2

Electrical Fundamentals

In order to understand electrochemical impedance spectroscopy (EIS), we first need to learn and understand the principles of electronics. In this chapter, we will introduce the basic electric circuit theories, including the behaviours of circuit elements in direct current (DC) and alternating current (AC) circuits, complex algebra, electrical impedance, as well as network analysis. These electric circuit theories lay a solid foundation for understanding and practising EIS measurements and data analysis.

2.1 Introduction

An electric circuit or electric network is an integration of electrical elements (also known as circuit elements). Each element can be expressed as a general two-terminal element, as shown in Figure 2.1. The terminals “a” and “b” are accessible for connections with other elements. These circuit elements can be interconnected in a specified way, forming an electric circuit. Figure 2.2 demonstrates an example of an electric circuit.

Circuit elements can be classified into two categories, passive elements and active elements. The former consumes energy and the latter generates energy. Examples of passive elements are resistors (measured in ohms), capacitors (measured in farads), and inductors (measured in henries). The two typical active elements are the current source (measured in amperes), such as generators, and the voltage source (measured in volts), such as batteries.

Two major parameters used to describe and measure the circuits and elements are current (I) and voltage (V). Current is the flow, through a circuit or an element, of electric charge whose direction is defined from high potential to low potential. The current may be a movement of positive charges or of negative charges, or of both moving in opposite directions. For example, in a metallic resistor the current is the movement of electrons, whereas in an electrolyte solution the current is the movement of ions, and in a proton exchange polymer it is the movement of protons. Voltage is the difference in electrical potential between two points of an electric circuit or an element, expressed in volts. As shown in Figure 2.1, the potential difference between terminal “a” and terminal “b” is the voltage, which drives current through the element [1, 2].

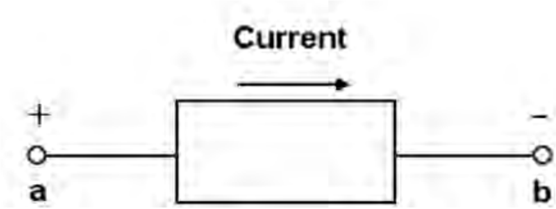


Figure 2.1. A general two-terminal electrical element

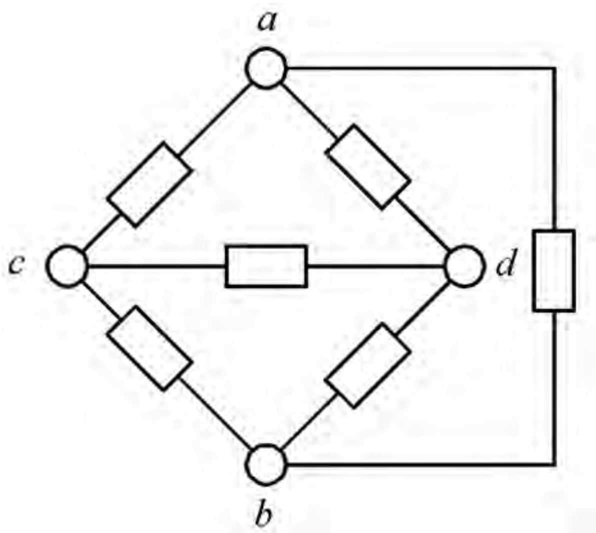


Figure 2.2. An example of an electric circuit

2.2 Direct Current Circuits

If the independent sources in a circuit are constant sources, such as batteries, all the currents and voltages remain constant and the circuit reaches its steady state. In this case, we say that the circuit is in a DC steady state.

2.2.1 Ohm's Law

The relationship between voltage and current in the circuit can be described by Ohm's law, which states that the current passing through a conductor between two points is directly proportional to the voltage across the two points, and inversely proportional to the resistance between them. The mathematical equation that describes this relationship is

$$V = IR \tag{2.1}$$

where V is the driving voltage in volts (V), R is the resistance in ohms (Ω), and I is the current in amperes (A).

Two common concepts are relevant to resistance. One is the short circuit, which is the direct connection externally between two nodes using an electrically conductive wire that has a theoretical resistance of zero. The opposite of a short circuit is an open circuit, in which the two nodes have no external connection or an infinite resistance connection [3]. Note that a point of connection of two or more circuit elements is called a node, as seen in Figure 2.3*b*.

Another important quantity, known as conductance, is defined by

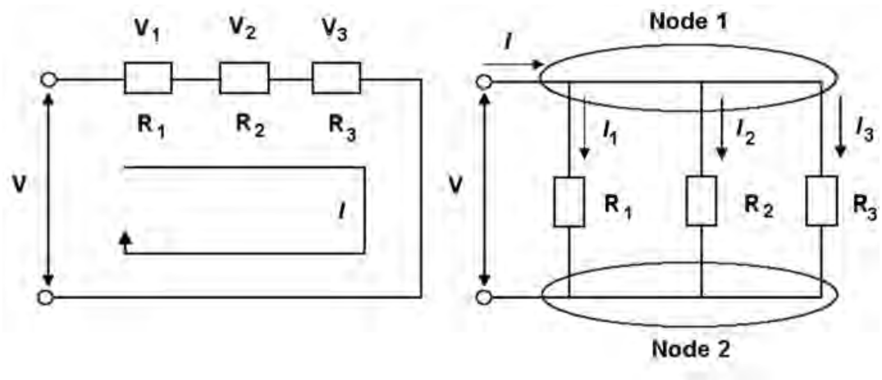
$$G = 1/R \tag{2.2}$$

where G is the conductance in siemens (S). Obviously, in this case Ohm's law can also be expressed as

$$I = GV \tag{2.3}$$

2.2.2 Series and Parallel Circuits

There are two basic circuit connections: series circuit and parallel circuit. If two or more circuit components are connected end to end, as shown in Figure 2.3*a*, they are connected in series. A series circuit has only one path for the electric current to run through all of its components. If two or more circuit components are connected like the rungs of a ladder, as shown in Figure 2.3*b*, they are connected in parallel. A parallel circuit has different paths for the electric current through each of its components, with the same voltage across.



a *b*

Figure 2.3. *a* Series and *b* parallel circuits

2.2.3 Kirchhoff's Laws

Electric circuits can be very complicated. For example, they may include series-connected sections, parallel-connected sections, or both. No matter how complex they are, the behaviours of these sections are governed by fundamental laws, which provide basic tools for the analysis of all the circuits.

The fundamental laws for circuit analysis are Ohm's law and Kirchhoff's laws. Ohm's law, described above, can be used to find the current, voltage, and power associated with a resistor. However, in some cases Ohm's law by itself cannot analyze the circuit. Analytical solutions for most electric networks need to combine Ohm's law and Kirchhoff's laws, the latter being also known as Kirchhoff's current law (KCL) and Kirchhoff's voltage law (KVL).

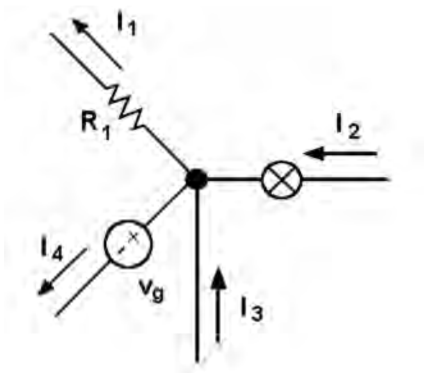


Figure 2.4. Principle schematic of Kirchhoff's current law

Kirchhoff's current law states that the algebraic sum of the currents entering a node is equal to the algebraic sum of the currents leaving the node. The principle schematic of KCL is shown in Figure 2.4, and the mathematical equation that describes KCL in Figure 2.4 is

$$I_1 + I_4 = I_2 + I_3 \tag{2.4}$$

More commonly, the current has a reference direction indicating entrance to or exit from the node. If the current enters the node, the arrow points to the node and a positive value is denoted for this current. Conversely, if the current leaves the node, the arrow points away from the node and a negative value is assigned to this current. So, KCL can also be expressed as

$$\sum I = 0 \tag{2.5}$$

Applying KCL to the circuit in Figure 2.3*b*, we have

$$I - I_1 - I_2 - I_3 = 0 \tag{2.6}$$

Kirchhoff's voltage law states that the algebraic sum of the voltage over the circuit elements around any closed circuit loop must be zero. The principle schematic of KVL is shown in Figure 2.5. The mathematical equation that describes KVL in Figure 2.5 can be expressed as

$$V_1 + V_2 + V_3 + V_4 = 0 \tag{2.7}$$

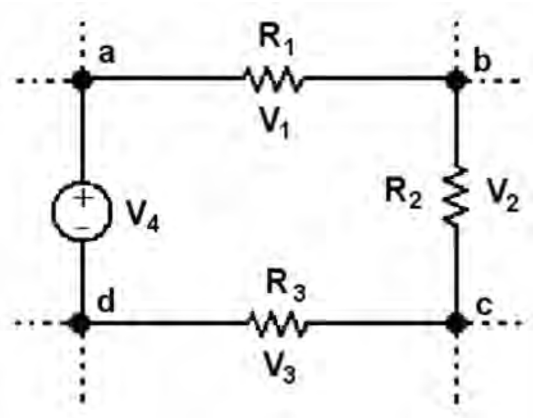


Figure 2.5. Principle schematic of Kirchhoff's voltage law

More commonly, KVL can be expressed as

$$\sum V = 0 \tag{2.8}$$

According to KVL, in a closed circuit loop, the sum of the voltage drops caused by the current across the elements, such as the resistor, capacitor, or inductor, is equal to the sum of the driving voltages produced by a voltage source such as a battery or a generator:

$$\sum \text{Driving voltages} = \sum \text{Voltage drops} \tag{2.9}$$

2.2.4 Resistors in DC Circuits

Electric circuits or networks can be analyzed using both Ohm's law and Kirchhoff's laws. For a circuit of resistors in series, as shown in Figure 2.6, the current flow in each resistor is the same (I_R).

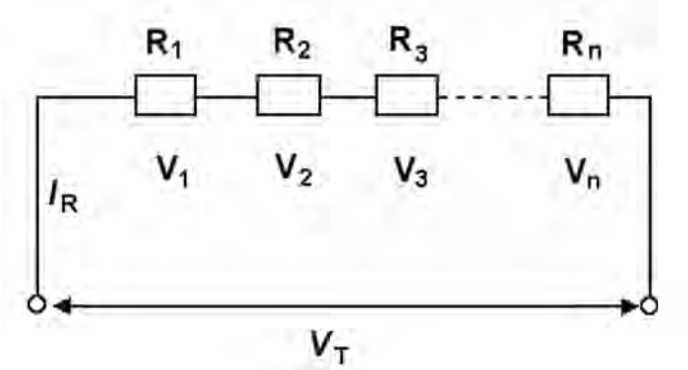


Figure 2.6. Resistors in series

Applying KVL to the circuit in Figure 2.6, we have

$$V_T = V_1 + V_2 + V_3 + ... + V_n \tag{2.10}$$

Applying Ohm's law to Equation 2.10, we can obtain

$$V_T = I_R R_1 + I_R R_2 + I_R R_3 + \ldots + I_R R_n \tag{2.11}$$

Equation 2.10 can be rearranged as Equation 2.12:

$$V_T = I_R (R_1 + R_2 + R_3 + ... + R_n) \tag{2.12}$$

Thus, the equivalent resistance R of n resistors connected in series can be expressed as

$$R = \frac{V_T}{I_R} = R_1 + R_2 + R_3 + ... + R_n \tag{2.13}$$

For a circuit of resistors in parallel, as shown in Figure 2.7, the voltage across each resistor is the same (V_T). Applying KCL to the circuit in Figure 2.7, we have

$$I_T = I_1 + I_2 + I_3 + ... + I_n \tag{2.14}$$

Then,

$$I_T = (\frac{V_T}{R_1} + \frac{V_T}{R_2} + \frac{V_T}{R_3} + ... + \frac{V_t}{R_n}) \tag{2.15}$$

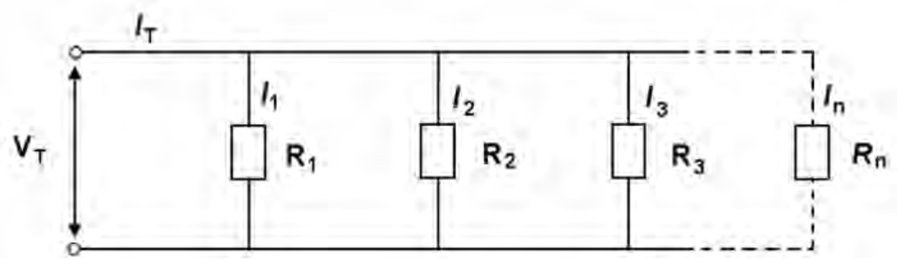


Figure 2.7. Resistors in parallel

Therefore, the equivalent resistance of the parallel combination of *n* resistors is

$$R = \frac{V_T}{I_T} = \left(\frac{1}{R_1} + \frac{1}{R_2} + \frac{1}{R_3} + ... + \frac{1}{R_n} \right)^{-1} \tag{2.16}$$

The equivalent conductance of *n* resistors in parallel, *G*, can be expressed as

$$G = \frac{I_T}{V_T} = G_1 + G_2 + G_3 + ... + G_n = \frac{1}{R_1} + \frac{1}{R_2} + \frac{1}{R_3} + ... + \frac{1}{R_n} \tag{2.17}$$

2.2.5 Capacitors in DC Circuits

Capacitance represents the energy-storing capability of a capacitor. The most common form of charge storage device is a two-plate capacitor, as shown in Figure 2.8. A parallel-plate capacitor is a circuit element with two conducting plates at the terminals and a nonconductive material, known as the dielectric material, to separate them. When a charge source, such as a battery, transfers charges to a capacitor, the voltage builds up across the two conductive terminals. The charges accumulate at the two plates of the capacitor, and can be expressed as

$$q = CV \tag{2.18}$$

where *C* is the capacitance in farads (F), *q* is the accumulated charge in coulombs (C), and *V* is the voltage measured between the two conducting plates in volts (V). The capacitance value (*C*) of a parallel-plate capacitor is related to the geometry of the capacitor and to the dielectric constant of the nonconductive material in the capacitor by the following equation:

$$C = \frac{KA(8.854 \times 10^{-12})}{d} \tag{2.19}$$

where *C* is the capacitance in farads (F), *K* is the dielectric constant of the insulating material, *A* is the surface area in square metres (m^2), and *d* is the thickness of the dielectric material in metres (m).

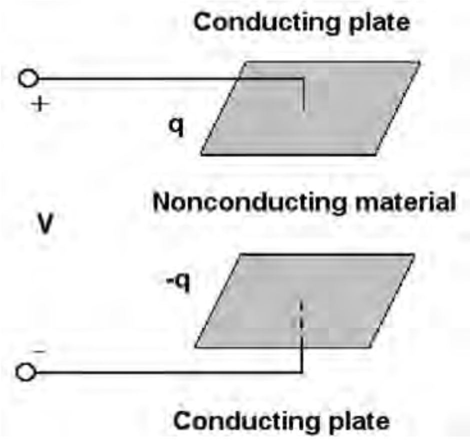


Figure 2.8. A parallel-plate capacitor

Some representative dielectric constants are 1.0 for air, 5 for mica, 6 for glass, and 7500 for ceramic.

In a DC circuit, a capacitor behaves like an open circuit. In other words, the current through it is zero when the circuit reaches its steady state. However, if a current or voltage source is impressed on or switched out of the circuit with a capacitor (or capacitors), as shown in Figure 2.9, there will be a transitory change in the current and voltage. Between the moment of switching and the steady state, the current passing through the capacitor is not zero. The time dependence of the voltage across the capacitor during the transient state in a DC circuit like Figure 2.9 can be obtained using Laplace transforms (for these, please refer to Appendix B).

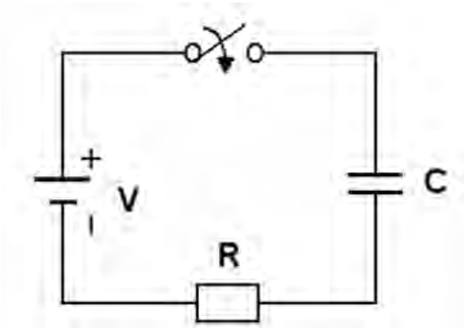


Figure 2.9. A DC circuit containing a capacitor and a switch

Since the current is defined as the change rate of the charge, by differentiating Equation 2.18 we can obtain

$$I(t) = C\frac{dV(t)}{dt} \tag{2.20}$$

Equation 2.20 is the current–voltage relation for a capacitor.

Figure 2.10 shows the transient process of a capacitor when charging. In the charging process, the electric field in the nonconductive material changes due to the charge increase in the conductive terminals of the capacitor. The charging process stops when the voltage *V* across the capacitor is equal to the DC charge source.

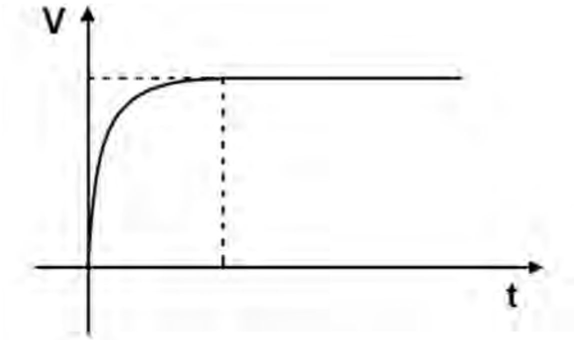


Figure 2.10. Voltage build-up versus charging time in a capacitor

2.2.5.1 Equivalent Capacitance of Capacitors in Series

Applying KVL to the circuit in Figure 2.11, we have

$$V_T = V_1 + V_2 + V_3 + \ldots + V_n \tag{2.21}$$

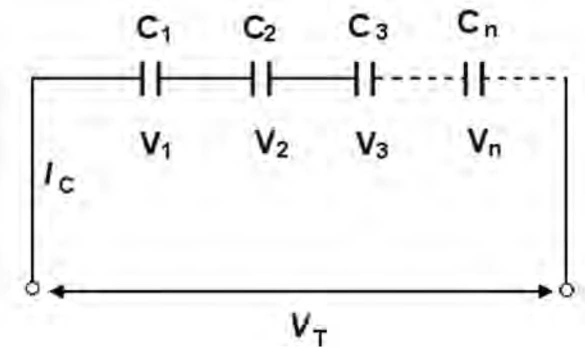


Figure 2.11. Capacitors in series

Substituting voltages according to Equation 2.18, we obtain

$$V_T = \frac{q_1}{C_1} + \frac{q_2}{C_2} + \frac{q_3}{C_3} + \ldots + \frac{q_n}{C_n} \tag{2.22}$$

Since the current to all the elements in a series circuit is the same, the accumulation of charge in every capacitor must be the same. Thus,

$$q_1 = q_2 = q_3 = q_n = q \tag{2.23}$$

Equation 2.22 becomes

$$V_T = q(\frac{1}{C_1} + \frac{1}{C_2} + \frac{1}{C_3} + \ldots + \frac{1}{C_n}) \tag{2.24}$$

Then, the equivalent capacitance of *n* capacitors in series, C_s, is determined by

$$\frac{1}{C_s} = \frac{V_T}{q} = \frac{1}{C_1} + \frac{1}{C_2} + \frac{1}{C_3} + \ldots + \frac{1}{C_n} \tag{2.25}$$

In other words, the total capacitance of capacitors in series is equal to the reciprocal of the sum of the reciprocals of the individual capacitances.

2.2.5.2 Equivalent Capacitance of Capacitors in Parallel

Applying KCL to the circuit in Figure 2.12, we have

$$I_T = I_1 + I_2 + I_3 + ... + I_n \tag{2.26}$$

As the voltage across each element in a parallel circuit is the same, by substituting currents using Equation 2.20 we can obtain

$$I_T = C_1 \frac{dV}{dt} + C_2 \frac{dV}{dt} + C_3 \frac{dV}{dt} + \ldots + C_n \frac{dV}{dt} \tag{2.27}$$

Therefore,

$$I_T = (C_1 + C_2 + C_3 + ... + C_n) \frac{dV}{dt} \tag{2.28}$$

Thus, the equivalent capacitance of *n* parallel capacitors, C_p, is simply the sum of the individual capacitances:

$$C_p = C_1 + C_2 + C_3 + ... + C_n \tag{2.29}$$

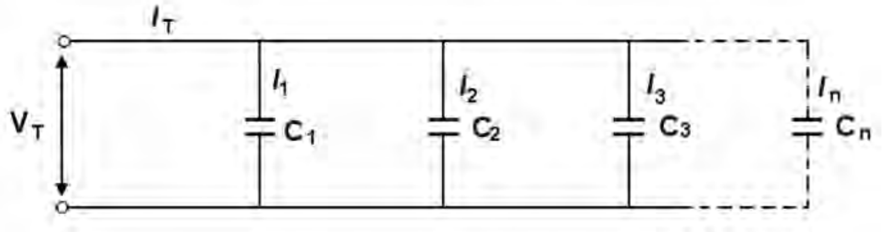


Figure 2.12. Capacitors in parallel

2.2.6 Inductors in DC Circuits

An inductor is commonly a coiled conducting wire wrapped around a core (e.g., ferromagnetic material) with two terminals. When current passes through the inductor, magnetic flux is produced, resulting in inductance. The number of loops, the size of each loop, and the core material all affect the inductance value.

In a DC circuit, an inductor is like a short circuit, which means the voltage across it is zero when the circuit reaches its steady state. However, if a current or voltage source is impressed on or switched out of the circuit with an inductor, as shown in Figure 2.13, there will be a transitory change in the current and voltage. During the time period from the moment of switching to the steady state, the voltage across the inductor is not zero.

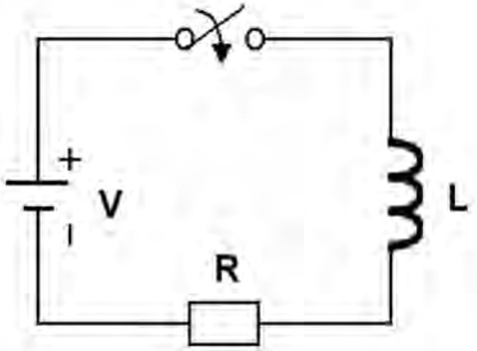


Figure 2.13. A DC circuit containing an inductor and a switch

While a capacitor delays changes in voltage, an inductor delays changes in current. Generally, the relationship between the time-varying voltage *V*(*t*) across an inductor with an inductance of *L* and the time-varying current *I*(*t*) passing through it can be written as the differential equation:

$$V(t) = L\frac{dI(t)}{dt} \tag{2.30}$$

where *L* is the inductance (measured in henries).

Inductors in series and in parallel are shown in Figures 2.14 and 2.15, respectively. While the voltage across each inductor may be different, the current through inductors in series stays the same. Since the sum of the voltages is equal to the total voltage, the total inductance of inductors in series, L_s, can be expressed as

$$L_s = L_1 + L_2 + L_3 + ... + L_n \tag{2.31}$$

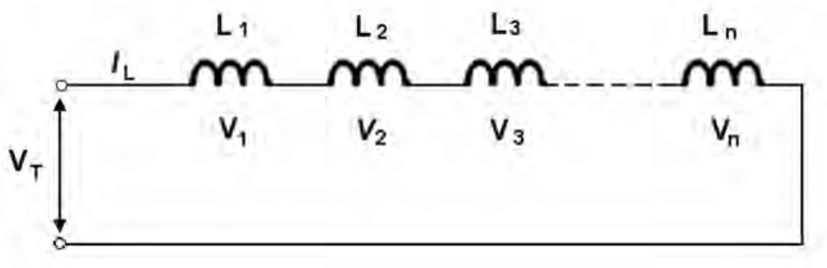


Figure 2.14. Inductors in series

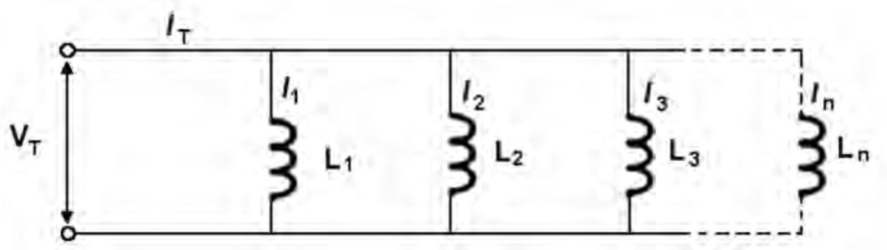


Figure 2.15. Inductors in parallel

In a parallel configuration of inductors, as shown in Figure 2.15, each inductor has the same voltage. Therefore, the total equivalent inductance of inductors in parallel, L_p, can be obtained:

$$\frac{1}{L_p} = \frac{1}{L_1} + \frac{1}{L_2} + \frac{1}{L_3} + \ldots + \frac{1}{L_n} \tag{2.32}$$

2.3 Alternating Current Circuits

2.3.1 Sinusoidal Systems

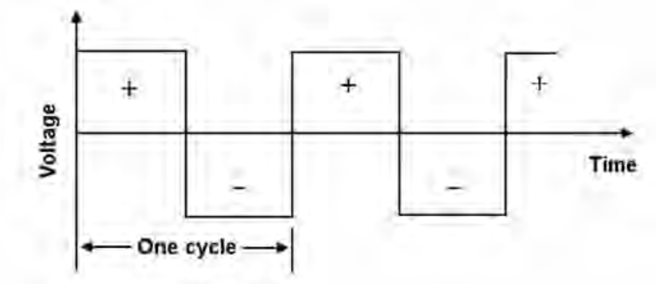
Alternating current or voltage (AC) refers to current or voltage that varies with time in a periodic manner. Figure 2.16 shows three examples of periodic voltage waves. As shown there, one cycle is a complete set of the periodic wave, the frequency of which, f (Hz), is the number of cycles completed in one second (one cycle per second is one hertz). The period of the periodic wave, T (s), is the time required to complete one cycle. Thus, the relation between the frequency and the period is as follows:

$$T = \frac{1}{f} \tag{2.33}$$

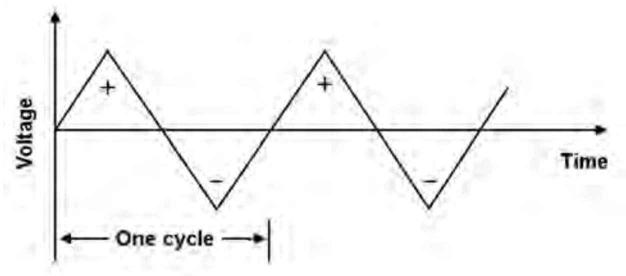
Among the periodic waves, the sinusoidal wave is extremely important, being the easiest to work with mathematically. The general mathematical expression for the sinusoidal wave (voltage) is given by

$$V(t) = V_m \sin(\omega t + \theta) \tag{2.34}$$

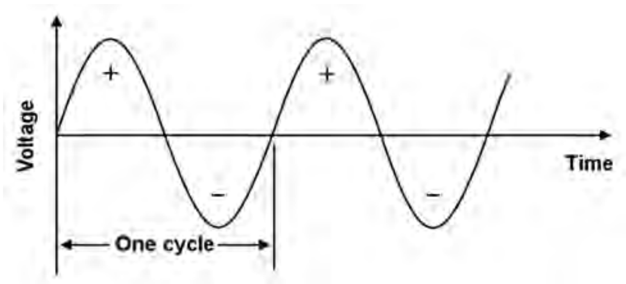
where $V(t)$ is the instantaneous voltage value at the instant of time t, V_m is the peak amplitude of the sinusoidal voltage wave (V), θ is the phase angle, ω is the angular frequency (rad/s), and T is the time (s).



a



b



c

Figure 2.16. Periodic voltage waves: *a* rectangular, *b* triangular, *c* sinusoidal

Since the angle spun in one cycle is 2π radians, we have

$$\omega = 2\pi f \tag{2.35}$$

Thus,

$$T = \frac{2\pi}{\omega} \tag{2.36}$$

Substituting for ω using Equation 2.35, we obtain

$$V(t) = V_m \sin(2\pi f t + \theta) \tag{2.37}$$

Similarly, the equation for a sinusoidal current wave is

$$I(t) = I_m \sin(2\pi f t + \phi) \tag{2.38}$$

where $I(t)$ is the instantaneous current value at the instant of time t; I_m is the amplitude or the maximum value of the sinusoidal current wave (A); ϕ is the phase angle; f is the frequency (Hz); and T is the time (s).

Direct current or voltage can be considered a special type of sinusoidal current wave or sinusoidal voltage wave whose frequency is at the lower limit of zero hertz.

2.3.2 Resistors in AC Circuits

In an AC circuit, assuming the voltage across the resistor is described by a sinusoidal wave (as shown in Equation 2.37), the current through the resistor, based on Ohm's law, is

$$I_R(t) = \frac{V_R(t)}{R} = \frac{V_m \sin(2\pi f t + \theta)}{R} = \frac{V_m}{R}\sin(2\pi f t + \theta) \tag{2.39}$$

As can be seen in Equation 2.39, both $I_R(t)$ (the current through the resistor) and $V_R(t)$ (the voltage across the resistor) have the same frequency and phase.

According to Equation 2.38, we have

$$I_R(t) = I_m \sin(2\pi f t + \phi) \tag{2.40}$$

Comparing Equations 2.39 and 2.40, we can obtain

$$I_m = \frac{V_m}{R} \tag{2.41}$$

Since there is no angular difference between the current in a resistor and the voltage across it, we have

$$\phi = \theta \tag{2.42}$$

2.3.3 Capacitors in AC Circuits

In a sinusoidal AC circuit, the current through a pure capacitor leads the voltage drop across this capacitor by 90°. The 90° phase relationship between $I_C(t)$ (the current through the capacitor) and $V_C(t)$ (the voltage across the capacitor) can be written as

$$I_C(t) = C\frac{dV_C(t)}{dt} \tag{2.43}$$

For example, if the voltage across the capacitor, $V_C(t)$, is

$$V_C(t) = V_m \sin 2\pi ft \tag{2.44}$$

then substituting $V_C(t)$ in Equation 2.43 with Equation 2.44, we have

$$I_C(t) = C\frac{d(V_m \sin 2\pi ft)}{dt} = CV_m(2\pi f)\cos 2\pi ft = \omega CV_m \sin(2\pi ft + 90°) \tag{2.45}$$

The current through the capacitor, $I_C(t)$, will be

$$I_C(t) = I_m \sin(2\pi ft + 90°) \tag{2.46}$$

where

$$I_m = \omega CV_m \tag{2.47}$$

2.3.4 Inductors in AC Circuits

In a sinusoidal AC circuit, the voltage drop across a pure inductor advances the current through it by 90°. The 90° phase relationship between $I_L(t)$ (the current through the inductor) and $V_L(t)$ (the voltage across the inductor) is expressed by

$$V_L(t) = L\frac{dI_L(t)}{dt} \tag{2.48}$$

For example, if the current through the inductor, $I_L(t)$, is

$$I_L(t) = I_m \sin 2\pi ft \tag{2.49}$$

then substituting $I_L(t)$ from Equation 2.49 into Equation 2.48, we have

$$V_L(t) = L\frac{d(I_m \sin 2\pi ft)}{dt} = LI_m(2\pi f)\cos 2\pi ft = \omega LI_m \sin(2\pi ft + 90°) \tag{2.50}$$

The voltage across the inductor, $V_L(t)$, will be

$$V_L(t) = V_m \sin(2\pi ft + 90°) \tag{2.51}$$

where

$$V_m = \omega LI_m \tag{2.52}$$

2.4 Complex Algebra and Impedance

Complex algebra is a powerful tool for solving problems in AC electric circuits, including sinusoidal systems. The complex number *Z* can be written in the rectangular form

$$Z = Z_{re} + iZ_{im} \tag{2.53}$$

where Z_{re} (or Z') and Z_{im} (or Z'') are the real and imaginary parts of *Z*, respectively, and $i = \sqrt{-1}$.

The complex number *Z* can also be expressed in the polar form

$$Z = |Z|e^{i\phi} \tag{2.54}$$

or

$$Z = |Z|(\cos\phi + i\sin\phi) \tag{2.55}$$

where $|Z|$ is the magnitude of *Z*:

$$|Z| = \sqrt{(Z_{re})^2 + (Z_{im})^2} \tag{2.56}$$

and ϕ is called the argument or the angle of *Z*:

$$\phi = \tan^{-1}\frac{Z_{im}}{Z_{re}} \tag{2.57}$$

Complex algebra is associated with a two-dimensional plane, called the complex plane. The complex plane of the complex number *Z* is presented in Figure 2.17. As can be seen there, the horizontal and vertical axes are called the real and imaginary axes, respectively. Complex algebra applications will be employed in the following sections and in Chapter 4.

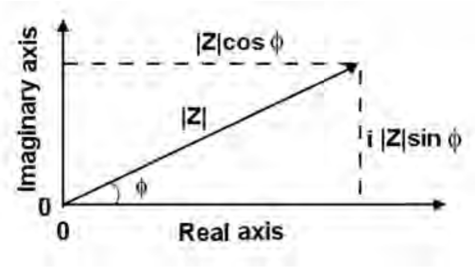


Figure 2.17. Complex plane of the complex number *Z*

Let us recall the general sinusoidal voltage and current:

$$V(t) = V_m \sin(2\pi f t + \theta) \tag{2.58}$$

$$I(t) = I_m \sin(2\pi f t + \phi) \tag{2.59}$$

These can be displayed in related complex numbers:

$$\boldsymbol{V} = V_m e^{i\theta} = V_m \angle\theta \tag{2.60}$$

$$\boldsymbol{I} = I_m e^{i\phi} = I_m \angle\phi \tag{2.61}$$

which are defined as phasors, or phasor representations. To distinguish them from other complex numbers, phasors are printed in bold.

Having introduced complex algebra, we are now able to go further, to the concept of electrical impedance or simply impedance. Electrical impedance extends the concept of resistance to AC circuits and therefore is also called AC impedance. As impedance is a complex quantity, the term complex impedance may also be used. Based on the definition of resistance described by Ohm's law, the current–voltage relationship in impedance can be expressed as

$$Z = \frac{V(t)}{I(t)} \tag{2.62}$$

where $V(t)$ and $I(t)$ are measurements of voltage and current in an AC system.

For a sinusoidal system, the AC impedance of a resistor, Z_R, in the complex plane can be expressed as

$$Z_R = R \tag{2.63}$$

The AC impedance of a capacitor, Z_C, in the complex plane can be expressed as

$$Z_C = \frac{1}{i\omega C} \tag{2.64}$$

because

$$Z_C = \frac{V_m e^{i0^0}}{I_m e^{i90^0}} = \frac{V_m e^{i0^0}}{\omega C V_m e^{i90^0}} = \frac{e^{i(-90^0)}}{\omega C} \tag{2.65}$$

Applying Euler's formula, we have

$$e^{i(-90°)} = \cos(-90°) + i\sin(-90°) \tag{2.66}$$

Therefore,

$$Z_C = \frac{e^{i(-90^0)}}{\omega C} = \frac{-i}{\omega C} = \frac{1}{i\omega C} \tag{2.67}$$

The AC impedance of an inductor, Z_L, in the complex plane can be expressed as

$$Z_L = i\omega L \tag{2.68}$$

because

$$Z_L = \frac{V_m e^{i90^0}}{I_m e^{i0^0}} = \frac{\omega L I_m e^{i90^0}}{I_m e^{i0^0}} = \omega L e^{i90^0} \tag{2.69}$$

Again, applying Euler's formula, we obtain

$$Z_L = \omega L e^{i90^0} = i\omega L \tag{2.70}$$

2.4.1 AC Impedance of a Resistor–Capacitor Circuit

In a parallel resistor–capacitor (RC) circuit (R/C), the overall AC impedance of the circuit is denoted as $Z_{R/C}$. Since

$$\frac{1}{Z_{R/C}} = \frac{1}{Z_R} + \frac{1}{Z_c} \tag{2.71}$$

$Z_{R/C}$ can be expressed as

$$Z_{R/C} = \left(\frac{1}{R} + \frac{1}{(i\omega C)^{-1}}\right)^{-1} = (\frac{1}{R} + i\omega C)^{-1} \tag{2.72}$$

Then we have

$$Z_{R/C} = \frac{R}{1 + i\omega RC} \tag{2.73}$$

Ultimately, Equation 2.73 can be transferred to the standard form of a complex number:

$$Z_{R/C} = \frac{R}{1 + (\omega RC)^2} - i\frac{\omega R^2 C}{1 + (\omega RC)^2} \tag{2.74}$$

Therefore, the real and imaginary components, Z_{re} and Z_{im}, in the AC impedance of the parallel RC circuit are given by

$$Z_{re} = \frac{R}{1 + (\omega RC)^2} \tag{2.75}$$

$$Z_{im} = -\frac{\omega R^2 C}{1 + (\omega RC)^2} \tag{2.76}$$

while the phase angle ϕ is given by

$$\tan\phi = -\omega RC \tag{2.77}$$

At low frequency ($\omega RC << 1$, $Z_{re} \approx R$ and $Z_{im} \approx 0$), this RC circuit acts as a resistor, and at high frequency ($\omega RC >> 1$, $Z_{re} \approx 0$ and $Z_{im} \approx \frac{1}{\omega C}$), as a capacitor. The time constant τ of this circuit is equal to *RC*.

Combining Equation 2.77 with Equations 2.75 and 2.76 yields

$$\left(Z_{re} - \frac{R}{2}\right)^2 + Z_{im}{}^2 = \left(\frac{R}{2}\right)^2 \tag{2.78}$$

Equation 2.78 represents a half-circle in the fourth quadrant of the complex plane, with a radius of *R*/2 and circle centre of (*R*/2, 0), as shown in Figure 2.18. Note that the frequency range in Figure 2.18 is from 1 MHz to 0.001 Hz. The same frequency range is kept for the following figures in this chapter, unless otherwise stated.

It can be seen from Figure 2.18 that at $\omega \to 0$, the plot crosses the real axis at (R, 0). At $\omega \to \infty$, the plot crosses the origin. The frequency at $\frac{\partial(Z_{im})}{\partial \omega} = 0$ is designated the characteristic frequency, ω_C. At the characteristic frequency, $\omega_C \tau_C$ is equal to one.

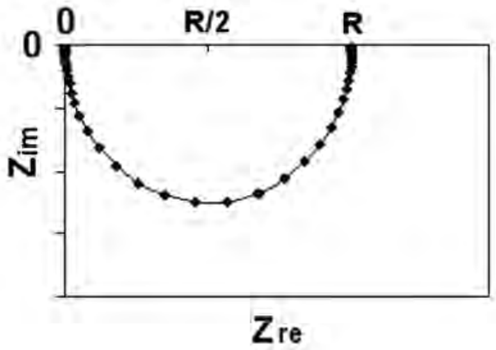


Figure 2.18. Graphical representation of the AC impedance of a parallel RC circuit

In a series RC circuit (R-C), according to the primary rules, the overall impedance, Z_{R-C}, is expressed as

$$Z_{R-C} = R + (i\omega C)^{-1} \tag{2.79}$$

Then we have

$$Z_{R-C} = R - i(\omega C)^{-1} \tag{2.80}$$

The real and imaginary components Z_{re}, Z_{im} in the AC impedance of the series RC circuit are given by

$$Z_{re} = R \tag{2.81}$$

$$Z_{im} = -(\omega C)^{-1} \tag{2.82}$$

The phase angle ϕ is given by

$$\tan \phi = -\frac{(\omega C)^{-1}}{R} \tag{2.83}$$

According to the above calculations, a graphical representation of the AC impedance of a series RC circuit is presented in Figure 2.19. As shown in the complex plane of Figure 2.19, the AC impedance of a series RC circuit is a straight vertical line in the fourth quadrant with a constant Z' value of R.

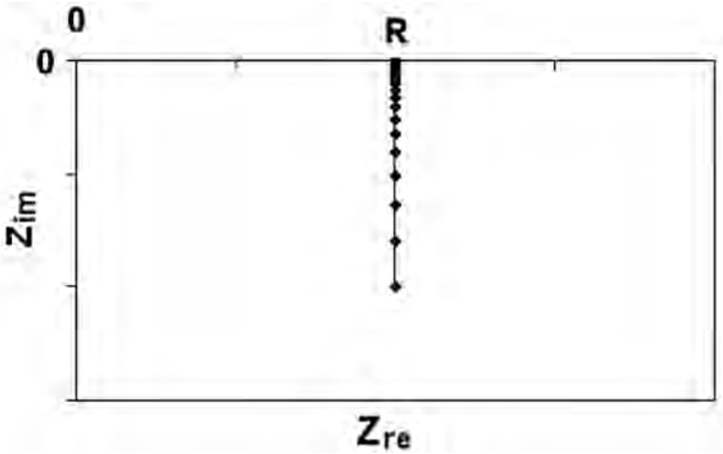


Figure 2.19. Graphical representation of the AC impedance of a series RC circuit

2.4.2 AC Impedance of a Resistor–Inductor Circuit

In a parallel resistor–inductor (RL) circuit (R/L), the overall AC impedance, $Z_{R/L}$, can be expressed as

$$Z_{R/L} = [(R^{-1} + (i\omega L)^{-1}]^{-1} \tag{2.84}$$

Then, we have

$$Z_{R/L} = \frac{\omega^2 RL^2}{R^2 + \omega^2 L^2} + i\frac{\omega R^2 L}{R^2 + \omega^2 L^2} \tag{2.85}$$

So, the real and imaginary components in the AC impedance of a parallel RL circuit are given by

$$Z_{re} = \frac{\omega^2 RL^2}{R^2 + \omega^2 L^2} \tag{2.86}$$

$$Z_{im} = \frac{\omega R^2 L}{R^2 + \omega^2 L^2} \tag{2.87}$$

and the impedance phase angle is given by

$$\tan\phi = \frac{R}{\omega L} \tag{2.88}$$

In the complex plane, the AC impedance of a parallel RL circuit is represented by a semicircle in the first quadrant with a radius of R/2 and the centre at (R/2, 0), as shown in Figure 2.20. The curve crosses the real axis at R and 0 at the frequencies of $\omega \to \infty$ and $\omega = 0$, respectively.

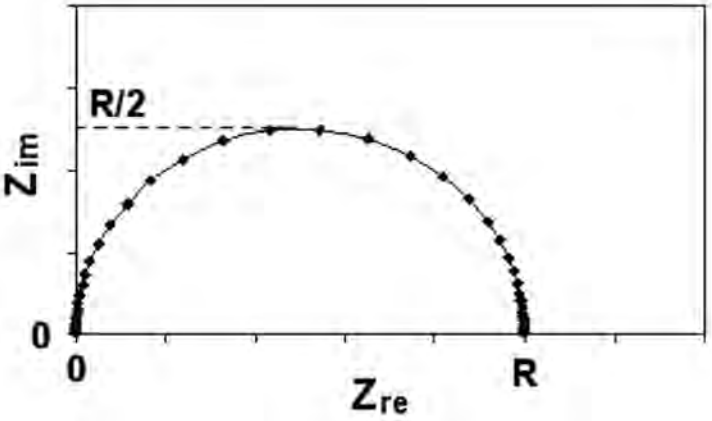


Figure 2.20. Graphical representation of the AC impedance of a parallel RL circuit

In a series RL circuit (R-L), the overall impedance of the RL circuit in series, Z_{R-L}, is written as

$$Z_{R-L} = R + i\omega L \quad (2.89)$$

The real and imaginary components, Z_{re} and Z_{im}, in the AC impedance can be obtained:

$$Z_{re} = R \quad (2.90)$$

$$Z_{im} = \omega L \quad (2.91)$$

The phase angle ϕ is as follows

$$\tan \phi = \frac{\omega L}{R} \quad (2.92)$$

A graphical representation of the AC impedance of a series RL circuit, according to the above calculations, is shown in Figure 2.21. In the complex plane of this figure, the AC impedance of a series RL circuit is a straight vertical line in the first quadrant with a constant Z' value of R.

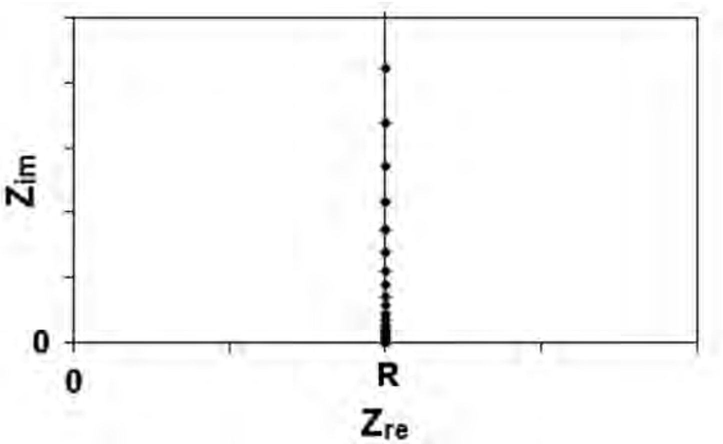


Figure 2.21. Graphical representation of the AC impedance of a series RL circuit

2.4.3 AC Impedance of a Capacitor–Inductor Circuit

In a parallel capacitor–inductor (CL) circuit (C/L), the overall AC impedance, $Z_{C/L}$, can be expressed as

$$Z_{C/L} = [(i\omega L)^{-1} + i\omega C]^{-1} \tag{2.93}$$

Then

$$Z_{C/L} = \left(\frac{1}{\frac{1}{\omega L} - \omega C}\right)i \tag{2.94}$$

So, the real and imaginary components of the AC impedance of the parallel CL circuit are given by

$$Z_{re} = 0 \tag{2.95}$$

$$Z_{im} = \frac{1}{\frac{1}{\omega L} - \omega C} \tag{2.96}$$

and the phase angle is 90°.

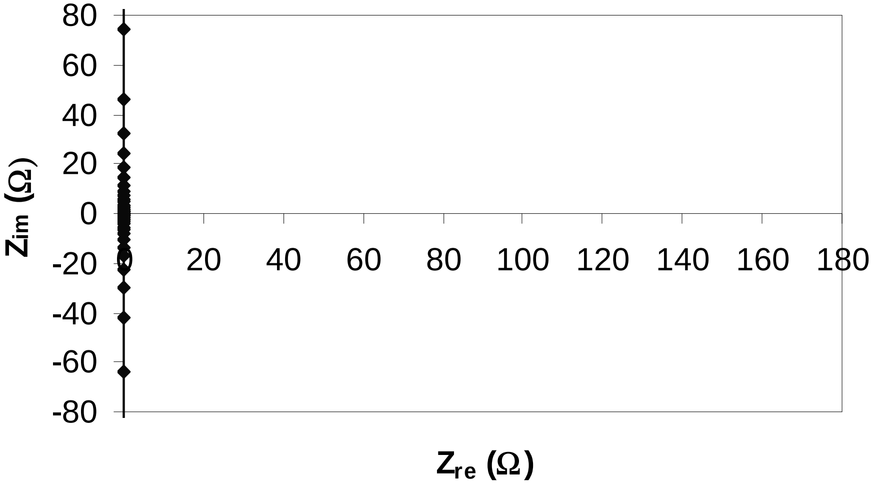


Figure 2.22. Graphical representation of the AC impedance of a simple parallel CL circuit (L = 0.04 H, C = 0.00001 F)

According to the above calculations, a graphical representation of the AC impedance of a parallel CL circuit is depicted in Figure 2.22. In the complex plane, the AC impedance of the parallel CL circuit is represented by a straight vertical line on the Z''-axis with a constant Z' value of zero.

In a series CL circuit (C-L), according to the primary rules, the overall AC impedance of a CL circuit in series, Z_{C-L}, is expressed as

$$Z_{C-L} = (i\omega C)^{-1} + i\omega L \tag{2.97}$$

Therefore,

$$Z_{C-L} = (\omega L - \frac{1}{\omega C})i \tag{2.98}$$

The real and imaginary components, Z_{re} and Z_{im}, in the AC impedance can then be obtained:

$$Z_{re} = 0 \tag{2.99}$$

$$Z_{im} = \omega L - \frac{1}{\omega C} \tag{2.100}$$

and the phase angle is again 90°.

According to the above calculations, a graphical representation of the AC impedance of a series CL circuit is given in Figure 2.23. As shown in the complex plane, the AC impedances of a series CL circuit are also located on the Z''-axis with a constant Z' value of zero.

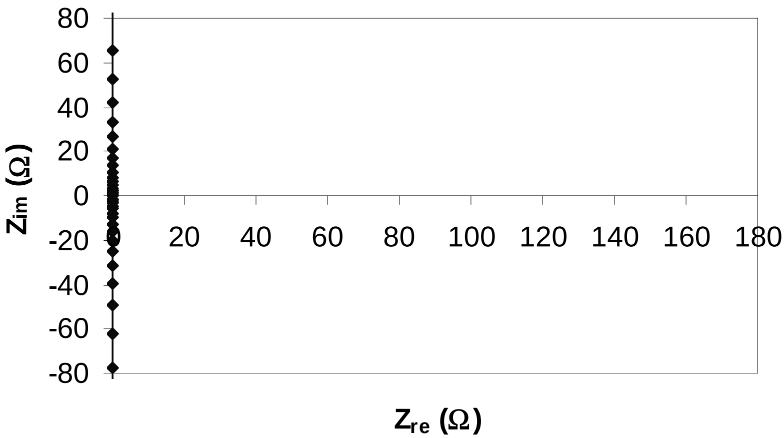


Figure 2.23. Graphical representation of the AC impedance of a series CL circuit (L = 0.04 H, C = 0.01 F)

2.4.4 AC Impedance of a Resistor–Capacitor–Inductor Circuit

2.4.4.1 R-(C/L) Circuit

If a circuit of parallel CL is in series with R (R-(C/L)), the overall AC impedance, $Z_{R-(C/L)}$, can be expressed as

$$Z_{R-(C/L)} = R + [(i\omega L)^{-1} + i\omega C]^{-1} \tag{2.101}$$

Then, we have

$$Z_{R-(C/L)} = R + \left(\frac{1}{\frac{1}{\omega L} - \omega C}\right)i \tag{2.102}$$

So, the real and imaginary components of the AC impedance of the R-(C/L) circuit are given by

$$Z_{re} = R \tag{2.103}$$

$$Z_{im} = \frac{1}{\frac{1}{\omega L} - \omega C} \tag{2.104}$$

and the phase angle ϕ is given by

$$\tan\phi = \frac{1}{R(\frac{1}{\omega \mathrm{L}} - \omega C)} \tag{2.105}$$

Based on these equations, Figure 2.24 gives a graphical representation of the AC impedance of the R-(C/L) circuit. In the complex plane, the AC impedance of the circuit is represented by a straight vertical line with a constant Z' value of R.

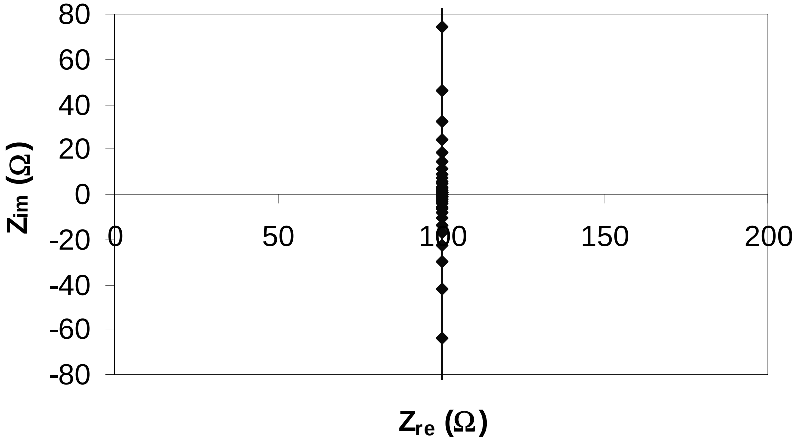


Figure 2.24. Graphical representation of the AC impedance of the R-(C/L) circuit (L = 0.04 H, C = 0.00001 F, R = 100 Ω)

2.4.4.2 R-C-L Circuit

In a series RCL circuit (R-C-L), the overall impedance, Z_{R-C-L}, is expressed as

$$Z_{R-C-L} = R + (i\omega C)^{-1} + i\omega L \tag{2.106}$$

Then we obtain

$$Z_{R-C-L} = R + (\omega L - \frac{1}{\omega C})i \tag{2.107}$$

The real and imaginary components, Z_{re} and Z_{im}, in the AC impedance of the R-C-L circuit in series are given by

$$Z_{re} = R \tag{2.108}$$

$$Z_{im} = \omega L - \frac{1}{\omega C} \tag{2.109}$$

The phase angle ϕ is then described by

$$\tan\phi = \frac{\omega L - \dfrac{1}{\omega C}}{R} \tag{2.110}$$

Based on these equations, a graphical representation of the AC impedance of the (R-C-L) circuit is given in Figure 2.25. As shown in the complex plane of this figure, the AC impedance of the series RCL circuit is a straight line with a constant Z' value of R.

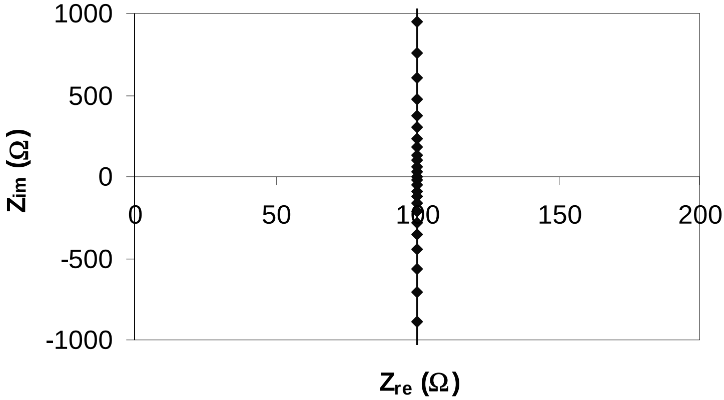


Figure 2.25. Graphical representation of the AC impedance of a series RCL circuit (L = 0.04 H, C = 0.00001 F, R = 100 Ω)

2.4.4.3 R/C/L Circuit

In a circuit of parallel RCL (R/C/L), the overall AC impedance, $Z_{R/C/L}$, can be expressed as

$$Z_{R/C/L} = [R^{-1} + (i\omega L)^{-1} + i\omega C]^{-1} \tag{2.111}$$

After a series of transformations, the standard form of the impedance is obtained:

$$Z_{R/C/L} = \frac{\dfrac{1}{R}}{(\dfrac{1}{R})^2 + (\omega C - \dfrac{1}{\omega L})^2} - \frac{\omega C - \dfrac{1}{\omega L}}{(\dfrac{1}{R})^2 + (\omega C - \dfrac{1}{\omega L})^2} i \tag{2.112}$$

Thus, the real and imaginary components of the AC impedance of the parallel RCL circuit are given by

$$Z_{re} = \frac{\dfrac{1}{R}}{(\dfrac{1}{R})^2 + (\omega C - \dfrac{1}{\omega L})^2} \tag{2.113}$$

$$Z_{im} = -\frac{\omega C - \frac{1}{\omega L}}{(\frac{1}{R})^2 + (\omega C - \frac{1}{\omega L})^2} \quad (2.114)$$

and the phase angle ϕ is given by

$$\tan\phi = R(\omega C - \frac{1}{\omega L}) \quad (2.115)$$

Based on these equations, Figure 2.26 gives a graphical representation of the AC impedance of the (R/C/L) circuit.

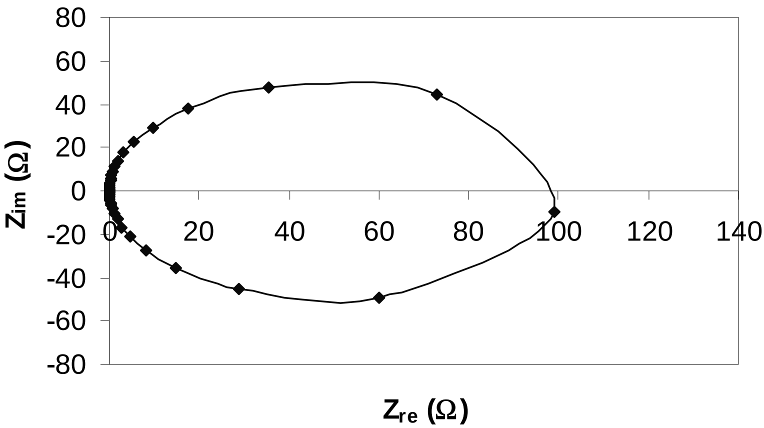


Figure 2.26. Graphical representation of the AC impedance of a simple parallel RCL circuit (L = 0.04 H, C = 0.00001 F, R = 100 Ω)

2.4.4.4 R/(C-L) Circuit

If a series CL is in parallel with R (R/C-L) in a circuit, the overall impedance, $Z_{R/(C-L)}$, is expressed as

$$Z_{R/(C-L)} = [R^{-1} + ((i\omega C)^{-1} + i\omega L)^{-1}]^{-1} \quad (2.116)$$

Then, we have

$$Z_{R/(C-L)} = \frac{\frac{1}{R}}{(\frac{1}{R})^2 + (\frac{\omega C}{\omega^2 CL - 1})^2} + \frac{\frac{\omega C}{\omega^2 CL - 1}}{(\frac{1}{R})^2 + (\frac{\omega C}{\omega^2 CL - 1})^2} i \quad (2.117)$$

Thus, the real and imaginary components, Z_{re} and Z_{im}, in the AC impedance of the R/C-L circuit are:

$$Z_{re} = \frac{\frac{1}{R}}{(\frac{1}{R})^2 + (\frac{\omega C}{\omega^2 CL - 1})^2} \tag{2.118}$$

$$Z_{im} = \frac{\frac{\omega C}{\omega^2 CL - 1}}{(\frac{1}{R})^2 + (\frac{\omega C}{\omega^2 CL - 1})^2} \tag{2.119}$$

The phase angle ϕ is then given by

$$\tan\phi = \frac{\omega CR}{\omega^2 CL - 1} = R(\omega L - \frac{1}{\omega C})^{-1} \tag{2.120}$$

Based on these, a graphical representation of the AC impedance of the R/C-L circuit can be calculated and is depicted in Figure 2.27.

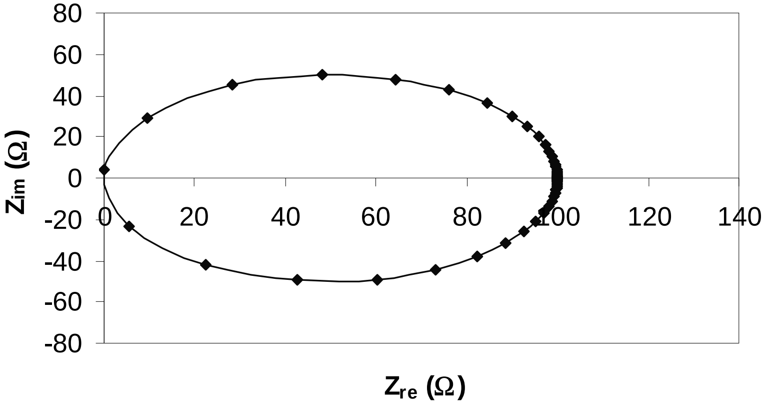


Figure 2.27. Graphical representation of the AC impedance of the R/(C-L) circuit (L = 0.04 H, C = 0.00001 F, R = 100 Ω)

2.4.4.5 C-(R/L) Circuit

In a circuit of a parallel RL in series with C (C-R/L), the overall AC impedance, $Z_{C-(R/L)}$, can be expressed as

$$Z_{C-(R/L)} = (i\omega C)^{-1} + [(R^{-1} + (i\omega L)^{-1}]^{-1} \tag{2.121}$$

Based on the previous calculation in Equation 2.85, we have

$$Z_{C-(R/L)} = (i\omega C)^{-1} + \frac{\omega^2 RL^2}{R^2 + \omega^2 L^2} + i\frac{\omega R^2 L}{R^2 + \omega^2 L^2} \tag{2.122}$$

Then

$$Z_{C-(R/L)} = \frac{\omega^2 RL^2}{R^2 + \omega^2 L^2} + i\left(\frac{\omega R^2 L}{R^2 + \omega^2 L^2} - \frac{1}{\omega C}\right) \tag{2.123}$$

So, the real and imaginary components of the AC impedance of the C-R/L circuit are given by

$$Z_{re} = \frac{\omega^2 RL^2}{R^2 + \omega^2 L^2} \tag{2.124}$$

$$Z_{im} = \frac{\omega R^2 L}{R^2 + \omega^2 L^2} - \frac{1}{\omega C} \tag{2.125}$$

and the phase angle is written as

$$\tan\phi = \frac{\omega^2 R^2 LC - R^2 - \omega^2 L^2}{\omega^3 RL^2 C} \tag{2.126}$$

In the complex plane, an example of the AC impedance of the C-(R/L) circuit is shown in Figure 2.28.

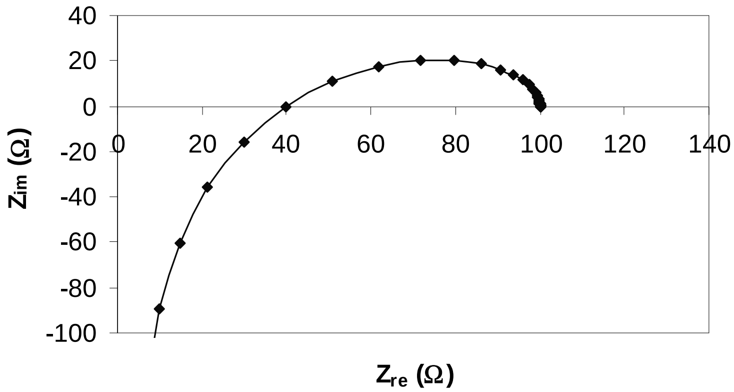


Figure 2.28. Graphical representation of the AC impedance of the C-(R/L) circuit (L = 0.04 H, C = 0.00001 F, R = 100 Ω)

2.4.4.6 C/(R-L) Circuit

In a circuit of a series RL in parallel with C (C/(R-L)), the overall impedance, $Z_{C/(R-L)}$, is expressed as

$$Z_{C/(R-L)} = [(i\omega C) + (R + i\omega L)^{-1}]^{-1} \tag{2.127}$$

Then, we have

$$Z_{C/(R-L)} = \frac{R}{(1-\omega^2 LC)^2 + (R\omega C)^2} + \frac{\omega L(1-\omega^2 LC) - R^2\omega C}{(1-\omega^2 LC)^2 + (R\omega C)^2} i \qquad (2.128)$$

The real and imaginary components, Z_{re} and Z_{im}, of the AC impedance of the C/(R-L) circuit are then written as

$$Z_{re} = \frac{R}{(1-\omega^2 LC)^2 + (R\omega C)^2} \qquad (2.129)$$

$$Z_{im} = \frac{\omega L(1-\omega^2 LC) - R^2\omega C}{(1-\omega^2 LC)^2 + (R\omega C)^2} \qquad (2.130)$$

The phase angle ϕ is given by

$$\tan\phi = \frac{\omega L(1-\omega^2 LC) - R^2\omega C}{R} \qquad (2.131)$$

An example, in the complex plane, of the AC impedance of the C/(R-L) circuit is presented in Figure 2.29.

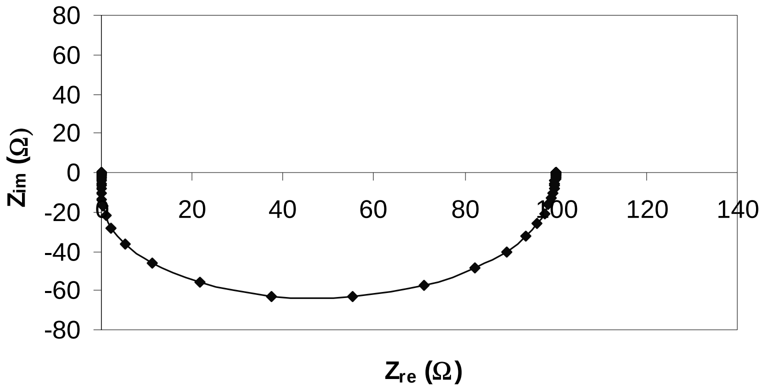


Figure 2.29. Graphical representation of the AC impedance of the C/(R-L) circuit (L = 0.04 H, C = 0.00001 F, R = 100 Ω)

2.4.4.7 L-(R/C) Circuit

In a circuit of a parallel RC in series with L (L-R/C), the overall AC impedance, $Z_{L-(R/C)}$, can be expressed as

$$Z_{L\text{-}(R/C)} = i\omega L + \left(R^{-1} + i\omega C\right)^{-1} \qquad (2.132)$$

Based on Equation 2.74, we have

$$Z_{L-(R/C)} = i\omega L + \frac{R}{1+(\omega RC)^2} - i\frac{\omega R^2 C}{1+(\omega RC)^2} \tag{2.133}$$

Then

$$Z_{L-(R/C)} = \frac{R}{1+(\omega RC)^2} + i(\omega L - \frac{\omega R^2 C}{1+(\omega RC)^2}) \tag{2.134}$$

The real and imaginary components, Z_{re} and Z_{im}, of the AC impedance of the L-R/C circuit are written as

$$Z_{re} = \frac{R}{1+(\omega RC)^2} \tag{2.135}$$

$$Z_{im} = \omega L - \frac{\omega R^2 C}{1+(\omega RC)^2} \tag{2.136}$$

The phase angle ϕ is given by

$$\tan\phi = \frac{\omega L + \omega^3 R^2 L C^2 - \omega R^2 C}{R} \tag{2.137}$$

In the complex plane, an example of the AC impedance of the L-(R/C) circuit is depicted in Figure 2.30.

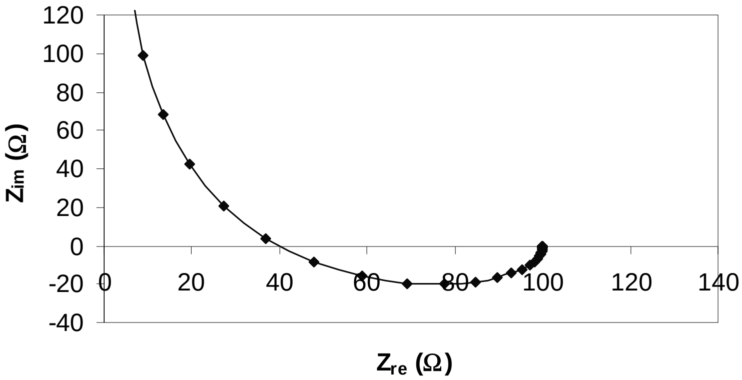


Figure 2.30. Graphical representation of the AC impedance of the L-(R/C) circuit (L = 0.04 H, C = 0.00001 F, R = 100 Ω)

2.4.4.8 L/(R-C) Circuit

In a circuit of a series RC in parallel with L (L/(R-C)), the overall impedance, $Z_{L/(R-C)}$, is expressed as

$$Z_{L/(R-C)} = [(i\omega L)^{-1} + (R + (i\omega C)^{-1})^{-1}]^{-1} \tag{2.138}$$

Then we have

$$Z_{L/(R-C)} = \frac{R}{(1-\frac{1}{\omega^2 LC})^2 + (\frac{R}{\omega L})^2} + \frac{\frac{R^2}{\omega L} - \frac{1}{\omega C}(1-\frac{1}{\omega^2 LC})}{(1-\frac{1}{\omega^2 LC})^2 + (\frac{R}{\omega L})^2} i \tag{2.139}$$

The real and imaginary components, Z_{re} and Z_{im}, of the AC impedance of the L/(R-C) circuit are given by

$$Z_{re} = \frac{R}{(1-\frac{1}{\omega^2 LC})^2 + (\frac{R}{\omega L})^2} \tag{2.140}$$

$$Z_{im} = \frac{\frac{R^2}{\omega L} - \frac{1}{\omega C}(1-\frac{1}{\omega^2 LC})}{(1-\frac{1}{\omega^2 LC})^2 + (\frac{R}{\omega L})^2} \tag{2.141}$$

The phase angle ϕ is given by

$$\tan\phi = \frac{R^2 - \frac{L}{C} + \frac{1}{\omega^2 C^2}}{R\omega L} \tag{2.142}$$

In the complex plane, an example of the AC impedance of the L/(R-C) circuit is shown in Figure 2.31.

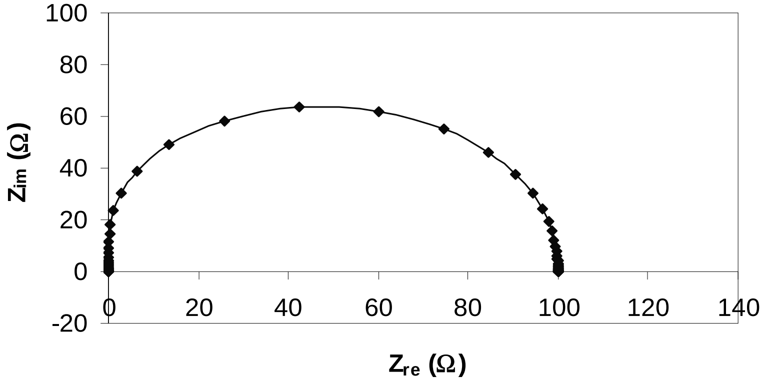


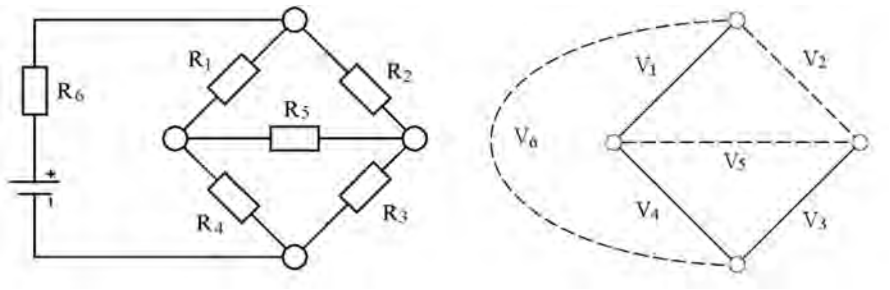
Figure 2.31. Graphical representation of the impedance of the L/(R-C) circuit (L = 0.04 H, C = 0.00001 F, R = 100 Ω)

2.5 Network Circuit Analysis

To construct an equivalent circuit of a complicated electrode process (e.g., a porous electrode) and calculate its impedance, more knowledge about the network circuit may be necessary. In this section, we will spend some time discussing network circuit analysis.

2.5.1 Topological Features of a Network

Two major factors shape an electric network: the type of elements it contains and the manner in which the elements are connected. The latter is called the network topology. To analyze an electric network, one needs to know the number of independent voltage and current variables. To facilitate the following discussion of a network topology, we keep the nodes and replace the elements with lines in the network circuit, thus simplifying the network topology, as depicted in Figure 2.32. Figure 2.32*a* shows a regular network circuit while the configuration in Figure 2.32*b* is called the line graph of a network.



a *b*

Figure 2.32. A regular circuit and its network line graph: *a* circuit diagram; *b* line graph of circuit

2.5.1.1 Some Terms Used in Network Topology

Several terms are frequently used in network analysis: node, branch, tree, link, loop, and mesh.

A *node* is a terminal or junction at which two or more circuit elements are connected.

A *branch* is a portion of a network which contains either a single element or a certain connection of elements between two nodes.

A *tree* is a connected portion or sub-graph of the entire graph that contains all the nodes but no loops. For example, the solid lines in Figure 2.32*b* form a tree, which consists of all the four nodes in the graph; there are no loops within the tree.

In Figure 2.32*b*, the dashed lines are called *links*, i.e., the branches which are not in the chosen tree. A graph usually has more than one tree, and the entire graph is the sum of the links and tree branches. Assuming that there are N nodes in a network, the number of tree branches is N–1.

A *loop* comprises a set of branches that form a closed path in a network. This set of branches passes through no node or element more than once.

A *mesh* is a loop which contains no other loops within the contour of its closed path. Basically, the term “loop” is applicable to a closed path in both planar and non-planar circuits, whereas “mesh” is only applicable to planar circuits. The meshes in a planar circuit are in fact the contours of the “windows” seen in the circuit diagram. For example, Figure 2.32*a* has three windows, and thus the circuit is a three-mesh circuit.

A *planar network* or *circuit* is one that can be drawn on a plane surface without any of the branches crossing each other. Conversely, a non-planar network or circuit cannot be drawn on a plane surface without the crossing of branches.

2.5.1.2 Independent Voltages

Assuming that there are N nodes and B branches in a network, if all the branch voltages of any tree are made zero by short-circuiting the branches, all the nodes of the circuit are at the same potential, and thus all the voltages of the links are zero. In other words, the link voltages depend on the tree branch voltages. Assuming that there is one link voltage independent of the tree branch voltages, it could not be forced to zero by short-circuiting the tree branches. Consequently at least one node voltage is different from the voltage of the rest of the nodes. Therefore, we conclude that the (N–1) tree branch voltages are independent and can be used to obtain the link voltages. For example, there are four nodes and three independent voltages, namely V1, V3, and V4 in Figure 2.32*b*. The link voltages V2, V5, and V6 can be calculated from the three independent voltages.

2.5.1.3 Independent Currents

Since a tree in a graph contains no loops, all the tree branch currents depend on the link currents. In other words, all the tree branch currents can be expressed in terms of the link currents. Assuming the number of branches in a circuit is B, there will be B–(N–1) link currents, which are independent. Therefore, B–(N–1) independent equations are needed to analyze the circuit. For example, Figure 2.32*b* needs three independent current equations.

2.5.2 Network Theorems [4]

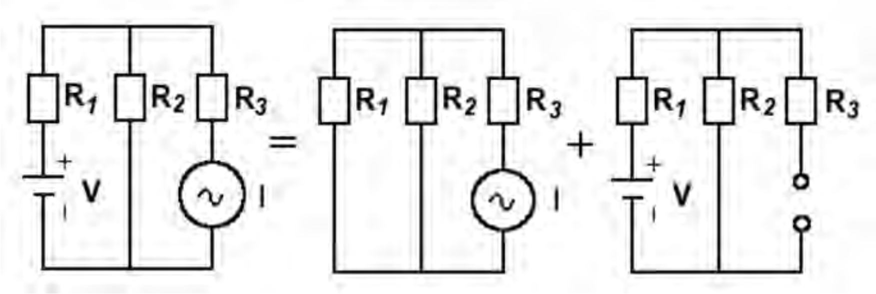
Although the application of Kirchhoff’s laws offers basic tools to analyze a network, knowledge of certain network theorems, use of network equivalence, and use of reduction procedures simplify the process of network analysis. Basically, these theorems are applicable for linear networks.

2.5.2.1 Network Reduction

One of the most important strategies to simplify or reduce a linear circuit is superposition. The superposition theorem states that the response of a linear network to a number of simultaneously applied sources is equal to the sum of the individual responses due to each source acting alone.

By analyzing separately a single-input circuit, superposition allows us to analyze linear circuits with more than one independent source. For example, Figure

2.33*a* shows one voltage source and one current source. According to the superposition theorem, the current flowing through resistor R_1 is the sum of the individual response to the voltage source and current source. By replacing the voltage source with a short circuit, as depicted in Figure 2.33*b*, the current through resistor R_1 is the response of R_1 to the current source. To find the response of R_1 to the voltage source, we can replace the current source with an open circuit, as depicted in Figure 2.33*c*. Then the current flowing through resistor R_1 with a voltage source and a current source can be obtained. Compared with the straight analysis of the current through resistor R_1, superposition simplifies the circuit.



a *b* *c*

Figure 2.33. Superposition of a linear circuit

Other methods to simplify the circuit are Thevenin’s and Norton’s theorems. These two theorems can be used to replace the entire circuit by employing equivalent circuits. For example, Figure 2.34 shows a circuit separated into two parts. Circuit A is linear. Circuit B contains non-linear elements. The essence of Thevenin’s and Norton’s theorems is that no dependent source in circuit A can be controlled by a voltage or current associated with an element in circuit B, and vice versa.

Thevenin’s theorem states that a section of a linear circuit containing one or more sources and impedances can be replaced with an equivalent circuit model containing only one voltage source and one series-connected impedance, as shown in Figure 2.35.

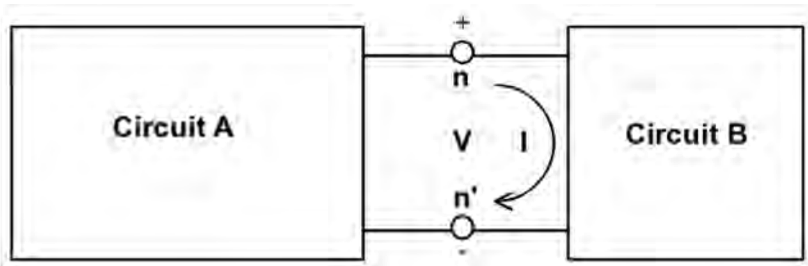


Figure 2.34. Partitioned circuit

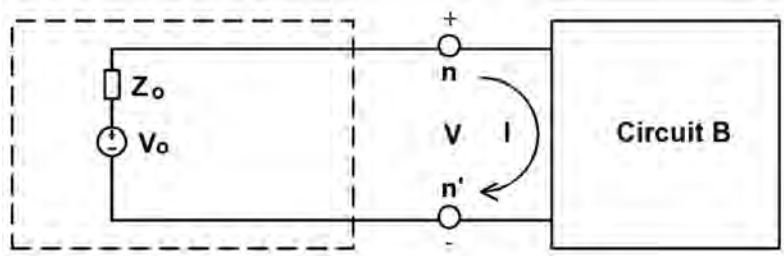


Figure 2.35. Graphical presentation of Thevenin's theorem

To determine V_o, we can remove circuit B and calculate the voltage drop across the terminals n and n'. This voltage drop is the Thevenin voltage. To determine the impedance Z_o, we can kill all the sources in circuit A, as we did in Figure 2.33, and then calculate the impedance from n-n' terminals by looking back into circuit A. This impedance Z_o is the Thevenin impedance, which is also called the output impedance of circuit A.

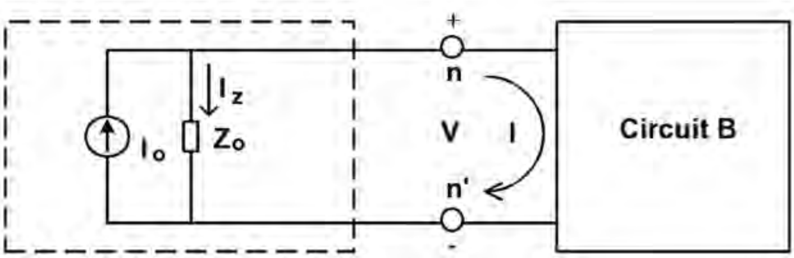


Figure 2.36. Graphical presentation of Norton's theorem

Similar to Thevenin's theorem, Norton's theorem states that a section of a linear circuit containing one or more sources and impedances can be replaced with an equivalent circuit model containing only one constant current source and one parallel-connected impedance, as shown in Figure 2.36.

To determine the Norton equivalent impedance Z_o in Figure 2.36, we can kill all the sources in circuit A and then calculate the impedance from n-n' terminals by looking back into circuit A. Thus, the Norton impedance Z_o is equal to the Thevenin impedance. The Norton current I_o is a constant current that remains the same regardless of the impedance of circuit B. It can be determined by

$$I_o = \frac{V_o}{Z_o} \tag{2.143}$$

Note that only at the output terminals n-n' are the Thevenin and Norton equivalents the same. In other words, at the output terminals n-n' the voltage and current of the Thevenin equivalent circuit and the Norton equivalent circuit are identical.

2.5.2.2 Loop and Mesh Analysis

A commonly used network analysis method is loop and mesh analysis, which is generally based on KVL. As defined previously, loop analysis refers to the general method of current analysis for both planar and non-planar networks, whereas mesh analysis is reserved for the analysis of planar networks. In loop or mesh analysis, the circulating currents are selected as the unknowns, and a circulating current is assigned to each independent loop or mesh of the network. Then a series of equations can be formed according to KVL.

The series of equations in the form of $[Z][I]=[V]$ can be established by equating the sum of the externally applied voltage sources acting in each loop to the sum of the voltage drops across the branches forming the loop. The number of equations is equal to the number of independent loops in the network. The general equation in loop or mesh analysis is given by

$$\begin{pmatrix} Z_{11} & Z_{12} & Z_{13} & \dots & Z_{1N} \\ Z_{21} & Z_{22} & Z_{23} & \dots & Z_{2N} \\ Z_{31} & Z_{32} & Z_{33} & \dots & Z_{3N} \\ \dots & \dots & \dots & \dots & \dots \\ Z_{N1} & Z_{N2} & Z_{N3} & \dots & Z_{NN} \end{pmatrix} \bullet \begin{pmatrix} I_1 \\ I_2 \\ I_3 \\ \dots \\ I_N \end{pmatrix} = \begin{pmatrix} V_1 \\ V_2 \\ V_3 \\ \dots \\ V_N \end{pmatrix} \tag{2.144}$$

where the impedance matrix [Z] is an $N \times N$ matrix, as described in Equation 2.144. The following rules describe how to determine the values of the voltages, currents, and impedances in Equation 2.144.

1. The voltages in Equation 2.144 are equal to the voltage sources in a given loop. If the direction of the current caused by the voltage is the same as that of the assigned current, the voltage is positive. Otherwise, the voltage is negative.
2. The series of mesh impedances, known as the self-mesh impedances, Z_{11}, Z_{22}, Z_{33}, …, Z_{NN}, are given by the sum of all impedances through the loop in which the circulating current flows.
3. Each mesh mutual impedance, denoted by Z_{ik} ($i \neq k$), is given by the sum of the impedances through which both mesh currents I_i and I_k flow. In other words, the mesh mutual impedances are equal to the sum of the impedances shared by meshes i and k. If the direction of the current I_i in loop i is opposite to that of the current I_k in the adjacent loop k, the mutual impedance equals the negative sum of the impedances, whereas if the direction of the current I_i is the same as that of the current I_k, then the mutual impedance equals the positive sum. In a linear network, the following can be obtained:

$$Z_{ik} = Z_{ki} \tag{2.145}$$

A linear matrix equation can be solved by the application of Cramer's rule. Assuming the determinant Δ of the matrix Z is non-zero, the solution of the current can be expressed as

$$[I] = [Z]^{-1}[V] \tag{2.146}$$

where $[Z]^{-1}$ is the inverse of [Z], which can be expressed as

$$[Z]^{-1} = \frac{1}{\Delta}(\Delta_{ik})^T = \frac{1}{\Delta}\Delta_{ki} \tag{2.147}$$

where Δ_{ik} is the matrix cofactor and $(\Delta_{ik})^T = \Delta_{ki}$ represents the matrix transpose. Δ and Δ_{ki} can be expressed as follows:

$$\Delta = \|[Z]\| = \begin{vmatrix} Z_{11} & Z_{12} & \dots & Z_{1i} & \dots & Z_{1N} \\ Z_{21} & Z_{22} & \dots & Z_{2i} & \dots & Z_{2N} \\ \dots & \dots & \dots & \dots & \dots & \dots \\ Z_{N1} & Z_{N2} & \dots & Z_{Ni} & \dots & Z_{NN} \end{vmatrix} \tag{2.148}$$

$$\Delta_{ki} = \begin{bmatrix} \Delta_{11} & \Delta_{21} & \Delta_{31} & \dots & \Delta_{N1} \\ \Delta_{12} & \Delta_{22} & \Delta_{32} & \dots & \Delta_{N2} \\ \Delta_{13} & \Delta_{23} & \Delta_{33} & \dots & \Delta_{N3} \\ \dots & \dots & \dots & \dots & \dots \\ \Delta_{1N} & \Delta_{2N} & \Delta_{3N} & \dots & \Delta_{NN} \end{bmatrix} \tag{2.149}$$

where |[Z]| is the determinant of [Z].

2.5.2.3 Nodal Analysis

In nodal analysis, the voltages between adjacent nodes of the network are chosen as the unknowns. This can commonly be achieved by selecting a reference node from the graph of the network. Equations are then formed if KCL is employed. By equating the sum of the currents flowing through admittances associated with one node to the sum of the currents flowing out of the current sources associated with the same node, a set of equations can be established with the form of $[Y][V] = [I]$:

$$\begin{pmatrix} Y_{11} & Y_{12} & Y_{13} & \dots & Y_{1,N-1} \\ Y_{21} & Y_{22} & Y_{23} & \dots & Y_{2,N-1} \\ Y_{31} & Y_{32} & Y_{33} & \dots & Y_{3,N-1} \\ \dots & \dots & \dots & \dots & \dots \\ Y_{N-1,1} & Y_{N-1,2} & Y_{N-1,3} & \dots & Y_{N-1,N-1} \end{pmatrix} \begin{pmatrix} V_1 \\ V_2 \\ V_3 \\ \dots \\ V_{N-1} \end{pmatrix} = \begin{pmatrix} I_1 \\ I_2 \\ I_3 \\ \dots \\ I_{N-1} \end{pmatrix} \tag{2.150}$$

where the admittance matrix [Y] is an $(N-1)\times(N-1)$ matrix given in Equation 2.150. The following rules describe how to determine the values in Equation 2.150.

1. The currents in Equation 2.150 are equal to the sum of the source currents associated with one given node. The currents are positive if they go into the nodes. Otherwise, the currents are negative.
2. Y_{11}, Y_{22}, Y_{33}, …, $Y_{N-1,N-1}$, known as the self node admittances, are given by the sum of all admittances directed to a given node with all other nodes shorted to the reference node.
3. Each node mutual admittance Y_{ik} $(i \neq k)$ is the sum of the admittances between two given nodes i and k. The current $Y_{ik}V_i$ in the mutual admittances between nodes i and k is negative if the voltages of nodes i and k have the same assumed polarity relative to the reference node. The current $Y_{ik}V_i$ is positive if the voltages of nodes i and k have the opposite assumed polarity relative to the reference node. In a linear network, we have

$$Y_{ik} = Y_{ki} \tag{2.151}$$

2.5.3 Transient Network Analysis

If a generator is imposed on a network or switched out of the circuit with capacitors and/or inductors, there will be a transitory change in the currents and voltages until a new equilibrium state is established. These changing currents and voltages are defined as transients. The time period from the moment of switching to the time equilibrium established is called the transient state. In transient analysis, we always come across linear differential, integral, or integro-differential equations of either the first or the second order when Kirchhoff's laws are applied. In this section, we will solve these equations using a classical method.

The first order circuit with one storage element is described by

$$\frac{dx}{dt} + a_0 x = f(t) \tag{2.152}$$

The second order circuit with two storage elements can be described by

$$\frac{d^2x}{dt^2} + a_1\frac{dx}{dt} + a_0 = f(t) \tag{2.153}$$

In Equations 2.152 and 2.153, a_1 and a_0 are the constant coefficients; x may be either voltage, current, or charge; $f(t)$ is the driving voltage or current; and t is time. The solution of these equations consists of two parts:

$$x = x_n + x_f \tag{2.154}$$

where x_n is the natural response and x_f is the forced response. The natural response is the general solution of the differential equation with the driving function $f(t)$ set to zero. The forced response is a particular solution of the differential equation for a given driving function. For example, the complete solution of Equation 2.152 can be derived as follows.

The characteristic equation of Equation 2.153 can be expressed as

$$s^2 + a_1 s + a_0 = 0 \tag{2.155}$$

Providing s_1 and s_2 are the two eigenvalues of Equation 2.155, the two natural responses can be obtained:

$$x_{n1} = A_1 e^{s_1 t} \tag{2.156}$$

$$x_{n2} = A_2 e^{s_2 t} \tag{2.157}$$

where A_1 and A_2 are arbitrary constants.

As this is a linear equation, the natural response x_n can simply be summed up as

$$x_n = A_1 e^{s_1 t} + A_2 e^{s_2 t} \tag{2.158}$$

The eigenvalues are also known as the natural frequencies of the circuit, which are the reciprocals of the circuit response time constant. The eigenvalues of Equation 2.155 could be real or complex numbers. If the natural frequencies are complex, we have

$$s_{1,2} = \alpha \pm i\beta \tag{2.159}$$

The natural response is given by

$$x_n = A_1 e^{(\alpha + i\beta)t} + A_2 e^{(\alpha - i\beta)t} \tag{2.160}$$

Based on Euler’s formula, the above equation can be rewritten as

$$x_n = [B_1 \cos \beta t + iB_2 \sin \beta t]\, e^{\alpha t} \tag{2.161}$$

where

$$B_1 = A_1 + A_2 \tag{2.162}$$

$$B_2 = A_1 - A_2 \tag{2.163}$$

In a circuit, if the real part in the eigenvalues is negative, then the response decays with time. The imaginary part in the eigenvalues implies that this decayed response is accompanied by oscillation.

If there are two real and equal roots for Equation 2.155, the natural response is given by

$$x_n = \left(A_1 + A_2 t\right) e^{st} \tag{2.164}$$

This demonstrates that the response is the superposition of two parts: the linear response and the exponential decayed response.

One solution of the forced response x_f is the undetermined coefficient method. Assuming the forced response has the same form of source function $f(t)$ but a different coefficient, putting this trial forced response into the differential equation yields the coefficients in the forced response x_f.

For a higher order equation, the general form is given by

$$a_n \frac{d^n x}{dt^n} + a_{n-1} \frac{d^{n-1} x}{dt^{n-1}} + \ldots + a_r \frac{d^r x}{dt^r} + \ldots + a_1 \frac{dx}{dt} + a_0 x = f(t) \tag{2.165}$$

The characteristic equation of the above equation is given by

$$a_n s^n + a_{n-1} s^{n-1} + \ldots + a_r s^r + \ldots + a_1 s + a_0 = 0 \tag{2.166}$$

The eigenvalues of $s_1, \ldots, s_n$ are the natural frequencies of this circuit, otherwise known as the poles of the circuit network. If the poles are all different, the natural response is given by

$$x_n = A_1 e^{s_1 t} + A_2 e^{s_2 t} + \ldots + A_r e^{s_r t} + \ldots + A_n e^{s_n t} \tag{2.167}$$

If r poles are equal, then we have

$$x_n = \left(A_1 + A_2 t + \ldots + A_r t^{r-1}\right) e^{s_r t} + A_{r+1} e^{s_{r+1} t} + \ldots + A_n e^{s_n t} \tag{2.168}$$

where $A_1 \ldots A_n$ are arbitrary constants.

In general, x_n satisfies

$$a_n \frac{d^n (x_n)}{dt^n} + a_{n-1} \frac{d^{n-1} (x_n)}{dt^{n-1}} + \ldots + a_r \frac{d^r (x_n)}{dt^r} + \ldots + a_1 \frac{d(x_n)}{dt} + a_0 x_n = 0 \tag{2.169}$$

and x_f is a solution of

$$a_n \frac{d^n (x_f)}{dt^n} + a_{n-1} \frac{d^{n-1} (x_f)}{dt^{n-1}} + \ldots + a_r \frac{d^r (x_f)}{dt^r} + \ldots + a_1 \frac{d(x_f)}{dt} + a_0 x_f = f(t) \tag{2.170}$$

Summing the above two equations, we have

$$\begin{aligned} &a_n \frac{d^n (x_n + x_f)}{dt^n} + a_{n-1} \frac{d^{n-1}(x_n + x_f)}{dt^{n-1}} + \dots \\ &+a_r \frac{d^r (x_n + x_f)}{dt^r} + \dots + a_1 \frac{d(x_n + x_f)}{dt} + a_0 (x_n + x_f) = f(t) \end{aligned} \tag{2.171}$$

Thus, $x = x_n + x_f$ is the complete solution of Equation 2.165.

2.6 Basic Knowledge for Understanding EIS

2.6.1 Introduction

Ohm's law defines the resistance, R, in terms of the ratio between voltage V and current I. Its use is limited to the ideal resistor for a DC system, which is independent of frequency. The relationship between the resistance, current, and voltage can be expressed as

$$R = \frac{V}{I} \tag{2.172}$$

However, real electrochemical systems exhibit much more complex behaviours. They are not simply resistive. The electrochemical double layer adds a capacitive term. Other electrode processes, such as diffusion, are time and/or frequency dependent. Therefore, for an actual electrochemical system, impedance is used instead of resistance. The impedance of an electrochemical system (defined as $Z(\omega)$) is the AC response of the system being studied to the application of an AC signal (e.g., sinusoidal wave) imposed upon the system. The form of the current–voltage relationship of the impedance in an electrochemical system can also be expressed as

$$Z(\omega) = \frac{V(t)}{I(t)} \tag{2.173}$$

where $V(t)$ and $I(t)$ are the measurements of voltage and current in an AC system.

The technique that measures the AC impedance of a circuit element or an electric circuit is called *AC impedance spectroscopy*. As described in Section 2.4, the impedances of a resistor (Z_R), a capacitor (Z_C), and an inductor (Z_L) for a sinusoidal system can be expressed, respectively, as follows:

$$Z_R(\omega) = \frac{V(t)}{I(t)} = R \tag{2.174}$$

$$Z_C(\omega) = \frac{V(t)}{I(t)} = \frac{1}{i\omega C} \tag{2.175}$$

$$Z_L(\omega) = \frac{V(t)}{I(t)} = i\omega L \tag{2.176}$$

If AC impedance spectroscopy is used in an electrochemical system, this technique is generally called *electrochemical impedance spectroscopy*, known as EIS. The impedance of an electrochemical system can also be expressed typically in Cartesian coordinates:

$$Z(\omega) = Z_{re} + iZ_{im} \tag{2.177}$$

where Z_{re} (or Z') and Z_{im} (or Z'') are the real and imaginary parts of the impedance, respectively. In polar coordinates, this becomes

$$Z(\omega) = |Z|e^{i\theta} \tag{2.178}$$

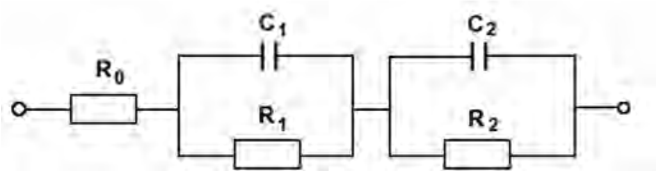
where $|Z| = \sqrt{(Z_{re}^2 + Z_{im}^2)}$ is the modulus and θ is the phase corresponding to a given frequency.

2.6.2 Nyquist and Bode Plots

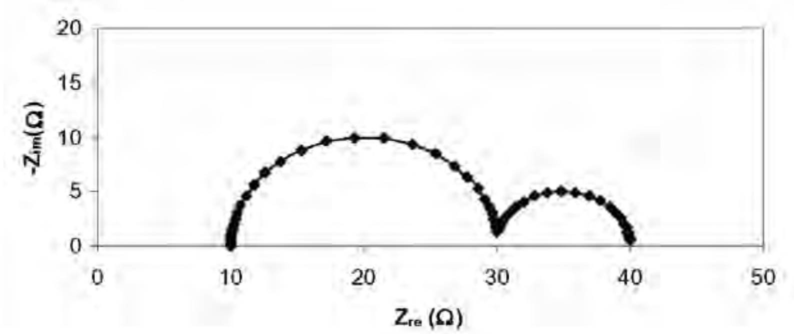
Generally, the impedance spectrum of an electrochemical system can be presented in Nyquist and Bode plots, which are representations of the impedance as a function of frequency. A Nyquist plot is displayed for the experimental data set $Z(Z_{re,i}, Z_{im,i}, \omega_i)$, ($i$ = 1, 2, …, n) of n points measured at different frequencies, with each point representing the real and imaginary parts of the impedance $(Z_{re,i} \sim Z_{im,i})$ at a particular frequency ω_i.

A Bode plot is an alternative representation of the impedance. There are two types of Bode diagram, $\log|Z| \sim \log\omega$ (or $|Z| \sim \log\omega$) and $\theta \sim \log\omega$, describing the frequency dependencies of the modulus and phase, respectively. A Bode plot is normally depicted logarithmically over the measured frequency range because the same number of points is collected at each decade. Both plots usually start at a high frequency and end at a low frequency, which enables the initial resistor to be found more quickly.

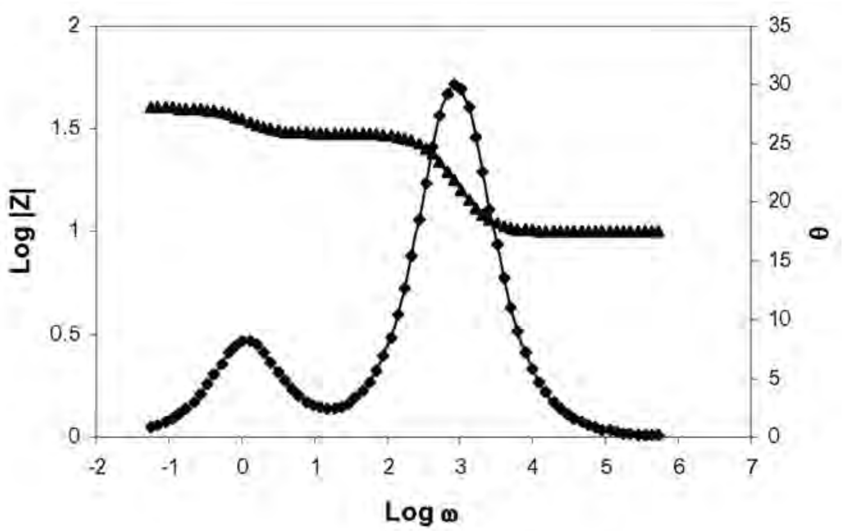
Figure 2.37 shows an example impedance spectrum of an electrochemical system with two time constants. Figure 2.37*a*, *b*, and *c* are the equivalent circuit, simulated Nyquist diagram, and Bode plot, respectively.



a



b



c

Figure 2.37. *a* The equivalent circuit of an electrochemical system with two time constants; *b* Nyquist diagram of a two time constants model simulated over the frequency range 100 kHz–0.0 1Hz (R_0 = 10 Ω, R_1 = 20 Ω, C_1 = 0.0001 F, R_2 = 10 Ω, C_2 = 0.1 F); *c* Bode plot of a two time constants model simulated over the frequency range 100 kHz–0.01 Hz (R_0 = 10 Ω, R_1 = 20 Ω, C_1 = 0.0001 F, R_2 = 10 Ω, C_2 = 0.1 F) (◆) $\log|Z| \sim \log\omega$, (▲) $\theta \sim \log\omega$.

The most common graphical representation of experimental impedance is a Nyquist plot (complex-plane diagram), which is more illustrative than a Bode plot. However, a Bode plot sometimes can provide additional information.

Some typical Nyquist plots for an electrochemical system are shown in Figure 2.38. The usual result is a semicircle, with the high-frequency part giving the solution resistance (for a fuel cell, mainly the membrane resistance) and the width of the semicircle giving the charge-transfer resistance.

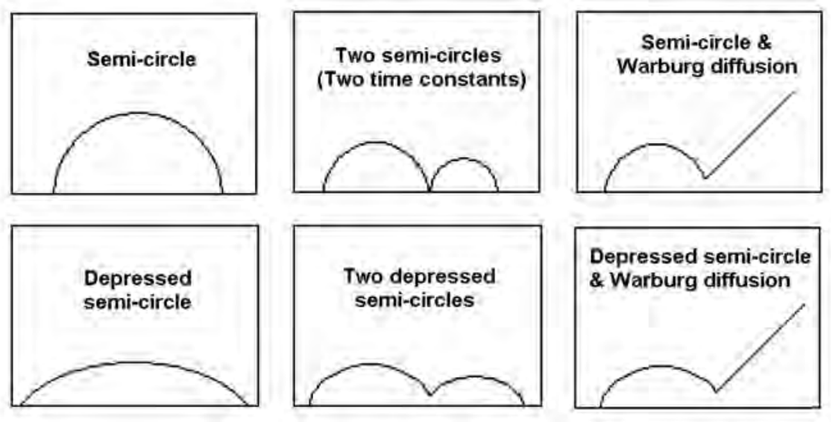


Figure 2.38. Typical Nyquist plots for electrochemical systems

2.6.3 Equivalent Circuit Models

EIS data analysis is commonly carried out by fitting it to an equivalent electric circuit model. An equivalent circuit model is a combination of resistances, capacitances, and/or inductances, as well as a few specialized electrochemical elements (such as Warburg diffusion elements and constant phase elements), which produces the same response as the electrochemical system does when the same excitation signal is imposed. Equivalent circuit models can be partially or completely empirical. In the model, each circuit component comes from a physical process in the electrochemical cell and has a characteristic impedance behaviour. The shape of the model's impedance spectrum is controlled by the style of electrical elements in the model and the interconnections between them (series or parallel combinations). The size of each feature in the spectrum is controlled by the circuit elements' parameters.

However, although powerful numerical analysis software, e.g., Zview, is available to fit the spectra and give the best values for equivalent circuit parameters, analysis of the impedance data can still be troublesome, because specialized electrochemical processes such as Warburg diffusion or adsorption also contribute to the impedance, further complicating the situation. To set up a suitable model, one requires a basic knowledge of the cell being studied and a fundamental understanding of the behaviour of cell elements.

The equivalent circuit should be as simple as possible to represent the electrochemical system and it should give the best possible match between the model's impedance and the measured impedance of the system, whose equivalent circuit contains at least an electrolyte resistance, a double-layer capacity, and the impedance of the Faradaic or non-Faradaic process. Some common equivalent circuit elements for an electrochemical system are listed in Table 2.1. A detailed description of these elements will be introduced in Section 4.1.

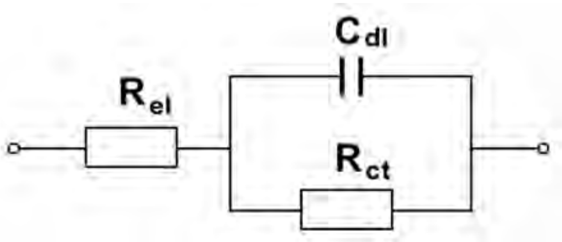
Table 2.1. Common circuit elements used in equivalent circuit models

Equivalent element	**Name**
R	Resistance
C	Capacitance
L	Inductance
W	Infinite Warburg
BW	Finite Warburg (Bounded Warburg)
CPE	Constant phase element
BCPE	Bounded CPE

The following are two examples of the standard equivalent circuits used in electrochemical systems.

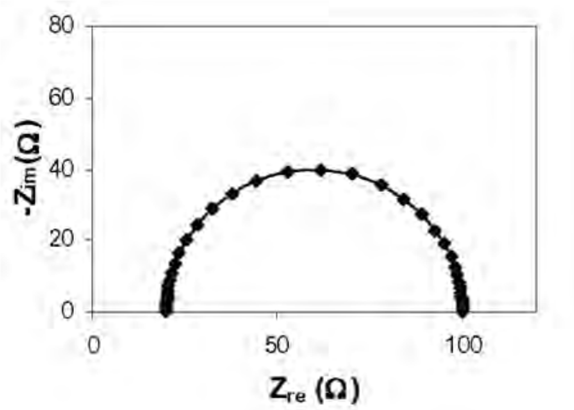
2.6.3.1 The Randles Cell

The simplest and most common model of an electrochemical interface is a Randles circuit. The equivalent circuit and Nyquist and Bode plots for a Randles cell are all shown in Figure 2.39. The circuit includes an electrolyte resistance (sometimes solution resistance), a double-layer capacitance, and a charge-transfer resistance. As seen in Figure 2.39*a*, R_{ct} is the charge-transfer resistance of the electrode process, C_{dl} is the capacitance of the double layer, and R_{el} is the resistance of the electrolyte. The double-layer capacitance is in parallel with the charge-transfer resistance.

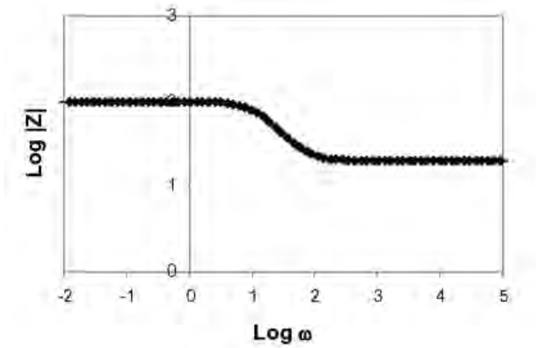


a

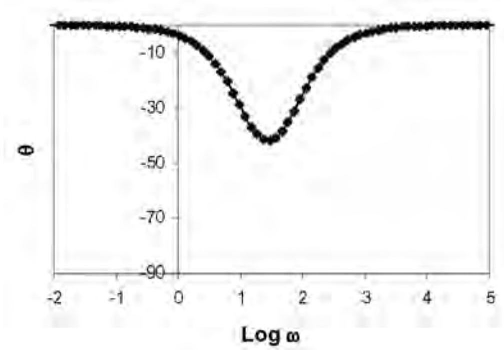
Figure 2.39. Graphic presentations of the Randles cell: *a* equivalent circuit, *b* Nyquist plot, *c* Bode magnitude plot, *d* Bode phase plot (R_{el} = 20 Ω, R_{ct} = 80 Ω, C_{dl} = 0.001 F)



b



c



d

Figure 2.39. (continued)

The Nyquist plot of a Randles cell is always a semicircle. At high frequencies the impedance of C_{dl} is very low, so the measured impedance tends to R_{el}. At very low frequencies the impedance of C_{dl} becomes extremely high, and thus, the measured impedance tends to R_{ct} + R_{el}. Accordingly, at intermediate frequencies, the impedance falls between R_{el} and R_{ct} + R_{el}. Therefore, the high-frequency intercept is associated with the electrolyte resistance, while the low-frequency intercept corresponds to the sum of the charge-transfer resistance and the electrolyte resistance. The diameter of the semicircle is equal to the charge-transfer resistance.

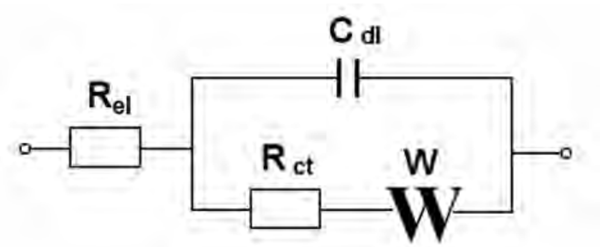
The Bode plot contains a magnitude plot and a phase angle plot. For a Randles cell, the values of the electrolyte resistance and the sum of the electrolyte resistance and the polarization resistance can easily be identified from the horizontal line in the magnitude plot. At high or low frequencies, the phase angles are close to 0°. Otherwise, at intermediate frequencies, the phase angles fall between 0° and 90°.

The Randles cell model is not only useful but also serves as a starting point for more complex models, created by adding more components.

2.6.3.2 Mixed Kinetic and Diffusion Control

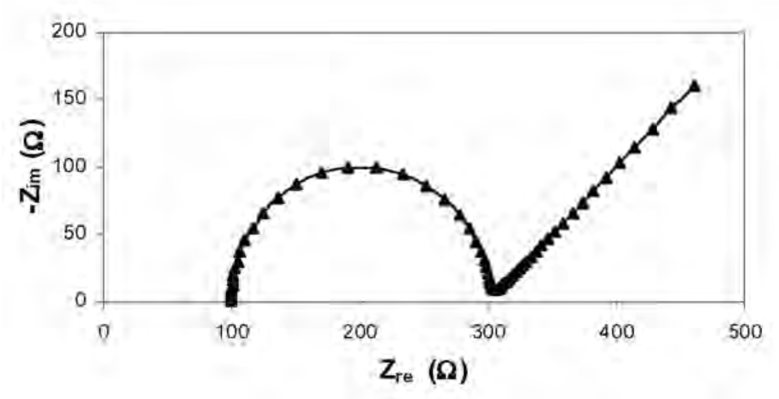
In a situation where a charge transfer is also influenced by diffusion to and from the electrode, the Warburg impedance will be seen in the impedance plot. This circuit model presents a cell in which polarization is controlled by the combination of kinetic and diffusion processes. The equivalent circuit and the Nyquist and Bode plots for the system are all shown in Figure 2.40. It can be seen that the Warburg element is easily recognizable by a line at an angle of 45° in the lower frequency region.

When investigating an electrochemical system using EIS, the equivalent circuit model that has been constructed must be verified. An effective way to do so is to alter a single cell component and see if the expected changes in the impedance spectrum occur, or to keep adding components to the circuit to see if a suitable circuit can be achieved, until reaching a perfect fit. Nevertheless, empirical models should use as few components as possible.

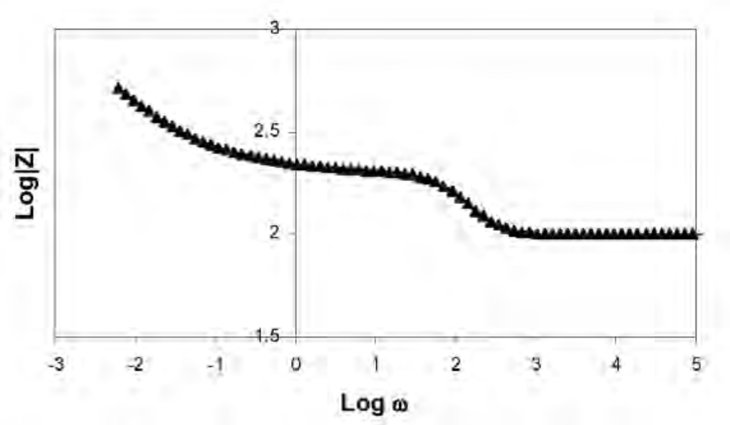


a

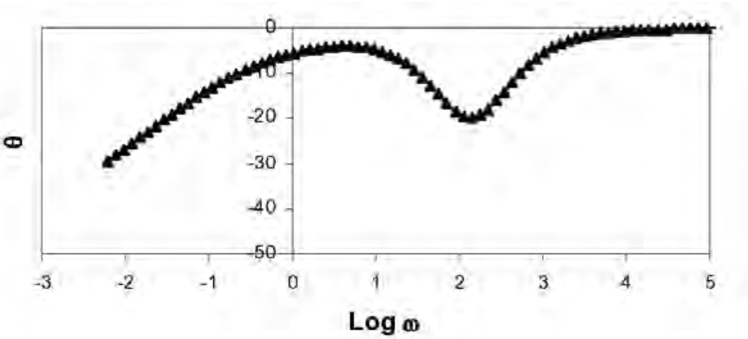
Figure 2.40. Graphic presentations of a mixed kinetic and diffusion control circuit: *a* equivalent circuit, *b* Nyquist plot, *c* Bode magnitude plot, *d* Bode phase plot (R_{el} = 100 Ω, R_{ct} = 100 Ω, C_{dl} = 0.001 F, σ = 20 Ωs$^{-1/2}$)



b



c



d

Figure 2.40. (continued)

It should also be pointed out that an equivalent circuit is not unique. In describing the same AC impedance spectrum, several circuits may exhibit the same result. For example, a model that includes elements without any chemical basis and practical meaning can demonstrate a perfect fit. Various equivalent circuit models used in PEM fuel cells will be discussed in detail in Chapter 4.

2.6.4 Data Fitting of EIS

It has been recognized that the analysis of EIS spectra is not straightforward. An effective approach is to fit the data using equivalent circuit models. Different methods for data fitting exist, such as the graphic method, the non-linear least square method, and the deconvolution approach. Although the graphic method is extremely simple and sufficiently accurate, with the rapid development of computer technology fewer people are using it. Here we briefly introduce the widely used non-linear least squares (NLLS) method and the deconvolution approach.

2.6.4.1 Non-Linear Least Squares Method

The rapid development of computer technology has yielded powerful tools that make it possible for modern EIS analysis software not only to optimize an equivalent circuit, but also to produce much more reliable system parameters. For most EIS data analysis software, a non-linear least squares fitting method, developed by Marquardt and Levenberg, is commonly used. The NLLS Levenberg–Marquardt algorithm has become the basic engine of several data analysis programs.

The core of the NLLS Levenberg–Marquardt algorithm is the use of the chi-squared parameter, χ^2, which is defined as follows

$$\chi^2 = \sum_{i=1}^{n} [(y_i - f(x_i))/\sigma_i]^2 \tag{2.179}$$

where σ_i, y_i, and $f(x_i)$ represent the standard deviation of measurement, the data, and the known function, respectively. By minimizing the object function, χ^2, this method makes it possible to measure the “goodness of fit”.

For the complex non-linear least squares (CNLS) method, the object function, S, is defined as [5, 6]

$$S = \sum_{i=1}^{n} w_i \left\{ [Z_{re,i} - Z_{re}(\omega_i, \alpha_k)]^2 + [Z_{im,i} - Z_{im}(\omega_i, \alpha_k)]^2 \right\} \tag{2.180}$$

where

$Z_{re,i} + jZ_{im,i}$ is the measured impedance at frequency ω_i (here, $j = \sqrt{-1}$ is used for differentiation);

$Z(\omega_i, a_k) = Z_{re}(\omega_i, a_k) + jZ_{im}(\omega_i, a_k)$ is the model function, which can be altered using the adjustable parameters; the model function can often be presented by an equivalent circuit, involving such elements as resistance, capacitance, and Warburg in series and/or in parallel;

α_k (k = 1… M) is the adjustable parameters; and

w_i is the weight factor, which is the inverse of the square of the vector length of the impedance.

Other parameters, such as CNLS-fit residuals (Δ_{re} and Δ_{im}), also indicate the "goodness of fit". They are defined as

$$\Delta_{re} = \frac{Z_{re,i} - Z_{re}(\omega_i, a_k)}{|Z(\omega_i, a_k)|} \quad (2.181)$$

$$\Delta_{im} = \frac{Z_{im,i} - Z_{im}(\omega_i, a_k)}{|Z(\omega_i, a_k)|} \quad (2.182)$$

For an optimum fit, the residuals should distribute over the full range of frequencies.

NLLS or CNLS starts with the selection of the equivalent circuit, followed by the initial value estimation for all the model parameters. Estimation of the initial values is one of the most difficult tasks in the analysis of an equivalent circuit model. A good initial value estimation needs a solid understanding of the element behaviours in the circuit. If the initial estimations are far from the "real values", the optimum fit may not be found. An estimated value within a factor of ten of the true value is a good start for determining a model parameter [7].

The simplest case for estimating the initial values of the circuit parameters is when the semicircle arcs in the impedance spectrum are not overlapping. In this situation the charge-transfer resistance, R_{ct}, can be estimated using the intercepts of the arc with the real axis, and the associated double-layer capacitance, C_{dl}, is then obtained from $\omega_{\max} = (R_{ct}C_{dl})^{-1}$, where $\omega_{\max}$ is the peak value of the frequency.

Experimental arcs in the spectrum are not always ideal semicircles, and this complicates parameter estimation. Nevertheless, there are still basic rules for estimating the initial values [8, 9]. The key is to identify the region of the spectrum in which one element dominates and then estimate the value of the element in this region. For example, the resistor's impedance dominates the spectrum at a low frequency, while the impedance of a capacitor approaches zero at a high frequency and infinity at a low frequency; also, individual resistors can be recognized based on the horizontal regions in a Bode plot.

Using the estimated initial values of the parameters, the software will adjust several or all of the parameters and evaluate the resulting fit. The process is repeated again and again until the goodness of fit is satisfactory. Generally speaking, the NLLS algorithm optimizes the fit over the entire frequency range rather than over a small section of the spectrum. Sometimes the fit looks poor due to an inappropriate choice of model, or poor estimates of the initial values, or noise. In such cases, the model should be adjusted and the procedure repeated.

2.6.4.2 Deconvolution

Assuming that the Nyquist plot of the impedance does not display an ideal semicircle (e.g., it shows a depressed semicircle or a wide arc), it might be described using two or more discrete time constants or a continuous distribution of time constants. In the former case, the equivalent circuit may involve two or more parallel RCs in series. In the latter case, it may involve one or more parallel CPEs and Rs in series. As mentioned, one solution could be to use several CNLS fittings; however, a more direct method would be the deconvolution of the imaginary part of the impedance data.

One of the advantages of the deconvolution method is to make it possible to decide whether the Nyquist plot of the impedance is describable by discrete time constants or by a continuous distribution of time constants, according to the width of the individual relaxation. Also, from the values of the peak relaxation time, τ_p, one may calculate the approximate frequency region as well, from $\omega_p = \tau_p^{-1}$. These results may then be used to build an appropriate equivalent circuit and estimate the initial values of the parameters for subsequent CNLS fittings.

Starting with Equation 2.183, the basic equations for attaining the distribution of relaxation times, $g_z(\tau)$, can be derived:

$$Z(\omega) = R_0 \int_0^{\infty} \frac{g_z(\tau)dt}{1 + i\omega\tau} \tag{2.183}$$

where R_0 is the $\omega \rightarrow 0$ value of $Z(\omega)$.

Assuming that ω_0 is approximately the central value of all frequencies measured, the following transformations can be performed:

$$\omega_0 \equiv 2\pi f_0 \tag{2.184}$$

$$\tau_0 \equiv \omega_0^{-1} \tag{2.185}$$

$$\omega\tau_0 \equiv \exp(-z) \tag{2.186}$$

$$\tau \equiv \tau_0 \exp(s) \tag{2.187}$$

$$G_z(s) \equiv \tau g_z(\tau) \tag{2.188}$$

where s and z are the new logarithmic variables. Then, the relation presented in Equation 2.183 can be transferred into the convolution form

$$Z(z) = R_0 \int_{-\infty}^{\infty} \frac{G_z(s)ds}{1 + i\exp[-(z - s)]} \tag{2.189}$$

The standard convolution forms can be obtained by separating Equation 2.189 into real and imaginary parts, each having an expression related to $G_z(s)$. Normally, it is preferable to calculate the imaginary part of the impedance Z, denoted as Z_{im}, instead of the real part denoted as Z_{re}, since the imaginary part shows more structure than the real part. The imaginary part of Z is then expressed in the following form:

$$Z_{im}(z) = -(R_0 / 2)\int_{-\infty}^{\infty} G_z(s)\,\mathrm{sech}(z-s)ds \tag{2.190}$$

The deconvolution process is basically complicated, but using modern computer techniques, calculating $G_z(s)$ and $g_z(\tau)$ is quite easy [8].

2.6.5 Applications

EIS has proven to be a useful technique for the analysis of electrochemical systems, such as corrosion systems and batteries. In comparison with DC electrochemical techniques, EIS has tremendous advantages, as it can provide a wealth of information about the system being studied. Also, due to the small perturbation in the AC signal, the electrode response is in a linear potential region, causing no destructive damage to the electrode. Therefore, EIS can be used to evaluate the time relation of interface parameters.

EIS thus has been demonstrated to be a powerful technique for investigating the electrical properties of materials, including gaseous, liquid, and solid materials, and the interfaces of conducting electrodes in different research areas. Miscellaneous applications of EIS are listed below:

- Mechanisms, such as reaction mechanisms, electrode kinetics, state of charge, change of active surface area
- Processes, such as complicated corrosion, crystallization, sintering, transport through membranes
- Interfaces, including blocked interfaces, liquid/liquid interfaces, electrode/solid electrolyte interfaces, etc.

In recent decades, research has intensified to develop commercially viable fuel cells as a cleaner, more efficient source of energy, due to the global shortage of fossil fuels. The challenge is to achieve a cell lifetime suitable for transportation and stationary applications. Among the possible fuel cell types, it is generally believed that PEM fuel cells hold the most promise for these uses [10, 11]. In order to improve fuel cell performance and lifetime, a suitable technique is needed to examine PEM fuel cell operation. EIS has also proven to be a powerful technique for studying the fundamental components and processes in fuel cells [12], and is now widely applied to the study of PEM fuel cells as well as direct methanol fuel cells (DMFCs), solid oxide fuel cell (SOFCs), and molten carbonate fuel cells (MCFCs).

2.7 Chapter Summary

This chapter has provided basic electrical fundamentals, including concepts and definitions for circuit elements, and their relationships within electric circuits. Various basic AC electric circuits were also presented. Following upon primary circuit theories, the concept of electrochemical impedance spectroscopy and basic information about EIS was introduced. This chapter lays a foundation for readers to expand their study of EIS and its applications in PEM fuel cell research and development.

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