Electrochimica Acta 259 (2018) 517–533

Contents lists available at ScienceDirect

Electrochimica Acta

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

A new method to compensate impedance artefacts for Li-ion batteries with integrated micro-reference electrodes

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ARTICLE INFO

Article history:
Received 22 July 2017
Received in revised form
10 October 2017
Accepted 19 October 2017
Available online 2 November 2017

Keywords:
Electrochemical Impedance Spectroscopy
Lithium ion batteries
Three-electrode cell
Micro-reference electrodes
Impedance measurement artefacts

ABSTRACT

In order to measure the electrochemical characteristics of both electrodes inside Li-ion batteries, micro-reference electrodes (μREF) turned out to be very useful. However, measuring the electrochemical impedance with respect to μREF can lead to severe measurement artefacts, making a detailed analysis of the impedance spectra complicated. In the present work a new method is developed in which high-frequency measurement artefacts can be compensated. A theoretical analysis, using equivalent circuit models of the measurement setups, shows that if two different impedance measurements are averaged, the impedance contributions from the measurement leads can be completely eliminated. The theoretical analysis is validated using Li-ion batteries with seven integrated μREF, having all different impedances. The measurement results show that artefacts are dominating for high-impedance μREF in the high frequency range. However, these artefacts can be fully compensated by averaging two separate impedance measurements, as predicted by theory. This easily makes it possible to perform artefact-free impedance measurements, even at high frequencies.

1. Introduction

Lithium-based batteries are today's most favourable systems to provide energy to battery powered applications, such as (Hybrid) Electric Vehicles ((H)EV), laptops and smartphones. Since (commercial) Li-ion batteries are two-electrode systems, only the total battery potential and impedance can be measured. However, for research purposes and to develop more advanced Battery Management Systems (BMS) it is of interest to distinguish between both electrodes with the use of reference electrodes (REF), hence making it possible to measure the electrochemical characteristics of the individual electrodes.

REF have already been introduced in many studies [1–14]. However, in particular Electrochemical Impedance Spectroscopy (EIS) measurements at three-electrode Li-ion battery systems are prone to measurement artefacts [15–26]. These artefacts cause a divergence in impedance spectra and, as a consequence, the analyses of the measurements become unreliable and inaccurate. Moreover, underlying physical phenomena can be hidden by artefacts. Therefore, it is important to either prevent or to compensate these artefacts as much as possible.

Many studies on EIS measurement artefacts in the field of Li-ion batteries focuses on the cell geometry and/or the position of the REF, since improper three-electrode measurement setups are highly sensitive to artefacts. In general, it can be concluded that EIS measurement artefacts can be prevented to a large extend by using an appropriate cell geometry and REF position. Often these measurement setups are based on Swagelok-type cells in which perfect electrode alignment can be realized and where the REF can be easily introduced coaxially with respect to the electrodes [16,18,21,22]. Obviously, these setups are suitable for small-scale laboratory experiments. However, perfect electrode alignment and coaxially positioning of REF are more complicated to realize in large-size (commercial) Li-ion batteries, which are used in for example (H)EVs. Therefore these cells are often equipped with integrated micro-reference electrodes (μREF) [1,3,6,8,10,27].

Not only the cell geometry and electrode positions, but also the REF impedance and measurement equipment like, for instance cables, potentiostats, capillaries, frits, *etc.* can lead to EIS

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https://doi.org/10.1016/j.electacta.2017.10.132
0013-4686/

measurement artefacts [15,24,28–34]. Obviously, the input impedance of the measurement device should be selected high and the REF impedance low [31]. Baker et al. [35] found by modelling and simulations that artefacts are a function of the REF size, its surface resistance, the resistance of the separator and both the working and counter electrodes. Furthermore, the length of the measurement cables should be reduced as much as possible [24,28], although this is sometimes difficult due to measurements which have to be performed at remote locations, such as glove-boxes and temperature-controlled climate chambers.

A solution to suppress high-frequency artefacts caused by the measurement equipment and the high-impedance REF, is to use so-called dual REF [29,32,33]. This is based on a second reference electrode which is carefully positioned in the cell and connected in series with a conventional REF through a capacitor. Recently, another successful technique is introduced in which a capacitor bridge between the counter electrode (CE) and the REF is used to suppress high-frequency EIS artefacts of three-electrode geometries [15]. The capacitor bridge balances the leakage current through the REF. However, it is not straightforward to determine the compensating value of the capacitor for systems, using dual REF or capacitor bridges. The capacitance must be carefully aligned to the measurement setup under consideration, which can lead to elaborate investigations.

This study presents a new method in which high frequency EIS measurement artefacts at three-electrode Li-ion batteries can be fully compensated by averaging two individual three-electrode EIS measurements. Strikingly, this results in artefact-free EIS measurements in the high frequency range of the impedance spectra, which is essential for *e.g.* characterizing the individual electrodes, for modelling purposes, State-of-Health indication and impedance-based temperature measurements [36–39]. The proposed method is similar to the method presented by Hsieh et al. [31], in which they correct artefacts arising from a so-called voltage divider effect. However, their work was performed on solid-state electrochemical devices in which the platinum REF impedance approaches the input impedance of the measurement device. Moreover, Hsieh et al. [31] combined one two-point and two three-point measurements in order to correct the artefacts, which is not required for the method presented in this work.

Models, including all electrode, device input and lead impedances are systematically developed in the present contribution in order to provide a deeper insight into the measurement artefacts of three-electrode Li-ion battery systems. It will be shown that the lead impedances, which can significantly contribute to artefacts, can be easily compensated by reversing the measurement device connections to the battery. In addition, multiple μREF with various active tip areas are used to investigate the influence of the REF impedance on the artefacts.

In order to experimentally show the artefacts and the strength of the proposed compensation method, EIS measurements are performed with conventional electrochemical measurement equipment on pouch-type Li-ion batteries with seven integrated μREF. The proposed compensation method is compared to the successfully applied capacitor bridging method, applied by Battistel et al. [15]. Finally, it will be shown that the impedance measurements can be accurately simulated by the developed artefact models.

2. Experimental

2.1. Battery construction

Pouch-type batteries are made with electrode dimensions of 72 × 190 mm (width x length). Each battery consists of six positive (P) and seven negative electrodes (N), which are separated by Celgard 2400 separators. Each electrode has an external current collector extension of 20 × 20 mm. A schematic representation of such an electrode stack is shown in Fig. 1a. The P and N electrodes are stacked in parallel and the complete battery stack is inserted into an Al-polymer pouch which is sealed after the electrolyte has been added. In order to put some pressure on the as-produced cells,

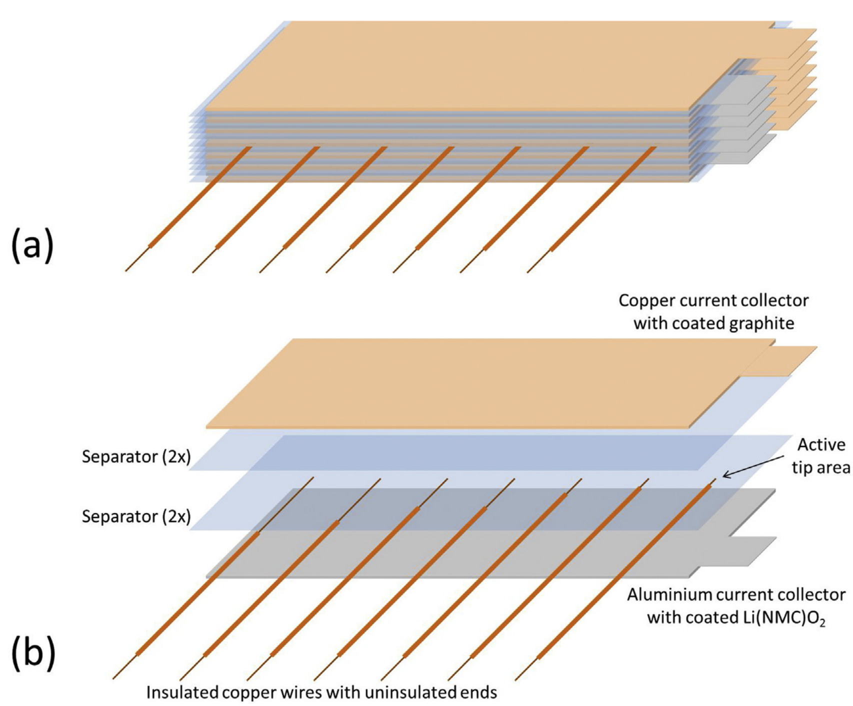

Fig. 1. Schematic representation of an electrode stack with seven integrated μREF (a) and enlargement of seven μREF in-between the P and N electrode (b). Note that on both sides of the μREF two separator sheets are used to isolate them from the electrodes.