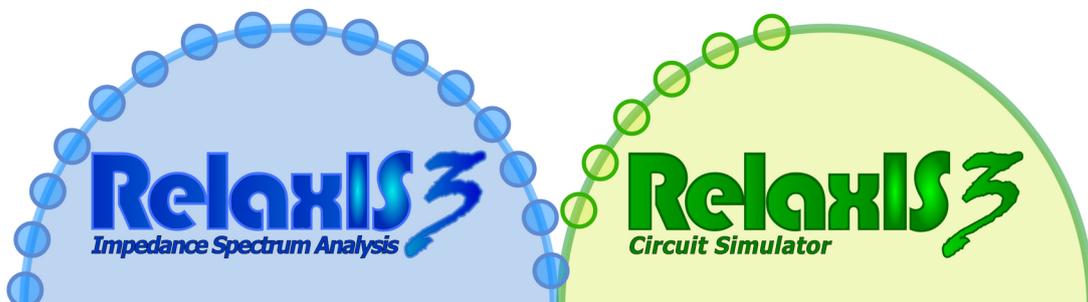
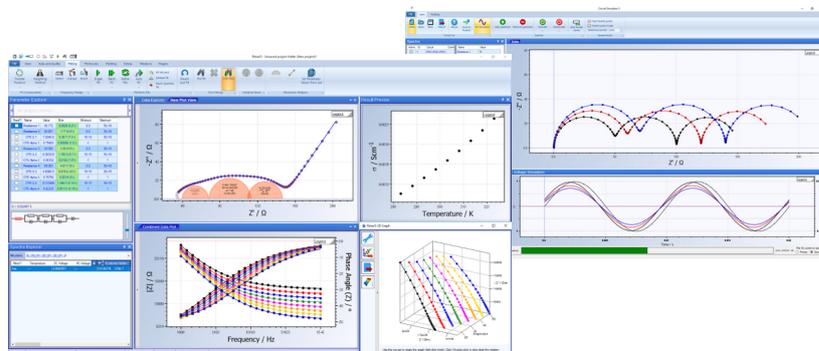


Application note

2-electrode and 3-electrode setups

A comparison of experiment and simulation



Introduction

Impedance spectroscopy is a versatile, powerful and non-destructive analysis technique for material characterization.[1]-[4] It is applied for instance for the investigation of dielectrics, passivation effects, redox reactions or even of fully assembled batteries. With alternating current (AC) measuring frequencies ranging from MHz down to mHz, EIS allows for studying processes taking place on timescales from microseconds up to hours or even days.

One of the biggest challenges in practical impedance spectroscopy is the analysis of the measured data in a physically meaningful way. The analysis is complicated by the fact, that most electrochemical systems do not consist of a homogeneous phase in contact with the electrodes, but of a lot of different phases with phase boundaries between them. For example, a typical 2-electrode impedance spectrum of a battery will show contributions of every material, interface and electrode reaction inside the cell. To distinguish between individual impedance contributions, electrochemical experiments are often carried out in a 3-electrode setup. But why and how can this help?

This application note will focus on answering this question both from theoretical considerations and simulation as well as with practical experiments.

Theory

We first consider a simplified, ideal electrochemical system, consisting of two different electrode materials **a** and **b**, which are in contact with an electrolyte and electrically connected. At both electrodes electrochemical double layers are formed and Faradaic reactions may take place. To describe such a system, typically a connection of two parallel R_iC_r -elements - one for each electrode interface - is used. In each RC -element the resistor represents the charge transfer resistance of the Faradaic reaction, $R_{CT,i}$. The capacitor describes the double layer capacitance $C_{DL,i}$ at the electrode/electrolyte-interface. Ionic charge trans-

port through the electrolyte is represented by an Ohmic resistor R_{elec} in series to the interface RC -elements. A schematic sketch together with the equivalent circuit is shown in **Figure 1** for different electrode setups. For simplicity, contributions of diffusion processes are neglected.

In a 2-electrode potentiostatic measurement a sinusoidal potential $\hat{V}_{WE/CE}$ is applied between the working electrode (WE) and counter electrode (CE) and the resulting sinusoidal current $\hat{i}_{WE/CE}$ is measured. Both quantities are complex valued to accommodate the phase difference between the voltage and current. In this formulation, the impedance is defined similar to Ohm's law as the ratio between complex voltage and current.

The voltage drops over the whole cell. However, this drop is not uniform over the distance between the electrodes. Instead, the individual phases in the system have individual impedance contributions and therefore drop different amounts of voltage at a given current. The total impedance can therefore be written as the sum of the individual impedances, e.g. in the example above:

$$\hat{Z}_{2E} = \frac{\hat{V}_{WE/CE}}{\hat{i}_{WE/CE}} = \hat{Z}_{WE} + \hat{Z}_{CE} + \hat{Z}_{elec}$$

In a 3-electrode setup, a third electrode is introduced between the WE and CE, which measures the voltage at this point versus the WE. In practice, the voltage applied between WE and CE is regulated in a feedback-loop to keep a defined voltage drop between WE and RE.

When the impedance is calculated using the partial voltage drop between WE and RE, it only contains the voltage drops caused by the phases between WE and RE. Likewise, if the voltage drop between RE and CE is used, only the phases between RE and CE contribute. This means, that the 2-E impedance spectrum is the sum of the WE/RE spectrum and the RE/CE spectrum. The WE/RE spectrum is typically referred as 3-E impedance spectrum.

$$\hat{Z}_{3E} = \frac{\hat{V}_{WE/RE}}{\hat{i}_{WE/CE}} = \hat{Z}_{2E} - \hat{Z}_{RE/CE}$$

As a consequence, the 3-electrode spectrum is also influenced by the position of the RE relative to the WE in the cell, schematically shown in **Figure 1**. Placing the RE at a larger distance from the WE (**Figure 1(b)**) causes the spectrum to contain a higher electrolyte resistance as compared to the position of the RE shown in **Figure 1(c)**. When the RE is located directly in the middle between WE and CE, the measured electrolyte resistance is half of the total electrolyte resistance (**Figure 1(c)**).

Most importantly, the 3-E spectrum does not contain any contributions of the CE interface, which often overlaps the processes at the WE. This allows for an easier analysis and characterization of the WE interface processes.

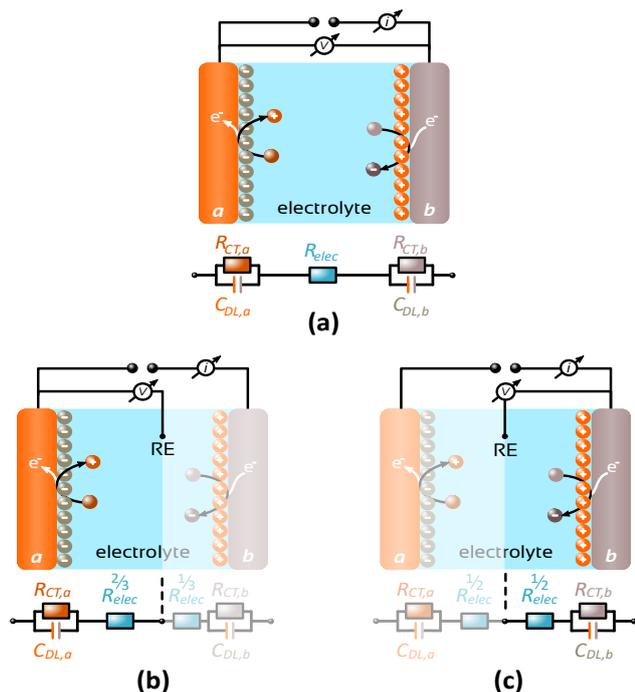


Figure 1: Illustration of different measurement setups/electrode positions inside an electrochemical cell and expected influence on the impedance behavior. **(a)** 2-electrode setup, **(b)** 3-electrode setup with RE positioned closer to the CE, **(c)** 3-electrode setup with RE positioned exactly in the middle of the cell.

Experiment

a) Measurement setup

For this application note, a set of different resistors and capacitors were combined and connected on a breadboard as shown in **Figure 2**, imitating the cell considered in the previous section. The used components have a tolerance in their nominal values of 5% or 10% for resistors and capacitors, respectively.

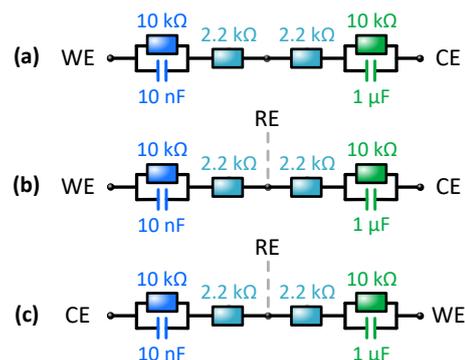


Figure 2: Electric circuit, imitating an ideal battery impedance behavior with different electrode arrangements for the individual experiments **(a)**, **(b)** and **(c)**.

To allow for positioning the RE in the “middle between WE and CE”, the resistor representing the electrolyte resistance was divided into two equal resistors, connected in series.

A PGStat302N potentiostat/galvanostat equipped with a FRA32-module (Metrohm Autolab B.V.) was used for the impedance experiments. For data acquisition, the NOVA 2.1.4 software was used. The connection and arrangements of WE, CE and RE were changed as shown in **Figure 2** after every measurement (in the sequence: **(a)** → **(b)** → **(c)**).

Impedance analysis as well as spectra plotting was done using the RelaxIS 3 software suite (developed by rhd instruments GmbH & Co. KG).

b) Impedance measurement parameters

The impedance measurements were performed within a frequency range of 100 kHz to 1 Hz and with an amplitude of $V_{AC,rms} = 10$ mV.

c) Simulated impedance spectra

Impedance data for equivalent circuits with arbitrary parameter values and frequency range was generated using the RelaxIS Circuit Simulator 3, which is included in the RelaxIS 3 software suite.

Results and comparison

Figure 3 shows the measured spectra for both the 2-electrode and the 3-electrode experiments. In addition, a simulated impedance spectrum based on the nominal component values for the 2-E spectrum is included in **Figure 3(a)**. Both simulated and measured data was overlaid in a single plot in the RelaxIS 3 combined data plot feature.

For analysis, the spectra were fitted in RelaxIS with the corresponding full or partial equivalent circuit. The fitted values can then be compared to the nominal component values, as shown in the following table. For easier reference, the parameters are colored similar to their appearance in **Figure 2**.

Parameter	Nominal value	Fitted value 2-electrode	Fitted value 3-electrode
R_1	4.4 k Ω	4.43 k Ω	2.20 k Ω
R_2	10 k Ω	9.75 k Ω	9.74 k Ω
C_2	10 nF	10.00 nF	10.07 nF
R_3	10 k Ω	9.75 k Ω	9.76 k Ω
C_3	1 μ F	1.03 μ F	1.03 μ F

Please note, that R_1 in the 2-electrode experiment shows double the value of the individual (“electrolyte”) resistors, because these are connected in series. All fitted values are well within the component tolerances. The largest discrepancies are found for the resistors R_2 and R_3 , with a difference of 2.5%.

The parameter values illustrate, that even though the processes overlap moderately in the frequency domain, the fit is still able to retrieve the correct values. However, if the processes

show a larger overlap this can become problematic. To overcome this problem, the 3-electrode spectra illustrate, that you can completely eliminate one side of the cell by measuring a 3-electrode spectrum, while still measuring the correct parameter values.

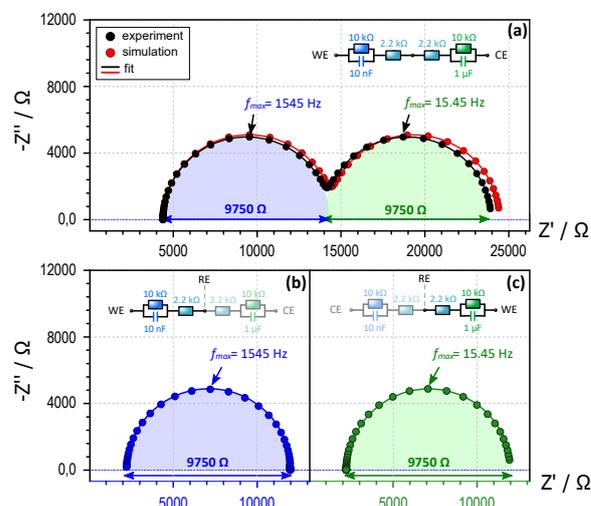


Figure 3: (a) Nyquist plots of fitted experimental and simulated 2-electrode impedance spectra of the shown circuit (simulation for $R_2 = R_3 = 10$ k Ω); (b) and (c) individual 3-electrode impedance spectra or the indicated circuit parts according to the electrode arrangements shown in **Figure 2**.

The 2-E spectrum poses another challenge: How can you assign the two R_iC_i -processes in the 2-E spectrum to the corresponding 3-electrode spectrum? Unfortunately, both semicircles show the same diameter, meaning equal resistance values in the Nyquist plot.

It is important to know, that in impedance spectroscopy parallel R_iC_i -processes are resolved by their specific time constants τ_i . The time-constant is directly related to the angular frequency at the maximum $-Z''$ value of a semicircle, $\omega_{max,i}$:

$$\tau_i = R_i \cdot C_i$$

$$\omega_{max,i} = \frac{1}{\tau_i} = 2\pi f_{max,i} = \frac{1}{R_i \cdot C_i}$$

Here, the corresponding specific frequencies for the R_2C_2 - and R_3C_3 -processes at the maximum f_{max} and f_{max} are:

$$f_{max} = \frac{1}{2\pi \cdot 9.75 \cdot 10^3 \text{ V A}^{-1} \cdot 10^{-8} \text{ As V}^{-1}} = 1539.00 \text{ Hz}$$

$$f_{max} = \frac{1}{2\pi \cdot 9.75 \cdot 10^3 \text{ V A}^{-1} \cdot 10^{-6} \text{ As V}^{-1}} = 15.39 \text{ Hz}$$

This means, that the R_2C_2 process is found at higher frequencies in the spectrum than the R_3C_3 process. Therefore, the left semicircle in the Nyquist plot corresponds to the R_2C_2 process and the right semicircle to the R_3C_3 process.

In impedance spectroscopy experiments the frequency dependence of the processes is very important. The Bode-plot can be of great help in identifying processes between 2-E and 3-E spectra, because it contains the frequency information directly (Figure 4).

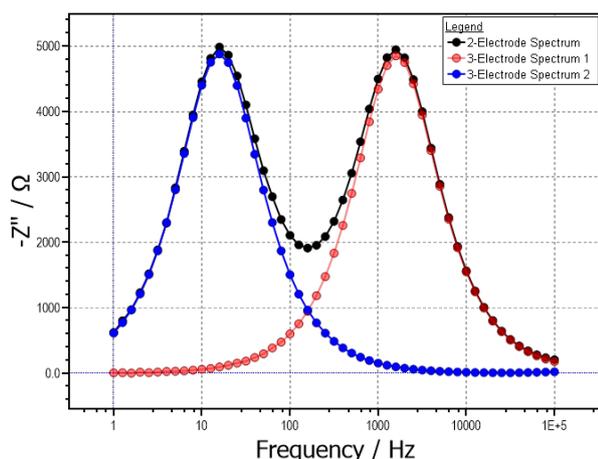


Figure 4: Bode-plot overlay of the negative imaginary part of the 2-E and 3-E impedance spectra, to illustrate the assignment of the Nyquist-semicircles in the frequency domain.

Simulating multiple spectra with gradually changing parameters can illustrate how processes can overlap. In Figure 5, spectra for the example model were simulated. All parameters were kept constant except for the C_3 parameter, which was gradually decreased until it matched C_2 . In the overlapping spectra, only a single semicircle is visible and the determination of the correct R_2 and R_3 values is hardly possible. You could produce the same spectrum

by increasing R_2 and decreasing R_3 and vice versa - the case is ambiguous. In that case, the 2-E spectrum is not suitable to determine correct values for R_2 and R_3 . The 3-E spectra however would still show the individual processes and allow a correct determination.

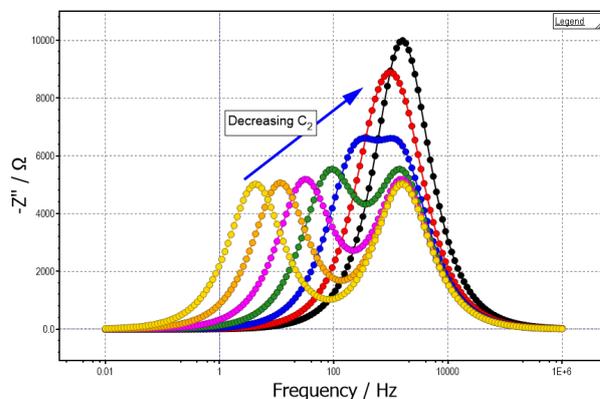


Figure 5: Bode-plot overlay of the negative imaginary part of simulated spectra of the example model, where the value of C_3 was gradually decreased, to illustrate the possible overlap of two processes in the frequency range.

Summary

This application note shows the advantage of eliminating one half-cell of an electrochemical system from an impedance spectrum by employing a 3-electrode measurement setup. Introducing a reference electrode at a location between the working and counter electrode results in an impedance spectrum that contains only the contributions of the relevant processes between WE and RE. In case of a cell with drastically different half-cells, an evaluation of the full 2-electrode spectrum may be possible, but we show here that you can eliminate the possible problems caused by the overlap and still retrieve the correct parameter values from the 3-electrode spectrum. If only a 2-electrode experiment is performed, it is not trivial to attribute the processes in the spectrum to the correct half-cells. In this application note's example the attribution could be done using the process time-constants or the Bode-plot, but this method is not easily generalizable to more complex electrode processes or to cases where the electrode processes show a large overlap in similar frequency ranges.

Are you interested in learning more about impedance spectroscopy in general, its application, analysis, pitfalls and features? Then our impedance spectroscopy course could be the right choice. We are looking forward to your registration!



<https://www.rhd-instruments.de/en/products/software/relaxis>



Training Course: Impedance Spectroscopy

<https://www.rhd-instruments.de/en/products/services/training-course-impedance>

Literature

- [1] V. F. Lvovich, *Impedance spectroscopy. Applications to Electrochemical and Dielectric Phenomena*, 1st edition, Wiley, Hoboken, N.J., **2012**.
- [2] M. E. Orazem, B. Tribollet, *Electrochemical impedance spectroscopy*, Wiley, Hoboken, New Jersey, **2008**.
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