robertson, *J. Power Sources*, 43, 103 (1993).
- [15] J. B. Bates, N. J. Dudney, D. C. Lubben, G. R. Gruzalski, B. S. Kwak, Y. Xiaohua, and R. A. Zuhr, *J. Power Sources*, 54, 58 (1995).
- [16] P. H. L. Notten, in *Interstitial Intermetallic Alloys*, F. Grandjean, G. J. Long, and K. H. J. Buschow, Editors, Chap. 7, p. 151 Kluwer, Dordrecht (1995).