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 → WE potential fixed

→ lock-in amplifier, frequency-response analyzer: faster & convenient

Electrochemical impedance spectroscopy (EIS): impedance vs. frequency

ac voltammetry: three-electrode cell $\rightarrow$ 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, ω the angular frequency (rad/sec, 2π x Hz)

The response is a current

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

where ϕ is the phase angle between perturbation and response

Pure resistance (R)

$V = IR$, Ohm's law, $e = E\sin \omega t$

$$I = (E/R)\sin\omega t$$

and $\phi = 0 \rightarrow$ no phase difference between potential & current

Pure capacitance (C)

For capacitor ($q = Ce$, $i = dq/dt = C(de/dt)$)

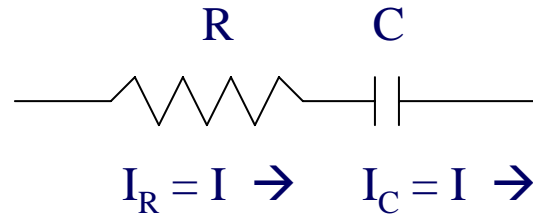$$i = \omega CE\cos \omega t = \omega CE\sin(\omega t + \pi/2) = (E/X_c)\sin(\omega t + \pi/2)$$

$\phi = \pi/2 \rightarrow$ current leads the voltage by $\pi/2$.

$X_c = (\omega C)^{-1}$; capacitive reactance (ohms): unlike R $\rightarrow$ magnitude falls with frequency $\uparrow$

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

$$E = -jX_C I$$

Resistance & capacitance in series

$$I_R = I \rightarrow \quad I_C = I \rightarrow$$

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), $$\mathbf{Z} = R - jX_C$$

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

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

The magnitude of the impedance

$$|\mathbf{Z}| = (R^2 + X_C^2)^{1/2} = (Z_{Re}^2 + Z_{Im}^2)^{1/2}$$

The phase angle

$$\phi = \arctan(Z_{Im}/Z_{Re}) = \arctan(|X_C|/|R|) = \arctan[1/(\omega RC)]$$

<u>Impedance (**Z**)</u>: the proportionality factor between V and I $\rightarrow$ Z consists of resistances, reactances (derived from capacitive elements), inductances (at very high frequencies > 1 MHz)

<u>Impedance plot</u>
Bode plot: $\log|Z|$ & ϕ vs. $\log \omega$
Nyquist plot: Z_{Im} vs. Z_{Re} for different ω

For a series RC circuit

For a parallel RC circuit

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_{tot}) is the sum of the two parts
Potential difference across the two components is equal

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

$$\left| I_{tot} \right| = (I_R{}^2 + I_C{}^2)^{1/2} = V(1/R^2 + 1/X_C{}^2)^{1/2}$$

the magnitude of the impedance
$$|\mathbf{Z}| = (1/R^2 + 1/X_C^2)^{-1/2}$$

the phase angle

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

$$1/\mathbf{Z} = 1/R + i\omega C$$
$$\mathbf{Z} = R/(1 + i\omega RC) = R(1 - i\omega RC)/[1 + (\omega RC)^2]$$

$Z' = R/[1 + (\omega RC)^2]$, $Z'' = -\omega R^2 C/[1 + (\omega RC)^2]$
Semicircle in the complex plane of radius R/2 and maximum $|Z''|$ at $\omega RC = 1$

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

→**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: Y', phase angle of $\pi/2$: Y''

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

$Y' = Z'/[(Z')^2 + (Z'')^2] = G_p, \quad G_p;$ conductance

$Y'' = -Z''/[(Z')^2 + (Z'')^2] = B_p = \omega C_p, \quad B_p;$ susceptance

$$\mathbf{Z} = Ze^{j\Phi}, \qquad \mathbf{Y} = (1/Z)e^{-j\Phi}$$

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) $\mathbf{Z}_f$

- - the uncompensated resistance R_Ω (the solution resistance)

The combination of these elements: $\mathbf{Z}_f$ & C_d in parallel

Equivalent electrical circuit of an electrochemical cell for a simple electrode process.

R_Ω 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.

$\mathbf{Z}_f$ can be subdivided in two equivalent way

   (1) subdivision into *series resistance* R_s and *pseudocapacity* C_s

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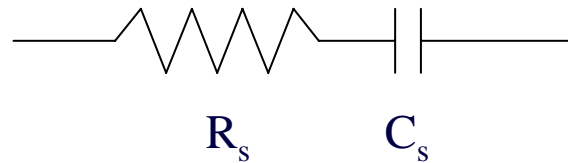
   (2) subdivision into $\underline{R_{ct}}$ (*charge-transfer resistance*) and *Warburg impedance*, $\underline{Z_w}$ (a kind of resistance to mass transport of the electroactive species)

R_{ct}
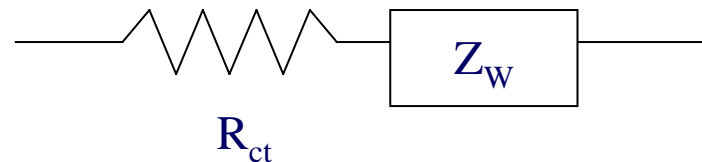
kinetically favored reactions: $R_{ct} \rightarrow 0$ and Z_w predominates
kinetically difficult reactions: $R_{ct} \rightarrow \infty$ and R_{ct} predominates "Randles circuit"

Interpretation of the faradaic impedance
Characteristics of the equivalent circuit
For a series RC circuit, total voltage drop
$$E = iR_s + q/C_s, \qquad i = I\sin\omega t$$
By differentiation
$$dE/dt = R_s di/dt + i/C_s = R_s I\omega\cos\omega t + (I/C_s)\sin\omega t$$

Properties of the chemical system
simple charge transfer reaction
$$O + ne^- = R$$

chage transfer process; $E = E[i, C_O(0,t), C_R(0,t)]$

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

$\partial E/\partial i$ is the charge transfer resistance, R_{ct}

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

where $\sigma = (I/nFA\sqrt{2})(\beta_O/D_O^{1/2} - \beta_R/D_R^{1/2})$, $\beta = (\partial E/\partial C(0,t))$

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

$R_s, C_s \rightarrow$ 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 σ, 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

$$O + e^- \underset{k_b}{\overset{k_f}{=}} R$$

[Equation (3.4.30), p.106]

$$\eta = (RT/F)\{[C_O(0,t)/C_O^*] - [C_R(0,t)/C_R^*] + i/i_0\}$$

Hence

$$R_{ct} = RT/Fi_0$$
$$\beta_O = RT/FC_O^*$$
$$\beta_R = -RT/FC_R^*$$

$$R_s - 1/\omega C_s = R_{ct} = RT/Fi_0$$

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

Experimentally, frequency dependency measurement → slope σ

$$\sigma = (RT/F^2 A\sqrt{2})(1/D_O^{1/2}C_O^* - 1/D_R^{1/2}CR^*)$$

R_s plot: intercept $R_{ct} \rightarrow i_0$ (extrapolating at infinite frequency)
Warburg impedance drops out at high frequencies because time scale is so short that diffusion cannot manifest itself as a factor influencing the current $\rightarrow$ surface conc never change $\rightarrow$ charge-transfer kinetics alone dictate the current

If non-linear $\rightarrow$ complex situation

Quasireversible multistep mechanism

$$R_{ct} = RT/nFi_0$$

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 $\rightarrow$ reduce mass-transfer impedance

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

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 $R_{ct} \rightarrow \infty$
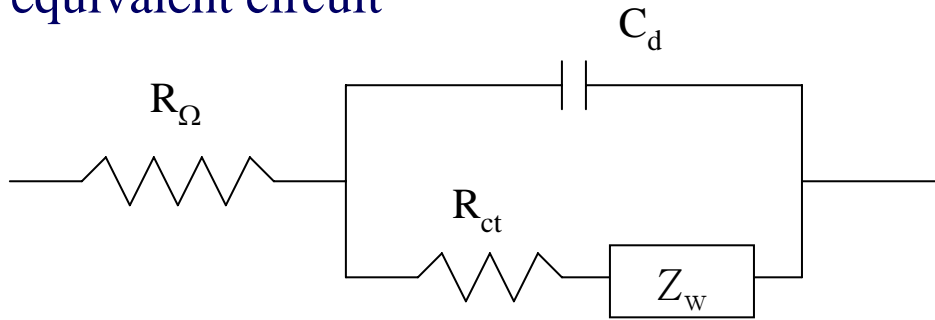
For reversible multi-electron mechanisms

$$\sigma = (RT/n^2F^2A\sqrt{2})(1/D_O^{1/2}C_O^* - 1/D_R^{1/2}CR^*)$$

<u>Electrochemical impedance spectroscopy</u>
Real electrochemical system: R_{Ω}, C_d, $\mathbf{Z_f}$
- measure in the absence of the electroactive species $\rightarrow \mathbf{Z_f} = 0 \rightarrow$ directly R_{Ω}, C_d
- study the variation of Z with frequency $\rightarrow \mathbf{Z_f}$, R_{Ω}, C_d, R_{ct} can be extracted

Full Randles equivalent circuit

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

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

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 $\pi/2$.
$\to$ "diffusion-controlled electrode process"

(b) high-frequency limit: $\omega \rightarrow \infty$, At the high-frequency limit the control is purely kinetic, and $R_{ct} >> \mathbf{Z_w}$. The electrical analogy is an RC parallel combination.

$$Z' = R_{\Omega} + [R_{ct}/(1 + \omega^2 C_d^2 R_{ct}^2)]$$
$$Z'' = [\omega C_d R_{ct}^2/(1 + \omega^2 C_d^2 R_{ct}^2)]$$

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

$$(Z' - R_{\Omega} - R_{ct}/2)^2 + (Z'')^2 = (R_{ct}/2)^2$$

(c) Application to real systems

If kinetically sluggish $\rightarrow$ large R_{ct} kinetically facile

Equivalent Circuit   **Impedance**   **Equivalent Circuit**   **Impedance**

Bulk resistance R_{el} → Ionic conductivity of electrolyte

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

G: Conductance (Ω^{-1} or S), κ : 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

<u>a.c. bridge</u>

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

$$Z_s = R_s - i/\omega C_s$$

$$Z_{cell}/R_1 = Z_s/R_2$$

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

$$= R_{cell} - i/\omega C_{cell}$$

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

$\rightarrow$ sensitive, low cost, but slow, low frequency range
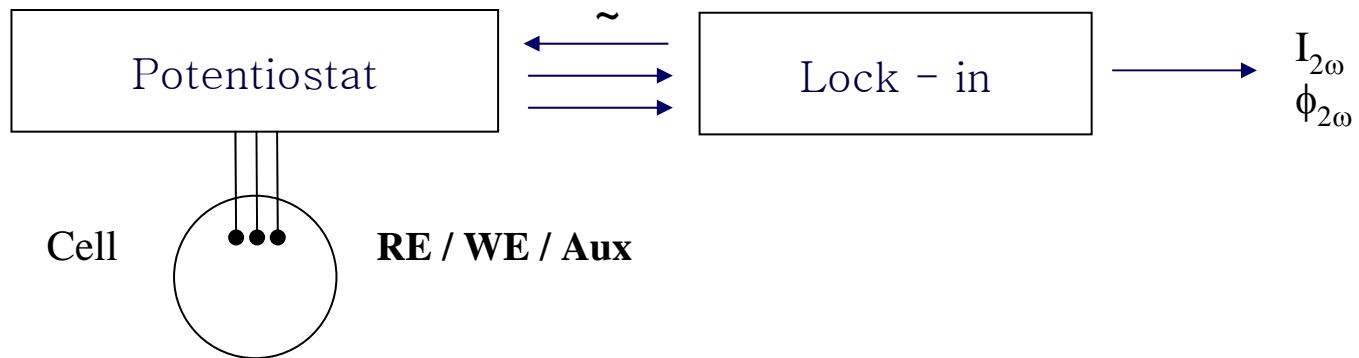
FRA: fast, easy to operate, digitallized, expensive