Simulation of the Behavior of the Lithium Ion Battery

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Abstract:

The lithium-ion battery is an ideal candidate for a wide variety of applications due to its high energy/power density and operating voltage. In the military it is used in numerous types of communications and army robotic applications. Lithium-ion batteries are used as a primary and a secondary power source. We focus on the use of secondary power sources. The real lithium ion battery is compared with simulation results and with real measurements.

Keywords:

Lithium ion battery, numerical simulation, mathematical model, simulation, measuring

1. Introduction

Lithium ion batteries gains more and more importance due to their higher specific capacity, longer life and lower self-discharging compared with conventional batteries such as NiCd or NiMH. These properties are based on the use of lithium and intercalation materials from which the electrodes are formed. These substances are characterized by the ability to release and then incorporate lithium ions in their structure, thereby these batteries differ from the conventional ones, in which chemical conversion of anode and cathode material takes place. Another advantage is that these accumulators use only a small amount of electrolyte, which serves only as ion conductor, thus again leads to reducing the size of these batteries. The following equations describe the function of lithium-ion batteries. In these equations $LiMO_2$ metal oxide stands for cathode materials as $LiCoO_2$ or $LiNiO_2$. C is typically used as the anode material [1].

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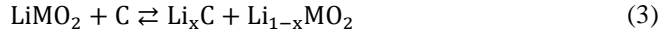
Reaction at the positive electrode of Li-Ion cells:

$$LiMO_2 \rightleftarrows Li_{1-x}MO_2 + xLi^+ + xe^- \tag{1}$$
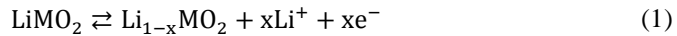
Reaction at the negative electrode of Li-Ion cells:

$$C + xLi^+ + xe^- \rightleftarrows Li_xC \tag{2}$$

Summary reaction:

$$LiMO_2 + C \rightleftarrows Li_xC + Li_{1-x}MO_2 \tag{3}$$

Currently the material most frequently used for positive electrode in lithium-ion cells is LiCoO2 and its modifications. This type of material was used in the first commercial lithium-ion batteries made by Sony in 1991. It is a material with a layered structure, its voltage against lithium in pure form is 3.88 V and capacity ~155 mAh/g. Its disadvantage is worse temperature and cycling stability. A modification by using Ni is very common. Material LiNi1-xCoxO2 shows better stability and higher capacity than the default material, but it is slightly less thermally stable. The final properties depend on the content of Co. Specific capacity of the material is between 190 mAh/g and 220 mAh/g. Similarly, the voltage against lithium varies from 3.72 to 3.78 V depending on the content of Co. The first notes about $LiFePO_4$, which was created as its possible replacement, are dated from 1997. $LiFePO_4$ material is the newest one in the group of materials for lithium-ion cells and it is characterized by olivine structure, high stability and long shelf life. It is composed of ecological and cheap materials and shows the voltage of 3.3 V versus lithium and capacity of 170 mAh/g. This material gradually begins to replace older types of cathode materials [2]. Fig. 1 shows the principle of function of lithium ion battery - charging and discharging processes.
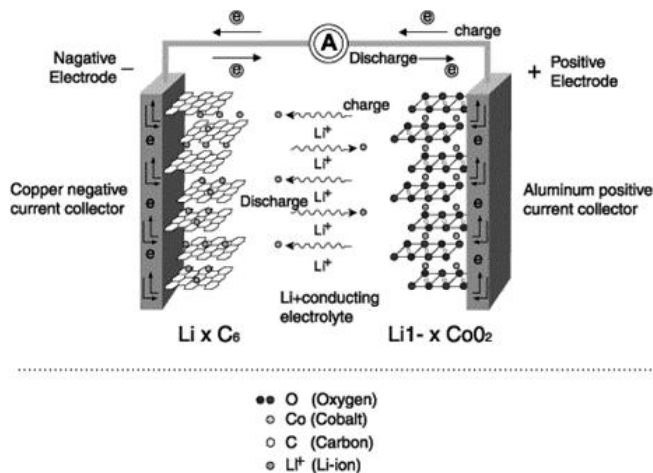

Fig. 1 The principle of function of lithium ion battery – charging and discharging model [4].

Modern simulation programs (e.g. Comsol, Matlab) have found a place in electrochemistry. It is important to describe chemical processes mathematically

correctly. The output can be the charging and discharging curves, the concentration profiles of electrolyte during charging and discharging, state of charge characteristic, or in more complex simulations for example heat loss caused by charging and discharging. Comsol allows simulating chemical reactions and provides computational modules dealing with specific types of batteries.

2. Measuring Devices and Methods

The Samsung ICR18650-30A battery with a capacity of 3000 mAh and a nominal voltage 3.7 V was selected as a sample for real measurement (the battery structure is shown in Fig. 2 [4]).
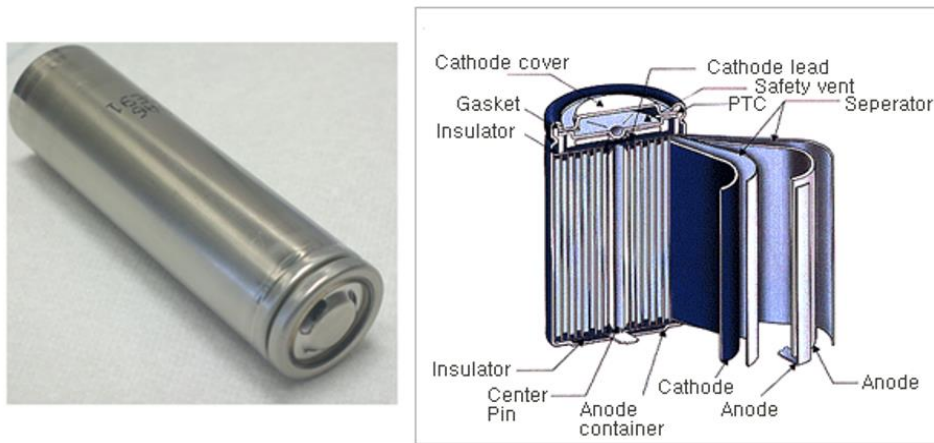

Fig. 2 a) The battery used for measuring and preparing geometrical model.
b) Cross section of measured lithium-ion cylindrical cell [4].

The VMP3 potentiostat (Biologic) with attached VMP3B-20 booster was used for the measuring of discharge curves. Fig. 3 shows the bloc diagram of the measured cell (the measuring was released at the room temperature 20 °C).
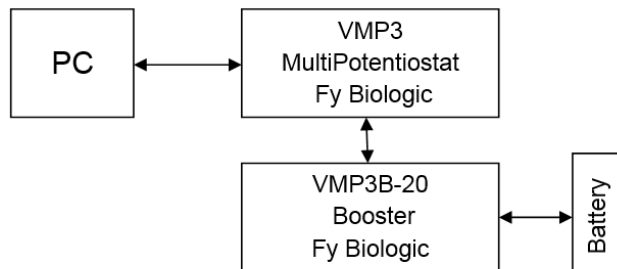

Fig. 3: Block diagram of measuring cell.

The measurement procedure was set according to the datasheet. Two discharging currents were selected - namely 0.2 C and 0.5 C. The charging was done using the CC-CV method. For the first measurement charging current was set to 0.2 C (600 mA)

and the maximum charging potential was set to 4.2 V. This was followed by CV charging until the current dropped to 0.05 C (150 mA). Discharging was done by discharging current 0.2 C (600 mA), cut-off potential was set to 2.75 V.

Charging current for the second measurement was set to 0.5 C (1500 mA) and the maximum charging potential was set to 4.2 V. This was followed by CV charging until the current dropped to 0.05 C (150 mA). After that, discharging by a current of 0.5 C (1500 mA) was used. Cut-off potential was set to 2.75 V (Fig. 4). Fig. 5 shows the comparison between 0.2 C and 0.5 C discharge current and Fig. 6 shows the equilibrium potentials of electrode materials.
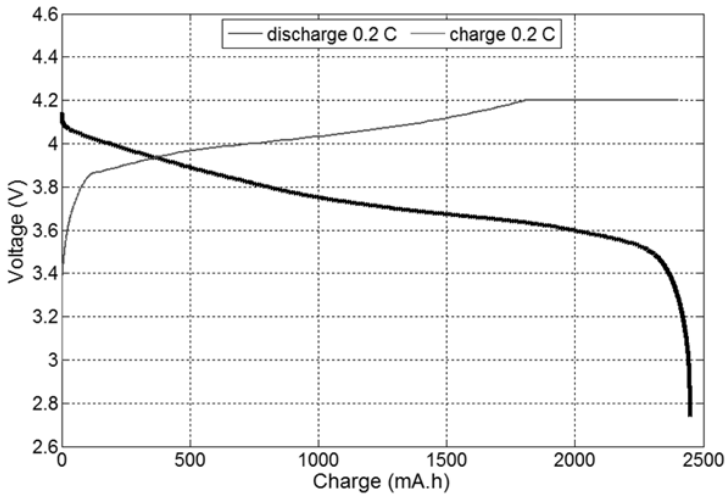

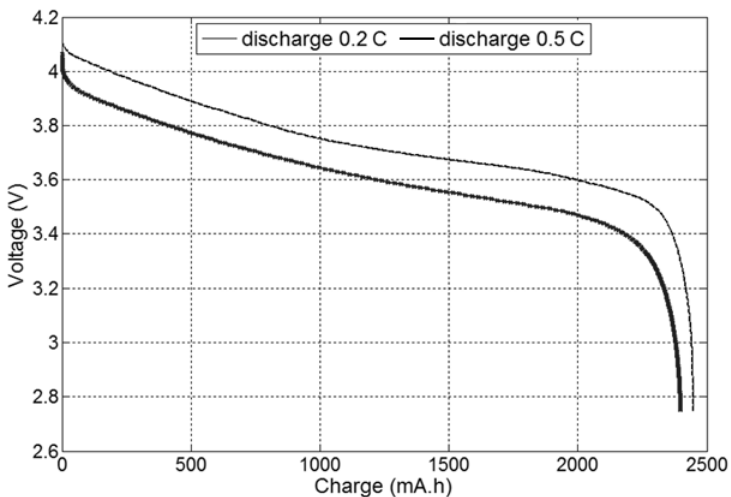*Fig. 4 Charging and discharging characteristics of lithium ion battery for 0.2 C.*

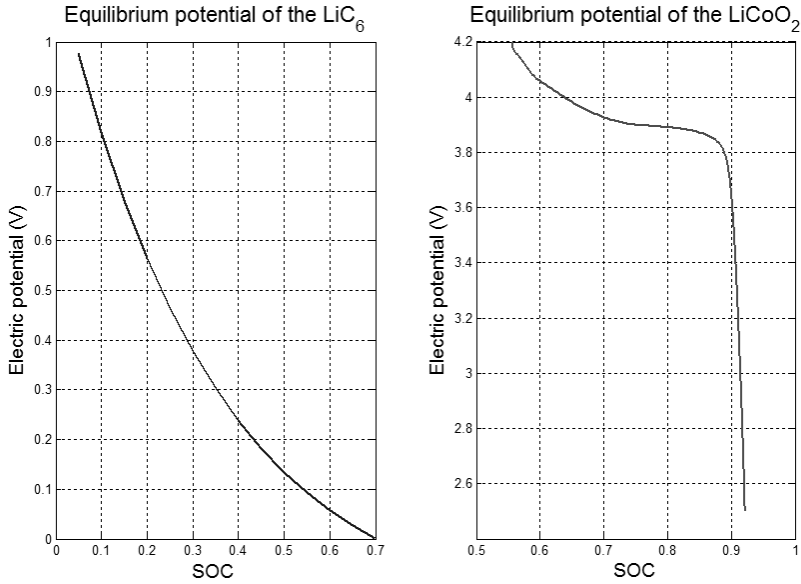*Fig. 5 Comparison between 0.2 and 0.5 C discharge.*

Fig. 6 Equilibrium potential of electrode materials.

3. Matlab Simulink 2012b

The Battery block implements a generic dynamic model parameterized to represent the most popular types of rechargeable batteries:

- Lead-Acid Model
- Lithium-Ion Model
- Nickel-Cadmium Model
- Nickel-Metal-Hydride Model

The general model for charge and discharge is in this form:

$$E_{\text{charge}} = f_1(it, i^*, Exp, \text{BattType}) \tag{4}$$

and

$$E_{\text{discharge}} = f_2(it, i^*, Exp, \text{BattType}) \tag{5}$$

where E_{charge} and $E_{\text{discharge}}$ are the functions of it (Extracted capacity (Ah)), i^* (Low frequency current dynamics (A)), Exp (Exponential zone dynamics (V)) and BattType (type of the battery). Fig. 7 shows the equivalent circuit of the battery in Matlab Simulink.
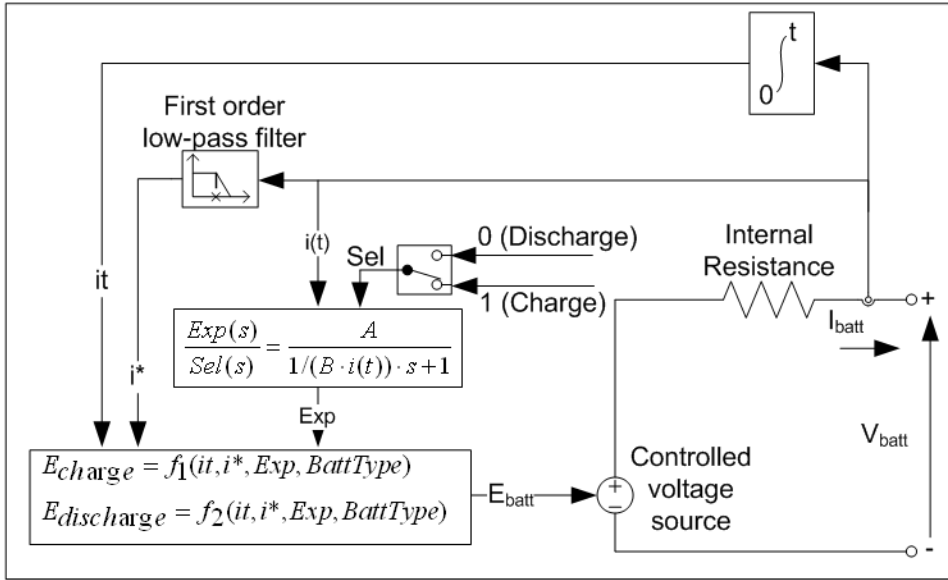
Fig. 7: Equivalent circuit of battery.

In these equations $Exp(s)$ is the Exponential zone dynamics and (V) $Sel(s)$ represents the battery mode. $Sel(s) = 0$ during battery discharge, $Sel(s) = 1$ during battery charging and E_{batt} is the Nonlinear voltage (V).

The $Exp(s)/Sel(s)$ transfer function represents the hysteresis phenomenon for the Lead-Acid, NiCd and NiMH batteries during charge and discharge cycles. The exponential voltage increases when battery is charging, no matter what the SOC of the battery is. When the battery is discharging, the exponential voltage decreases immediately.

Lithium ion battery model

Discharge model for $i^* > 0$

$$f_1(it, i^*, i) = E_0 - K \cdot \frac{Q}{Q - it} \cdot i^* - K \cdot \frac{Q}{Q - it} \cdot it + A \cdot \exp(-B \cdot it) \tag{6}$$

Charge model for $i^* < 0$

$$f_2(it, i^*, i) = E_0 - K \cdot \frac{Q}{it + 0 \cdot 1 \cdot Q} \cdot i^* - K \cdot \frac{Q}{Q - it} \cdot it + A \cdot \exp(-B \cdot it) \tag{7}$$

where i is the battery current (A), E_0 is the constant voltage (V), K is the polarization constant (Ah^{-1}) or polarization resistance (Ω), Q is the maximum battery capacity (Ah), A is the exponential voltage (V) and B is the Exponential capacity (Ah^{-1}). Fig. 8 shows the Simulink model for charging and discharging of the battery [3].

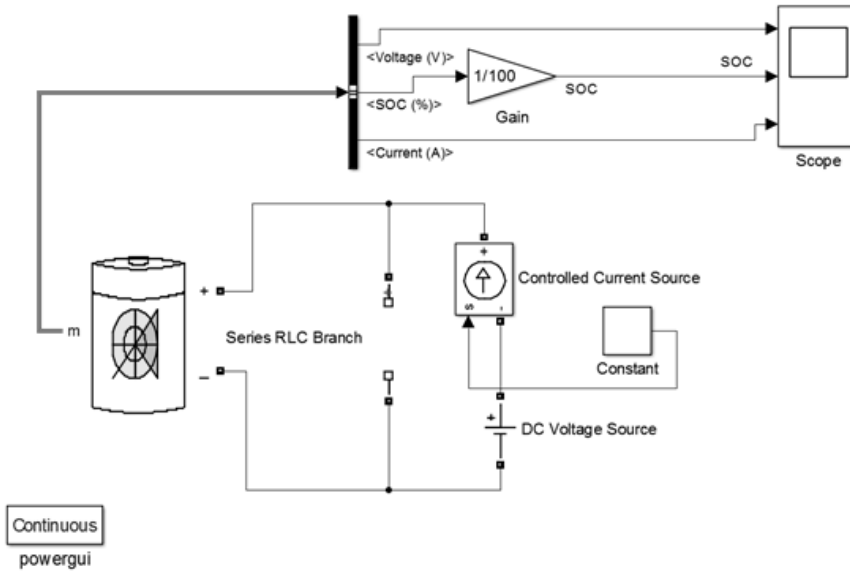**Lithium - Ion Battery Charging and Discharging Model**

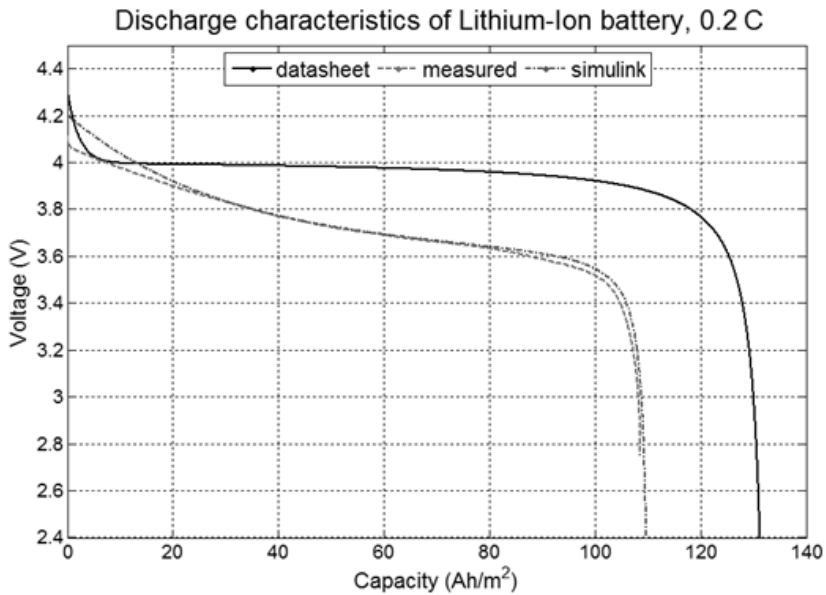*Fig. 8 Simulink model for charging and discharging of the battery.*

Fig. 9 Discharge characteristics of lithium ion battery – comparison between datasheet, Matlab Simulink and real measurement.
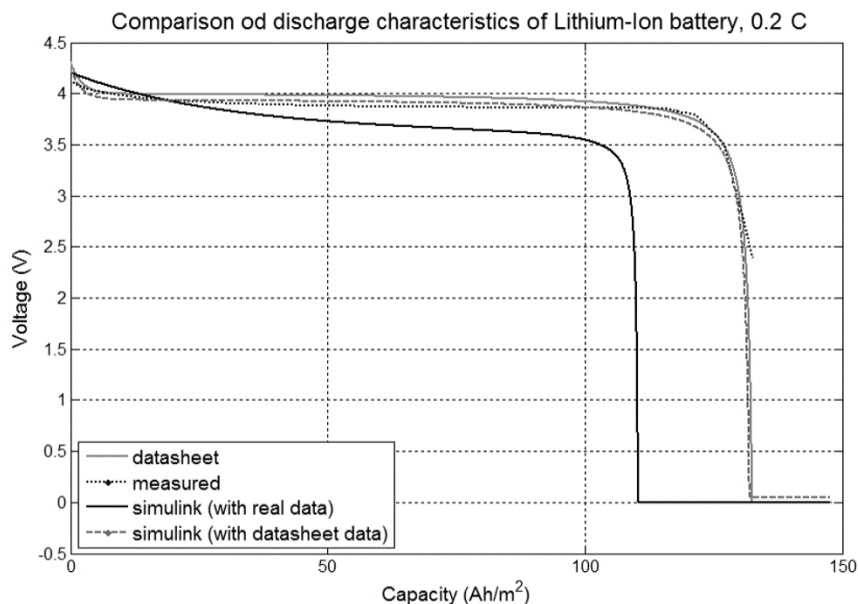
Fig. 10 Discharge characteristics of lithium ion battery – comparison of datasheet and Matlab Simulink with real data and real measurement.

4. Discussion

The results of the measurements made with the potentiostat have revealed that the capacity stated by the manufacturer and the real capacity differ by approximately 25 % even when charged and discharged accordingly to the manufacturer's recommendations (see Figs 4 and 10). It can be assumed that the cathode contains $LiCoO_2$ combined with Ni. We can see from the comparison of the real values and manufacturer's discharge curve that the values in the datasheet are rather idealistic; it is rather similar to the discharge curve of pure $LiCoO_2$ material.

It is obvious from the graphs that the simulation made in Matlab Simulink and the real values are almost identical (see Fig. 10). This is because we used the output values from real measurement as an input for Simulink simulation, not the values from the datasheet.

5. Conclusion

This article deals with the possibilities of simulations of Lithium-ion batteries. We used Matlab for the demonstration of these possibilities. This system (or its integrated part Simulink) is one of the best programs for mathematical analysis.

Our goal was to investigate how this solver works from the view point of numerical analysis and to compare the results with the real measurement. Then we have analyzed the production sample of the battery. We can say that the real discharge characteristics significantly differ from the ones stated by the manufacturer.

There are differences both in the shape of the curve and the capacity of the cell. The discharge curve shown in the datasheet is rather an ideal curve, not a real one.

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