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Influence of the settling behavior on the measurement uncertainty of EIS and how to decrease the measurement duration

Abstract: To obtain a spectrum, different frequencies are applied stepwise. In an ideal system the measurement uncertainty is only influenced by the noise of the voltage and current measurements. But since a switched sine includes transient signal parts, the system's settling behavior leads to systematic errors. Usually the first periods after the start of the excitation are thus not included in the measurement. A method based on a model of the measurement system will be shown, allowing for compensation of the error. Thus the measurement duration can be reduced significantly.

Keywords: Uncertainty, settling behavior, measurement model

1 Introduction

The electrochemical impedance spectroscopy is widely used in laboratories as a tool for the parameterization of electrochemical energy storage models based on equivalent circuits [1]. It is also used as a tool to investigate changing processes in aging batteries [4]. A good knowledge of the measurement uncertainty is needed in both cases to be able to evaluate the determined parameters.

Another growing field of application is quality assurance during the manufacturing of battery packs. In a series production line the reduction of cycle time has top priority. Therefore, the goal is to decrease the measurement duration of an impedance spectrum, without increasing the measurement uncertainty considerably.

The most common way to measure the electrochemical impedance is to apply a sinusoidal excitation signal. The excitation and response signals are acquired using a constant sample rate. Both signals are then transferred to the frequency domain by using the discrete Fourier transformation and divided to obtain the impedance. To acquire a spectrum, different frequencies are applied stepwise, one after another.

To reduce the measurement duration, multiple frequencies can be applied simultaneously [2, 3]. Since the information density of an electrochemical system is not

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scaled linearly with frequency, only a finite number of distinct frequencies has to be included in the signal. The phase angles can further be chosen in a way to minimize the crest factor [5]. Overall suitable signal-to-noise ratios can be reached.

2 Measurement uncertainty

The main influence on the uncertainty of measured impedance values, which cannot be reduced by calibration, is the noise of the voltage and current measurement.

With the Fourier transformation the noise component at the examined frequency gets isolated and results in a Gaussian distribution around the true impedance value [6]. This behavior was verified by 22,000 measurements on a Sanyo/Panasonic UR18650E Li-ion cell, each with one period at 220 Hz. The resulting histogram (Fig. 1) shows the analytically proven Gaussian distribution.

Fig. 1: Gaussian distribution of impedance measurement values due to noise in the excitation and response signals.

The standard deviation of the distribution depends on the noise magnitude at the considered frequency, the magnitude of the excitation and response signals and the number of samples used for the calculation.

3 Settling influence

Electrochemical energy storage devices exhibit processes with different time constants. This results in a transient response, when the excitation signal is being switched on. It takes a specific time until the amplitude and phase shift can be considered stable. To apply a Fourier transformation to this unstable part can be considered wrong, since the assumption of a periodic signal is not valid. But still it can be computed without numerical difficulties and provide information about the system.

To quantify the influence of the settling 20 periods at 220 Hz where applied to the previously introduced Li-ion cell. This procedure was repeated 100 times with breaks without excitation in between. Every period was individually evaluated, resulting in the impedance points seen in Fig. 2. For the first cycle the error due to the settling behavior is quite significant compared to the uncertainty due to noise. The error decreases exponentially with increased cycle number, but in this case has to be considered as a systematic error up to cycle number five.

Fig. 2: Results of multiple repeated measurements on a Li-ion cell marked depending on the number of the considered excitation period.

The error is not constant but depends on the time constants and resistive magnitude of the analyzed system and changes in magnitude and direction with the frequency being applied.

The usual way to overcome this effect is to apply the first period but start the acquisition afterwards, during the second cycle. This is documented by the different instrument manufactures in different detail (e. g., as “pre-wave” [7]). Beginning from the second cycle the following cycles are usually averaged to reduce the noise level. The effect of the settling is also being reduced by this averaging.

4 Reduction of measurement duration

If the measurement duration should be reduced, long averaging cannot be used anymore. It would further be favorable to not have to apply at least two periods of the signal. Especially at lower frequencies, in the mHz range, this is considerably influencing the measurement duration.

In Fig. 3 the resulting spectrum of the first excitation period and the true system response (from the 20th period) are shown. For these measurements a multisine signal with 39 frequencies, logarithmically spaced from 8 kHz to 100 mHz, was applied to the previously introduced cell. The length of the signal is 10 seconds (one period of the lowest frequency). It can be seen that the influence in the lower frequencies is greater than in the higher frequencies. This is due to deviating numbers of periods of the different frequency components and therefore a variation in the averaging.

Fig. 3: Spectra measured with multisine excitation. The settling error can clearly be identified within the first period.

In the measurement model (see Fig. 4) the signal source, amplifier and input filter are assumed to be ideal. The multisine signal is periodic, so the gating in the current measurement path has no effect. But the gating of the voltage signal is the source of the settling error and thus has to be considered in the model.

Fig. 4: Model of the measurement system.

Overall, equation (1) can be derived from the model, where $H(\omega)$ denotes the true impedance of the system, $H_r\omega$ is the transfer function of an ideal rectangular window and V, I can be observed. A response impedance $H^*(\omega)$ can be calculated, including the settling error. The equation cannot be de-convoluted to be solved with respect to H , since the problem is ill defined and would lead to massive noise amplification. We have

$$V(\omega) = (I(\omega) \cdot H(\omega)) * H_r(\omega), \quad (1)$$

$$H^*(\omega) = \frac{V(\omega)}{I(\omega)}. \quad (2)$$

To reconstruct the true impedance, an iterative method has to be developed only computing the measurement model in forward direction.

1. Set the system impedance input $H_{n=0}$ to the measured response impedance H^* interpolating in between the measured frequencies.
2. Calculate the new response impedance H_n^* with the measurement model.
3. Change the input by the difference of the responses $H_{n+1} = H_n + (H_n^* - H_{n-1}^*)$ at the frequency points excited. Apply an interpolation as above.
4. Repeat from step 2 until the iteration converges.

An interpolation can be used without introducing errors, since electrochemical energy storage devices exhibit continuous impedance functions not including discontinuities.

The first three iterations on the previously shown measurement results are shown in Fig. 5. It can be seen that the curve of the input impedance starts to smoothen and the response impedance converges towards the measured curve. It is therefore possible to reconstruct the true impedance of the system only taking the measurement values from the first period into account.

Fig. 5: Presentation of the first three iterations of the proposed method to reconstruct the true impedance.

5 Conclusion

The settling behavior is a significant error source for impedance determination within the first to sixth excitation period. A method was given to reconstruct an impedance

spectrum utilizing a measurement model. It is sufficient to excite the system with a multisine excitation with the length of one period of the lowest frequency. The measurement duration for impedance spectra can thus be significantly reduced.

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