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Fast and Accurate Measurement of Entropy Profiles of Commercial Lithium-Ion Cells

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ABSTRACT

We report on an effective approach to speed up the measurement of thermodynamic characterization curves (entropy of reaction $\Delta_r S(x)$) of rechargeable batteries, in particular commercial 18650 lithium ion cells. We propose and demonstrate a measurement and data processing protocol that reduces the time required to record entropy profiles from time scales of weeks to time scales of hours – without loss in accuracy. For time consuming studies such as investigations on ageing of battery cells, entropy profile measurements thus become as feasible as conventional electrochemical characterisation techniques like dV/dQ or cyclic voltammetry. We demonstrate this at the examples of two ageing protocols applied to a commercial high power and a commercial high energy cell, respectively: (i) accelerated calendric aging by storing cells at 100% state of charge at 60 °C and (ii) continuous cycling with a 1C current at 25 °C.

1. Introduction

Improvement in materials and fabrication processes continuously increased power and energy density of lithium ion batteries over the past years. As these improvements have almost been stretched out to their maximum, new developments of anode and cathode materials are needed to satisfy the increasing global need for energy storage devices [1]. Applications from consumer electronics over plug-in electric vehicles (PEV) up to full battery electric vehicles (BEV) require, besides a high power and energy density, a stable cycle life and must guarantee a safe use during their span of life. Optimization of the operational strategy demands fundamental understanding of electrochemical processes within the cell during charge and discharge is crucial. Non-destructive measurement techniques are a central pre-requisite for such a deeper understanding.

In a typical lithium ion battery, using graphite as the anode and a metal oxide as the cathode, the lithium contents in anode and cathode linearly follow the advancement of the overall cell reaction, denoted as x.

$$Li_{0.5}MO_2 + LiC_6 \rightarrow Li_{(0.5+0.5x)}MO_2 + Li_{(1-x)}C_6 \qquad (1)$$

M is a placeholder for one or a combination of the following elements: Mn, Co, Ni, Al. Here, we report on $Li_{0.5+0.5x}Ni_{1/3}Mn_{1/3}Co_{1/3}O_2$ (NMC) and $Li_{0.5+0.5x}Ni_{0.8}Co_{0.15}Al_{0.05}O_2$ (NCA). The advancement x of the overall cell reaction is in this special case equal to the amount of Li extracted from Li_xC_6. Varying Li contents in anode and cathode imply changes of their electrochemical potentials, in turn resulting in variations of the system enthalpy H and entropy S. In this context, the "system" involves the overall cell.

According to textbooks of electrochemistry, the cell's electromotive force E_{EMF} is related to the Gibbs free energy G via

$$E_{EMF}(x) = -\frac{\Delta_r G(x)}{nF} \qquad (2)$$

where F is the Faraday constant and n the number of electrons involved in the reaction. The Gibbs free energy can be expressed by the enthalpy H, the entropy S and the temperature T

$$G(x) = H(x) - TS(x) \qquad (3)$$

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Combining Eqs. (2) and (3) leads to

$$E_{EMF}(x) = -\frac{\Delta_r H(x) - T\Delta_r S(x)}{nF} \tag{4}$$

for constant pressure, and cell temperature T. H and S both depend on x and Δ_r denotes the derivative with respect to x. Since the crystal structure of anode and cathode often vary significantly with changing x,$H(x)$ and $S(x)$ have non-linear characteristics and thus sometimes distinctive profiles [2–5]. For this paper, the key formula, derived from Eq. (4) is

$$\left(\frac{\partial E_{EMF}(x)}{\partial T}\right)_{p,x} = -\frac{1}{nF}\left(\frac{\partial}{\partial x}S(x)\right)_{p,x} = -\frac{1}{nF}\Delta_r S(x) \tag{5}$$

which describes that any variation of S as a function of x is reflected in the temperature dependency of E_{EMF} (x). First comprehensive measurements to determine $\Delta_r S(x)$ using the temperature dependency of the open circuit voltage were conducted by A. H. Thompson in 1981 on Li_xTiS_2, using a sinusoidal temperature profile [4]. Later, Baffier et al. used temperature steps between −20° and 30 °C with a relaxation time of 10 hours after each discharge step for voltage stabilization (±1mV) to investigate the thermodynamic behaviour of $Li_xMn_2O_4$ [5]. Selman et al. used electrochemical-calorimetric measurements on $LiCoO_2$ based cathodes and full cells respectively [6,7], with every step lasting 25 hours. The temperature dependency of the open circuit voltage to calculate the entropy profile of $LiCoO_2$ cathodes and graphite anodes in half cells vs. Li/Li^+ metal was investigated intensively by Reynier et al. [3,8]. The authors could directly relate the measured entropy profiles of $LiCoO_2$ to the phase change mechanisms, described by Reimers and Dahn [9]. As a compromise between measurement time and measurement accuracy, approximately 21 [3] to 26 [5,10] data points, which are equivalent to 5% and 4% changes in the SOC respectively, were chosen. Depending on the cell's chemistry [5,10–13], the conducted entropy profile measurements needed between 10 and 30 hours per state of charge, leading to an overall measurement time of up 600 hours (25 days) per measurement.

In this paper, we will demonstrate that the measurement time for entropy profiles can be drastically reduced by a rational redesign of the measurement procedure. Most of the time in entropy measurements is wasted on voltage relaxation after (dis-) charge steps. We will demonstrate that for an accurate measurement of the $^{\partial}E_{EMF}(x)/_{\partial}T$ response it is sufficient to measure the temperature response of the open circuit voltage (OCV) even if that potential is still relaxing towards the equilibrium. The time dependent drift can be automatically determined and subtracted from the raw data. Kashiwagi et al. measured entropy profiles for different kind of metal doping in $Mn_{2-y}O_4$ spinel structures. Due to the long measurement time of 10h/step, the self-discharge of the half cells was approximated with a quadratic function to correct the measured results [14]. Thomas et al. followed this basic idea and were able to reduce the measurement time for entropy profiles to some extent. Their attempt relies on a determination of the drift background by applying the same charge/discharge programme, but without any temperature variations [11]. This approach may bear the risk that it relies on an ideal thermodynamic behaviour of the battery. Specifically, such a method of background identification can only be relied on if the state of charge of the battery is not influenced by the temperature variations between the intended charge steps.

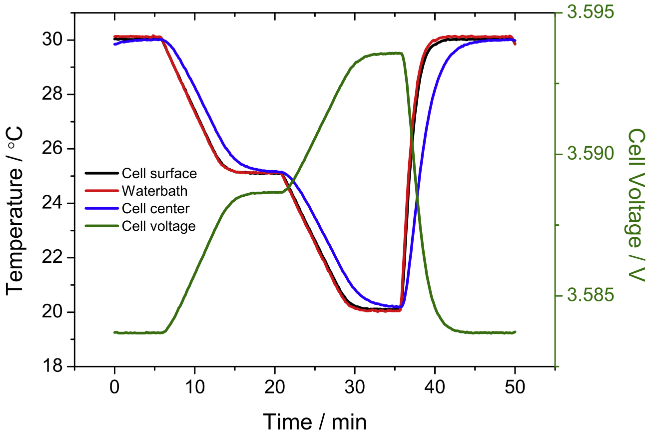

Fig. 1. Optimised temperature profile: Temperature of water bath (red), cell surface (black) and cell core (blue) as well as the cell's voltage response (green). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Here, we follow an even simpler approach. Similar to Hudak et al. [15], we assume that all information necessary to eliminate the drift from the temperature-programme response curves is actually contained in those curves themselves if the temperature programme is chosen carefully. Unlike Pei et al. who recently demonstrated an elegant extrapolation approach to predict the equilibrated OCV using a second-order RC circuit model, [16] we postulate that we do not really need to know the equilibrium OCV but can still measure the voltage/temperature slopes with sufficient accuracy. Waiting periods were trimmed down to the minimum necessary for sufficient thermal equilibration of the cells (measured by retrofitted thermocouples). That reduces the overall measurement time by one or more orders of magnitude as compared to all entropy studies reported in the literature so far.

The paper is organized as follows. After a brief description of the experimental setup, we will describe the background correction approach in some detail. We will then demonstrate that the derived entropy profiles cannot be distinguished from such obtained in slow measurements with long voltage relaxation times. Furthermore, we will highlight that a proper treatment of the background drift is necessary even for slow measurements with long voltage relaxation period. The drift behaviour strongly varies between cell types and for different states of charge, and it is much more pronounced for aged cells. Finally, as a "real world example", we will show some preliminary results of how ageing due to repetitive cycling and storage at higher temperature is reflected in the entropy profiles. In this context, we will discuss to what extent this method can be applied as a standard non-destructive technique for battery characterization in a laboratory scale and how far applications for mobile battery monitoring are conceivable.

2. Experimental set-up

For the measurements, we studied commercial 18650 cells with different cathodes; specifically $Ni_{1/3}Co_{1/3}Mn_{1/3}O_2$ (NMC) and $Ni_{0.8}Co_{0.15}Al_{0.05}O_2$ (NCA). All cells contain a graphite-based anode. The cells were charged and discharged with a BasyTec CTS battery cycler. To improve the accuracy of voltage and temperature measurement, an Agilent 39720A with a 34901A 20 channel armature multiplexer was connected to the set-up via a programmable software interface. The Agilent 39720A was used as a 5 digit multi meter with a maximum voltage error of 0.0020% of the 10V range as well as 0.0005% for the measured value over a time period of 90 days at room temperature. For temperature control, the cells were embedded into a custom-made copper block with a cylindrical hole, which itself was coupled to a Julabo F12-MA Refrigerated/Heating Circulator with heating and cooling capacities of 2kW and 0.16kW, respectively. It should be noted that we also achieved good results using a simple climate chamber for the