Chapter 2
Definition of Impedance and Impedance of Electrical Circuits

2.1 Introduction

To understand the impedance of electrochemical objects, it is necessary to understand the behavior of simple electrical circuits, first in steady state, then in transient conditions. Such circuits contain simple linear electrical elements: resistance, capacitance, and inductance. Then the concept of electrical impedance will be introduced. It demands an understanding of the Laplace and Fourier transforms, which will also be presented. To understand impedance, it is necessary to thoroughly understand the complex plane and Bode plots, which will be presented for a few typical connections of the electrical elements. They can be computed using Excel, Maple, Mathematica, and specialized programs such as ZView. Several examples and exercises will be included.

2.2 Electrical Circuits Containing Resistances

2.2.1 Ohm's Law

The total resistance of complex electrical circuits can be determined using two fundamental laws of Ohm and Kirchhoff. Ohm's law relates current passing through resistance i in A, with voltage V in V, and resistance R in Ω:

$$V = Ri. \tag{2.1}$$

It allows one to determine the current if the applied voltage is known or the voltage (ohmic drop) when the current is flowing through the resistance. It also shows that current follows the potential without delay. Additionally, in electrical engineering, by convention, the current is positive when it flows from the positive

A. Lasia, *Electrochemical Impedance Spectroscopy and its Applications*,
DOI 10.1007/978-1-4614-8933-7_2, © Springer Science+Business Media New York 2014

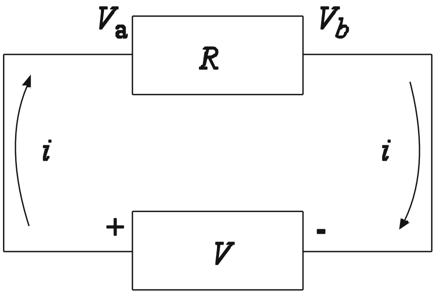


Fig. 2.1 Illustration of Ohm's law

to the negative side of the potential source that is the potential drop is related to the direction of the current. This is illustrated in Fig. 2.1. The direction of the current was chosen, and Ohm's law may be written as

$$i = \frac{V_{\mathrm{a}} - V_{\mathrm{b}}}{R} = \frac{V}{R}, \tag{2.2}$$

where $V_{\mathrm{a}} > V_{\mathrm{b}}$ for the chosen direction of the current. From Ohm's law it follows that the equivalent resistance, R_{eq}, of the connection of resistances, R_{i}, in series equals the sum of the resistances:

$$R_{\mathrm{eq}} = \sum_i R_{\mathrm{i}}. \tag{2.3}$$

2.2.2 Kirchhoff's Laws

There are two Kirchhoff laws, one for nodes and one for loops. The first law says that the sum of the currents entering any point is equal to zero:

$$\sum_k i_{\mathrm{k}} = 0, \tag{2.4}$$

that is, the algebraic sum of currents entering one point is equal to the sum of all currents leaving this point. It simply states that there can be no accumulation of charges in conductors. The second law applies to loops and says that the algebraic sum of voltage drops in a closed loop equals zero:

$$\sum_k V_{\mathrm{k}} = 0. \tag{2.5}$$

These laws allow for resolving any connection of resistances and voltage sources. They will be illustrated in the following examples.

Example 2.1 Find the relation between the total current and voltage and the equivalent resistance of the circuit in Fig. 2.2.

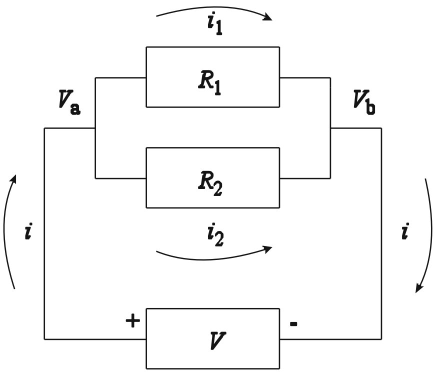


Fig. 2.2 Illustration of Kirchhoff's law for Example 2.1

The total current, i, flows from the positive to the negative connection of the source V. It separates into two currents, i_1 and i_2, and, according to Kirchhoff's first law,

$$i = i_1 + i_2. \tag{2.6}$$

Using Ohm's law one can write

$$\begin{aligned} i_1 &= \frac{(V_\mathrm{a} - V_\mathrm{b})}{R_1} = \frac{V}{R_1}, \\ i_2 &= \frac{V}{R_2}. \end{aligned} \tag{2.7}$$

Combining these equations with Eq. (2.6) gives

$$i = \frac{V}{R_1} + \frac{V}{R_2} = V\left(\frac{1}{R_1} + \frac{1}{R_2}\right) = \frac{V}{R_\mathrm{eq}}, \tag{2.8}$$

which means that the two resistances can be replaced by one equivalent resistance R_eq:

$$\begin{aligned} &R_{eq} = \frac{1}{\dfrac{1}{R_1} + \dfrac{1}{R_2}} = \frac{R_1 R_2}{R_1 + R_2} \\ &\text{or} \\ &\frac{1}{R_{eq}} = \frac{1}{R_1} + \frac{1}{R_2}. \end{aligned} \tag{2.9}$$

The equivalent resistance is the harmonic mean of two parallel resistances. This formula should always be used for the parallel connection of resistances.

The problem may also be solved using Kirchhoff's second law. It is easy to see that there are three loops in the circuit, one containing the source V and the resistance R_1, the second containing V and R_2, and the third containing R_1 and R_2. For these loops, in the clockwise direction, one can write Kirchhoff's law for loops:

$$\left.\begin{array}{l} i_1R_1 - V = 0 \\ i_2R_2 - V = 0 \end{array}\right\} \quad \text{or} \quad i_1R_1 - i_2R_2 = 0. \tag{2.10}$$

The negative sign in the first two equations for V appears because the direction of the loop goes from negative to positive voltage. The third equation is equivalent to the Eq. (2.8) and comes from the two first equations; therefore, it is redundant. The solution is, of course, the same as the previous one. Such equations written for any circuit lead to the system of linear equations for which programs were developed in electrical engineering.

Example 2.2 Calculate the currents, voltages, and equivalent resistances for the schema of the circuit in Fig. 2.3.

From Kirchhoff's first law one obtains

$$i = i_1 + i_2 \tag{2.11}$$

and from the second law

$$\left.\begin{array}{l} iR_1 + i_1R_2 - V = 0 \\ iR_1 + i_2R_3 - V = 0 \end{array}\right\} \quad \text{or} \quad i_1R_2 + i_2R_3 = 0. \tag{2.12}$$

As happened earlier, the third equation arises from the first two previous equations. Elimination of i_2 gives

$$i_1 = i\frac{R_3}{R_2 + R_3}. \tag{2.13}$$

The total voltage drop may be described as

$$\begin{aligned} V &= (V_a - V_b) + \left(V_b - V_c\right) = iR_1 + i_1R_2 = iR_1 + i\frac{R_2R_3}{R_2 + R_2} \\ &= i\left(R_1 + \cfrac{1}{\cfrac{1}{R_2} + \cfrac{1}{R_3}}\right) = iR_{eq}. \end{aligned} \tag{2.14}$$

Therefore, all the resistances in the circuit may be substituted by one equivalent resistance, R_{eq}, equal to the sum of R_1 and the parallel connection of resistances R_2 and R_3.

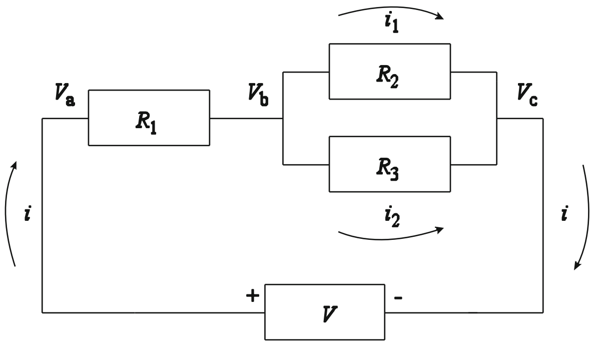


Fig. 2.3 Circuit for Example 2.2

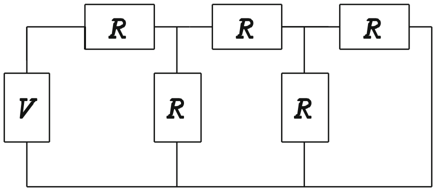


Fig. 2.4 Circuit for Example 2.3

Example 2.3 Find the equivalent resistance in Fig. 2.4.

To determine the total resistance, a circuit can be divided into parts starting from the right. First there are two resistances in parallel, then in series, etc. Answer: $8R/5$.

2.3 Capacitance

Electrical circuits may contain three passive elements: resistors, capacitors, and inductors. The behavior of the capacitance and inductance is different from that of the resistance. A constant current cannot flow through a capacitance, but an electrical charge can accumulate in it, and it is different at each voltage applied. The fundamental relation between charge and voltage is given as

$$V = \frac{Q}{C}, \tag{2.15}$$

where Q is the charge stored in the capacitor in coulombs, C, and C is the capacitance in farads, F. The charge is related to the current flowing in the circuit:

$$Q(t) = \int_0^t i(t)\mathrm{d}t. \tag{2.16}$$

Substitution of Eq. (2.16) into (2.15) gives an integral equation:

$$V(t) = \frac{1}{C}\int_{0}^{t} i(t)\mathrm{d}t. \tag{2.17}$$

If there is a circuit consisting of a resistor and a capacitor in series connected to the voltage source V, the voltage applied to the system is the sum of the potentials on the resistance (ohmic drop) and on the capacitance:

$$E(t) = i(t)R + \frac{1}{C}\int_{0}^{t} i(t)\mathrm{d}t. \tag{2.18}$$

This constitutes an integral equation where the unknown current is outside and under the integral. The solution of such an equation may be easily accomplished using a Laplace transform. It should be added that in electrochemical systems double layer capacitance is potential dependent and the differential capacitance, $C = \mathrm{d}Q/\mathrm{d}E$ should be used.

2.4 Inductance

The inductance is usually represented as a coil in which current induces an electromotive force that opposes a change in current. The ideal inductance has a zero resistance and resists changes in the current. The potential difference developed at the inductance is

$$V(t) = L\frac{\mathrm{d}i(t)}{\mathrm{d}t}, \tag{2.19}$$

where L is the inductance in henrys, H. This means that the constant current flows through the inductance without resistance, that is, $V(t) = 0$. In the case of the connections of the resistance and inductance in series the equation describing the system is

$$V = i(t)R + L\frac{\mathrm{d}i(t)}{\mathrm{d}t}. \tag{2.20}$$

To obtain the solution of a transient current, this differential equation must be solved. It can be easily solved using a Laplace transform.

2.5 Laplace Transform

The Laplace transform is a tool that allows for an easy solution of differential or integral equations by changing them into algebraic equations in the Laplace plane. It is also well suited for solving problems in electrical engineering and impedance spectroscopy. The Laplace transform is defined as

$$L[f(t)] = F(s) = \bar{f}(s) = \int_0^\infty f(t)e^{-st}\mathrm{d}t. \tag{2.21}$$

This is an integral transform that maps the function of time, $f(t)$, into a function called $F(s)$ or $\bar{f}(s)$ of the parameter s, called the frequency, because if t is in s, then s must be in s^{-1}. Of course, integration over the parameter t between 0 and ∞ assures that t will not appear after integration. During the transformation, no information about $f(t)$ is lost and the transform contains the same amount of information, only displayed in the frequency domain. Complex equations are usually much simpler in the Laplace domain. In general, the parameter s can be complex (see Sect. 2.6),

$$s = \sigma + j\omega, \tag{2.22}$$

but usually a real transform is used $s = \sigma$, and for complex s it is a Heaviside transform. Let us first look at the restrictions on the function $f(t)$ because not all functions can be transformed:

(1) $f(t) \equiv 0$ for $t < 0$, that is, the function must always be zero at $t < 0$.
(2) $f(t)$ has a finite number of discontinuities.
(3) $f(t)$ is of exponential order, that is, there are always two constants $\lambda \geq 0$ and $M \geq 0$ for which $|f(t)| < M\,\mathrm{e}^{\lambda t}$ for all values of t. Functions t^n and e^{at} are of exponential order, but the function e^{x^2} is not and cannot be transformed.

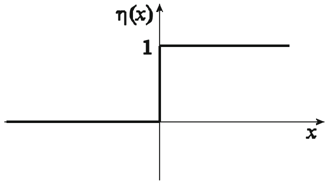
The Laplace transform is linear, that is, the transform of the sum of functions is equal to the sum of transforms:

$$L\{af_1(t) + bf_2(t)\} = a\bar{f}_1(s) + b\bar{f}_2(s). \tag{2.23}$$

To better understand this transform, let us work out a few examples.

Example 2.4 Determine the Laplace transform of the Heaviside step function $\eta(t)$ defined as

Fig. 2.5 Heaviside step function



$$f(t) = \eta(t) = \begin{cases} 0 & t < 0, \\ 1 & t > 0, \end{cases} \tag{2.24}$$

displayed in Fig. 2.5. This function is equal to zero for $t < 0$ (as specified in restriction 1 given earlier) and equal to 1 elsewhere.

Application of the definition given by Eq. (2.21) yields

$$L[\eta(t)] = \int_0^\infty 1e^{-st}\mathrm{d}t = -\frac{e^{-st}}{s}\bigg|_0^\infty = \frac{1}{s}, \tag{2.25}$$

and the transform is simply equal to 1/s.

Example 2.5 Find the transform of the exponential function $f(t) = \exp(-at)$:

$$L(e^{-at}) = \int_0^\infty e^{-at}e^{-st}\mathrm{d}t = \int_0^\infty e^{-(a+s)t}\mathrm{d}t = \frac{e^{-(a+s)t}}{-(a+s)}\bigg|_0^\infty = \frac{1}{s+a}. \tag{2.26}$$

The exponential function is transformed into a simpler form: $1/(s + a)$.

Example 2.6 Find the transform of the first derivative of the function

$$\begin{aligned} L\{f'(t)\} &= \int_0^\infty e^{-st}f'(t)\mathrm{d}t = e^{-st}f(t)\Big|_0^\infty - \int_0^\infty \left(e^{-st}\right)' f(t)\mathrm{d}t \\ &= -f(0^+) + s\int_0^\infty e^{-st}f(t)\mathrm{d}t = s\bar{f}(s) - f(0^+), \end{aligned} \tag{2.27}$$

where the following formula for integration by parts was used:

$$\int uv'\mathrm{d}x = uv - \int u'v\mathrm{d}x, \tag{2.28}$$

and $f(0)^+$ is the initial value of the function $f(x)$ at time equal to zero; it is taken as the right-hand-side limit, $\lim_{x\to 0^+} f(x)$.

Similarly, the transform of the second derivative may be obtained as follows:

$$L[f''(t)] = s^2\overline{f}(s) - sf(0^+) - f'(0^+). \tag{2.29}$$

It can also be shown that the transform of the integral equals

$$L\left\{\int_0^t f(\tau)\mathrm{d}\tau\right\} = \frac{1}{s}L\{f(t)\} = \frac{\overline{f}(s)}{s}. \tag{2.30}$$

The preceding examples show that the differentiation is equivalent to the multiplication by the parameter s and the integration is equivalent to the division by s in the Laplace domain. This allows for an easy transformation of differential or integral equations into algebraic equations, solving them in the Laplace domain and then carrying an inverse transformation into the time domain. This is schematically shown below:

$$\text{Time domain}\left\{\begin{array}{ccc} \text{Differential eqn.} & \xrightarrow{L} & \text{Algebraic eqn.} \\ & & \downarrow \\ \text{solution } (t) & \xleftarrow[L^{-1}]{} & \text{solution } (s) \end{array}\right\}\text{Laplace domain} \tag{2.31}$$

To understand this method, let us work out two examples.

Example 2.7 Solve the following differential equation of first-order kinetics:

$$\frac{\mathrm{d}y(t)}{\mathrm{d}t} = -ky(t) \quad \text{with} \quad y(0) = y_0. \tag{2.32}$$

Application of the Laplace transform to both sides of the equation using Eqs. (2.27) and (2.23) gives

$$s\overline{y}(s) - y_0 = -k\overline{y}(s), \tag{2.33}$$

from which $\overline{y}(s)$ is the solution in the Laplace domain:

$$\overline{y}(s) = y_0\frac{1}{s+k}. \tag{2.34}$$

The inverse transform using Eq. (2.26) gives the solution in the time domain:

$$y = y_0e^{-kt}. \tag{2.35}$$

The differential equation was solved only by transformation, which can be done using Laplace transform tables, the solution of an algebraic equation, and the inverse Laplace transform using tables. Tables of Laplace transforms can be easily found in the literature [73, 74], and several of the most often used ones are shown in the appendix.

Example 2.8 Solve the following differential equation:

$$\frac{\mathrm{d}^2 y(t)}{\mathrm{d}t^2} - a^2 y(t) + b = 0 \tag{2.36}$$

if the initial values of $y(0)$ and $y'(0)$ are known and a and b are constants.

Transformation into the Laplace domain by applying the formula for the second derivative, Eq. (2.29), and for the constant (2.25) leads to

$$s^2\overline{y}(s) - sy(0) - y'(0) - a^2\overline{y}(s) + \frac{b}{s} = 0, \tag{2.37}$$

from which the value of $\overline{y}(s)$ may be isolated:

$$\overline{y}(s) = \frac{-\frac{b}{s} + y'(0) + sy(0)}{s^2 - a^2} = \frac{+s^2 y(0) + sy'(0) - b}{s(s-a)(s+a)}. \tag{2.38}$$

To carry out the inverse Laplace transform, Eq. (2.38) must be separated into simple fractions:

$$\begin{aligned}\overline{y}(s) &= \frac{A}{s+a} + \frac{B}{s-a} + \frac{C}{s} = \frac{A(s^2 - as) + B(s^2 + as) + C(s^2 - a^2)}{s(s^2 - a^2)} \\ &= \frac{s^2(A + B + C) + s(-aA + aB) - Ca^2}{s(s^2 - a^2)}.\end{aligned} \tag{2.39}$$

The constants A, B, and C may be obtained by comparison of the coefficients at s^2, s, and s^0 between Eqs. (2.38) and (2.39). This gives three equations:

$$\begin{cases} A + B + C = y(0), \\ -aA + aB = y'(0), \\ -Ca^2 = -b, \end{cases} \tag{2.40}$$

from which the following parameters are obtained:

$$\begin{cases} C = \dfrac{b}{a^2}, \\ A = \dfrac{y(0)}{2} - \dfrac{y'(0)}{2a} - \dfrac{b}{2a^2}, \\ B = \dfrac{y(0)}{2} + \dfrac{y'(0)}{2a} - \dfrac{b}{2a^2}. \end{cases} \tag{2.41}$$

The inverse transform of Eq. (2.39),

$$\overline{y}(s) = \frac{A}{s+a} + \frac{B}{s-b} + \frac{C}{s}, \tag{2.42}$$

leads to the solution in the time domain:

$$y(t) = Ae^{-ax} + Be^{ax} + \frac{b}{a^2}. \tag{2.43}$$

Example 2.9 Solve the differential equation

$$y(t)'' + ky(t) = 0 \tag{2.44}$$

with the following conditions: $y\ (0) = a$; $y'\ (0) = b$.

Application of a Laplace transform gives

$$\begin{aligned} &s^2\overline{y}(s) - sy(0) - y'(0) + k\overline{y}(s) = 0, \\ &s^2\overline{y}(s) - as - b + k\overline{y}(0) = 0. \end{aligned} \tag{2.45}$$

The solution in the Laplace domain is

$$\overline{y}(s) = \frac{as+b}{s^2+k} = a\frac{s}{s^2+k} + b\frac{1}{s^2+k}. \tag{2.46}$$

From the Laplace transform tables we have

$$L[\sin(at)] = \frac{a}{s^2+a^2}; \quad L[\cos(at)] = \frac{s}{s^2+a^2}, \tag{2.47}$$

and the solution in the time domain is

$$y(t) = a\cos\left(\sqrt{kt}\right) + \frac{b}{\sqrt{k}}\sin\left(\sqrt{kt}\right). \tag{2.48}$$

This equation displays the sum of two periodic functions.

The use of the Laplace transform is relatively simple using either Laplace transform tables or programs that make it possible to perform symbolic operations such as Maple or Mathematica. Application of the Laplace transform to solve current-voltage relations in electrical circuits will be illustrated in Sect. 2.8 on the impedance of electrical circuits.

2.6 Complex Numbers

The use of complex numbers is not obligatory, but they greatly simplify mathematical operations.

Let us consider first a vector R rotating with a constant angular frequency $\omega = 2\pi f$, where f is the frequency in s^{-1} or Hz and ω is in radians s^{-1} (Fig. 2.6).

The projection of R on the x- and y-axes, R_x and R_y, can be calculated using simple trigonometry:

$$\begin{aligned} R_x &= |R| \cos(\varphi) = |R| \cos(\omega t), \\ R_y &= |R| \sin(\varphi) = |R| \sin(\omega t), \end{aligned} \tag{2.49}$$

where $|R|$ is the length of the vector and $\varphi = \omega t$. This means that the projections of the rotating vector are periodic cos and sin functions of time. It should be stressed that R_x is the function of the cosine and R_y that of the sine. Of course, using Pythagoras' rule and the trigonometric identity $\sin^2 x + \cos^2 x = 1$ the length of the vector is

$$|R| = \sqrt{R_x^2 + R_y^2}. \tag{2.50}$$

In complex analysis, a projection on the x-axis is called the real part of vector R, and a projection on the y-axis is called the imaginary part. This is a simple way of distinguishing between these two projections, but, as we will see below, it simplifies considerably the calculations. The angle φ can be obtained as

$$\tan(\varphi) = \frac{R_y}{R_x}; \quad \varphi = \operatorname{atan}\left(\frac{R_y}{R_x}\right). \tag{2.51}$$

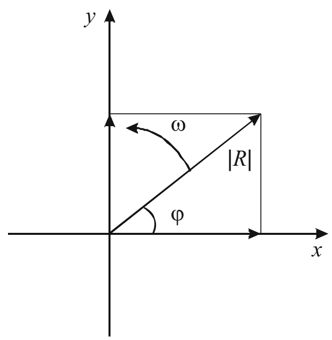
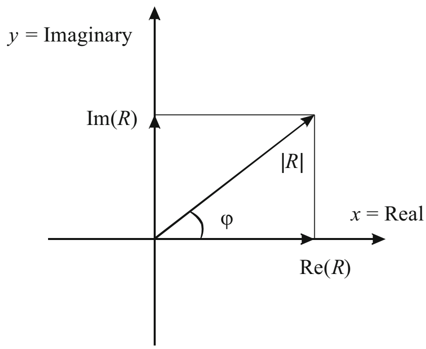


Fig. 2.6 Vector R rotating with constant angular frequency ω

Fig. 2.7 Representation of vector R on complex plane



The imaginary unit is defined as $j^2 = -1$, and the complex plane has two axes, x, which is real, and y, which is imaginary; all the real numbers on the y-axis are multiplied by the imaginary unit j. This means that any point on the complex plane has two parts: a real part on the x-axis and an imaginary part on the y-axis. This is illustrated in Fig. 2.7. Vector R may be written as

$$\hat{R} = \mathrm{Re}(R) + j\,\mathrm{Im}(R) = R' + jR'', \tag{2.52}$$

where the following definitions were used for the real and imaginary parts of the vector R:

$$\mathrm{Re}\left(\hat{R}\right) = R' \text{ and } \mathrm{Im}(R) = R''. \tag{2.53}$$

Of course, the length of the vector $|R|$ is

$$|R| = \sqrt{(R')^2 + (R'')^2}. \tag{2.54}$$

The phase angle of a complex number is called an argument, $\arg\left(\hat{R}\right)$, and the same point may be described by the angles $\varphi + 2\pi n$, where $n = \pm 1, \pm 2, \ldots$. However, we usually need the principal value of the argument denoted by $\mathrm{Arg}\left(\hat{R}\right)$ which is between 0 and 2π i.e. between 0° and 360°:

$$\varphi = \mathrm{Arg}\left(\hat{R}\right) = \mathrm{atan}\left(\frac{R''}{R'}\right). \tag{2.55}$$

Complex numbers can be written in exponential form keeping in mind that

$$e^{j\varphi} = \cos\varphi + j\sin\varphi; \tag{2.56}$$

therefore, each complex number may be written in polar form:

$$R = |R|e^{j\varphi} = |R|(\cos\varphi + j\sin\varphi). \tag{2.57}$$

The length of the vector $|R|$ is found by multiplying R by its complex conjugate R^*:

$$|R| = \sqrt{RR^*} = \sqrt{(R' + jR'')(R' - jR'')} = \sqrt{(R')^2 + (R'')^2}. \tag{2.58}$$

From Eqs. (2.56) and (2.58) it follows that

$$|e^{j\varphi}| = 1. \tag{2.59}$$

It should be kept in mind that addition, multiplication, and division of the complex numbers should be carried out correctly:

$$\begin{aligned}
&(a + jb) + (c + jd) = (a + c) + j(b + d),\\
&(a + jb)(c + jd) = (ac - bd) + j(ad + bc),\\
&\frac{1}{a + jb} = \frac{(a - jb)}{(a + jb)(a - jb)} = \left(\frac{a}{a^2 + b^2}\right) - j\left(\frac{b}{a^2 + b^2}\right),\\
&\frac{a + jb}{c + jd} = \frac{(a + jb)(c - jd)}{(c + jd)(c - jd)} = \left(\frac{ac + bd}{c^2 + d^2}\right) + j\left(\frac{bc - ad}{c^2 + d^2}\right).
\end{aligned} \tag{2.60}$$

Complex calculations may be carried out in Excel using built-in functions. Further applications of complex calculations will be shown later.

2.7 Fourier Transform

Techniques based on the FT are often used in chemical instrumentation and spectroscopy [e.g., Fourier transform-infrared (FTIR), Fourier transform nuclear magnetic resonance (FT-NMR), FT Raman] and in EIS. They can also be applied to smooth noisy experimental data. To comprehend these methods, a good understanding of the FT technique and its limitations is necessary.

Each periodic function may be presented as an infinite Fourier series composed of sine and cosine functions:

$$f(t) = a_0 + \sum_{k=1}^{\infty} a_\mathrm{k}\cos(k\omega_1 t) + b_\mathrm{k}\sin(k\omega_1 t), \tag{2.61}$$

where a_0 is a constant and all the parameters a_0, a_k, and b_k may be found by integration over the function f(t) with cosine and sine functions over one period:

$$a_k = \frac{2}{T}\int_0^T f(t)\cos(k\omega_1 t)\mathrm{d}t, \tag{2.62}$$

$$b_k = \frac{2}{T}\int_0^T f(t)\sin(k\omega_1 t)\mathrm{d}t. \tag{2.63}$$

The FT of the continuous function $f(t)$ is defined similarly to Eq. (2.21) with the parameter, $s = j\omega$, Eq. (2.22), but with integration from $-\infty$ to ∞ [75–77]:

$$F(\omega) = \int_{-\infty}^{\infty} f(t)e^{-j\omega t}\mathrm{d}t. \tag{2.64}$$

It maps the function of time, $f(t)$, into the function of frequency, $F(\omega)$. As with the Laplace transform, no information is lost during this operation. In practice, one uses integration between 0 and T assuming that the function is periodic before and after this time window, which means that this time window is exactly repeated until infinity:

$$F(\omega) = \int_0^T f(t)e^{-j\omega t}\mathrm{d}t. \tag{2.65}$$

Taking into account Eq. (2.57) this equation corresponds to two parts of the integral: a real part,

$$F'(\omega) = \int_0^T f(t)\cos(\omega t)\mathrm{d}t, \tag{2.66}$$

and an imaginary part,

$$F''(\omega) = j\int_0^T f(t)\sin(\omega t)\mathrm{d}t. \tag{2.67}$$

This operation corresponds simply to the integration of our function $f(t)$ with $\cos(\omega t)$ and $\sin(\omega t)$, respectively.

Electrochemistry deals with digitized signals acquired with a constant frequency determined by the analog to digital (A/D) converter, that is, instead of the continuous function we deal with the collection of N points every Δt during the time period T. The points i are numbered from 0 to $N - 1$, but only the point number is indicated and the corresponding time must be calculated from the sampling rate:

$$\begin{array}{cc}
\text{Function of time} & \text{Point number} \\
f[0] & f(0) \\
f[\Delta t] & f(1) \\
f[2\Delta t] & f(2) \\
\dots & \dots \\
f[(N-2)\Delta t] & f(N-2) \\
f[(N-1)\Delta t] & f(N-1)
\end{array} \tag{2.68}$$

The acquired series of points may be integrated using Eq. (2.65), rewritten for the discretized function (the integral is written as a sum):

$$F(u) = \frac{1}{N}\sum_{i=0}^{N-1} f(i)\exp(-j\omega_{\mathrm{u}} t_{\mathrm{i}}), \tag{2.69}$$

where ω_{u} is a series of harmonic frequencies and u is a whole number between 0 and $N - 1$,

$$\omega_{\mathrm{u}} = u\omega_1, \tag{2.70}$$

and the fundamental angular frequency ω_1 is related to the fundamental frequency ν_1 determined by the data acquisition time:

$$\omega_1 = 2\pi\nu_1 = \frac{2\pi}{T} = \frac{2\pi}{N\Delta t}. \tag{2.71}$$

Taking into account that

$$t_i = i\Delta t \tag{2.72}$$

and substituting these values into Eq. (2.69), the following equation is obtained:

$$F(u) = \frac{1}{N}\sum_{i=0}^{N-1} f(i)\exp\left(-\frac{j2\pi ui}{N}\right). \tag{2.73}$$

This equation represents the so-called discrete Fourier transform (DFT) and shows how the series of points $f(i)$ in the time domain is transformed into a series of points in the frequency domain $F(u)$. The exponent depends only on the numbers u (point number in frequency domain), i (point number in the time domain), and the total number of points N. It should be noticed that Δt cancels and does not appear in the equation. This operation can be shown in a schema, where the parameters i and u change from 0 to $N - 1$:

$$\begin{array}{cc} \text{Time domain} & \text{Frequency domain} \\ f(0) & F(0) \\ f(1) & F(1) \\ f(2) & F(2) \\ \dots & \dots \\ f(i) & F(u) \\ \dots & \dots \\ f(N-1) & F(N-1) \end{array} \tag{2.74}$$

However, the highest frequency for which information can be obtained corresponds to the point $N/2$. This is the so-called *Nyquist frequency* and it expresses the fact that in order to obtain information about a periodic function (sine or cosine), this function must be sampled at least two times per period. The Nyquist frequency is

$$v_{\max} = \frac{Nv_1}{2} = \frac{N}{2T} = \frac{N}{2(N\Delta t)} = \frac{1}{2\Delta t}. \tag{2.75}$$

Although N points in the frequency domain are obtained, the information about the frequency is contained for u from 0 (constant) up to $N/2$. After this point the values are repeated, and no new information is found. Nevertheless, to carry out the inverse FT, all N points must be used (for u from $u = 0$ to $N - 1$):

$$f(i) = \sum_{u=0}^{N-1} F(u) \exp\left(\frac{j2\pi ui}{N}\right). \tag{2.76}$$

The frequencies at each point are calculated using the equation

$$v_{\mathrm{u}} = \frac{u}{N\Delta t} \text{ for } u = 0 \dots N/2. \tag{2.77}$$

The DFT is numerically inefficient and demands many multiplications/divisions. Cooley and Tukey have developed a more efficient algorithm that reduces the number of calculations for N^2 to $N \log_2 N$. This is the so-called fast Fourier transform (FFT) [75], which is implemented in many programs including Microsoft Excel. However, it requires that the number of data points be a power of 2, that is, $\mathrm{N} = 2^k$, where k is an integer number, e.g., 4, 8, 16, 32, 64, 128,. . .. Although manual calculation of the FT is possible for a few points, it is always done by computer. To better understand this transform, let us look at a few examples. They can be completed using Excel. In Exercise 2.1, the function $E(t) = \cos(2\pi t_i/0.32)$ is generated for 64 points and its FT is computed in Excel. Plots of the functions are

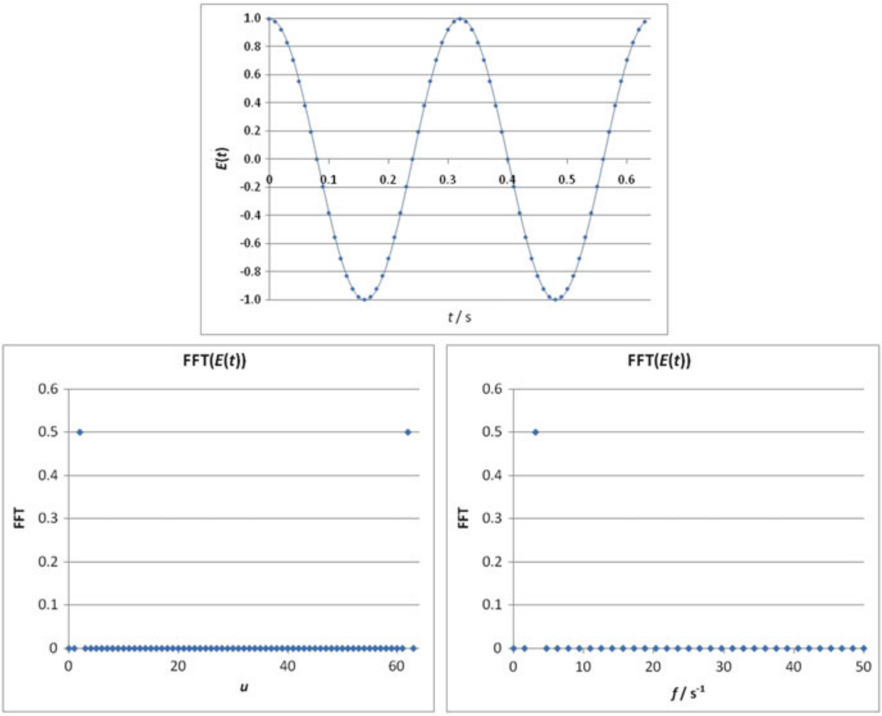


Fig. 2.8 Assumed function $E(t) = \cos(2\pi t_i/0.32)$ (64 points) and its FT in Excel plotted versus u and versus frequency

displayed in Fig. 2.8. The FT displays only one point at the frequency $\nu = 1/0.32\ \mathrm{s}^{-1} = 3.125\ \mathrm{s}^{-1}$, with the real part 0.5 and the imaginary part 0. This indicates that the function transformed was the cosine without a phase shift. The phase angle is calculated using Eq. (2.78):

$$\varphi = \mathrm{Arg}\left(\frac{0}{0.5}\right) = 0. \tag{2.78}$$

The value of 0.5 is simply the FT of the cosinus function with an amplitude of one:

$$\frac{1}{T}\int_0^T \cos\left(2\pi t/T\right) e^{-j(2\pi/T)t} \mathrm{d}t = 0.5 \tag{2.79}$$

for $\nu = 3.125\ \mathrm{s}^{-1}$. It should be stressed that the FT of the cosine function is always real.

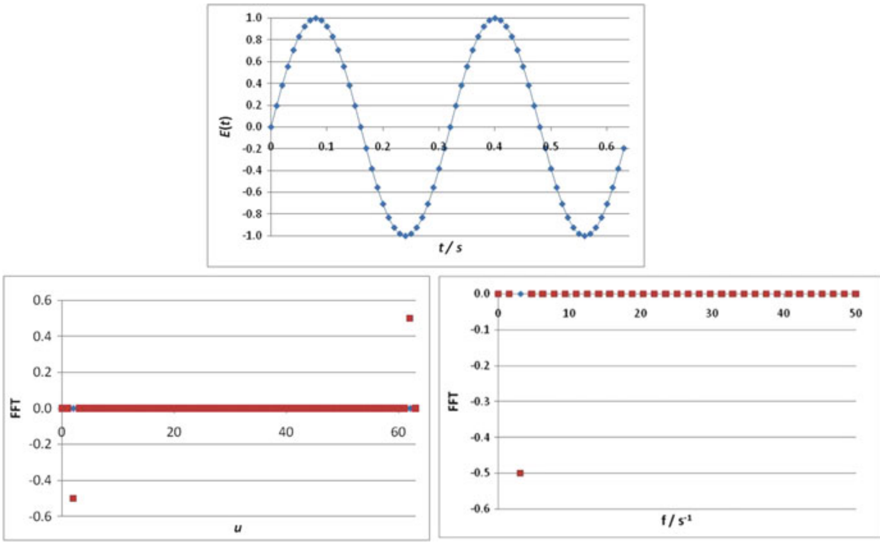


Fig. 2.9 Assumed function $\sin(2\pi t_i\,/\,0.32)$ (64 points) and its FT (imaginary part) in Excel plotted versus u and versus frequency up to Nyquist frequency

The FT of the sinus function $E(t) = \sin(2\pi t/T_a)$ is studied in Exercise 2.2. It is simply the cosine function studied in Exercise 2.1 but shifted in phase by $-\pi/2 = -90°$:

$$\sin\left(\frac{2\pi t}{T_a}\right) = \cos\left(\frac{2\pi t}{T_a} - \frac{\pi}{2}\right) \tag{2.80}$$

The assumed function and its FT are presented in Fig. 2.9.

The FT of this function shows that all the real values are equal to 0. The FT displays two imaginary values: $-0.5j$ for $u = 2$ and $0.5j$ for $u = 62$. The frequency of the function is 3.125 s^{-1}. The phase angle is

$$\varphi = \mathrm{Arg}\left(\frac{-0.5}{0}\right) = -\frac{\pi}{2}, \tag{2.81}$$

that is, $-90°$. FT is characterized by three parameters: the real (0) and imaginary (-0.5) parts and the frequency 3.125 s^{-1}. The equivalent representation is by the modulus 0.5, the phase angle $-\pi/2$, and the frequency 3.125 s^{-1}.

Let us consider now what happens if the cosine function is shifted by the phase angle φ. This is also illustrated in Exercise 2.3, where the function $E(t) = \cos(2\pi t\,/\,T + \pi\,/\,3)$ is transformed. The function and its FT are displayed in Fig. 2.10.

In this case the FT versus u presents values different from 0 for $u = 2$ and 62; they are both complex, the real part is the same, and the imaginary is just of the

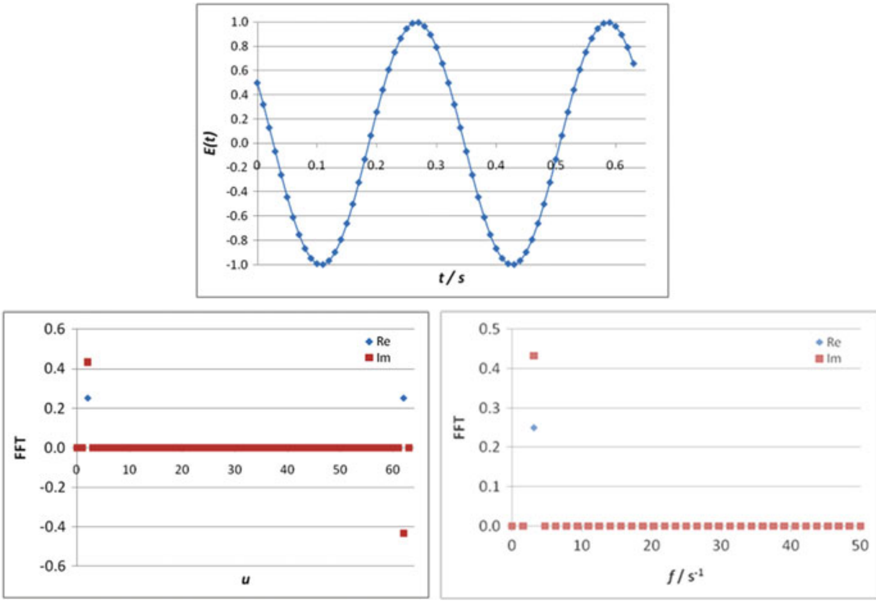


Fig. 2.10 Assumed function $E(t) = \cos(2\pi t_i/0.32 + \pi/3)$ (64 points) and its FT (real and imaginary parts) in Excel plotted versus u and versus frequency, f

opposite sign. The plot versus frequency displays real and imaginary values different from zero for one frequency $f = 3.125\ \mathrm{s}^{-1}$. The phase angle is

$$\varphi = \mathrm{Arg}\left(\frac{\mathrm{Im}}{\mathrm{Re}}\right) = \frac{\pi}{3} = 60^\circ. \tag{2.82}$$

From these values one can write that the original function is $\cos(2\pi\, 3.125\ t + \pi/3)$. The modulus of the FT is $\sqrt{0.25^2 + 0.43301^2} = 0.5$, and it is the same as in Exercises 2.1 and 2.2. In all these exercises the amplitude of the periodic functions was assumed to be one.

In general, the cosine function (without the phase shift) always produces real values and the sine only imaginary values. A cosine function shifted in phase produces the real and imaginary parts from which the phase shift can be determined.

In the next example we will examine the FT of an intrinsically nonperiodic function. This is also illustrated in Exercise 2.4, in which the function $E(t) = \exp(-3t_i)$ for 32 points is transformed. This function and its FT are displayed in Fig. 2.11. It is evident that nonzero values of the FT are obtained at all frequencies; with the exception of $u = 0$ and 16, they are all complex. The first constant value for $f = 0$ is simply the average value of all the experimental points. Note that from $u > N/2$ that is form $u = 17$ the real values are repeated in inverse order, that is, $\mathrm{Re}_{17} = \mathrm{Re}_{15}$, $\mathrm{Re}_{18} = \mathrm{Re}_{14}$, etc., while the imaginary parts change sign: $\mathrm{Im}_{17} = -\mathrm{Im}_{15}$, $\mathrm{Im}_{18} = -\mathrm{Im}_{14}$, etc., around the central value for $u = N/2 = 16$. It must be

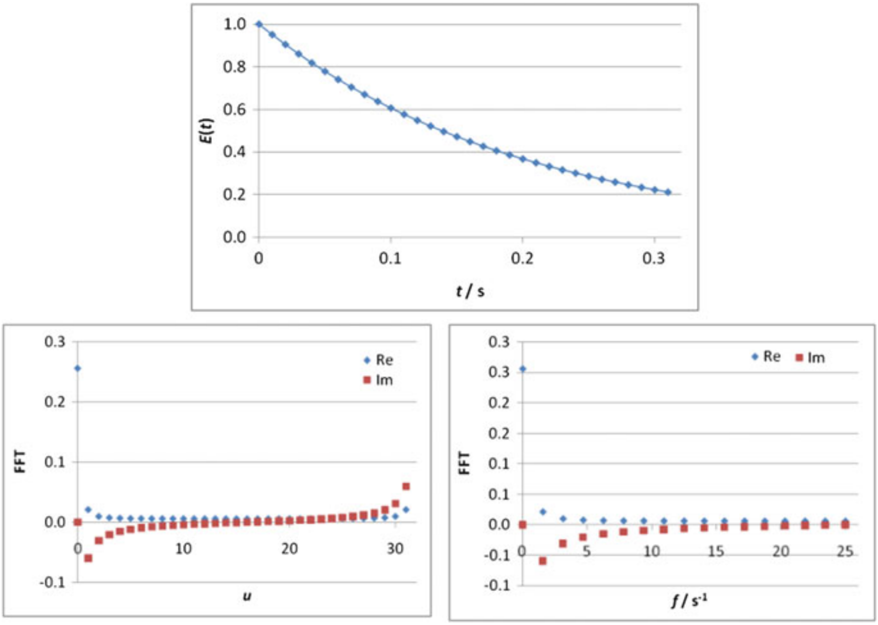


Fig. 2.11 Assumed function $E(t) = \exp(-3t_i)$ (32 points) and its FT (real and imaginary parts) in Excel plotted versus u and versus frequency

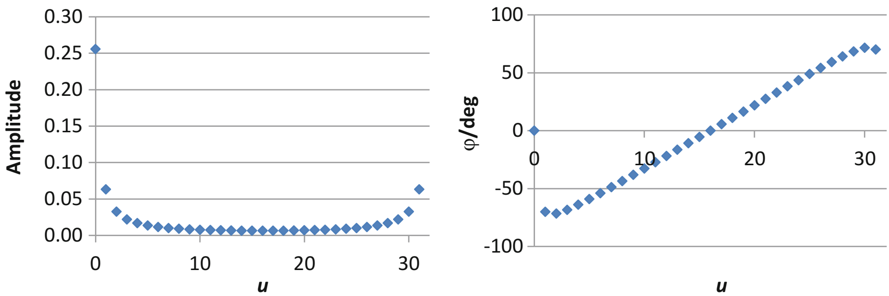


Fig. 2.12 Amplitude and phase angle of FT of exponential function in Fig. 2.11

stressed that all the frequencies are necessary to approximate the experimental points. The experimental points of the exponential function are approximated by a sum of the cosine functions with different amplitudes and different phase angles. The amplitude (modulus) at each frequency and the phase angle are displayed in Fig. 2.12. The same information is contained in the real and imaginary values at each frequency as in the amplitude and the phase angle. It should be stressed that FT gives an exact approximation of the experimental function at each point by the sum of the periodic functions. Of course, one cannot use the sum of the obtained periodic functions to interpolate it between the experimental points.

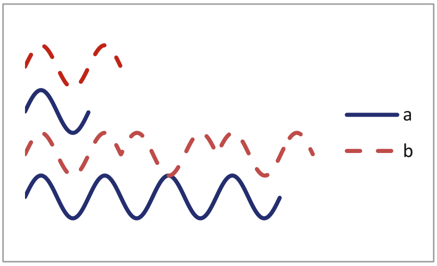


Fig. 2.13 *Top: curve a* containing whole number of periods (here one); *curve b* containing 1.5 periods. *Bottom*: FT assumes that this element is periodically repeated producing discontinuities for *curve b*

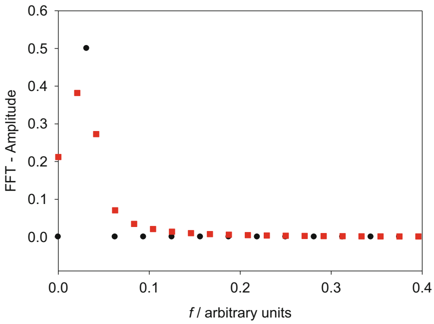


Fig. 2.14 Fourier transform (amplitude) of function in Fig. 2.13a, bottom, containing whole number (one) of periods (●) and Fig. 2.13b, bottom, containing three blocks of 1.5 periods each (■) during data acquisition time

2.7.1 Leakage

There are some limitations of the FT technique connected with so-called leakage. The FFT works well if there is a whole number of periods of the function $f(t)$ in the total acquisition time, T. As was mentioned at the beginning, the FT is an integral from $-\infty$ to ∞, and the transform assumes that what is observed in the total data acquisition time is repeated before and after our time window from 0 to T. This is illustrated in Fig. 2.13; curve a, containing a whole number of periods (here one), produces a smooth curve (without discontinuities) when it is repeated before and after the time window. However, when the number of periods is not a whole or integer number, curve b (in this example 1.5 periods), repetition of this curve produces discontinuities, as at the end of the period the curve is decreasing and at the beginning of a new block it is increasing. The FT of curve a, Fig. 2.14, produces one point in the frequency domain corresponding to the frequency of the wave. However, in the case of curve b, in the list of frequencies calculated using Eq. (2.77), there is no frequency corresponding to the natural frequency of that sine function (there are others around this number; see Fig. 2.14), and a dispersion of frequencies appears. This problem is called leakage and always appears when there are no whole numbers of periods in the data acquisition time T, that is, the

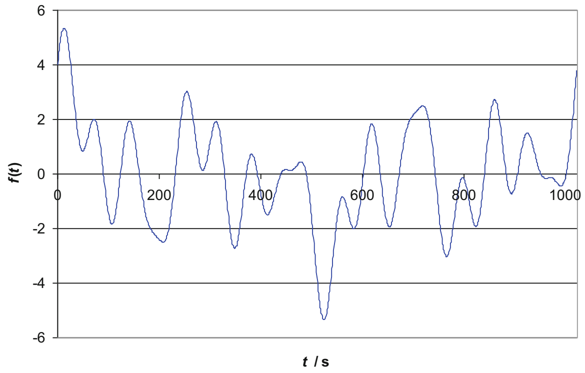


Fig. 2.15 Plot of a complex function composed of the sum of seven simple periodic functions

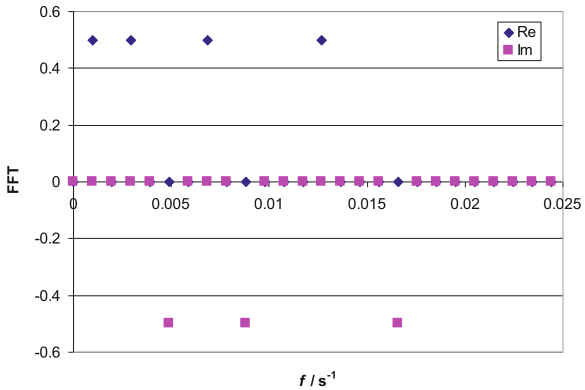


Fig. 2.16 Fourier transform of function displayed in Fig. 2.15

ratio of T/T_a, where T_a is the period of the studied function, is not a whole number. An example of leakage is illustrated in Exercise 2.5.

The main conclusion of this part is that to avoid leakage, one always should keep a whole number of periods in the total acquisition time. The problem of leakage may be minimized (but not completely eliminated) when the total time and number of periods of the function increase, which means that more frequencies are added to the list and their separation becomes smaller (Exercise 2.5). Some authors have proposed that using a digital filter that decreases the importance of the initial and final points decreases the effect of leakage.

Therefore, when using a sum of frequencies in impedance (Chap. 3.7.3) one must also ensure that the number of periods of each function during the data acquisition time is a whole number.

The advantage of the FFT is that this analysis allows one to determine the response of each periodic function when their sum is applied. It should be stressed, however, that the frequency information is for f between $f_{min} = 1/T$ and the Nyquist frequency $f_{max} = 1/2\Delta t$. For example, the FT of the curve displayed in Fig. 2.15 shows that it is composed of four cosine (only real values in the Fourier domain) and three sine functions (only imaginary values in the Fourier domain) (Fig. 2.16).

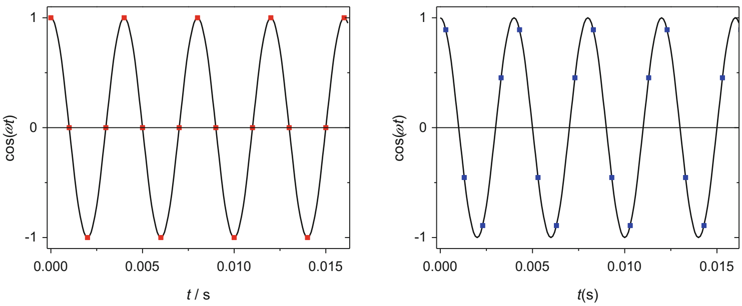


Fig. 2.17 Examples of sampling wave of frequency 250 Hz at rate of 1,000 Hz. The wave is sampled four times per period, which can be at different places (phases) of the wave

Although the shape of the function $f(t)$ seems quite complex, the FT analysis reveals all the underlying functions and their frequencies. Details are presented in Exercise 2.6.

2.7.2 Aliasing

Another problem with the FFT is related to the Nyquist sampling theorem. As was shown earlier, the highest frequency for which information can be found from the FFT is given by Eq. (2.75); this is the so-called Nyquist frequency, ν_{max}. If the experimental frequency is larger than this value, it cannot be found with the FFT. Instead, new frequencies lower than ν_{max} appear. This can be illustrated in the following example. Let us suppose that the sampling frequency is 1 kHz, that is, samples are measured every 1 ms. This means that the Nyquist frequency is $f_{max} = 1/(2 \times 0.001\ \mathrm{s}) = 500$ Hz. When a cosine wave of frequency 250 Hz is applied, the FT is able to find it because the periodic wave is sampled four times per period. This is illustrated in Fig. 2.17. When the wave frequency is 500 Hz (Nyquist frequency), the wave is sampled two times per period. This is a minimum sampling rate necessary to determine the frequency (Fig. 2.18). While sampling with the Nyquist frequency one can find, by accident, that all the sampled values are zero or very small. In the second case, the measurements might not be precise enough (noisy), although theoretically the FFT should give correct values (Fig. 2.18). In such a case, the waveform should be resampled. In practice, sampling with the Nyquist frequency might be less reliable and should be repeated.

Finally, when the wave frequency is 625 Hz, which is larger than the Nyquist frequency (500 Hz), the FT cannot find it. Instead, it finds a different frequency, lower than the Nyquist frequency, in this case 375 Hz. This frequency does not exist in the system but is reconstructed by the FT. It is illustrated in Fig. 2.19. This example indicates that when performing FFT one should ensure that the sampling rate is sufficiently large, larger than the Nyquist frequency. It could be verified by doubling the sampling frequency; no changes in the frequencies found should appear. Sometimes, it is advantageous to use a low-pass filter to cut off all

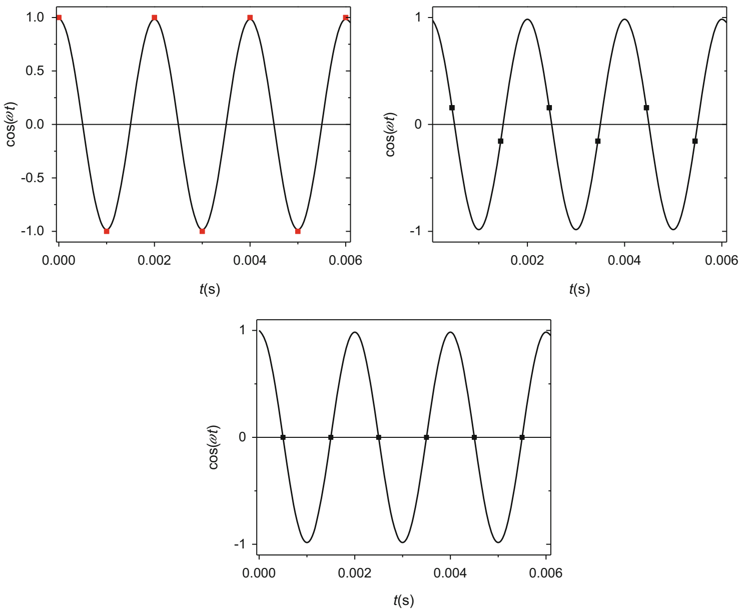


Fig. 2.18 Sampling of wave of frequency 500 Hz with Nyquist frequency of 1,000 Hz. It may appear in some cases that the measured signal is either zero or very small; in such cases, the wave should be resampled

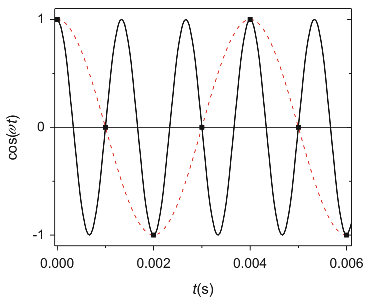


Fig. 2.19 Example of wave of 750 Hz (*continuous line*) being sampled with frequency of 1,000 Hz. The Nyquist frequency is 500 Hz. The Fourier transform finds a "phantom" frequency of 250 Hz (*dashed line*) that does not exist in the system

frequencies larger than the Nyquist frequency. A problem with leakage is presented in Exercise 2.5.

In summary, the sampled waveform should contain a whole number of periods to avoid leakage and the sampling should be with at least the Nyquist frequency or faster to avoid aliasing. In EIS practice, a waveform containing a predetermined number of frequencies and whole number of periods of waveforms is used and sampling is synchronized (Chap. 3.7).

2.8 Impedance of Electrical Circuits

Knowledge of the Laplace and Fourier transforms allows us to determine the system impedance and to solve the equations $i(t) = f[E(t)]$ for an arbitrary perturbation.

2.8.1 Application of Laplace Transform to Determination of Impedances

Let us assume that an arbitrary potential function $E(t)$ is applied to a simple connection of the resistance R and capacitance C in series. Such a circuit is described by Eq. (2.18):

$$E(t) = i(t)R + \frac{1}{C}\int_0^t i(t)\mathrm{d}t. \tag{2.18}$$

To solve the problem, which is an integral equation, we could use the Laplace transform:

$$\overline{E}(s) = R\overline{i}(s) + \frac{1}{Cs}\overline{i}(s), \tag{2.83}$$

where an integral equation in the time domain was transformed into an algebraic equation in the frequency domain s. From this equation one can easily find $\overline{i}(s)$:

$$\overline{i}(s) = \frac{1}{R + \frac{1}{sC}}\overline{E}(s). \tag{2.84}$$

Similarly, one can solve differential Eq. (2.20) describing the connection of the resistance, R, and inductance, L, in series:

$$E(t) = i(t)R + L\frac{\mathrm{d}i(t)}{\mathrm{d}t}. \tag{2.20}$$

Applying the Laplace transform to this equation and keeping in mind Eq. (2.27) for the transform of the first derivative the following form is obtained:

$$\overline{E}(s) = \overline{i}(s)R + \overline{i}(s)sL, \tag{2.85}$$

Table 2.1 Operational impedance of linear electrical elements

Element	Impedance
R	R
C	$\frac{1}{sC}$
L	sL

from which a current in the Laplace domain may be easily obtained:

$$i(s) = \frac{E(s)}{R + sL}. \tag{2.86}$$

To obtain a current as a function of time, the form of the potential program must be known. In the case of a simple resistance in the circuit, the solution is obvious:

$$i(t) = \frac{E(t)}{R} \text{ and } \bar{i}\,(s) = \frac{\overline{E}\,(s)}{R}. \tag{2.87}$$

2.8.2 Definition of Operational Impedance

Analysis of Eqs. (2.84), (2.86), and (2.87) reveals that the relation between current and potential in the presence of resistance, capacitance, and inductance may be represented in a general form:

$$\hat{Z}\,(s) = \frac{L[E(t)]}{L[i(t)]} = \frac{\overline{E}\,(s)}{i(s)}, \tag{2.88}$$

where $\hat{Z}\,(s)$ is called the operational impedance and has units of the resistance, Ω, and for each electrical element one can write the corresponding impedance (Table 2.1) and calculate the total impedance using Ohm's and Kirchhoff's laws.

The *operational impedance is the ratio of the Laplace transform of the potential to the Laplace transform of the current* (Eq. 2.88). It is usually used for an arbitrary perturbation signal. For the periodic signal it is equivalent to the definition using Fourier transformation. What follows are examples of the application of the Laplace technique to the determination of the current–potential relations and the impedances.

Example 2.10 Determine the current after application of the potential step $E_0\eta(t)$ [see Fig. 2.5 for a definition of the Heaviside function $\eta(t)$ and its transform] to the connection of the resistance, R, and capacitance, C, in series.

The system is described by Eq. (2.84). The transform of the potential step $E_0\,\eta(t)$ is

$$L[E_0\eta(t)] = E_0 L[\eta(t)] = \frac{E_0}{s}, \tag{2.89}$$

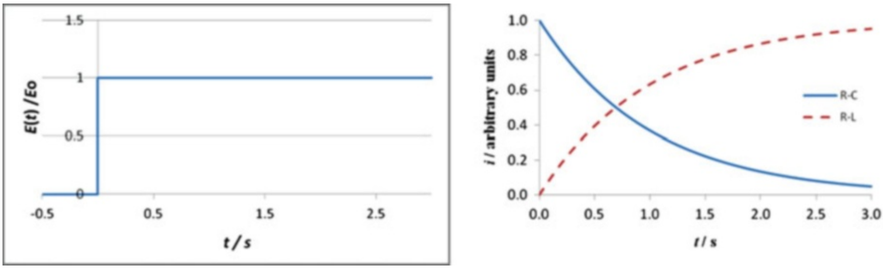


Fig. 2.20 Current–time transients due to application of step function to connection *R-C* and *R-L* in series; the time constant in both cases is 1 s

where Eq. (2.25) was used for the transform of the $\eta(t)$ function. The operational impedance corresponds to the connection of the impedances of the R and C elements in series. Using the impedances from Table 2.1 the total impedance is

$$\hat{Z}(s) = R + \frac{1}{Cs}, \tag{2.90}$$

and from Eq. (2.88)

$$\bar{i}(s) = \frac{\overline{E}(s)}{\hat{Z}(s)} = \frac{E_0}{s}\frac{1}{R + \frac{1}{Cs}} = \frac{E_0}{R}\frac{1}{s + 1/RC}. \tag{2.91}$$

An inverse Laplace transform using Eq. (2.26) gives the solution in the time domain:

$$i(t) = \frac{E_0}{R}\exp\left(-\frac{t}{RC}\right) = \frac{E_0}{R}\exp\left(-\frac{t}{\tau}\right). \tag{2.92}$$

The current starts at $i = E_0/R$ at $t = 0$ then decreases exponentially with time to zero as the capacitor is charged from 0 to E_0; the constant current cannot flow through the capacitance. The potential step and the response of the system are displayed in Fig. 2.20. The rate at which the current decreases with time depends on RC, which is called the system time constant $\tau = RC$; if the time constant is smaller (smaller resistance or capacitance), then the current decay is faster.

Let us consider an application of the same potential step function to the R-L connection in series.

Example 2.11 Determine the current after application of the potential step $E_0\,\eta(t)$ to the connection of the resistance, R, and inductance, L, in series.

The proposed system is described by the differential Eq. (2.20). The impedance of the system is

$$\hat{Z}(s) = R + Ls. \tag{2.93}$$

Substitution into the expression for the current gives

$$\bar{i}(s) = \frac{\overline{E}(s)}{\hat{Z}(s)} = \frac{E_0}{s(R+sL)} = \frac{E_0}{L}\frac{1}{s(s+R/L)} = \frac{E_0}{R}\left(\frac{1}{s} - \frac{1}{s+R/L}\right). \tag{2.94}$$

The inverse transform gives

$$i(t) = \frac{E_0}{R}\left[1 - \exp\left(-\frac{Rt}{L}\right)\right]. \tag{2.95}$$

A plot of current versus time is given in Fig. 2.20. At time $t = 0$ the exponential term is equal to 1 and the current is zero. This corresponds to the properties of a coil that resists fast changes in a current. Then the current increases to the limiting value E_0/R as the coil does not oppose the passage of the constant current [$L\mathrm{d}i(t)/\mathrm{d}t = 0$ in Eq. (2.20)]. The characteristic time constant of the system is $\tau = L/R$.

Let us consider a more difficult example.

Example 2.12 Determine the current after application of the potential step $E_0\eta(t)$ to the connection of the resistance, R, capacitance, C, and inductance, L, in series.

The operator impedance of the circuit is simply a connection of the three elements in series:

$$\hat{Z}(s) = R + \frac{1}{Cs} + Ls. \tag{2.96}$$

Substitution into the equation for the current gives

$$\bar{i}(s) = \frac{E_0}{s\left(R + \frac{1}{Cs} + Ls\right)} = \frac{E_0}{L}\frac{1}{\left(s^2 + \frac{R}{L}s + \frac{1}{RL}\right)}. \tag{2.97}$$

To be able to carry out the inverse transform, the second-order expression for s must be separated into simple fractions:

$$s^2 + \frac{R}{L}s + \frac{1}{RL} = (s - s_1)(s - s_2), \tag{2.98}$$

$$\begin{aligned} s_1 &= \frac{R}{2L}\left(-1 - \sqrt{1 - \frac{4L}{R^2C}}\right) = \frac{1}{2\tau_1}\left(-1 - \sqrt{1 - \frac{4\tau_1}{\tau_2}}\right), \\ s_2 &= \frac{R}{2L}\left(-1 + \sqrt{1 - \frac{4L}{R^2C}}\right) = \frac{1}{2\tau_1}\left(-1 + \sqrt{1 - \frac{4\tau_1}{\tau_2}}\right), \end{aligned} \tag{2.99}$$

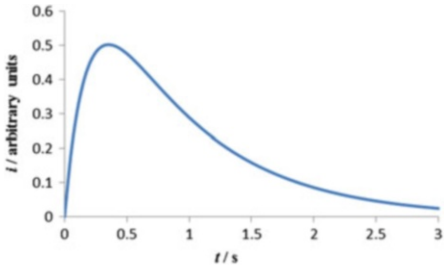


Fig. 2.21 Current–time transients due to application of step function to connection *R*-*C*-*L* in series; $\tau_1 = 0.15$ s, $\tau_2 = 3$ s

assuming that $\Delta > 0$, that is, $1 - 4\tau_1 / \tau_2 > 0$

$$\frac{1}{s^2 + \frac{R}{L}s + \frac{1}{RL}} = \frac{1}{(s - s_1)(s - s_2)} = \frac{A}{s - s_1} + \frac{B}{s - s_2} = \frac{s(A + B) - As_2 - Bs_1}{(s - s_1)(s - s_2)},$$

$$A = -B = -\frac{2L}{R\sqrt{1 - \frac{4L}{R^2C}}} = -\frac{2}{\tau_1\sqrt{1 - \frac{4\tau_1}{\tau_2}}}. \tag{2.100}$$

After substitution into the expression for the Laplace transform of the current,

$$\bar{i}(s) = \frac{E_0}{R\sqrt{1 - \frac{4\tau_1}{\tau_2}}}\left(\frac{1}{s - s_2} - \frac{1}{s - s_1}\right), \tag{2.101}$$

the inverse transform is

$$\begin{aligned} i(t) &= \frac{E_0}{R\sqrt{1 - \frac{4L}{R^2C}}}\left(e^{s_2 t} - e^{s_1 t}\right) \\ &= \frac{E_0}{R\sqrt{1 - \frac{4\tau_1}{\tau_2}}}\left[e^{-\frac{1}{2\tau_1}\left(1-\sqrt{1-\frac{4\tau_1}{\tau_2}}\right)t} - e^{-\frac{1}{2\tau_1}\left(1+\sqrt{1-\frac{4\tau_1}{\tau_2}}\right)t}\right]. \end{aligned} \tag{2.102}$$

The current relaxation is controlled by two time constants, $\tau_1 = L/R$ and $\tau_2 = RC$, which correspond to the relaxation of the system corresponding to *R*-*L* and *R*-*C* connections. A plot of the current versus time is presented in Fig. 2.21. At $t = 0$ the current is zero, and then it increases as in the case of the connection *R*-*L*. Then it starts to decrease to zero as with the connection *R*-*C*.

The method of the Laplace transform may also be used to determine the $i(t)$ relation in the case where the ac signal is applied. This is illustrated in Example 2.13.

Example 2.13 Determine the current after application of the periodic function $E(t) = E_0 \sin(\omega t)$ to the connection of the resistance, R, and capacitance, C, in series.

As in Example 2.10, the relation between current and potential in the Laplace domain is described as

$$\bar{i}(s) = \frac{\overline{E}(s)}{\hat{Z}(s)} = \frac{E(s)}{R + \frac{1}{Cs}} \tag{2.103}$$

The Laplace transform of the sine function is found in Appendix 1:

$$L[\sin(\omega t)] = \frac{\omega}{s^2 + \omega^2}. \tag{2.104}$$

Substitution into Eq. (2.103) gives, after rearrangements,

$$\begin{aligned}\bar{i}(s) &= E_0 \frac{\omega}{s^2 + \omega^2} \frac{1}{R + \dfrac{1}{Cs}} = E_0 \frac{\omega}{(s^2 + \omega^2)} \frac{s}{R\left(s + \dfrac{1}{RC}\right)} = \\ &= \frac{E_0 \omega}{R} \frac{s}{(s^2 + \omega^2)\left(s + \dfrac{1}{RC}\right)}.\end{aligned} \tag{2.105}$$

The last term in Eq. (2.105) must be separated into simple fractions:

$$\begin{aligned}\bar{i}(s) &= \frac{As + B}{s^2 + \omega^2} + \frac{D}{s + \dfrac{1}{RC}} = \\ &= \frac{s^2(A + D) + s\left(B + \dfrac{A}{RC}\right) + \left(\dfrac{B}{RC} + D\omega^2\right)}{(s^2 + \omega^2)\left(s + \dfrac{1}{RC}\right)}.\end{aligned} \tag{2.106}$$

Comparison of Eqs. (2.106) and (2.105) allows for the determination of the parameters A, B, and D:

$$\begin{aligned} &A + D = 0 \quad B + \frac{A}{RC} = 1 \quad \frac{B}{RC} + D\omega^2 = 0, \\ &A = -D = \frac{RC}{1 + (\omega RC)^2} \quad B = \frac{(\omega RC)^2}{1 + (\omega RC)^2}. \end{aligned} \tag{2.107}$$

Substitution of these parameters into Eq. (2.106) leads to

$$\bar{i}(s) = \frac{E_0\omega}{R}\left[\begin{array}{l} \dfrac{RC}{\left[1 + (\omega RC)^2\right]}\dfrac{s}{(s^2 + \omega^2)} + \dfrac{(\omega RC)^2}{\left[1 + (\omega RC)^2\right]}\dfrac{1}{(s^2 + \omega^2)} \\ + \dfrac{RC}{\left[1 + (\omega RC)^2\right]}\dfrac{1}{s + \dfrac{1}{RC}} \end{array}\right] = \tag{2.108}$$

$$\begin{aligned} &= \frac{E_0\omega}{R(\omega RC)^2\left(1 + \dfrac{1}{(\omega RC)^2}\right)}\left[RC\frac{s}{(s^2 + \omega^2)} + (\omega RC)^2\frac{1}{(s^2 + \omega^2)}\right] = \\ &= \frac{E_0}{R}\frac{1}{\left[1 + \dfrac{1}{(\omega RC)^2}\right]}\left[\frac{1}{\omega RC}\frac{s}{(s^2 + \omega^2)} + \frac{\omega}{(s^2 + \omega^2)}\right], \end{aligned} \tag{2.109}$$

where the third term displaying a transient exponential relaxation was neglected because it disappears in the steady state. This equation can be transformed into the time domain keeping in mind that

$$L[\cos(\omega t)] = \frac{s}{s^2 + \omega^2}, \tag{2.110}$$

and the following expression is obtained:

$$i(t) = \frac{E_0}{R}\frac{1}{1 + \frac{1}{(\omega RC)^2}}\left[\frac{1}{\omega RC}\cos(\omega t) + \sin(\omega t)\right]. \tag{2.111}$$

Note that any real number can be represented as $\tan(x)$; in our case we can use

$$\tan\varphi = \frac{1}{\omega RC}. \tag{2.112}$$

Substitution of Eq. (2.112) into (2.111) gives

$$i(t) = \frac{E_0}{R}\frac{1}{1+\frac{1}{(\omega RC)^2}}[\tan(\varphi)\cos(\omega t) + \sin(\omega t)]$$
$$= \frac{E_0}{R}\frac{1}{1+\frac{1}{(\omega RC)^2}}[\cos(\omega t)\sin(\varphi) + \sin(\omega t)\cos(\varphi)] \tag{2.113}$$

Using the trigonometric identities

$$\cos(\varphi) = \sqrt{\frac{1}{1+\tan^2(\varphi)}} = \sqrt{\frac{1}{1+\frac{1}{(\omega RC)^2}}} \tag{2.114}$$
$$\cos(\omega t)\sin(\varphi) + \sin(\omega t)\cos(\varphi) = \sin(\omega t + \varphi)$$

one obtains the final form:

$$i(t) = \frac{E_0}{\sqrt{R^2 + \frac{1}{(\omega c)^2}}}\sin(\omega t + \varphi) = \frac{E_0}{|Z|}\sin(\omega t + \varphi). \tag{2.115}$$

Comparison of the applied voltage and obtained current reveals that the current oscillates with the same frequency as the potential but is shifted in phase by the angle φ depending on the frequency, according to Eq. (2.112). The term $|Z|$ is the modulus of the impedance:

$$|Z| = \sqrt{R^2 + \frac{1}{(\omega C)^2}} \tag{2.116}$$

is a sum of two perpendicular vectors, R and $1/\omega C$. We will find later that the same answer will be obtained using FT.

An exercise where the sine function is replaced by the cosine is presented in Example 2.14.

Example 2.14 Determine the current following application of the periodic function $E(t) = E_0\cos(\omega t)$ to the connection of the resistance, R, and capacitance, C, in series.

This example is analogous to Example 2.13, with the exception of the periodic function, which is now the cosine. Using the Laplace transform of the cosine function the transformed current is obtained and must be separated into simple fractions:

$$\bar{i}(s) = E_0 \frac{s}{\left(s^2+\omega^2\right)\left(R+\dfrac{1}{sC}\right)} = \frac{E_0}{R} \frac{s^2}{\left(s^2+\omega^2\right)\left(s+\dfrac{1}{RC}\right)}$$
$$= \frac{E_0}{R\left(1+(\omega RC)^2\right)}\left[(\omega RC)^2 \frac{s}{\left(s^2+\omega^2\right)} - \omega RC \frac{\omega}{\left(s^2+\omega^2\right)} + \frac{1}{\left(s+\dfrac{1}{RC}\right)}\right]$$
$$= \frac{E_0}{R}\frac{(\omega RC)^2}{1+(\omega RC)^2}\left[\frac{s}{\left(s^2+\omega^2\right)} - \frac{1}{\omega RC}\frac{\omega}{\left(s^2+\omega^2\right)}\right]$$
$$= \frac{E_0}{R}\frac{1}{1+\dfrac{1}{(\omega RC)^2}}\left[\frac{s}{\left(s^2+\omega^2\right)} - \frac{1}{\omega RC}\frac{\omega}{\left(s^2+\omega^2\right)}\right]. \tag{2.117}$$

As before, the transient term was neglected. The inverse Laplace transform may be rearranged as before:

$$i(t) = \frac{E_0}{R}\frac{1}{1+\dfrac{1}{(\omega RC)^2}}\left[\cos(\omega t) - \tan(\varphi)\sin(\omega t)\right]$$
$$= \frac{E_0}{R}\frac{1}{1+\dfrac{1}{(\omega RC)^2}}\left[\frac{\cos(\omega t)\cos(\omega t) - \sin(\varphi)\sin(\omega t)}{\cos(\omega)}\right], \tag{2.118}$$

and using the trigonometric identity, Eq. (2.114), and

$$\cos(\omega t)\cos(\omega t) - \sin(\varphi)\sin(\omega t) = \cos(\omega t + \varphi) \tag{2.119}$$

the final expression is obtained:

$$i(t) = \frac{E_0}{R}\cos^2(\varphi)\frac{\cos(\omega t+\varphi)}{\cos(\varphi)} = \frac{E_0}{R}\frac{1}{\sqrt{1+\dfrac{1}{(\omega RC)^2}}}\cos\left(\omega t+\varphi\right)$$
$$i(t) = \frac{E_0}{\sqrt{R^2+\dfrac{1}{(\omega C)}}}\cos\left(\omega t+\varphi\right) = \frac{E_0}{|Z|}\cos\left(\omega t+\varphi\right). \tag{2.120}$$

As in Example 2.13, the current is shifted in phase by angle φ and the modulus of the impedance is the same. Such an exercise is mathematically simple but time consuming. It should be added that the program Maple, which allows for symbolic calculations, allows for automatic separation of expressions into simple fractions using the function `convert(f, parfrac, s)`, in which function f of the parameter s is transformed into simple fractions, for example:

$$
\begin{aligned}
&> \mathrm{f} := \mathrm{s}^2/(\mathrm{s}^2+\mathrm{a}^2)/\left(\mathrm{s}+\mathrm{b}\right);\\
&\qquad f := \frac{s^2}{(s^2+a^2)(s+b)}\\
&> \mathrm{yy} := \mathrm{convert}(\mathrm{f}, \mathrm{parfrac}, \mathrm{s});\\
&\qquad yy := -\frac{a^2(b-s)}{\left(b^2+a^2\right)(s^2+a^2)} + \frac{b^2}{\left(b^2+a^2\right)(s+b)}.
\end{aligned}
\tag{2.121}
$$

2.8.3 Application of Fourier Transform to Determination of Impedances

In the Laplace transform above, we assumed a real transform with $s = \sigma$. As in the impedance technique, we usually apply a periodic cosine perturbation, and in such a case it is simpler to use the FT with $s = j\omega$. In general, a periodic potential perturbation, ΔE, applied to a circuit may be written as a complex analog of the simple periodic perturbation, see Eq. (2.56):

$$\Delta E = E_0 \exp(j\omega t) \tag{2.122}$$

or, in a more general form, assuming that there is an initial phase shift at $t = 0$:

$$\Delta E = E_0 \exp[j(\omega t + \phi_1)] = E_0 \exp(j\phi_1)\exp(j\omega t) = \widetilde{E}\exp(j\omega t). \tag{2.123}$$

Equation (2.123) represents a vector of length E_0 rotating with a constant frequency ω and with the initial phase shift ϕ_1, and projections of this vector on the x- and y-axes are called real and imaginary parts, respectively. The value of ΔE oscillates between $\pm E_0$. This is represented schematically in Fig. 2.22. Vector $\widetilde{E}$ can be written as a product of the amplitude and exponential:

$$\widetilde{E} = E_0 \exp(j\phi_1), \tag{2.124}$$

which represents a vector of lengths E_0 shifted by the angle ϕ_1 and the term exp ($j\omega t$), which is responsible for the rotation of the vector $\widetilde{E}$ at a constant rate ω. The parameter $\widetilde{E}$ is called a *phasor* and represents an immobile vector shifted by the angle ϕ_1. Similarly, for the vector corresponding to the current we can write

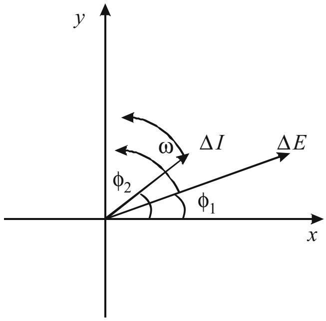


Fig. 2.22 Representation of rotating vectors ΔE, Eq. (2.124), and ΔI on complex plane. They both rotate with a constant angular frequency ω, but there is a constant phase difference between them, $\phi_1 - \phi_2$

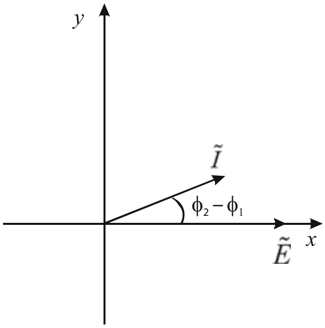


Fig. 2.23 Representation of phasors of $\widetilde{E}$ and $\widetilde{I}$ on complex plane plot. These vectors are immobile and there is a constant phase difference, $\phi_2 - \phi_1 = \phi$, between them. The initial phase angle for the potential $\widetilde{E}$ was chosen as zero

$$\Delta I = I_0 \exp[j(\omega t + \phi_2)] = I_0 \exp(j\phi_2)\exp(j\omega t) = \widetilde{I}\exp(j\omega t), \tag{2.125}$$

where $\widetilde{I}$ is the phasor of the current. The rotating vectors of $E(t)$ and $I(t)$ are shown in Fig. 2.22 and the corresponding phasors in Fig. 2.23. The initial phase shift for $\widetilde{E}$ is usually assumed to be zero because it is the signal of reference created by the signal generator and all other signals are referred to it. The *ac impedance of the system is defined as the ratio of phasors* $\widetilde{E}$ and $\widetilde{I}$:

$$\hat{Z}(j\omega) = \frac{\Delta E}{\Delta I} = \frac{\widetilde{E}}{\widetilde{I}}. \tag{2.126}$$

In other words, the impedance is the ratio of the FTs of the potential and current, which is equal to the ratio of the corresponding phasors:

$$\hat{Z}(j\omega) = \frac{F[E(t)]}{F[I(t)]} = \frac{\widetilde{E}}{\widetilde{I}}. \tag{2.127}$$

To better understand how the impedance is determined, let us suppose that the applied ac voltage and measured current are described by the following equations: $E(t) = E_0\cos(\omega t)$ and $I(t) = I_0\cos(\omega t + \pi/3)$, where $E_0 = 0.01$ V, $I_0 = 0.002$ A, $\omega = 2\pi f = 2\pi/T_a$, $T_a = 0.32$ s. The calculations are carried out in Exercise 2.7.

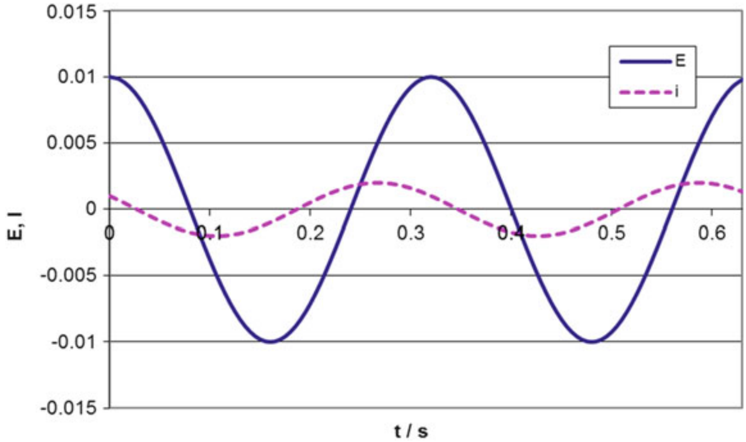


Fig. 2.24 Potential and current functions for calculation of impedance using following data: $E(t) = E_0 \cos(\omega t)$ and $I(t) = I_0 \cos(\omega t + \pi / 3)$,where $E_0 = 0.01$ V, $I_0 = 0.002$ A, $\omega = 2\pi f = 2\pi/T_a$, $T_a = 0.32$ s (Exercise 2.7)

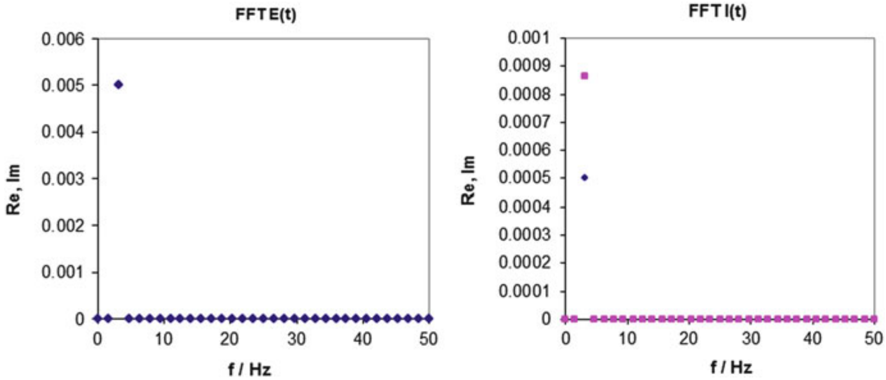


Fig. 2.25 Fast Fourier transform of potential and current functions in: real part – diamonds, imaginary – squares of functions in Fig. 2.24

The potential and current functions are displayed in Fig. 2.24 and their FTs in Fig. 2.25. Using complex calculations in Excel the ratio of the FT of the potential and the current gives the total impedance:

$$\widetilde{E} = 0.005 \text{ V}, \qquad \widetilde{I} = 3.20 \times 10^{-2} + 5.54256 \times 10^{-2} j \text{ A},$$
$$\hat{Z} = \widetilde{E}/\widetilde{I} = 2.5 - 4.33013 j \ \Omega,$$
$$\phi = -60^\circ, |Z| = 5 \ \Omega \text{ at } f = 3.125 \text{ Hz}.$$

Modern impedance measuring equipment is able to extract the impedance from the experimentally measured potential and current.

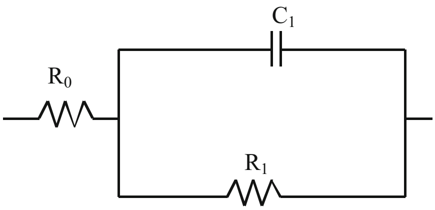


Fig. 2.26 Circuit for Example 2.15

2.8.4 Definition of Impedance

From the preceding section we can write a general definition of impedance. The general operational definition of impedance is described by Eq. (2.88):

$$\hat{Z}(s) = \frac{L[E(t)]}{L[i(t)]} = \frac{\overline{E}(s)}{\overline{i}(s)}, \tag{2.88}$$

where the symbol L denotes the Laplace transform, Eq. (2.21). As was mentioned earlier, the parameter s, called the frequency, may be complex: $s = \sigma + j\omega$. In the classical Laplace transform the parameter s is real: $s = \sigma$. To obtain the impedance of electrical circuits, the impedance of the elements R, C, and L are defined in Table 2.1 and the impedance of the total circuit is written using Ohm's and Kirchhoff's laws. The following examples illustrate this method.

Example 2.15 Write the impedance of the circuit in Fig. 2.26.

Applying the laws for the connections of impedances in series and in parallel, and substituting the impedance of the elements from Table 2.1, the total impedance of this circuit may be written as

$$\hat{Z}(s) = R_0 + \frac{1}{sC_1 + \frac{1}{R_1}}. \tag{2.128}$$

Example 2.16 Write the impedance of the circuit in Fig. 2.27.

The impedance of this circuit may be written as

$$\hat{Z}(s) = R_0 + \frac{1}{sC_1 + \frac{1}{R_1 + \frac{1}{sC_2 + \frac{1}{R_2}}}}. \tag{2.129}$$

From the preceding examples one can see that writing the impedance of the circuits is straightforward.

The foregoing examples are valid for any potential perturbation. In the particular case of ac impedance, that is, when the applied potential perturbation is sinusoidal, one uses the FT (Eq. 2.127):

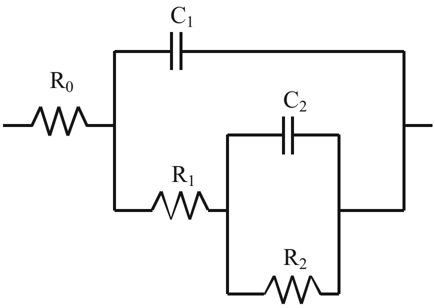


Fig. 2.27 Circuit for Example 2.16

$$\hat{Z}(j\omega) = \frac{F[E(t)]}{F[I(t)]} = \frac{\widetilde{E}(j\omega)}{\widetilde{I}(j\omega)}, \tag{2.127}$$

where the parameter s is imaginary: $s = j\omega$. It should be stressed that all the definitions presented above are equivalent for periodic signal perturbation while the operator impedance applies better to any perturbation. Besides *impedance* other terms are also used; the inverse of impedance is *admittance:*

$$\hat{Y}(s) = \frac{1}{\hat{Z}(s)}. \tag{2.130}$$

Both impedance and admittance are called *immittances*. Between other related functions, *complex dielectric constant* should also be mentioned [78]. It is used in the analysis of dielectric relaxation and is obtained from the measured admittance (impedance) of a cell with a given dielectric (liquid or solid):

$$\hat{\varepsilon} = \frac{\hat{Y}}{j\omega C_c}, \tag{2.131}$$

where $\hat{Y}$ is the admittance of the cell $\hat{Y} = j\omega\hat{C}$, and

$$\hat{C} = \frac{\hat{\varepsilon}\,\varepsilon_0 A_c}{d} \tag{2.132}$$

is the capacitance of the studied material, $\hat{\varepsilon}$ is the complex dielectric constant (function of the frequency), $\varepsilon_0 = 9.8542 \times 10^{-14}$ F/cm is the dielectric permittivity of a vacuum, d is the distance between electrodes, A_c is their surface area, and C_c is the capacity of the empty cell (containing air or in vacuum) $C_c = \varepsilon_0 A_c/d$. Another function used in dielectric research is the modulus, $\hat{M} = 1/\hat{\varepsilon}$.

To obtain the ac impedance of circuits represented by Eqs. (2.128) and (2.129) substitution of s must be done, and the appropriate equations become

$$\hat{Z}(j\omega) = R_0 + \frac{1}{j\omega C_1 + \frac{1}{R_1}}, \tag{2.133}$$

Table 2.2 Operational and ac impedance of linear electrical elements

Element	Operational impedance	Ac impedance
R	R	R
C	$\frac{1}{sC}$	$\frac{1}{j\omega C}$
L	sL	$j\omega L$

$$\hat{Z}(j\omega) = R_0 + \frac{1}{j\omega C_1 + \frac{1}{R_1 + \frac{1}{j\omega C_2 + \frac{1}{R_2}}}}. \tag{2.134}$$

Therefore, in general, the impedance of the electrical elements used is displayed in Table 2.2.

Equations (2.133) and (2.134) can be further rearranged using the complex calculus. For example, Eq. (2.133) may be rearranged into

$$\begin{aligned}\hat{Z}(j\omega) &= R_0 + \frac{R_1}{1 + j\omega R_1 C_1} = R_0 + \frac{R_1(1 - j\omega R_1 C_1)}{1 + (\omega R_1 C_1)^2} = \\ &= R_0 + \frac{R_1}{1 + (\omega R_1 C_1)^2} - j\frac{\omega R_1 C_1}{1 + (\omega R_1 C_1)^2}\end{aligned} \tag{2.135}$$

and the impedance consists of two parts, one real and positive and one imaginary and negative:

$$\begin{aligned}\mathrm{Re}\left[\hat{Z}(j\omega)\right] &= R_0 + \frac{R_1}{1 + (\omega R_1 C_1)^2}, \\ \mathrm{Im}\left[\hat{Z}(j\omega)\right] &= -\frac{\omega R_1 C_1}{1 + (\omega R_1 C_1)^2},\end{aligned} \tag{2.136}$$

and both parts are frequency dependent. Similarly, Eq. (2.134) may be rearranged into

$$\hat{Z}(j\omega) = R_0 + \frac{R_1 + R_2 + j\omega R_1 R_2 C_2}{1 - \omega^2 R_1 R_2 C_1 C_2 + j\omega[R_2 C_2 + C_1(R_1 + R_2)]}, \tag{2.137}$$

and multiplying by the conjugated form of the denominator yields

$$\begin{aligned}\mathrm{Re}\left[\hat{Z}(j\omega)\right] &= R_0 \frac{(R_1 + R_2)(1 - \omega^2 R_1 R_2 C_1 C_2) + \omega^2 R_1 R_2 C_2[R_2 C_2 + C_1(R_1 + R_2)]}{(1 - \omega^2 R_1 R_2 C_1 C_2)^2 + \omega^2[R_2 C_2 + C_1(R_1 + R_2)]^2}, \\ \mathrm{Im}\left[\hat{Z}(j\omega)\right] &= \frac{\omega R_1 R_2 C_2(1 - \omega^2 R_1 R_2 C_1 C_2) - \omega(R_1 + R_2)[R_2 C_2 + C_1(R_1 + R_2)]}{(1 - \omega^2 R_1 R_2 C_1 C_2)^2 + \omega^2[R_2 C_2 + C_1(R_1 + R_2)]^2}.\end{aligned} \tag{2.138}$$

The calculations are simple but time consuming and may be carried out easily using Maple (see below):

```
>Z: = 1/(I * om * C1 + 1/(R1 + 1/(I * om * C2 + 1/R2)));
```

$$Z: = \frac{1}{I\ om\ C1 + \frac{1}{R1 + \frac{1}{I\ om\ C2 + \frac{1}{R2}}}}$$

```
> Z1: = simplify(Z);
```

$$Z1 := -\frac{I\,R1\ om\ C2\,R2 + R1 + R2}{om^2\ C1\,R1\,C2\,R2 - I\ om\ C1\,R1 - I\ om\ C1\,R2 - I\ om\ C2\,R2 - 1}$$

```
> evalc(Re(Z1));
```

$$-\frac{(R1 + R2)(om^2\ C1\,R1\,C2\,R2 - 1)}{(om^2\ C1\,R1\,C2\,R2 - 1)^2 + (-om\ C1\,R1 - om\ C1\,R2 - om\ C2\,R2)^2} - \frac{R1\ om\ C2\,R2(-om\ C1\,R1 - om\ C1\,R2 - om\ C2\,R2)}{(om^2\ C1\,R1\,C2\,R2 - 1)^2 + (-om\ C1\,R1 - om\ C1\,R2 - om\ C2\,R2)^2}$$

```
>evalc(Im(Z1));
```

$$-\frac{R1\ om\ C2\,R2\ (om^2\ C1\,R1\,C2\,R2 - 1)}{(om^2\ C1\,R1\,C2\,R2 - 1)^2 + (-om\ C1\,R1 - om\ C1\,R2 - om\ C2\,R2)^2} + \frac{(R1 + R2)(-om\ C1\,R1 - om\ C1\,R2 - om\ C2\,R2)}{(om^2\ C1\,R1\,C2\,R2 - 1)^2 + (-om\ C1\,R1 - om\ C1\,R2 - om\ C2\,R2)^2}.$$

The obtained results might be visualized using impedance plots.

2.9 Circuit Description Code

Boukamp [79] has proposed a simple notation for the connection of various electrical elements. It can be used instead of circuit schematics.

A simple connection of the elements in series, for example R, L, and C in series, is $R\ L\ C$. The use of parentheses means a change from a connection in series to a connection in parallel. That is, the connection of R and C in parallel (Fig. 2.33) is (RC), and the connection of R, L, and C parameters in parallel is (RLC). The connection of R_s with a parallel connection of R and C becomes (Fig. 2.34) $R_s(RC)$.

The next parentheses indicate a subsequent change from parallel to series connection. Inserting the capacitance in series with the resistance in a nested circuit (Fig. 2.35) is described as $R_s(C_{dl}(R_{ct}C_p))$, that is, R_s in series with the parallel connection of C_{dl} and a series connection of R_{ct} and C_p.

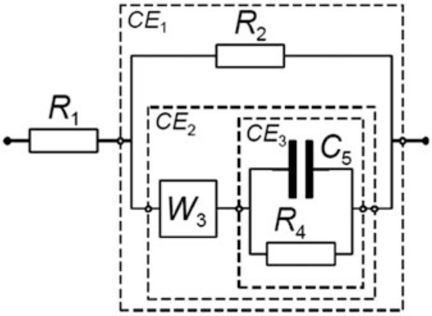


Fig. 2.28 Example of a more complex circuit from ref. [79] with permission of author

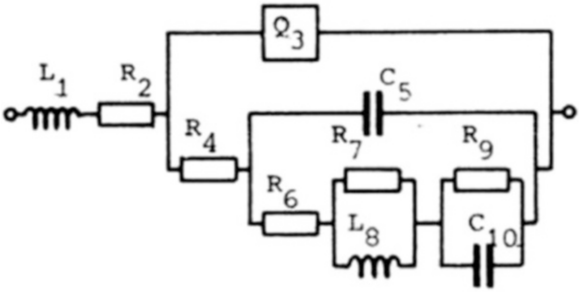


Fig. 2.29 Example of a more complex circuit from ref. [79] with permission of author

The two circuits in Fig. 2.37 in series and nested are described by $R_0(C_1R_1)(R_2C_2)$ and $R_0(C_1(R_1(C_2R_2)))$. Other distributed circuit elements can also be used: Q represents a constant phase element, CPE, W a semi-infinite Warburg element, W_s a finite length transmissive element, W_o a finite length reflecting element, and so forth. In the case of distributed elements, it is preferable to define them specifically.

Let us look at a more complex example (Fig. 2.28). It can be represented as $R_1(R_2(W_3(C_5R_4)))$. In this example, R_1 is in series with the circuit CE_1, which is R_2 in parallel with CE_2, which is W_3 in series with CE_3, that is, a parallel connection of C_5 and R_4.

Another, more complex, example is shown in Fig. 2.29. It is described using Boukamp's notation as follows: $L_1R_2(Q_3(R_4(C_5(R_6(R_7L_8)(R_9C_{10})))))$.

In this way, almost any arbitrary circuit may be simply represented.

2.10 Impedance Plots

Impedance measurements produce numerical results, usually as real Z′ and imaginary Z″ impedances or modulus |Z| and phase angle φ as functions of frequency. Visual (graphical) inspection of the obtained results usually makes it possible to identify the electrical equivalent circuit containing R, C, and L elements.

However, this inspection is insufficient, and mathematical modeling involving fit to the circuit or equation should be carried out (Chap. 14). In the case of real electrochemical systems, the situation is more complex because the studied objects are not electrical circuits but systems involving interfaces, electrochemical reactions, transport of species, etc. Nevertheless, graphical inspection usually helps in deciding whether the experiments are proceeding correctly and in making a first assessment of data.

There are two fundamental types of graph:

1. Complex plane plots, also called Argand diagrams (or, less correctly, Nyquist plots). They are plots of imaginary versus real impedance. In these plots -Z″ is plotted versus Z′ as the imaginary impedances of the electrochemical systems are usually negative. It should be added that, although the name Nyquist plot is often used in the electrochemical literature, it is not precise because Nyquist plots are used for assessing the stability of a system with feedback.
2. Bode plots. There are two types of Bode plot:
   (a) log |Z| (magnitude) versus log f (frequency)
   (b) phase angle φ versus log f

It should be stressed that in complex plane plots, the unit length of real and imaginary parts should be the same; otherwise, deformation of the plots is observed. Moreover, these plots do not contain all the information about frequency, and some frequencies are often added in these plots to better visualize the frequency domain. They are preferred by electrochemists because a model can be more easily found from them (especially by inexperienced researchers). On the other hand, two Bode plots contain all the necessary information. From a practical point of view, typical data acquisition and analysis programs display both plots. It is strongly recommended that both types of plots be used, especially when comparing experimental data with the fit to the appropriate model. In some cases other plots are also presented, for example, complex admittance plots, complex capacitance plots, and tridimensional impedance plots. Admittance plots can be useful when dealing with blocking systems, where very small and very large impedances are present (Fig. 2.30).

An example of a tridimensional plot, Z″, Z′, log f, created automatically in ZView, is displayed in Fig. 2.31.

Several examples of impedance plots are presented in Exercises 2.8 and 2.10.

First, let us look at the complex plane and Bode plots obtained for an R-C connection in series, RC in Boukamp's notation, with $R = 150\ \Omega$, $C = 40\ \mu\text{F}$, Exercise 2.8. The impedance of such a circuit is described as

$$\hat{Z}(j\omega) = R + \frac{1}{j\omega C} = R - j\frac{1}{\omega C}. \tag{2.139}$$

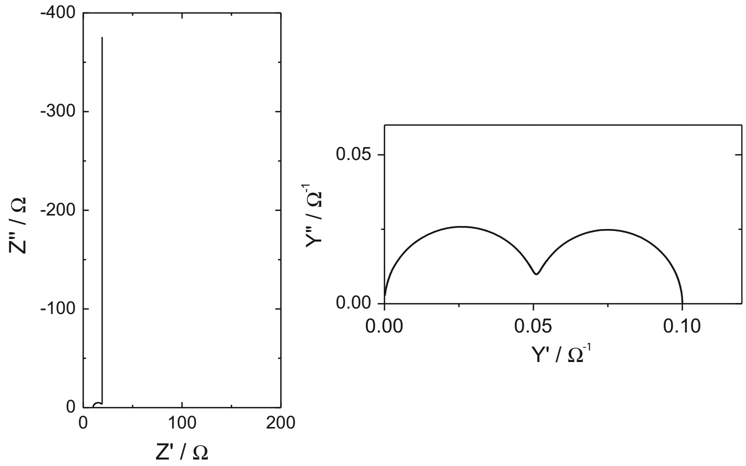


Fig. 2.30 Complex plane impedance, Z′ vs. Z″, Eq. (2.139), and admittance, Y′ vs. Y″, Eq. (2.141), plots for circuit $R_s(C_{dl}(R_pC_p))$ with $R_s = 10\ \Omega$, $C_{dl} = 4 \times 10^{-5}$ F, $R_p = 10\ \Omega$, $C_p = 0.001$ F

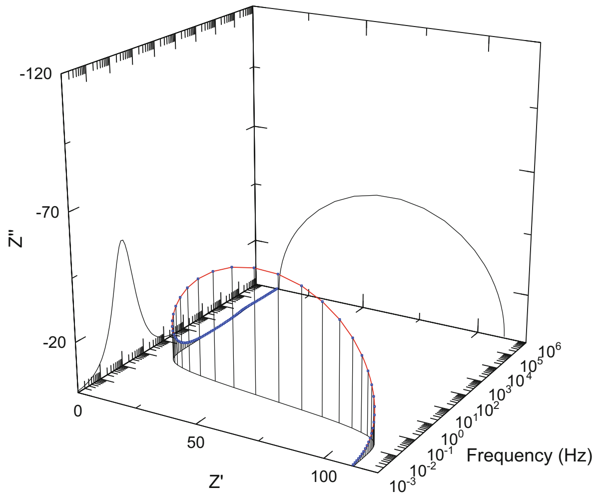


Fig. 2.31 Example of tridimensional impedance (in Ω) plot generated by ZView

The modulus and the phase angle are

$$|Z| = \sqrt{R^2 + \frac{1}{(\omega C)^2}}$$
$$\varphi = \operatorname{atan}\left(\frac{Z''}{Z'}\right) = \operatorname{atan}\left(-\frac{1}{\omega RC}\right) = \operatorname{atan}\left(\frac{1}{\omega RC}\right), \tag{2.140}$$

and the admittance is

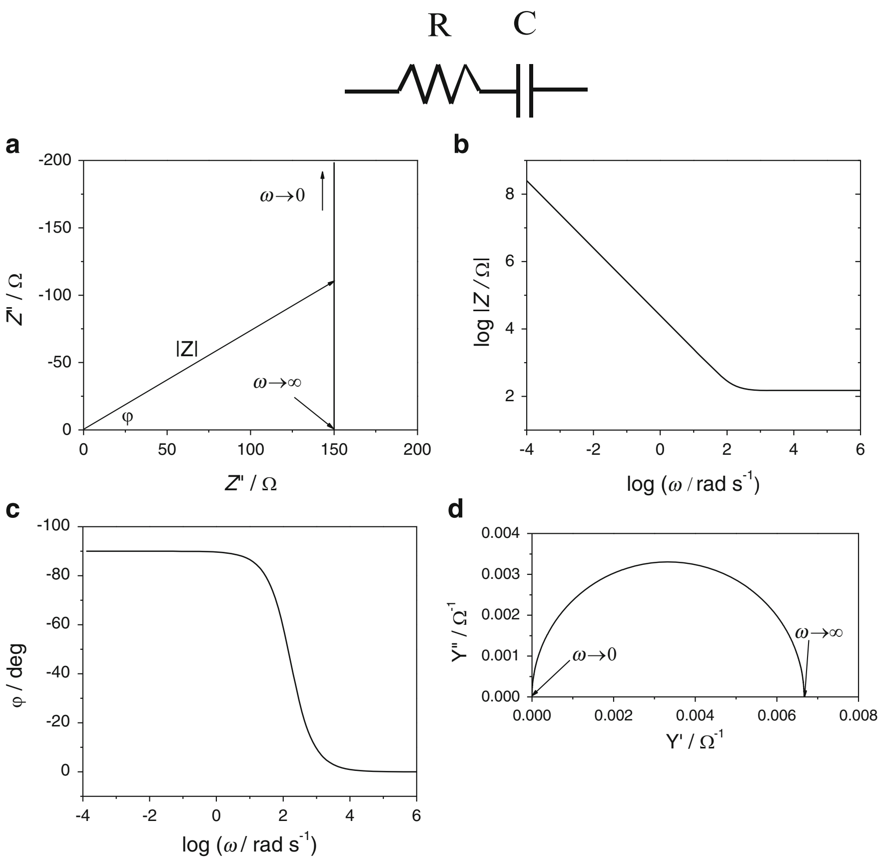


Fig. 2.32 Complex plane (**a**), Bode magnitude (**b**), Bode phase angle (**c**), and complex admittance (**d**) plots for R-C connection in series; $R = 150\ \Omega$, $C = 40\ \mu\mathrm{F}$

$$\hat{Y}(j\omega) = \frac{1}{\hat{Z}(j\omega)} = \frac{1}{R - j\frac{1}{\omega C}} = \frac{R}{R^2 + \frac{1}{\omega^2 C^2}} + j\frac{1}{\omega C\left(R^2 + \frac{1}{\omega^2 C^2}\right)}. \tag{2.141}$$

Equation (2.140) should be compared with Eq. (2.115); it is evident that the same equation describing impedance was obtained from Eq. (2.139) using complex algebra. The plots are displayed in Fig. 2.32.

In a complex plane plot, the real part is always constant, $Z' = R$, and the imaginary part, $Z'' = -1/\omega C$, changes from zero at infinite frequency to infinity at zero frequency. A dc current cannot circulate through such a circuit because $|Z|$ also goes to infinity as f goes to zero.

The Bode magnitude contains two elements: R and $1/\omega C$. The plot presents a constant value $\log|Z| = \log R$ at high frequencies and a straight line with a slope -1:

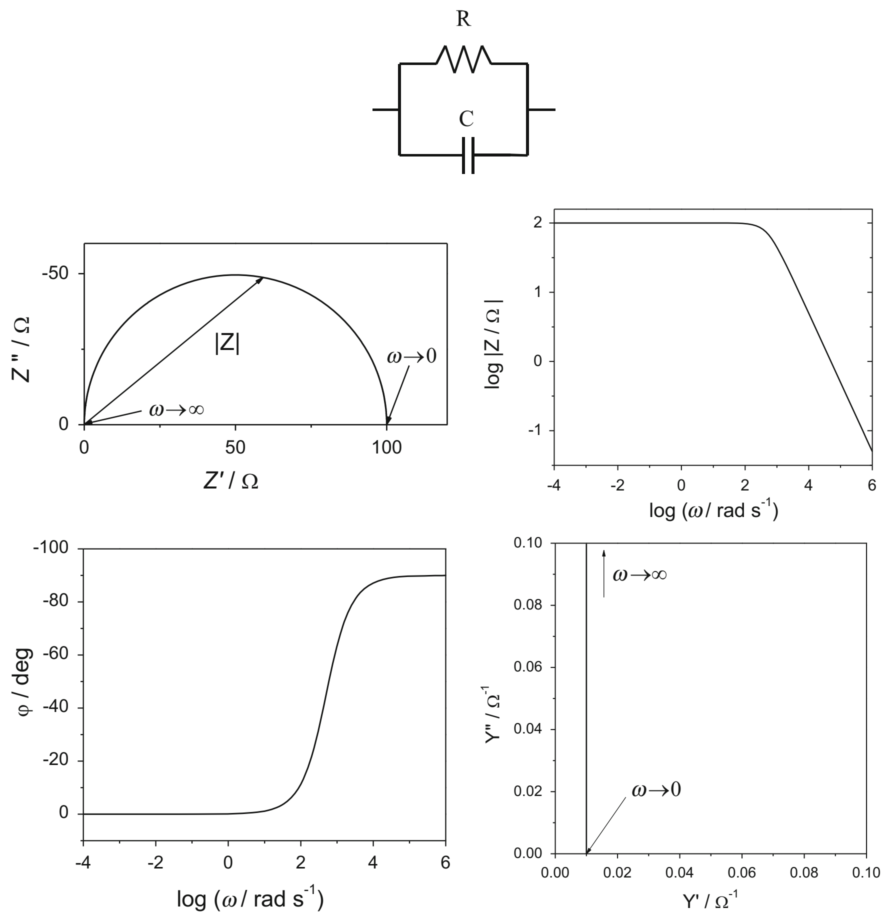


Fig. 2.33 Complex plane impedance, Bode, and complex plane admittance plots for a connection of R and C in parallel (RC), $R = 100\ \Omega$, $C = 20\ \mu\text{F}$

$\log |Z| = -\log \omega - \log C$ at low frequencies. There is an inflection point where these two elements are identical, giving the break-point frequency $\omega = 1/RC$. The Bode phase angle plot represents two bend points and changes between angle zero at high frequencies and 90° at very low frequencies.

The admittance presents a semicircle (Eq. 2.141); at very low frequencies the admittance is zero (impedance infinite), and at high frequencies it is equal to $1/R$ because the impedance of the capacitance is zero. The maximum of admittance is at $\omega = 1/RC$.

Let us now look at the R-C connection in parallel, i.e., the circuit (RC) using Boukamp's notation (Exercise 2.10). The impedance of the system is

$$Z = \frac{1}{\frac{1}{R} + j\omega C} = \frac{R}{1 + j\omega RC} = \frac{R}{1 + (\omega RC)^2} - j\frac{\omega R^2 C}{1 + (\omega RC)^2}, \tag{2.142}$$

$$|Z| = \frac{\sqrt{R^2 + \left(\omega R^2 C\right)^2}}{1 + (\omega RC)^2} \quad \varphi = \operatorname{atan}(-\omega RC) = -\operatorname{atan}(\omega RC), \tag{2.143}$$

and the admittance is

$$\hat{Y} = \frac{1}{R} + j\omega C. \tag{2.144}$$

The impedance presents a semicircle; when the frequency goes to infinity, the impedance goes to zero because the impedance of the capacitor becomes zero and when the frequency goes to zero the impedance becomes real $Z = R$ because a constant dc current can flow through the circuit. The maximum of the imaginary part is observed at the frequency $\omega = 1/RC$, and RC is called the time constant of the system. As in the preceding example, the imaginary part of the impedance is always negative.

There are two linear parts of the Bode magnitude plot; when the frequency is very low, Eq. (2.142) reduces to $|Z| = R$, and when the frequency is very large, the real part becomes small and $|Z| = 1/\omega C$. There is one break-point frequency on a Bode magnitude plot, when $R = 1/\omega C$, and the break-point frequency corresponds to the system time constant:

$$\omega = \frac{1}{\tau} = \frac{1}{RC}. \tag{2.145}$$

The admittance plot for (RC) connections is similar in shape to the impedance plot for an R-C connection in series. The difference is that for circuits containing capacitances the imaginary part of the impedance is negative and that of the admittance positive.

Next, let us consider R_s in series with a parallel connection of R and C, that is, circuit $R_s(CR)$ (Exercise 2.11 and Fig. 2.34).

The total impedance of the system is

$$\begin{aligned} \hat{Z} &= R_s + \frac{1}{\frac{1}{R} + j\omega C} = R_s + \frac{R}{1 + j\omega RC} \\ &= R_s + \frac{R}{1 + (\omega RC)^2} - j\frac{\omega R^2 C}{1 + (\omega RC)^2}, \end{aligned} \tag{2.146}$$

and the complex plane plots are displayed in Fig. 2.34.

A complex plane plot represents a semicircle shifted to higher values by a constant resistance R_s. The high-frequency current flows through the capacitance C and the total impedance is real and equal to R_s. The dc current ($\omega = 0$) flows through R_s and R and the impedance is real and here equal to $R_s + R$.

The phase angle is

$$\varphi = \operatorname{atan}\left(\frac{Z''}{Z'}\right) = -\operatorname{atan}\left[\frac{\omega R^2 C}{R_s + R + R_s(\omega RC)^2}\right], \tag{2.147}$$

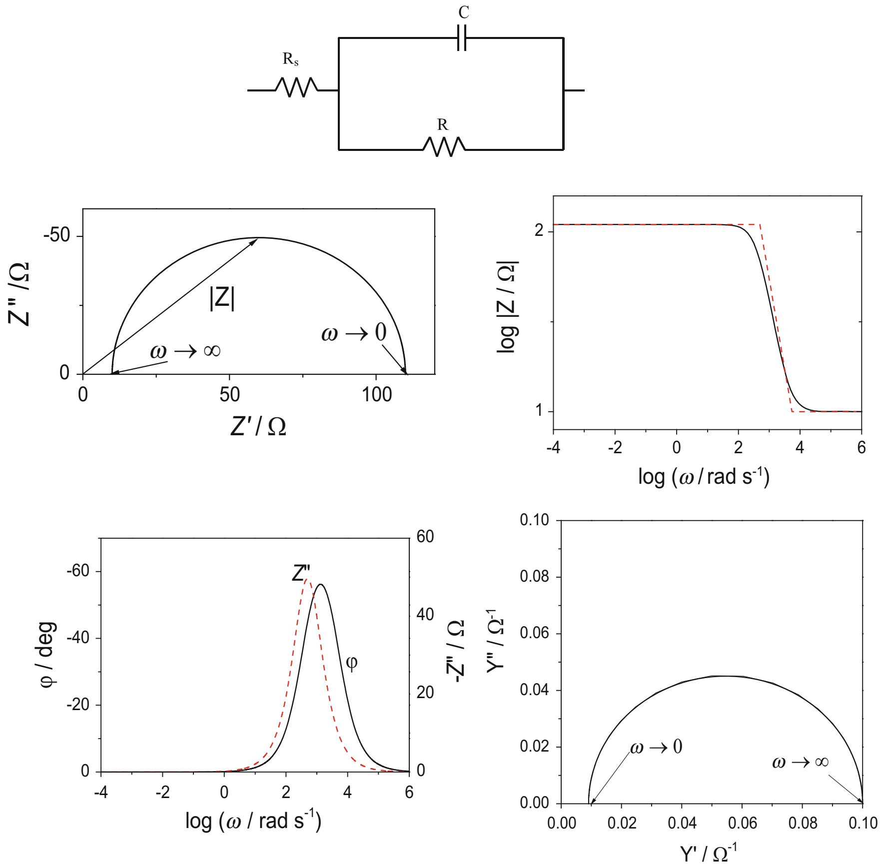


Fig. 2.34 Complex plane impedance, Bode, and complex plane admittance plots for resistance R_s with connection of R and C in parallel, $R_s = 10\ \Omega$, $R = 100\ \Omega$, $C = 20\ \mu F$

and the maximum of the phase angle is observed at the frequency

$$\omega_{\max} = \frac{1}{RC}\sqrt{\frac{R_s}{R} + 1}, \tag{2.148}$$

which in this example appears at $\omega_{\max} = 1658$ rad s^{-1}. One notices that the maximum of the phase angle appears at a frequency higher than the maximum of the imaginary part of the semicircle, which is at $\omega_{\max,\ \mathrm{Im}} = 1/RC = 500$ rad s^{-1}, as in the simple (RC) parallel circuit. This is schematically displayed in Fig. 2.34, Bode phase angle. The value of $\omega_{\max}$ approaches that of $\omega_{\max,\ \mathrm{Im}}$ when $R_s / R \ll 1$, that is, when the series resistance R_s is very small.

2.10.1 Interpretation of Bode Magnitude Plots

The total impedance of the circuit in Fig. 2.34 can be rewritten as

$$\begin{aligned}\hat{Z} &= R_s + \frac{1}{1+j\omega RC} = \frac{R_s + R + j\omega R_s RC}{1+j\omega RC} = (R_s+R)\frac{1+j\omega\left(\dfrac{R_s R}{R_s+R}C\right)}{1+j\omega(RC)} \\ &= (R_s+R)\frac{1+j\omega\tau_2}{1+j\omega\tau_1},\end{aligned} \tag{2.149}$$

where τ_1 and τ_2 are the two characteristic time constants of the circuit in Fig. 2.34; these time constants are $\tau_1 = 2$ ms and $\tau_1 = 0.1818$ ms, corresponding to two break-point frequencies, $\omega_1 = 500$ rad s^{-1} and $\omega_2 = 5500$ rad s^{-1}. From Eq. (2.149) the Bode magnitude plot can be evaluated:

$$\log|Z| = \log(R_s + R) + \log(|1 + j\omega\tau_2|) - \log(|1 + j\omega\tau_1|). \tag{2.150}$$

Depending on the frequencies, the logarithmic terms $\log(|1 + j\omega\tau|)$ may take two different values; when $\omega\tau \ll 1$, $\log(|1 + j\omega\tau|) = 0$, and when $\omega\tau \gg 1$, $\log(|1 + j\omega\tau|) = \log\omega + \log\tau$, which gives a line with a slope of one. From this equation three asymptotes can be constructed. When $\omega\tau \ll 1$ $\log|Z| = \log(R_s + R)$, in the intermediate frequency zone, taking into account that $\tau_2 < \tau_1$, $\log|Z| = \log(R_s + R) + \log\omega + \log\tau_2$, and at high frequencies the third term in Eq. (2.150) must also be taken into account, and the impedance becomes $\log|Z| = \log(R_s + R) + \log\omega + \log\tau_2 - \log\omega - \log\tau_1 = \log R_s$. This produces three straight lines and two break-point frequencies on the Bode magnitude plot. This is schematically shown in Fig. 2.34 (Bode magnitude) as a dashed line. The method presented above allows for a quick visualization of Bode magnitude plots.

Let us look now at the circuit in Fig. 2.35, denoted as $R_s(C_{dl}(R_{ct}C_p))$; it is described in detail in Exercise 2.12. The impedance of the system is easily written as

$$\hat{Z} = R_s + \cfrac{1}{j\omega C_{dl} + \cfrac{1}{R_{ct} + \cfrac{1}{j\omega C_p}}}. \tag{2.151}$$

The total impedance can be separated into real and imaginary parts, although the calculations are laborious and it is easy to make a mistake. It can be done easily in Maple (Exercise 2.12), and the obtained impedances are

$$Z' = \frac{R_s\left(C_{dl}^2 + 2C_{dl}C_p\right) + C_p^2(R_s + R_{ct}) + \left(R_s R_{ct} C_{dl} C_p \omega\right)^2}{\left(C_{dl} + C_p\right)^2 + \left(R_{ct} C_{dl} C_p \omega^2\right)^2}, \tag{2.152}$$

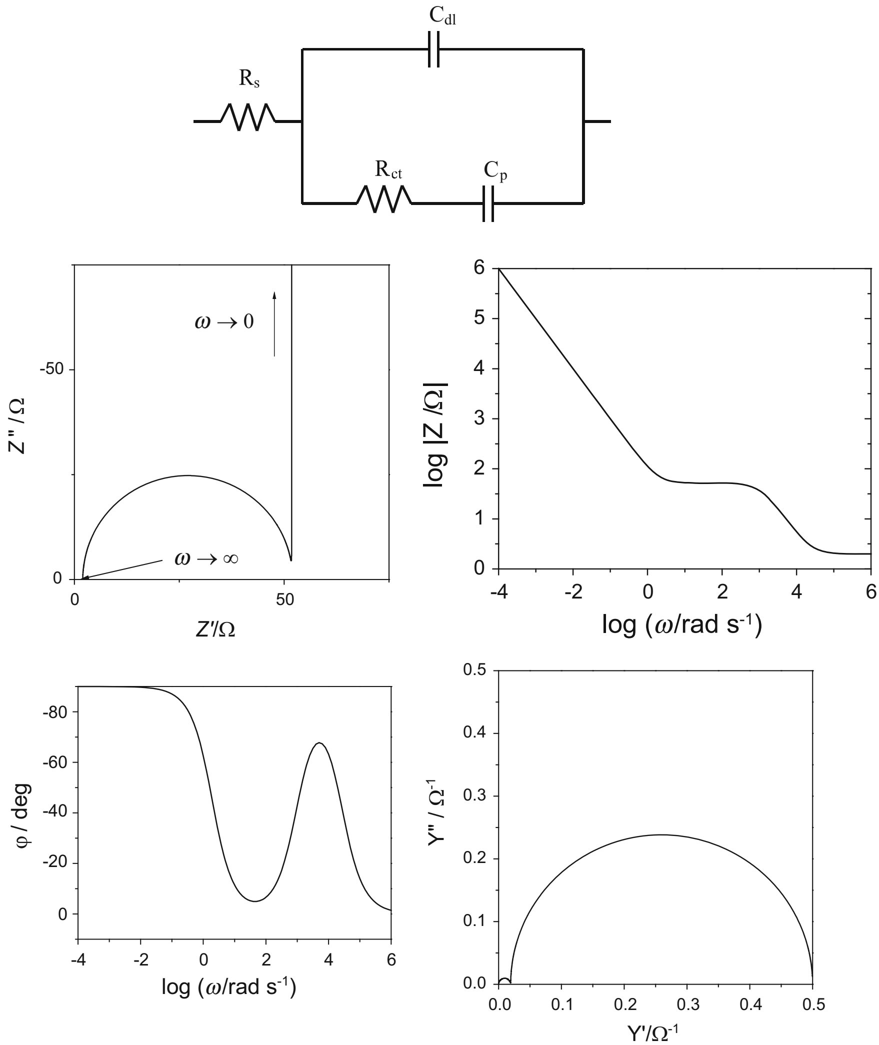


Fig. 2.35 Complex plane impedance, Bode, and complex plane admittance plots for circuit $R_s(C_{dl}(R_{ct}C_p))$; $R_s = 2\ \Omega$, $R_{ct} = 50\ \Omega$, $C_{dl} = 20\ \mu\text{F}$, $C_p = 0.01$ F

$$Z'' = -\frac{C_{dl} + C_p + C_{dl}\left(R_{ct}C_p\omega\right)^2}{\left[\left(C_{dl} + C_p\right)^2 + \left(R_{ct}C_{dl}C_p\omega^2\right)^2\right]\omega}. \tag{2.153}$$

To calculate the impedances, either the preceding equations may be used or they can be calculated stepwise in Excel starting from $\hat{Z}_f$:

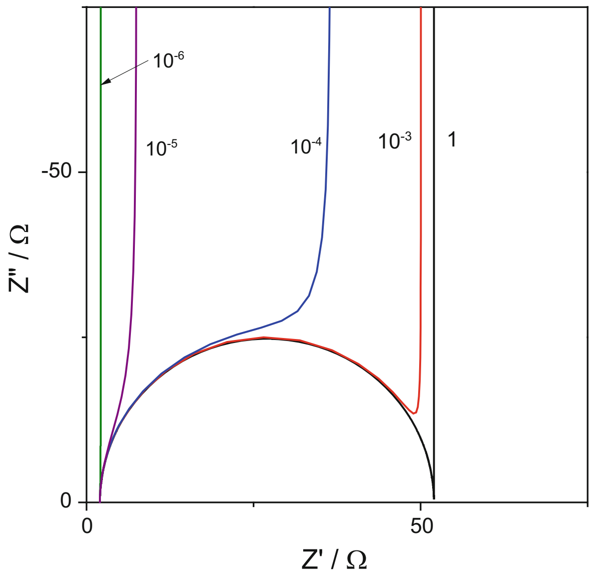


Fig. 2.36 Complex plane plots for circuit in Fig. 2.35 and different values of parameter C_p indicated in figure in farads

$$
\begin{aligned}
\hat{Z}_f &= R_{ct} + \frac{1}{j\omega C_p} = R_{ct} - j\frac{1}{\omega C_p},\\
\hat{Y}_f &= \frac{1}{\hat{Z}_f},\\
\hat{Y}_{el} &= \hat{Y}_f + j\omega C_{dl},\\
\hat{Z}_{el} &= \frac{1}{\hat{Y}_{el}},\\
\hat{Z} &= R_s + \hat{Z}_{el}.
\end{aligned}
\tag{2.154}
$$

The complex plane and the Bode plots are displayed in Fig. 2.35.

Looking at the circuit, it is evident that a dc current cannot flow through it because the two parallel branches are blocked by capacitances. This means that the low-frequency imaginary impedance part must go to negative infinity. On the other hand, at very high frequencies the capacitances do not obstruct current flow (impedance of the capacitance goes to zero), and the total ac current flows through R_s and the upper branch; therefore, the impedance is R_s. In the medium frequencies, the coupling of R_{ct} and C_{dl} produces a semicircle with the time constant $\tau = R_{ct}C_{dl} = 1$ ms. On Bode plots a semicircle produces an S-shaped wave followed by a straight line with a slope of -1. The phase angle plots show a peak at higher frequencies, corresponding to the semicircle, and then the phase angle goes to $-90°$ as the imaginary part of the impedance goes to $-\infty$. On the complex admittance at high frequencies the admittance is $1/2\ \Omega = 0.5\ \Omega^{-1}$, at low frequencies it goes to

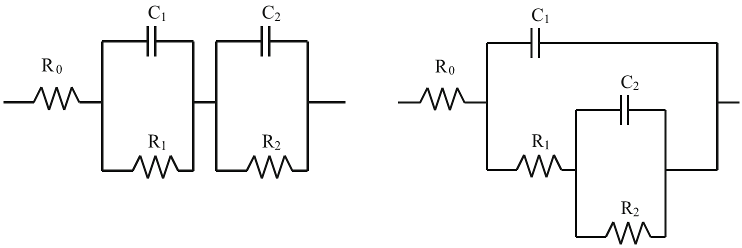


Fig. 2.37 Examples of two circuits producing two semicircles on complex plane plots: left series $R_0(R_1C_1)(R_2C_2)$ and right nested $R_0(C_1(R_1(R_2C_2)))$

zero as the impedance goes to $-\infty$. Two semicircles are observed on the complex admittance plots. The radius of the small low-frequency semicircle corresponds to $1/(R_s + R_{ct}) = 1/52\ \Omega^{-1}$, which is the total low-frequency real resistance in the complex impedance plots.

It is interesting to note that the shape of complex plane plots depends on the relative ratio of both capacitances. Figure 2.36 shows a series of plots for different values of C_p and the same values of all other parameters as previously. When C_p is very large ($C_p \gg C_{dl}$), a full semicircle touching the real part is formed. With a decrease of C_p, a smaller part of the semicircle is produced. Finally, when $C_{dl} \gg C_p$, the current flows not through the branch R_p-C_p but through R_s-C_{dl}, which produces a straight line on the complex plane plots, as in Fig. 2.32.

2.10.2 Circuits with Two Semicircles

Let us consider two circuits leading to the formation of two semicircles on complex plane plots, one consisting of two parallel (RC) circuits in series and another a nested circuit (Fig. 2.37), i.e., $R_0(R_1C_1)(R_2C_2)$ and $R_0(C_1(R_1(R_2C_2)))$. In the simulations, the following parameters were used: $R_0 = 10\ \Omega$, $R_1 = R_2 = 100\ \Omega$, $C_1 = 20\ \mu\text{F}$, and different values of $C_2 = 0.1$, 10^{-3}, 10^{-4}, 2×10^{-5}, and 10^{-5} F. This circuit contains two time constants: $\tau_1 = R_1C_1 = 2$ ms and $\tau_2 = R_2C_2 = 10$, 0.1, 0.01, 0.001, and 0.002 s. The results of simulations of the complex plane and Bode plots are displayed in Fig. 2.38. The numerical values recopied from ZView can be found in files (Exercise 2.13). When the two time constants are very different, two well-separated semicircles are formed on the complex plane plots. At the same time, two steps are observed on the Bode magnitude plots and two peaks on the Bode phase angle plots. When the two time constants merge, separation of the two semicircles becomes less obvious, a large semicircle is formed, $\tau_2 = 0.01$ s, and later it is difficult to decide just by looking at the plots that there still are two semicircles, $\tau_2 = 0.001$ s. In this case, only an analysis of the impedances (i.e., fit to the appropriate circuit) may determine whether there is one or two semicircles. Finally, when the time constants of the two circuit elements

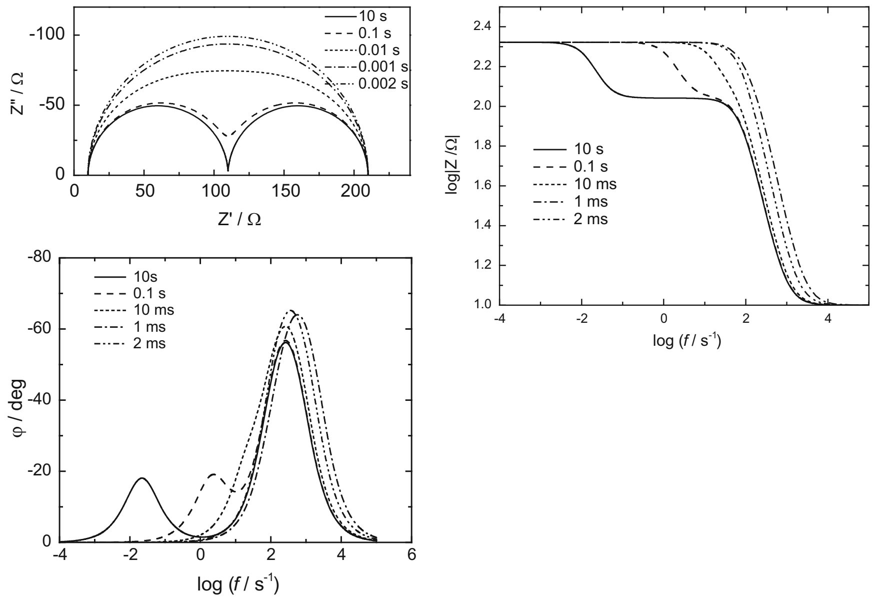


Fig. 2.38 Complex plane and Bode plots for a series circuit in Fig. 2.37, $R_0(R_1C_1)(R_2C_2)$, using following parameters: $R_0 = 10\ \Omega$, $R_1 = R_2 = 100\ \Omega$, $C_1 = 20\ \mu\text{F}$, and different values of $C_2 = 0.1, 10^{-3}, 10^{-4}, 2 \times 10^{-5}$, and 10^{-5} F. Values of τ_2 are indicated on plots

are identical, one semicircle appears in the complex plane plots. This effect is confirmed by the equation

$$Z = R_0 + \frac{1}{\frac{1}{R_1} + j\omega C_1} + \frac{1}{\frac{1}{R_2} + j\omega C_2} = R_0 + \frac{1}{\frac{1}{R_1} + j\omega C_1} + \frac{1}{\frac{1}{R_1} + j\omega C_1} =$$

$$= R_0 + \frac{2}{\frac{1}{R_1} + j\omega C_1} = R_0 + \frac{1}{\frac{1}{(2R_1)} + j\omega\left(\frac{C_1}{2}\right)}. \tag{2.155}$$

In such a case, one semicircle on the complex plane plots has a diameter of $2R_1 = 200\ \Omega$ and a capacitance of $C_1/2 = 10\ \mu\text{F}$. In this case, analysis of the circuit reveals only one time constant, although two identical parallel (RC) elements were used in simulations.

Let us look now at the impedance plots for a nested circuit using the same parameters as for a circuit in series. The results are presented in Fig. 2.39.

Note that, using the same set of parameters R_1, C_1, R_2, and C_2, different plots are obtained for both circuits. Nevertheless, exactly the same plots as in the case of a nested circuit can be obtained using a circuit in series but with different parameters.

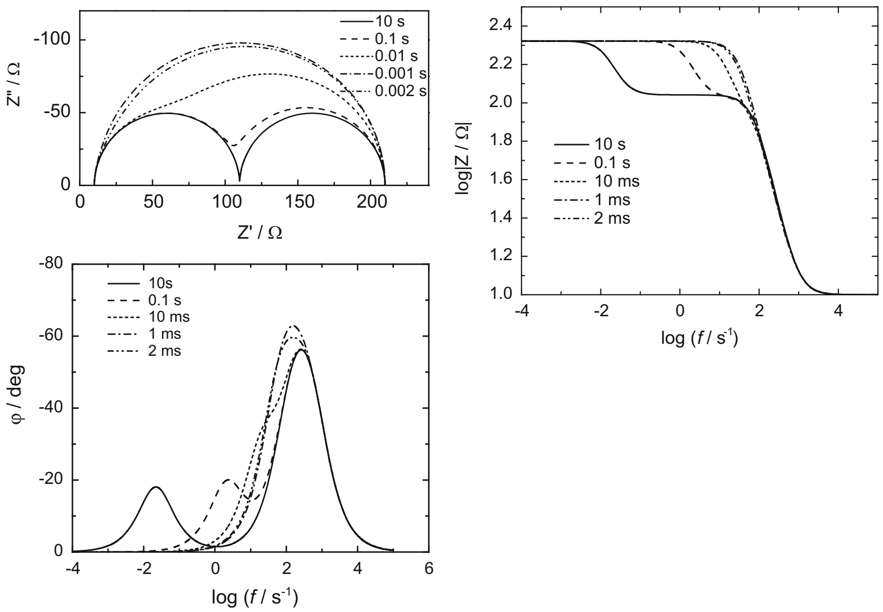


Fig. 2.39 Complex plane and Bode plots for a nested circuit in Fig. 2.37, $R_0(C_1(R_1(R_2C_2)))$, using parameters as in Fig. 2.38. Values of τ_2 are indicated on plots

Table 2.3 Results of fit of impedances in Fig. 2.39 to circuit containing two parallel (RC) elements in series. The parameters of the nested circuit are as follows: $R_0 = 10\ \Omega$, $R_1 = R_2 = 100\ \Omega$, $C_1 = 20\ \mu$F, and different assumed values of C_2 indicated below; the parameters found using fit to the series circuit are indicated

C_2 assumed / F	R_1 found / Ω	C_1 found / F	R_2 found / Ω	C_2 found / F
0.100	99.96	2.00×10^{-5}	100.0	1.53×10^{-6}
1.00×10^{-3}	96.00	2.04×10^{-5}	104.0	1.35×10^{-8}
1.00×10^{-4}	62.86	2.57×10^{-5}	137.1	1.54×10^{-9}
2.00×10^{-5}	10.56	7.24×10^{-5}	189.4	3.02×10^{-10}
1.00×10^{-5}	2.99	1.47×10^{-4}	197.0	1.57×10^{-10}

In fact, plots for the nested circuit can be obtained using the circuit in series and the parameters shown in Table 2.3, where the resistance R_0 is always the same, $R_0 = 10\ \Omega$, and other parameters are different. It should be stressed that the fit is exact, which means that the two circuits give exactly the same values of impedances.

This effect arises from the fact that impedances of circuits in series and nested circuits (Fig. 2.37) can be represented by the same equation:

$$\hat{Z} = R_0 \frac{(s - z_1)(s - z_2)}{(s - p_1)(s - p_2)}, \tag{2.156}$$

where $s = j\omega$. This equation comes from the expressions for the impedances of both circuits:

$$\hat{Z} = R_0 + \frac{1}{\frac{1}{R_1} + sC_1} + \frac{1}{\frac{1}{R_2} + sC_2}, \tag{2.157}$$

$$\hat{Z} = R_0 + \frac{1}{sC_1 + \frac{1}{R_1 + \frac{1}{\frac{1}{R_2} + sC_2}}}. \tag{2.158}$$

The values of the zeros z_i and poles p_i of the equation are

$$z_{1,2} = \frac{\frac{1}{R_1C_1} + \frac{1}{R_2C_2} + \frac{1}{R_0C_1} + \frac{1}{R_0C_2}}{2}\left[-1 \pm \sqrt{1 - \frac{\frac{4}{C_1C_2}\left(\frac{1}{R_1R_2} + \frac{1}{R_0R_1} + \frac{1}{R_0R_2}\right)}{\left(\frac{1}{R_1C_1} + \frac{1}{R_2C_2} + \frac{1}{R_0C_1} + \frac{1}{R_0C_2}\right)^2}}\right]$$

$$p_1 = -\frac{1}{R_1C_1}, \quad p_2 = -\frac{1}{R_2C_2} \tag{2.159}$$

for the circuit in series and

$$z_{1,2} = \frac{1}{2}\left(\frac{1}{R_1C_1} + \frac{1}{R_0C_1} + \frac{1}{R_1C_2} + \frac{1}{R_2C_2}\right) \times \left[-1 \pm \sqrt{1 - \frac{4\left(\frac{1}{R_1C_1R_2C_2} + \frac{1}{R_0R_2C_1C_2} + \frac{1}{R_0R_1C_1C_2}\right)}{\left(\frac{1}{R_1C_1} + \frac{1}{R_0C_1} + \frac{1}{R_1C_2} + \frac{1}{R_2C_2}\right)^2}}\right]$$

$$p_{1,2} = \frac{1}{2}\left(\frac{1}{R_1C_1} + \frac{1}{R_1C_2} + \frac{1}{R_2C_2}\right)\left[-1 \pm \sqrt{1 - \frac{4\left(\frac{1}{R_1C_1R_2C_2}\right)}{\left(\frac{1}{R_1C_1} + \frac{1}{R_1C_2} + \frac{1}{R_2C_2}\right)^2}}\right] \tag{2.160}$$

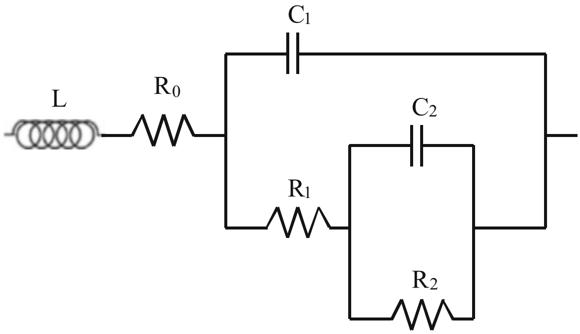


Fig. 2.40 Nested circuit with inductance L in series; $L = 2 \times 10^{-4}$ H, $C_2 = 0.1$ F; other parameters as in Fig. 2.39

for the nested circuit. From the preceding equations it is obvious that the impedances for both circuits have exactly the same general form with different formulas for zeros and poles. These are only two out of three possible circuits that will be discussed in Example 14.2.

2.10.3 Circuits Containing Inductances

Until now, only circuits containing resistances and capacitances have been discussed. Inductive effects in electrical circuits appear when alternative electrical current flow creates a magnetic field interacting with the flowing current; of course, in a strait wire the inductance is very small, but in looped wires or a coil it becomes larger. The inductive effects always lead to positive imaginary impedances, as will be shown in what follows. Let us first consider the circuit in Fig. 2.40, which contains inductance L in series with resistance R_0 and a nested connection of two (RC) circuits, i.e., $LR_0(C_1(R_1(R_2C_2)))$. The complex plane and Bode plots for this circuit without inductance were presented in Fig. 2.39.

From the impedance plots it follows that the presence of inductance in series does not affect low-frequency data. At high frequencies a positive imaginary straight line appears on the complex plane plots and the phase angle changes sign from negative to positive, while the modulus of the frequency displays a minimum at $R_0 = 10\ \Omega$. This positive imaginary impedance is characteristic of the presence of inductance.

Finally, let us consider a simple circuit containing an RLC connection in series. The impedance of such a circuit is

$$\hat{Z} = R + j\omega L - j\frac{1}{\omega C} = R + j\left(\omega L - \frac{1}{\omega C}\right). \tag{2.161}$$

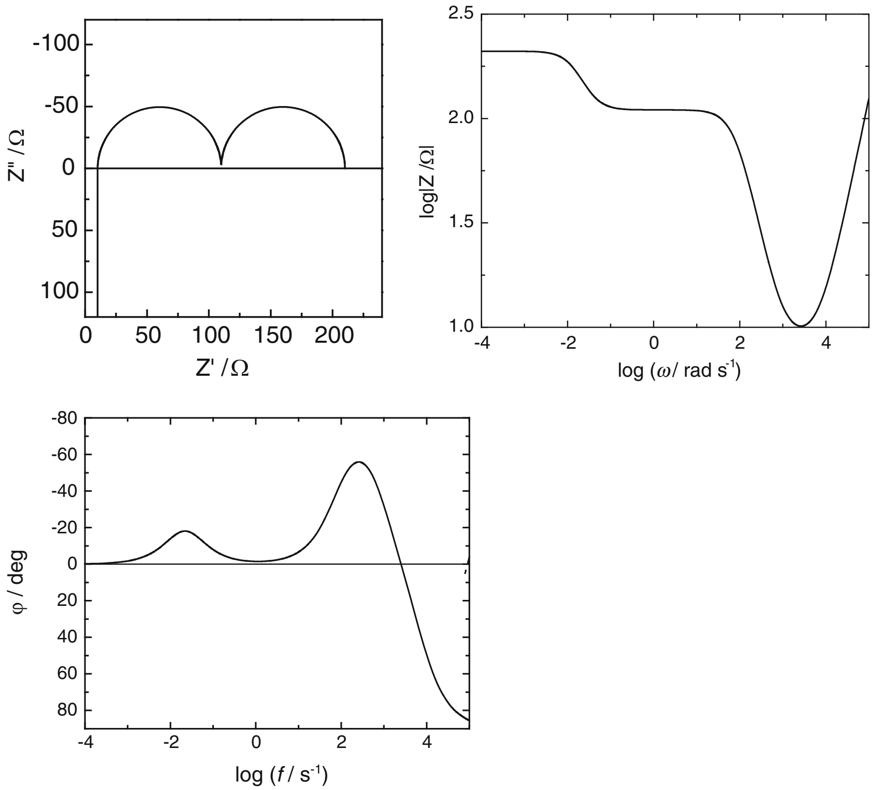


Fig. 2.41 Complex plane and Bode plots for circuit in Fig. 2.40

The real part of the impedance is constant and equal to R, while the imaginary impedance may be positive at high frequencies or negative at low frequencies. The imaginary impedance becomes zero when $\omega_{\mathrm{rez}} = 1/\sqrt{LC}$; this is the so-called resonant frequency. An example of the complex plane and Bode plots for such a circuit is presented in Fig. 2.42. A complex plane plot is a straight line perpendicular to the real axis. The upper negative part corresponds to low frequencies and is identical to an RC connection in series. The lower positive part corresponds to an RL connection in series. The Bode magnitude plot shows two lines at 45° corresponding to the capacitive (negative slope) and inductive (positive slope) parts. The phase angle plot passes through $Z'' = 0$ at the resonant frequency and goes to $-90°$ or $90°$ at very low or very high frequencies, respectively.

These results are shown in Exercise 2.14.

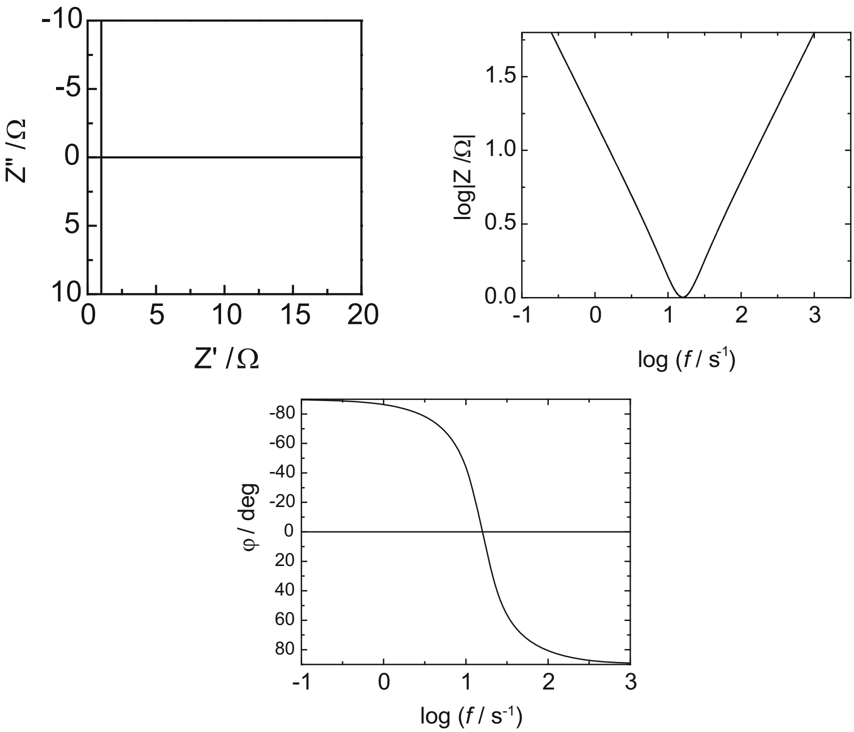


Fig. 2.42 Complex plane and Bode plots for *RLC* connection in series; $R = 1\ \Omega$, $C = 0.01$ F, $L = 0.01$ H

2.11 Summary

Impedance of an electrical circuit containing linear electrical elements *R*, *C*, and *L* can be calculated using the impedance of these elements and Ohm's and Kirchhoff's laws. The complex plane and Bode plots can be easily produced using programming in Excel, Zplot, Maple, Mathematica, etc., which are readily available. It should be stressed that these electrical elements are linear, that is, their impedance is independent of the applied ac amplitude. In subsequent chapters, we will see how the impedance of electrochemical systems can be described.

2.12 Exercises

Exercise 2.1 Generate a digitalized function $E(t) = \cos(2\pi t/T_a)$ containing 64 points from 0 to 63 for the sampling time 0.01 s and wave period $T_a = 0.32$ s for 0.63 s. Then use Excel to carry out a FFT. Show the plots of the function and its FT. What information can be obtained from it?

Exercise 2.2 Generate a digitalized function $E(t) = \sin(2\pi t/T_a)$ containing 64 points from 0 to 63 for the sampling time 0.01 s and for wave period $T_a = 0.32$ s for 0.63 s. Then use Excel to carry out a FFT. Show the plots of the function and its FT. What information can be obtained from it?

Exercise 2.3 Generate a digitalized function $E(t) = \cos(2\pi t/T_a + \pi/3)$ containing 64 points from 0 to 63 for the sampling time 0.01 s and for $T_a = 0.32$ s for 0.63 s. Then use Excel to carry out a FFT. Show the plots of the function and its FT. What information can be obtained from it?

Exercise 2.4 Generate a digitalized function $E(t) = \exp(-3t_i)$ containing 32 points for the sampling time 0.01 s. Use Excel to carry out a FFT. What information can be obtained from it?

Exercise 2.5 Generate a digitalized function $E(t) = \sin(2\pi t/T_a)$ containing 256 points for the sampling time 0.2 s and $T_a = 34$ s. Use Excel to carry out a FFT. What information can be obtained from it? Is it possible to obtain the studied function frequency from FT analysis?

Exercise 2.6 Simulate the sum of frequencies curve consisting of the following functions: $\cos(k\ 2\pi t/1024)$ for $k = 1, 3, 7$, and 13 and $\sin(\mathrm{k}\ 2\pi t/1024)$ for $k = 5$, 9, and 17, and t from 0 to 1023. Perform a FFT, determine the frequencies, and compare with the frequencies of assumed individual functions.

Exercise 2.7 To determine the impedance of a system, data of the applied voltage and circulating current were measured for 0.64 s every 0.01 s. To calculate the impedance, generate "experimental" data (normally they would be presented as series of numbers) using the following equations: $E(t) = E_0\cos(\omega t)$ and $I(t) = I_0 \cos(\omega t + \pi / 3)$, where $E_0 = 0.01$ V, $I_0 = 0.002$ A, $\omega = 2\pi f = 2\pi/T_a$, $T_a = 0.32$ s.

Exercise 2.8 Determine impedance using data obtained from D/A data acquisition of voltage and current. These data, containing time, potential, and current: t, $E(t)$, $I(t)$ in s, V, and A, respectively, can be found in the file Ex2_8.txt. What is the frequency of these functions?

Exercise 2.9 Make complex plane, Bode, and complex admittance plots of an RC connection in series; $R = 150\ \Omega$, $C = 40\ \mu$F.

Exercise 2.10 Make complex plane, Bode, and complex admittance plots of an (RC) connection in parallel; $R = 100\ \Omega$, $C = 20\ \mu$F.

Exercise 2.11 Make complex plane, Bode, and complex admittance plots of R_s in series with the parallel connection of (RC), $R_s(RC)$; $R_s = 10\ \Omega$, $R = 100\ \Omega$, $C = 20\ \mu$F.

Exercise 2.12 Make complex plane and Bode plots for the circuit $R_s(C_{dl}(R_{ct}C_p))$ with the following elements: $R_s = 2\ \Omega$, $R_{ct} = 50\ \Omega$, $C_{dl} = 2 \times 10^{-5}$ F, and $C_p = 0.01$ F.

Exercise 2.13 Simulate using ZView the impedance of the two models displayed in Fig. 2.37, in series $R_0(R_1C_1)(R_2C_2)$ and nested $R_0(C_1(R_1(R_2C_2)))$, using the following parameters: $R_s = 10\ \Omega$, $R_1 = 100\ \Omega$, $C_1 = 2 \times 10^{-5}$ F, $R_2 = 100\ \Omega$, $C_2 = 10^{-1}, 10^{-3}, 10^{-4}, 2 \times 10^{-5}, 10^{-5}$ F. Make the approximations of the impedances of the nested circuit using those in series. Compare with the results in Ch2.xlsx, Worksheets Ex2.13 serial, Ex2.13 nested, and Ex2.13 approx.

Exercise 2.14 Simulate impedances for the circuit *RCL* in series for $R = 1\ \Omega$, $C = 0.01$ F, and $L = 0.01$ H. Make simulations using ZView and Excel. Make complex plane and Bode plots.