

# Chapter 14

## Modeling of Experimental Data

### 14.1 Acquisition of “Good” Data

The purpose of analyzing EIS data is to determine the nature of the electrode process and its characteristic parameters. As was mentioned earlier, EIS is a very sensitive technique, but it does not provide a direct measure of physical phenomena. Other electrochemical experiments (dc, transients) should also be carried out, assuming good physical knowledge of the system (e.g., solution and surface composition, electrode geometry, dimensions, porosity, presence of various layers, hydrodynamic conditions). The interpretation of impedance data requires the use of an appropriate model. This is a rather difficult and sensitive task that must be carried out very carefully.

Initially, the experimental data must be acquired in a wide frequency range; usually ten points per frequency decade are registered. The lowest frequency is determined by the system stationarity. Usually, one should wait until the current following application of the steady-state potential (or potential in the galvanostatic mode) becomes stationary. It is also advisable to repeat the measurements at each potential twice and compare complex plane and Bode plots to check whether or not they are the same. Other tests may involve running measurements from low to high and then from high to low frequencies. When experiments are carried out at different potentials, they should be repeated from high to low and from low to high potentials and compared. Only stationary, i.e., repeatable, results should be used in the analysis.

For species in solution undergoing diffusion (without forced convection) the lowest frequency that can be used depends also on the hydrodynamic conditions. It is well known that the chronoamperometric curves in solutions might be measured up to 60 s, after which natural convection affects the linearity of diffusion. This means that measurements of the mass transport impedance are limited to approximately 0.1 Hz (or slightly lower). However, measuring diffusion in solid materials (e.g., hydrogen absorption in metals and alloys, lithium intercalation) is not influenced by convection, and the measurements might be carried out to the

millihertz range or lower. One should keep in mind that one ac cycle at 1 mHz takes 16.7 min and taking only one cycle might not always be sufficient because of system noise. Data are usually registered sequentially from high to low (or vice versa) frequencies, so the experimental time is longer than that of one cycle of the lowest frequency. To decrease the experimental time, the EG&G software uses single frequency scans at higher frequencies and applies the sum of frequencies at lower frequencies, followed by Fourier transform analysis. A sum of all odd frequencies might be used, although the experimental noise for individual frequencies is often larger as the individual amplitudes must be reduced to assure system linearity (Sect. 13.2).

If differences are detected, they indicate that the system is not stationary and further modifications must be made to assure data reproducibility. This might involve waiting longer at each potential or shortening the time of the experiment by abandoning lower frequencies (which require longer measurement times). Some systems evolve with time, e.g., during corrosion measurements, and each experiment is carried out in a different surface state. In such cases, one must be sure that during one experiment there are no important surface modifications and that reproducible data can be obtained by repetition of the experiment with a new sample.

Then the acquired data must be validated using Kramers-Kronig transforms. Such validated data can be used in subsequent analysis and modeling.

## 14.2 Types of Modeling

Modeling of experimental data may be divided into two types, as follows.

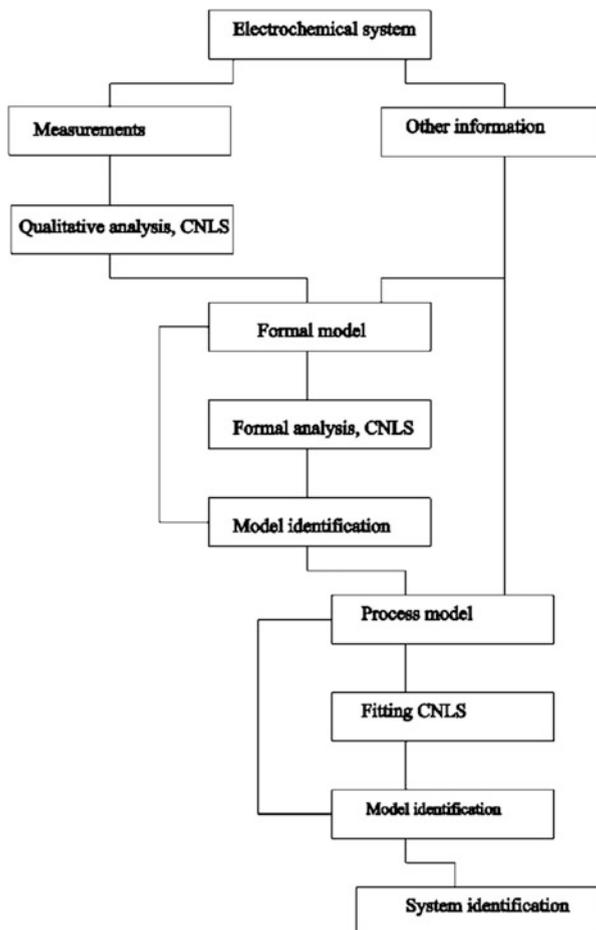
Measurement [606, 607], formal [27], or mathematical [608, 609] modeling explains experimental impedances in terms of mathematical functions or equivalent electrical circuits to obtain a good fit between the calculated and experimental impedances with a minimum number of parameters.

Physicochemical, process [566, 572, 606, 607], or structural [27, 610–612] modeling links measured impedances with physicochemical parameters of the electrochemical process (e.g., kinetic parameters, concentrations, diffusion coefficients, sample geometry, hydrodynamic conditions).

It is clear that in the measurement modeling, the parameters obtained often do not have a clear physicochemical significance. It should be stressed that proper modeling is the most difficult part of analysis and is often misunderstood and wrongly interpreted.

Zoltowski [608, 609] proposed that one should first use measurement modeling to determine the number and nature of the circuit elements and parameters describing the studied system. One could use equivalent circuits containing simple  $R$ ,  $C$ , and  $L$  parameters, or one could use more complex distributed elements such as the CPE and other analytically described elements such as, for example, mass transfer impedance and a porous model.

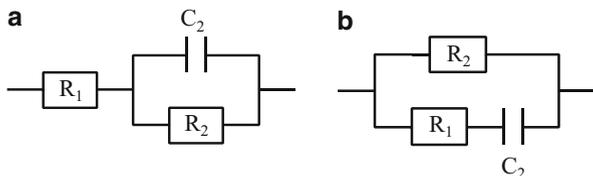
**Fig. 14.1** Steps in modeling process as suggested by Zoltowski [608, 609]



The next step would be to construct a physicochemical model for a given process. As was shown in earlier chapters, one can write faradaic impedance equations for any mechanism. The problem is that complex mechanisms produce equations (models) containing more parameters than really are observed in the experimental data (determined by measurement modeling). It must be stressed that a physicochemical model cannot contain more adjustable parameters than the corresponding measurement model. More complex physicochemical models must be correctly simplified. Several additional experiments are usually necessary to determine the origin of certain elements, for example, by changing the concentration, hydrodynamic conditions, adding poisons, or changing the temperature.

The modeling process proposed by Zoltowski is schematically displayed in Fig. 14.1. To characterize an electrochemical system, one performs impedance measurements and the results are qualitatively analyzed. This analysis allows the construction of a formal model and determination of the nature and number of the

**Fig. 14.2** Two electrical equivalent circuits producing one semicircle on complex plane plot and characterized by one time constant



parameters describing such a system. With information from other electrochemical and physicochemical methods, the process model is constructed leading to model identification and determination of the physicochemical parameters. The process is interactive, and repetitions/corrections might be necessary to finally describe the electrochemical system.

It must be added that such a process is not always possible. Certain phenomena cannot be described by analytical equations, for example, porous electrodes in the presence of a faradaic current and potential gradient, nonhomogeneous porous materials, diffusion to disk electrodes, and nonuniform diffusion. However, such phenomena might often be approximated by simpler analytical equations, although the obtained parameters might not have a clear meaning. For example, a semi-infinite porous model in the presence of a potential gradient may be approximated using a CPE, but the obtained parameters do not directly correspond to the electrode capacitance [435] (Fig. 9.29).

The main problem with equivalent circuit modeling is related to the fact that the same data may be exactly represented by different equivalent models. This problem will be illustrated in the following examples.

*Example 14.1* A complex plane plot displaying one semicircle (Fig. 2.34) may be exactly described by two equivalent circuits (Fig. 14.2). The impedances of these circuits are

$$\hat{Z}_a = R_1 + \frac{1}{\frac{1}{R_2} + j\omega C_2} = \frac{(R_1 + R_2) + j\omega(R_1 R_2 C_2)}{1 + j\omega(R_2 C_2)}, \quad (14.1)$$

$$\hat{Z}_b = \frac{1}{\frac{1}{R_2} + \frac{1}{R_1 + \frac{1}{j\omega C_2}}} = \frac{R_1 + j\omega(R_1 R_2 C_2)}{1 + j\omega C_2(R_1 + R_2)}. \quad (14.2)$$

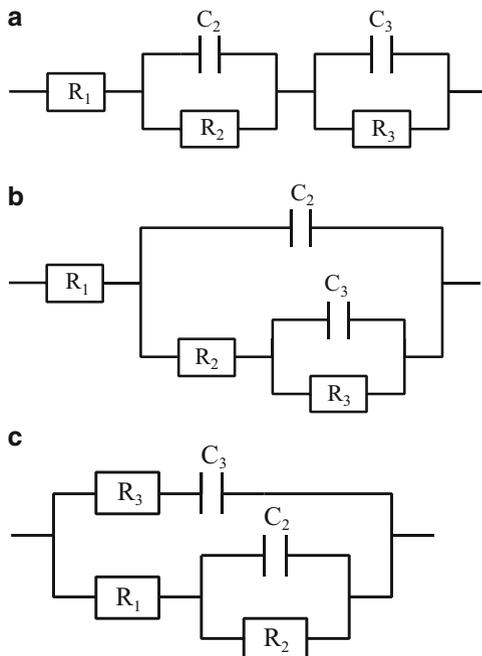
These two equations may be written in a unified form:

$$\hat{Z} = \frac{a_0 + a_1 j\omega}{b_0 + b_1 j\omega} = \frac{a_0 + a_1 j\omega}{1 + b_1 j\omega}, \quad (14.3)$$

where the parameters  $a_i$  and  $b_i$  are different for these two circuits:

$a_0 = R_1 + R_2$ ,  $a_1 = R_1 R_2 C_2$ ,  $b_0 = 1$ , and  $b_1 = R_2 C_2$  for circuit (a) and  $a_0 = R_1$ ,  $a_1 = R_1 R_2 C_2$ ,  $b_0 = 1$ , and  $b_1 = C_2(R_1 + R_2)$  for circuit (b).

**Fig. 14.3** Three circuits representing a system characterized by two time constants: (a) Voigt, (b) ladder, and (c) mixed



It is evident that these two forms are indistinguishable and produce exactly the same impedances and impedance complex plane and Bode plots for these two circuits. All the equations have three adjustable parameters. However, additional information is necessary to decide which circuit has a physical meaning in the given case. For example, when studying a redox process on an electrode in solution, circuit (a) is more probable because  $R_1$  and  $C_2$  have a meaning of solution resistance in series, with the electrode impedance consisting of a parallel connection of the double-layer capacitance,  $C_2$ , and the charge transfer resistance,  $R_2$  (Sect. 4.1 and Fig. 4.1).

*Example 14.2* Let us consider now a circuit characterized by two time constants producing two semicircles on complex plane plots. Three possible circuits explaining the impedances are shown in Fig. 14.3. Circuit (a) represents so-called a Voigt circuit consisting of the resistance in series with two ( $RC$ ) circuits in parallel; circuit (b) is a so-called ladder or nested circuit, and circuit (c) is a mixed circuit. The impedance of each circuit can be written as

$$\begin{aligned} \hat{Z}_a &= R_1 + \frac{1}{\frac{1}{R_2} + j\omega C_2} + \frac{1}{\frac{1}{R_3} + j\omega C_3} \\ &= \frac{(R_1 + R_2 + R_3) + j\omega(R_1 R_2 C_2 + R_1 R_3 C_3 + R_2 R_3 C_3 + R_2 R_3 C_2) + (j\omega)^2 (R_1 R_2 R_3 C_2 C_3)}{1 + j\omega(R_2 C_2 + R_3 C_3) + (j\omega)^2 (R_2 R_3 C_2 C_3)}, \end{aligned} \quad (14.4)$$

$$\hat{Z}_b = R_1 + \frac{1}{j\omega C_2 + \frac{1}{R_2 + \frac{1}{\frac{1}{R_3} + j\omega C_3}}}$$

$$= \frac{(R_1 + R_2 + R_3) + j\omega(R_1 R_2 C_2 + R_1 R_3 C_2 + R_1 R_3 C_3 + R_2 R_3 C_3) + (j\omega)^2 (R_1 R_2 R_3 C_2 C_3)}{1 + j\omega(R_2 C_2 + R_3 C_3 + R_3 C_2) + (j\omega)^2 (R_2 R_3 C_2 C_3)}, \quad (14.5)$$

$$\hat{Z}_c = \frac{1}{R_3 + \frac{1}{j\omega C_3}} + \frac{1}{R_1 + \frac{1}{\frac{1}{R_2} + j\omega C_2}}$$

$$= \frac{(R_1 + R_2) + j\omega(R_1 R_2 C_2 + R_1 R_3 C_3 + R_2 R_3 C_3) + (j\omega)^2 (R_1 R_2 R_3 C_2 C_3)}{1 + (j\omega)(R_1 C_3 + R_2 C_2 + R_2 C_3 + R_3 C_3) + (j\omega)^2 (R_1 R_2 C_2 C_3 + R_2 R_3 C_2 C_3)}. \quad (14.6)$$

All these equations can be written in one simpler form:

$$\hat{Z} = \frac{a_0 + a_1(j\omega) + a_2(j\omega)^2}{b_0 + b_1(j\omega) + b_2(j\omega)^2} = \frac{a_0 + a_1(j\omega) + a_2(j\omega)^2}{1 + b_1(j\omega) + b_2(j\omega)^2}, \quad (14.7)$$

which indicates that all three circuits will produce the same impedances at all frequencies after proper adjustments of the parameters. All the equations have five adjustable parameters (because  $b_0 = 1$ ).

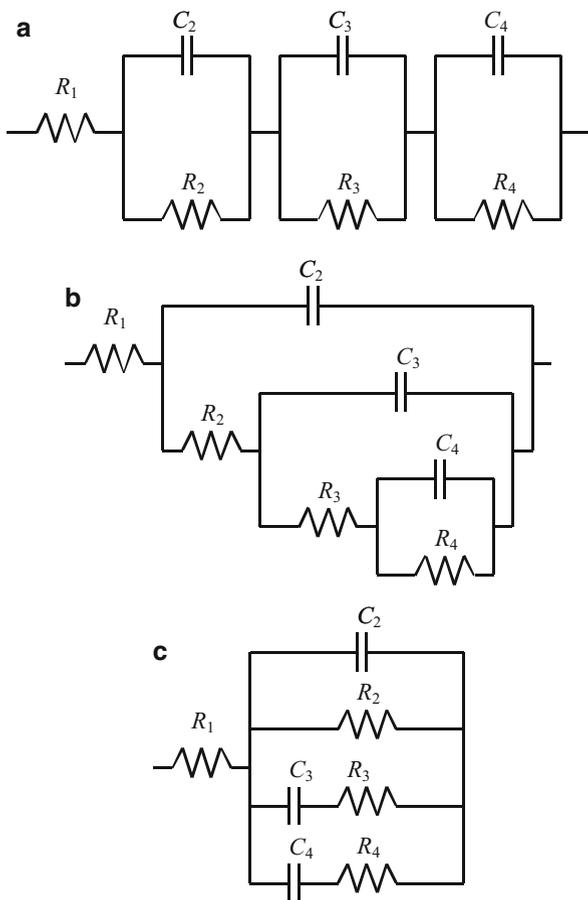
It should also be added that use of the equivalent circuits may introduce ambiguities. It is clear that in the Voigt circuit (a), permutation of the values of elements  $R_2 - C_2$  and  $R_3 - C_3$  does not change the impedance values and the attribution of values to one or another set is arbitrary, i.e. when fitting one can converge on either set. This fact is important when the system is studied as a function of the electrode potential (or other experimental parameter) to not exchange of these parameters (e.g. set of parameters 2 and 3). However, such an ambiguity does not appear in the ladder circuit (b).

*Example 14.3* Compare systems with three time constants.

Three circuits characterized by three time constants are presented in Fig. 14.4: (a) Voigt, (b) ladder, and (c) Maxwell circuits. Their impedances might be written in one common form,

$$\hat{Z} = \frac{a_0 + a_1(j\omega) + a_2(j\omega)^2 + a_3(j\omega)^3}{b_0 + b_1(j\omega) + b_2(j\omega)^2 + b_3(j\omega)^3}, \quad (14.8)$$

**Fig. 14.4** Three circuits representing systems with three time constants: (a) Voigt, (b) ladder, (c) Maxwell

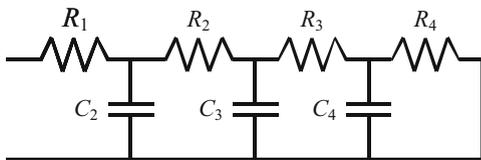


with  $b_0 = 1$  and they produce identical impedance characteristics. Only by using the additional mechanistic information can one decide which model should be used. For example, the ladder circuit might appear in systems with two adsorbed species (Sect. 5.3), while the Maxwell circuit appears in studies of dielectric phenomena [574].

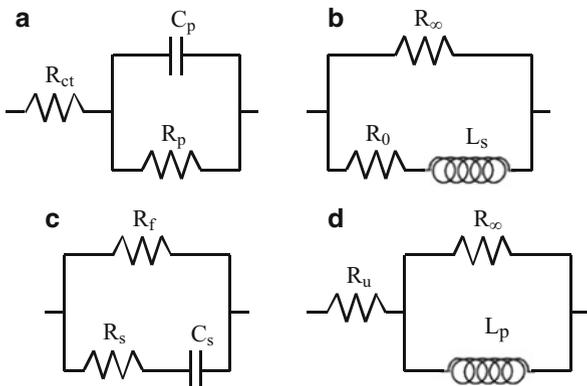
Note that the same equivalent circuits can be presented in different forms; for example, the same ladder circuit is presented in Figs. 14.4b and 14.5, although at first glance they look different.

It should be added that sometimes CPEs must be used and the corresponding impedance adjusted to include such parameters [611]; however, using polynomial notation for impedances makes the model more complicated. For example, replacing  $C_2$  in Fig. 14.3b by the CPE ( $T_2, \phi_2$ ) changes Eq. (14.5) into

**Fig. 14.5** Another representation of ladder circuit presented in Fig. 14.4b



**Fig. 14.6** Electrical equivalent circuits describing faradaic impedance of hydrogen evolution reaction



$$\hat{Z}_b = R_1 + \frac{1}{(j\omega)^{\phi_2} T_2 + \frac{1}{R_2 + \frac{1}{\frac{1}{R_3} + j\omega C_3}}}$$

$$= \frac{(R_1 + R_2 + R_3) + (j\omega)^{\phi_2} (R_1 R_2 T_2 + R_1 R_3 T_2) + j\omega (R_1 R_3 C_3 + R_2 R_3 C_3) + (j\omega)^{1+\phi_2} (R_1 R_2 R_3 T_2 C_3)}{1 + (j\omega)^{\phi_2} (R_2 T_2 + R_3 T_2) + j\omega (R_3 C_3) + (j\omega)^{1+\phi_2} (R_2 R_3 T_2 C_3)}$$

(14.9)

In such cases, it is simpler to use a direct fit to the equivalent circuit.

The same impedance behavior might be represented not only by permutation of  $R$  and  $C$  elements but also by replacing capacitance by inductance and using negative values of the parameters. This will be illustrated in Example 14.4.

*Example 14.4* The faradaic impedance of a hydrogen evolution reaction can be represented by four different circuits displaying the same values of impedances and frequency dependence [211]. These circuits are displayed in Fig. 14.6. The faradaic impedances of circuits (a)–(d) are

$$\begin{aligned}
 (a) \hat{Z}_f &= R_{ct} + \frac{1}{\frac{1}{R_p} + j\omega C_p} = \frac{(R_{ct} + R_p) + j\omega(R_{ct}R_pC_p)}{1 + j\omega(R_pC_p)} \\
 &= (R_{ct} + R_p) \frac{\left(1 + j\omega \frac{R_{ct}R_pC_p}{R_{ct} + R_p}\right)}{1 + j\omega(R_pC_p)},
 \end{aligned} \tag{14.10}$$

$$(b) \hat{Z}_f = \frac{1}{\frac{1}{R_\infty} + \frac{1}{R_0 + j\omega L_s}} = \frac{R_\infty R_0}{R_\infty + R_0} \frac{1 + j\omega \frac{L_s}{R_0}}{1 + j\omega \frac{L_s}{R_\infty + R_0}}, \tag{14.11}$$

$$(c) \hat{Z}_f = \frac{1}{\frac{1}{R_f} + \frac{1}{R_s + \frac{1}{j\omega C_s}}} = \frac{R_f + j\omega(R_f R_s C_s)}{1 + j\omega(R_f C_s + R_s C_s)}, \tag{14.12}$$

$$(d) \hat{Z}_f = R_u + \frac{1}{\frac{1}{R_L} + \frac{1}{j\omega L_p}} = \frac{R_u + j\omega\left(L_p + \frac{L_p R_u}{R_L}\right)}{1 + j\omega\left(\frac{L_p}{R_L}\right)}, \tag{14.13}$$

and the parameters of other circuits can be expressed in terms of the circuit (a) parameters:

$$\begin{aligned}
 (b) R_\infty &= R_{ct}; R_0 = -\frac{R_{ct}(R_{ct} + R_p)}{R_p}; L_s = -R_{ct}^2 C_p; \\
 (c) R_f &= R_{ct} + R_p; R_s = \frac{R_{ct}(R_{ct} + R_p)}{R_p}; C_p = \frac{R_p^2 C_p}{(R_{ct} + R_p)^2}; \\
 (d) R_u &= R_{ct} + R_p; R_L = -R_p; L_p = -R_p^2 C_p.
 \end{aligned} \tag{14.14}$$

That is, assuming the following values for the elements of circuit (a):

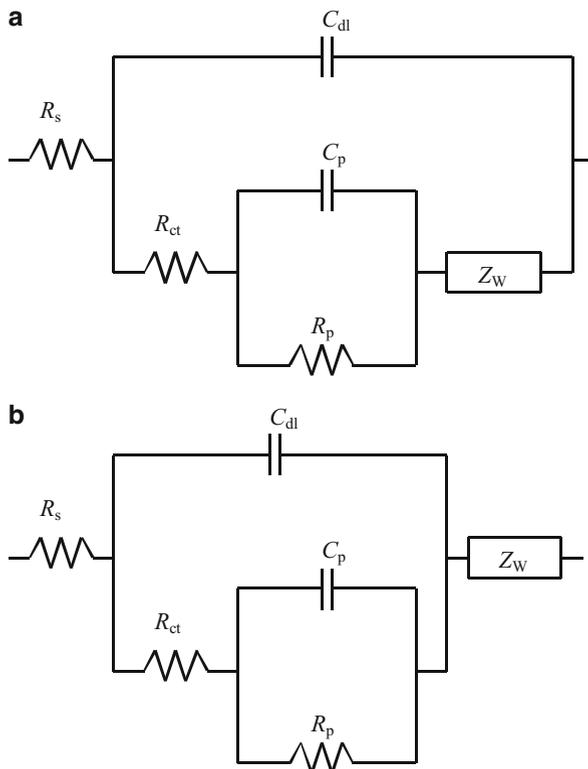
$$(a) R_{ct} = 70 \Omega; R_p = 100 \Omega; C_p = 0.01 \text{ F} \tag{14.15}$$

the parameters of the other circuits are

$$\begin{aligned}
 (b) R_\infty &= 70 \Omega; R_0 = -119 \Omega; L_s = -49 \text{ H}; \\
 (c) R_f &= 170 \Omega; R_s = 119 \Omega; C_s = 0.0346 \text{ F}; \\
 (d) R_u &= 170 \Omega; R_L = -100 \Omega; L_p = -100 \text{ H}.
 \end{aligned} \tag{14.16}$$

This means that a simple complex plot presenting one capacitive semicircle can be represented by other connections of  $R$  and  $C$  elements (as shown earlier) but also by circuits containing negative inductance and resistance. Of course, as has been proven in the literature, only the parameters of circuit (a) are more directly related

**Fig. 14.7** Electrical equivalent model of mechanism involving one adsorbed species with diffusion (a) and a model with different position of Warburg element (b)



to the mechanism, although other circuits give exactly the same frequency-dependent impedances.

*Example 14.5* Another example illustrates ambiguity in the position of the Warburg element. In Chap. 6, Eq. (6.28), and Fig. 6.1, a model was developed for the case of one adsorbed species with diffusion. However, the position of the Warburg impedance element (Fig. 14.7a) can be changed to 14.7b without practically affecting the quality of the fit that is both fits may be experimentally indistinguishable. Nevertheless, only the model in (a) has a physical meaning. Of course, the total impedance might be fitted to the model in Fig. 4.1b, expressing the faradaic impedance by Eq. (6.26).

### 14.3 Fitting the Experimental Data

The purpose of data fitting is to determine the values of the model parameters together with their standard deviations.

## 14.4 Error Classification

The observed impedance errors at each frequency,  $i$ , that is, the difference between the experimental,  $Z_i$ , and a fitted model impedance,  $Z_{i,\text{calc}}$ , arises from three major contributions [3]:

$$Z_i - Z_{i,\text{calc}} = \varepsilon_{i,\text{fit}} + \varepsilon_{i,\text{stoch}} + \varepsilon_{i,\text{bias}}, \quad (14.17)$$

where  $\varepsilon_{i,\text{fit}}$  is the systematic error attributed to an incorrect model used in approximation,  $\varepsilon_{i,\text{stoch}}$  is the stochastic (random) error intrinsic to each experiment with the average equal to zero, and  $\varepsilon_{i,\text{bias}}$  is the systematic error in the experiment arising from drift and instrumental artifacts. The statistical methods of data analysis deal with the stochastic errors only, but other more complex methods allow one to deal with bias errors [613–615].

## 14.5 Methods for Finding the Best Parameters

The problem of fitting impedances is nonlinear, and the method usually used is the complex nonlinear least-squares (CNLS) method [3, 24, 25, 616–618]. In this method, a weighted sum of squares,  $S$ , of the differences between the experimental,  $Z'_i$  and  $Z''_i$ , and the model,  $Z'_{i,\text{calc}}$  and  $Z''_{i,\text{calc}}$  impedances is minimized by choosing the best values of the adjustable parameters and minimizing the weighted differences between the experimental and model (calculated) impedances:

$$S = \sum_{i=1}^N \left\{ w'_i \left[ Z'_i - Z'_{i,\text{calc}} \right]^2 + w''_i \left[ Z''_i - Z''_{i,\text{calc}} \right]^2 \right\}, \quad (14.18)$$

where  $w'_i$  and  $w''_i$  are the statistical weights of the data points and the summation runs over all the  $N$  frequencies. This minimization is usually carried out using the iterative Marquardt-Levenberg algorithm [619]. The initial estimation of the model parameters must be supplied. Because the method is iterative and nonlinear, the initial estimation of the parameters *must be relatively close to the experimental values*; otherwise, a divergence is obtained and a message, for example “singular matrix,” is obtained or the parameters are found with errors exceeding several times their values. The latter case may be related to a local flat minimum and a new set of initial parameters should be chosen. These problems are often observed for more complicated circuits characterized by many adjustable parameters and in the presence of distributed elements as in porous electrodes or those with semi-infinite-length or finite-length diffusion.

In more complicated cases, a part of the total circuit (usually the high-frequency part) might be fitted, the elements found fixed, and additional elements added as free parameters. Finally, all the parameters should be set as free and the final

approximation parameters found. Examples of this type of modeling will be shown in subsequent exercises.

Another method for finding the minimum is the so-called downhill simplex method [3, 619]. It requires only a function evaluation and does not use either function derivatives or matrix inversion. It may be relatively slow if one is trying to optimize many parameters and a shallow minimum, but it will always find a minimum (at least a local minimum). The problem with this technique is that it does not calculate the parameters' standard deviations directly. In such cases, it is advisable, after finding the minimum by the simplex method, to use these parameters in the CNLS approximation, which should converge quickly and provide standard deviations of the parameters.

Some new methods are based on the use of genetic algorithm optimization, but although they are very promising they are still rarely used [620]. They could be used in future to distinguish between some complex reaction mechanism, e.g. in corrosion.

## 14.6 Weighting Procedures

The proper choice of the statistical weighting in Eq. (14.18) is very important for the determination of the system parameters. There are several popular choices:

- a. Statistical weighting:  $w'_i = 1/(\sigma'_i)^2$  and  $w''_i = 1/(\sigma''_i)^2$
- b. Unit weighting:  $w'_i = w''_i = 1$
- c. Modulus weighting [617, 622]:  $w'_i = w''_i = 1/|Z_i|^2$
- d. Proportional weighting [24, 615, 623]:  $w'_i = 1/(Z'_i)^2$  and  $w''_i = 1/(Z''_i)^2$
- e. Weighting from measurement model [3, 613, 624, 625]:

$$\sigma'_i = \sigma''_i = \alpha |Z''_i| + \beta |Z'_i - R_s| + \gamma \frac{|Z_i|^2}{R_m}.$$

These weighting choices will be discussed below.

### 14.6.1 Statistical Weighting

Statistical weighting is the statistically most straightforward method. The impedance data should be acquired several ( $n$ ) times and standard deviations calculated for the real and imaginary parts separately using the average impedance  $\bar{Z}_i$  at each frequency,  $i$ :

$$\sigma'_i = \sum_{k=1}^n \frac{(Z'_i(k) - \bar{Z}'_i)^2}{n-1} \quad \text{and} \quad \sigma''_i = \sum_{k=1}^n \frac{(Z''_i(k) - \bar{Z}''_i)^2}{n-1}. \quad (14.19)$$

Then the statistical weight is calculated and used to calculate the sum of squares,  $S$ , Eq. (14.18). However, the biggest problem with this method is that, besides the fact that it is time consuming, the impedances may slowly change with time and the average will contain a systematic (drift) error. Because of this problem, it is rarely used. It could be replaced by weighting from the measurement model method.

The next three methods use information from one set of impedance measurements to estimate the weighted sum of squares. In these cases, assumptions about the weighting functions must be made.

### 14.6.2 Unit Weighting

Unit weighting is the simplest approach. It is assumed that each measured impedance is characterized by the same standard deviation, that is, each measured value has the same precision. This method might be useful for finding initial model parameters for relatively simple models. However, the biggest problem with this method is related to the fact that if the measured impedances change by orders of magnitude, the large values determine the sum of squares,  $S$ , and the small features may not be approximated at all. For example, for a model displaying one very small and one large semicircle on the complex plane plot, the smaller semicircle might be completely unnoticed by the approximating program. Of course, this deviation will be easily noticed on Bode phase angle plots.

### 14.6.3 Modulus Weighting

If impedance measurements are carried out at the same sensitivity scale for the real and imaginary components, the stochastic errors of the real and imaginary impedances will be similar, and one can use modulus weighting. Modulus weighting assumes the same statistical weights for real and imaginary parts, and they are proportional to the impedance modulus. This means that small and large impedances contribute in a similar way to the sum of squares and are equally important.

There are two possible choices for calculations of the modulus:

- a. Modulus of experimental impedances:  $|Z_i| = \sqrt{Z_i'^2 + Z_i''^2}$
- b. Modulus of calculated impedances:  $|Z_i| = \sqrt{Z_{i,\text{calc}}'^2 + Z_{i,\text{calc}}''^2}$

Because of the existence of random errors and the possibility of bias, it is recommended to use modulus weightings based on calculated impedances [626]. Macdonald [626] claims that modulus weighting introduces some bias to approximations.

### 14.6.4 Proportional Weighting

Proportional weighting was suggested by Macdonald [24, 615, 623, 626]. This method is especially important when the real and imaginary components have much different values. As in the case of modulus weighting, two choices are possible:

- a. Using experimental data:  $w'_i = 1/(Z'_i)^2$  and  $w''_i = 1/(Z''_i)^2$
- b. Using calculated data:  $w'_i = 1/(Z'_{i,\text{calc}})^2$  and  $w''_i = 1/(Z''_{i,\text{calc}})^2$

As before, it is recommended that calculated data be used [626]. Care must be taken in those cases where the imaginary impedances pass the real axes and become zero or very close to zero because their weight will go to infinity, exaggerating the importance of such points.

Modern approximation programs usually provide users with a choice of the weighting procedures and might contain other more advanced functions [626].

### 14.6.5 Weighting from Measurement Model

Orazem and coworkers [3, 624, 625] modified the method of statistical weighting in such a way that it could be used in cases of mildly nonstationary systems. Data should be acquired several times and fitted to the Voigt model, retaining a statistically significant number of circuit elements. From the differences between the experimental and model impedance values (each of which might be different for sequentially acquired impedances), the standard deviations might be determined at each frequency and then fitted to the model described earlier in (e). The calculated values are used in the calculation of the sum of squares, Eq. (14.18). The proposed procedure is detailed below:

- a. Impedance measurements should be repeated several times (six repetitions were used in Ref. [625]) in the same experimental conditions and at the same frequencies. The authors suggested that the standard deviations of the real and imaginary impedance components should be lower than 3 % of the impedance modulus at each frequency.
- b. A measurement series Voigt model, Figure 13.2, Eq. (13.10), should be fitted to each experimental data set, keeping the time constants positive and the resistances positive or negative. The number of Voigt elements should be increased until the confidence intervals  $2\sigma$  (i.e., 95.4 %) for one of the parameters include zero. Then the number of the circuit elements should be decreased by one. If for one data set the number of Voigt elements is lower, then all other approximations should be recalculated with this reduced number of elements. This procedure satisfies the condition that the maximum number of parameters must be statistically important.
- c. The standard deviations of the residuals of the impedances, i.e., the differences between the experimental and corresponding model values, should be calculated

at each frequency. Such standard deviations should be bias free because they are calculated from the differences for all data sets, which were approximated separately.

- d. These standard deviations were fitted to the model for the data structure described earlier in point (e), p. 312.

The obtained standard deviations are used in the subsequent CNLS analysis of one of the impedance data files. Unfortunately, typical software programs, such as ZView, cannot perform this fitting. However, it can be easily done with Macdonald's LEVM program, although the experimental data should be prepared in a special format. An example of such an analysis is presented in Exercise 14.1. Several examples are discussed in the literature [613, 624, 627–632].

In practical approximations, modulus and proportional weighting procedures are usually used.

## 14.7 Statistical Tests

The purpose of modeling is to find an appropriate model described by an electrical circuit or equation by minimization of the sum of squares. Such model impedances should lie very close to the experimental ones without any systematic deviations. The first test is a visual comparison of the complex plane and Bode plots, which should agree. To assure that the approximating model is correct, several statistical tests might be used.

### 14.7.1 Chi-Square

The quality of fit may be verified by examining a  $\chi^2$  (chi-square) test.  $\chi^2$  is defined as

$$\chi^2 = \sum_{i=1}^N \left\{ \left[ \frac{Z'_i - Z'_{i,\text{calc}}}{\sigma'_i} \right]^2 + \left[ \frac{Z''_i - Z''_{i,\text{calc}}}{\sigma''_i} \right]^2 \right\}. \quad (14.20)$$

This parameter should be small. Because it depends on the number of points (i.e., frequencies), usually the reduced [617] value, which is  $\chi^2$  divided by the number of degrees of freedom,  $\nu = 2N - m$ , is calculated:

$$\chi^2_\nu = \frac{\chi^2}{\nu} = \frac{\chi^2}{2N - m}, \quad (14.21)$$

where  $N$  is the number of frequencies, i.e., there are  $2N$  measured impedance values ( $N$  real and  $N$  imaginary), and  $m$  is the number of adjustable parameters used in the

model. If the estimates of  $\sigma_i$  are correct, this parameter should approach unity [619]. If the values of  $\chi_v^2$  are much larger than unity, the approximation or estimation of  $\sigma_i$  is incorrect. Values much lower than unity might indicate overestimation (too many parameters). The estimation of  $\sigma_i$  values might be accomplished by repeating the impedance measurements several times, as described earlier in Sects. 14.6.1 and 14.6.5. However, such data are not always available.

In CNLS approximations, modulus or proportional weightings are used. One can define the reduced sum of squares, for example, for proportional weighting:

$$S_v = \frac{S}{\nu} = \frac{1}{\nu} \sum_{i=1}^N \left\{ \left[ \frac{Z'_i - Z'_{i,\text{calc}}}{Z'_{i,\text{calc}}} \right]^2 + \left[ \frac{Z''_i - Z''_{i,\text{calc}}}{Z''_{i,\text{calc}}} \right]^2 \right\}. \quad (14.22)$$

If proportional or modulus errors are assumed, then the standard deviations of impedances are supposed to be proportional to the impedance values,  $\sigma_i = \varepsilon Z_i$ , where  $\varepsilon$  is the relative error of the measured impedances. A comparison of Eqs. (14.21) and (14.22) shows that

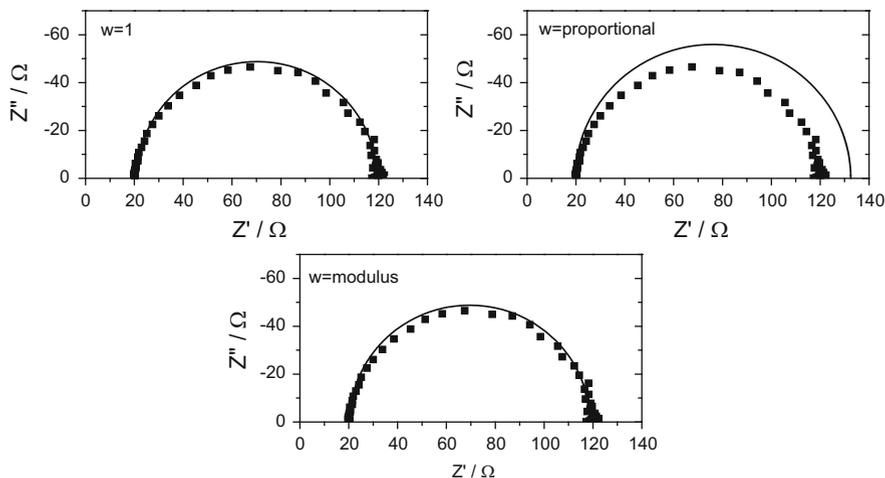
$$S_v = \varepsilon^2 \chi_v^2 \approx \varepsilon^2, \quad (14.23)$$

and the square root of the calculated reduced sum of squares is a measure of the relative error of the measured impedances.

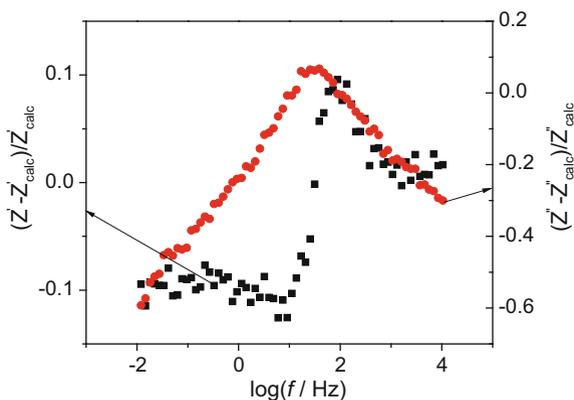
In practice, the values of  $S_v$  are shown in commercial programs (however, the calculation details are rarely well documented). It should be stressed that for each weighting choices the values  $S_v$  are much different. This will be illustrated in the following example.

*Example 14.6* Analysis of the experimental data are illustrated below. A numerical example is shown in Exercise 14.2. The impedance data are shown as symbols in Fig. 14.8. One should always start with the simplest possible model. The simplest model that can be used in this case is  $R(RC)$ ; it contains three adjustable parameters. There are 67 data points, and  $\nu = 2 \times 67 - 3 = 131$  degrees of freedom. In the same figure, the results of approximations using three weighting methods – (a) unity, (b) proportional, and (c) modulus – are presented. For these three models the following values of  $S$  and  $S_v$  were obtained: (a)  $S = 205.4$ ,  $S_v = 1.57$ ; (b)  $S = 1.657$ ,  $S_v = 0.0126$ ; (c)  $S = 0.0524$ ,  $S_v = 0.00040$ . Of course, they cannot be simply compared between the models because different weighting procedures were used. Closer inspection of the results indicates that large differences were obtained for the proportional model, but for other models some systematic differences between the experimental and model data exist, which are visible on the Bode plots.

The differences can also be easily visualized by plotting the relative residuals, that is, the differences between the experimental and model impedances. If the model is correct, then the residuals should be randomly distributed around the zero line. An example of such a plot is shown in Fig. 14.9. It is evident that the residuals display systematic differences, which suggests that the model is not correct.

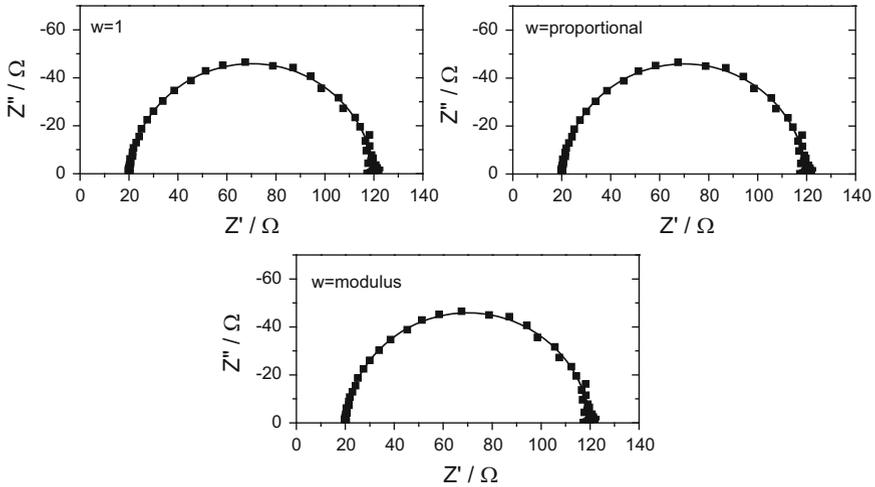


**Fig. 14.8** Approximation of experimental data by model  $R(RC)$  using unit, proportional, and modulus weighting

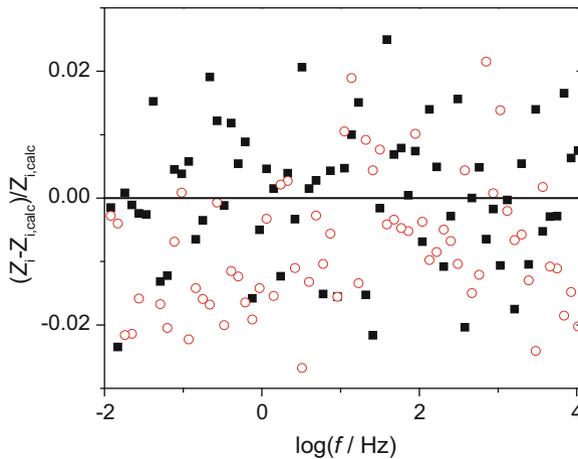


**Fig. 14.9** Relative differences between experimental and calculated impedances for modulus weighting from Fig. 14.8

The next model one can use is one in which the capacitance is replaced by the CPE, that is, one more parameter is added. The results of the approximation to the model  $R(QR)$  using different weighting methods are shown in Fig. 14.10. This time the approximation looks better. The values of the parameters  $S$  and  $S_v$  for the three weighting methods are as follows: (a)  $S = 56.9$ ,  $S_v = 0.434$ ; (b)  $S = 0.0141$ ,  $S_v = 0.00011$ ; (c)  $S = 0.00708$ ,  $S_v = 0.000054$ . An important decrease in the sum of squares is observed after replacing the capacitance by the CPE. The plot of



**Fig. 14.10** Fit of experimental data to model containing CPE:  $R(QR)$  for different weighting models



**Fig. 14.11** Relative differences between experimental and calculated impedances for modulus weighting from Fig. 14.10

residuals is shown in Fig. 14.11. This time the residuals of the real and imaginary parts seem to be distributed randomly, and the fit is satisfactory.

In summary, analysis of the values of  $\chi_v^2$  or  $S_v$  is not sufficient to determine the goodness of fit. Additional analysis of the residuals and their randomness is also necessary.

### 14.7.2 Test F

The Fisher-Snedecor test F [633] is used to compare two different variances (square of standard deviations):

$$F = \frac{\sigma_1^2}{\sigma_2^2}. \quad (14.24)$$

This experimental value must be compared with  $F(\alpha, \nu_1, \nu_2)$ , where  $\alpha$  is the confidence level, and  $\nu_1$  and  $\nu_2$  are the degrees of freedom of the numerator and denominator, respectively. The theoretical values  $F(\alpha, \nu_1, \nu_2)$  are tabulated or might be calculated in Excel using the function F.INV.RT (former FINV). In practice, the most often used value for the confidence level are 0.05 and 0.01, corresponding to probabilities of 95 % and 99 %.

In the modeling of the impedance data one can use the F-test for the importance of the additional term [633]. One can add another parameter in the model only if this produces a statistically important decrease in the sum of squares. In general, if the sum of squares for the model containing  $m$  parameters is  $S_1$  and after adding  $k$  parameters it is  $S_2$ , the corresponding degrees of freedom are  $2N - m$  and  $2N - m - k$ , respectively. Then one can write the following equation for the F-test:

$$F_{\text{exp}} = \frac{\frac{S_1 - S_2}{(2N - m) - (2N - m - k)}}{\frac{S_2}{2N - m - k}} = \frac{\frac{S_1 - S_2}{k}}{\frac{S_2}{2N - m - k}} = \frac{S_1^2}{S_2^2}. \quad (14.25)$$

This should be compared with the theoretical value of  $F(\alpha, k, 2N - m - k)$ . If  $F_{\text{exp}} > F(\alpha, k, 2N - m - k)$ , then the improvement is important and the new model may be accepted. If it is lower, then there is no reason to accept the new model and the simpler one should be retained. It is important to keep the number of new parameters as low as possible, that is, to add one parameter each time. In some cases, such as when a new (RC) parallel element is added to the Voigt circuit, one can use  $k = 2$ .

*Example 14.7* Let us apply this test to the data in Example 14.6. In this case,  $N = 67$ , for the simpler model  $R(CR)$  there are three parameters, and for the  $R(QR)$  model there are four. Therefore,  $\nu_1 = 1$  and  $\nu_2 = 2 \times 67 - 4 = 130$ . Let us apply this test to the unit weighting, where  $S_1 = 205.4$  and  $S_2 = 56.9$ :

$$F_{\text{exp}} = \frac{\frac{205.4 - 56.9}{1}}{\frac{56.9}{130}} = 339.3. \quad (14.26)$$

The theoretical value is  $F(0.05, 1, 130) = 3.91$ ; therefore,  $F_{\text{exp}}$  is much larger than the theoretical value and the addition of this one term is statistically justified at the confidence level assumed. Of course, this addition is justified for all three weighting procedures.

### 14.7.3 *t*-test for Importance of Regression Parameters

Another factor that should be considered is the standard deviation of the obtained parameters. When the standard deviation of a parameter is comparable to or larger than its value, such a parameter is unimportant in regression. This can be tested using a *t*-test:

$$t = \frac{p}{s_p}, \quad (14.27)$$

where  $p$  is the value of the parameter and  $s_p$  its standard deviation. The experimental value should be compared with that from the tables for  $t(\alpha, 2N - m)$  for the confidence level of  $\alpha$  and the number of degrees of freedom  $2N - m$ . If  $t_{\text{exp}} > t(\alpha, 2N - m)$ , this means that the parameter is much larger than its standard deviation and its presence is justified, but if it is lower, the parameter should be rejected.

Macdonald [634] proposed checking the precision of fitting parameters using Monte Carlo data simulations followed by CNLS approximations. This provides information about how accurately the parameters can be determined for an assumed amount of error in impedances and may be used in the design of experiments to extract such data precisely.

## 14.8 Conclusion

The experimental data that were checked by the Kramers-Kronig transforms may be used in modeling. First, usually, fit to an electrical equivalent model is carried out. It is important to use a proper weighting procedure and start with the simplest model. Then additional parameters can be added and their importance verified by the appropriate *F*- and *t*-tests. The number of adjustable parameters must be kept to a minimum. Additionally, comparison of the experimental and model impedances on complex plane and Bode plots should be carried out. Furthermore, plots of the residuals indicate the correctness of the model used. Next, on the basis of this fit, a physicochemical model might be constructed. One should check how the obtained parameters depend on the potential, concentration, gas pressure, hydrodynamic conditions, etc. If a strange or unusual dependence is obtained, one should check whether the assumed model is physically correct in the studied case. This is the most difficult part of modeling.

Exercises on impedance modeling are presented below.

## 14.9 Exercises

**Exercise 14.1** Determine the error structure of the impedance in the files Z1.z, Z2.z, Z3.z, and Z4.z using Orazem's measurement model approach and determine the impedance parameters for Z1.z using the circuit  $R_s(C_{dl}(R_{ct}Z_{FLW}))$ , where  $Z_{FLW}$  is the finite-length transmissive mass transfer impedance.

**Exercise 14.2** Find an electrical equivalent model describing data in the file 2.z. Try different weighting techniques. Calculate the sum of squares,  $S$ , and reduce the sum of squares,  $S_v$ . Carry out an  $F$ -test.

**Exercise 14.3** Fit data 3.z into the nested model  $R_s(C_{dl}(R_{ct}(C_p R_p)))$ . Check whether the use of CPEs instead of capacitances is statistically justified.

**Exercise 14.4** Fit 4.z into the model  $R_s(C_{dl}(R_{ct} C_p))$ . Check whether the use of CPEs instead of capacitances is statistically justified.

**Exercise 14.5** Fit the data in 5.z to the model  $R(C(RW_s))$ , where  $W_s$  is the transmissive mass transfer impedance. Check whether the use of the CPE is justified.