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 problems presented in this chapter is to introduce the subject of complex variables at a level sufficient to understand the development of interpretation models for impedance spectroscopy. Problems 1.1–1.6 are based on problems taken from Orazem and Tribollet.[1]

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Problems

1.1 Calculate the phase angle and modulus for the following:
(a) $Z = 1/(\mathrm{j}\omega C)$
(b) $Z = R$



Solution 1.1.

(a) The equation $Z = 1/(\mathrm{j}\omega C)$ corresponds to the electrical behavior of a capacitor. As $1/\mathrm{j} = -\mathrm{j}$, the impedance is an imaginary number $Z = -\mathrm{j}/\omega C$ with phase $\varphi = -90^\circ$ and magnitude $|Z| = 1/\omega C$. This result may also be obtained from the definitions of phase angle and magnitude. The phase angle is given by

$$\varphi = \tan^{-1}\frac{Z_\mathrm{j}}{Z_\mathrm{r}} = \tan^{-1}(-\infty) = -\pi/2 \tag{1.1}$$

or $\varphi = -90^\circ$. The magnitude is given by

$$|Z| = \sqrt{Z_\mathrm{r}^2 + Z_\mathrm{j}^2} = 1/\omega C \tag{1.2}$$

(b) The equation $Z = R$ corresponds to the electrical behavior of a resistor and is a real number. For a real number, the phase angle is equal to zero, and the magnitude is the value of the real number, thus $|Z| = R$. These results may also be

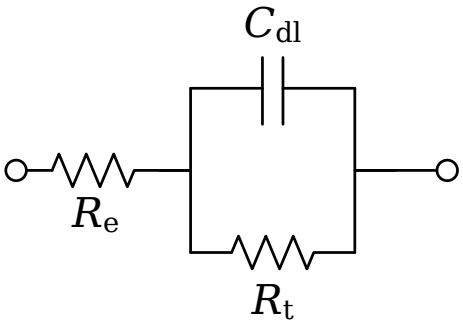


Figure 1.1: Circuit representation of equation (1.5). Taken from Orazem and Tribollet[1] with permission of John Wiley & Sons.

obtained from the definitions of phase angle and magnitude. The phase angle is given by

$$\varphi = \tan^{-1}\frac{Z_{\mathrm{j}}}{Z_{\mathrm{r}}} = \tan^{-1} 0 = 0 \tag{1.3}$$

and the magnitude is given by

$$|Z| = \sqrt{Z_{\mathrm{r}}^2 + Z_{\mathrm{j}}^2} = R \tag{1.4}$$

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

$$Z(\omega) = R_{\mathrm{e}} + \frac{R_{\mathrm{t}}}{1 + \mathrm{j}\omega R_{\mathrm{t}} C_{\mathrm{dl}}} \tag{1.5}$$

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.



Solution 1.2. Equation (1.5) is the response of the electrical circuit presented in Figure 1.1, which can also account for the impedance response of a simple potential-dependent electrochemical reaction on an electrode surface.

(a) Expressions for the real and imaginary parts of Z are found by multiplying nu-

merator and denominator by the complex conjugate, i.e.,

$$Z = R_e + \frac{R_t}{1 + j\omega R_t C_{dl}} \frac{1 - j\omega R_t C_{dl}}{1 - j\omega R_t C_{dl}} \tag{1.6}$$

or

$$Z = R_e + \frac{R_t}{1 + \omega^2 R_t^2 C_{dl}^2} - j\frac{R_t^2 \omega C_{dl}}{1 + \omega^2 R_t^2 C_{dl}^2} \tag{1.7}$$

The real part of the impedance is given by

$$Z_r = R_e + \frac{R_t}{1 + \omega^2 R_t^2 C_{dl}^2} \tag{1.8}$$

and the imaginary part is given by

$$Z_j = -\frac{\omega R_t^2 C_{dl}}{1 + \omega^2 R_t^2 C_{dl}^2} \tag{1.9}$$

As the frequency becomes small, i.e., $\omega \to 0$, the real part of the impedance approaches $R_e + R_t$ and the imaginary part of the impedance approaches zero. As the frequency becomes large, i.e., $\omega \to \infty$, the real part of the impedance approaches R_e and the imaginary part of the impedance again approaches zero.

(b) The magnitude is given by

$$|Z| = \sqrt{Z_r^2 + Z_j^2} \tag{1.10}$$

A compact notation may be used in which

$$x = \left(1 + \omega^2 R_t^2 C_{dl}^2\right) \tag{1.11}$$

Application of equation (1.10) yields

$$|Z| = \frac{1}{x}\sqrt{R_t^2 + \omega^2 R_t^4 C_{dl}^2 + 2R_e R_t x + R_e^2 x^2} \tag{1.12}$$

which can be simplified to

$$|Z| = \frac{1}{x}\sqrt{R_t^2 x + 2R_e R_t x + R_e^2 x^2} \tag{1.13}$$

The phase angle is given by

$$\varphi = \tan^{-1}\left(\frac{Z_j}{Z_r}\right) \tag{1.14}$$

which can be expressed as

$$\varphi = \tan^{-1}\left(\frac{-R_t^2 \omega C_{dl}}{R_e\left(1 + \omega^2 R_t^2 C_{dl}^2\right) + R_t}\right) \tag{1.15}$$

As the frequency becomes small, i.e., $\omega \to 0$, the magnitude of the impedance approaches $R_e + R_t$ and the phase angle approaches zero. As the frequency becomes large, i.e., $\omega \to \infty$, the magnitude of the impedance approaches R_e and the phase angle again approaches zero.

(c) Expressions for the real and imaginary parts of the admittance can be obtained in terms of the impedance by using the complex conjugate, i.e.,

$$Y = \frac{1}{Z} = \frac{1}{Z_r + jZ_j}\left(\frac{Z_r - jZ_j}{Z_r - jZ_j}\right) \tag{1.16}$$

yielding

$$Y = \frac{1}{|Z|^2}\left(Z_r - jZ_j\right) \tag{1.17}$$

The real part of the resulting admittance is

$$Y_r = \frac{R_e + R_t + \omega^2 R_e R_t^2 C_{dl}^2}{R_e^2 + 2R_e R_t + R_t^2 + \omega^2 R_e^2 R_t^2 C_{dl}^2} \tag{1.18}$$

and the imaginary part is given by

$$Y_j = \frac{\omega R_t^2 C_{dl}}{R_e^2 + 2R_e R_t + R_t^2 + \omega^2 R_e^2 R_t^2 C_{dl}^2} \tag{1.19}$$

As the frequency becomes small, i.e., $\omega \to 0$, the real part of the admittance approaches $1/(R_e + R_t)$ and the imaginary part of the admittance approaches zero. As the frequency becomes large, i.e., $\omega \to \infty$, the real part of the admittance approaches $1/R_e$ and the imaginary part of the admittance again approaches zero.

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

$$Z(\omega) = R_e + \frac{1}{j\omega C_{dl}} \tag{1.20}$$

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.



Solution 1.3. This problem is very much like Problem 1.1.a with the exception that an ohmic resistance has been added to the capacitance.

(a) As $1/j = -j$, the impedance is given by

$$Z = R_e - j\frac{1}{\omega C_{dl}} \tag{1.21}$$

where

$$Z_r = R_e \tag{1.22}$$

is the real part of the impedance and

$$Z_j = -\frac{1}{\omega C_{dl}} \tag{1.23}$$

is the imaginary part.

(b) The phase angle, expressed by equation (1.14), can be written

$$\varphi = \tan^{-1}\left(\frac{-1}{\omega R_e C_{dl}}\right) \tag{1.24}$$

At a frequency $\omega = 1/R_e C_{dl}$, $\varphi = -\pi/4 = -45°$. As the frequency becomes small, i.e., $\omega \to 0$, the phase angle approaches $-90°$. As the frequency becomes large, i.e., $\omega \to \infty$, the phase angle approaches zero.

The magnitude, expressed by equation (1.10), can be written

$$|Z| = \sqrt{\frac{1 + \omega^2 R_e^2 C_{dl}^2}{\omega^2 C_{dl}^2}} \tag{1.25}$$

When $\omega = 1/R_e C_{dl}$, $|Z| = \sqrt{2} R_e$. As the frequency becomes small, i.e., $\omega \to 0$, the magnitude approaches $1/\omega C_{dl}$. As the frequency becomes large, i.e., $\omega \to \infty$, the magnitude approaches R_e.

(c) Following equation (1.17),

$$Y_r = \frac{\omega^2 R_e C_{dl}^2}{1 + \omega^2 R_e^2 C_{dl}^2} \tag{1.26}$$

and

$$Y_j = \frac{\omega C_{dl}}{1 + \omega^2 R_e^2 C_{dl}^2} \tag{1.27}$$

As the frequency becomes small, i.e., $\omega \to 0$, the real and imaginary parts of the admittance approach zero. As the frequency becomes large, i.e., $\omega \to \infty$, the real part of the admittance approaches $1/R_e$ and the imaginary part of the admittance again approaches zero.

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

$$Z(\omega) = R_e + \frac{1}{(j\omega)^{\alpha} Q} \tag{1.28}$$

where α and Q are parameters associated with a constant-phase element (CPE). When $\alpha = 1$, Q has units of a capacitance, i.e., $\mu F/cm^2$, 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.



Solution 1.4.

(a) Equation (1.28) may be expressed as

$$Z(\omega) = R_e + \frac{j^{-\alpha}}{\omega^{\alpha} Q} \tag{1.29}$$

Introduction of

$$j^{-\alpha} = \cos\left(\frac{\alpha\pi}{2}\right) - j\sin\left(\frac{\alpha\pi}{2}\right) \tag{1.30}$$

yields

$$Z = R_e + \frac{\cos\left(\frac{\alpha\pi}{2}\right)}{\omega^{\alpha} Q} - j\frac{\sin\left(\frac{\alpha\pi}{2}\right)}{\omega^{\alpha} Q} \tag{1.31}$$

Thus, the real part of the impedance is given by

$$Z_r = R_e + \frac{\cos(\alpha\pi/2)}{\omega^{\alpha} Q} \tag{1.32}$$

and imaginary part of the impedance is given by

$$Z_j = -\frac{\sin(\alpha\pi/2)}{\omega^{\alpha} Q} \tag{1.33}$$

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

$$\lim_{\alpha \to 1} Z_{CPE} = -j\frac{1}{\omega C} \tag{1.34}$$

which is the impedance for a capacitor.

(b) Following equation (1.14),

$$\varphi = \tan^{-1}\left(\frac{-\sin(\alpha\pi/2)}{\omega^{\alpha}R_{\mathrm{e}}Q + \cos(\alpha\pi/2)}\right) \tag{1.35}$$

If $R_{\mathrm{e}} = 0$, $\varphi = -\alpha\pi/2 = -\alpha 90^{\circ}$. Following equation (1.10),

$$|Z| = \frac{1}{\omega^{\alpha}Q}\sqrt{1 + R_{\mathrm{e}}^2\omega^{2\alpha}Q^2 + 2R_{\mathrm{e}}\omega^{\alpha}Q\cos(\alpha\pi/2)} \tag{1.36}$$

If $R_{\mathrm{e}} = 0$, $|Z| = 1/\omega^{\alpha}Q$.

(c) Following equation (1.17),

$$Y_{\mathrm{r}} = \frac{\omega^{2\alpha}R_{\mathrm{e}}Q^2 + \omega^{\alpha}Q\cos(\alpha\pi/2)}{1 + \omega^{2\alpha}R_{\mathrm{e}}^2Q^2} \tag{1.37}$$

and

$$Y_{\mathrm{j}} = \frac{\omega^{\alpha}Q\sin(\alpha\pi/2)}{1 + \omega^{2\alpha}R_{\mathrm{e}}^2Q^2} \tag{1.38}$$

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

$$Z_1(\omega) = \frac{R_1}{1 + \mathrm{j}\omega R_1C_1} \tag{1.39}$$

and the impedance of a second layer is given by

$$Z_2(\omega) = \frac{R_2}{1 + \mathrm{j}\omega R_2C_2} \tag{1.40}$$

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



Solution 1.5. Sum impedances by adding the real parts and adding the imaginary parts. The sum of complex numbers z and w may be expressed as

$$z + w = (z_{\mathrm{r}} + w_{\mathrm{r}}) + \mathrm{j}(z_{\mathrm{j}} + w_{\mathrm{j}}) \tag{1.41}$$

As

$$Z_1 = \frac{R_1}{1 + \mathrm{j}\omega R_1C_1} = \frac{R_1}{1 + \omega^2R_1^2C_1^2} - \mathrm{j}\frac{\omega R_1^2C_1}{1 + \omega^2R_1^2C_1^2} \tag{1.42}$$

and

$$Z_2 = \frac{R_2}{1 + \mathrm{j}\omega R_2C_2} = \frac{R_2}{1 + \omega^2R_2^2C_2^2} - \mathrm{j}\frac{\omega R_2^2C_2}{1 + \omega^2R_2^2C_2^2} \tag{1.43}$$

the real part of the sum of Z_1 and Z_2 is given by

$$\mathrm{Re}\{Z_1 + Z_2\} = \frac{R_1}{1 + \omega^2R_1^2C_1^2} + \frac{R_2}{1 + \omega^2R_2^2C_2^2} \tag{1.44}$$

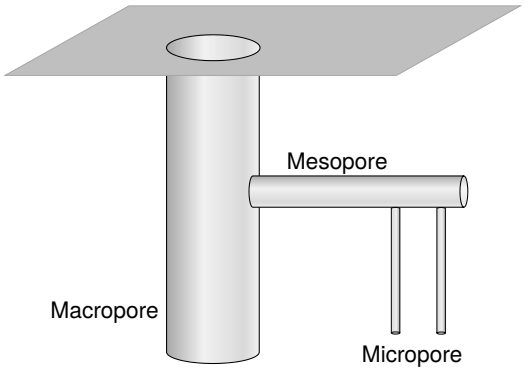


Figure 1.2: Schematic representation of a pore-within-a-pore hierarchy as suggested by Itagaki et al.[13] Taken from Orazem and Tribollet[1] with permission of John Wiley & Sons.

and the imaginary part is given by

$$\mathrm{Im}\left\{Z_1 + Z_2\right\} = -\left(\frac{\omega R_1^2 C_1}{1+\omega^2 R_1^2 C_1^2} + \frac{\omega R_2^2 C_2}{1+\omega^2 R_2^2 C_2^2}\right) \tag{1.45}$$

1.6 Gourbeyre et al.[14] and Itagaki et al.[13] have proposed that pores can appear inside a macropore structure as illustrated in Figure 1.2. The pore-in-pore model, involving macropores and mesopores, yields an impedance

$$Z = \sqrt{R_0 \sqrt{R_1 Z_1}} \tag{1.46}$$

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

$$Z_1 = \frac{1}{\mathrm{j}\omega C_{\mathrm{dl}}} \tag{1.47}$$

(b) The impedance Z_1 is given by

$$Z_1 = \frac{R_{\mathrm{t}}}{1+\mathrm{j}\omega R_{\mathrm{t}} C_{\mathrm{dl}}} \tag{1.48}$$



Solution 1.6. Two approaches were taken to solve this problem. The solution for part (a) makes use of the relationships between rectangular and polar coordinates for complex variables to derive real and imaginary parts of the impedance from which the modulus and phase angle may be derived. The solution for part (b) derives directly the modulus and phase angle from which the real and imaginary parts of the

impedance may be derived.

(a) The imaginary number may be expressed in polar coordinates as

$$\mathrm{j} = \cos(\frac{\pi}{2}) + \mathrm{j}\sin(\frac{\pi}{2}) \tag{1.49}$$

Therefore, Z_1 can be expressed as

$$Z_1 = \frac{1}{\mathrm{j}\omega C_{\mathrm{dl}}} = -\mathrm{j}\frac{1}{\omega C_{\mathrm{dl}}} = \frac{\cos(-\frac{\pi}{2}) + \mathrm{j}\sin(-\frac{\pi}{2})}{\omega C_{\mathrm{dl}}} \tag{1.50}$$

Equation (1.46) may be expressed as

$$\begin{aligned} Z &= \sqrt{R_0\sqrt{R_1 Z_1}} \\ &= R_0^{1/2}(R_1 Z_1)^{1/4} \\ &= R_0^{1/2} R_1^{1/4} \left(\frac{\cos(-\frac{\pi}{2}) + \mathrm{j}\sin(-\frac{\pi}{2})}{\omega C_{\mathrm{dl}}} \right)^{1/4} \\ &= R_0^{1/2} R_1^{1/4} \frac{\cos(\frac{-\pi}{8}) + \mathrm{j}\sin(\frac{-\pi}{8})}{(\omega C_{\mathrm{dl}})^{1/4}} \\ &= \left(\frac{R_0^2 R_1}{\omega C_{\mathrm{dl}}} \right)^{1/4} \left(\cos(\frac{\pi}{8}) - \mathrm{j}\sin(\frac{\pi}{8}) \right) \end{aligned} \tag{1.51}$$

The expressions of real and imaginary parts of Z are

$$Z_{\mathrm{r}} = (\frac{R_0^2 R_1}{\omega C_{\mathrm{dl}}})^{1/4} \cos(\frac{\pi}{8}) \tag{1.52}$$

$$Z_{\mathrm{j}} = -(\frac{R_0^2 R_1}{\omega C_{\mathrm{dl}}})^{1/4} \sin(\frac{\pi}{8}) \tag{1.53}$$

The phase angle is expressed as

$$\begin{aligned} \varphi &= \tan^{-1}\left(\frac{Z_{\mathrm{j}}}{Z_{\mathrm{r}}} \right) \\ &= -\frac{\pi}{8} \end{aligned} \tag{1.54}$$

The phase angle is -22.5° (or $-\pi/8$), which is half of the -45° (or $-\pi/4$) phase angle associated with a single pore.

(b) The impedance Z_1 given by equation (1.48) may be expressed in terms of real and imaginary parts as

$$Z_1 = \frac{R_{\mathrm{t}}}{1 + \mathrm{j}\omega R_{\mathrm{t}} C_{\mathrm{dl}}} \frac{1 - \mathrm{j}\omega R_{\mathrm{t}} C_{\mathrm{dl}}}{1 - \mathrm{j}\omega R_{\mathrm{t}} C_{\mathrm{dl}}} \tag{1.55}$$

where the real part of the impedance is given by

$$Z_{1,r} = \frac{R_t}{1 + \omega^2 R_t^2 C_{dl}^2} \tag{1.56}$$

and the imaginary part is given by

$$Z_{1,j} = -\frac{\omega R_t^2 C_{dl}}{1 + \omega^2 R_t^2 C_{dl}^2} \tag{1.57}$$

The modulus of Z_1 may be expressed as

$$|Z_1| = \sqrt{\frac{R_t^2}{\left(1 + \omega^2 R_t^2 C_{dl}^2\right)^2} + \frac{\omega^2 R_t^4 C_{dl}^2}{\left(1 + \omega^2 R_t^2 C_{dl}^2\right)^2}} = \sqrt{\frac{R_t^2 + \omega^2 R_t^4 C_{dl}^2}{\left(1 + \omega^2 R_t^2 C_{dl}^2\right)^2}} \tag{1.58}$$

and the modulus of Z may be obtained as

$$|Z| = R_0^{1/2} R_1^{1/4} \sqrt{\sqrt{|Z_1|}} \tag{1.59}$$

The phase of Z_1 is given by

$$\varphi_1 = \tan^{-1}\left(-\omega R_t C_{dl}\right) \tag{1.60}$$

and the phase of Z may be obtained as

$$\varphi = \frac{\varphi_1}{4} = \frac{\tan^{-1}\left(-\omega R_t C_{dl}\right)}{4} \tag{1.61}$$

In the high-frequency limit, the impedance given as equation (1.48) approaches equation (1.47), and the phase angle approaches a value of $-\pi/8$ or -22.5°, just as was seen for part (a).

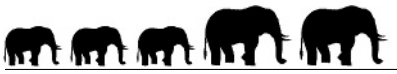
The real part of Z is obtained from the modulus and phase angle as

$$Z_r = R_0^{1/2} R_1^{1/4} \left(\frac{R_t^2 + \omega^2 R_t^4 C_{dl}^2}{\left(1 + \omega^2 R_t^2 C_{dl}^2\right)^2} \right)^{1/8} \cos\left(\frac{\varphi_1}{4}\right) \tag{1.62}$$

and the imaginary part is given as

$$Z_j = R_0^{1/2} R_1^{1/4} \left(\frac{R_t^2 + \omega^2 R_t^4 C_{dl}^2}{\left(1 + \omega^2 R_t^2 C_{dl}^2\right)^2} \right)^{1/8} \sin\left(\frac{\varphi_1}{4}\right) \tag{1.63}$$

A similar treatment can be applied for a pore-in-pore-in-pore model in which macro-, meso-, and micropores are considered.



1.7 A phasor notation is commonly used in the development of mathematical models for the transfer function, or impedance, response of electrochemical systems.

(a) 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

$$i(t) = \bar{i} + |\Delta i| \cos(\omega t + \varphi) \tag{1.64}$$

can be expressed as

$$i(t) = \bar{i} + \mathrm{Re}\left\{\widetilde{i} \exp(\mathrm{j}\omega t)\right\} \tag{1.65}$$

where the phasor

$$\widetilde{i} = |\Delta i| \exp(\mathrm{j}\varphi) \tag{1.66}$$

is a complex number for $\varphi \neq 0$.

(b) Under galvanostatic modulation, $\widetilde{i}$ may be considered a real number. Explain.

(c) Under potentiostatic modulation, the difference between the working and the reference electrode potentials $\widetilde{\Phi}_{\mathrm{m}} - \widetilde{\Phi}_{\mathrm{ref}}$ may be considered a real number, but the interfacial potential $\widetilde{\Phi}_{\mathrm{m}} - \widetilde{\Phi}_0$, where $\widetilde{\Phi}_0$ corresponds to a position just outside the diffuse part of the double layer, is a complex number. Explain.



Solution 1.7.

(a) Following

$$\exp(\mathrm{j}x) = \cos(x) + \mathrm{j}\sin(x) \tag{1.67}$$

the oscillating component of equation (1.64) can be expressed in terms of an exponential as

$$|\Delta i| \cos(\omega t + \varphi) = |\Delta i| \exp(\mathrm{j}(\omega t + \varphi)) - \mathrm{j}|\Delta i| \sin(\omega t + \varphi) \tag{1.68}$$

or

$$|\Delta i| \cos(\omega t + \varphi) = \widetilde{i} \exp(\mathrm{j}\omega t) - \mathrm{j}|\Delta i| \sin(\omega t + \varphi) \tag{1.69}$$

where $\widetilde{i}$ is given by equation (1.66). The quantity on the left-hand side of equation (1.66) must be a real number. Equation (1.69) is formally equivalent to

$$|\Delta i| \cos(\omega t + \varphi) = \mathrm{Re}\left\{|\Delta i| \cos(\omega t + \varphi)\right\} = \mathrm{Re}\left\{\widetilde{i} \exp(\mathrm{j}\omega t) - \mathrm{j}\sin(\omega t + \varphi)\right\} \tag{1.70}$$

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

$$|\Delta i| \cos(\omega t + \varphi) = \mathrm{Re}\left\{\widetilde{i} \exp(\mathrm{j}\omega t)\right\} \tag{1.71}$$

(b) The phase angle is referenced to the input signal. Under galvanostatic modulation, current is the input signal and the phase angle of the current signal is equal to zero, as it is referenced to itself. The phasor for current $\widetilde{I}$ (or current density $\widetilde{i}$) is given by equation (1.66). The real and imaginary parts are given by

$$\widetilde{i}_{\mathrm{r}} = |\Delta i| \cos(\varphi) \tag{1.72}$$

and

$$\widetilde{i}_{\mathrm{j}} = |\Delta i| \sin(\varphi) \tag{1.73}$$

For $\varphi = 0$, $\widetilde{i}_{\mathrm{r}} = |\Delta i|$ and $\widetilde{i}_{\mathrm{j}} = 0$.

(c) Under potentiostatic modulation, the potential difference between the working and reference electrodes is controlled. Thus, using the arguments presented in part (b), $\widetilde{\Phi}_{\mathrm{m}} - \widetilde{\Phi}_{\mathrm{ref}}$ may be considered a real number. The difference between the potential of the working electrode and the potential outside the diffuse part of the double layer cannot be controlled. Thus, the phase of $\widetilde{\Phi}_{\mathrm{m}} - \widetilde{\Phi}_0$ is referenced to the input signal $\widetilde{\Phi}_{\mathrm{m}} - \widetilde{\Phi}_{\mathrm{ref}}$ and cannot be assumed to be equal to zero. The difference $\widetilde{\Phi}_{\mathrm{m}} - \widetilde{\Phi}_0$ is therefore considered a complex number.

1.8 The impedance may be expressed in the form of a complex capacitance following

$$\mathcal{C} = \frac{1}{\mathrm{j}\omega (Z - R_{\mathrm{e}})} \tag{1.74}$$

Find an expression for the complex capacitance for:

(a) $Z = R_{\mathrm{e}} + 1/\mathrm{j}\omega C$.

(b) $Z = R_{\mathrm{e}} + R_{\mathrm{t}}/(1 + \mathrm{j}\omega R_{\mathrm{t}} C)$.

(c) $Z = R_{\mathrm{e}} + 1/(\mathrm{j}\omega)^{\alpha} Q$.



Solution 1.8.

(a) For $Z = R_{\mathrm{e}} + 1/\mathrm{j}\omega C$, equation (1.74) yields

$$\mathcal{C} = \frac{1}{\mathrm{j}\omega \left(\frac{1}{\mathrm{j}\omega C}\right)} = C \tag{1.75}$$

The complex capacitance for an impedance associated with an ohmic resistance in series with a capacitor is a real number with the value of the capacitance. The imaginary part is equal to zero.

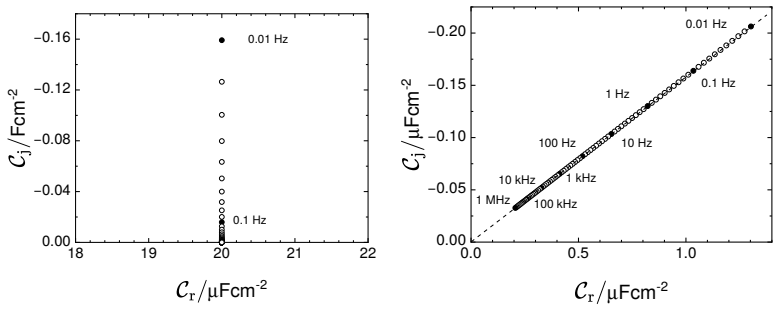


Figure 1.3: Complex capacitance plots for Problem 1.8: (a) solution to part b for parameters $R_t = 100\ \Omega\text{cm}^2$ and $C = 20\ \mu\text{F/cm}^2$ and (b) solution to part c for parameters $\alpha = 0.9$ and $Q = 10^{-6}\ \text{F/cm}^2\text{s}^{1-\alpha}$.

(b) For $Z = R_e + R_t/(1 + j\omega R_t C)$,

$$\mathcal{C} = \frac{1}{j\omega\left(\frac{R_t}{1+j\omega R_t C}\right)} = C + \frac{1}{j\omega R_t} = C - j\frac{1}{\omega R_t} \tag{1.76}$$

The real part of the complex capacitance is C and the imaginary part is $-1/\omega R_t$. The calculated complex capacitance presented in Figure 1.3(a) was obtained for parameters $R_t = 100\ \Omega\text{cm}^2$ and $C = 20\ \mu\text{F/cm}^2$. These calculations confirm that the real part of the complex capacitance yields the input value for capacitance.

(c) For an ohmic resistance in series with a constant-phase elements (CPE), e.g., $Z = R_e + 1/(j\omega)^\alpha Q$,

$$\mathcal{C} = \frac{1}{j\omega\left(\frac{1}{(j\omega)^\alpha Q}\right)} = \frac{Q}{(j\omega)^{1-\alpha}} \tag{1.77}$$

Introduction of equation (1.30) yields

$$\mathcal{C} = \frac{Q}{\omega^{1-\alpha}}\cos\left(\frac{\pi(\alpha-1)}{2}\right) + \frac{Q}{\omega^{1-\alpha}}j\sin\left(\frac{\pi(\alpha-1)}{2}\right) \tag{1.78}$$

or

$$\mathcal{C} = \frac{Q}{\omega^{1-\alpha}}\cos\left(\frac{\pi(1-\alpha)}{2}\right) - j\frac{Q}{\omega^{1-\alpha}}\sin\left(\frac{\pi(1-\alpha)}{2}\right) \tag{1.79}$$

Equation (1.79) shows that, for a CPE, where $0 < \alpha < 1$, $\mathcal{C}_r \to 0$ as frequency tends toward infinity. Thus, the pure CPE with $0 < \alpha < 1$ cannot be represented by a capacitance. A value for capacitance is seen only if $\alpha = 1$, for which $\mathcal{C}_r = Q$ and $\mathcal{C}_j = 0$.

The calculated complex capacitance presented in Figure 1.3(b) was obtained for $\alpha = 0.9$ and $Q = 10^{-6}\ \text{F/cm}^2\text{s}^{1-\alpha}$. In contrast to the results shown in Figure 1.3(a), the real part of the complex capacitance does not approach a finite value for capacitance.