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Electrothermal impedance spectroscopy as a cost efficient method for determining thermal parameters of lithium ion batteries: Prospects, measurement methods and the state of knowledge

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ABSTRACT

Current lithium-ion battery research aims in not only increasing their energy density but also power density. Emerging applications of lithium-ion batteries (hybrid electric vehicles, plug-in hybrid electric vehicles, grid support) are becoming more and more power demanding. The increasing charging and discharging power capability rates of lithium-ion batteries raises safety concerns and requires thermal management of the entire battery system. Moreover, lithium-ion battery's temperature influences both battery short term (capacity, efficiency, self-discharge) and long-term (lifetime) behaviour. Thus, thermal modelling of lithium-ion battery cells and battery packs is gaining importance. Equivalent thermal circuits' models have proven to be relatively accurate with a low computational burden for the price of low spatial resolution; nevertheless, they usually require expensive equipment for parametrization. Recent research initiated by Barsoukov et al. proposed electrothermal impedance spectroscopy as a novel and non-destructive method of characterizing the thermal properties of batteries by defining frequency dependent thermal impedance. Despite its usefulness, the electrothermal impedance spectroscopy method can be still improved in terms of e.g. accuracy and measurement time and it has a potential to be extended to new applications. Performed review indicates that the electrothermal impedance spectroscopy is a very promising, non-destructive, simple and especially cost-efficient method for thermal characterization of batteries. The scientific intention of this paper is to collect and systematize the state of knowledge about electrothermal impedance spectroscopy and present different measurement methods on the example of a high-power lithium battery cell and finally to discuss the prospect.

1. Introduction

Lithium-ion (li-ion) batteries have dominated very quickly the market of portable electronics and they currently start to enter markets of electro-mobility and grid energy storage (Oliveira et al., 2015; Golembiewski et al., 2015). Nevertheless, the standards for li-ion batteries are constantly raised in order to meet the requirements of the more and more demanding applications (Kushnir and Sandén, 2011; Sen et al., 2016). Undergoing research on li-ion batteries results in increasing both energy and power densities of the state of the art li-ion batteries. Some li-ion battery technologies, e.g. lithium metal oxide cathode and lithium titanate oxide anode ($LiMO_2/Li_4Ti_5O_{12}$) have currently continuous power capabilities higher than 10 C (full discharge within 6 min) and pulse power capabilities higher than 20 C (13Ah Altair Nano lithium titanate battery cell datasheet, 2011).

For many years, there was very little interest in thermal modelling of the li-ion batteries because they were mainly employed in low-power applications. However, this has changed recently together with the development of high-power li-ion batteries. Nowadays ambitious goals of new battery applications, e.g. 10–15 years lifetime of electric vehicles (EVs), impose a good understanding of lithium-ion battery thermal issues.

The high power capability of the most state of the art battery cells drives the need for accurate and cost-efficient thermal modelling of the li-ion batteries in order to estimate heat generation on the cell level. Moreover, battery thermal models are required to facilitate the optimal battery pack design with a cost-effective heat management. Battery temperature has an influence on many parameters of the li-ion battery like capacity, efficiency,

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self-discharge and internal resistance (Bandhauer et al., 2011). On the other hand, thermal modelling of the li-ion battery cells is also required to avoid overheating damage or thermal runaway (Miyamoto et al., 1996; Hatchard et al., 2001). Furthermore, the knowledge about the thermal behaviour of a li-ion battery is essential because the temperature is the most degrading stress factor which accelerates battery ageing and limits its lifetime (Markovsky et al., 2003; Vetter et al., 2005). Fleckenstein et al. pointed to a need for looking into thermal gradients for the high power battery cells which may lead to the large decoupling between battery internal and surface temperature (Fleckenstein et al., 2013). In consequence, both battery safety and accuracy of battery lifetime models can be compromised because the inner battery temperature may be different than average surface temperature (with up to 10 °C) (Onda et al., 2006). The similar mismatch between the inner and outer temperature of a battery cell was obtained by Barsoukov et al. (2002). where authors report even one-third higher temperature inside battery than on its surface for a cylindrical battery cell.

Thermal behaviour of the li-ion batteries has been studied in a number of publications (Bernardi et al., 1985; Doyle et al., 1993). Thermal models of li-ion batteries usually are complex and they require coupled electrochemical model and, in consequence, precise knowledge about the inner structure and physical and material properties of the li-ion battery. These are usually finite element models (FEM) where Fourier's law of conductivity is being solved and they require high computation power what limits their applicability (Gomadam et al., 2003; Song and Evans, 2000).

FEMs, though accurate, are not appropriate for applications where real-time calculations of the battery temperature are required. Thus, in order to shorten calculation time, equivalent thermal circuit (ETC) models with a different degree of complexity are utilized, where resistors, capacitors and current sources are used for representing heat transfer, heat accumulation and heat source, respectively (Forgez et al., 2010; Fleckenstein et al., 2011a). ETC models are a good compromise between the complexity and accuracy for the price losing spatial resolution. However, ETC models require expensive calorimeters or time consuming and destructive disassembling and the opening of battery cells in order to determine battery parameters like heat capacity, thermal conductivity and convective heat exchange with the environment (Keil et al., 2013; Fleckenstein et al., 2011b).

In order to simplify ETC parametrization and reduce model parametrization cost, the electrothermal impedance spectroscopy (ETIS) concept was proposed (Barsoukov et al., 2002).

The goal of this paper is to collect knowledge and own experience and present thorough state of the art on ETIS, its challenges and prospect with an emphasis on the ETIS measurements on li-ion batteries.

In the next section of this paper, the ETIS concept and applications will be presented. This will be followed by a section which deals with different ETIS measurement methods. In the next section results from ETIS measurements on the high-power $LiMO_2$/$Li_4Ti_5O_{12}$ (M stands for metal) pouch battery cell will be presented (Table 1 and Fig. 1). These battery cells are becoming very important for the grid applications and renewables integration due to their 25 years calendar and more 16 000 cycles lifetime. Finally, prospects for ETIS measurements will be discussed.

2. The principle of electrothermal impedance spectroscopy

Battery thermal characterization methods focus on determining the key thermal properties of the battery: heat capacity, heat thermal conductivity and battery entropy. Expensive calorimeters are usually used for heat capacity determination (Maleki and Hallaj, 1999). The thermal conductivity of battery cell is usually measured by applying a heat flux perpendicular to the measured samples (Maleki and Hallaj, 1999; Brooman and McCallum, 1971). An alternative method for determining the thermal conductivity of battery cell is based on applying a short flash pulse from a xenon lamp and determining the temperature function of time (Maleki and Hallaj, 1999; Nagpure et al., 2010). All of the above-mentioned methods usually requires the deep discharge of the cell (destructive) and/or costly equipment.

ETIS is a non-destructive method for obtaining thermal parameters of the battery cells. It was first introduced by Barsoukov et al. (2002). The concept was derived from the electrochemical impedance spectroscopy (EIS), which is now a standard method applied in the electrochemistry and in many different applications (Orazem and Tribollet, 2008; Andre et al., 2011). ETIS concept is an alternative method for characterizing the thermal properties of the entire battery cell. It is based on defining a frequency dependent thermal impedance and it allows for determining heat capacity and thermal conductivity of the entire battery cell. The huge advantage of ETIS method is that the user does not need to possess a priori knowledge about the electrical cell behaviour and the electrical battery cell model.

The ETIS measurement is based on applying a defined heat flow to the battery (by an external heat source or internally by inducing internal heat generation with a specific current profile) and measuring the temperature response of the battery cell at different frequencies of the applied heat flow. Thus, the ETIS is based on examining the thermal transfer of the battery in the frequency domain (1). The obtained results are presented in the Nyquist plot and represented by an equivalent circuit model. Finally, battery

Table 1
Parameters of the high power lithium titanate oxide battery used for ETIS measurements.

Property	$LiMO_2$/$Li_4Ti_5O_{12}$
Cathode	$LiMO_2$ (M-metal) (combination of $LiCoO_2$ and $LiCo_xNi_yAl_zO_2$)
Anode	$Li_4Ti_5O_{12}$
Nominal capacity	13 Ah
Nominal voltage	2.26 V
Max. charging voltage	2.9 V
Min. voltage	1.5 V
Max. charge current	130 A
Max. discharge current	130 A
Operating temperature	-40°C to +55°C
Design life	25 years

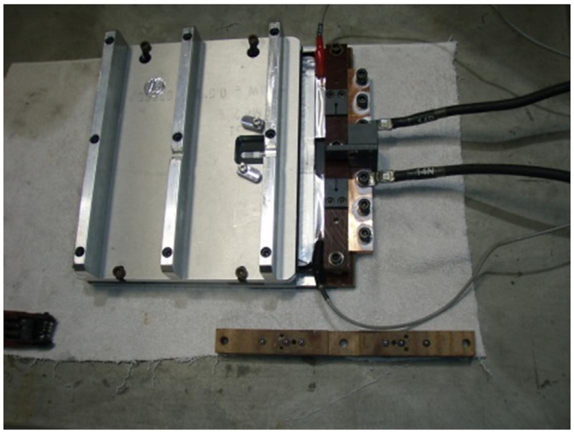

Fig. 1. $LiMO_2$/ $Li_4Ti_5O_{12}$ 13 Ah battery cell under test.

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