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A new approach to measure the non-linear Butler–Volmer behavior of electrochemical systems in the time domain

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ABSTRACT

A new approach to measure the non-linear Butler–Volmer behavior of electrochemical systems in the time domain is presented. The method is based on two superimposed currents, one large pulse as an offset and a small pulse which is transformed into the frequency domain. The advantage of this new method is the decreased measurement time compared to frequency domain measurements. This allows the characterization at lower frequencies with less distortion from change in SOC and temperature. In order to reduce spectral leakage of the fast Fourier transform the derivative of the measured signals is taken. The measurement time can be as small as the theoretical limit $T = 1/f$ with a negligible error. For the characterization of large automotive cells high currents are needed which were provided by a reprogrammed BaSyTeC HPS cell test system, also used to conduct dynamic electrochemical impedance spectroscopy measurements to validate the new method. The equality of the two completely different hardware and software systems is shown for a 50 Ah cell for automotive applications at −20 °C in a current range from 0 to 100 A.

1. Introduction

In order to predict the performance of Li-ion cells under all operating conditions it is necessary to use precise cell models. In practice physically motivated equivalent circuits (ECs) are common to describe the electric behavior of the cell [1–3]. The parametrization of such models is often done by electrochemical impedance spectroscopy measurements (EIS) in the frequency domain (FD). Measurements in the time domain (TD) with subsequent transformation into the frequency domain are also possible to obtain the impedance spectrum, as reported in [4–6]. EIS and TD measurements usually give small signal parameters of the cell. Dynamic impedance measurements (DEIS) are necessary to determine the large signal behavior. These measurements determine the non-linear current dependency of the charge transfer resistance R_{ct}, which is described by the Butler–Volmer equation [2,3,7–11].

To measure the large signal behavior of automotive Li-ion cells with >20 Ah commercial impedance measurement devices are not suitable. These devices are typically designed for small currents in the range up to several amps. To avoid this problem a BaSyTec HPS cell test system, which can provide currents up to 240 A, is programmed as an impedancemeter. It will be described in detail in Section 3.1.

In this paper a new large signal method using dynamic time domain analysis (DTD) is presented for high bias currents and frequencies up to 1 kHz. It is based on two superimposed currents, one large pulse as an offset and a small pulse to measure the impedance which is then transformed into the frequency domain.

Due to the considerable time saving (see Section 4) of this method, which also means a shorter span of the DC offset current, lower frequencies can be measured with less deviations caused by self-heating or SOC shift. This enables a highly precise cell characterization and results in better parametrization of cell models.

2. Theory

Details of EIS and TD measurements can be found in the literature. All the aspects concerning EIS are illustrated in [12] and the relevant source of errors in the evaluation of TD measurements, which are signal to noise ratio (SNR), aliasing for high frequencies and spectral leakage, are described in [4].

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2.1. Comparison of frequency and time domain measurements

The principle of DEIS (see Fig. 1(a)) is to superimpose a small sinusoidal current for cell characterization with a DC offset current. The new approach presented here is based on the same principle. Instead of a sinusoidal signal a small arbitrary excitation pulse, from which the impedance is calculated, is superimposed onto a much larger DC offset current (see Fig. 1(b)). For DEIS the non-linear Butler–Volmer behavior (large signal) of the cell can be directly calculated by measuring the amplitude and phase of the input and output signals. This is not possible for time domain measurements which require a more complicated data analysis because all frequencies up to the Nyquist frequency are included in the small excitation pulse. Lohmann et al. [6] investigated different waveforms (rectangular, Gaussian and sinc pulse) regarding the signal to noise ratio (SNR) and concluded that a sinc pulse leads to the best results due to the concentrated signal energy in the frequency range under test. In this paper a rectangular pulse with a rise time of 0.5 ms is used, because it can be easily generated by discharging the cell for a certain time through a shunt. Our experimental setup as described below with high current excitation and low noise voltage measurement down to μV leads to a sufficient SNR even for the simple rectangular pulse in the frequency range up to 1 kHz.

The advantages of this measurement technique in the TD compared to EIS/DEIS in the FD are: (1) simple signal generation, (2) the excitation signal contains all frequencies up to the Nyquist-frequency and (3) a time saving factor of 4 is achieved (see Section 4). The disadvantages of the TD approach are the more complicated data analysis as well as the reduced signal energy which requires extremely low noise measurement equipment.

2.2. Error sources of large signal measurements

The DC current for the large signal characterization leads to a shift in state of charge (SOC) as well as self-heating of the cell. To meet the necessary conditions for stationarity (see [8]) the acceptable change in SOC should be less than 2% and the change in temperature <1 K at the end of the pulse. The AC should be small enough to avoid distortion of the sine wave signal. The same applies to the excitation pulse in DTD. The influence of the current magnitude on the measurement result is investigated in Section 4.

A further non-negligible aspect in the evaluation of both DEIS and dynamic pulse measurements is the voltage drift that comes with the large DC-offset current. There are two main reasons for the drift which are the change in open circuit voltage (OCV) and the over-voltage of the diffusion in the active material (described by the Warburg impedance). This aspect is demonstrated schematically for DEIS and a dynamic pulse in Fig. 2. Note that drift can also be caused by insufficient relaxation time after charging/discharging to a certain SOC, which is also relevant for all measurements.

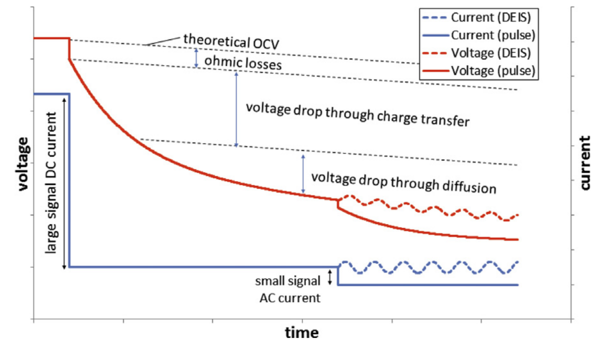

Fig. 2. Detailed current and voltage waveforms during DEIS and dynamic pulse measurements. Due to the DC current a significant voltage drift is observed which is caused by change in OCV as well as diffusion in the active material.

The impact of drift is quite severe. Without a correction an evaluation of the dynamic impedance is impossible. The ramp- or square root-like drift is interpreted by the Fourier transform as a saw tooth wave, which also contains frequency parts of the excitation signal. For FD measurements there are several approaches in the literature to correct the drift:

- A baseline correction which is possible down to frequencies of 1 Hz [13].
- A numerical approximation based on the average values of voltage during each period of the exciting sine current [8].
- A subtraction of the mean value of the neighbor lines of the spectrum [14].

We propose a different method which is based on a shift of the evaluation window. For a linear drift the method leads analytically to a perfect compensation. This can be proved mathematically by solving Eq. (1):

$$U_k = \frac{1}{2}V_{k,w1} + \frac{1}{2}V_{k,w2}, \tag{1}$$

where U_k is the discrete Fourier transform (DFT) of frequency k of one period of a signal without drift. $V_{k,w1}$ and $V_{k,w2}$ are the DFTs of the same signal with a ramp-like drift and $w1$ and $w2$ denote the different evaluation windows with a shift of 180 degrees in between (see Fig. 3).

In Li-ion cells the Warburg diffusion leads to a square root-like drift. The slope of this drift becomes less with proceeding time which results in a spiral form in the Nyquist plot, as can be seen in Fig. 3). An analytic compensation of the root-like drift is very difficult because the Fourier coefficients have to be calculated for

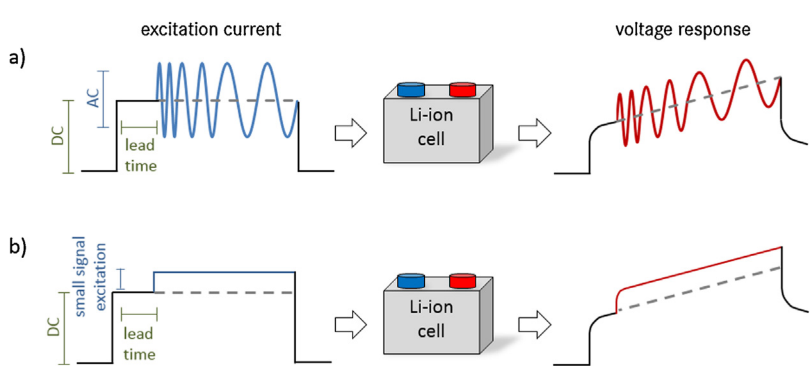

Fig. 1. Schematic picture of (a) DEIS and (b) dynamic pulse. The cell is excited by a large DC offset current which is superimposed by a small sinusoidal excitation current for DEIS and a rectangular excitation current for dynamic pulse.