Electrochemical Impedance Spectroscopy (EIS)
(a.k.a. a.c. impedance)
- this is a transient technique, but one that requires a general steady state condition...

- can be used for determining both:
  Interfacial parameters
  - reaction rates
  - rate constants
  - capacitance/charge storage abilities
  - diffusion coefficients
  - adsorption rate constants
  - reaction mechanisms

  and
  Material parameters
  - conductivity
  - dielectric constants
  - charge mobilities
  - bulk generation-recombination rates
  - equilibrium conc. of charged species
  - film thicknesses
  - presence of pores and cracks
Like other spectroscopy experiments, we apply an excitation to the system under study and observe its response (generally as a function of frequency).

(a) General concept

- Excitation → System → Response

(b) Spectrophotometric experiment

- Lamp-Monochromator → Optical cell with sample → Phototube

(c) Electrochemical experiment

- Power supply → Current response

- In EIS, we apply a potential perturbation (usually a sine wave) and observe the current response, which is a sine wave at the same frequency, but with a different amplitude and phase than the potential signal.

\[ V_{DC}(I_{DC}) \]  \[ V_{AC}^{in} \]  \[ V_{AC}^{in} \]  \[ I_{AC}^{out} \]
Advantageous Features of EIS

- Measurements are made under steady state conditions
- All electrical parameters of the system can be determined in a single experiment
- A simple measurement, easy to automate
- Characterizes bulk and interfacial properties of all sorts of materials (conductors, semiconductors, ionic transport media, dielectrics (insulators).)
- Can be used to help verify mechanistic models
- Works even in low conductivity electrolyte solutions (IRu is not a big problem!)
- Signal can be averaged over long periods to achieve high precision
- Non-destructive

Caution: Because it is easy to do, it is also easy to collect large amounts of meaningless data!
to understand what is happening in E15, we need to consider Ohm's Law

\[ \Delta E = IR \]

- the above holds for a resistor at a constant potential (the d.c. case) - what about a.c.?
- now consider a sinusoidally varying potential, \( \nu \)

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

Where \( \nu \) is the potential difference at any time \( t \), \( \omega \) is the angular frequency of the sine wave, and \( V \) is its amplitude.

- if such a potential waveform is applied to a circuit containing only a resistor, the resulting current will be
\[ i = \left( \frac{V}{R} \right) \sin(\omega t) \]

- \( V \) and \( i \) oscillate with the same frequency and they are in phase. The amplitudes are related by \( R \) \( \left( \frac{|v|}{|i|} = R \right) \)

Now consider the potential sine wave applied to a circuit with only a capacitor:

\[ C \]

- Current only flows when the potential is changing, according to

\[ i = C \frac{dv}{dt} \]

\[ = C \frac{d(V\sin(\omega t))}{dt} \]

\[ = C \omega V \cos(\omega t) \]

\[ = \omega CV \sin(\omega t + \frac{\pi}{2}) \]

- \( V \) and \( i \) still oscillate with the same frequency, but now they are \( \frac{\pi}{2} \) radians (90°) out of phase. The relative amplitudes depend on \( \omega \) and \( C \).
\[
\frac{|v|}{|i|} = \frac{1}{\omega C} \quad \text{(after the phase shift is accounted for)}
\]

we can then develop the concept of "impedance"

\[
Z(\omega) = \frac{V(\omega)}{I(\omega)}
\]

which describes the restriction of current flow under conditions of changing potential.

- This is the "a.c." form of Ohm's Law.

- Thus, for a resistor

\[
Z(\omega) = R
\]

and for a capacitor

\[
Z(\omega) = \frac{1}{j\omega C}
\]

where \( j \) represents the \( 90^\circ \) phase shift.

- Impedances add in series as

\[
Z = Z_1 + Z_2
\]
therefore, for a resistor and capacitor in series

\[
\begin{align*}
Z &= \frac{1}{j\omega C} \\
\end{align*}
\]

\( Z(\omega) = R + \frac{1}{j\omega C} \) \text{ a complex number}

\[
\begin{align*}
\text{in-phase component (real)} \quad \frac{1}{\omega C} \\
\text{out-of-phase component (imaginary)} \quad j
\end{align*}
\]

\( j^2 = -1 \)

Note that:

\[
\frac{1}{j\omega C} = \frac{j}{j^2\omega C} = -j\left(\frac{1}{\omega C}\right)
\]

4th quadrant (real)}
- Impedances add in parallel as reciprocals \(116\)

\[
\frac{1}{Z} = \frac{1}{Z_1} + \frac{1}{Z_2}
\]

(So the smallest \(z\) dominates)

- Thus, for a resistor and capacitor in parallel:

\[
\frac{1}{Z(\omega)} = \frac{1}{R} + j \omega C
\]

\[
Z(\omega) = \frac{1}{\left(\frac{1}{R} + j \omega C\right)} = \frac{1}{\left(1 + j \omega CR\right)}
\]

\[
= \frac{R}{1 + j \omega CR} = \frac{R}{(1 + j \omega CR)} \cdot \frac{(1 - j \omega CR)}{(1 - j \omega CR)}
\]
$$Z(\omega) = \frac{R - j\omega CR^2}{1 - j^2 \omega^2 C^2 R^2}$$

$$= \frac{R - j\omega CR^2}{1 + \omega^2 C^2 R^2}$$ (since $j^2 = -1$)

$$= \left(\frac{R}{1 + \omega^2 C^2 R^2}\right) - j\left(\frac{\omega CR^2}{1 + \omega^2 C^2 R^2}\right)$$

^ in-phase component (real)

^ out-of-phase component (imaginary)

---

Now consider a typical electrode-solution interface in a cell. We have a capacitance due to charging/discharging the electrochemical double layer. In parallel with the double layer we may have a faradaic reaction proceeding at some potential-dependent rate. This is equivalent to a resistance (remember linear polarization $\frac{\Delta E}{\Delta I} = R_{ct}$). Finally, in series with those, there is the ever-present solution resistance $R_a$ (here called $R_s$).
Apply $v = V \sin(\omega t)$ to this cell, observe $L = \frac{V}{Z(\omega)}$ and calculate the value of $Z$ at a variety of $\omega$.

Plot of the imaginary component vs. the real component of $Z(\omega)$ for various values of $\omega$.

Nyquist Plot (a.k.a. complex plane plot)

$$Z = R_s + \frac{R_{ct}}{1 + \omega^2 C_{dl}^2 R_{ct}^2} - j \left( \frac{\omega C_{dl} R_{ct}^2}{1 + \omega^2 C_{dl}^2 R_{ct}^2} \right)$$

- The plot traces a semicircle with diameter $R_{ct}$, centred on the real axis at $Z_{RE} = R_s + \frac{R_{ct}}{2}$.
- The Nyquist plot makes it easy to determine $R_{ct}$.
- $R_s$ simply translates the semicircle along the real axis, so it doesn't really interfere with the measurement.
\[
(Z_{Re} - R_g - \frac{R_{ct}}{2})^2 + Z_{Im}^2 = \left(\frac{R_{ct}}{2}\right)^2
\]

- the above equation rearranges to: (11')

Which (remember grade-12/13 Functions + Relations) is the equation of a circle \( x^2 + y^2 = r^2 \)

- disadvantages of this type of plot are:
  - \( \omega \) information is lost
  - plot looks the same for any value of \( C \)
- to highlight other features we may want to plot other parameters

Using Pythagorus:

\[
Z^2 = Z_{RE}^2 + Z_{Im}^2
\]

\[|Z| = \sqrt{Z_{RE}^2 + Z_{Im}^2}\]

and

\[
\frac{Z_{Im}}{Z_{RE}} = \tan \Theta
\]

\[
\Theta = \arctan\left(\frac{Z_{Im}}{Z_{RE}}\right)
\]

- plots of \(|Z|\) and \( \Theta \) vs. \( \log \omega \) are called Bode plots
Nyquist Plot

\[ |Z| = \frac{1}{\omega C_{dl}} \]

Bode plot

\[ \log |Z| \]

\[ \log \omega \]
- advantages of Bode plot
  - can get R values from plateaus of the magnitude plot
  - can get C from the values of |Z|
  - ω information is not lost.

- there are many other plotting possibilities using derivative parameters. These may highlight specific features and minimize others. It depends on the application which plots will be the most useful. The most common are Nyquist and Bode plots.

Admittance: \( Y = Z^{-1} \)

\[ = Y' + jY'' \]
\[ i = Yv \]

Modulus: \( M = j\omega \epsilon Z \)

\[ = M' + jM'' \]
\[ = \epsilon^{-1} \]

\( \epsilon = \text{complex dielectric constant} \)

\( \epsilon = \mu^{-1} \)

\[ \epsilon = \epsilon' + j\epsilon'' \]

| Relations Between the Four Basic Immittance Functions* |
|-----------------|--------|--------|--------|
| \( M \)         | \( Z \) | \( Y \) | \( \epsilon \) |
| \( M \)         | \( M \) | \( \mu Z \) | \( \mu Y^{-1} \) | \( \epsilon^{-1} \) |
| \( Z \)         | \( \mu^{-1} M \) | \( Z \) | \( Y^{-1} \) | \( \mu^{-1} \epsilon^{-1} \) |
| \( Y \)         | \( \mu M^{-1} \) | \( Z^{-1} \) | \( Y \) | \( \mu \epsilon \) |
| \( \epsilon \)  | \( M^{-1} \) | \( \mu^{-1} Z^{-1} \) | \( \mu^{-1} Y \) | \( \epsilon \) |

* \( \mu = j\omega \epsilon_c \), where \( \epsilon_c \) is the capacitance of the empty cell.
Effect of Changing Rs

Nyquist plots handle changes in Rs better than Bode plots.
$C_{dl} = \frac{1}{Z(\omega=1)}$

$|Z|$

$\omega = 1 \text{ rad/s}$

Rs shifts intercept - overestimates $C_{dl}$

Response of RC pair +Rs

Response of RC pair
Effect of Changing $R_p$

- $R_p = 1400$ Ohms
- $R_p = 1200$ Ohms
- $R_p = 1000$ Ohms

As $R_p$ decreases, the slope of the line changes, and the peak height of the plateau increases.

For lower $C$, the phase angle shifts to the right. Increasing $C$ decreases, shift of peak height.

The imaginary component moves to the left side of the graph.
Effect of Changing Cdl

Frequency (Hz)

Phase Angle (degrees)

Magnitude (Ω)

Real Component (Ω)

Imaginary Component (Ω)

-750

0

750

1,600

0

-1,600

Peak shifts to lower C

Slope is constant, but

Burke height is low

Effect of Changing Cdl
For two time constants:

\[ \tau_1 = R_2 C_1 \quad \tau_2 = R_3 C_2 \]

Note: there will be an error introduced in the capacitance value calculated by this method as the ratio of \( R_s / R_p \) increases.

If the ratio is 1/500, the error is ca. 2%.
1/100, the error is ca. 10%.
1/10, the error is ca. 50%.
*** should either deconvolute or use CNLS fitting ***
Simple analysis of impedance data:

\[ \omega_{\text{max}} = \frac{1}{R_{\text{ct}}C_{\text{dl}}} \]

\( \omega_{\text{max}} \) is the frequency which determines the top of the semicircle

\[ \omega_{\text{max}} = \frac{1}{\tau} \]

where \( \tau = R_{\text{ct}}C_{\text{dl}} \)

**Bode Plot**

\[ |Z| = \frac{1}{\omega C_{\text{dl}}} \]

* this slope will decrease as the ratio \( R_s/R_{\text{ct}} \) increases

To have a measurement at \( \omega_{\text{max}} \), use Nyquist to get \( |Z| = \sqrt{Z'^2 + Z''^2} \) at max; then use Bode mag plot to get \( \omega_{\text{max}} \).
Inductive Behaviour

- observed in batteries and corroding systems
- also often an experimental artifact
- inductor "L" has 90° phase shift like capacitor, but leads the voltage (ie, +90°) rather than following it (-90° for capacitor).

\[ Z_L = j\omega L \]

\[ Z_T = R + j\omega L \]

"pseudo-inductance"

\[ Z_T = \frac{\omega^2 L^2 / R}{1 + \omega^2 L^2 / R^2} + \frac{\omega L}{1 + \omega^2 L^2 / R^2} j \]

\[ \omega_{\text{max}} = \frac{R}{L} \]
- experimentally, poor cell design will also give inductance-like response

Caused by very resistive reference electrode, such as commercial SCE with ceramic frit.

- Can also result from non-steady state conditions

\[ T_1 \to T_0 \] imagine that you could know instantly the complete impedance spectrum, and you do this for an electrode covered with a resistive layer that is dissolving with time.

Your "instant" spectra the actual data you record, and apparent spectrum.
Proposed origins of h.f. inductive behavior in batteries:

- cell geometry, electrical leads, and connectors


- viscoelastic property of the electrolyte


  concludes that whenever electrode system behaves as a negative
  resistance and supplies energy to the measuring device, an inductive
  component is present

  a viscous electrolyte may produce harmonics in the current response at
  the electrode interphase which gives rise to a lag in response and
  corresponding energy storage and inductive behavior

  (but does not explain dependence on battery size and surface topology,
  e.g. flat Pb electrode in H$_2$SO$_4$ generates no inductance)

- porous texture of electrode (Pb-acid battery)


  (not supported by porous electrode theory. $Z_L$ porous = $[Z_L$ flat]$^{1/2}$

- reaction within pores

  (1980).

  (disproven by M. Keddam, C. Rakotomavo, H. Takenouti, J. Appl.

- ferromagnetism of electrode material (e.g. Ni in Ni-Cd battery)

Proposed origins of l.f. inductive behavior:

termed pseudo-inductance, a.k.a. inductive loop

A real inductance requires storage of energy in a magnetic field and there is no appreciable ac magnetic field energy present in low-current IS measurement.

*interpretation requires elimination of non-linear aspect


- adsorbate reacting with the metal in a 2-step charge transfer reaction producing an adsorbed soluble intermediate


- desorption of an inhibitor


- exchange of both cations and anions constituting thin passive film


- bulk diffusion to a partially blocked electrode/non-homogeneity of corroding interface


- electrorecrystallization

Mass transport control

\[ \text{Log } I \]

mass transport limit

\[ E = \frac{dE}{dI} = 0 \]

- like very big resistance

EXCEPT \( I \neq 0 \)

and I continues for both \( \pm V \)

- results in a resistive term called the WARBURG impedance

- Faradaic impedance with mass transport is then:

\[ Z_F(\omega) = Rct \left( 1 + \frac{K}{VjwD_0} + \frac{K}{VjwD_R} \right) \]

Where \( K \) and \( K \) are the rate constants of the forward and reverse reactions, respectively, and \( D_0 \) and \( D_R \) are the diffusion coefficients of the oxidized and reduced species.

- note the \( \sqrt{E} \) dependence (in the form \( \frac{1}{\sqrt{\omega}} \)) like Cottrellian diffusion

- the phase angle is a constant 45°
- Commonly seen in corroding systems or when redox chemistry occurs deep within pores on a porous electrode.

Models for anodic processes on the Li electrode in a Li-SOCl\(_2\) battery (Chenenbault, Vallin, Thevenin, Wiart (1989))
$Z_{im}$

$\text{Re}$ = "pore" resistance

$\theta$ = area covered by passive film (LiCl)

$R_{gb}$ and $C_{gb}$ = resistance of LiCl grain boundaries and capacitance

$Z_d$ = diffusional impedance

$R_t$ = charge transfer resistance

↑ a pretty example of how impedance spectroscopy takes advantage of the different speeds of electrode processes. By probing the system at different frequencies we can "tune in" to each process one at a time.
Distributed Elements

- Single time constant behaviour (Debye) with well-defined semi-circles in the Nyquist plots is actually rare in real systems.
- More commonly, real systems give us:
  - Depressed or flattened semicircles
  - Skewed arcs
  - Wranges with constant phase angle

- Many proposed sources of these non-ideal impedance responses, and much effort has gone into modelling them:
  - Mass transport - Can occur even in homogeneous media
  - Electrode porosity
  - Surface roughness - Variable capacitance across surface
  - Nonuniform current distribution - Non-equipotential surface
  - Distribution of activation energies - Distribution of time constants for thermally activated processes.
Different $R$ and $C$ at different spots on surface

Oxide layer

Electrode

$Z_{im}$

Semicircle, centre on real axis

Overall response apparently "depressed" semicircle (centre below real axis)

Various of different local time constants

$Z_{Re}$

Phase angle $\theta - 90^\circ$

Individual Debye peaks.

Overall response phase angle not $90^\circ$ but constant over a large frequency range $\log \omega$
Criteria for Valid Impedance Spectroscopy Measurements

For a valid impedance measurement, the response to the applied perturbation must be:

1. Linear
2. Stable
3. Causal
4. Finite

1. Linearity - we are trying to apply Ohm's Law $V(w) = I(w)Z(w)$ which is linear. If the $V-I$ relationship is nonlinear, then Ohm's Law cannot apply.

- We know (from Butler-Volmer) that the $I-E$ relationship in electrochemistry is exponential...

- But over a small enough $\Delta E$, it is approximately linear

- In practice, one can try a few small $\Delta E$s, and if $Z$ doesn't change, then $I-E$ is linear enough over that range of $\Delta E$. 

\[ I(t) = I_0 + \Delta I \sin(\omega t - \phi) \]
2 Stability - the system must not change during the course of the measurement, and should return to its original state after the perturbation is removed.

3 Causality - the measured response must be caused only by the applied perturbation and must not contain contributions from other sources (e.g. pitting, 60Hz power supply, electrode rotator, etc.)

4 Finiteness - there can never be an infinite response to a perturbation.

How can you tell if it's valid?

Do a Kramers-Kronig Transformation.

- A mathematical operation that can transform real impedance values into imaginary ones, and imaginary impedance into real. If, after transformation, you get the same impedance spectrum back, then the measurement is valid.

- Drawback is that the entire impedance spectrum must be integrated (from \( \omega = 0 \) to \( \omega = \infty \)) for a proper transformation. If one cannot get close enough to \( \omega = 0 \) (common in corrosion) then one must use polynomial fitting or equivalent circuit response to estimate \( Z_{\omega \to 0} \).
Other ways of determining invalid results

Failure of Linearity  - try different perturbation amplitudes
   (if response changes, then the system may
   not be linear).
   - use an oscilloscope to examine the
     I and E signals. If a sine wave is
     applied, the response should be a sine
     wave too.

Failure of Stability  - repeat the experiment (should not change)
   - repeat the experiment using fewer data
     points (should not change)
   - reverse the frequency scan direction,
     or try random frequency values.

Failure of Causality  - Spurious/noisy impedance data may indicate
   failure of causality
   - try testing the equipment using an equivalent
     circuit with element values above and below
     those measured to see if they can be
     accurately measured.

Failure of Finiteness  - generally not a problem in electrochemical systems
   (potentiostat hits a maximum).
1. **Bridges** → adjust values of circuit elements to get a particular (often zero) signal
   - Very slow
   - Very precise

2. **Fourier Transform of Time Domain Signal from Potentiostat**
   → sharp potential step contains contributions from a wide range of frequencies.
   - has linear frequency spacing
   - limited range of frequencies (truncated)
   - noisy (no integration/averaging)

   - one frequency at a time
   - precise
   - excellent noise rejection by averaging/integration

4. **Frequency Response Analyzer (\(+\) Potentiostat)**
   - qualities similar to L.I.A., but usually contains more features specific to impedance spectroscopy and more flexible.
Potentiostat/Galvanostat Requirements

- wide frequency range
- bandwidth should be 100x highest frequency desired ampl
  \[ \text{Log } \omega \]
- stable
- must be sensitive enough to measure small signal on small \( \Delta E \) perturbation, with possible d.c. background
- many commercial potentiostats are unsuitable.

Cell Requirements

- reasonably low overall impedance (especially in non-aqueous systems). \( \text{(Ru not usually a problem)} \)
- low impedance reference electrode
- symmetrical design/electrode placement to avoid non-uniform current distributions.
- short leads, good connections, driven shields

Software

- not required, but makes life much easier during:
  1. data acquisition - runs quickly by itself
  2. data analysis - plots and measures parameters
does least-squares fitting to refine models.