Journal of Power Sources 330 (2016) 61–69

Contents lists available at ScienceDirect

Journal of Power Sources

journal homepage: www.elsevier.com/locate/jpowsour

Determination of the entropy change profile of a cylindrical lithium-ion battery by heat flux measurements

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HIGHLIGHTS

- ΔS measurements by using a gradient heat flux sensor are presented.
- Time required for the ΔS measurements by the potentiometric method is evaluated.
- Uncertainty and limitations of the methods under consideration are given.
- Comparison of the proposed method with the potentiometric method is made.

ARTICLE INFO

Article history:
Received 15 June 2016
Received in revised form
9 August 2016
Accepted 30 August 2016

Keywords:
Li-ion battery
Entropy change
Thermal diffusivity
Heat flux measurements
Sensor
Thermal model

ABSTRACT

The popularity of lithium-ion (Li-ion) batteries has increased over the recent years. Because of the strong dependence of the Li-ion battery operation characteristics on temperature, heat generation in the battery has to be taken into account. The entropy change of a Li-ion battery has a significant influence on heat generation, especially at a low C-rate current. Therefore, it is necessary to consider the entropy change profile in the estimation of heat generation. In the paper, a method to determine the entropy change (ΔS) profile by heat flux measurements of a cylindrical Li-ion cell is proposed. The method allows simultaneous measurements of the thermal diffusivity and ΔS of the cylindrical cell. The thermal diffusivity and ΔS measurements are carried out by a gradient heat flux sensor (GHFS). The comparison between the ΔS profile determined by the GHFS method with that obtained using a standard potentiometric method clearly shows that the entropy change measurements could be made by using a GHFS. Even though the uncertainty of the reported method is higher than that of the potentiometric method, a significant decrease in the experiment time compared with the potentiometric method is a major advantage of this method.

1. Introduction

The increasing popularity of electric and hybrid vehicles over the recent years is caused by a number of factors, including an increase in CO_2 emissions and high energy costs. An energy storage device is one of the main parts in electric vehicles (EVs). Nowadays, because of their large number of usable operation cycles and low self-discharge rate, lithium-ion (Li-ion) batteries are considered the most promising technology for the energy storage in EVs. Despite the advantages of the Li-ion batteries, they also have certain disadvantages such as the high sensitivity to overcharge and overdischarge and the risk of a thermal runaway, which can even be a reason of fire. Therefore, a battery management system and a thermal management system are required in the operation of Li-ion batteries. An appropriate thermal management system becomes more important when the surface area per volume ratio of a battery decreases with the increasing battery size, resulting in a lower heat transfer rate per unit rate of heat generation [1]. Therefore, a good thermal management system is required to ensure safe operation of a lithium-ion battery system.

The construction of a thermal management system calls for information about heat generated during the operation of the battery system. It was shown in Ref. [2] that the entropy change can account for more than 50% of the total heat generated (in Joules) at the 1 C-rate discharge, which is significant for the battery system operation in EVs, where the typical discharge current is from 0.125 to 0.25 C-rate [3].

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http://dx.doi.org/10.1016/j.jpowsour.2016.08.130

In addition, the entropy change has to be taken into account in plug-in hybrid electrical vehicles, where batteries are typically discharged with a 0.25 C-rate current [3]. Therefore, information about the entropy change is important and should be taken into consideration in the thermal management system. This prevents the system overheating and enhances the reliability and safety of the system.

The measurements of ΔS can be carried out by calorimetric [4,5] or potentiometric [3,6–10] methods. The calorimetric method requires an expensive calorimeter for the measurement of heat generation in a Li-ion battery. Application of the potentiometric method is typically less expensive than the calorimetric method and requires an option to adjust the temperature of the Li-ion battery, which can be done for example by using an environmental chamber. However, the relaxation time of the Li-ion battery strongly affects the measurement results in the potentiometric method. As it was shown in Ref. [8], the entropy profile measurements require 10–30 h per a single state of charge (SoC). The influence of the cell relaxation time can be taken into account as it was done in Ref. [8], where the effective approach to speed up the ΔS profile measurement was proposed to investigate the Li-ion battery aging and to determine its state of health (SoH). However, also in Ref. [8], 2.5 h was required to measure ΔS for a single value of the SoC.

In this paper, a method for the determination of the entropy change profile is proposed, which is based on heat flux measurements on the surface of a cylindrical Li-ion cell. The cylindrical cell was chosen for two reasons: it is one of the most common cell types, and the heat generation in a cylindrical cell is usually lower than in pouch or prismatic cells. The low heat generation allows to assume that if the heat generation can be estimated with a low uncertainty by heat flux measurements in the cylindrical cell, it could also be estimated in pouch or prismatic cells with an acceptable uncertainty. However, in the case of other cell types than the cylindrical ones, a special thermal model should be established to calculate the heat generation based on the information of temperature and heat dissipation from the cell surface. The proposed method for the cylindrical cell is similar to the calorimetric method; however, it does not require an expensive calorimeter for the measurements of heat generation. The proposed method allows simultaneous measurements of the thermal diffusivity and ΔS of the cylindrical cell. By using this method, it is possible to reduce the time of the experiment to only 80 min per a single value of the SoC. The quality of the ΔS measurements was analyzed by comparing the values of ΔS obtained by the heat flux sensor with the values of ΔS measured by the potentiometric method. In addition, the limitations of the ΔS profile determination method and the potentiometric method were analyzed based on the proposed cylindrical cell thermal model.

2. Entropy measurement by the potentiometric method

2.1. Test setup and procedure

At a constant temperature T (K) and pressure, the following dependence of the enthalpy H (J mol^{-1}) on the Gibbs free energy G (J mol^{-1}), the entropy change ΔS (J mol^{-1} K^{-1}), and the temperature can be given [5,6]:

$$\Delta H = \Delta G + T\cdot\Delta S, \tag{1}$$

$$\Delta G = -n\cdot U_{\mathrm{ocv}}\cdot F, \tag{2}$$

$$\Delta S = n\cdot F\cdot\left(\frac{\partial U_{\mathrm{ocv}}}{\partial T}\right), \tag{3}$$

where F is the Faraday constant (F = 96485 C mol^{-1}), n is the stoichiometric number of electrons participating in the cell reaction (for a Li-ion cell, $n = 1$), and U_{ocv} is the open-circuit voltage of the cell (V).

In this work, ΔS of a 2.3 A h A123 Systems cylindrical cell (ANR26650M1A) was estimated by the potentiometric method applying Equation (3). The parameters of the cylindrical cell were measured and are given in Table 1. The values of the theoretical heat capacity and thermal conductivity in the radial direction were assumed, as it was done in Refs. [11,12], to determine the limitations of the ΔS measurements.

The cylindrical cell was placed in an environmental chamber (Jeio Thech TH-KE-025), where the temperature and humidity of air can be controlled. The terminal voltage of the cell was measured by a 34420A nanoVolt/micro-Ohm meter. The Potentiostat/Galvanostat Gamry Reference 3000 was used for charging and discharging. A PT100 temperature sensor and a Keithley 2701 bench digital multimeter were used to measure the temperature on the cell surface. The step of the ΔS measurements was chosen to be 10% of the SoC as a compromise between the number of measured points and the time required to perform the measurements.

The ΔS measurement process consisted of three steps. In the first step, the test preparation was carried out. The available capacity of the cylindrical cell was measured by discharging the cell with a 3.0 A constant current in order to determine the discharge capacity of the cell at the operation current under study. The 3.0 A constant current, that is the maximum operation current of the Potentiostat/Galvanostat Gamry Reference 3000, was chosen for the cell discharge to reduce the duration of the test. Then, the cell was fully charged according to the manufacturers recommendations [13]. In the second step, the cylindrical cell was discharged with a 3.0 A current for 264 s, and the relaxation period of the cylindrical cell after charging and discharging was 12 h. The internal pressure of the cell was assumed to be constant during charging and discharging. The relaxation time was chosen based on [8], where it was found that the entropy profile measurements require between 10 and 30 h per SoC. The charging, discharging, and relaxation of the cylindrical cell took place at a room temperature of about 24° C. At the end of the second step, the cell was placed in an environmental chamber. Then, the measurements of ΔS were performed for the considered value of the SoC. The temperature in the chamber was set to 30° C. When the temperature in the cylindrical cell became constant and equal to the air temperature in the chamber, the OCV of the cell was measured. The profile of the temperature changes in the environmental chamber during the ΔS measurements was similar to that in Ref. [8]. The OCV measurements were made at the temperatures of 30° C, 25° C, 20° C, and 30° C, in this order. In addition, to compensate for the influence of the cell relaxation process on the entropy measurements, a similar method as in Ref. [8] was applied. The change in the OCV, caused by the relaxation process in the cylindrical cell during the ΔS measurements, was subtracted from the measured data.

2.2. Thermal transient processes in the cylindrical cell

The measurements of the OCV after changing the air temperature inside the environmental chamber should be made only after the attenuation of all thermal transient processes in the cell when the temperature in all parts of the cell is equal to the air temperature in the chamber. The time after which the measurements can be carried out was estimated based on the thermal model of the cylindrical cell, which was constructed based on the thermal model of an infinitely long cylinder, presented in Ref. [14].

To simplify the thermal model of the cylindrical cell, ceramic fiber wool was used to provide the thermal isolation of the ends of the cylindrical cell. In this case, the cylindrical cell can be