

Heat Capacity and Internal Thermal Resistance Measurements in Lithium-ion

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Abstract. *The heat capacity and the internal thermal resistance of lithium-ion batteries are two important parameters for the thermal modelling of cells. These parameters are not generally available from manufactures or stated on cell datasheets. Particularly, measurements of the specific heat capacity of the cell would require disassembly of the cell and the use of an expensive calorimeter. This work describes a simple method for the measurement of both the heat capacity and the internal resistance of a cell. The method only requires an electrical characterization of the cell from which a good estimate of the thermal parameters is obtained. The method has been verified on a cylindrical lithium-ion cell. Experimental data are in excellent agreement to those obtained by conventional method of specific heat capacity measurements, thus validating the proposed setup for the thermal modelling of lithium-ion cells.*

Keywords. Lithium-ion battery, heat capacity, internal thermal resistance, overvoltage, thermal Modelling

1 Introduction

Recently, energy storage has attracted a significant amount of research attention, mainly with the final target in transportations. Among the several types of batteries, lithium-ion cells have emerged for their high capacity, high efficiency, long life and low self-discharge rate. Accurate thermal model of battery cells is fundamental for adequate design of battery-pack especially for designing devices guaranteeing the safety during operation.

The thermal model of lithium-ion cells is often referred to the single point heat generation [1]. The heat is generated inside the cell in a point having a known mass and a specific heat capacity. Heat is then transferred from the inside to the surface of the cell and finally to the external environment. Different methods are adopted for the measurement of the specific heat capacity of a cell [2]. Depending on the adopted thermal model, heat capacity of the entire cell may be either: (i) a function of the values found for the different materials of the cell; or (ii) a single value expressing the heat capacity of the entire cell. In the former, to find the value for each component, the simplest approach involves disassembly of the cell, i.e. its destruction. In this case, the weighted sum of the heat capacities of each component gives the heat capacity of the cell. For the latter, the cell is characterized as is and a calorimeter is employed to measure its heat-capacity [3].

In this paper, a non-destructive method to determine both the heat capacity and the internal thermal resistance of lithium-ion cells is illustrated. The method implies the estimation of the two thermal parameters by cell's overvoltage measurements. Although referred to a specific cell, the two mentioned terms remain the same also in a more complex scenario, i.e. battery packs.

The report is structured as follows. Section 2 illustrates the theoretical background of the proposed approach. The experimental setup and the experimental results are described in Section 3 and Section 4, respectively. The conclusions are summarized in Section 5.

2 Theory

In an electrochemical cell, the available electrical energy can be calculated from the change in Gibbs free energy of the electrochemical couple [4]:

$$\Delta G = -n \cdot F \cdot OCV \quad (1)$$

where n is the number of electrons exchanged in the reaction, F the Faraday constant and OCV the open circuit voltage. When the cell is at equilibrium, not all the available energy can be converted into useful electrical energy: when a current flows in the cell, its voltage (V_{cell}) deviates from the value found at equilibrium. This effect reduces the amount of energy that the cell can convert. Depending on the direction of the current, this voltage deviation is termed as overvoltage or undervoltage [5]. In this work, simply referring on overvoltage, voltage deviation is calculated as:

$$\eta = OCV - V_{cell} \quad (2)$$

which is directly related to the energy dissipated as heat during transport and transfer phenomena [2].

Overtoltage contributions can be due to ohmic and non-ohmic effects. In ohmic conduction, only purely resistive effects are taken into account [6]. Non-ohmic contributions relate to polarizations losses that include: (i) concentration of a polarization, caused by spatial variations in the reactant concentration occurring in the bulk of the electrolyte or at the electrodes [7]; (ii) activation of a polarization deriving from the energy required to overcome the activation barrier of chemical reactions [6, 8].

Overtoltage value can be measured on a cell if discharged under a constant current [9]. In this case, the heat dissipated during the discharge process is given by:

$$P = \eta \cdot I \tag{3}$$

Integration of Eq. (3) over time represents the total energy the cells dissipates as heat. The heat capacity is then calculated by:

$$C = \frac{Pdt}{\Delta T} \tag{4}$$

where P is the heating power, T the battery temperature, and t the time.

The internal thermal resistance of a cell is simply given by:

$$R_i = \frac{\eta}{i} \tag{5}$$

i.e. a linear relationship between the current and the overvoltage amplitude.

The method used in this work and described in the following involved several charging-discharging cycles of the cell. In each cycle, the cell was maintained into its nominal operating conditions declared by the manufacturer.

3 Experimental setup

A lithium-ion cell (mod. 18650, Samsung) was characterized during this work. In order to simulate the optimal operating conditions, a constant-current source circuit was realized (Fig. 1). A fixed source/sink current of 2.5 A was adjusted for the experiments. However, a 10 mΩ shunt was also inserted in series to the cell for the continuous monitoring of the current value.

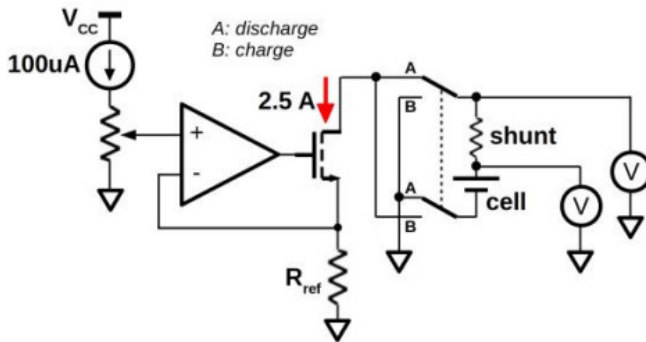


Figure 1. Simplified schematic of the circuit used during charge/discharge cycles

Three platinum resistance sensors (PT100 RS 158-985 PTFE) have been used for the temperature monitoring of the cell surface. The sensors were glued with silver paste at the centre and close the two poles of the cell. The voltage and the sink current of the cell, as well as the three temperatures, have been measured by means of a multi-channel acquisition system from National Instruments. A specifically designed Labview® program was developed for acquisition, processing and recording of data during the charge/discharge cycles. Figure 2 shows a picture of the adopted setup.

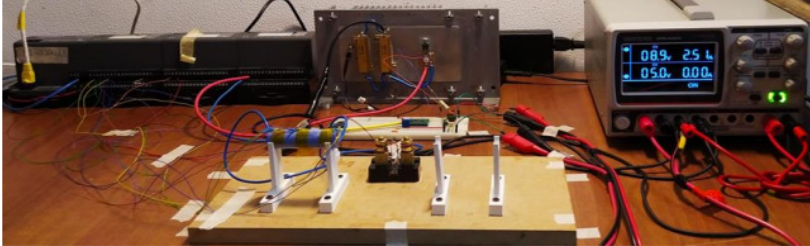


Figure 2. Experimental setup

4 Results and discussion

Up to 100 charge/discharge cycles have been carried out on the cell. Figure 3 shows four cycles as examples of the typical overvoltage behaviour. During a discharge cycle, η is approximately constant around 0.13 V.

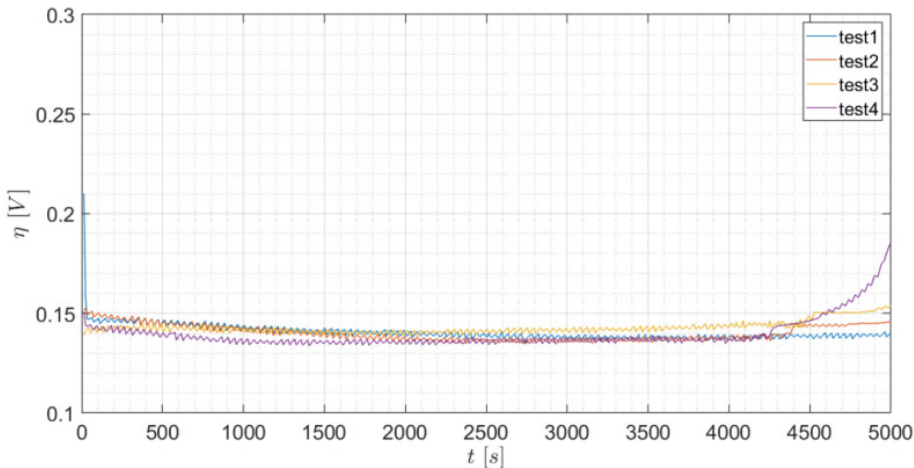


Figure 3. Overvoltage trend

The dissipated power can be calculated according to Eq. (3). As already mentioned, integrating the dissipated power over time gives the total energy dissipated as heat. By the energy dissipated as heat and the temperature changes over time, the heat capacity of the cell was calculated (see Eq. (4)). For the temperature, the values acquired by the sensor

located at the centre of the cell surface was used, being the highest found in all the acquisitions. Based on the data collected during the cycles, the heat capacity of the cell resulted of about $280 \text{ J} \cdot \text{K}^{-1}$. Moreover, from Eq. (5), and internal thermal resistance of about 0.18Ω was also evaluated.

To validate the obtained results, a conventional method [2] was employed. A thermos-insulating container was filled with deionized water and a cell was then immersed into the water. After hermetical closure of the container, the temperature of the water was monitored over time by means of a PT100 sensor. If T_{end} is the temperature at system equilibrium, the heat capacity of the cell, C_{cell} , can be calculated as:

$$C_{cell} = \frac{c_{ref}m_{ref}(T_{end}-T_{ref})}{m_{cell}(T_{cell}-T_{end})} \quad (6)$$

where C_{ref} is the heat capacity of deionized water, T_{ref} , T_{cell} , m_{cell} and m_{ref} the start temperatures and masses of the water and the cell, respectively. To enhance the accuracy, the measurements were performed by immersing three cells into the bath. A specific heat capacity of $286 \text{ J} \cdot \text{K}^{-1}$ was obtained, in excellent agreement with the value calculated by overvoltage measurements.

5 Conclusion

The thermal modelling of lithium-ion batteries is fundamental for battery-packs applications. Cell datasheets do not report any data useful to evaluate the thermal parameter of a cell. In this report, a measurement method for the specific heat capacity of lithium-ion cells has been described. Overvoltage measurement during several charge/discharge cycles allowed estimating both the heat capacity and the internal thermal resistance of a cell. These parameters are fundamental for the thermal modelling of single cell, but can be easily adapted to battery modules or packs.

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