

Charge-discharge studies of lithium-ion batteries

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Abstract: A lithium-ion battery comprises of two intercalating electrodes separated by a lithium-ion conducting matrix, sandwiched between an aluminum and copper current collecting plates. The battery performance generally depends upon several parameters and it is important to better the cell performance by varying these parameters. In this work we have optimized some parameters of a lithium iron phosphate (LiFePO₄) battery model and validated our results with experimental charge-discharge curves. The studies could help in the development of analytics for products where the lithium ion battery will be used as a component.

Keywords: LiFePO₄, Lithium-ion battery

1. Introduction

Performance of a battery depends upon several parameters, such as, charge-discharge current, active material particle radius, temperature, volume fraction of active mass in the electrodes, reaction rates at the electrodes, separator thickness, electrode thickness, etc. These quantities must be optimized to ensure a) high electrical storage capacity; b) uniform electrical energy storage within the device; c) avoid hot-spots during charge-discharge cycles; d) avoid build-up of significant Li⁺-ion concentration differentials within an electrode domain (cathode or anode) and hence e) avoid build-up of significant potential differentials within an electrode. How the diverse parameters and operating conditions affect the battery performance can be well understood by modeling the device.

Today, several industries are interested in putting Li⁺-ion based energy storage devices in their products. However, the original equipment manufacturer (OEM) of lithium-ion batteries is often reluctant to give details of the working of

the devices in order to protect their IP rights. This can lead to a less-than-optimum usage of the energy storage device within an equipment where the battery works as a component.

In this paper we developed a model of a lithium ion battery provided by a vendor. The model is based on Batteries and Fuel Cell Module of COMSOL Multiphysics. The battery consists of LiFePO₄ as the cathode material, carbon as the anode material and LiPF₆ as the electrolyte. Several model parameters are taken from the literature [1] and some parameters have been varied depending upon the chemistry. The results of the model has been validated with the experimental tests done in the laboratory.

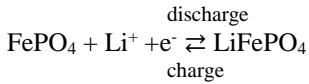
2. Experimental studies of lithium-ion battery

A lithium-ion battery of dimensions 362 mm (L) x 55mm (W) x 249 mm (H), weight of 7.2kg, operating voltage between 2.8V and 3.8V, and cell capacity of 200Ah was obtained from a vendor. The cell was charged and discharged for five cycles at a very slow rate (about C/25) at room temperature, in order to reach a stable capacity. After this Galvanostatic charging and discharging at 1C rate was conducted at 10°C, 30°C and 45°C with voltage range of 2.8V and 3.8V. These experimental results were used to validate our model of lithium ion battery.

3. Modeling lithium-ion battery using COMSOL Multiphysics

The fit to the above polarization data was obtained from models developed using the one-dimensional isothermal lithium-ion battery model available in COMSOL Multiphysics 5.0 model library. While the mathematical formalism to simulate the negative electrode and the electrolyte

was used as such, significant changes were made in the positive electrode. The cathode material for this battery is lithium iron phosphate (LiFePO₄). During charging, electrochemical de-intercalation reaction occurs at the surface of the iron phosphate particles. And during discharging intercalation reaction takes. These changes can be represented by the equation



The equilibrium potential with respect to the Li⁺ content obtained from galvanostatic intermittent titration technique (GITT) method was used [2]. The equation was found to be

$$U = 3.4245 + 0.85\exp(-800 x^{1.3}) - 17\exp(-0.98/x^{14})$$

where x in the above equation is the ratio of the surface concentration to the maximum concentration of lithium that can be incorporated into an FePO₄ lattice.

Table 1. Parameters used in the model

Description	Value
Cathode thickness (μm)	160
Anode thickness (μm)	160
Separator thickness (μm)	75
Median active-particle diameter (nm)	52
Total active material volume fraction	0.357
Maximum solid-phase lithium concentration (mol m ⁻³)	20950
Initial salt concentration in electrolyte (mol m ⁻³)	2000
Bulk diffusion coefficient of electrolyte (m ² s ⁻¹)	7.5×10^{-11}
Li ⁺ transference number	0.363
Effective electronic conductivity in cathode (S m ⁻¹)	6.75
Cell cross-section area (m ²)	10
Bruggeman exponent	1.5

The full cell model solves the set of coupled partial differential equations as in the one-dimensional isothermal lithium-ion battery model available in COMSOL Multiphysics 5.0 model

library. This simulation used the various model parameters applicable to Li_xC₆ | Li_yFePO₄. Table 1 summarizes the model parameters used in the study.

4. Results and Discussions

The results of this work is shown in the following Figures 1-6.

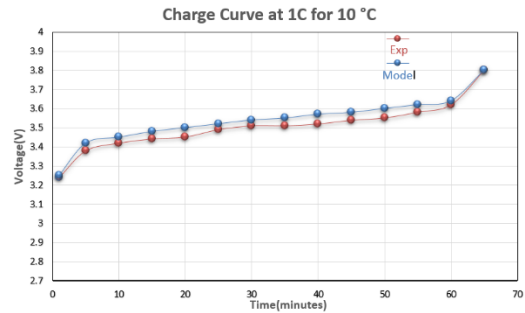


Figure 1. Comparison of the model with experimental data for 1C charging at 10°C

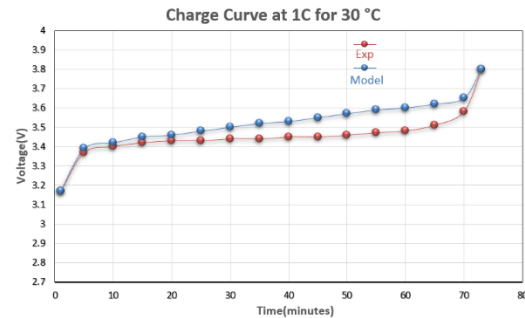


Figure 2. Comparison of the model with experimental data for 1C charging at 30°C

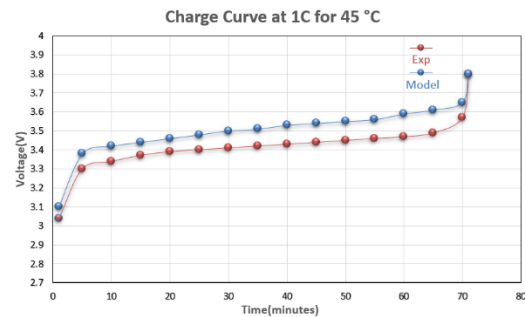


Figure 3. Comparison of model with experimental data for 1C charging for 1C charging at 45°C

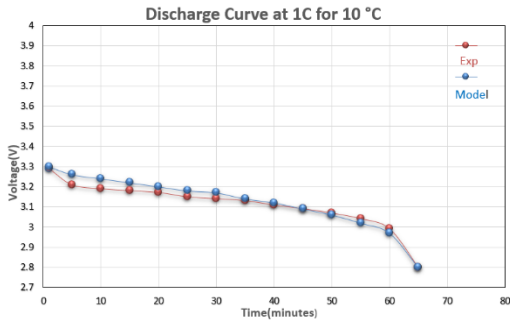


Figure 4. Comparison of model with experimental data for 1C discharging at 10°C

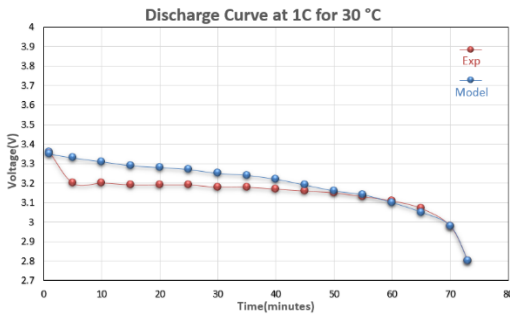


Figure 5. Comparison of model with experimental data for 1C discharging at 30°C

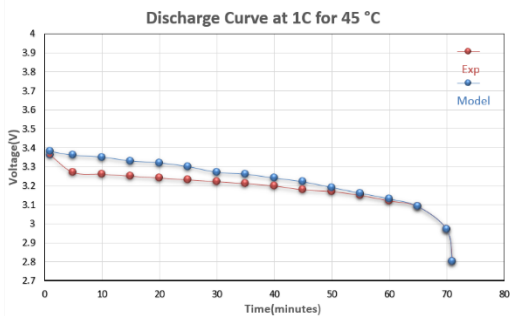


Figure 6. Comparison of model with experimental data for 1C discharging at 45°C

We note that the results obtained from our model are in general agreement with respective experimental data. We also note that the effective diffusion coefficient and the reaction rates in cathode during charging and the cell can be different while charging and discharging. This is an indication of the system being away from equilibrium condition. In a recent study, Farkhondeh et. al. also found that the model used during charging could not accurately represent the

conditions during discharging [3]. They solved the issue by introducing different equilibrium potentials during charging and discharging. In the present study we provide an alternate approach to look into the problem. Reaction rates at cathodes/anodes and the diffusion of Li^+ in LiFePO_4 particles are activated barrier crossing processes within the working battery. Hence they change with temperature and morphology at the microscopic length-scales. However, this issue merits a detailed study.

Table 2. Additional parameters used in the different studies

Description	Value	Study
Reaction rate in cathode (m/s)	2.5×10^{-13}	Fig 1
Diffusion coefficient of Li^+ in LiFePO_4 particles ($\text{m}^2 \text{s}^{-1}$)	2.0×10^{-17}	Fig 1
Reaction rate in cathode (m/s)	8×10^{-13}	Fig 2
Diffusion coefficient of Li^+ in LiFePO_4 particles ($\text{m}^2 \text{s}^{-1}$)	7.0×10^{-16}	Fig 2
Reaction rate in cathode (m/s)	8×10^{-13}	Fig 3
Diffusion coefficient of Li^+ in LiFePO_4 particles ($\text{m}^2 \text{s}^{-1}$)	9.0×10^{-16}	Fig 3
Reaction rate in cathode (m/s)	2.5×10^{-13}	Fig 4
Diffusion coefficient of Li^+ in LiFePO_4 particles ($\text{m}^2 \text{s}^{-1}$)	8.0×10^{-18}	Fig 4
Reaction rate in cathode (m/s)	5×10^{-13}	Fig 5
Diffusion coefficient of Li^+ in LiFePO_4 particles ($\text{m}^2 \text{s}^{-1}$)	8.0×10^{-18}	Fig 5
Reaction rate in cathode (m/s)	8×10^{-13}	Fig 6
Diffusion coefficient of Li^+ in LiFePO_4 particles ($\text{m}^2 \text{s}^{-1}$)	8.0×10^{-18}	Fig 6

5. Conclusions

In this work we have carried out COMSOL Multiphysics simulation of a lithium-ion single cell at different temperatures using the one-dimensional isothermal lithium-ion battery model available in the COMSOL Multiphysics 5.0 model library. This simulation uses model parameters applicable to $\text{Li}_x\text{C}_6 \mid \text{Li}_y\text{FePO}_4$ system. Few model parameters were determined by comparing simulated polarization data with experimental data. Using these parameters further simulations were performed for different temperatures under charging and discharging conditions. It is observed that the cell cycled at 10°C showed lower capacity, due to decrease in ionic conductivity of electrolyte at low temperature and also due to the sluggish kinetics for Li-ion diffusion into electrodes. The results are matching with the experimental results with good accuracy.

We however note that the system is away from equilibrium. Hence few parameters needs to be changed for reproducing the charging and discharging experimental results of the single cell.

The study could be used to further build models for thermal management and capacity fading of the battery available in the market. Also it will help in understanding the optimal usage conditions for their long cycle life. Further, it can be used in designing electronics and battery management systems.

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