Part I

Background

Chapter 1

Complex Variables

A working understanding of complex variables is essential for the analysis of experiments conducted in the frequency domain, such as impedance spectroscopy. The objective of this chapter is to introduce the subject of complex variables at a level sufficient to understand the development of interpretation models in the frequency domain. Complex variables represent an exciting and important field in applied mathematics, and textbooks dedicated to complex variables can extend the introduction provided here.[88,89] The overview presented in this chapter is strongly influenced by the compact treatment presented by Fong et al.[90]

1.1 Why Imaginary Numbers?

The terminology used in the study of complex variables, in particular the term imaginary number, is particularly unfortunate because it provides an unnecessary conceptual barrier to the beginning student of the subject. Complex variables are ordered pairs of numbers, where the imaginary part represents the solution to a particular type of equation. As suggested by Cain in his introduction to complex variables,[89] complex numbers can be compared to other ordered pairs of numbers.

Rational numbers, for example, are defined to be ordered pairs of integers. For example, $(3, 8)$ is a rational number. The ordered pair (n, m) can be written as $(\frac{n}{m})$. Thus the rational number $(3, 8)$ can be represented as well by 0.375.

Two rational numbers (n, m) and (p, q) are defined to be equal whenever $nq = pm$. The sum of (n, m) and (p, q) is given by

$$(n, m) + (p, q) = ((nq + pm), mq) \tag{1.1}$$

and the product by

$$(n, m)(p, q) = (np, mq) \tag{1.2}$$

Subtraction and division are defined to be the inverses of the addition and multiplication operations, respectively.

Irrational numbers were introduced because the set of rational numbers could not provide solutions to such equations as $z = \sqrt{2}$. As seen in the subsequent section, the set of real numbers, which encompasses rational and irrational numbers, is not adequate to provide solutions to yet other classes of equations. Thus, complex numbers were introduced, which can be seen in the following sections to be defined as ordered pairs (x, y) of real and imaginary numbers.[89]

1.2 Terminology

The concept of complex variables is used widely in mathematical and engineering analysis. Some definitions and concepts commonly encountered in the field of impedance spectroscopy are presented in this section.

1.2.1 The Imaginary Number

The imaginary number $\mathrm{j} = \sqrt{-1}$ is the solution to the algebraic equation

$$z^2 = -1 \tag{1.3}$$

which yields $z = \pm\mathrm{j}$. The imaginary number arises as well in the solution to differential equations such as

$$\frac{\mathrm{d}^2 y}{\mathrm{d}x^2} + by = 0 \tag{1.4}$$

which, as shown in Example 2.3 on page 30, has the characteristic equation

$$m^2 = -b \tag{1.5}$$

with solution

$$m = \pm\sqrt{-b} = \pm\mathrm{j}\sqrt{b} \tag{1.6}$$

The homogeneous solution to equation (1.4) is given by

$$y = \mathrm{C}_1 \exp\left(\mathrm{j}\sqrt{b}x\right) + \mathrm{C}_2 \exp\left(-\mathrm{j}\sqrt{b}x\right) \tag{1.7}$$

Some useful identities for the complex number j are presented in Table 1.1.

1.2.2 Complex Variables

The solution to the quadratic equation

$$az^2 + bz + c = 0 \tag{1.13}$$

given as

$$z = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a} \tag{1.14}$$

is a complex number if the argument $b^2 - 4ac < 0$. The complex variables can be written as

$$z = z_\mathrm{r} + \mathrm{j}z_\mathrm{j} \tag{1.15}$$

where z_r and z_j are real numbers that represent the real and imaginary parts of z, respectively. Often the notations $\mathrm{Re}\{z\}$ and $\mathrm{Im}\{z\}$ are used to designate real and imaginary components of the complex number z, respectively.

1.2.3 Conventions for Notation in Impedance Spectroscopy

The IUPAC convention, as described in the overview by Sluyters-Rehbach,[91] is that $\sqrt{-1}$ should be denoted by the symbol i. To avoid confusion with current density, given the symbol i, and the index i used to indicate specific chemical species, we have chosen here to follow the electrical engineering convention in which $\sqrt{-1}$ is given the symbol j.

We also depart from the IUPAC convention in the notation used to denote real and imaginary parts of the impedance. The IUPAC convention is that the real part of the impedance is given by Z' and the imaginary part is given by Z''. We consider that the IUPAC notation can be confused with the use of primes and double primes to denote first and second derivatives, respectively. Thus, we choose to identify the real part of the impedance by Z_r and the imaginary part of the impedance by Z_j.

1.3 Operations Involving Complex Variables

As z is a single value with real and imaginary components, z can be represented as a point on a complex plane, as shown in Figure 1.1. The complex conjugate of a complex number $z = z_\mathrm{r} + \mathrm{j}z_\mathrm{j}$ is defined to be $\overline{z} = z_\mathrm{r} - \mathrm{j}z_\mathrm{j}$. Thus, in Figure 1.1, $\overline{z}$ is seen to be the reflection of z about the real axis.

As is evident in the graphical representation of a complex number in Figure 1.1, two complex numbers are equal if and only if both the real and the imaginary parts are equal. Thus, an equation involving complex variables requires that two equations are

Table 1.1: Identities for the imaginary number j.

$$\mathrm{j} = \sqrt{-1} \tag{1.8}$$

$$\mathrm{j}^2 = -1 \tag{1.9}$$

$$\mathrm{j}^3 = -\mathrm{j} \tag{1.10}$$

$$\mathrm{j}^4 = 1 \tag{1.11}$$

$$1/\mathrm{j} = -\mathrm{j} \tag{1.12}$$

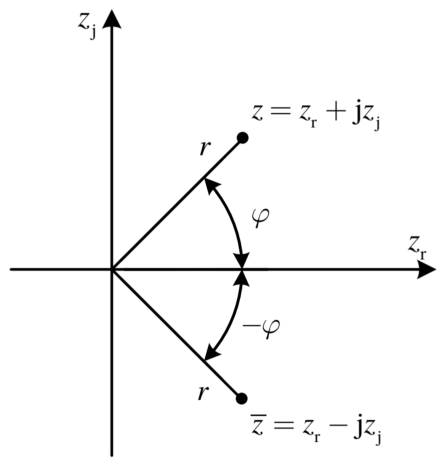

Figure 1.1: Argand diagram showing the position of a complex number and its complex conjugate on a complex plane.

satisfied, one involving the real terms and one involving the imaginary terms. Commutative, associative, and distributive laws hold for complex numbers. Some useful relationships for complex variables are presented in Table 1.2, which demonstrate the commutative, associative, and distributive properties.

The commutative property states that, in addition and multiplication, terms may be arbitrarily interchanged. Thus, equation (1.16) applies for addition and equation (1.17) applies for multiplication of complex numbers z and w. The distributive property is demonstrated by equation (1.18), and the associative property is demonstrated by equation (1.19).

1.3.1 Multiplication and Division of Complex Numbers

Equations (1.20)-(1.24) illustrate the manner in which mathematical operations are carried out in terms of real and imaginary components. These results provide a foundation for the followings series of examples.

Example 1.1 Multiplication of Complex Numbers: *Does the imaginary part of the product of two complex numbers equal the product of the imaginary parts?*

Remember! 1.1 *Complex numbers are ordered pairs (x, y) of real and imaginary numbers that represent the solution to a class of problems that cannot be solved using rational and irrational numbers.*

Table 1.2: Relationships for complex variables $z = z_\mathrm{r} + \mathrm{j}z_\mathrm{j}$ and $w = w_\mathrm{r} + \mathrm{j}w_\mathrm{j}$.

$$z + w = w + z \tag{1.16}$$

$$zw = wz \tag{1.17}$$

$$a(z + w) = az + aw \tag{1.18}$$

$$a(zw) = (az)w \tag{1.19}$$

$$z + w = (z_\mathrm{r} + w_\mathrm{r}) + \mathrm{j}(z_\mathrm{j} + w_\mathrm{j}) \tag{1.20}$$

$$z - w = (z_\mathrm{r} - w_\mathrm{r}) + \mathrm{j}(z_\mathrm{j} - w_\mathrm{j}) \tag{1.21}$$

$$zw = (z_\mathrm{r}w_\mathrm{r} - z_\mathrm{j}w_\mathrm{j}) + \mathrm{j}(z_\mathrm{r}w_\mathrm{j} + z_\mathrm{j}w_\mathrm{r}) \tag{1.22}$$

$$w\overline{w} = w_\mathrm{r}^2 + w_\mathrm{j}^2 \tag{1.23}$$

$$\begin{aligned} \frac{z}{w} &= \frac{z\overline{w}}{w\overline{w}} \\ &= \frac{(z_\mathrm{r}w_\mathrm{r} + z_\mathrm{j}w_\mathrm{j}) + \mathrm{j}(z_\mathrm{j}w_\mathrm{r} - z_\mathrm{r}w_\mathrm{j})}{w_\mathrm{r}^2 + w_\mathrm{j}^2} \end{aligned} \tag{1.24}$$

Solution: *Consider two numbers $z = z_\mathrm{r} + \mathrm{j}z_\mathrm{j}$ and $w = w_\mathrm{r} + \mathrm{j}w_\mathrm{j}$. The multiplication of z and w follows equation (1.22), i.e.,*

$$\begin{aligned} zw &= (z_\mathrm{r} + \mathrm{j}z_\mathrm{j})(w_\mathrm{r} + \mathrm{j}w_\mathrm{j}) \\ &= \left(z_\mathrm{r}w_\mathrm{r} + j^2 z_\mathrm{j}w_\mathrm{j}\right) + \mathrm{j}\left(z_\mathrm{r}w_\mathrm{j} + w_\mathrm{r}z_\mathrm{j}\right) \\ &= (z_\mathrm{r}w_\mathrm{r} - z_\mathrm{j}w_\mathrm{j}) + \mathrm{j}\left(z_\mathrm{r}w_\mathrm{j} + w_\mathrm{r}z_\mathrm{j}\right) \end{aligned} \tag{1.25}$$

The imaginary part of zw is $\left(z_\mathrm{r}w_\mathrm{j} + w_\mathrm{r}z_\mathrm{j}\right)$, which is not equal to the product of the imaginary parts, i.e.,

$$\left(z_\mathrm{r}w_\mathrm{j} + w_\mathrm{r}z_\mathrm{j}\right) \neq z_\mathrm{j}w_\mathrm{j} \tag{1.26}$$

Thus, the imaginary part of the product of two complex numbers does not equal the product of the imaginary parts.

Example 1.2 Division of Complex Numbers: *In a new experimental technique developed by Antaño-Lopez et al.,*[92] *an approximate formula for capacitance was used; i.e.,*

$$C = \frac{Y_\mathrm{j}(\omega)}{\omega} \tag{1.27}$$

Remember! 1.2 *The notation used in this text provides that $\mathrm{j} = \sqrt{-1}$ and that real and imaginary parts of complex numbers are denoted by subscripts r and j, respectively.*

where Y is the complex admittance $Y = Z^{-1}$, and ω is angular frequency. At frequencies sufficiently high to eliminate the contribution of faradaic resistance, the capacitance is shown in Section 17.4 to be obtained correctly from

$$C = -\frac{1}{\omega Z_{\mathrm{j}}(\omega)} \tag{1.28}$$

where Z_{j} is the imaginary part of the complex impedance Z. For capacitive systems, $Z_{\mathrm{j}} < 0$. Under what conditions will equation (1.27) be accurate?

Solution: *Equation (1.27) would agree with equation (1.28) if*

$$Y_{\mathrm{j}} = \mathrm{Im}\{Z^{-1}\} \stackrel{?}{=} -Z_{\mathrm{j}}^{-1} \tag{1.29}$$

To test the validity of equation (1.29), consider the inverse of the complex number $Z = Z_{\mathrm{r}} + \mathrm{j}Z_{\mathrm{j}}$.

$$\frac{1}{Z} = \frac{1}{Z_{\mathrm{r}} + \mathrm{j}Z_{\mathrm{j}}} \tag{1.30}$$

Division is possible only after the denominator is converted into a real, rather than complex, number. Both the numerator and the denominator are multiplied by the complex conjugate (see equations (1.23) *and* (1.24)*).*

$$\begin{aligned} \frac{1}{Z} &= \left\{\frac{1}{Z_{\mathrm{r}} + \mathrm{j}Z_{\mathrm{j}}}\right\}\left\{\frac{Z_{\mathrm{r}} - \mathrm{j}Z_{\mathrm{j}}}{Z_{\mathrm{r}} - \mathrm{j}Z_{\mathrm{j}}}\right\} \\ &= \frac{Z_{\mathrm{r}} - \mathrm{j}Z_{\mathrm{j}}}{Z_{\mathrm{r}}^2 + Z_{\mathrm{j}}^2} \\ &= \frac{Z_{\mathrm{r}}}{Z_{\mathrm{r}}^2 + Z_{\mathrm{j}}^2} - \mathrm{j}\frac{Z_{\mathrm{j}}}{Z_{\mathrm{r}}^2 + Z_{\mathrm{j}}^2} \end{aligned} \tag{1.31}$$

Thus,

$$Y_{\mathrm{j}} = \mathrm{Im}\{Z^{-1}\} = -\frac{Z_{\mathrm{j}}}{Z_{\mathrm{r}}^2 + Z_{\mathrm{j}}^2} \neq -\frac{1}{Z_{\mathrm{j}}} \tag{1.32}$$

Equation (1.29) is satisfied only if $Z_{\mathrm{r}} = 0$. As discussed in Chapter 10, the real part of the impedance Z_{r} approaches the electrolyte resistance at high frequencies. The capacitance obtained by Antaño-Lopez et al.[92] is correct at high frequencies only if the electrolyte resistance can be neglected, i.e., $Z_{\mathrm{r}}^2 \ll Z_{\mathrm{j}}^2$.

Remember! 1.3 *The impedance is a complex number defined to be the ratio of complex potential and complex current.*

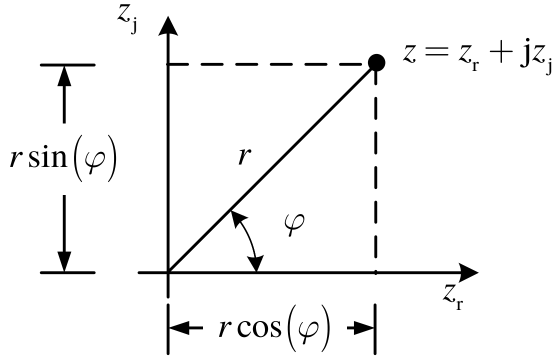

Figure 1.2: Argand diagram showing relationships among complex impedance, magnitude, and phase angle.

Example 1.3 Rectangular Coordinates: *The impedance of a parallel combination of a resistor and a capacitor can be expressed as*

$$Z = \frac{R}{1 + j\omega\tau} \tag{1.33}$$

where τ is the time constant $\tau = RC$. Express equation (1.33) in rectangular coordinates, i.e., find the real and imaginary components of Z.

Solution: *To express equation (1.33) in rectangular coordinates, the denominator must be converted into a real, rather than complex, number. Both the numerator and the denominator are multiplied by the complex conjugate (see equations (1.23) and (1.24)).*

$$\begin{aligned} Z &= \left\{\frac{R}{1 + j\omega\tau}\right\}\left\{\frac{1 - j\omega\tau}{1 - j\omega\tau}\right\} \\ &= \frac{R - j\omega R\tau}{1 + \omega^2\tau^2} \\ &= \frac{R}{1 + \omega^2\tau^2} - j\frac{\omega R\tau}{1 + \omega^2\tau^2} \end{aligned} \tag{1.34}$$

Thus,

$$\mathrm{Re}\{Z\} = \frac{R}{1 + \omega^2\tau^2}; \quad \mathrm{Im}\{Z\} = -\frac{\omega R\tau}{1 + \omega^2\tau^2} \tag{1.35}$$

1.3.2 Complex Variables in Polar Coordinates

The transformation from rectangular to polar coordinates is shown schematically in Figure 1.2. The variable r is the modulus or absolute value $|z|$, which always has a positive value. The phase angle is written as $\varphi = \arg(z)$. In the mathematical development (see Section 1.4.1), the phase angle has units of radians; however, it is often presented

Table 1.3: Relationships between polar and rectangular coordinates for the complex variable $z = z_{\mathrm{r}} + \mathrm{j}z_{\mathrm{j}}$.

$$z_{\mathrm{r}} = r\cos(\varphi) \tag{1.36}$$

$$z_{\mathrm{j}} = r\sin(\varphi) \tag{1.37}$$

$$r = |z| = \sqrt{z_{\mathrm{r}}^2 + z_{\mathrm{j}}^2} \tag{1.38}$$

$$\varphi = \tan^{-1}\left(\frac{z_{\mathrm{j}}}{z_{\mathrm{r}}}\right) \tag{1.39}$$

$$|z| = \sqrt{z\overline{z}} \tag{1.40}$$

$$z = r\left(\cos(\varphi) + \mathrm{j}\sin(\varphi)\right) \tag{1.41}$$

$$z^n = r^n\left(\cos(n\varphi) + \mathrm{j}\sin(n\varphi)\right) \tag{1.42}$$

$$z^{1/n} = r^{1/n}\left[\cos\left(\frac{\varphi}{n} + \frac{2\pi k}{n}\right) + \mathrm{j}\sin\left(\frac{\varphi}{n} + \frac{2\pi k}{n}\right)\right];\ \ k = 0, 1, \ldots, n-1 \tag{1.43}$$

in units of degrees where $90^\circ = \pi/2$. The angle $\arg(z)$ has an infinite number of possible values because any multiple of 2π radians can be added to it without changing the value of z. The value of φ that lies between $-\pi$ and π is called the principal value of $\arg(z)$.

Some useful relationships between polar and rectangular coordinates for complex variables are summarized in Table 1.3. Equation (1.42) is known as De Moivre's theorem. It is valid for all rational values of n.

Example 1.4 Polar Coordinates: *The impedance of a parallel combination of a resistor and a capacitor can be expressed as*

$$Z = \frac{R}{1 + \mathrm{j}\omega\tau} \tag{1.44}$$

where τ is the time constant $\tau = RC$. Express equation (1.44) in polar coordinates; i.e., find the modulus and phase angle for Z.

Solution: *As shown in Example 1.3, equation (1.44) can be expressed in rectangular coordinates by*

$$\mathrm{Re}\{Z\} = \frac{R}{1 + \omega^2\tau^2}; \quad \mathrm{Im}\{Z\} = -\frac{\omega R\tau}{1 + \omega^2\tau^2} \tag{1.45}$$

Equations (1.38) and (1.39) can be used to convert equation (1.45) into polar coordinates. Thus,

$$r = \sqrt{\left(\frac{R}{1 + \omega^2\tau^2}\right)^2 + \left(\frac{\omega R\tau}{1 + \omega^2\tau^2}\right)^2} \tag{1.46}$$

or

$$r = \sqrt{\frac{R^2}{1+\omega^2\tau^2}} \tag{1.47}$$

$$\begin{aligned}\varphi &= \tan^{-1}\left[-\frac{\omega R\tau}{1+\omega^2\tau^2}\frac{1+\omega^2\tau^2}{R}\right] \\ &= \tan^{-1}(-\omega\tau)\end{aligned} \tag{1.48}$$

The phase angle φ is a function only of frequency ω and the time constant τ. The modulus r depends on the value of R as well as on the frequency ω and the time constant τ.

The solution can be obtained more rapidly by casting the impedance in terms of admittance (see Section 17.2 on page 478). The admittance can be expressed as

$$Y = \frac{1}{Z} = \frac{1+\mathrm{j}\omega\tau}{R} \tag{1.49}$$

The modulus of the admittance is given by

$$|Y| = \sqrt{\frac{1+\omega^2\tau^2}{R^2}} \tag{1.50}$$

and the argument is given by

$$\varphi_Y = \tan^{-1}(\omega\tau) \tag{1.51}$$

The modulus of the impedance and the corresponding argument can be deduced immediately as

$$|Z| = \frac{1}{|Y|} \tag{1.52}$$

and

$$\varphi = -\varphi_Y \tag{1.53}$$

respectively.

Example 1.5 Square Roots of Complex Variables: *The Warburg impedance associated with diffusion in an infinite medium takes the form $Z = 1/\sqrt{\mathrm{j}\omega\tau}$. Find the roots of Z.*

Solution: *The polar form of $z = 1/\mathrm{j}\omega\tau = -\mathrm{j}/\omega\tau$ is expressed as*

$$z = \frac{1}{\omega\tau}\left(\cos\left(\frac{3\pi}{2}\right) + \mathrm{j}\sin\left(\frac{3\pi}{2}\right)\right) \tag{1.54}$$

From equation (1.43)

$$z^{1/2} = \sqrt{\frac{1}{\omega\tau}}\left(\cos\left(\frac{3\pi}{4}+k\pi\right) + \mathrm{j}\sin\left(\frac{3\pi}{4}+k\pi\right)\right); \quad k = 0,1 \tag{1.55}$$

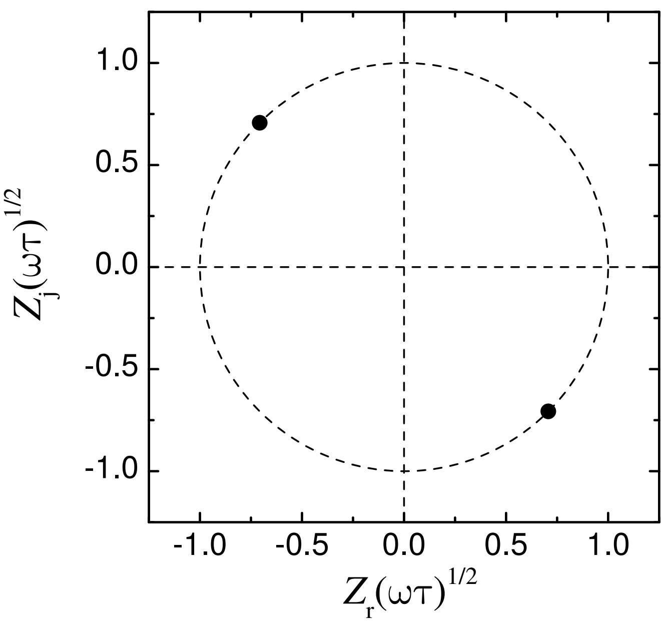

Figure 1.3: Argand diagram showing the two roots of $Z = 1/\sqrt{j\omega\tau}$ as calculated in Example 1.5.

The roots of $1/\sqrt{j\omega\tau}$ *are shown in Figure 1.3. The root with* $k = 0$ *can be rejected using the physical reasoning that the resistance associated with diffusion cannot have a negative sign. Thus, the Warburg impedance can be expressed in rectangular coordinates as*

$$Z = \sqrt{\frac{1}{2\omega\tau}} - j\sqrt{\frac{1}{2\omega\tau}} \tag{1.56}$$

The real and the negative imaginary components have the same magnitude and increase according to $\sqrt{1/\omega}$ *as frequency tends toward zero.*

As shown in the following examples, equation (1.41) is very useful for expressing complex quantities in rectangular coordinates. The imaginary number can be expressed as

$$j = \cos\left(\frac{\pi}{2}\right) + j\sin\left(\frac{\pi}{2}\right) \tag{1.57}$$

where evaluation of equations (1.38) and (1.39) yields $r = 1$ and $\varphi = \pi/2$, respectively

Remember! 1.4 *The expression* $j = \cos(\pi/2) + j\sin(\pi/2)$ *is very useful for finding real and imaginary parts of complex expressions involving the imaginary number raised to a power.*

Example 1.6 Square Roots of Complex Variables 2: *Use equation* (1.57) *to find real and imaginary parts of the Warburg impedance in the form* $Z = 1/\sqrt{j\omega\tau}$.

Solution: *From equation* (1.57), *the Warburg impedance may be expressed as*

$$Z = \frac{1}{\sqrt{j\omega\tau}} = \frac{1}{\sqrt{\omega\tau}\left(\cos\left(\frac{\pi}{4}\right) + j\sin\left(\frac{\pi}{4}\right)\right)} \tag{1.58}$$

Multiplication of numerator and denominator by the complex conjugate yields

$$Z = \frac{\cos\left(\frac{\pi}{4}\right) - j\sin\left(\frac{\pi}{4}\right)}{\sqrt{\omega\tau}\left(\cos^2\left(\frac{\pi}{4}\right) + \sin^2\left(\frac{\pi}{4}\right)\right)} \tag{1.59}$$

Introduction of the identity

$$\cos^2(x) + \sin^2(x) = 1 \tag{1.60}$$

yields

$$Z = \frac{\cos\left(\frac{\pi}{4}\right) - j\sin\left(\frac{\pi}{4}\right)}{\sqrt{\omega\tau}} \tag{1.61}$$

As $\cos\left(\frac{\pi}{4}\right) = \sin\left(\frac{\pi}{4}\right) = 1/\sqrt{2}$,

$$Z = \sqrt{\frac{1}{2\omega\tau}} - j\sqrt{\frac{1}{2\omega\tau}} \tag{1.62}$$

This is the same result as obtained in Example 1.5.

Example 1.7 Blocking Constant-Phase Element: *Use equation* (1.57) *to find real and imaginary parts for a constant-phase element given as*

$$Z_{\mathrm{CPE}} = \frac{1}{(j\omega)^{\alpha}Q} \tag{1.63}$$

where α *is a real number, generally with value* $0.5 \leqq \alpha \leqq 1$.

Solution: *Introduction of equation* (1.57) *yields*

$$Z = \frac{1}{(j\omega)^{\alpha}Q} = \frac{1}{\omega^{\alpha}Q\left(\cos\left(\frac{\alpha\pi}{2}\right) + j\sin\left(\frac{\alpha\pi}{2}\right)\right)} \tag{1.64}$$

multiplication by the complex conjugate yields

$$Z = \frac{\cos\left(\frac{\alpha\pi}{2}\right) - j\sin\left(\frac{\alpha\pi}{2}\right)}{\omega^{\alpha}Q\left(\cos^2\left(\frac{\alpha\pi}{2}\right) + \sin^2\left(\frac{\alpha\pi}{2}\right)\right)} \tag{1.65}$$

From equation (1.60),

$$Z = \frac{\cos\left(\frac{\alpha\pi}{2}\right)}{\omega^{\alpha}Q} - j\frac{\sin\left(\frac{\alpha\pi}{2}\right)}{\omega^{\alpha}Q} \tag{1.66}$$

When $\alpha = 1$, the parameter Q can be expressed as a capacitance C, and

$$\lim_{\alpha \to 1} Z_{\mathrm{CPE}} = -\mathrm{j}\frac{1}{\omega C} \tag{1.67}$$

which is the impedance for a capacitor.

Example 1.8 Reactive Constant-Phase Element: *Use equation* (1.57) *to find real and imaginary parts for a constant-phase element in the expression*

$$Z_{\mathrm{CPE}} = \frac{R}{1 + (\mathrm{j}\omega)^{\alpha} QR} \tag{1.68}$$

where α is a real number, generally with value $0.5 \leqq \alpha \leqq 1$.

Solution: *Introduction of equation* (1.57) *yields*

$$Z_{\mathrm{CPE}} = \frac{R}{1 + (\mathrm{j}\omega)^{\alpha} QR} = \frac{R}{1 + \omega^{\alpha} QR \left(\cos\left(\frac{\alpha\pi}{2}\right) + \mathrm{j}\sin\left(\frac{\alpha\pi}{2}\right)\right)} \tag{1.69}$$

multiplication by $1 + \omega^{\alpha} RQ \cos\left(\frac{\alpha\pi}{2}\right) - \mathrm{j}\omega^{\alpha} RQ \sin\left(\frac{\alpha\pi}{2}\right)$ *yields*

$$Z_{\mathrm{CPE}} = \frac{R\left(1 + \omega^{\alpha} RQ \cos\left(\frac{\alpha\pi}{2}\right)\right) - \mathrm{j}\omega^{\alpha} RQ \sin\left(\frac{\alpha\pi}{2}\right)}{1 + 2\omega^{\alpha} RQ \cos\left(\frac{\alpha\pi}{2}\right) + \omega^{2\alpha} R^2 Q^2} \tag{1.70}$$

or

$$\begin{aligned} Z_{\mathrm{CPE}} \quad = \quad & \frac{R\left(1 + \omega^{\alpha} RQ \cos\left(\frac{\alpha\pi}{2}\right)\right)}{1 + 2\omega^{\alpha} RQ \cos\left(\frac{\alpha\pi}{2}\right) + \omega^{2\alpha} R^2 Q^2} \\ & -\mathrm{j}\frac{\omega^{\alpha} R^2 Q \sin\left(\frac{\alpha\pi}{2}\right)}{1 + 2\omega^{\alpha} RQ \cos\left(\frac{\alpha\pi}{2}\right) + \omega^{2\alpha} R^2 Q^2} \end{aligned} \tag{1.71}$$

When $\alpha = 1$, the parameter Q can be expressed as a capacitance C, and

$$\lim_{\alpha \to 1} Z_{\mathrm{CPE}} = \frac{R}{1 + \omega^2 R^2 C^2} - \mathrm{j}\frac{\omega R^2 C}{1 + \omega^2 R^2 C^2} \tag{1.72}$$

Equation (1.72) *is the expression given as equation* (1.34), *where the time constant is expressed as $\tau = RC$.*

The rectangular forms developed in Examples 1.6, 1.7, and 1.8 can be expressed easily in polar form using equations (1.38) and (1.39). For example, the phase angle for the Warburg impedance analyzed in Example 1.6 can be expressed as

$$\begin{aligned} \varphi \quad &= \quad \tan^{-1}\left(\frac{Z_{\mathrm{j}}}{Z_{\mathrm{r}}}\right) = \tan^{-1}\left(\frac{-\sqrt{1/2\omega\tau}}{\sqrt{1/2\omega\tau}}\right) \\ &= \quad \tan^{-1}(-1) = -\pi/4 = -45^{\circ} \end{aligned} \tag{1.73}$$

Table 1.4: Properties for the complex conjugates of $z = z_{\mathrm{r}} + \mathrm{j}z_{\mathrm{j}}$ and $w = w_{\mathrm{r}} + \mathrm{j}w_{\mathrm{j}}$.

$$\overline{z+w} = \overline{z} + \overline{w} \tag{1.76}$$

$$\overline{zw} = \overline{z}\,\overline{w} \tag{1.77}$$

$$\overline{\left[\frac{1}{z}\right]} = \frac{1}{\overline{z}} \tag{1.78}$$

$$\overline{\overline{z}} = z \tag{1.79}$$

Similarly, the phase angle for the blocking CPE of Example 1.7 can be expressed as

$$\begin{aligned} \varphi &= \tan^{-1}\left(\frac{-\sin\left(\frac{\alpha\pi}{2}\right)/\omega^{\alpha}Q}{\cos\left(\frac{\alpha\pi}{2}\right)/\omega^{\alpha}Q}\right) \\ &= -\frac{\alpha\pi}{2} = -\alpha 90^{\circ} \end{aligned} \tag{1.74}$$

The phase angle for the reactive CPE presented in Example 1.8 is given by

$$\varphi = \tan^{-1}\left(\frac{-\sin\left(\frac{\alpha\pi}{2}\right)}{\frac{1}{\omega^{\alpha}RQ} + \cos\left(\frac{\alpha\pi}{2}\right)}\right) \tag{1.75}$$

As the frequency $\omega \rightarrow \infty$, the phase angle approaches $-\alpha 90^{\circ}$. Each of these types of models can be described as constant-phase elements as the phase angle is either constant or approaches a constant value at high frequency.

1.3.3 Properties of Complex Variables

Some useful properties of the complex conjugates of $z = z_{\mathrm{r}} + \mathrm{j}z_{\mathrm{j}}$ and $w = w_{\mathrm{r}} + \mathrm{j}w_{\mathrm{j}}$ are presented in Table 1.4, and some relationships for the absolute value of $z = z_{\mathrm{r}} + \mathrm{j}z_{\mathrm{j}}$ and $w = w_{\mathrm{r}} + \mathrm{j}w_{\mathrm{j}}$ are presented in Table 1.5.

1.4 Elementary Functions of Complex Variables

The definition of many elementary functions can be extended to complex variables. Polynomial, exponential, and logarithmic functions are discussed here.

1.4.1 Exponential

The exponential function e^{z} is of fundamental importance in impedance spectroscopy. The exponential function is defined such that it retains the properties of the real function e^{x} that

Table 1.5: Properties for the absolute value of $z = z_\mathrm{r} + \mathrm{j}z_\mathrm{j}$ and $w = w_\mathrm{r} + \mathrm{j}w_\mathrm{j}$.

$$|z| = |\overline{z}| \tag{1.80}$$

$$z\overline{z} = |z|^2 \tag{1.81}$$

$$z_\mathrm{r} \leq |z| \tag{1.82}$$

$$z_\mathrm{j} \leq |z| \tag{1.83}$$

$$|zw| = |z||w| \tag{1.84}$$

$$\left|\frac{1}{z}\right| = \frac{1}{|z|};\ \ z \neq 0 \tag{1.85}$$

$$|z + w| \leq |z| + |w| \tag{1.86}$$

1. e^z, with argument $z = x + \mathrm{j}y$, is single valued and analytic (see Appendix A.1),
2. $\mathrm{de}^z/\mathrm{d}z = \mathrm{e}^z$, and
3. $\mathrm{e}^z \to \mathrm{e}^x$, when $y \to 0$.

As a consequence of the above requirements, the exponential function with argument $z = x + \mathrm{j}y$ can be shown to conform to

$$\begin{aligned} \mathrm{e}^z &= \mathrm{e}^{x+\mathrm{j}y} \\ &= \mathrm{e}^x\left[\cos(y) + \mathrm{j}\sin(y)\right] \end{aligned} \tag{1.87}$$

Equation (1.87) can be considered to be the definition of e^z, which can be readily shown to meet the requirements expressed above.

Equation (1.87) is written in the standard polar form, equation (1.41), in which the modulus of e^z is

$$r = |\mathrm{e}^z| = \mathrm{e}^x \tag{1.88}$$

and the argument, or phase angle, is given by

$$\varphi = \arg\left(\mathrm{e}^z\right) = y \tag{1.89}$$

It is evident, then, that the exponential function is periodic, i.e.,

$$\mathrm{e}^z = \mathrm{e}^{z+\mathrm{j}2k\pi} \tag{1.90}$$

for integer values of k.

Any complex number can be written in exponential form. For example, if $x = 0$ and $y = \varphi$, application of equation (1.87) yields

$$\cos(\varphi) + \mathrm{j}\sin(\varphi) = \mathrm{e}^{\mathrm{j}\varphi} \tag{1.91}$$

In addition,

$$\begin{aligned} e^{-j\varphi} &= \cos(-\varphi) + j\sin(-\varphi) \\ &= \cos(\varphi) - j\sin(\varphi) \end{aligned} \tag{1.92}$$

Equations (1.91) and (1.92) yield the Euler formulas

$$\cos(\varphi) = \frac{e^{j\varphi} + e^{-j\varphi}}{2} \tag{1.93}$$

and

$$\sin(\varphi) = \frac{e^{j\varphi} - e^{-j\varphi}}{2j} \tag{1.94}$$

These can be extended for $x \neq 0$ as

$$\cos(z) = \frac{e^{jz} + e^{-jz}}{2} \tag{1.95}$$

and

$$\sin(z) = \frac{e^{jz} - e^{-jz}}{2j} \tag{1.96}$$

Equations (1.95) and (1.96) provide relationships between trigonometric functions and complex variables. These can be manipulated to find relationships with hyperbolic function. Some important definitions and identities are presented in Table 1.6.

1.4.2 Logarithmic

Given

$$z = e^{w} \tag{1.114}$$

where z and $w = u + jv$ are complex numbers, the natural logarithm can be defined as

$$w = \ln(z) \tag{1.115}$$

As $w = u + jv$, equation (1.114) can be expressed as

$$z = e^{u}\left[\cos(v) + j\sin(v)\right] \tag{1.116}$$

The modulus of equation (1.116) is given as

$$|z| = e^{u} \tag{1.117}$$

Remember! 1.5 *The exponential representation of a complex number plays an important role in impedance analysis. Remember that* $e^{\pm j\varphi} = \cos(\varphi) \pm j\sin(\varphi)$.

Table 1.6: Trigonometric and hyperbolic relationships for the complex variable $z = z_\mathrm{r} + \mathrm{j}z_\mathrm{j}$.

$$\sin(z) = \left(\mathrm{e}^{\mathrm{j}z} - \mathrm{e}^{-\mathrm{j}z}\right)/2\mathrm{j} \tag{1.97}$$

$$\cos(z) = \left(\mathrm{e}^{\mathrm{j}z} + \mathrm{e}^{-\mathrm{j}z}\right)/2 \tag{1.98}$$

$$\frac{\mathrm{d}\sin(z)}{\mathrm{d}z} = \cos(z) \tag{1.99}$$

$$\frac{\mathrm{d}\cos(z)}{\mathrm{d}z} = -\sin(z) \tag{1.100}$$

$$\tan(z) = \frac{\sin(z)}{\cos(z)} \tag{1.101}$$

$$\cot(z) = \frac{\cos(z)}{\sin(z)} \tag{1.102}$$

$$\cos^2 z + \sin^2 z = 1 \tag{1.103}$$

$$\cos(z_1 \pm z_2) = \cos(z_1)\cos(z_2) \mp \sin(z_1)\sin(z_2) \tag{1.104}$$

$$\sin(z_1 \pm z_2) = \sin(z_1)\cos(z_2) \pm \cos(z_1)\sin(z_2) \tag{1.105}$$

$$\sinh(z) = \left(\mathrm{e}^{z} - \mathrm{e}^{-z}\right)/2 \tag{1.106}$$

$$\cosh(z) = \left(\mathrm{e}^{z} + \mathrm{e}^{-z}\right)/2 \tag{1.107}$$

$$\tanh(z) = \frac{\sinh(z)}{\cosh(z)} \tag{1.108}$$

$$\coth(z) = \frac{\cosh(z)}{\sinh(z)} \tag{1.109}$$

$$\cos(z) = \cos(x)\cosh(y) - \mathrm{j}\sin(x)\sinh(y) \tag{1.110}$$

$$\sin(z) = \sin(x)\cosh(y) + \mathrm{j}\cos(x)\sinh(y) \tag{1.111}$$

$$\cosh(z) = \cosh(x)\cos(y) + \mathrm{j}\sinh(x)\sin(y) \tag{1.112}$$

$$\sinh(z) = \sinh(x)\cos(y) + \mathrm{j}\cosh(x)\sin(y) \tag{1.113}$$

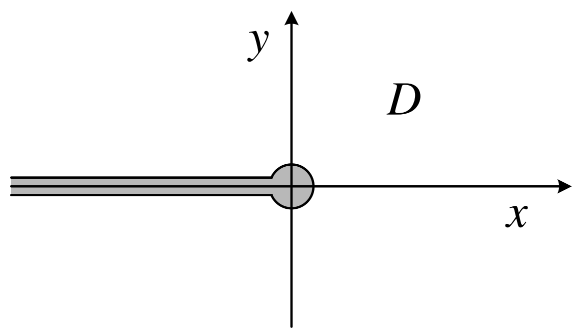

Figure 1.4: Representation of the domain D in which $\text{Ln}(z)$ is analytic.

and the phase angle is given by

$$\arg(z) = v \tag{1.118}$$

The complex number z can therefore be expressed as

$$z = |z|e^{j\arg(z)} = |z|e^{jv} \tag{1.119}$$

or

$$\ln(z) = \ln(|z|) + \text{j}\arg(z) = \ln(e^u) + \text{j}v \tag{1.120}$$

There are an infinite number of values of $\ln(z)$ because $\arg(z)$ can differ by multiples of 2π. The principal value of $\ln(z)$ is defined for the principal value of $\arg(z)$, both designated by initial capital letters. Thus,

$$\text{Ln}(z) = \ln(|z|) + \text{j}\text{Arg}(z) \tag{1.121}$$

where

$$-\pi < \text{Arg}(z) \leq \pi \tag{1.122}$$

The function $\text{Ln}(z)$ is not defined at $z = 0$ and is not continuous anywhere on the negative real axis $z = x + 0j$, where $x < 0$. The negative real axis is a line of discontinuity because, on that line, the imaginary part of $\text{Ln}(z)$ has a jump discontinuity of 2π. If a cut is made, as shown in Figure 1.4, to remove the origin and the negative real axis, $\text{Ln}(z)$ is analytic in the resulting domain, and the derivative of $\text{Ln}(z)$ is given by

$$\frac{\text{dLn}(z)}{\text{d}z} = \frac{1}{z} \tag{1.123}$$

The derivative of $\ln(z)$ is also given by equation (1.123) because $\text{Ln}(z)$ and $\ln(z)$ differ by a constant, $2\pi k\text{j}$.

Some functional relationships commonly used in impedance spectroscopy are presented in Table 1.7.

Table 1.7: Functional relationships of complex variables commonly encountered in impedance spectroscopy, where x and y are real numbers, and $z = x + \mathrm{j}y$.

$$\exp(\mathrm{j}x) = \cos(x) + \mathrm{j}\sin(x) \tag{1.124}$$

$$\exp(\mathrm{j}(x+y)) = \exp(\mathrm{j}x)\cdot\exp(\mathrm{j}y) \tag{1.125}$$

$$\cos(\omega t + \varphi) = \mathrm{Re}\left\{\exp(\mathrm{j}(\omega t + \varphi))\right\} \tag{1.126}$$

$$= \mathrm{Re}\left\{\exp(j\varphi)\cdot\exp(\mathrm{j}\omega t)\right\} \tag{1.127}$$

$$\mathrm{Re}\{\ln(z)\} = \ln|z| \tag{1.128}$$

$$\mathrm{Im}\{\ln(z)\} = \arg(z) \tag{1.129}$$

Example 1.9 Exponential Form: *Show that a time-dependent variable $i(t)$, expressed in terms of the steady-state value $\bar{i}$ and a sinusoidal time-dependent contribution as*

$$i(t) = \bar{i} + |\Delta i|\cos(\omega t + \varphi) \tag{1.130}$$

can be expressed as

$$i(t) = \bar{i} + \mathrm{Re}\left\{\widetilde{i}\exp(\mathrm{j}\omega t)\right\} \tag{1.131}$$

where

$$\widetilde{i} = |\Delta i|\exp(\mathrm{j}\varphi) \tag{1.132}$$

is a complex number for $\varphi \neq 0$. Equation (1.131) is commonly used in the development of mathematical models for the transfer function, or impedance, response of electrochemical systems.

Solution: *From equation (1.124), the oscillating component of equation (1.130) can be expressed in terms of an exponential as*

$$|\Delta i|\cos(\omega t + \varphi) = |\Delta i|\exp(j(\omega t + \varphi)) - \mathrm{j}|\Delta i|\sin(\omega t + \varphi) \tag{1.133}$$

or

$$|\Delta i|\cos(\omega t + \varphi) = \widetilde{i}\exp(\mathrm{j}\omega t) - \mathrm{j}|\Delta i|\sin(\omega t + \varphi) \tag{1.134}$$

where $\widetilde{i}$ is given by equation (1.132). The quantity on the left-hand side of equation (1.132) must be a real number. Equation (1.134) is formally equivalent to

$$|\Delta i|\cos(\omega t + \varphi) = \mathrm{Re}\left\{|\Delta i|\cos(\omega t + \varphi)\right\} = \mathrm{Re}\left\{\widetilde{i}\exp(\mathrm{j}\omega t) - \mathrm{j}\sin(\omega t + \varphi)\right\} \tag{1.135}$$

The imaginary term $j\sin(\omega t + \varphi)$ does not contribute to the real part of the complex number inside the brackets; thus,

$$|\Delta i|\cos(\omega t + \varphi) = \mathrm{Re}\left\{\widetilde{i}\exp(\mathrm{j}\omega t)\right\} \tag{1.136}$$

The above development could be considered to be a verification of equation (1.127) and justifies the treatment of the current and potential response of electrical circuits expressed as equation (4.8).

Example 1.10 Verification of Expression for Impedance: *Show that the impedance may be expressed as $Z = \widetilde{V}/\widetilde{i}$.*

Solution: *From equation* (1.132),

$$\widetilde{i} = |\Delta i| \exp\left(\mathrm{j}\varphi_i\right) \tag{1.137}$$

where φ_i is the phase associated with the current density signal. Similarly, an expression for $\widetilde{V}$ may be obtained to be

$$\widetilde{V} = |\Delta V| \exp\left(\mathrm{j}\varphi_V\right) \tag{1.138}$$

The ratio yields

$$\frac{\widetilde{V}}{\widetilde{i}} = \frac{|\Delta V|}{|\Delta i|} \exp\left(\mathrm{j}\left(\varphi_V - \varphi_i\right)\right) \tag{1.139}$$

Equation (1.139) *yields a complex number with magnitude $|\Delta V|/|\Delta i|$ and phase $\varphi = \varphi_V - \varphi_i$. This is the impedance.*

1.4.3 Polynomial

A polynomial function of degree n is defined to be

$$P_n(z) = a_n z^n + a_{n-1} z^{n-1} + \ldots + a_1 z + a_0 \tag{1.140}$$

where $a_n \neq 0$, a_{n-1}, ..., a_0 are all complex constants. The rational algebraic function

$$w(z) = \frac{P(z)}{Q(z)} \tag{1.141}$$

is defined where $P(z)$ and $Q(z)$ are polynomials.

A continued overview of complex variables is presented in Appendix A in the context of the complex integration used to establish the Kramers–Kronig relations.

Problems

1.1 Calculate the phase angle and modulus for the following:

(a) $Z = 1/(j\omega C)$

(b) $Z = R$

1.2 The impedance associated with a single electrochemical reaction on a uniform surface can be expressed as

$$Z(\omega) = R_e + \frac{R_t}{1 + j\omega R_t C_{dl}} \tag{1.142}$$

where R_e is the electrolyte resistance, R_t is the charge-transfer resistance, and C_{dl} is the capacity of the double layer.

(a) Find expressions for the real and imaginary parts of the impedance as a function of frequency.

(b) Find expressions for the magnitude and phase angle of the impedance.

(c) Find expressions for the real and imaginary parts of the admittance as a function of frequency.

1.3 The impedance associated with an ideally polarized (blocking) electrode can be expressed as

$$Z(\omega) = R_e + \frac{1}{j\omega C_{dl}} \tag{1.143}$$

where R_e is the electrolyte resistance and C_{dl} is the capacity of the double layer.

(a) Find expressions for the real and imaginary parts of the impedance as a function of frequency.

(b) Find expressions for the magnitude and phase angle of the impedance.

(c) Find expressions for the real and imaginary parts of the admittance as a function of frequency.

1.4 The impedance associated with a constant phase element can be expressed as

$$Z(\omega) = R_e + \frac{1}{(j\omega)^\alpha Q} \tag{1.144}$$

where α and Q are parameters associated with a constant-phase element (CPE). When $\alpha = 1$, Q has units of a capacitance, i.e., μFcm^{-2}, and represents the capacity of the interface. When $\alpha \neq 1$, the system shows behavior that has been attributed to surface heterogeneity, oxide films, or to continuously distributed time constants for charge-transfer reactions.

(a) Find expressions for the real and imaginary parts of the impedance as a function of frequency.

(b) Find expressions for the magnitude and phase angle of the impedance.

(c) Find expressions for the real and imaginary parts of the admittance as a function of frequency.

1.5 Consider a situation where the impedance of one layer is given by

$$Z_1(\omega) = \frac{R_1}{1 + j\omega R_1 C_1} \tag{1.145}$$

and the impedance of a second layer is given by

$$Z_2(\omega) = \frac{R_2}{1 + j\omega R_2 C_2} \tag{1.146}$$

Add the two impedances to find the overall impedance of the two layers.

1.6 The pore-in-pore model described in Section 13.1.3 on page 328 yields an impedance

$$Z = \sqrt{R_0 \sqrt{R_1 Z_1}} \tag{1.147}$$

Develop an expression for the real and imaginary parts of the associated impedance and the associated phase angle:

(a) The impedance Z_1 is given by

$$Z_1 = \frac{1}{j\omega C_1} \tag{1.148}$$

(b) The impedance Z_1 is given by

$$Z_1 = \frac{R_1}{1 + j\omega R_1 C_1} \tag{1.149}$$