Ch. 10

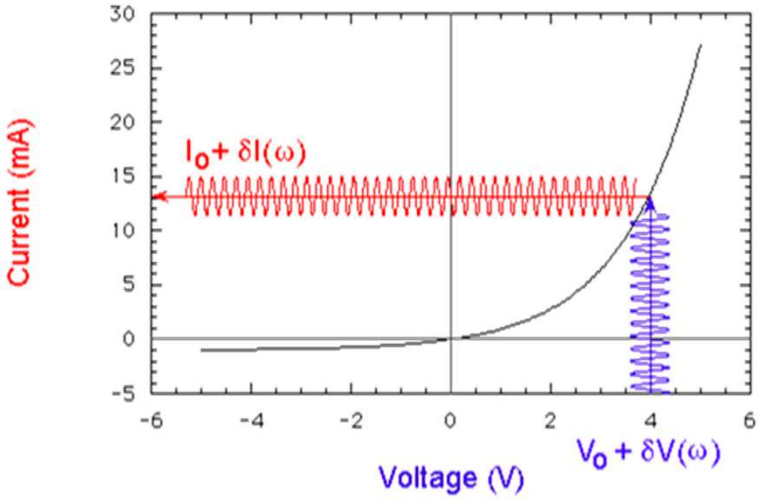
TECHNIQUES BASED ON CONCEPTS OF IMPEDANCE

10.1 INTRODUCTION

- In previous chapters we have discussed ways of studying electrode reactions through large perturbations on the system.

- By imposing potential sweeps, potential steps, or current steps, we typically drive the electrode to a condition far from equilibrium.
→ we observe the response, which is usually a transient signal.

- Another approach is to perturb the cell with an alternating signal of small magnitude and to observe the way in which the system follows the perturbation at steady state.



10.1 INTRODUCTION

- Many advantages

(a) an experimental ability to make high-precision measurements because the response may be indefinitely steady and can therefore be averaged over a long term,

(b) an ability to treat the response theoretically by linearized (or otherwise simplified) current-potential characteristics,

(c) measurement over a wide time (or frequency) range (10^4 to 10^{-6} s or 10^{-4} to 10^6 Hz).

- Since one usually works close to equilibrium,

→ one often does not require detailed knowledge about the behavior of the i-E response curve over great ranges of overpotential.

→ This advantage leads to important simplifications in treating kinetics and diffusion.

10.1 INTRODUCTION

- A purely sinusoidal voltage can be expressed as

$$e = E \sin \omega t$$

→ where ω is the angular frequency, which is 2π times the conventional frequency in Hz.

- It is convenient to think of this voltage as a rotating vector (or phasor) quantity like that pictured in Figure 10.1.3.

→ Its length is the amplitude E and its frequency of rotation is ω.

→ The observed voltage at any time, e, is the component of the phasor projected on some particular axis (normally that at 0°).

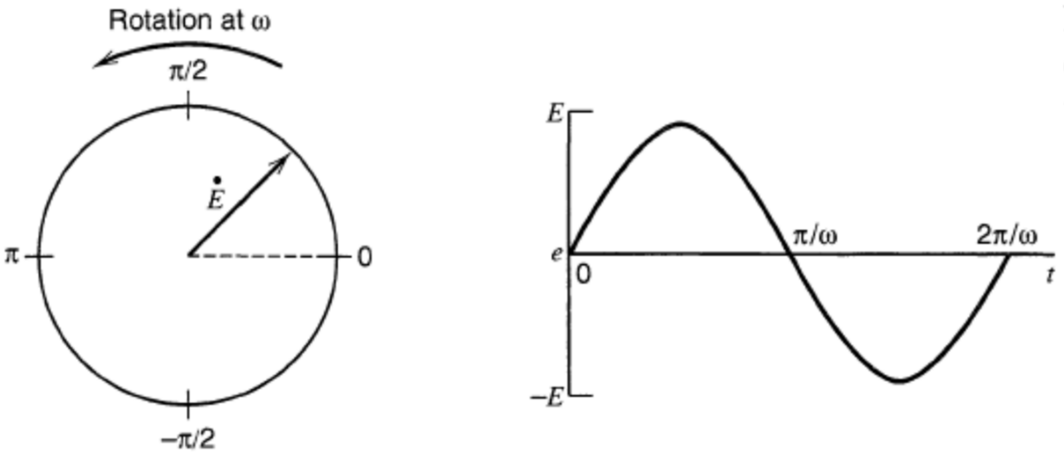


Figure 10.1.3 Phasor diagram for an alternating voltage, $e = E \sin \omega t$.

10.1 INTRODUCTION

- One frequently wishes to consider the relationship between two related sinusoidal signals, such as the current, i, and the voltage, e.

- Each is then represented as a separate phasor, $\dot{I}$ or $\dot{E}$, rotating at the same frequency.

- As shown in Figure 10.1.4, they generally will not be in phase;

→ thus their phasors will be separated by a phase angle, ϕ.

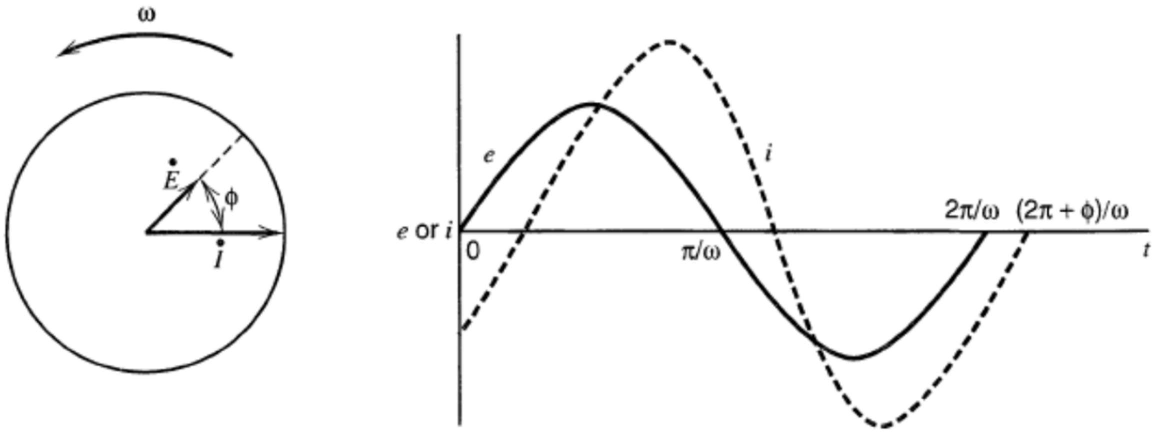


Figure 10.1.4 Phasor diagram showing the relationship between alternating current and voltage signals at frequency ω.

10.1 INTRODUCTION

- One of the phasors, usually $\dot{E}$, is taken as a reference signal, and ϕ is measured with respect to it.

- In the figure, the current lags the voltage. It can be expressed generally as

$$i = I \sin(\omega t + \phi)$$

- The relationship between two phasors at the same frequency remains constant as they rotate
→ hence the phase angle is constant.

10.1 INTRODUCTION

- Let us apply these concepts to the analysis of some simple circuits.
- Consider first a pure resistance, R, across which a sinusoidal voltage, e = E sin ωt, is applied.
- Since Ohm's law always holds,

  → the current is (E/R)sin ωt or, in phasor notation,

$$\dot{I} = \frac{\dot{E}}{R}$$

$$\dot{E} = \dot{I}R$$

- The phase angle is zero, and the vector diagram is that of Figure 10.1.5.

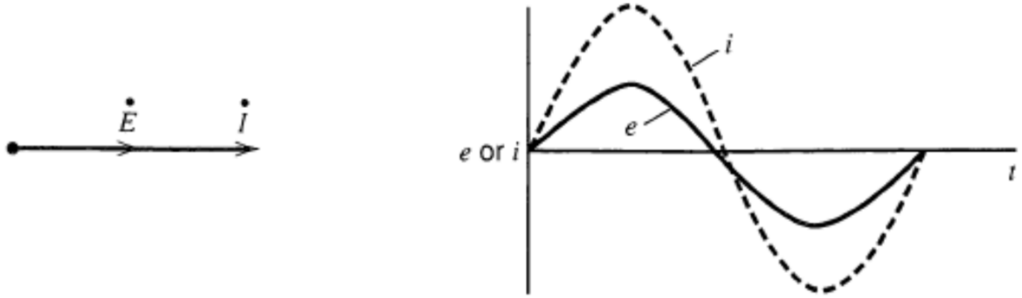


Figure 10.1.5
Relationship between the voltage across a resistor and current through the resistor.

10.1 INTRODUCTION

- Suppose we now substitute a pure capacitance, C, for the resistor.
- The fundamental relation of interest is then $q = Ce$, or $i = C(de/dt)$; thus

$$i = \omega C E \cos \omega t$$

$$i = \frac{E}{X_C} \sin\left(\omega t + \frac{\pi}{2}\right)$$

→ where X_c is the capacitive reactance, $1/\omega C$.

- The phase angle is π/2, and the current leads the voltage, as shown in Figure 10.1.6.

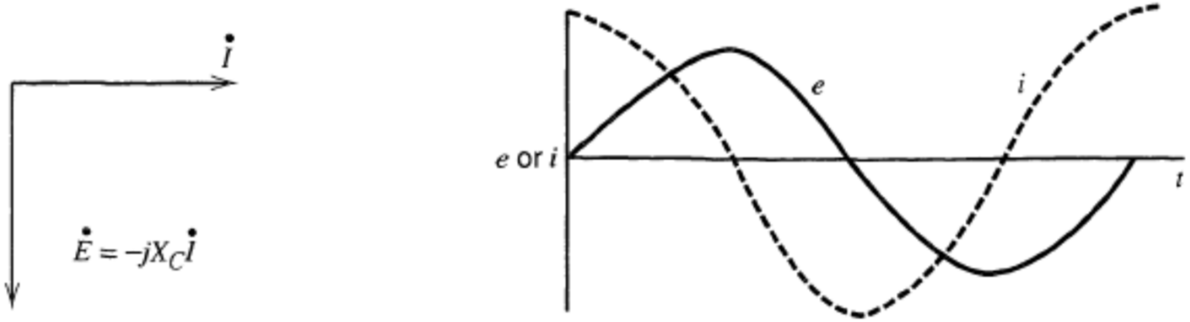


Figure 10.1.6
Relationship between an alternating voltage across a capacitor and the alternating current through the capacitor.

10.1 INTRODUCTION

- Since the vector diagram has now expanded to a plane, it is convenient to represent phasors in terms of complex notation.

→ Components along the ordinate are assigned as imaginary and are multiplied by $j = \sqrt{-1}$.

→ Components along the abscissa are real.

- We handle vector components mathematically as "real" or "imaginary," but both types are real in the sense of being measurable by phase angle.

$$i = \frac{E}{X_C}\sin\left(\omega t + \frac{\pi}{2}\right) \quad \Rightarrow \quad \dot{E} = -jX_C\dot{I}$$

10.1 INTRODUCTION

- Now consider a resistance, R, and a capacitance, C, in series.

- A voltage, $\dot{E}$, is applied across them, and at all times it must equal the sum of the individual voltage drops across the resistor and the capacitor; thus

$$\dot{E} = \dot{E}_R + \dot{E}_C$$
$$\dot{E} = \dot{I}(R - jX_C)$$
$$\dot{E} = \dot{I}\mathbf{Z}$$

- The impedance is a kind of generalized resistance,
  → The equation is a generalized version of Ohm's law.

10.1 INTRODUCTION

- In this way we find that the voltage is linked to the current through a vector **Z** = R - jX_c called the impedance.
- Figure 10.1.7 is a display of the relationships between these various quantities.

(*a*) (*b*)

Figure 10.1.7 (*a*) Phasor diagram showing the relationship between the current and the voltages in a series *RC* network. The voltage across the whole network is $\dot{E}$, and $\dot{E}_R$ and $\dot{E}_C$ are its components across the resistance and the capacitance. (*b*) An impedance vector diagram derived from the phasor diagram in (*a*).

10.1 INTRODUCTION

- In general the impedance can be represented a

$$\boxed{\mathbf{Z}(\omega) = \mathrm{Z}_{\mathrm{Re}} - j\mathrm{Z}_{\mathrm{Im}}}$$

→ where Z_{RE} and Z_{Im} are the real and imaginary parts of the impedance.

- For the example

here, $Z_{RE} = R$ and $Z_{Im} = X_C = 1/\omega C$.

- The magnitude of **Z**, written lZl or Z, is given by

$$|Z|^2 = R^2 + X_C^2 = (Z_{\mathrm{Re}})^2 + (Z_{\mathrm{Im}})^2$$

- and the phase angle, ϕ, is given by

$$\tan\phi = Z_{\mathrm{Im}}/Z_{\mathrm{Re}} = X_C/R = 1/\omega RC$$

10.1 INTRODUCTION

- The variation of the impedance with frequency is often of interest and can be displayed in different ways.

(1) In a **Bode plot**, log lZl and ϕ are both plotted against log ω.

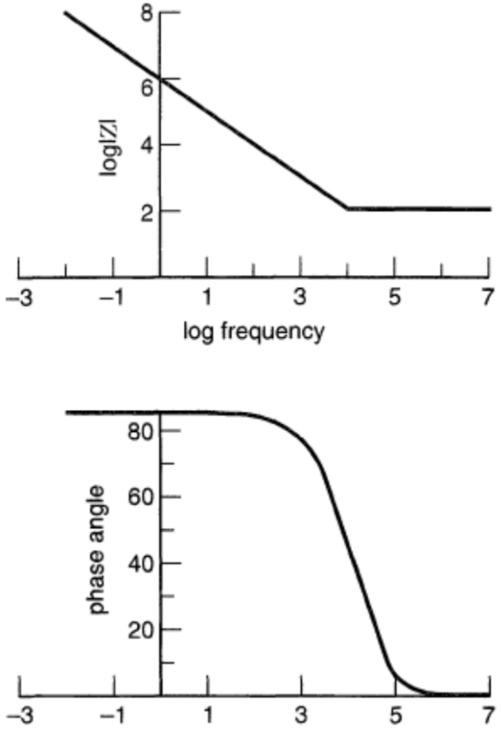
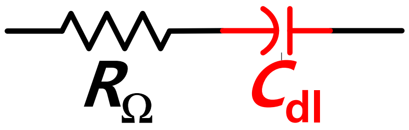
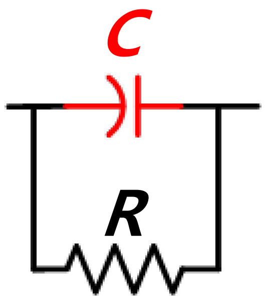


Figure 10.1.8 Bode plots for a series RC circuit with $R = 100\ \Omega$ and $C = 1\ \mu F$.



Plots for the series RC circuit

10.1 INTRODUCTION



Plots for a parallel RC circuit

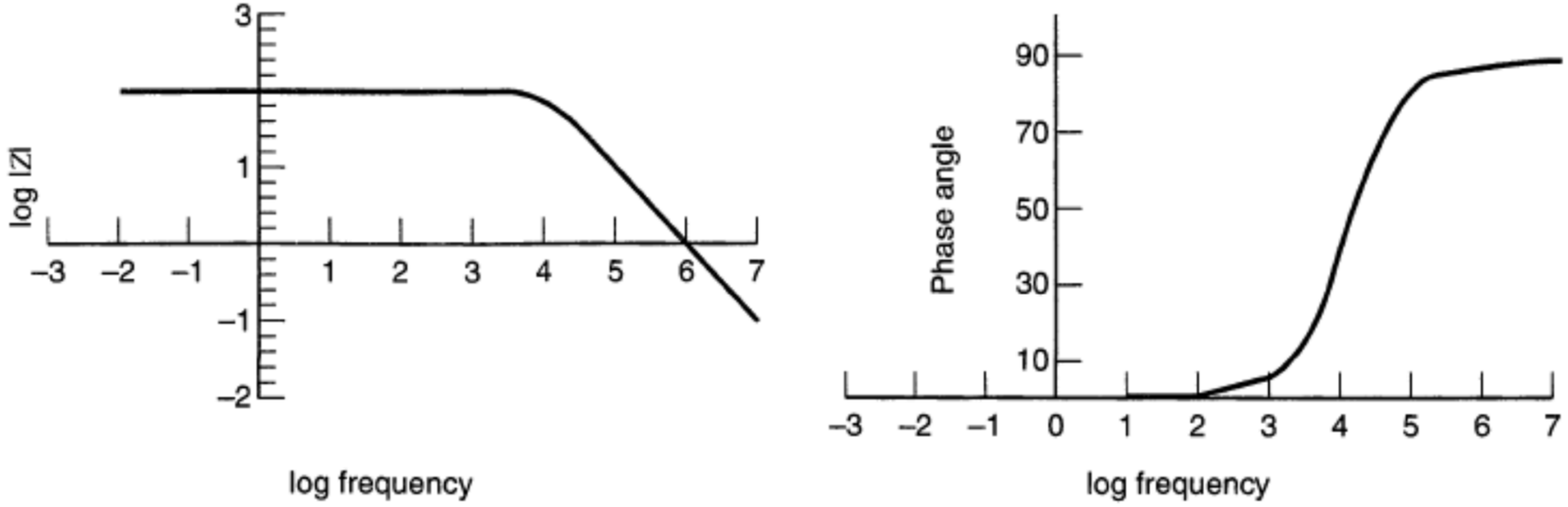
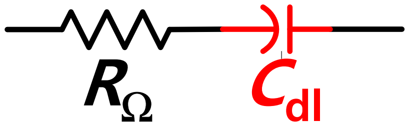


Figure 10.1.10 Bode plots for a parallel *RC* circuit with $R = 100\ \Omega$ and $C = 1\ \mu\mathrm{F}$.

10.1 INTRODUCTION

(2) An alternative representation, a **Nyquist plot**, displays Z_{Im} vs. Z_{Re} for different values of ω.



Plots for the series RC circuit

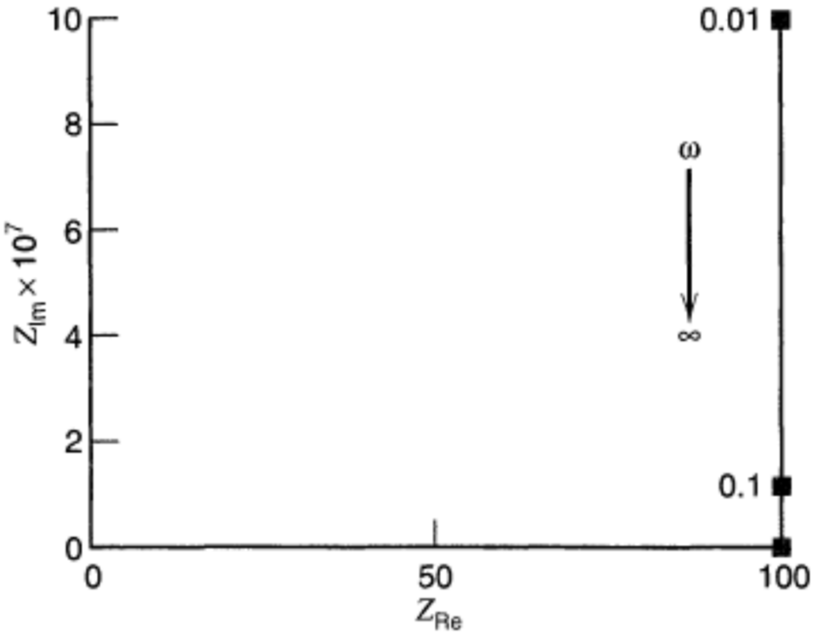
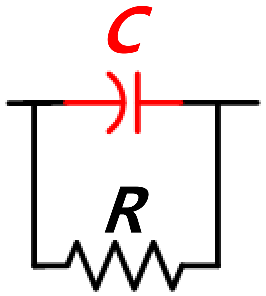


Figure 10.1.9 Nyquist plot for a series *RC* circuit with $R = 100\ \Omega$ and $C = 1\ \mu F$.

10.1 INTRODUCTION



Plot for a parallel RC circuit

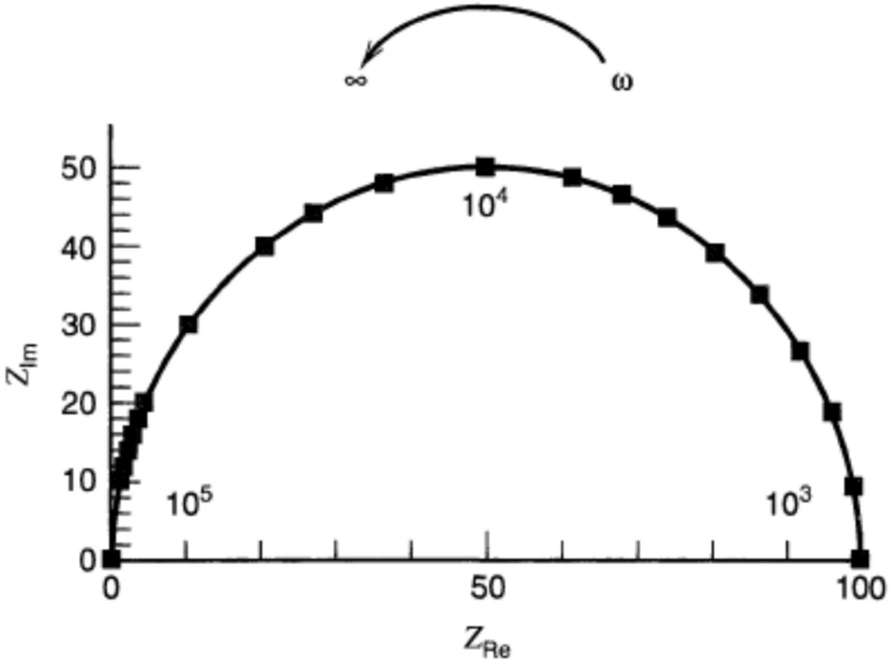
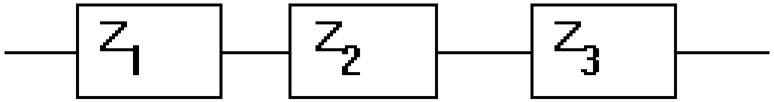


Figure 10.1.11 Nyquist plot for a parallel *RC* circuit with $R = 100\ \Omega$ and $C = 1\ \mu F$.

10.1 INTRODUCTION

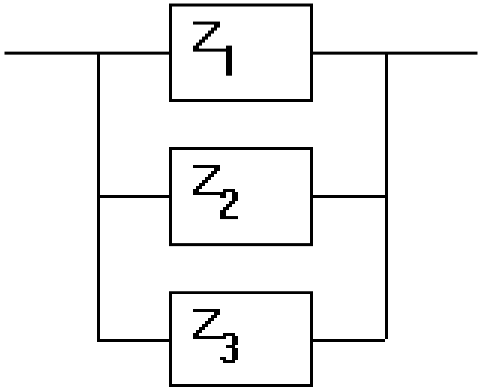
- For impedances in series, the overall impedance is the sum of the individual values
- For impedances in parallel, the inverse of the overall impedance is the sum of the reciprocals of the individual vectors.

(a) Impedances in Series:



$$Z_{eq} = Z_1 + Z_2 + Z_3$$

(b) Impedances in Parallel;



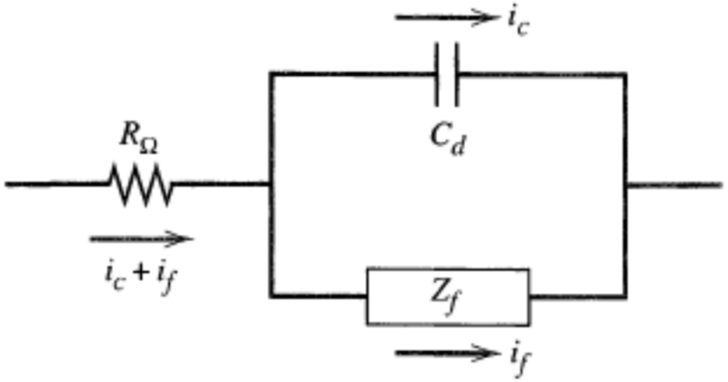
$$\frac{1}{Z_{eq}} = \frac{1}{Z_1} + \frac{1}{Z_2} + \frac{1}{Z_3}$$

10.1 INTRODUCTION

- An electrochemical cell can be considered simply an impedance to a small sinusoidal excitation

→ hence we ought to be able to represent its performance by an equivalent circuit of resistors and capacitors that pass current with the same amplitude and phase angle that the real cell does under a given excitation.

- A frequently used circuit, called the Randies equivalent circuit, is shown in Figure 10.1.14a.

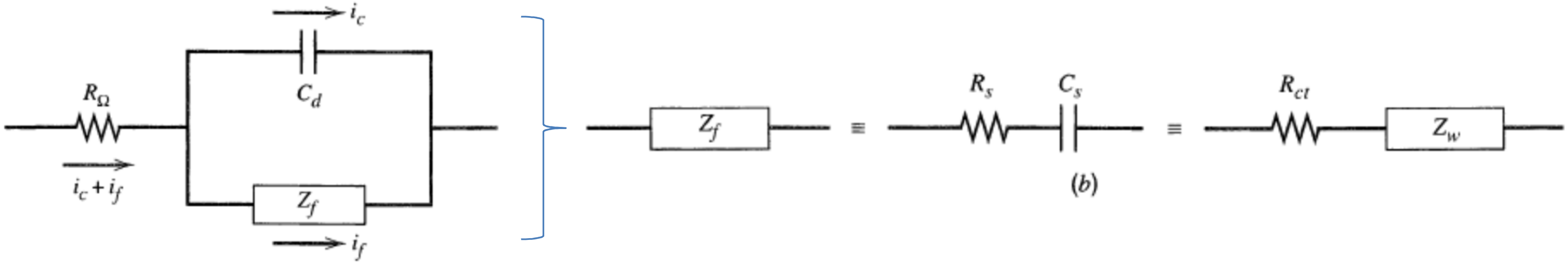


10.1 INTRODUCTION

- The faradaic impedance has been considered in the literature in various ways.
- Figure 10.1.14b shows two equivalences that have been made.

(1) The simplest representation is to take the faradaic impedance as a series combination comprising the series resistance, R_s, and the pseudocapacity, C_s.

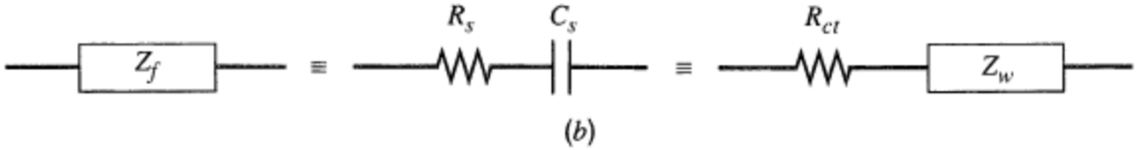
(2) An alternative is to separate a pure resistance, R_{ct} the charge-transfer resistance, from another general impedance, Z_w, the Warburg impedance, which represents a kind of resistance to mass transfer.



- In contrast to R_Ω and C_d, which are nearly ideal circuit elements, the components of the faradaic impedance are not ideal, because they change with frequency, ω.

10.2 INTERPRETATION OF THE FARADAIC IMPEDANCE

- Let us assume that the faradaic impedance, expressed as the series combination R_s and C_s, is evaluable from the total impedance.



- Now consider the behavior of this impedance as a sinusoidal current is forced through it. The total voltage drop is.

$$E = iR_s + \frac{q}{C_s}$$

$$\frac{dE}{dt} = R_s\frac{di}{dt} + \frac{i}{C_s}$$

$$i = I \sin \omega t$$

$$\frac{dE}{dt} = (R_s I\omega)\cos\ \omega t + \left(\frac{I}{C_s}\right)\sin\ \omega t$$

10.2 INTERPRETATION OF THE FARADAIC IMPEDANCE

- For our standard system, O + ne ↔ R, with both O and R soluble, we can write

$$E = E[i, C_O(0, t), C_R(0, t)]$$

$$\frac{dE}{dt} = \left(\frac{\partial E}{\partial i}\right)\frac{di}{dt} + \left[\frac{\partial E}{\partial C_O(0, t)}\right]\frac{dC_O(0, t)}{dt} + \left[\frac{\partial E}{\partial C_R(0, t)}\right]\frac{dC_R(0, t)}{dt}$$

$$\frac{dE}{dt} = R_{ct}\frac{di}{dt} + \beta_O\frac{dC_O(0, t)}{dt} + \beta_R\frac{dC_R(0, t)}{dt}$$

$$R_{ct} = \left(\frac{\partial E}{\partial i}\right)_{C_O(0,t),C_R(0,t)}$$

$$\beta_O = \left[\frac{\partial E}{\partial C_O(0, t)}\right]_{i,C_R(0,t)}$$

$$\beta_R = \left[\frac{\partial E}{\partial C_R(0, t)}\right]_{i,C_O(0,t)}$$

$$i = I\sin\omega t$$

$$\frac{di}{dt} = I\omega\ \cos\ \omega t$$

10.2 INTERPRETATION OF THE FARADAIC IMPEDANCE

- Assuming semi-infinite linear diffusion with initial conditions $C_O(x,0) = C_O^*$ and $C_R(x,0) = C_R^*$, we can write from our experience in Section 8.2.1 that

$$\bar{C}_O(0, s) = \frac{C_O^*}{s} + \frac{\bar{i}(s)}{nFAD_O^{1/2}s^{1/2}}$$

$$\bar{C}_R(0, s) = \frac{C_R^*}{s} - \frac{\bar{i}(s)}{nFAD_R^{1/2}s^{1/2}}$$

- Inversion by convolution gives

$$C_O(0, t) = C_O^* + \frac{1}{nFAD_O^{1/2}\pi^{1/2}} \int_0^t \frac{i(t-u)}{u^{1/2}} du$$

$$C_R(0, t) = C_R^* - \frac{1}{nFAD_R^{1/2}\pi^{1/2}} \int_0^t \frac{i(t-u)}{u^{1/2}} du$$

10.2 INTERPRETATION OF THE FARADAIC IMPEDANCE

$$\int_0^t \frac{i(t-u)}{u^{1/2}}\,du \quad = \quad \int_0^t \frac{I\sin\omega(t-u)}{u^{1/2}}\,du = I\sin\omega t\int_0^t \frac{\cos\omega u}{u^{1/2}}\,du - I\cos\omega t\int_0^t \frac{\sin\omega u}{u^{1/2}}\,du$$

$i = I\sin\omega t$

$\sin\omega(t-u) = \sin\omega t\cos\omega u - \cos\omega t\sin\omega u$

- Now let us consider the range of times in which we are interested.
- Before the current is turned on, the surface concentrations are C_O^* and C_R^*, and after a few cycles we can expect them to reach a steady state in which they cycle repeatedly through constant patterns.
- We can be sure of this point because no net electrolysis takes place in any full cycle of current flow.
- Our interest is not in the transition from initial conditions to steady state, but in the steady state itself.

10.2 INTERPRETATION OF THE FARADAIC IMPEDANCE

$$\int_0^t \frac{I \sin \omega(t-u)}{u^{1/2}} du = I \sin \omega t \int_0^t \frac{\cos \omega u}{u^{1/2}} du - I \cos \omega t \int_0^t \frac{\sin \omega u}{u^{1/2}} du$$

- The two integrals on the right side of (10.2.17) embody the transition period.
- Because $u^{1/2}$ appears in their denominators, the integrands are appreciable only at short times.
- After a few cycles, each integral must reach a constant value characteristic of the steady state.
- We can obtain it by letting the integration limits go to infinity:

$$\int_{\substack{\text{Steady}\\\text{state}}} \frac{I \sin \omega(t-u)}{u^{1/2}} du = I \sin \omega t \int_0^\infty \frac{\cos \omega u}{u^{1/2}} du - I \cos \omega t \int_0^\infty \frac{\sin \omega u}{u^{1/2}} du$$

10.2 INTERPRETATION OF THE FARADAIC IMPEDANCE

$$\int_{\substack{\text{Steady}\\ \text{state}}} \frac{I\ \sin\ \omega(t-u)}{u^{1/2}}\,du = I\ \sin\ \omega t \int_0^\infty \frac{\cos\ \omega u}{u^{1/2}}\,du - I\ \cos\ \omega t \int_0^\infty \frac{\sin\ \omega u}{u^{1/2}}\,du$$

- both integrals on the right side of (10.2.18) are equal to $(\pi/2\omega)^{1/2}$;

$$C_{\mathrm{O}}(0,t) = C_{\mathrm{O}}^{*} + \frac{1}{nFAD_{\mathrm{O}}^{1/2}\pi^{1/2}} \int_0^t \frac{i(t-u)}{u^{1/2}}\,du$$

$$C_{\mathrm{R}}(0,t) = C_{\mathrm{R}}^{*} - \frac{1}{nFAD_{\mathrm{R}}^{1/2}\pi^{1/2}} \int_0^t \frac{i(t-u)}{u^{1/2}}\,du$$

$$C_{\mathrm{O}}(0,t) = C_{\mathrm{O}}^{*} + \frac{I}{nFA(2D_{\mathrm{O}}\omega)^{1/2}}(\sin\ \omega t - \cos\ \omega t)$$

$$C_{\mathrm{R}}(0,t) = C_{\mathrm{R}}^{*} - \frac{I}{nFA(2D_{\mathrm{R}}\omega)^{1/2}}(\sin\ \omega t - \cos\ \omega t)$$

$$\frac{dC_{\mathrm{O}}(0,t)}{dt} = \frac{I}{nFA}\left(\frac{\omega}{2D_{\mathrm{O}}}\right)^{1/2}(\sin\ \omega t + \cos\ \omega t)$$

$$\frac{dC_{\mathrm{R}}(0,t)}{dt} = -\frac{I}{nFA}\left(\frac{\omega}{2D_{\mathrm{R}}}\right)^{1/2}(\sin\ \omega t + \cos\ \omega t)$$

10.2 INTERPRETATION OF THE FARADAIC IMPEDANCE

$$\frac{dE}{dt} = R_{\mathrm{ct}}\frac{di}{dt} + \beta_{\mathrm{O}}\frac{dC_{\mathrm{O}}(0,t)}{dt} + \beta_{\mathrm{R}}\frac{dC_{\mathrm{R}}(0,t)}{dt}$$

$$\frac{di}{dt} = I\omega\cos\omega t$$

$$\frac{dC_{\mathrm{O}}(0,t)}{dt} = \frac{I}{nFA}\left(\frac{\omega}{2D_{\mathrm{O}}}\right)^{1/2}(\sin\omega t + \cos\omega t)$$

$$\frac{dC_{\mathrm{R}}(0,t)}{dt} = -\frac{I}{nFA}\left(\frac{\omega}{2D_{\mathrm{R}}}\right)^{1/2}(\sin\omega t + \cos\omega t)$$

$$\frac{dE}{dt} = \left(R_{\mathrm{ct}} + \frac{\sigma}{\omega^{1/2}}\right)I\omega\cos\omega t + I\sigma\omega^{1/2}\sin\omega t$$

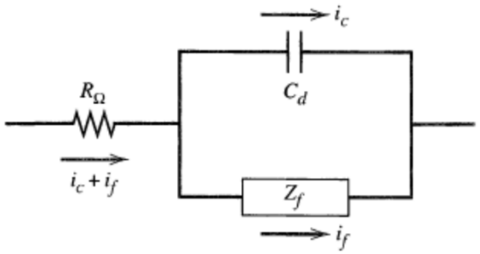
$$\sigma = \frac{1}{nFA\sqrt{2}}\left(\frac{\beta_{\mathrm{O}}}{D_{\mathrm{O}}^{1/2}} - \frac{\beta_{\mathrm{R}}}{D_{\mathrm{R}}^{1/2}}\right)$$

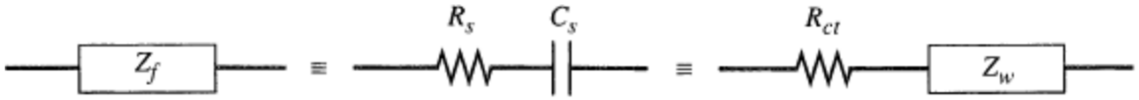
$$\frac{dE}{dt} = (R_{\mathrm{s}}I\omega)\cos\omega t + \left(\frac{I}{C_{\mathrm{s}}}\right)\sin\omega t$$

$$\boxed{R_{\mathrm{s}} = R_{\mathrm{ct}} + \sigma/\omega^{1/2}}$$

$$\boxed{C_{\mathrm{s}} = \frac{1}{\sigma\omega^{1/2}}}$$

10.2 INTERPRETATION OF THE FARADAIC IMPEDANCE





(*b*)

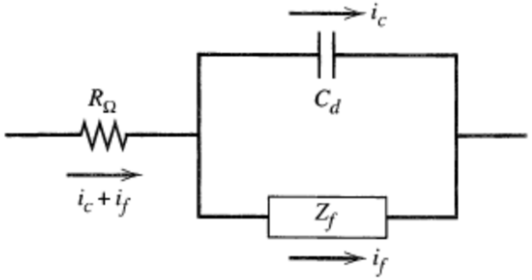
$$\boxed{R_s = R_{ct} + \sigma/\omega^{1/2}}$$

$$\boxed{C_s = \frac{1}{\sigma\omega^{1/2}}}$$

$$\mathbf{Z}_f = R_{ct} + R_w - j/(\omega C_w) = R_{ct} + \underbrace{[\sigma\omega^{-1/2} - j(\sigma\omega^{-1/2})]}_{\text{Warburg impedance}}$$

10.4 ELECTROCHEMICAL IMPEDANCE SPECTROSCOPY

- The measured total impedance of the cell, **Z**, is expressed as the series combination of R_B and C_B.
- These two elements provide the real and imaginary components of **Z**, that is, $Z_{Re} = R_B$ and $Z_{Im} = 1/\omega C_B$
- The electrochemical system is described theoretically in terms of an equivalent circuit such as that in Figure 10.1.14.



- The real and imaginary parts, which must equal the measured Z_{Re} and Z_{Im}, are

$$Z_{Re} = R_B = R_\Omega + \frac{R_s}{A^2 + B^2}$$

$$A = (C_d/C_s) + 1$$

$$Z_{Im} = \frac{1}{\omega C_B} = \frac{B^2/\omega C_d + A/\omega C_s}{A^2 + B^2}$$

$$B = \omega R_s C_d$$

10.4 ELECTROCHEMICAL IMPEDANCE SPECTROSCOPY

$$\boxed{R_s = R_{ct} + \sigma/\omega^{1/2}}$$

$$\boxed{C_s = \frac{1}{\sigma\omega^{1/2}}}$$

$$Z_{Re} = R_B = R_\Omega + \frac{R_s}{A^2 + B^2}$$

$$Z_{Im} = \frac{1}{\omega C_B} = \frac{B^2/\omega C_d + A/\omega C_s}{A^2 + B^2}$$

$$Z_{Re} = R_\Omega + \frac{R_{ct} + \sigma\omega^{-1/2}}{(C_d\sigma\omega^{1/2} + 1)^2 + \omega^2 C_d^2 (R_{ct} + \sigma\omega^{-1/2})^2}$$

$$Z_{Im} = \frac{\omega C_d (R_{ct} + \sigma\omega^{-1/2})^2 + \sigma\omega^{-1/2}(\omega^{1/2} C_d \sigma + 1)}{(C_d\sigma\omega^{1/2} + 1)^2 + \omega^2 C_d^2 (R_{ct} + \sigma\omega^{-1/2})^2}$$

10.4 ELECTROCHEMICAL IMPEDANCE SPECTROSCOPY

- Chemical information can be extracted by plotting Z_{Im} vs. Z_{Re} for different ω.

→ For simplicity, let us first consider the limiting behavior at high and low ω.

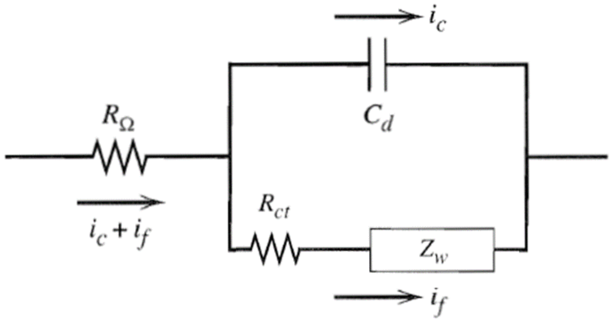
(a) Low-Frequency Limit

- As ω → 0, the functions (10.4.3) and (10.4.4) approach the limiting forms:

$$\left.\begin{aligned} Z_{\mathrm{Re}} &= R_{\Omega} + \frac{R_{\mathrm{ct}} + \sigma\omega^{-1/2}}{(C_{\mathrm{d}}\sigma\omega^{1/2}+1)^2 + \omega^2 C_{\mathrm{d}}^2(R_{\mathrm{ct}} + \sigma\omega^{-1/2})^2} \\ Z_{\mathrm{Im}} &= \frac{\omega C_{\mathrm{d}}(R_{\mathrm{ct}} + \sigma\omega^{-1/2})^2 + \sigma\omega^{-1/2}(\omega^{1/2}C_{\mathrm{d}}\sigma + 1)}{(C_{\mathrm{d}}\sigma\omega^{1/2}+1)^2 + \omega^2 C_{\mathrm{d}}^2(R_{\mathrm{ct}} + \sigma\omega^{-1/2})^2} \end{aligned}\right\} \qquad \begin{aligned} Z_{\mathrm{Re}} &= R_{\Omega} + R_{\mathrm{ct}} + \sigma\omega^{-1/2} \\ Z_{\mathrm{Im}} &= \sigma\omega^{-1/2} + 2\sigma^2 C_{\mathrm{d}} \end{aligned}$$

→ Elimination of ω between these two gives

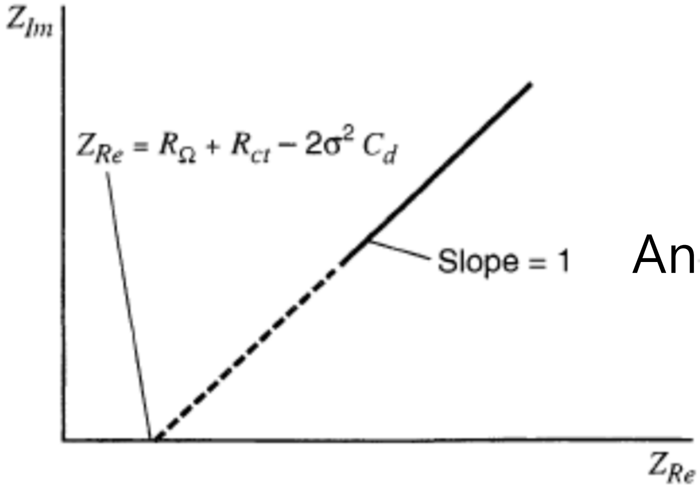
$$\boxed{Z_{\mathrm{Im}} = Z_{\mathrm{Re}} - R_{\Omega} - R_{\mathrm{ct}} + 2\sigma^2 C_{\mathrm{d}}}$$



10.4 ELECTROCHEMICAL IMPEDANCE SPECTROSCOPY

- Thus, the plot of Z_{Im} vs. Z_{Re} should be linear and have unit slope, as shown in Figure 10.4.1.

→ The extrapolated line intersects the real axis at $R_\Omega + R_{ct} - 2\sigma^2 Cd$.



Angle = 45°

Figure 10.4.1 Impedance plane plot for low frequencies.

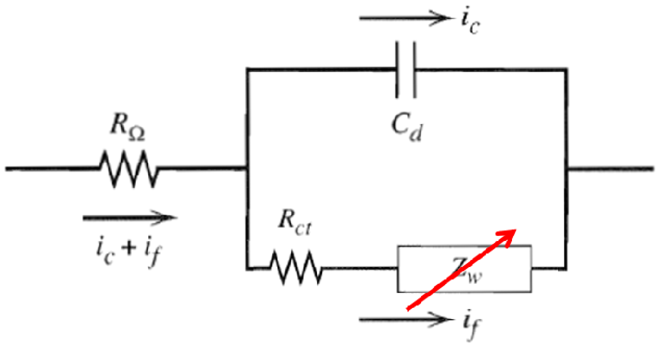
- The frequency dependence in this regime comes only from Warburg impedance terms;

→ thus the linear correlation of Z_{Re} and Z_{Im} is characteristic of a diffusion-controlled electrode process.

10.4 ELECTROCHEMICAL IMPEDANCE SPECTROSCOPY

(b) High-Frequency Limit

- At very high frequencies, the Warburg impedance becomes unimportant in relation to R_{ct} and the equivalent circuit converges to that of Figure 10.4.2.



$$Z_w = \sigma\omega^{-1/2} - j\sigma\omega^{-1/2} \cong 0$$

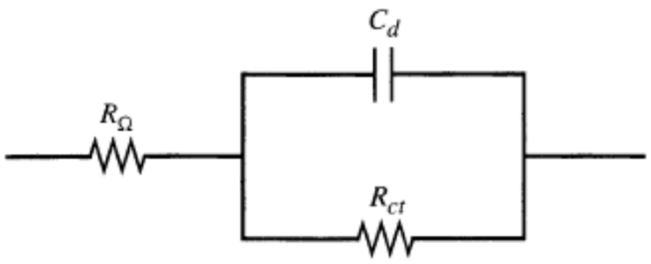
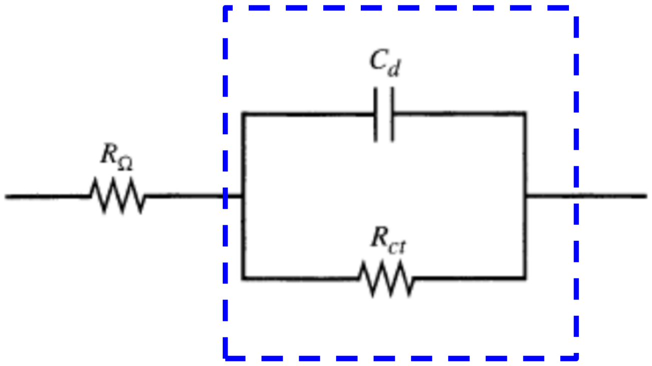


Figure 10.4.2 Equivalent circuit for a system in which the Warburg impedance is unimportant.

10.4 ELECTROCHEMICAL IMPEDANCE SPECTROSCOPY



$$\frac{1}{Z_{tot}} = \frac{1}{R} + \frac{1}{\frac{1}{j\omega C}} = \frac{1}{R} + j\omega C$$

$$Z_{tot} = \frac{R(1 - j\omega RC)}{1 + (\omega RC)^2}$$

$$= \underbrace{\boxed{\frac{R}{1 + (\omega RC)^2}}}_{Z_{\mathrm{Re}}} - j\underbrace{\boxed{\frac{\omega R^2 C}{1 + (\omega RC)^2}}}_{Z_{\mathrm{Im}}}$$

- The impedance is

$$\mathbf{Z} = R_\Omega - j\left(\frac{R_{\mathrm{ct}}}{R_{\mathrm{ct}} C_{\mathrm{d}} \omega - j}\right)$$

$$Z_{\mathrm{Re}} = R_\Omega + \frac{R_{\mathrm{ct}}}{1 + \omega^2 C_{\mathrm{d}}^2 R_{\mathrm{ct}}^2}$$

$$Z_{\mathrm{Im}} = \frac{\omega C_{\mathrm{d}} R_{\mathrm{ct}}^2}{1 + \omega^2 C_{\mathrm{d}}^2 R_{\mathrm{ct}}^2}$$

- Elimination of ω from this pair of equations yields

$$\boxed{\left(Z_{\mathrm{Re}} - R_\Omega - \frac{R_{\mathrm{ct}}}{2}\right)^2 + Z_{\mathrm{Im}}^2 = \left(\frac{R_{\mathrm{ct}}}{2}\right)^2}$$

10.4 ELECTROCHEMICAL IMPEDANCE SPECTROSCOPY

$$\boxed{\left(Z_{\mathrm{Re}} - R_{\Omega} - \frac{R_{\mathrm{ct}}}{2}\right)^2 + Z_{\mathrm{Im}}^2 = \left(\frac{R_{\mathrm{ct}}}{2}\right)^2}$$

- Hence Z_{Im} vs. Z_{Re} should give a circular plot centered at $Z_{\mathrm{Re}} = R_{\Omega} + R_{\mathrm{ct}}/2$ and $Z_{\mathrm{Im}} = 0$ and having a radius of $R_{\mathrm{ct}}/2$. Figure 10.4.3 depicts the result.

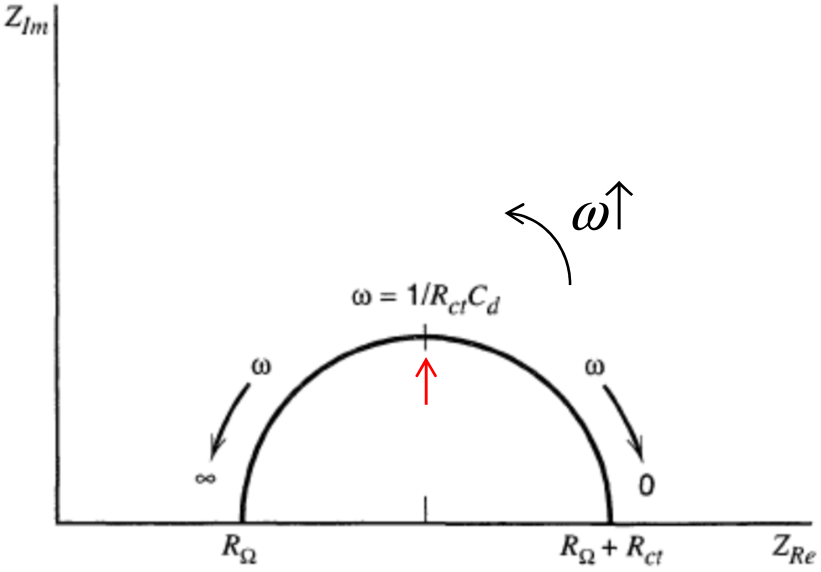


Figure 10.4.3 Impedance plane plot for the equivalent circuit of Figure 10.4.2.

10.4 ELECTROCHEMICAL IMPEDANCE SPECTROSCOPY

- An actual plot of impedance in the complex plane will combine the features of our two limiting cases as in Figure 10.4.4.

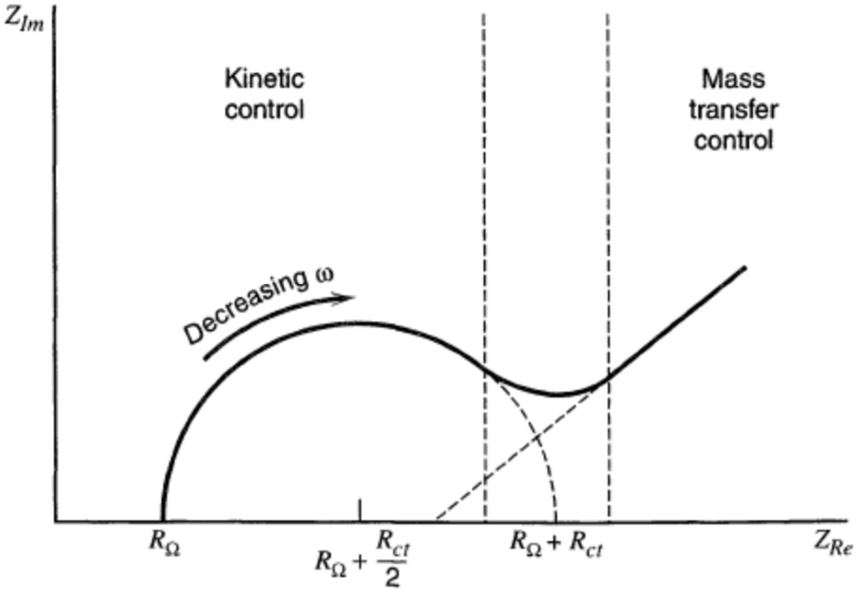
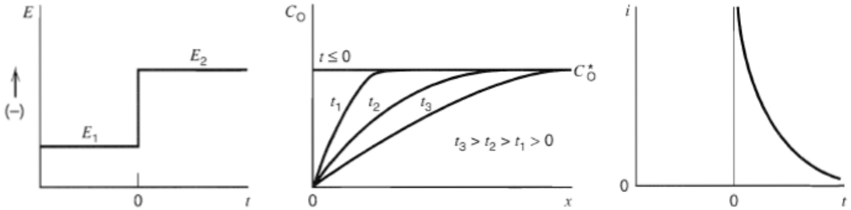


Figure 10.4.4 Impedance plot for an electrochemical system. Regions of mass-transfer and kinetic control are found at low and high frequencies, respectively.

Electrochemical methods

Ch 5 Potential step

Chronoamperometry



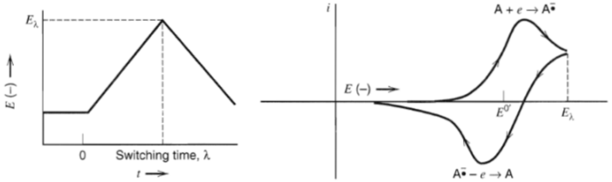
$$i(t) = i_d(t) = \frac{nFAD_O^{1/2}C_O^*}{\pi^{1/2}t^{1/2}}$$

Cottrell equation

Chronocoulometry

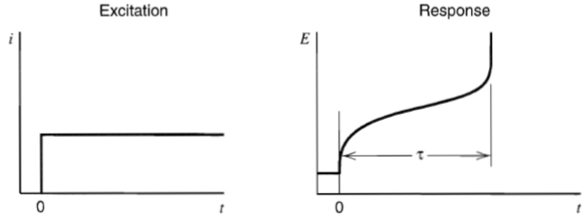
Ch 6 Potential sweep

CV (cyclic voltammetry)



Ch 8 Controlled-current techniques

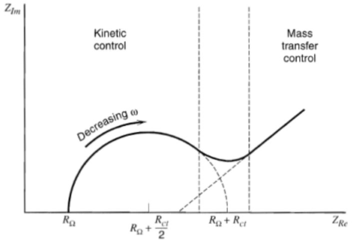
Chronopotentiometry



$$\frac{i\tau^{1/2}}{C_O^*} = \frac{nFAD_O^{1/2}\pi^{1/2}}{2} = 85.5\,nD_O^{1/2}A\,\frac{\text{mA-s}^{1/2}}{\text{m}M}\ (\text{with } A \text{ in cm}^2)$$

Sand equation

Ch 10 EIS (electrochemical impedance spectroscopy)



Summary

- **Ch. 1**

  → overview of electrode process

- **Ch. 2**

  → thermodynamics and potential

- **Ch. 3, 4**

  → charge-transfer and mass transfer

- **Ch. 5, 6, 8, 10**

  → various electrochemical methods