Journal of Power Sources 282 (2015) 335–347

Contents lists available at ScienceDirect

Journal of Power Sources

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

Modeling graphite anodes with serial and transmission line models

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HIGHLIGHTS

- Extensive impedance analysis of graphite anode providing a physical interpretation.
- DRT and microstructure reconstruction are combined to obtain a new understanding.
- Impact of electrode microstructure on impedance spectra and model design.

ARTICLE INFO

Article history:
Received 19 November 2014
Received in revised form
18 January 2015
Accepted 6 February 2015
Available online 12 February 2015

Keywords:
Lithium-ion
Graphite anode
Impedance model
DRT
Transmission line model
FIB tomography

ABSTRACT

Electrochemical impedance spectroscopy (EIS) is an indispensable technique for the investigation of polarization processes in Lithium-ion Batteries. These cause performance limitation or degradation. A physically meaningful impedance model is key when drawing conclusions on further cell improvement.

This study introduces an in-depth impedance analysis of a commercial high-power graphite anode. The impedance spectra measured between 0 °C and 30 °C and 0%–100% SOC were analyzed by the distribution of relaxation times (DRT-method), enabling a separation of loss processes by their individual time constants. Using this method, we separated charge transfer resistance and solid electrolyte interface resistance at medium frequencies (10 Hz–200 Hz) and the contact resistance anode/current collector in the at high frequency range (5 kHz–100 kHz). Two fundamentally different model structures were set up, either (i) two modifications of a serial model connecting RQ-elements and a Warburg element for solid state diffusion, or (ii) three modifications of a transmission line model with one-path or two-path design. The suitability of all serial and TLM model structures was tested, and the fitting procedure was supported using microstructure parameters gained from x-ray tomography. The favored one-path transmission line model reveals that the lithium-ion transport in the electrolyte contributes more to polarization than expected. Impediment of lithium-ion transport is caused by the pore structure and the tortuosity of the high-power graphite anode, and has to be considered for meaningful interpretation of impedance spectra.

1. Introduction

Lithium-ion batteries for electric vehicles necessitate new efforts to understand their performance limitations and degradation mechanisms. Electrochemical Impedance Spectroscopy supports, if the obtained data are reviewed properly and a physically meaningful equivalent circuit model can be established. This study strives for an in-depth analysis of a commercial high-power graphite anode. There are already a multitude of published equivalent circuit models of carbon-based anodes. However, interpretation of impedance data without having access to "real" microstructure parameters calls the presented model structures into question. Graphite anode impedance spectra often show a depressed semicircle at medium frequencies. This makes a clear identification of the number and nature of loss processes difficult. Usually, an additional high frequency loss process is identified, as shown for a commercial high-power graphite anode in Fig. 1.

To appropriately describe both semicircles Levi et al. [1] were the first and proposed an equivalent circuit model of five serially connected RC-elements. This approach was motivated by the existence of a multilayer solid electrolyte interface (SEI) between electrolyte and individual graphite particles. However, this model remains uncertain, as the Nyquist plot does neither disclose the number of processes nor the number of SEI layers.

Other studies applied simpler equivalent circuit models by

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http://dx.doi.org/10.1016/j.jpowsour.2015.02.038
0378-7753/

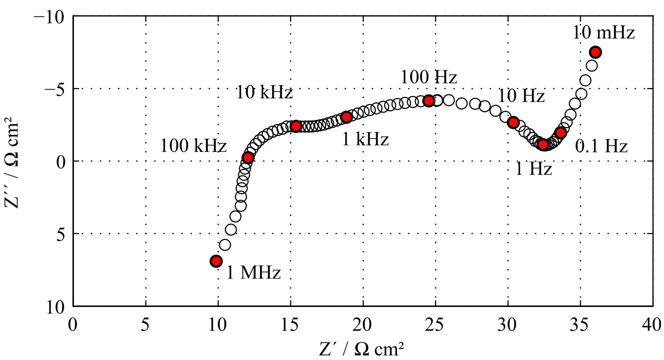

Fig. 1. Typical Impedance spectrum of a graphite anode measured via reference electrode at 100% SOC in an experimental full cell at 23 °C.

describing each “visible” semicircle with one RQ-element. The medium frequency semicircle is usually assigned to the charge transfer process [2–5] whereas the high frequency semicircle is interpreted either as SEI [3,4,6] or as contact resistance [2,5]. These studies proposed serial models or applied Randles circuits to connect the impedance elements. Table 1 lists contributions and model structures introduced in these studies.

None of the publications had access to precise microstructure parameters of the graphite anode investigated, and thus, did not account for its possible influence on the impedance spectrum. Barsoukov et al. [7] were the first to apply a transmission line model (TLM) to describe the graphite anode impedance spectrum. The TLM model structure is ideal for consideration of the ionic path in the electrolyte volume of the porous anode structure and the electronic paths in the individual graphite particles. However, as Barsoukov could not utilize measured microstructure parameters at that time, a reliable parameterization was impeded.

At this point, we want to contribute to the challenge of establishing a “true” model structure for graphite anodes. In this study, we perform a series of impedance measurements on a commercial high-power graphite anode versus temperature and SOC and evaluate these data by the distribution of relaxation times (DRT-method). DRT has proven advantageous when designing impedance models for $LiFePO_4$-cathodes [8] and gives better insight into polarization processes in commercial cells [9].

In the following, the DRT method will be presented, and the impedance of a commercial high-power graphite anode will be assessed in a (small area) experimental cell in the temperature range from 0 °C to 30 °C and from 0% to 100% SOC. It will be demonstrated, that the DRT analysis of impedance data facilitates the separation of (i) charge transfer, (ii) SEI and (iii) contact resistance as major contributors to the graphite-anode impedance spectrum. For the first time, the characteristic shape of the relaxation curve gives evidence that ion transport through the pores is a significant contributor.

Table 1
Published impedance studies and number/interpretation of loss processes identified for graphite anodes.

Study	SEI	Charge transfer	Contact resistances	Consideration of the microstructure
Yamada et al.	x	x		
Momma et al.	x	x		
Xu et al.	x	x		
Holzapfel et al.		x	x	
Chang et al.		x	x	
Levi et al.	x	x		
Barsoukov et al.	x	x	x	x

Five different equivalent circuit models are designed, based on DRT analysis: two serial and three transmission line models. All models were then compared by fit quality and parameter dependencies in order to select the most suitable model for a high-power graphite anode. Microstructure parameters gained from X-ray tomography enabled a further suitability assessment. Finally, a one-path transmission line model was favored and applied to quantify the individual polarization resistance of each loss process depending on operating condition.

2. Theory of impedance analysis

2.1. Kramers Kronig residuals

Meaningful impedance spectra evaluation requires high quality measurement data. The Kramers Kronig (KK) residuals are a suitable, proven, method of checking measurement data quality and the time invariance condition of impedance measurements. They are based on the relation between real and imaginary parts of a linear time invariant system, given by the following equations [10–12]:

$$Z'(\omega) = Z'(\infty) + \frac{2}{\pi} \cdot \int_0^\infty \frac{xZ''(x) - \omega Z''(\omega)}{x^2 - \omega^2} dx \qquad (1)$$

and

$$Z''(\omega) = -\frac{2\omega}{\pi} \cdot \int_0^\infty \frac{Z'(x) - Z'(\omega)}{x^2 - \omega^2} dx. \qquad (2)$$

These equations have a problem with integration over the 0 to ∞ frequency range as impedance measurements never cover this entire range. One approach for overcoming these limitations was initially proposed by Agarwal et al. [13]. It is based on RC-elements connected in series (the measurement model), known to be KK-transformable.

The RC-elements are used to fit either the real or the imaginary part of the measured impedance data by a Complex Non-linear Least Squares fit (CNLS-fit) and to predict the other component. The relative deviation of the predicted figures from the measured values is called the KK residual. This can be used to measure whether or not the impedance data is KK-transformable. The approach was improved by Boukamp et al. [12]. Therein, the time constants of the RC-elements are fixed and the only free fit parameter is the polarization. A complex linear least squares fit results in, and allows for, a stabler impedance data fit. It can be further complemented by a series connected inductor and/or capacitance. This will describe pure capacitive or pure inductive behavior [12] as they occur in lithium-ion cells.

2.2. Distribution of relaxation times

EIS is a powerful tool for the identification and separation of electrochemical loss processes that proceed at a differing rate. Occasionally, however, their number and physical nature are identified ambiguously.

In the following we present an alternative method of analyzing impedance spectra which reduces this problem by increasing the resolution by an alternative visualization. The DRT method was developed for the impedance assessment of solid oxide fuel cells and presented in detail in Refs. [14–16]. The basic concept of DRT evaluation is described in the next subchapter.