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# New approach for the calculation of impedance spectra out of time domain data

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ABSTRACT

A technique for fast impedance measurement in the time domain is presented. It is based on the Fourier transformation and includes various improvements compared to previous work in the literature. Namely, it minimizes the influence of spectral leakage and aliasing and reduces noise. This is proved by the theoretical error estimate for different model systems. The technique is independent of the excitation signal and is demonstrated by a voltage step. Measurement results for a commercial Li-ion cell are presented and compared with results obtained by electrochemical impedance spectroscopy. Finally, a combination of the two techniques is proposed to cover a wide frequency range in minimum measurement time for the characterization of electrochemical systems.



## 1. Introduction

In recent years electrochemical impedance spectroscopy (EIS) has been established as one of the most important characterization methods for electrochemical systems such as batteries or fuel cells. EIS is effective for model systems as well as for commercial consumer products. EIS is a powerful method for the analysis of the dynamics of basic electrochemical processes as well as for parameter identification by diagnosis systems for commercial applications.

The measured physical quantity is the complex and frequency dependent resistance of the tested system. The data set obtained is the so-called impedance spectrum, which has to fulfil the criteria of causality, linearity, and stability [1]. Information gained from an impedance spectrum comprises the static behavior of a system at very low frequencies. It allows judging the performance by the inner resistance in different operation points, as well as the dynamic behavior by mapping the polarization processes of the system. While the spectrum itself is obtained as a non-parametric process model, it nevertheless allows for a detailed analysis of the polarization processes with regard to relaxation times and polarization resistances often used as model parameters. The analysis of such an impedance spectrum is thereby neither restricted to a predefined evaluation method nor to model assumptions. This opens the possibility to use a variety of specifically capable evaluation methods for analysis. For example measurement series with varying temperatures are used to determine activation energies of electrochemical processes. Given impedance models of electrochemical processes can be validated or rejected by a complex nonlinear least-squares fit.

In Ref. [2] an integrated approach was presented to analyze the impedance spectrum of a Li-ion battery by equivalent circuit models (ECMs) and the distribution of relaxation times (DRT). A detailed description of the DRT method and its application on fuel cells can be found in Ref. [3]. In combination with adequate ECMs, physical parameters of the system can be obtained as demonstrated for Li-ion batteries in Ref. [4] and for fuel cells in Ref. [5].

Different measurement techniques in the time domain and the frequency domain generate an impedance spectrum of a practical system. EIS measures the impedance successively by applying only mono frequent harmonic excitation signals (alternating current, AC). The multisine technique applies sine-waves of several frequencies simultaneously [6]. Because of the reduction in measurement time and the simultaneous measurement of different frequencies, it is used for dynamic electrochemical impedance spectroscopy (DEIS) [7]. The excitation signals of time domain techniques can have arbitrary waveforms such as white noise or step functions. Spectra are calculated by Fourier transformation (FT-EIS) [8,9] or Laplace transformation [10]. One realisation of a time domain measurement is the so-called current-interrupt technique. The (high) current drawn from a system is simply cut off at a certain time and the voltage response is measured. This technique is proposed to determine the impedance of low impedance systems such as PEM fuel cell stacks [11] at high frequencies. The current-interrupt technique is favored for this purpose because it reduces inductive effects, which have to be considered for AC methods. Current-interrupt is also proposed for fast diagnosis of electrochemical cells with large time constants. This is done by directly fitting the time domain data to a pre-assigned ECM as described for the current-interrupt technique in [12] and in general in [13,14]. The point

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at issue for these methods is that the choice of the ECM is based on assumptions determined before the measurement. This is only suitable when a distinct model is widely accepted for the system under test. Potential Intermittent Titration Technique (PITT) and Galvanostatic Intermittent Titration Technique (GITT) also work on this principle [15,16]. Both of them are used to determine the effective diffusion coefficient in Li-ion batteries and assume a model equation including the diffusion coefficient. This coefficient can be obtained by a linear fit of the time domain data if displayed adequately.

All impedance measurement techniques lead to the same results as shown and discussed in Ref. [13]. In contrast, time domain techniques are generally faster because of the simultaneous excitation of several frequencies. A reduction of measurement time is advantageous, for example, for the analysis of the solid-state diffusion processes in electrodes for Li-ion batteries. Here fore, the measurement has to be extended to very low frequencies [17], which intensifies degradation effects in the active materials. Furthermore, for measurement times of several days, the steady-state of the system under test is questionable and the current drift of the measurement equipment becomes a critical issue.

Therefore, we propose a faster approach by time domain measurement (TDM), which covers the low frequencies down to a few μHz. The excitation signal for this TDM is a voltage step. The proposed algorithm for the calculation of the impedance spectrum is based on the method presented by Takano et al. [18], but significant improvement will be presented for the processing of the time domain data. This is achieved by (i) an optimization of the window function, (ii) a transformation of the time domain data using a straight line sequence, (iii) a variable sampling rate, and (iv) a stepwise evaluation within sections.

It is worth mentioning that it is possible to calculate the DRT directly from the recorded time domain data as pointed out in Ref. [19], for example with the LEVM software [20]. However, this technique fails, if the system under test shows capacitive behavior as Li-ion batteries do. Then the time response cannot be expressed as a pure sum of exponential functions and a pre-identification and subtraction of the system capacity would be necessary as done in Ref. [4]. That is why a direct calculation of the impedance spectrum out of time domain data is favored in this study to analyze Li-ion batteries comprehensively over the necessarily large frequency range comprising the very slow solid state diffusion [17]. The presented approach is valid for all kinds of electrochemical systems and is also capable of displaying the capacitive behavior at low frequencies. Results obtained from measurement data of a commercial Li-ion cell are presented and discussed.

## 2. Experimental

The capability of the presented technique is demonstrated by experimental data of a commercial Li-ion pouch bag cell with a capacity of 120 mAh. The starting conditions of 95% state of charge (SOC) at a constant ambient temperature of 21 °C were adjusted and the cell voltage settled at 4.1882 V after 3 days, so that all processes in the relevant frequency range can be assumed to have decayed.

First an impedance spectrum (IS 1) was recorded using an alpha-AK analyzer together with a POT/GAL10V/15A (novocontrol technologies, Hundsangen, Germany) in a 4-wire-setup. The excitation was chosen to $\hat{u}$ = 10 mV. The frequency range was 33.4 μHz to 10 kHz. There was a delay of one period before three periods were recorded for impedance calculation for every frequency point. The focus for this measurement was set on accuracy. Therefore, less frequency points were measured with longer integration time than for a standard cell characterization. This added up to a measurement time for IS 1 of approximately 2 days. Afterwards, the cell was again held for 2 days at 4.1882 V. Then, the time domain measurement (TDM) was started. At $t_{start}$ = 0, a voltage step of −50 mV was applied using the same measurement device. Current and voltage were monitored for 1.5 days. The sampling frequency was varied in intervals shown in Table 1.

**Table 1**
Measurement intervals for the time domain measurement (TDM) in Figs. 4 and 5 with corresponding sampling rate.

| Interval | Sampling rate |
|---|---|
| 0...3 s | 2 kHz |
| 3...33 s | 1 kHz |
| 33...183 s | 200 Hz |
| 183...783 s | 50 Hz |
| 783...3783 s | 20 Hz |
| 3783...33,783 s | 2 Hz |
| 33,783...120,000 s | 1 Hz |

Afterwards, a voltage step of 50 mV was applied to restore the starting conditions. When the cell had settled at 4.1882 V after 3 days, another impedance spectrum (IS 2) was recorded with the same specifications as IS 1. To reduce measurement time, IS 2 was stopped after reaching 680 μHz after approximately 2 h.

## 3. Theory

The time domain data, namely the voltage and current signals over time, can be transformed into an impedance spectrum by division of the corresponding Fourier coefficients obtained by the direct application of the fast Fourier transformation (FFT), which is a fast algorithm to perform a discrete Fourier transformation (DFT). This technique is valid for arbitrary excitation signals. As a consequence it is robust against faulty excitation signals. However, for optimization of the measurement time an accurate excitation signal is required. But the technique also entails two major shortcomings, (i) spectral leakage and (ii) aliasing. They are originated in the fact that the monitored signals are normally nonzero at the end of the finite monitoring interval and in the finite sampling frequency, respectively. A detailed description of these effects can be found in Ref. [21]. Also, the trade-off between information and data volume is an important issue.

### 3.1. Data volume

In order to cover a wide frequency range up to high frequencies with the time domain measurement, a high sampling frequency is required. This reduces the aliasing and results in a better signal to noise ratio for high frequencies. On the other hand, a long measurement time is required. Otherwise low frequencies could not be evaluated.

If these requirements are combined the resulting data files become extremely large. So the first innovation of our method is a step-wise reduction of the sampling rate. A similar approach was used by Takano et al. [18] who used three data acquisition units that worked on different sampling rates with the same memory resulting in different observation intervals. The impedance spectrum was calculated in sections – one section for every device covering a different frequency range. For the technique proposed here, the sampling time of the measurement device is varied during the experiment according to Table 1.

### 3.2. Spectral leakage

Spectral leakage is the distortion of the Fourier transformation caused by finite measurement time when the signal still has not properly converged to zero. By stopping the measurement, all the information contained in the signal at later times is implicitly