Charge-Discharge Studies of Lithium Iron Phosphate 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 a copper current collecting plates. The battery performance generally depends upon several parameters & it is important to know the cell performance by varying these parameters. In this work we have modeled a lithium iron phosphate (LiFePO$_4$) battery available commercially and validated our model with the experimental results of 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.

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, many manufacturers are interested in using Li$^+$-ion based batteries in their products. However, battery manufacturers often refuse to give details of the working of the devices in order to protect their IP rights. This leads to a less-than-optimum usage of the energy storage device within a device where the battery works as a component.

In this work, we developed a model of a Li$^+$-ion battery provided by a vendor. The model is based on Batteries and Fuel Cell Module of COMSOL Multiphysics. The battery consists of LiFePO$_4$ as a cathode material, carbon as anode material and LiPF$_6$ 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.
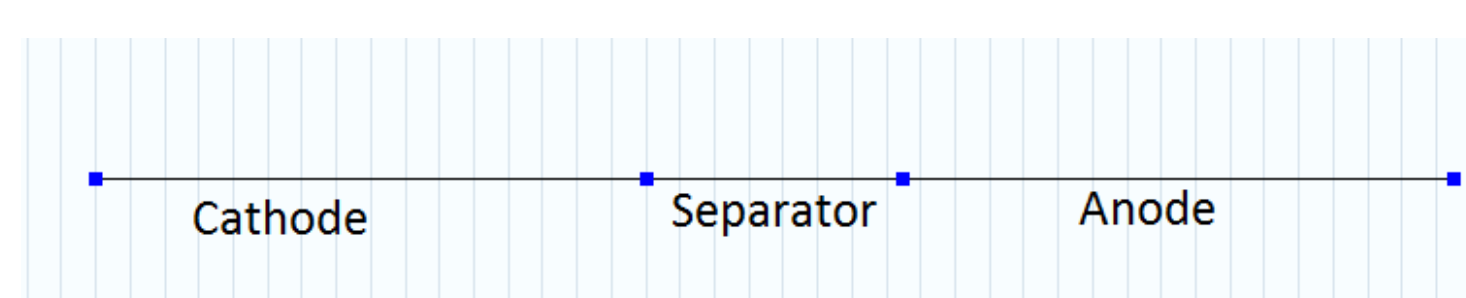
**Figure 1**. 1D model of the lithium-ion battery

Experimental studies: A Li$^+$-ion battery weighing 7.2kg with 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.

Modeling: 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 (LiFePO$_4$). During charging, electrochemical de-intercalation reaction occurs at the surface of the iron phosphate particle. And during discharging intercalation reaction takes place on the particle surface. The equilibrium potential with respect to the Li$^+$ intercalation was assumed to be [2]

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

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 FePO$_4$ lattice. This simulation used the various model parameters applicable to LixC$_6$ | Li$_y$FePO$_4$. Also the effective diffusion coefficient and the reaction rates in cathode was optimized to obtain good fit between experimental and simulation results.

Results:
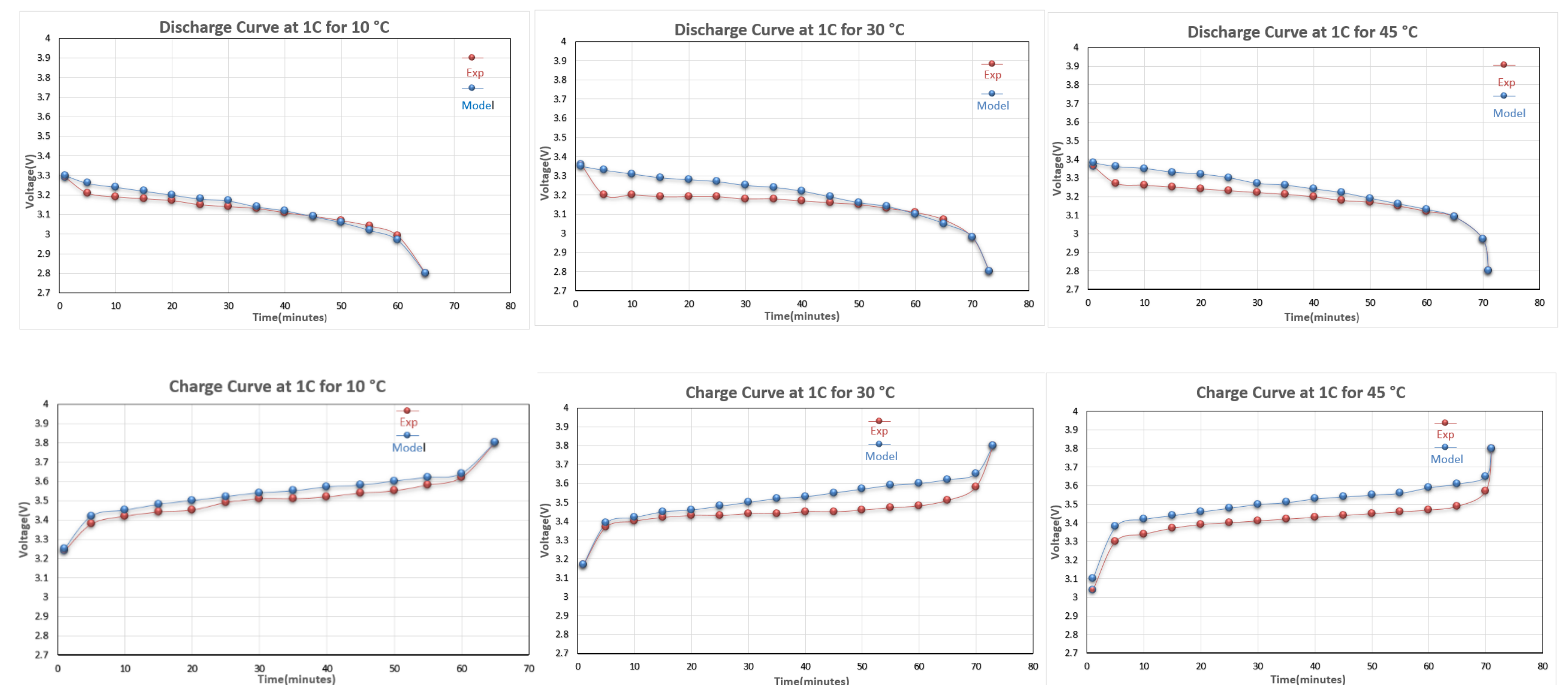
Figure 2. Comparison between the model and experimental results for 1C charging & discharging

We note that the results obtained from our model are in general agreement with the respective experimental data. The effective diffusion coefficient and the reaction rates in cathode during working of the cell can be different while charging and discharging. This is an indication of the system being away from equilibrium condition, contrary to what is normally assumed in most modeling studies. 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 work we provide an alternate approach to look into the problem. Reaction rates at cathodes/anodes and 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.

Conclusions: We carried out 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 used the various model parameters applicable to the Li$_x$C$_6$ | Li$_y$FePO$_4$ system. The 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.

References:

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