Short communication

Uncertainties in entropy due to temperature path dependent voltage hysteresis in Li-ion cells

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HIGHLIGHTS

- The existence of the temperature path dependent voltage hysteresis is shown.
- Minimal temperature pulse duration and amplitude reduce measurement uncertainty.
- Optimized temperature profile for potentiometric entropy measurement is presented.

GRAPHICAL ABSTRACT
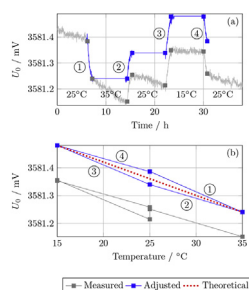
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ABSTRACT

The determination of reversible heat is often carried out by means of a potentiometric measurement of entropy related effects. In this work, the potentiometric method is more closely investigated regarding the often assumed linear relationship between the open circuit potential (OCP) and temperature and possible associated measurement inaccuracies. Four different, completely equalized lithium-ion cells comprising different chemistries and cell formats are object of this study. Two different temperature profiles with varying frequency and amplitude components were applied and according entropic coefficients were calculated based on the preceding data. The results obtained in this work clearly reveal a non-linear behavior of the voltage to temperature relationship regardless of the cell format, state of charge (SOC), cell chemistry or sign of the derived entropic coefficient. This non-linearity manifests in a certain hysteresis of the OCP depending on the temperature history of the cells. The results suggest to minimize the temperature pulse duration whilst still allowing for a thermal equalization of the cell. Additionally, the authors suggest to minimize the amplitude of the temperature pulse as much as possible, whilst still allowing for an acceptable signal to noise ratio (SNR) for the measured voltage response.

1. Introduction

The rising trend of decentralized energy production as well as growing market for electric vehicles (EV) has created a demand for economically reasonable, persistent and reliable energy storage systems. Lithium-ion technology has recently become a key player in the energy storage domain by improving its cycle life and safety properties.

Whilst currently used materials are reaching their maximum theoretical potential in terms of energy density, further improvements can be achieved on the system level. Thermal management can guarantee both, a high efficiency and a long lifetime of a battery pack. However, proper dimensioning and design of such thermal management systems requires precise thermal characterization of the battery cells.

The major heat losses in a lithium-ion cell can be divided into

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reversible and irreversible part [1]. Irreversible losses are usually attributed to charge transfer, finite conductivity of the electrolyte, the current collector foil, active materials and cell connectors [2]. The reversible heat losses on the other hand are connected to structural properties of the active materials, which might change during the lithiation and delithiation due to different arrangement of lithium-ions in the host lattice [2].

Thermodynamics of an electrochemical system can be described by Gibbs free energy ΔG, reaction enthalpy ΔH and reaction entropy ΔS. At constant pressure and physical composition, the maximum available electrical energy, the Gibbs free energy ΔG is given by

$$\Delta G = -nFU_0(x) \tag{1}$$

whereas n is the number of electrons participating in the reaction, F is the Faraday constant, $U_0(x)$ is the equilibrium voltage and x is the SOC. The overall energy of the reaction, the Gibbs free energy ΔG can be expressed by

$$\Delta G = \Delta H - T\Delta S \tag{2}$$

whereas T is the absolute temperature. The reaction entropy ΔS, which describes the reversible heat effect is then given by

$$\Delta S = nF\frac{\mathrm{d}U_0(x)}{\mathrm{d}T} \tag{3}$$

where the entropic coefficient for a constant pressure and a certain SOC is proportional to a change of the OCP for a change in temperature. This relationship holds, if ΔS and ΔH do not depend on temperature.

Considering equations (1)–(3) there are two major techniques for the determination of the entropic coefficients. The calorimetric method utilizes reversible heat effects, by separating the reversible and irreversible heat losses for a subsequent charge and discharge of the cell, which is only applicable in case other effects contributing to the energy balance are negligible [3]. The potentiometric method, however, utilizes the relationship from equation (3). A temperature pulse is applied under open circuit conditions and the terminal voltage is measured. Schmidt et al. have shown that both methods deliver results in good accordance to each other [4].

Due to its simplicity, the potentiometric method has been used repeatedly in the battery research. The entropy profiles of different cathode and anode materials have been analyzed in order to investigate theoretically feasible entropy profiles of full cells [5]. Hudak et al. and Osswald et al. have shown that there are trackable entropy changes during the cyclic aging [6] [7]. Forgez et al. have used the potentiometric method to implement a detailed thermal model of a lithium-ion cell [8].

In most cases, a temperature dependent change of the OCP is assumed to be linear, regardless of the positive or negative temperature change and regardless of the initial temperature [9]. However, a non-linear behavior of the entropy has been already observed. Schmidt et al. have shown an entropy hysteresis depending on the direction of the current [4]. Bazinksi et al. observed different entropy coefficients for the same temperature change at the same SOC at different initial temperatures [10].

This work deals with the effect of the temperature path dependent entropy hysteresis, which to the knowledge of the authors has not been reported yet. This paper is organized as follows. After a brief description of the experimental setup, different temperature excitations are specified and their influence on the non-linear behavior of the reaction entropy is discussed. Finally, an optimal temperature excitation is proposed for potentiometric entropy determination method.

2. Experimental

One 2032 coin type lithium-ion cell and three different 18650 type cells comprising different NMC and NCA cathodes and graphite anodes were object of this study. All cells rested for more than six months at

Table 1
Overview of tested cells and their respective properties.

Name	Manuf.	Cathode	SOC	ΔS sign	Format	Quantity
A	Moli	NMC111	48%	Positive	18650	3
B	Sanyo	NCA	50%	Positive	18650	3
C	LG	NMC811	30%	Negative	18650	3
D	Varta	NMC111	28%	Negative	Coin	2

different SOCs at room temperature in order to guarantee a most equalized state [11]. Similar to the 18650 cells, the investigated coin cell contains a jelly roll as well. Due to the large surface to volume ratio and the small height of the cell, thermal gradients along the jelly roll are considered to be negligible even during rapid temperature changes. Cylindrical 18650 cells, however, might exhibit a certain temperature gradient along the jelly roll, leading to possible equalization processes, which might interfere with the potentiometric measurement method. All considered cell types and their corresponding properties are summarized in Table 1. The results presented in the discussion section depict the averaged behavior of the considered quantity of each cell type.

During the experiment, all cells were placed in a Binder KT115 climate chamber, which guaranteed isothermal test condition with a temperature accuracy of 15 mK. The temperature was measured on the surface of each cell with mounted PT100 sensors.

The voltage was measured with a self-built, custom measurement unit on the basis of ADS1278 from Texas Instruments, a 24 Bit analog digital converter (ADC) with 8 differential input channels. All channels underwent gain and offset calibration with a high precision voltage source LTC6655 from Linear Technology. The noise level for each channel was under $15\,\mu V$ for a 10 Hz sampling rate. Due to the high input impedance of $20\,G\Omega$ it was insured, that no leakage current of the circuit interfered with the voltage measurement by slowly discharging the cell. The fact, that a potentiometric measurement of the entropic coefficient of a cell is based on the change of the cell's potential for a change in its temperature inevitably comes with a change of the temperature of the sense wires. That might cause a possible interference due to the Seebeck effect. However, by using the same length as well as the same material for the positive and negative sensing wire, the Seebeck effect can be neglected. Since all cell internal junctions between different materials exhibit the same temperature at all times, the Seebeck effect within the cell can be neglected as well.

In order to investigate a possible hysteresis of the reaction entropy, the following temperature profile was applied. The chosen generic temperature excitation was composed of a positive and a consequent negative temperature pulse, both starting at initial temperature of 25°C. Based on this concept two different temperature profiles were deployed.

Profile I, shown in Fig. 1a, was used to investigate the influence of the temperature pulse frequency on the entropic coefficient. The resting time at each temperature level was increased from 2 to 24 h. The amplitude of the temperature pulse was chosen to be 15°C with initial temperature of 25°C. As 2 h resting time showed to be not sufficient to reach a thermally equalized state for each cell, only the results from 4, 8 and 24 h resting time are discussed further. A distinct variation in the gained entropy data for a change in the dynamics of temperature excitation would be an evidence that the entropy measurement is corrupted by charge equalization or self-discharge processes in the cell. Profile II, shown in Fig. 1b, on the other hand investigates the dependency between the amplitude of the temperature pulse and the derived entropy coefficients. This profile verifies the linear characteristic of the entropy. The temperature pulse was increased from 5°C over 10°C to 15°C with 8 h resting time.