

Employing Real Automotive Driving Data for Electrochemical Impedance Spectroscopy on Lithium-Ion Cells

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ABSTRACT

Battery aging is a main concern within hybrid and electrical cars. Determining the current state-of-health (SOH) of the battery on board of a vehicle is still a challenging task. Electrochemical Impedance Spectroscopy (EIS) is an established laboratory method for the characterization of electrochemical energy storages such as Lithium-Ion (Li-Ion) cells. EIS provides a lot of information about electrochemical processes and their change due to aging. Therefore it can be used to estimate the current SOH of a cell. Standard EIS methods require the excitation of the cell with a certain waveform for obtaining the impedance spectrum. This waveform can be a series of monofrequent sinusoidal signals or a time-domain current pulse with a dedicated Fourier spectrum. However, any form of dedicated perturbation is not generally applicable on board of an electric vehicle.

This work presents a new passive spectroscopy method, which obtains the impedance spectrum directly out of real driving data. Results from an automotive 20Ah Li-Ion cell are compared with reference EIS measurements obtained from sinusoidal excitation. The main challenges for on-board measurements are identified, analyzed and their influences are separated. Findings of this analysis are used to optimize the measurement method. Results show good concordance with the spectrum obtained under laboratory conditions. Finally, equivalent resistances are calculated from the spectra and compared with time-domain reference measurements. Good concordance promises a possible implementation into an on-board state estimation algorithm.

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INTRODUCTION

Energy storage is still the most challenging and critical part in the process of vehicles powertrain electrification. Lithium-Ion (Li-Ion) is currently the most promising technology for hybrid and electrical cars. A lot of research has been done or is still ongoing for improving materials, composition and manufacturing processes [1] or investigating the aging behavior [2]. State estimation is another crucial issue regarding the practical implementation of electrochemical energy storages into vehicles. A robust and reliable estimation of the current state-of-charge (SOC) and state-of-health (SOH) of the energy storage is important for efficient battery management [3]. This is also indispensable for better customer acceptance of electric mobility, because the driver needs reliable information about the remaining cruising distance and battery lifetime.

Electrochemical Impedance Spectroscopy (EIS) is a well-known and powerful tool for characterizing electrochemical systems such as Li-Ion cells. It provides various information and a deep insight into the electrochemical processes [4, 5, 6, 7]. In general, two types of EIS investigations can be distinguished: The first group aims at separating cathode and anode impedance and therefore requires the insertion of a reference electrode into the cell or assembles experimental full or half cells for the measurement [8, 9, 10]. The second group performs

measurements on unmodified and original full cells without opening the cells or inserting a reference electrode [6, 7, 11, 12]. Therefore, the latter is closer to the application on board of a vehicle.

Nevertheless, both are laboratory methods, since they require special measurement equipment and apply a dedicated perturbation to the battery. In the standard EIS method, this excitation signal is a series of monofrequent sinusoidal signals. More sophisticated approaches aim at reducing the measurement time and apply sum-of-sine signals [13] or time-domain current pulses [14, 15]. In general, all kinds of dedicated waveforms are not applicable on board of a vehicle. Providing a complete impedance spectrum to the Battery Management System (BMS) would be helpful for robust state-diagnosis and estimation algorithms [3].

Previous work already discussed the integration of EIS into a vehicle. Tröltzsch et al. [16] proposed the active generation of multifrequent signals in rest periods, which requires additional signal generation electronics. Howey et al. [17] do not need additional electronics for generating dedicated waveforms. Instead, they propose to use the excitation of the motor controller. Although their approach works with arbitrary signals, they still have to be applied dedicatedly in rest periods. In addition, they only consider frequencies greater than 1 Hz. Since several electrochemical processes such as diffusion have long

time constants, lower frequencies are also interesting and should be considered. Walter, Bohlen et al. [18, 19] developed an algorithm employing digital filters for obtaining the impedance from arbitrary data. However, this method obtains the real part and the modulus of the complex-valued impedance. The imaginary part is not obtained directly, only its absolute value can be computed. Hence, the full spectrum information is not available.

The aim of this work is to present a method for obtaining impedance spectra directly from real arbitrary driving data with good concordance with laboratory reference spectra. The paper is organized as follows: First, the theoretical background of EIS, different laboratory measurement methods and an approach for investigating the validity of measured spectra are recapitulated. After this, the main challenges for obtaining impedance spectra during driving compared to laboratory conditions are discussed. In the experimental section, the cell used for demonstrating the methods, the test equipment and the employed driving data are described. Then, standard EIS measurements used as a reference are presented. The influence of SOC, temperature and SOH on the impedance spectrum is investigated. Subsequently, a general approach for obtaining the spectra from driving data is presented and detrimental impacts are analyzed stepwise before an optimized measurement procedure is suggested. Finally, the application into BMS and parameter estimators are discussed. In order to track the SOH, equivalent resistances obtained from laboratory and driving data EIS are compared with time-domain reference measurements.

BACKGROUND

For the reader's convenience this chapter recapitulates the theoretical background of Electrochemical Impedance Spectroscopy in general and introduces the methods employed in this paper.

Electrochemical Impedance Spectroscopy

EIS obtains the complex-valued inner impedance of a cell as a function of frequency:

$$\underline{Z}(f) = |Z| \cdot e^{j\varphi_z} \quad (1)$$

Standard method for deriving $\underline{Z}(f)$ is the excitation of the cell with a sinusoidal current $i(t) = \hat{i} \cdot \sin(\omega t)$ and measuring the voltage response $v(t) = \hat{v} \cdot \sin(\omega t + \Delta\varphi)$. The inner impedance is then given by

$$\underline{Z}(f) = |Z| \cdot e^{j\varphi_z} = \frac{\hat{v}}{\hat{i}} \cdot e^{j\Delta\varphi} \quad (2)$$

This is repeated for a discrete number of frequencies within a given range. A typical frequency range that covers the electrochemical processes of interest starts at the mHz scale and ends at the kHz range. Normally, several cycles of each frequency are applied. This enables averaging and therefore increases the robustness of the results. Also, transient effects occurring in the first cycles can be discarded so that the evaluation is done in a steady-state.

Exciting the cell with a current of constant amplitude and observing the voltage response is referred to as the galvanostatic mode. This method prevents an SOC drift, since the same charge quantity is transported in both the positive and the negative direction. In the potentiostatic mode the excitation signal is a voltage with constant amplitude and the current response is measured. This method ensures linearity, since in an electrochemical system linearity is controlled by voltage [20]. The pseudo-potentiostatic mode combines both methods: A current excitation is employed. The current amplitude remains constant for all cycles of one frequency but is adapted to achieve a certain nominal amplitude of the voltage response for all frequencies. This nominal voltage amplitude has to be sufficiently small to ensure linearity but also big enough to achieve a good signal-to-noise-ratio (SNR) in the measurement. A typical value for this nominal voltage amplitude is $\hat{v} = 10\text{mV}$.

Impedance spectra are often visualized with a Nyquist plot, which depicts the imaginary part of the impedance versus its real part. In literature the imaginary axis is normally inverted because of the inherent capacitive behavior of energy storages. An alternative visualization is the Bode plot, where magnitude and phase are separately plotted versus frequency.

Spectrum Validation

Measured impedance spectra are only valid as long as they are a representation of a linear and time-invariant system (LTI system). For causal and stable LTI systems with a finite frequency response, fixed relations between the real and the imaginary part of the frequency response are given [21]. These lead to the Kramers-Kronig (KK) relations, which are employed for validating measured transfer functions in general and EIS data in particular [22]. Unfortunately, the KK relations cannot be used directly, because they require integration from zero to infinity. In order to avoid an extrapolation of the measured data with additional assumptions about the system, Boukamp [23] developed a practical implementation of the KK relations, commonly referred to as Linear-Kramers-Kronig (Lin-KK) test. This test performs a fit of the real part of the measured spectra to the real part of an Equivalent Circuit Model (EQM), the frequency response of which is a-priori KK conform. The deviations between the imaginary part of the EQM and the imaginary part of the measured spectrum ("KK residuals Δ_{im} ") are then a measure for the KK conformity of the data. In this work, an automated and improved version of the Lin-KK test presented by Schönleber [24] is used.

Pulse Spectroscopy

Standard EIS can be a time consuming method, since every frequency is excited separately. In order to reduce measurement time, several frequencies have to be applied simultaneously. This can be achieved by generating sum-of-sine signals as proposed by Christophersen [13] or using broadband current pulses. Klotz et al. [14] presented a method using a rectangular voltage step. Our approach [15] for pulse spectroscopy is a Sinc function ($\sin(x)/x$), since the Fourier spectrum of the Sinc-Function has a rectangular shape and therefore enables the pulse energy to be optimally distributed into the desired frequency

range. The possibility to derive valid spectra from time-domain pulses motivates to obtain impedance spectra also from arbitrary data such as driving cycles.

Data Processing

Obtaining impedance spectra from time-domain data such as pulses or arbitrary driving profiles requires data processing in order to transform measured current and voltage data into the frequency domain. First step is segmenting of the whole data set for each investigated frequency f_k . The duration of each data segment is a multiple of the according cycle duration $1/f_k$. After subtracting the DC component a window function is applied. This is mandatory for reducing spectral leakage. As suggested by Klotz et al. [14] a Gaussian Window function is used in this work. Zero-Padding is performed in order to increase frequency resolution. After that, the spectrum is computed by means of a Discrete Fourier Transformation (DFT). Finally, the complex-valued impedance at frequency f_k is calculated by

$$\underline{Z}(f_k) = \frac{\underline{U}(f_k)}{\underline{I}(f_k)} \quad (3)$$

This process is repeated for each frequency f_k .

Real Driving Data

Electrochemical Impedance Spectroscopy is typically performed in a constant operating point regarding SOC and temperature. Furthermore, for obtaining a valid representation of an LTI system, the excitation has to be sufficiently small and the cell has to be in a state of stationary equilibrium. Normally, these preconditions are not fulfilled during driving. This leads to some challenges, when real driving data are used to obtain a spectrum that is supposed to be similar to a spectrum measured under laboratory conditions.

The first problem is constituted by the variation of SOC. During a driving cycle the SOC can vary over a broad range, depending on current magnitudes and the duration of the investigated data segment. As described above, the data segment has to be a multiple of the investigated frequency. Hence, it cannot be indefinitely small in order to also obtain the low frequency branch of the spectrum.

The second problem is related to the cell temperature and its variation. Every cycling causes self-heating of the cell. Even if a cooling system for the energy storage is applied, the inner cell temperature will still significantly increase during cycling.

The third issue refers to the requirement of a linear excitation. Real driving currents contain high peaks of up to several hundred amps exceeding the linear excitation range by far. Even if high current peaks were disregarded during data processing, they would still perturbate the cell outside the linear range and hence affect its behavior.

The last problem is caused by the non-stationary behavior of the cell. For a laboratory measurement, the cell is relaxed for a certain time in order to achieve an equilibrium state. Typically, this relaxation time is in the dimension of hours. During driving the cell generally is in a non-stationary state and time-invariance cannot be guaranteed.

EXPERIMENTAL

Test Cell

All methods in this work are demonstrated with measurements of a Li-Ion cell for automotive applications. The prismatic hard case cell is a prototype sample with LMO/NMC (blend of lithium manganese oxide with nickel manganese cobalt) technology. Nominal capacity of the cell is 20Ah, nominal voltage is 3.7V.

Test Equipment

Stressing Li-Ion cells with real automotive driving profiles and performing EIS measurements requires a test equipment capable of high currents of up to several hundred amps, a large bandwidth and precise measurement. Therefore our group developed a dedicated single-cell tester [15] which can cope with all requirements mentioned above. The development of this test equipment is beyond the scope of this paper, the main features of the tester are given in Table 1.

Table 1. Features of the single-cell tester used.

Maximum discharge current	600A
Maximum charge current	200A
Terminal voltage	1.5V - 4.9V
Maximum continuous power	2kW
Maximum signal frequency	3.5kHz
Measurement resolution	18bit
Voltage resolution	20μV
Current resolution	10mA
Maximum sampling rate	25kHz

Kelvin contacts are used to measure the cell voltage directly at the terminals. The cell is placed in a climate chamber and cell temperature is obtained with a PT100 sensor mounted between the terminals with constant contact pressure and isolated from ambient temperature.

Driving Profile

The driving profile used in this work is derived from real driving data and is typical for a Plug-In Hybrid Electrical Vehicle (PHEV) [25]. The profile has a duration of about one hour and discharges the cell from SOC=100% to SOC=40%. It contains current peaks of up to 300A. Due to a limited sampling rate of the original data the profile is superimposed with high frequency white noise.

The cell is cycled with this profile at an ambient temperature of $\vartheta = 25^\circ\text{C}$.