Impedance (Ch. 10)

ac circuits
Faradaic impedance
Kinetic parameters from impedance measurements
Electrochemical impedance spectroscopy
**Introduction**
To perturb the cell with an *ac* of small magnitude

**Types of techniques**
*Faradaic impedance*: electrochemical cell $\rightarrow$ WE potential fixed

$\rightarrow$ lock-in amplifier, frequency-response analyzer: faster & convenient

*Electrochemical impedance spectroscopy* (EIS): impedance vs. frequency
ac voltammetry: three-electrode cell → WE potential, $E_{dc} + ac$ component ($E_{ac}$, 5 mV peak-to-peak amplitude): dc potential to set the mean surface concentrations of O & R
Review of *ac* (alternating current) circuits

Pure sinusoidal voltage to an electric circuit (or EC cell)

\[ e = E \sin \omega t \]

where \( E \) is the maximum amplitude, \( \omega \) the angular frequency (rad/sec, \( 2\pi \times \text{Hz} \))

The response is a current

\[ i = I \sin(\omega t + \phi) \]

where \( \phi \) is the phase angle between perturbation and response
Pure resistance (R)

\[ V = IR, \text{ Ohm's law, } e = E \sin \omega t \]

\[ I = \left( \frac{E}{R} \right) \sin \omega t \]

and \( \phi = 0 \rightarrow \text{no phase difference between potential \& current} \)
Pure capacitance (C)
For capacitor \( q = C e, \ i = dq/dt = C (de/dt) \)
\[
i = \omega C e \cos \omega t = \omega C e \sin (\omega t + \pi/2) = (E/X_c) \sin (\omega t + \pi/2)
\]

\( \phi = \pi/2 \rightarrow \) current leads the voltage by \( \pi/2 \).
\( X_c = (\omega C)^{-1}; \) capacitive reactance (ohms): unlike \( R \rightarrow \) magnitude falls with frequency ↑

\( j = \sqrt{-1} \)

\[ E = -j X_c I \]
Resistance & capacitance in series

\[
\begin{align*}
R & \quad C \\
\end{align*}
\]

\[I_R = I \quad \Rightarrow \quad I_C = I \quad \Rightarrow\]

Total potential difference = the sum of potential differences across the two elements
\[E = E_R + E_C\]

Current have to be equal (Kirchhoff’s law): \[I = I_R = I_C\]
\[E = I(R - jX_C) = IZ\]

Impedance (vector), \[Z = R - jX_C\]

Generally, \[Z(\omega) = Z_{Re} - jZ_{Im}\]

Where \(Z_{Re}\), \(Z_{Im}\): real & imaginary parts of impedance

The magnitude of the impedance
\[|Z| = (R^2 + X_C^2)^{1/2} = (Z_{Re}^2 + Z_{Im}^2)^{1/2}\]

The phase angle
\[\phi = \arctan(Z_{Im}/Z_{Re}) = \arctan(|X_C|/|R|) = \arctan[1/(\omega RC)]\]
**Impedance (Z):** the proportionality factor between V and I \( \rightarrow \) Z consists of resistances, reactances (derived from capacitive elements), inductances (at very high frequencies > 1 MHz)
Impedance plot
Bode plot: $\log|Z|$ & $\phi$ vs. $\log \omega$
Nyquist plot: $Z_{\text{Im}}$ vs. $Z_{\text{Re}}$ for different $\omega$

For a series RC circuit
For a parallel RC circuit

For other textbooks

$Z'$: in-phase component of impedance

$Z''$: out-of-phase component, i.e. at $\pi/2$

$$Z = Z' + iZ''$$

$Z' = R$, $Z'' = -X_C$

A vertical line in the complex plane impedance plot since $Z'$ is constant but $Z''$ varies with frequency
Resistance & capacitance in parallel

Total current ($I_{\text{tot}}$) is the sum of the two parts
Potential difference across the two components is equal

$$I_{\text{tot}} = (E/R)\sin \omega t + (E/X_c)\sin(\omega t + \pi/2)$$

$$|I_{\text{tot}}| = (I_R^2 + I_C^2)^{1/2} = V(1/R^2 + 1/X_C^2)^{1/2}$$
the magnitude of the impedance

$$|Z| = (1/R^2 + 1/X_C^2)^{-1/2}$$

the phase angle

$$\phi = \arctan(I_C/I_R) = \arctan[1/(\omega RC)]$$

$$1/Z = 1/R + i\omega C$$

$$Z = R/(1 + i\omega RC) = R(1 - i\omega RC)/(1 + (\omega RC)^2)$$

$$Z' = R/[1 + (\omega RC)^2], \quad Z'' = -\omega R^2C/[1 + (\omega RC)^2]$$

Semicircle in the complex plane of radius R/2 and maximum $|Z''|$ at $\omega RC = 1$

$$\left(Z' - \frac{R}{2}\right)^2 + (Z'')^2 = \left(\frac{R}{2}\right)^2$$
\textbf{more complicated circuits}

At the top of semicircle: the value of capacitor and the time constant of the circuit can be calculated from the frequency (f) \( \omega = 2\pi f = 1/\tau = 1/RC \)

x-axis (real axis): intercepts give the values of resistor
Impedance in series and in parallel

in series: $\mathbf{Z} = \mathbf{Z}_1 + \mathbf{Z}_2$

in parallel: $1/\mathbf{Z} = 1/\mathbf{Z}_1 + 1/\mathbf{Z}_2$

Admittance

Admittance is the inverse of impedance

\[ \mathbf{Y} = 1/\mathbf{Z} \]

Useful in the analysis of parallel circuits

In phase: $\mathbf{Y}'$, phase angle of $\pi/2$: $\mathbf{Y}''$

\[ \mathbf{Y} = 1/\mathbf{Z} = 1/(\mathbf{Z}' + i\mathbf{Z}'') = (\mathbf{Z}' - i\mathbf{Z}'')/[(\mathbf{Z}')^2 + (\mathbf{Z}'')^2] = \mathbf{Y}' + i\mathbf{Y}'' \]

\[ \mathbf{Y}' = \mathbf{Z}'/[(\mathbf{Z}')^2 + (\mathbf{Z}'')^2] = \mathbf{G}_p, \quad \mathbf{G}_p; \text{ conductance} \]

\[ \mathbf{Y}'' = -\mathbf{Z}''/[(\mathbf{Z}')^2 + (\mathbf{Z}'')^2] = \mathbf{B}_p = \omega \mathbf{C}_p, \quad \mathbf{B}_p; \text{ susceptance} \]

\[ \mathbf{Z} = \mathbf{Z}e^{i\phi}, \quad \mathbf{Y} = (1/\mathbf{Z})e^{-i\phi} \]
Equivalent circuit of an electrochemical cell

Any electrochemical cell can be represented in terms of an *equivalent circuit* that comprises a combination of resistances and capacitances. This circuit should contain at the very least components:

- - the double layer: pure capacitor $C_d$
- - the impedance of the faradaic process (charge transfer process) $Z_f$
- - the uncompensated resistance $R_\Omega$ (the solution resistance)

The combination of these elements: $Z_f$ & $C_d$ in parallel
Equivalent electrical circuit of an electrochemical cell for a simple electrode process. 

$R_\Omega$ is the solution resistance, of the constants and electrode materials, $Z_f$ the impedance of the electrode process, and $C_d$ the double layer capacity.
$Z_f$ can be subdivided in two equivalent ways:

1. Subdivision into *series resistance* $R_s$ and *pseudocapacity* $C_s$

2. Subdivision into $R_{ct}$ (*charge-transfer resistance*) and *Warburg impedance*, $Z_w$ (a kind of resistance to mass transport of the electroactive species)

- Kinetically favored reactions: $R_{ct} \to 0$ and $Z_w$ predominates
- Kinetically difficult reactions: $R_{ct} \to \infty$ and $R_{ct}$ predominates “Randles circuit”
Interpretation of the faradaic impedance

Characteristics of the equivalent circuit

For a series RC circuit, total voltage drop

\[ E = iR_s + q/C_s, \quad i = Isin\omega t \]

By differentiation

\[ \frac{dE}{dt} = R_s \frac{di}{dt} + \frac{i}{C_s} = R_s \omega \cos \omega t + (I/C_s)\sin \omega t \]

Properties of the chemical system

Simple charge transfer reaction

\[ O + ne^- = R \]

Charge transfer process; \( E = E[i, C_O(0,t), C_R(0,t)] \)

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

\( \frac{\partial E}{\partial i} \) is the charge transfer resistance, \( R_{ct} \)

\[ \frac{dE}{dt} = (R_{ct} + \sigma/\omega^{1/2})\omega \cos \omega t + I\sigma \omega^{1/2} \sin \omega t \]

Where \( \sigma = (I/nFA^2)(\beta_O/D_O^{1/2} - \beta_R/D_R^{1/2}) \), \( \beta = (\partial E/\partial C(0,t)) \)
\[ R_s = R_{ct} + \sigma \omega^{-1/2} \]
\[ 1/C_s = \sigma \omega^{1/2} \]

\( R_s, C_s \rightarrow \) Randles circuit (\( R_{ct} + \) Warburg impedance \( Z_w \))

From \( Z = Z' + iZ'' \)

\[ Z_w' = R_w = \sigma \omega^{-1/2} \]
\[ Z_w'' = -X_w = -(\omega C_w)^{-1} = -\sigma \omega^{-1/2} \]

In terms of faradaic impedance \( Z_f \)

\[ Z_f' = R_{ct} + \sigma \omega^{-1/2} \]
\[ Z_f'' = -\sigma \omega^{-1/2} \]

Straight line: slope \( \sigma \), intercept \( R_{ct} \) (infinite frequency)
\( R_{ct} \rightarrow 0, Z_f = Z_w = \sigma \omega^{-1/2}(1 - i) \rightarrow \) phase angle \( \pi/2 \)
Kinetic parameters from impedance measurements
For faradaic impedance experiment: WE’s mean potential at equilibrium & small sinusoidal perturbation → linearized i-η characteristics to describe the electrical response to the departure from equilibrium

For one-step, one-electron process

\[ O + e^- = R \]

\[ k_f \]

\[ k_b \]

[Equation (3.4.30), p.106]

\[ \eta = \left( \frac{RT}{F} \right) \left\{ \frac{[CO(0,t)]}{[CO^*]} - \frac{[CR(0,t)]}{[CR^*]} + \frac{i}{i_0} \right\} \]

Hence

\[ R_{ct} = \frac{RT}{Fi_0} \]

\[ \beta_O = \frac{RT}{FC_O^*} \]

\[ \beta_R = -\frac{RT}{FC_R^*} \]

\[ R_s - 1/ \omega C_s = R_{ct} = \frac{RT}{Fi_0} \]

Exchange current \((i_0)\), therefore \(k^0\), can be evaluated from \(R_s\) & \(C_s\)

Experimentally, frequency dependency measurement → slope \(\sigma\)

\[ \sigma = \left( \frac{RT}{F^2A\sqrt{2}} \right) \left( \frac{1}{D_O^{1/2}C_O^*} - \frac{1}{D_R^{1/2}C_R^*} \right) \]
Warburg impedance drops out at high frequencies because time scale is so short that diffusion cannot manifest itself as a factor influencing the current. Surface concentration never changes, so charge-transfer kinetics alone dictate the current.

If the situation is non-linear, it is a complex situation.

**Quasireversible multistep mechanism**

\[ R_{ct} = \frac{RT}{nF}i_0 \]
General impedance properties of a reversible system
When charge-transfer kinetics are very facile, $i_0 \rightarrow \infty$: $R_{ct} \rightarrow 0$
$\rightarrow R_s \rightarrow \sigma / \omega^{1/2}$

Resistance & capacitive reactance are equal: $Z_f = (2/\omega)^{1/2} \sigma$
$\rightarrow$ magnitude of Warburg impedance alone (mass-transfer impedance)

If kinetics are observable: $R_{ct}$
Effect of concentration: high conc → reduce mass-transfer impedance

Phase angle between $I_{ac}$ & $E_{ac}$
\[ \phi = \tan^{-1}\left(1/\omega R_sC_s\right) = \tan^{-1}\left[\sigma / \omega^{1/2}/(R_{ct} + \sigma / \omega^{1/2})\right] \]

For the reversible case, $R_{ct} = 0 \rightarrow \phi = \pi/4$ or 45°
A quasireversible, $R_{ct} > 0 \rightarrow \phi < \pi/4$, $\phi > 0$ unless $R_{ct} \rightarrow \infty$

For reversible multi-electron mechanisms
\[ \sigma = (RT/n^2F^2A\sqrt{2})(1/D_{O}^{1/2}C_{O}^{*} - 1/D_{R}^{1/2}C_{R}^{*}) \]
**Electrochemical impedance spectroscopy**

Real electrochemical system: $R_\Omega$, $C_d$, $Z_f$
- measure in the absence of the electroactive species $\rightarrow Z_f = 0$ $\rightarrow$ directly $R_\Omega$, $C_d$
- study the variation of $Z$ with frequency $\rightarrow Z_f$, $R_\Omega$, $C_d$, $R_{ct}$ can be extracted

Full Randles equivalent circuit

\[
Z'_{Re} = R_\Omega + \frac{R_{ct} + \sigma \omega^{-1/2}}{(\sigma \omega^{1/2} C_d + 1)^2 + \omega^2 C_d^2 (R_{ct} + \sigma \omega^{-1/2})^2}
\]

\[
-Z''_{Im} = \frac{\omega C_d (R_{ct} + \sigma \omega^{-1/2})^2 + \sigma^2 C_d + \sigma \omega^{-1/2}}{(\sigma \omega^{1/2} C_d + 1)^2 + \omega^2 C_d^2 (R_{ct} + \sigma \omega^{-1/2})^2}
\]
Consider two limiting forms of these equation:
(a) Low frequency limit: $\omega \to 0$

\[
Z' = R_\Omega + R_{ct} + \sigma \omega^{-1/2}
\]
\[
Z'' = \sigma \omega^{-1/2} + 2\sigma^2 C_d
\]
\[
Z_{Im} = Z_{Re} - R_\Omega - R_{ct} + 2\sigma^2 C_d
\]

The low frequency limit is a straight line of unit slope, which extrapolated to the real axis gives an intercept of $R_\Omega + R_{ct} - 2\sigma^2 C_d$. The line corresponds to a reaction controlled solely by diffusion, and the impedance is the Warburg impedance, the phase angle being $\pi/2$.

$\rightarrow$ “diffusion-controlled electrode process”
(b) high-frequency limit: \( \omega \to \infty \), At the high-frequency limit the control is purely kinetic, and \( R_{ct} \gg Z_w \). The electrical analogy is an RC parallel combination.

\[
Z' = R_{\Omega} + \left[ \frac{R_{ct}}{1 + \omega^2 C_d^2 R_{ct}^2} \right] \\
Z'' = \left[ \frac{\omega C_d R_{ct}^2}{1 + \omega^2 C_d^2 R_{ct}^2} \right]
\]

Simplifying to the equation of a circle of radius \( R_{ct}/2 \) with intercepts on the \( Z' \) axis of \( R_{\Omega} (\omega \to \infty) \) and of \( R_{\Omega} + R_{ct} (\omega \to 0) \)

\[
(Z' - R_{\Omega} - R_{ct}/2)^2 + (Z'')^2 = \left( \frac{R_{ct}}{2} \right)^2
\]
(c) Application to real systems
If kinetically sluggish $\rightarrow$ large $R_{ct}$  

kinetically facile
Bulk resistance $R_{el} \rightarrow$ Ionic conductivity of electrolyte

$$G = 1 / R = \kappa \cdot A / L$$

$G$: Conductance ($\Omega^{-1}$ or S), $\kappa$: conductivity, $A$: area

$L$: distance between the electrodes

$$\kappa = G \cdot L / A$$

$L/A$: cell constant ($cm^{-1}$)

A simple equivalent circuit representing a solid electrolyte cell (a) and its response in the impedance plane (b). $R_L C_L$; $R_{gb} C_{gb}$; and $R_p$; $C_{dl}$ are resistances and capacitances associated with the electrolyte bulk (intragrain), the grain boundary (intergrain) and electrode processes, respectively.
Measurement of impedance

a.c. bridge
These bridge use the principle of balance between the electrochemical cell and a variable impedance ($Z_s$)

$$Z_s = R_s - i/\omega C_s$$
$$Z_{cell}/R_1 = Z_s/R_2$$
$$Z_{cell} = R_s R_1/R_2 - I(R_1/\omega C_s R_2)$$

That is,
$$R_{cell} = R_s R_1/R_2, \quad C_{cell} = C_s R_2/R_1$$
**Electrochemical Impedance spectroscopy (EIS)**

Impedance techniques involves applying a sinusoidal signal of low magnitude (mV range) to the electrochemical system under investigation and comparing the input and output responses to determine impedance and phase shift.

EIS based on lock-in amplifier or frequency response analyser (FRA)

lock-in amplifier: specialized AC voltmeter w/ typical frequency range 50 μHz-100 kHz

→ sensitive, low cost, but slow, low frequency range

FRA: fast, easy to operate, digitallized, expensive