Energy 61 (2013) 432–439

Contents lists available at ScienceDirect

Energy

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

Thermal characterization of a high-power lithium-ion battery: Potentiometric and calorimetric measurement of entropy changes

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ARTICLE INFO

Article history:
Received 28 February 2013
Received in revised form
10 September 2013
Accepted 12 September 2013
Available online 6 October 2013

Keywords:
Lithium-ion battery
Thermal behaviour
Accelerating rate calorimeter
Potentiometric method
Entropy change

ABSTRACT

This paper focuses on the thermal behaviour of high-power lithium-ion cells during charge-discharge at several current rates. A series of tests are conducted using an accelerating rate calorimeter to promote an adiabatic environment. Cell heat capacity is identified and the overall heat generated is quantified. Cell entropy is measured, using both potentiometric and calorimetric methods. The part of reversible reaction in the overall thermal behaviour is determined during charge-discharge tests and compared to joule losses. The influence of the state-of-charge variation and the impact of charge-discharge current rate on battery heat generation are highlighted. Experimental results for two lithium-ion technologies are presented and discussed.

1. Introduction

In order to reduce the environmental impact of their fleet, many companies have invested in researching and testing alternative technologies, such as hybrid and electric vehicles [1]. These technological innovations rely on an ESS (energy storage system), designed to meet the requirements of each application and enhance on-board energy management (auxiliaries, regenerative braking energy, etc.) [2].

Advanced energy storage technologies for the transportation industry all rely on a key component: lithium-ion batteries. Lithium-ion batteries present unmatched reliability, flexibility, and performance and are designed to provide advantages in terms of power, lifetime, safety, and energy [3].

Ferreira et al. [4] listed the relevant characteristics of energy storage technologies. They indicated that durability and reliability are among the important factors affecting battery selection.

Any investigation of lithium battery behaviour during use necessarily considers thermal aspects in addition to electrical ones. Indeed, battery characteristics depend strongly on the temperature range.

Actually, previous research on lithium battery ageing confirmed that performances, in particular capacity fade and impedance rise, are very sensitive to the operating temperature. This has been true for battery power cycling mode as well as in storage conditions [5,6].

In fact, Dubarry et al. [7] analysed irreversible phenomena and premature ageing caused by high temperatures and proved that this harms battery safety accelerating the growth and the crack of the SEI (Solid Electrolyte Interface). Moreover, the work presented by Vetter et al. [8] agreed with that and proved also that low temperatures are also damaging, as they lead to lithium plating and dendrite growth.

Furthermore, is necessary to manage the thermal behaviour of the battery in an EV (electric vehicle) or HEV (hybrid-electric vehicle) in order to optimize the energy balance of the whole system and ensure that it operates within a safety range [9,10]. Moreover, thermal factors are likely to be useful for developing a strategy to prolong battery pack lifetime [11].

In addition to the thermal runaway and safety issues, such as overcharge, short circuits, and other extreme working conditions, as illustrated in the reported case studies [12–14], it is very necessary to focus on the thermal behavior of lithium batteries, including the heat generating rate, under normal operating conditions. It will be very helpful for improving the efficiency of the cooling system, and maintaining the optimal battery performance [15,16].

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0360-5442/$ – see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.energy.2013.09.028

In Refs. [17], based on heat recovery examination, heat generated by the battery pack helped to optimize the cooling system of the cabin of a hybrid electric vehicle.

In this research, a calorimetric method was applied to measure the heat produced by lithium batteries during the charge and discharge processes at several C-rate (current rates), using an ARC (accelerating rate calorimeter). Indeed, the heat produced by the lithium-ion battery consists of irreversible and reversible parts due to joule losses and electrochemical reactions, respectively. Experiments were designed to quantify the reversible heat loss during battery use and study the impact of SOC (several states of charge) variation and current magnitude on overall heat generation.

In the first part, the thermal behaviour of an HEV lithium battery was investigated, using time-domain characterization and EIS (electrochemical impedance spectroscopy). This was followed by, a calorimetric thermal study, focussing on the battery's thermal behaviour during use under adiabatic conditions. Battery specific heat measurements were used in a later step for overall heat calculation and calorimetric analysis.

The battery entropy coefficient was then calculated using a potentiometric method at several SOC (states of charge) and a calorimetric method during charge and discharge for several C-rates. The findings highlighted entropy change dependency on SOC and its impact on thermal behaviour.

Finally, the difference between charge and discharge, the impact of C-rate and battery technology on heat generation are discussed.

2. Thermal characterization tests: equivalent circuit model based on impedance spectroscopy

2.1. Experimental setup

The 12 Ah high-power lithium cell used, based on NMC chemistry, is commercialized by Kokam. These cells have a carbon negative electrode and a positive electrode consisting of $LiMnNiCoO_2$ (lithium cobalt manganese nickel oxide). The $LiPF_6$ (lithium hexafluorophosphate) electrolyte is a solution in a mixture of organic solvents: EC (ethylene carbonates) + EMC (ethylmethyl carbonate). The overall chemical reaction inside the cell is given by:

$$Li_xC + Li_{1-x}MnNiCoO_2 \leftrightarrow C + LiMnNiCoO_2 \quad (1)$$

The cell was placed in a temperature-controlled climate chamber, maintained at SOC 60% using the IEC standard 62660-1 for HEV-battery performance testing [18]. Four temperature steps (25, 35, 45 and 55 °C) were then applied, each lasting 6 h, with an EIS test before each step. A thermocouple was attached to the battery's surface to measure temperature.

2.2. Electrochemical impedance spectroscopy

EIS is used to study system transfer behaviour in a wide range of scientific applications. In Lithium battery technology, this technique is a key tool for investigating battery behaviour under varying conditions, such as temperature, SOC, and current. As EIS is based on a frequency analysis, its main advantage is its capability to separate the influences of several physical effects occurring simultaneously [19]. Fig. 1 is a Nyquist plot showing variation with temperature.

Increasing temperature accelerates all phenomena inside the cell, including migration charge transfer and diffusion [20].

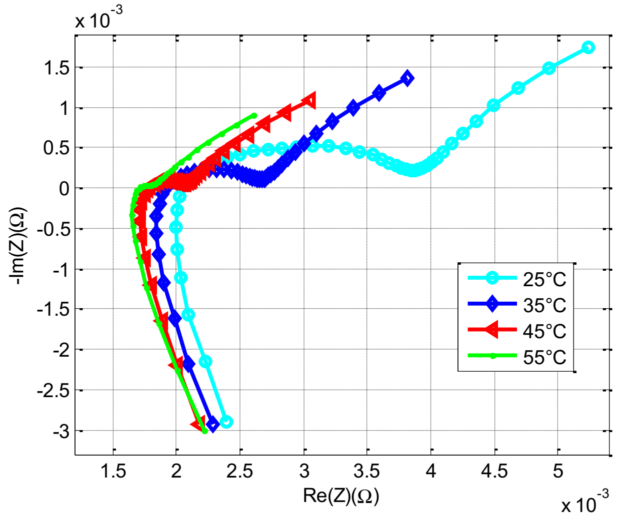

Fig. 1. Nyquist plots at SOC 60% and several *T*.

2.3. Equivalent circuit model and parameter identification

Impedance models provide an effective means of studying and modelling lithium batteries. In fact, the model parameters may be determined on the basis of EIS measurements and used to investigate variations with temperature change. Fig. 2 shows the model used to simulate lithium cell behaviour.

This impedance model consists of an SOC- and temperature-dependant voltage source (E), an ohmic resistance (R_1), a non-linearly SOC- and T-dependant resistance (R_2) connected in parallel with a CPE_1 (first constant phase element), and a CPE_2 (second constant phase element). The voltage source represents the OCV (open-circuit voltage) (OCV), corresponding to the voltage of the cell in a thermodynamic equilibrium state, and the ohmic resistance (R_1) represents the resistance of the active materials. The parallel connection of the second resistance (R_2) and (CPE_1) corresponds to the time-dependent overvoltage occurring during charging or discharging, i.e., charge transfer and double-layer processes. A CPE_2 (second constant-phase element) is used to model diffusion phenomena at low frequencies.

In fact, the resistance and capacitance values depend on the particular operating point of the cell, so they vary with time, temperature, SOC, power demand, and degradation [5]. Fig. 3 represents the variations in model parameters R_1 and R_2 with temperature. These parameters are useful for determining the irreversible heat generated when using the lithium cell.

Table 1 compares battery discharge capacity at several temperatures (25, 35, 45, and 55 °C) showing that battery capacity increases with temperature.

The impact of temperature on lithium battery characteristics is clear. The next step was a more detailed investigation of the lithium battery's thermal behaviour, including the difference between charge and discharge and the impact of SOC and C-rate on battery

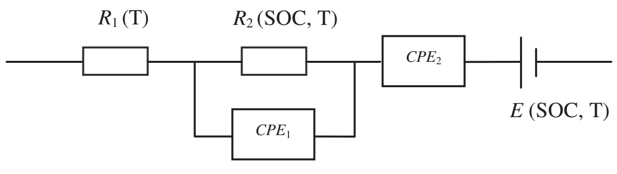

Fig. 2. EC model for lithium-ion cell.