Metrohm Autolab

Application Area: Fundamental

Electrochemical Impedance Spectroscopy (EIS) Part 5 – Parameter Estimation

Keywords

Electrochemical impedance spectroscopy; frequency response analysis; Nyquist and Bode presentations; data fitting; equivalent circuit; parameter estimation

Summary

In the application note AN-EIS-004 on equivalent circuit models, an overview of the different circuit elements that are used to build an equivalent circuit model was given. It was shown that these circuit elements provide the building blocks for more complex models. After identifying a suitable model for the system under investigation, the next step in the data analysis is estimation of the model parameters. This is done by the non-linear regression of the model to the data. Most impedance systems come with a data-fitting program. Although these programs can be used as a black box, care must be taken to avoid problems.

Weighting the data

The fitting of a model to data is the minimization of the objective function J, Equation 1.

$$J = \sum_k \frac{\left(Z_{r,k} - \hat{Z}_{r,k}\right)^2}{W_{r,k}^2} + \sum_k \frac{\left(Z_{j,k} - \hat{Z}_{j,k}\right)^2}{W_{j,k}^2} \qquad 1$$

Where:

- $Z_{r,k}$, $Z_{j,k}$ are the real and imaginary parts of the data
- $\hat{Z}_{r,k}$, $\hat{Z}_{j,k}$ are the real and imaginary parts of the model
- $W_{r,k}$, $W_{j,k}$ are the real and imaginary weights

The fit is performed using a non-linear regression routine. There are several different weighting strategies that are possible. The three most common strategies are described in this section.

No weighting

In impedance spectroscopy, the value of low frequency data points is usually much larger than that of the high frequency data points (sometimes by several orders of magnitude).

The no weighting strategy is expressed with Equation 2.

$$W_{r,k} = W_{j,k} = 1 \qquad 2$$

When no weighting is used then the low frequency points would have higher weight than the high frequency points. This introduces a bias and can give large errors in parameter estimation. Therefore, this weighting should not be used.

Proportional weighting

The proportional weighting is expressed with Equations 3

$$\begin{aligned} W_{r,k} &= Z_{r,k} \\ W_{j,k} &= Z_{j,k} \end{aligned} \qquad 3$$

Usually at high and low frequencies the imaginary part of the data goes to zero.

In that case, proportional weighting can cause numerical problems because of division by zero. Therefore, this weighting should not be used.

Modulus weighting

Weighting the data by the absolute value of impedance (Equation 4) is the most recommended weighting strategy, and is the default weighting in the NOVA software.

$$W_{r,k} = W_{j,k} = |Z| \qquad 4$$

Initial Guess

The models in impedance spectroscopy are highly non-linear in parameter space, which implies that the objective function can have several local minima. An initial guess of the parameters is required to begin the regression procedure. A poor choice of the initial guess can result in the procedure terminating at a local minimum with, for example, wrong estimates for the model parameters. A good initial guess requires some experience. An examination of asymptotes and inflection points in the Nyquist and Bode diagrams can give some clues for making a good initial guess.

In Figure 1, it is shown how the errors that can be introduced due to bad initial guess are illustrated.

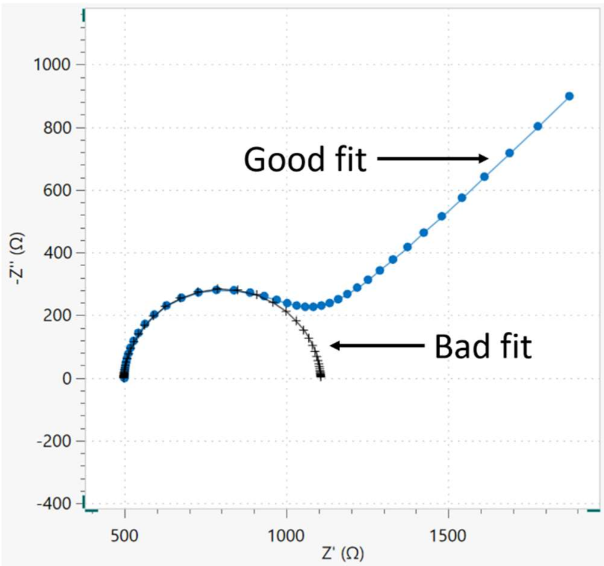

Figure 1 – The data (blue dots) are fitted with good initial guesses (blue line) and with bad initial guess (cross line)

Here, the circles represent the experimental data. The blue line is the result of fit to the data using a good initial guess, and the cross line represents the result with a poor initial guess. A poor initial guess can result in poor fit of the model to the data.

Non-uniqueness of circuit models

The Nyquist plot shown in Figure 2, shows two well-defined semi circles.

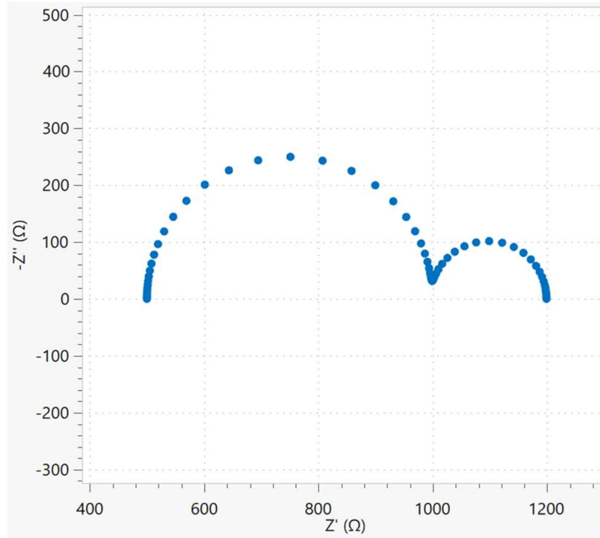

Figure 2 – They Nyquist plot with two well-defined semicircles

An equivalent circuit that consists of two RC time constants can model this spectrum. The two RC time constants can be produced by combining the resistances and capacitances in two different ways resulting in two equivalent circuits shown in Figure 3. Both the circuits would give an identical fit, with only the circuit parameters being different.

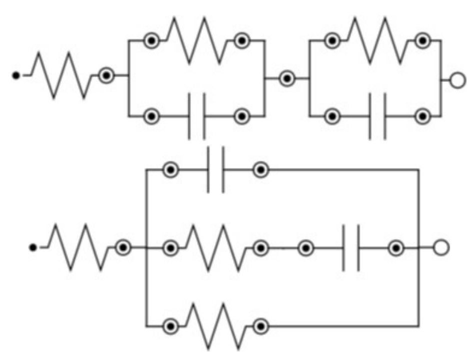

Figure 3 – Different arrangements of two RC time constants.

In this case, there is no unique equivalent circuit that describes the data in Figure 2.

It is not possible to assume that an equivalent circuit that produces a good fit represents an accurate physical model of the cell. Prior knowledge or complementary experiments are needed to determine the appropriate model for the data. This is one of the limitations of impedance spectroscopy.

Conclusions

In this application note, the ay the data are weighted during the fit is exposed, together with example of good and bat fit. Finally, limitations on data analysis is shown.

Date

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For more information

Additional information about this application note and the associated NOVA software procedure is available from your local **Metrohm distributor**. Additional instrument specification information can be found at **http://www.metrohm.com/electrochemistry**.