Experimental Methods of Electrochemistry
– a.c. impedance spectroscopy

Introduction
Application of a small perturbation
→ phase difference & amplitude (i.e. the impedance)
→ electrode process: diffusion, kinetics, double layer, reactions etc
→ corrosion, membranes, ionic solids, solid electrolytes, conducting polymers, liquid/liquid interfaces etc

Comparison between the electrochemical cell and an equivalent electrical circuit (a model) that contains combinations of resistances and capacitances (inductances at high perturbation frequencies, > 1 MHz)

Impedance measurement at different frequencies can furnish all the information about the electrochemical system
Basics of a.c. (alternating current) circuits

Consider the application of a sinusoidal voltage to an electric circuit (or EC cell)

\[ V = V_0 \sin \omega t \]

where \( V_0 \) is the maximum amplitude, \( \omega \) the frequency (rad/sec)

The response is a current

\[ I = I_0 \sin(\omega t + \phi) \]

where \( \phi \) is the phase angle between perturbation and response
**Impedance (Z):** the proportionality factor between V and I → Z consists of resistances, reactances (derived from capacitive elements), inductances (at very high frequencies > 1 MHz)

**Resistance (R)**

V = IR, Ohm’s law

\[ I = \frac{V_0}{R}\sin\omega t \]

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

**Capacitance**

For capacitor (\( q = CV, I = dq/dt \))

\[ I = C(dV/dt) \]

\[ I = \omega CV_0\sin(\omega t + \pi/2) = (V_0/X_c)\sin(\omega t + \pi/2) \]

\( \phi = \pi/2 \rightarrow \) current lag behind the potential by \( \pi/2 \). \( X_c = (\omega C)^{-1} \); reactance (ohms)
**Representation in the complex plane**

x-axis: zero phase angle, phase angle increase by rotating anticlockwise
x-axis: real axis for resistances
y-axis: imaginary axis for pure reactances, amplitude by distance
Resistance, capacitance, & inductance
Resistance & capacitance in series

\[ R \quad C \]

\[ I_R = I \rightarrow I_C = I \rightarrow \]

Total potential difference = the sum of potential differences across the two elements

Current have to be equal (Kirchhoff's law): \( I = I_R = I_C \)

The Impedance (vector)

\[ Z = R - iX_C \]

The magnitude of the impedance

\[ |Z| = (R^2 + X_C^2)^{1/2} \]

The phase angle

\[ \phi = \arctan\left( \frac{|X_C|}{|R|} \right) = \arctan\left[ \frac{1}{\omega RC} \right] \]
Impedance plot

\[ Z' \]: 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

$$I_{\text{tot}} = (V_0/R)\sin \omega t + (V_0/X_c)\sin(\omega t + \pi/2)$$

$$|I_{\text{tot}}| = (I_R^2 + I_C^2)^{1/2} = V(1/R^2 + 1/X_C^2)^{1/2}$$
the magnitude of the impedance
\[ |Z| = \left( \frac{1}{R^2} + \frac{1}{X_C^2} \right)^{-1/2} \]

the phase angle
\[ \phi = \arctan \left( \frac{I_C}{I_R} \right) = \arctan \left[ \frac{1}{\omega RC} \right] \]

\[ \frac{1}{Z} = \frac{1}{R} + i\omega C \]

\[ Z = \frac{R}{1 + i\omega RC} = \frac{R(1 - i\omega RC)}{[1 + (\omega RC)^2]} \]

\[ Z' = \frac{R}{[1 + (\omega RC)^2]} \], \quad Z'' = -\frac{\omega R^2 C}{[1 + (\omega RC)^2]} \]

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

\[ \left( Z' - \frac{R}{2} \right)^2 + (Z'')^2 = \left( \frac{R}{2} \right)^2 \]
Impedance in series and in parallel

in series: $Z = Z_1 + Z_2$
in parallel: $1/Z = 1/Z_1 + 1/Z_2$

Admittance
Admittance is the inverse of impedance

$$Y = 1/Z$$

Useful in the analysis of parallel circuits

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

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

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

$$Y'' = -Z''/[(Z')^2 + (Z'')^2] = B_p = \omega C_p$$, $B_p$; susceptance
**Equivalent circuit of an electrochemical cell**

Any electrochemical cell can be represented in terms of an equivalent electrical 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 way

(1) subdivision into $R_s$ and pseudocapacitance $C_s$

\[ \begin{array}{c}
R_s
\end{array} \quad \begin{array}{c}
C_s
\end{array} \]

(2) subdivision into $R_{ct}$ (the resistance to charge transfer) and Warburg impedance, $Z_w$ (impedance from the difficulty of mass transport of the electroactive species)

\[ \begin{array}{c}
R_{ct}
\end{array} \quad \begin{array}{c}
Z_w
\end{array} \]

kinetically favored reactions: $R_{ct} \to 0$ and $Z_w$ predominates

kinetically difficult reactions: $R_{ct} \to \infty$ and $R_{ct}$ predominates “Randles circuit”
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
Equivalent Circuit | Impedance
--- | ---
(a) | ![Diagram](image1)
(b) | ![Diagram](image2)
(c) | ![Diagram](image3)
(d) | ![Diagram](image4)
(e) | ![Diagram](image5)
(f) | ![Diagram](image6)

Equivalent Circuit | Impedance
--- | ---

\[
\omega = \frac{1}{R_p C_{el}}
\]

![Graph](image7)
Bulk resistance $R_{el} \rightarrow$ Ionic conductivity of electrolyte

\[ G = \frac{1}{R} = \kappa \cdot \frac{A}{L} \]

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

$\kappa = G \cdot \frac{L}{A}$

$L/A$: 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 $C_{dl}$ 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)

\[ Z_s = R_s - \frac{i}{\omega C_s} \]

\[ \frac{Z_{cell}}{R_1} = \frac{Z_s}{R_2} \]

\[ Z_{cell} = \frac{R_s R_1}{R_2} - \frac{I}{\omega C_s R_2} \]

That is,

\[ R_{cell} = \frac{R_s R_1}{R_2}, \quad C_{cell} = \frac{C_s R_2}{R_1} \]
**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

![Diagram of EIS setup](image)
FRA: fast, easy to operate, digitallized, expensive

**Examples**

(1) The faradaic impedance for a simple electrode process

simple charge transfer reaction

\[ O + ne^- = R \]

For a series RC circuit,

\[ E = I R_s + Q / C_s, \quad I = I_0 \sin \omega t \]

By differentiation

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

change transfer process; \( E f(I, C_O^s, C_R^s) \)

\[ \frac{dE}{dt} = (\frac{\partial E}{\partial I})(dI/dt) + (\frac{\partial E}{\partial C_O^s})(dC_O^s/dt) + (\frac{\partial E}{\partial C_R^s})(dC_R^s/dt) \]

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

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

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

\( R_s, C_s \rightarrow \text{Randles circuit (Rct + Wasberg impedance } Z_w) \)

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 \( \pi/2 \)

**Fig. 11.5.** Dependence of \( Z_i' \) and \( Z_i'' \) on the inverse square root of the frequency (Randles plot). The slope of the plots is \( \sigma \).
Experimental measurements
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

\[
\begin{align*}
Z' &= R_\Omega + \frac{R_{ct} + \sigma \omega^{-1/2}}{(\sigma \omega^{1/2} C_d + 1)^2 + \omega^2 C_d^2 (R_{ct} + \sigma \omega^{-1/2})^2} \\
-Z'' &= \frac{\omega C_d (R_{ct} + \sigma \omega^{-1/2})^2 + \sigma^2 C_d + \sigma \omega^{-1/2}}{(\sigma \omega^{1/2} C_d + 1)^2 + \omega^2 C_d^2 (R_{ct} + \sigma \omega^{-1/2})^2}
\end{align*}
\]
Consider two limiting forms of these equation:

(i) $\omega \to 0$

$$Z' = R_\Omega + R_{ct} + \sigma \omega^{-1/2}$$
$$Z'' = -\sigma \omega^{-1/2} - 2\sigma^2 C_d$$

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 Wasburg impedance, the phase angle being $\pi/2$.

(ii) $\omega \to \infty$, At the high-frequency limit the control is purely kinetic, and $R_{ct} \gg Z_w$. The electrical analogy is an RC parallel combination.

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

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 $R_\Omega + R_{ct} (\omega \to 0)$

$$(Z' - R_\Omega - R_{ct}/2)^2 + (Z'')^2 = (R_{ct}/2)^2$$
Solid electrolyte
Battery
Fuel cell
Semiconductor
Corrosion
Electrochromic device
Etc
- Applications of Impedance Spectroscopy


*Aqueous electrochemistry and fast in ion transport in solids.*
- Kinetics of charge transfer in slower than ion diffusion in the electrolyte e.g. Zn(Hg)/Zn$^{2+}$ in 1M NaClO$_4$ + 10$^{-3}$M HClO$_4$

The impedance results of a Zn(Hg)/Zn$^{2+}$ in 1M NaClO$_4$ + 10$^{-3}$M HClO$_4$
With $C_{Zn} = 8 \times 10^{-6}$ moles/cm$^3$ & $C_{Zn^{2+}} = 8 \times 10^{-6}$.
\[ R_2 = \frac{RT}{n^2 F^2 k \left( C_{Zn^2+} \right)^{\alpha} \left( C_{Zn(Hg)} \right)^{1-\alpha}} \]

\( n \): # of electrons transferred, \( k \): rate constant for charge transfer reaction, \( \alpha \): transfer coefficient

When \( C_{Zn} = C_{Zn^2+} \rightarrow k \)

**TABLE 1.4.1. Calculation of Rate Constant of Zn(Hg)/Zn^{2+} Couple**

<table>
<thead>
<tr>
<th>( C_{Zn} = C_{Zn^{2+}} ) (moles/cm³)</th>
<th>( R_2 ) (Ω·cm³)</th>
<th>( R_2 \times C_{Zn} ) (moles·Ω/cm)</th>
<th>( k ) (cm/sec)*</th>
</tr>
</thead>
<tbody>
<tr>
<td>2 \times 10^{-6}</td>
<td>10.17</td>
<td>20.3 \times 10^{-6}</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>4.95</td>
<td>19.8</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>4.26</td>
<td>21.3</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>2.41</td>
<td>19.3</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>2.13</td>
<td>21.3</td>
<td></td>
</tr>
<tr>
<td>16</td>
<td>1.27</td>
<td>20.3</td>
<td></td>
</tr>
<tr>
<td>16</td>
<td>1.28</td>
<td>20.5</td>
<td></td>
</tr>
</tbody>
</table>

*Calculated from the average value of \( R_2 \times C_{Zn} = 20.4 \times 10^{-6} \) by \( k = (R_2 C_{Zn} n^2 F^2)^{-1} RT \) according to Eq. (1).
- diffusion control: e.g., Hg/Hg²⁺ reaction in 1M HClO₄
Kinetics of the charge transfer at the electrode-electrolyte interface is much faster than the Hg²⁺ ions diffusion in the solution

<table>
<thead>
<tr>
<th>$C_{Zn}$ (moles/cm³)</th>
<th>$C_{Zn}^{*+}$ (moles/cm³)</th>
<th>$R_2$ (Ω·cm²)</th>
<th>log $R_2$</th>
<th>$-\log C_{Zn}^{*+}$</th>
<th>$\alpha^*$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$16 \times 10^{-6}$</td>
<td>$16 \times 10^{-6}$</td>
<td>1.28</td>
<td>0.107</td>
<td>4.796</td>
<td></td>
</tr>
<tr>
<td>16</td>
<td>8</td>
<td>2.00</td>
<td>0.301</td>
<td>5.097</td>
<td>0.70</td>
</tr>
<tr>
<td>16</td>
<td>4</td>
<td>3.29</td>
<td>0.517</td>
<td>5.398</td>
<td></td>
</tr>
<tr>
<td>16</td>
<td>2</td>
<td>5.37</td>
<td>0.730</td>
<td>5.699</td>
<td></td>
</tr>
</tbody>
</table>

*From slope of $-\log C_{Zn}^{*+}$ vs. log $R_2$ plot.

The impedance results of a Hg/Hg²⁺ couple in 1M HClO₄ with $C_{Hg²⁺} = 2 \times 10^{-6}$ moles/cm³.
Warburg impedance

\[ W = \sigma \omega^{-1/2} - j \sigma \omega^{-1/2} \]

constant

\[ \sigma = \frac{RT}{n^2 F^2 \sqrt{2}} \left[ \frac{1}{C_{\text{Hg}^2+} + (D_{\text{Hg}^2+})^{1/2}} + \frac{1}{C_{\text{Hg}}(D_{\text{Hg}})^{1/2}} \right] \]

\( D_{\text{Hg}^2+}, D_{\text{Hg}}: \) diffusion coefficient of mercurous ions in solution and mercury in amalgam

\( \sigma \rightarrow D \) at different concentration of \( \text{Hg}^{2+} \) in solution
**Characterization of materials:** microstructural + conductivity information
- polycrystalline solids: transport properties are strongly affected by microstructure → grains, grain boundaries, porosity …

- solid electrolyte (ionic conductor):
e.g. zirconia (ZrO$_2$) ceramic electrolytes at high temperature

Monoclinic (m) (ZrO$_2$ at ambient T) → tetragonal (t) → cubic (c)

CaO, MgO, Y$_2$O$_3$ alloying: occupy Zr$^{4+}$ sites & vacant oxygen lattice site → ionic conductivity

\[
\frac{1}{2} \text{O}_2(\text{g}) + 2e^- \leftrightarrow \text{O}^{2-} \text{(electrolyte)}
\]

Circuit equivalent for a ceramic electrolyte according to Bauerle (1969) and modeling the impedance of the grain interiors (gi) grain boundaries (gb) and electrode (e).
Comparison of admittance and impedance spectra for a zirconia solid electrolyte (ZrO$_2$:6 mole % Y$_2$O$_3$) at 240°C: (b) Experimental impedance spectrum. (c) Simulated impedance spectrum

<table>
<thead>
<tr>
<th>Circuit Parameters</th>
<th>Table 4.1.4. Circuit Parameters Graphically Obtained from the Impedance Spectrum of Figure 4.1.19b and Used to Simulate the Spectrum of Figure 4.1.19c</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C_{yi} = 4.8$ pF</td>
<td>$C_{eh} = 1.7$ nF</td>
</tr>
<tr>
<td>$R_{yi} = 2.1$ MΩ</td>
<td>$R_{eh} = 1.5$ MΩ</td>
</tr>
</tbody>
</table>

Materials design
i) Maximize conductivity
ii) Optimize ceramic structure for strength etc
$\rightarrow \text{ZrO}_2 + \text{Y}_2\text{O}_3$

$\text{ZrO}_2 + 3 \text{ mol} \% \text{ Y}_2\text{O}_3$ (tetragonal)
$\rightarrow \text{Grain size } \sim 600 \text{ nm}$
$\therefore \text{large contribution of gb to resistivity}$

$\text{ZrO}_2 + 6 \text{ mol} \% \text{ Y}_2\text{O}_3$ (cubic)
$\rightarrow \text{Grain size } \sim 10 \mu\text{m}$
$\therefore \text{small contribution of gb to resistivity}$

Impedance spectra for two zirconia ceramics, obtained at 300 °C using sputtered platinum electrode: (a) Tetragonal zirconia ceramic ($\text{ZrO}_2$: 3 mole \% $\text{Y}_2\text{O}_3$) with large grain boundary are due to continuous grain boundary phase. (b) Partially stabilized ceramic ($\text{ZrO}_2$: 6 mole \% $\text{Y}_2\text{O}_3$) with small grain boundary are due to discrete grain boundary phase.
Crystalline extrinsic ionic conductor conductivity

\[
\sigma = \left( \frac{\sigma_0}{T} \right) \exp\left( -\frac{\Delta H_m}{kT} \right)
\]

\(\Delta H_m\): activation enthalpy for ionic migration

\[\Rightarrow \text{Arrhenius plots of } \sigma \text{ vs. } 1/T \Rightarrow \text{slope } = \frac{\Delta H_m}{k}\]

Arrhenius plots of the grain interior and grain boundary resistivities for two zirconia ceramics: (a) Tetragonal zirconia ceramic (ZrO_2: 3 mole % Y_2O_3) in which the lines have different slopes, as expected from the brick layer model. (b) Partially stabilized ceramic (ZrO_2: 6 mole % Y_2O_3) in which the slopes of the lines are similar, as expected for discrete grain boundary phase.
→ Single crystals

\[ \text{gi arc, electrode arc} \]

Only t-phase → one arc

Comparison of the impedance spectra obtained at 300°C for two zirconia-yttria single crystals: (a) Tetragonal + monoclinic single crystal (ZrO\(_2\): 2.2 mole % Y\(_2\)O\(_3\)) showing large bulk are. (b) Fully tetragonal single crystal (ZrO\(_2\): 3.4 mole % Y\(_2\)O\(_3\)) showing small bulk are.

- polycrystalline & lacking a grain boundary response
  e.g., Bi\(_2\)O\(_3\):Er\(_2\)O\(_3\) → absence of grain boundary :: high solid solubility

Impedance spectrum obtained at 300°C for a pellet of Bi\(_2\)O\(_3\): 17 mole % Er\(_2\)O\(_3\) showing no grain boundary are.
- total conductivity: $g_i + g_b$ conductivities

$\text{ZrO}_2 : \text{Y}_2\text{O}_3$
Conductivity measurement

Pt/LiPON(Li conductor)/Pt sandwich structure

Ionic conductivity: $1.5 \times 10^{-6}$ S/cm

Cole-cole model
Gas sensor: solid electrolyte chemical sensors (SECS)
e.g., CO sensor

Structure of DAIS 585, an ion conducting sulfonated styrene/ethylene-butylene/styrene (S-SEBS) triblock copolymer.

Working electrode \[ 2\text{CO} + 2\text{H}_2\text{O} = 2\text{CO}_2 + 4\text{H}^+ + 4\text{e}^- \quad [1] \]
Counter electrode \[ \text{O}_2 + 4\text{H}^+ + 4\text{e}^- = 2\text{H}_2\text{O} \quad [2] \]
Cell reaction \[ 2\text{CO} + \text{O}_2 = 2\text{CO}_2 \quad [3] \]
Equivalent circuit model and predicted ac impedance plot.

Nyquist plots (at 60 % relative humidity and 22 ± 2°C) for sensor 5 in clean air (a) and in the presence of various CO concentrations, (b) 500, (c) 760, (d) 1000, (e) 1460, (f) 2500, and (g) 5000 ppm.
e.g., Zirconia-based electrolytes to measure oxygen concentration
gas/electrode/electrolyte

\[
\frac{1}{2}O_2 \text{(gas)} + 2e^- \text{(porous electrode)} \leftrightarrow O^2^- \text{(electrolyte)}
\]

Equivalent circuit model and
predicted ac impedance plot.

R$_3$: resistance from oxygen electrode rxn
R$_1$, R$_2$: bulk & grain boundary resistance
Solid state batteries

M/M⁺ electrolyte (solid or liquid)/I
M: Li or C, Na
I: insertion electrode (oxides….)
Ex) Li/1M LiAsF₆ in propylene carbonate/NaₓWO₃

Interfacial reaction resistance $\rightarrow$ exchange current density $i_0$

$$\theta = \frac{RT}{n_i F}$$
Diffusion coefficient of Li, $D_{Li}$

$$Z_w = (1 - j) \frac{V_m(dE/dy)}{nFS(2wD_{Li})^{1/2}}$$

dE/dy: slope of open circuit voltage vs. composition
S: surface area, $V_m$: molar volume

Solution resistance $R_i = 45 \ \Omega$

Charge transfer resistance = 105 $\ \Omega$

$(150 - 45)$

Impedance data for cell (B) with $x = 0.64$. Open circles are at $E = 1.85 \ \text{V vs. Li}$; closed circle are at $E = 2.00 \ \text{V vs. lithium.}$
ii) Li/15 wt % PAN-EC-PC-LiClO$_4$/Li (polyanilne)

$R_b$: bulk resistance of polymer electrolyte $\rightarrow$ conductivity

$R_e$: interfacial resistance

![Impedance spectra of Li/15 wt % PAN-EC-PC-LiClO$_4$/Li cell.](image)

**Ionic characteristic of various polymer electrolyte**

<table>
<thead>
<tr>
<th>sample</th>
<th>$T$ (cm)</th>
<th>$A$ (cm$^2$)</th>
<th>$R_b$ (Ω)</th>
<th>$C_{dl}$ (μF)</th>
<th>$R_e$ (Ω)</th>
<th>$\sigma$ (S/cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10 wt% PAN</td>
<td>$4.5 \times 10^{-2}$</td>
<td>4</td>
<td>34</td>
<td>0.51</td>
<td>1947</td>
<td>$2.30 \times 10^{-4}$</td>
</tr>
<tr>
<td>10 wt% PAN-Al$_2$O$_3$</td>
<td>$4.5 \times 10^{-2}$</td>
<td>4</td>
<td>8</td>
<td>2.19</td>
<td>1150</td>
<td>$8.92 \times 10^{-4}$</td>
</tr>
<tr>
<td>15 wt% PAN</td>
<td>$4.5 \times 10^{-2}$</td>
<td>4</td>
<td>131</td>
<td>0.90</td>
<td>1768</td>
<td>$0.57 \times 10^{-4}$</td>
</tr>
<tr>
<td>15 wt% PAN-Al$_2$O$_3$</td>
<td>$4.5 \times 10^{-2}$</td>
<td>4</td>
<td>74</td>
<td>1.06</td>
<td>1490</td>
<td>$1.00 \times 10^{-4}$</td>
</tr>
</tbody>
</table>
Li$^+$ transfer number of SPE electrolyte

\[
t_{Li^+} = \frac{R_b}{\left(\frac{\Delta V}{I_\infty}\right) - R_e}
\]

$\Delta V$: applied voltage
$I_\infty$: steady state current
iii) Carbon insertion materials

\[
\begin{align*}
\text{LiC}_6 & \rightarrow C_6 + \text{Li}^+ + x\text{e}^- \\
\text{Li}_y\text{CoO}_2 + x\text{Li}^+ + x\text{e}^- & \rightarrow \text{Li}_{x+y}\text{CoO}_2 \\
x\text{Li} + 6\text{C} & \Leftrightarrow \text{Li}_x\text{C}_6 \\
\end{align*}
\]

Impedance response of a LixC6 electrode in the LiClO4-PC electrolyte at various compositions (x = 0, x = 0.27, and x = 0.52) and at room temperature. Counter electrode: Li.
Photoelectrochemical solar cell (PESC)

- Impedance spec. \( \rightarrow \) excellent tool to examine the existence of surface states or other modifications of the ideal semiconductor-electrolyte interface

Mott-Schottky plot of the space charge capacitance

\[
\frac{1}{C_{se}^2} = \frac{2}{e \varepsilon_0 \varepsilon_N d} \left( |V - V_{fb}| - \frac{kT}{e} \right)
\]

C-2 vs. V at different frequencies for n-MoSe2 electrode in aqueous solution of 0.5 M Na2SO₄ at pH 4.5:

(□) 1KHz, (O) 3 kHz, (∆) 10 kHz.

Electrode area, 0.030 cm².
The diagram shows the redox potentials for various reactions in a pH scale. The redox couples include:

- \( H^+ / H_2^+ \) (pH = 0)
- \( \text{Fe(II)} \cdot \text{EDTA} / \text{Fe(III)} \cdot \text{EDTA} \) (pH = 5)
- \( \text{Fe(CN)}_{6}^{4-} / \text{Fe(CN)}_{6}^{3-} \) (pH = 6)
- \( \text{I}^{-} / \text{I}_2 \) (pH = 0)
- \( \text{Fe(II)} / \text{Fe(III)} \) (1 N \( \text{H}_2\text{SO}_4 \))
- \( \text{Br}^{-} / \text{Br}_2 \) (pH = 0)
- \( \text{H}_2\text{O} / \text{O}_2 \) (pH = 0)
- \( \text{Cl}^{-} / \text{Cl}_2 \) (pH = 0)

The energy levels are labeled as follows:

- \( E_{c} \)
- \( E_{f} \)
- \( E_{g} = 1.4 \text{ eV} \)
- \( E_{v} \)
(a) Energy of the edges of the valence ($E_v$) and conduction band ($E_c$) as a function of a position coordinate $x$ (perpendicular to the surface) for an n-type semiconductor under conditions of depletion. The arrow shows a one-step electron transfer process from the conduction band to the empty states of a redox system. (b) Equivalent scheme corresponding to Fig. (a).

(a) Band diagram for an n-type semiconductor electrode under conditions of weak depletion. The arrows show a transfer of a majority carrier from the electrode to a redox electrolyte in two steps. (b) General scheme for a semiconductor electrode taking into account two-step charge transfer processes. $Z_{sc}$ is the differential impedance due to localization of charge carriers in surface states or intermediates; $Z_H$ is the differential impedance for the transfer of electrons or ions though the Helmholtz layer.
dye-sensitized solar cell or photochemical solar cell: TiO$_2$

Mott-Schottky plot for the rutile and anatase electrodes
Fuel Cells
- Solid oxide fuel cells

Anode: \( H_2 + O^{2-} \iff H_2O + 2e^- \)

Cathode: \( \frac{1}{2}O_2 + 2e^- \iff O^{2-} \)

\[
H_2 + \frac{1}{2}O_2 \iff H_2O
\]

Issue: how to drop the operation temperature
A schematic illustration of the cell configuration. Note the size and shape of each electrode.

Evolution of ac impedance spectra at the $\text{Gd}_{0.8}\text{Ca}_{0.2}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_3$ cathode at 800 °C under air. The observed (O) and deconvoluted (solid line) spectra are displayed. The equivalent circuit is depicted in the inset.
Corrosion & corrosion protection

$t \uparrow \rightarrow \text{corrosion} \uparrow \text{in Cl}^-$

Impedance diagrams at the corrosion potential as a function of time for carbon steel exposed to a 0.997m NaCl + 0.001m FeCl$_3$ + 3500 ppb O$_2$ solution at 250 °C.

A= 11 h, B = 22 h, C= 35 h, D = 46 h, E = 58 h, F = 70 h, G= 86.5h, H = 112 h, I = 136 h, J= 216 h.

Polarization resistance ($R_p$)

$R_p = Z'(0) - Z'(\infty)$

Impedance diagram for Al-0.1P-0.1In-0.2Ga-0.01Tl alloy in 4M KOH at 25 °C and at the open-circuit potential (-1.760 V vs. Hg/HgO). The parameter is frequency in Hz.
Theoretical complex plane impedance diagrams for a passive film. $C_\infty = 5 \times 10^{-5}$ F, $R_\infty = 10^4$ Ω, $R_{\infty 2} = 1$ Ω, $\sigma_0 = 10^3$ Ω/s$^{1/2}$
Electrochromic devices

\[
WO_3 + yLi^+ + ye^- \leftrightarrow Li_yWO_3
\]

\begin{align*}
\text{colorless} & \quad \rightarrow \quad \text{blue} \\
\text{intrercalation} & \quad \leftrightarrow \quad \text{deintrercalation}
\end{align*}

1M LiClO_4 + PC at open circuit

Ni(OH)\text{x}

\[
O \rightarrow 3 \text{ V}
\]

Li deintercalation
\[ C_D = \frac{l^2}{3DR_D} \]

\( l \): thickness of sample  
\( C_D \): limiting capacity  
\( R_D \): limiting resistance

\[ D_{Li^+} = 1.72 \times 10^{-11} \text{ cm}^2/\text{s at 1.35 V, 20.5 nm thickness} \]