Electrochemical Impedance Spectroscopy (EIS)

Purpose (similar as for Cyclic Voltammetry):

- **characterize electrochemical systems**
- **rationalize interplay of physical and chemical processes (interfaces and bulk); widely different time scales (e.g. range of variation of k^0 !!!)**
- **electroanalysis, diagnostics: determine parameters**

What are relevant processes and parameters? We know many of them already …

- **Double layer charging** $\rightarrow C_{dl}$
- **Charge transfer** $\rightarrow k^0, \alpha, j^0$
- **Mass transport** $\rightarrow D, \delta, R_u$
- **Adsorption, desorption** $\rightarrow \theta, k_{ad}, k_{des}$

Complex coupling between processes and parameters!

There are two ways to disentangle this "mess":

- **Selective experimental techniques: probe one particular process, e.g.**
  - **use supporting electrolyte (eliminate migration)**
  - **use RDE, DME, UME (el. diffusion limitations).**

  Applicable
  - **simple structures (e.g. planar, smooth electrodes, semi-infinite diffusion)**
  - **well-defined conditions, controlled parameters (uniform concentrations, fixed temperature, …)**

  These are studies on model systems (ex-situ)

- **Cumulative methods, like CV and EIS: probe the dynamic behaviour of a system over a broad range of scales.**
  - **full coupling between different processes**
  - **real systems under in-situ conditions (e.g. operating fuel cell, corrosion processes).**

  Problem: Need simple analogues (e.g. equivalent circuits) or physical models to discriminate the processes and to extract parameters.

Impedance Spectroscopy

- **Sinusoidally varying potential** δE **(at electrochemical interface or complete electrochemical cell)**
- **Could be applied in addition to steady state potential.**
- **Potential variation in complex notation**

$$\delta E(t) = E_0 \exp(i\omega t)$$

where $i = \sqrt{-1}$ **is the complex unit.**

- **Defined: amplitude** E_0 **and angular frequency** ω
- **Measure current response (AC current) to** $\delta E(t)$
- **Small amplitude** E_0**, i.e.** $E_0 << \frac{RT}{F} \approx 25.7$ **mV** $\rightarrow$

  linear response in AC current density will be, i.e.

$$\delta j(t) = j_0 \exp(i\omega t)$$

- **amplitude** j_0 **generally complex**
- **Phase and amplitude of** $\delta j(t)$ **relative to** $\delta E(t)$

Complex impedance: extension of the well-known concept of **electrical resistance**

$$Z = \frac{\delta E(t)}{\delta j(t)} = \frac{E_0}{j_0}$$

- Impedance is a function of the frequency ω
- $Z(\omega)$ is complex quantity → decomposition into real and imaginary parts,

$$Z(\omega) = \mathrm{Re}\left(Z(\omega)\right) + i\,\mathrm{Im}\left(Z(\omega)\right) = \left|Z(\omega)\right| \exp\left(i\varphi(\omega)\right)$$

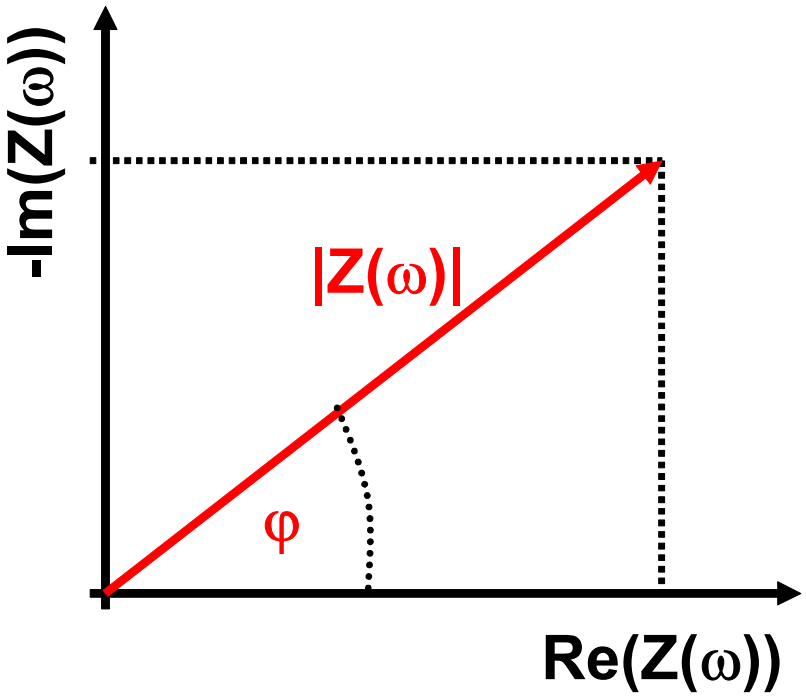
or alternatively into absolute value and phase angle

$$\left|Z(\omega)\right| = \left(\mathrm{Re}\left(Z(\omega)\right)^2 + \mathrm{Im}\left(Z(\omega)\right)^2\right)^{1/2}$$

and

$$\varphi(\omega) = \arctan\left(-\frac{\mathrm{Im}\left(Z(\omega)\right)}{\mathrm{Re}\left(Z(\omega)\right)}\right)$$

Complex plane representation displays these pieces of information



Impedance measurement

Impedance measurement performed in practice:

- **Fix working point: point of stationary operation of the electrochemical system, i.e. fixed point on the steady state current voltage curve:** j_s, E_s
- **Add small-signal harmonic variation, with frequency-response analyzer** $\delta E(t) = E_0 \exp(i\omega t)$ **to steady state potential.**

  Resulting electrode or cell potential is

$$E(t) = E_s + \delta E(t) = E_s + E_0 \exp(i\omega t)$$

- **Measure resulting current signal**

$$j(t) = j_s + \delta j(t) = j_s + j_0 \exp(i\omega t)$$

  and extract the AC part

$$\delta j(t) = j_0 \exp(i\omega t)$$

- **Determine impedance as** $Z = \frac{E_0}{j_0}$
- **Sample frequencies over relevant range (limitations of equipment, range of characteristic frequencies). Typical range of feasible frequencies:**

$$10^{-3}\,\mathrm{s}^{-1} < \omega < 10^{6}\,\mathrm{s}^{-1}$$

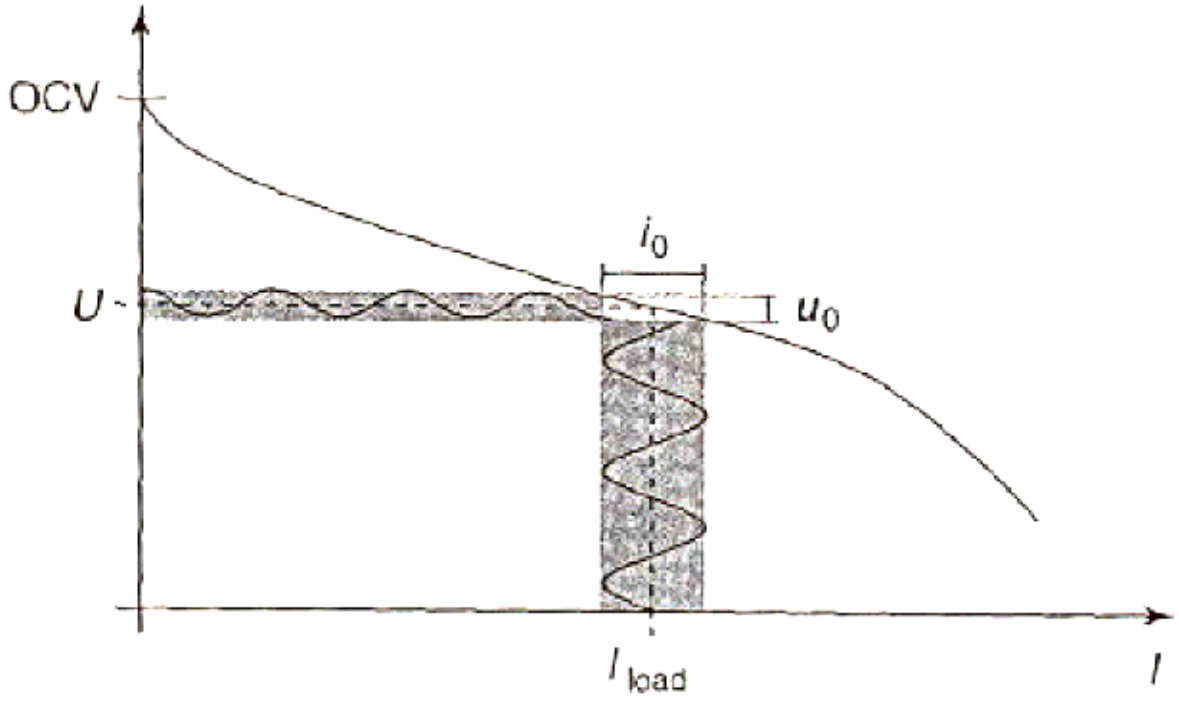
What determines this range?

- **Low frequency limit: stability of the system;**
  at 10^{-3} s^{-1}, one cycle corresponds to 17 min – difficult to provide stable conditions.
- **High frequency limit: limitations of equipment; electrical wiring interferes with measurement, unwanted inductivities.**

➢ **Sample interval of frequencies: determined on a log-scale by number N of sample points, and minimum and maximum frequencies:**

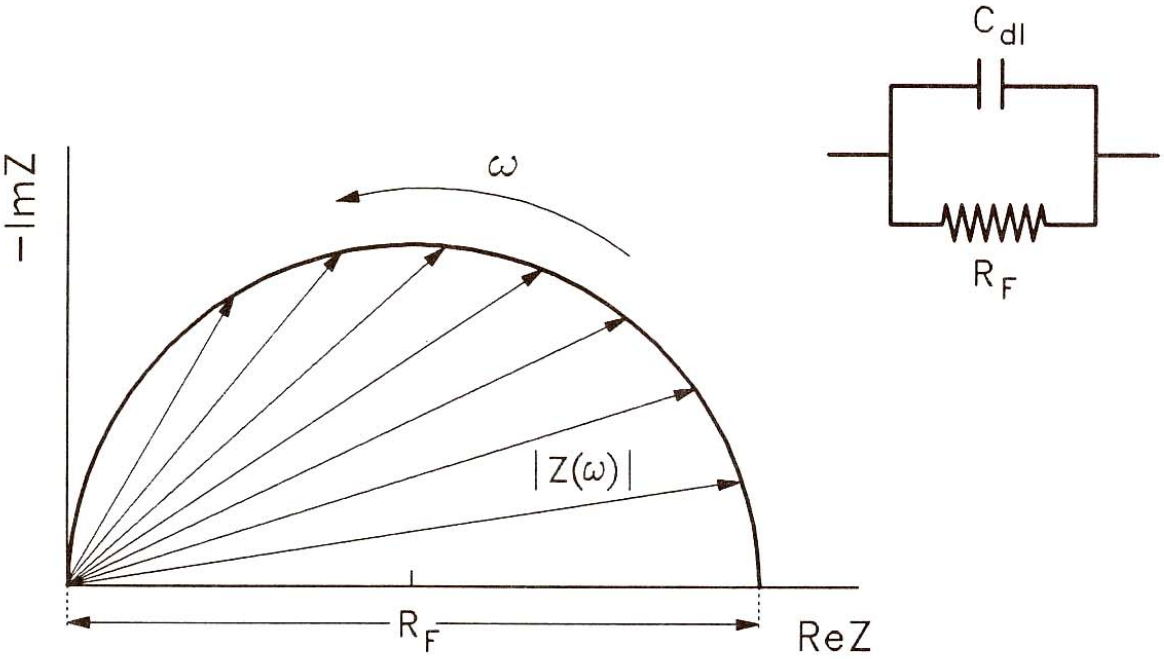
$$T = \frac{1}{N} \ln \frac{\omega_{\max}}{\omega_{\min}}$$

Sinusoidal perturbation of potential and AC current response at fixed working point:



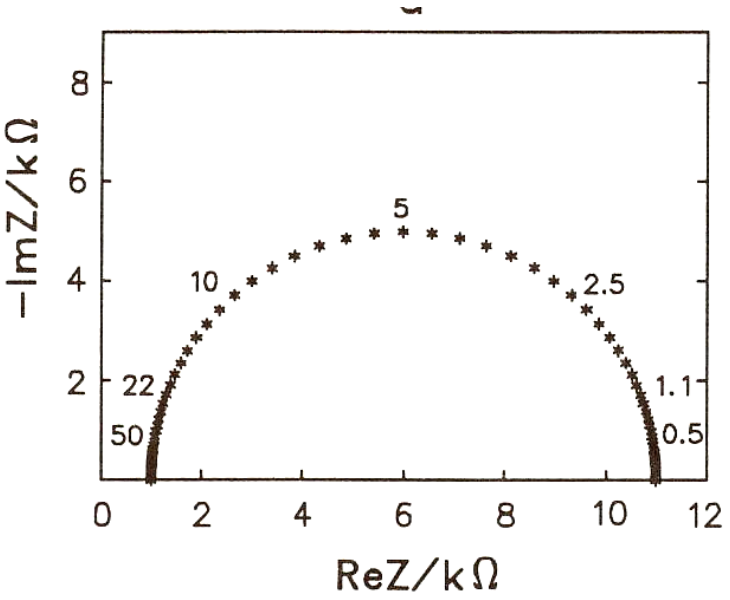
Recording impedances at various frequencies:

impedance spectrum, representing charge transfer and double layer charging at planar electrode (equivalent circuit indicated)



Different ways to display impedance spectra.

NYQUIST-plot (Cole-Cole plot):



$-\mathrm{Im}\left(Z\left(\omega\right)\right)$ **vs.** $\mathrm{Re}\left(Z\left(\omega\right)\right)$

Advantage: characteristic responses of typical elements can be immediately identified

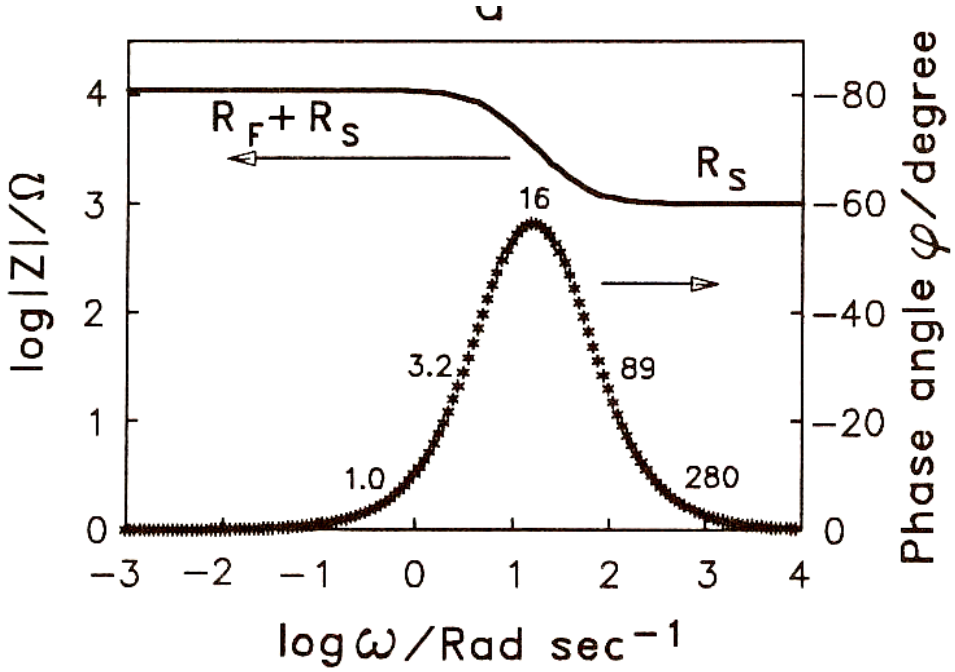
Disadvantage: frequency and phase information usually not explicitly shown - possible misinterpretation

The frequency information is important!!!!

At least frequency at maximum should be shown.

Most cases: $\mathrm{Im}\left(Z\left(\omega\right)\right) < 0$ **- negative imaginary part is plotted on the ordinate in Nyquist-plot.**

BODE-plot:



Absolute impedance $\log\left(\left|Z\left(\omega\right)\right|\right)$ **and phase angle** $\varphi\left(\omega\right)$ **plotted over** $\log\left(\omega\right)$**.**

Phase angle $\varphi = 0$**: real resistances dominates**

Maximum in $\left|\varphi\right|$**: large capacitive current approaching**

Pure capacitance: $\varphi = -90° \ (= -\pi / 2)$

Elements of an Electrochemical Cell

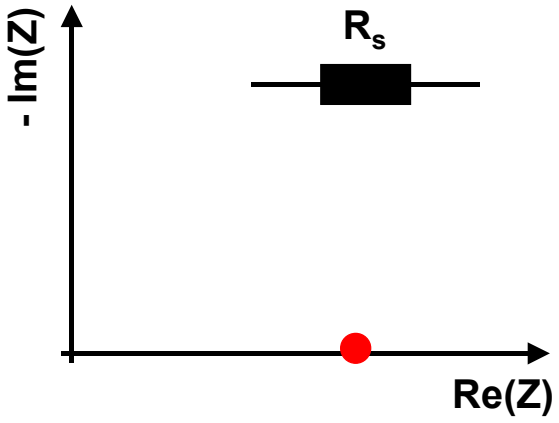
… and their representations in Nyquist plots

I would recommend that you try to figure out as an exercise, how the corresponding Bode-plots look like.

How to derive expressions for complex impedance?

- ❖ Equivalent circuit representation (analog)
- ❖ Kirchhoff equations

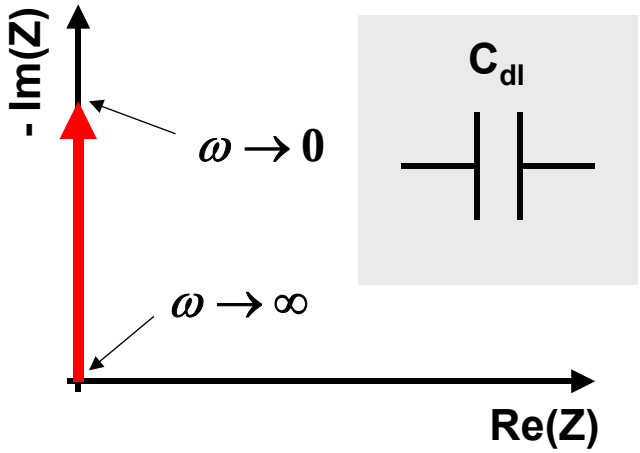
1. Simple resistance



(e.g. solution resistance or ideally non-polarizable electrode with $C_{dl} = 0$)

$$Z = R_s$$ (only real part)

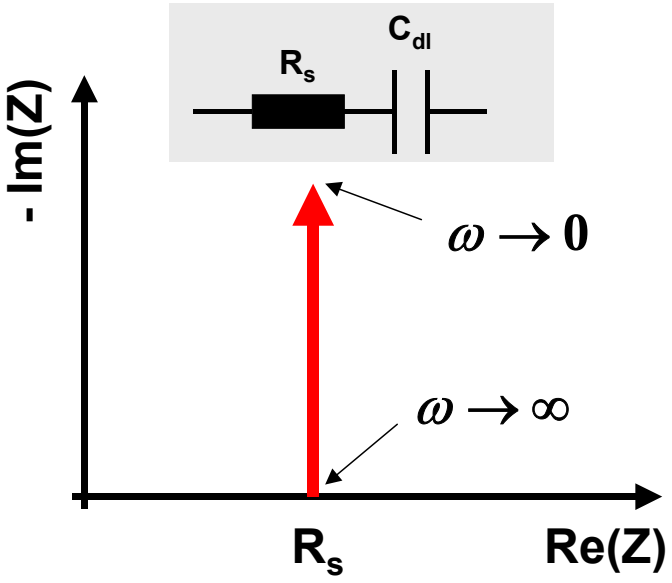
2. Simple capacitance



(e.g. ideally polarizable electrode, $R_F \to \infty$)

$$Z = -\frac{i}{\omega C_{dl}}$$ (only imaginary part)

3. Series of resistance and capacitance

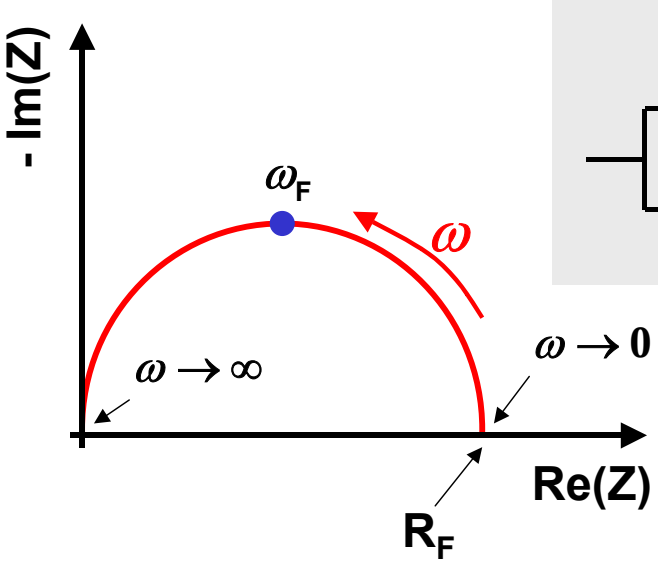


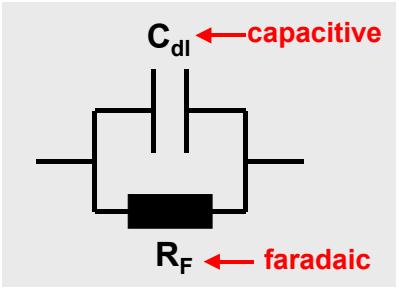
(e.g. charging ideal capacitor: solution resistance and capacitance)

$$Z = R_s - \frac{i}{\omega C_{dl}}$$

4. Capacitor and resistor in parallel

(double layer charging and charge transfer at real, planar electrode)



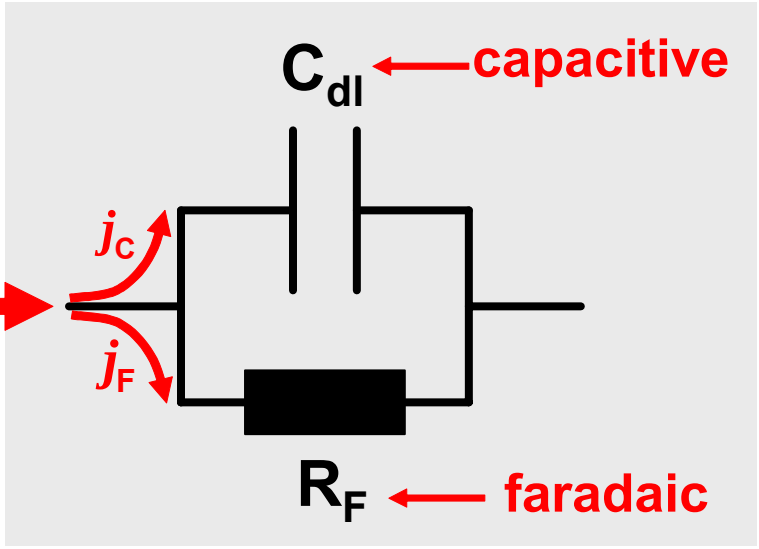


$$Z = \left(\frac{1}{R_F} + i\omega C_{dl} \right)^{-1}$$

$$= R_F \frac{1 - i\,\omega/\omega_F}{1 + \left(\omega/\omega_F\right)^2}$$

Response is semicircle

- **diameter** R_F
- **Frequency at maximum:** $\omega_F = \dfrac{1}{R_F C_{dl}}$



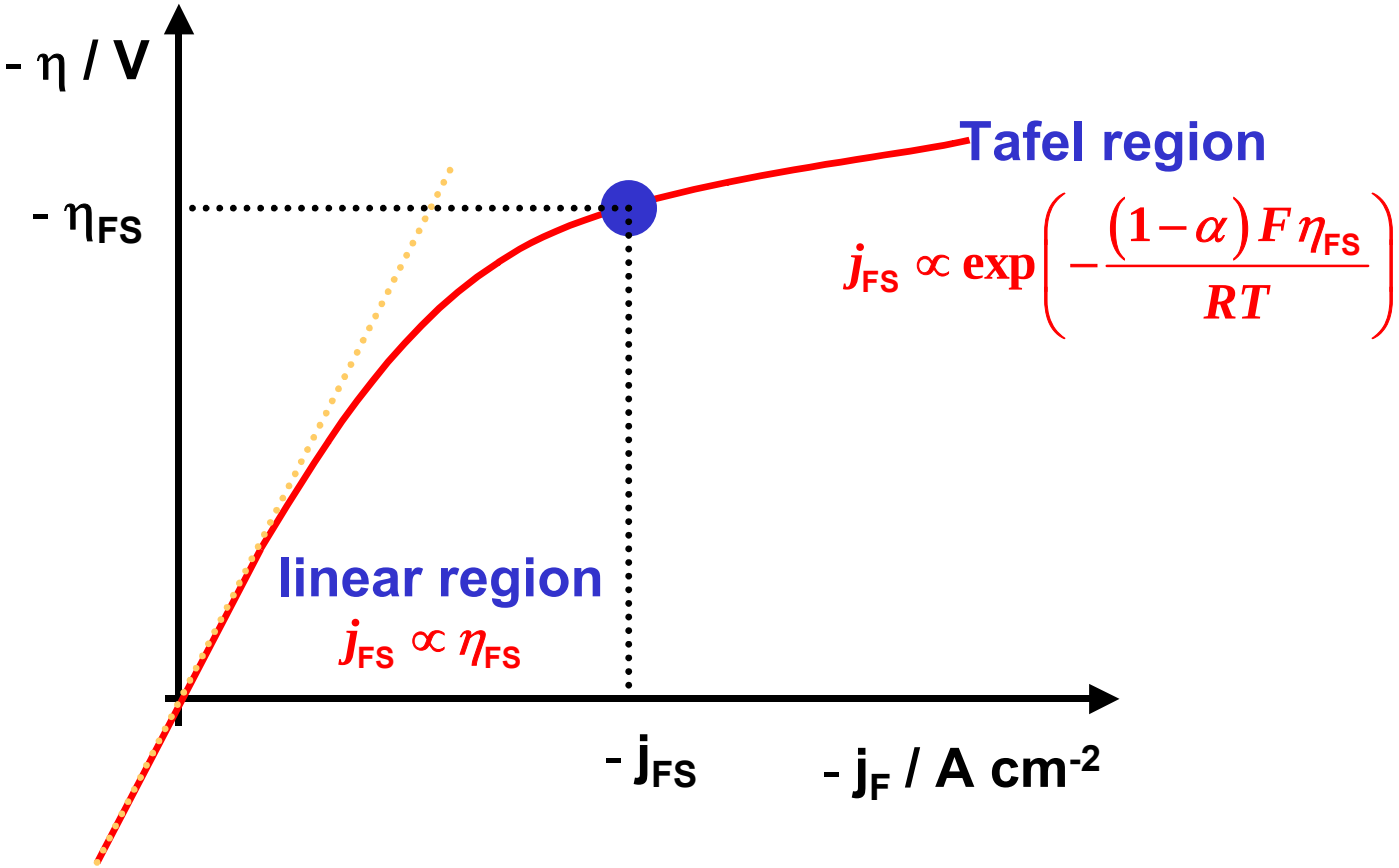
$\omega = \omega_F$: $j_C = j_F$

$\omega << \omega_F$: $j_C << j_F$ (faradaic)

$\omega >> \omega_F$: $j_C >> j_F$ (capacitive)

Now, let's consider response involving faradaic and capacitive processes at an electrode in more detail.

With respect to charge transfer: Can EIS only be used in the linear (reversible) region of the overpotential vs. current density plot?



Answer: EIS can also be used in Tafel-region, where relation between j_{FS} and η_{FS} is non-linear!

How does it work?

Working point (steady state): E_S and $j_S = j_{FS} + j_{CS} = j_{FS}$

(no stationary capacitive current!)

Consider perturbation and linear response:

$$\delta E = E_0 \exp(i\omega t) \quad \underset{\text{response}}{\overset{\text{linear}}{\longleftrightarrow}} \quad \delta j = j_0 \exp(i\omega t)$$

Relation between δE and δj in …

(1.) Linear region

$$\delta j = \delta j_F + \delta j_C$$

$$= \frac{\delta E}{R_{CT}} + \frac{d(\delta Q)}{A_s dt}$$

$$\delta Q = A_s C_{dl} \delta E \Rightarrow = \frac{\delta E}{R_{CT}} + C_{dl} \frac{d(\delta E)}{dt}$$

$$\frac{d(\delta E)}{dt} = i\omega \delta E \Rightarrow = \left(\frac{1}{R_{CT}} + i\omega C_{dl} \right) \delta E$$

$$j_0 \cancel{\exp(i\omega t)} = \left(\frac{1}{R_{CT}} + i\omega C_{dl} \right) E_0 \cancel{\exp(i\omega t)}$$

$$\Rightarrow \boxed{Z(\omega) = \frac{\delta E}{\delta j} = \frac{E_0}{j_0} = \frac{1}{\frac{1}{R_{CT}} + i\omega C_{dl}}}$$

Electrode impedance in linear region:

$$Z = R_{CT}\frac{1 - i\,\omega/\omega_{CT}}{1 + \left(\omega/\omega_{CT}\right)^2}$$

with

$$R_{CT} = \frac{RT}{Fj^0} \text{ and } \omega_{CT} = \frac{1}{R_{CT}C_{dl}} = \frac{Fj^0}{RTC_{dl}}$$

Response is determined by C_{dl} and j^0, independent of working point.

(2.) Tafel region

again: $\delta j = \delta j_F + \delta j_C,\ j = j_S + \delta j,\ E = E_S + \delta E$

Faradaic current (cathodic reaction):

$$-j_F = nFk^0 c_{ox}^b \exp\left(-\frac{(1-\alpha)F\left(E - E^0\right)}{RT}\right)$$

Can this be written as $-j_F = -j_{FS} + \delta j_F$ **?**

Insert $E = E_S + \delta E$

$$-j_F = nFk^0 c_{ox}^b \exp\left(-\frac{(1-\alpha)F\left(E_S - E^0\right)}{RT}\right)\exp\left(-\frac{(1-\alpha)F\delta E}{RT}\right)$$

$$\approx \quad -j_{FS} \quad \text{X} \quad \left(1-\frac{(1-\alpha)F}{RT}\delta E\right)$$

Taylor expansion on second line. Perturbation has to be small,

$$\delta E << \frac{RT}{(1-\alpha)F},$$

i.e. $E_0 \approx 5-10$ mV is usually sufficient for this.

Then, we finally get

$$-j_F = -j_{FS} + \frac{(1-\alpha)F}{RT} j_{FS}\delta E$$

This is exactly the relation we have been looking for. The response is linear:

$$\delta j = \frac{(1-\alpha)F}{RT} j_{FS}\delta E$$

or

$$\delta E = R_F \delta j \text{ with } R_F = \frac{RT}{(1-\alpha)F}\frac{1}{j_{FS}}$$

As you can see, differential faradaic resistance, R_F, in the Tafel region is determined by transfer coefficient α and by current density at the working point, j_{FS}.

Remember: The response to a small enough signal ($\delta E < 5$ - 10 mV) can be linear, even though the system is in the non-linear Tafel-region.

The impedance is given by

$$Z = R_F \frac{1 - i\,\omega/\omega_F}{1 + \left(\omega/\omega_F\right)^2}$$

Resulting Nyquist-plot is semicircle.

- diameter $$R_F = \frac{RT}{(1-\alpha)F}\frac{1}{j_{FS}}$$
- characteristic frequency (maximum of semicircle)

$$\omega_F = \frac{(1-\alpha)F}{RTC_{dl}} j_{FS}$$

Summary: impedance response of planar electrode gives

- … in the linear case: j^0 and C_{dl}
- … in the Tafel case: α and C_{dl}

EXAMPLE: Some results for electrode overpotential

- Consider cathode reaction
- Assume intermediate rate constant $k^0 = 10^{-3}\,\mathrm{cm\ s^{-1}}$

  Reversible or irreversible? Depends on working point.
- Equal concentrations of ox./red. species,

  $c_{ox}^{b} = c_{red}^{b} = 10^{-2}\,\mathrm{mol/l} = 10^{-5}\,\mathrm{mol/cm^3}$

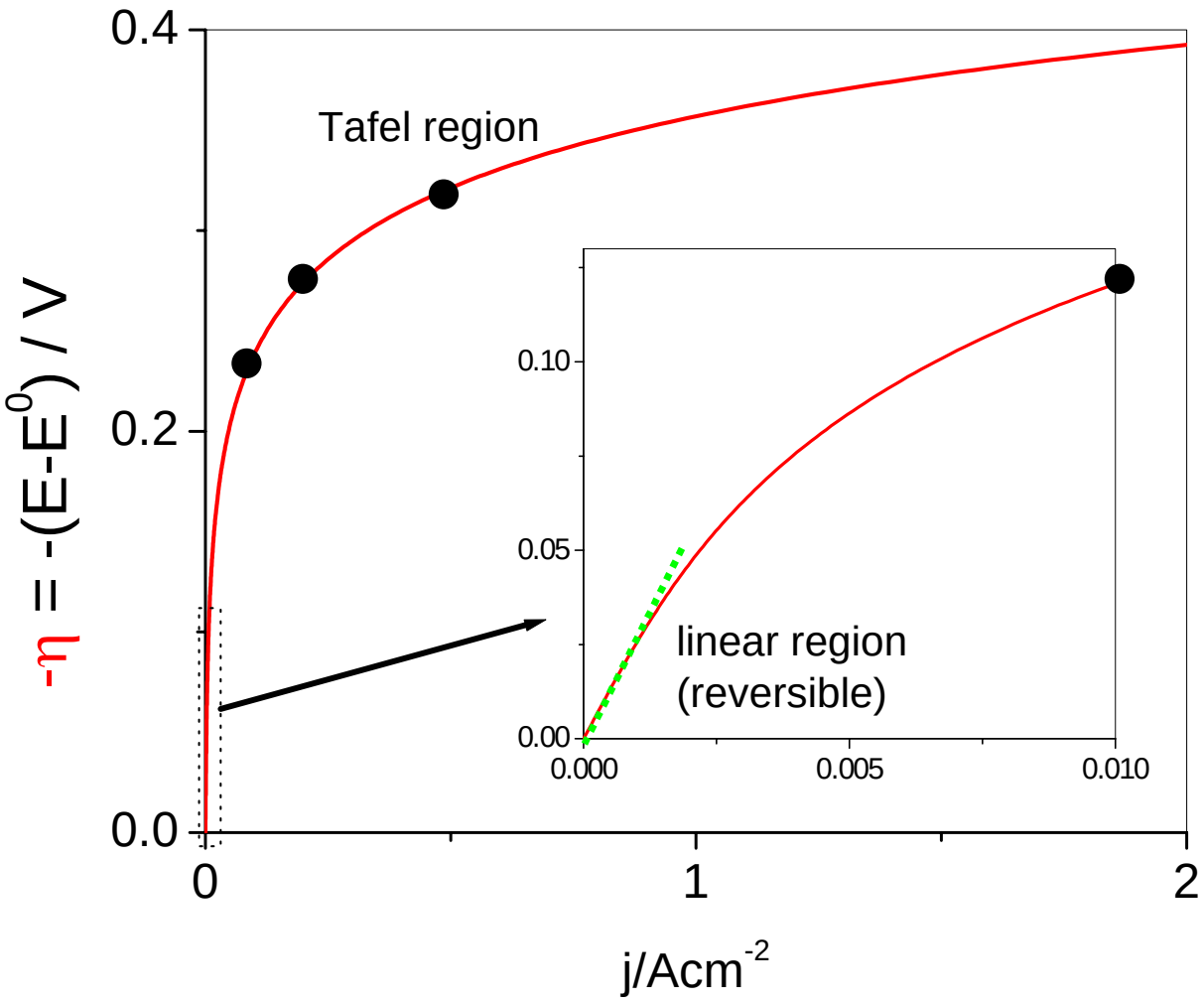
  What does this mean for the equilibrium potential?
- Exchange current density

  $j^0 = Fk^0 c_{red}^{b\ (1-\alpha)} c_{ox}^{b\ \alpha} = 0.965 \cdot 10^{-3}\,\mathrm{A\ cm^2}$ (with $n = 1$)
- Charge transfer resistance (linear region)

$$R_{CT} = \frac{RT}{F}\frac{1}{j^0} = \frac{b}{j^0} = 26.63\ \Omega\ \mathrm{cm^2}$$

- Transfer coefficient $\alpha = 0.5$

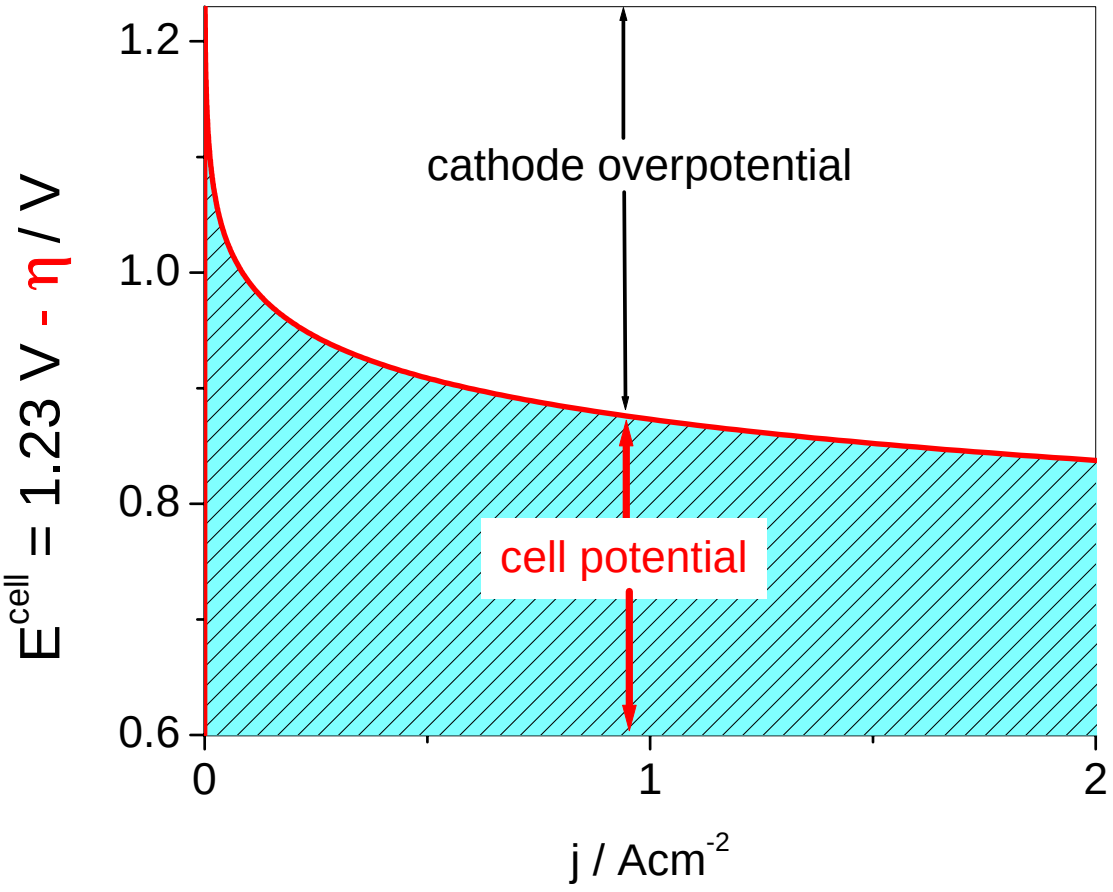
Overpotential vs. current density plot



Inset: small current densities (linear behavior)

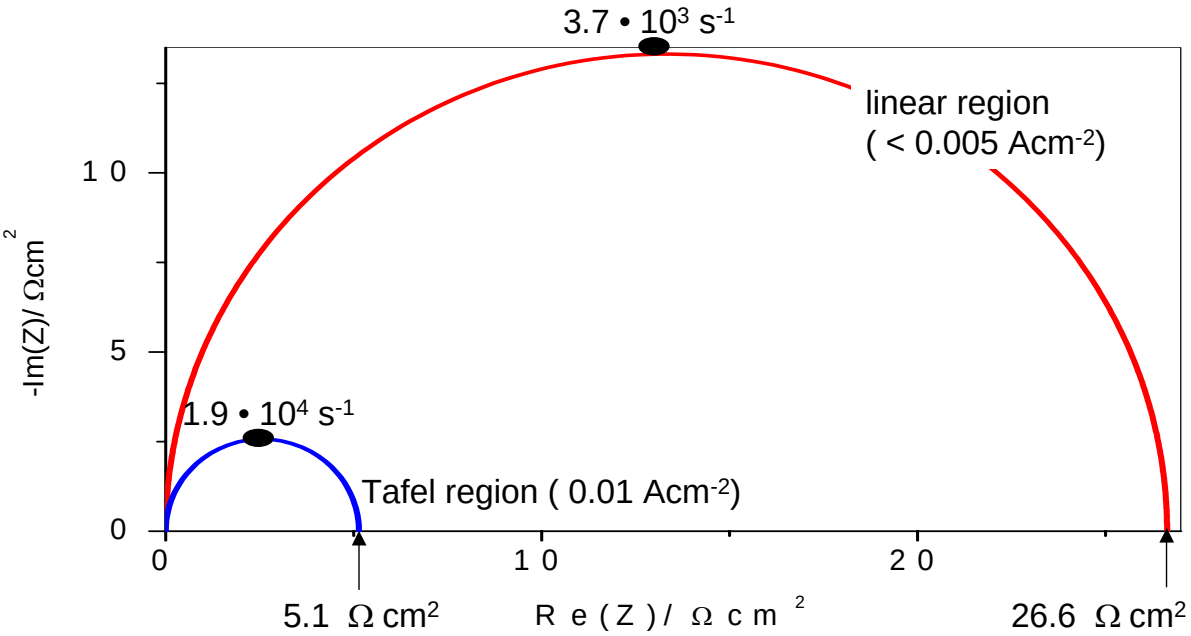
Next plot: cell potential, i.e. the difference of equilibrium potential and cathode overpotential (assume: all other overpotentials negligible), vs. current density

Cell potential vs. current density plot (H_2/O_2 fuel cell)

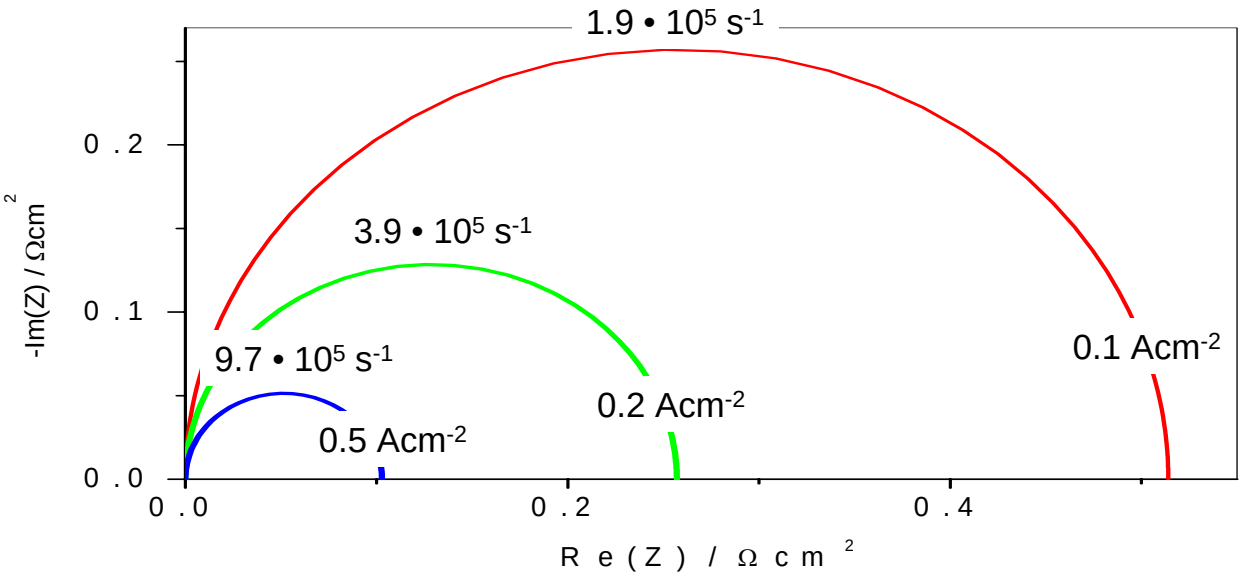


Impedance spectra (IS) shown below for linear region and for 4 points in Tafel region indicated in overpotential vs. current density plot.

Impedance spectra (IS): linear and Tafel region



Tafel region at different working points



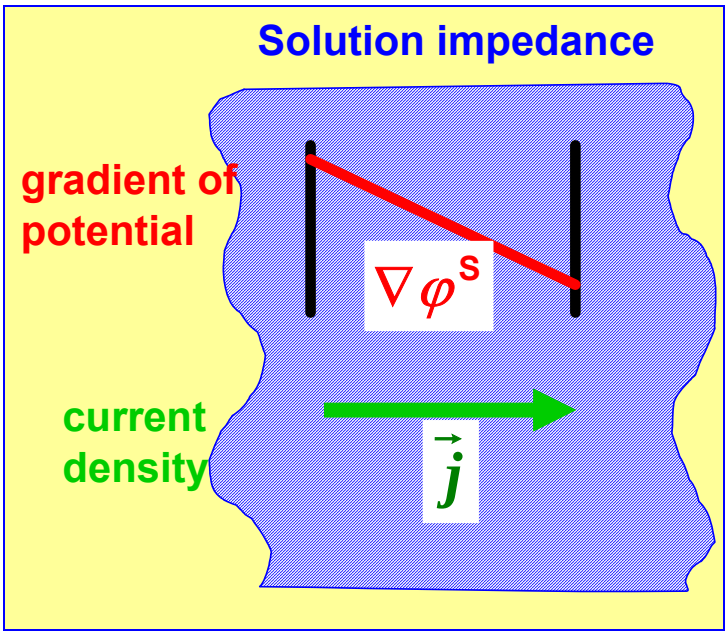
- **Linear region:** IS independent of working point, only determined by the exchange current density
- **Tafel region:** radius of semicircle decreases with increasing current density, whereas the characteristic frequency increases
- **Larger current densities**: ω_F exceeds upper limit of feasibility of IS (specified before as 10^6 s^{-1}). Only part of semicircle could be measured

Decrease of faradaic resistance R_F (= diameter of semicircle) with increasing j_{FS}: counterintuitive at first sight, right? How can we rationalize that?

R_F **: slope of overpotential vs. current density relation at working point. Due to exponential relation between current density and overpotential, slope decreases with increasing j_{FS} – obvious in the figure of η vs. j above.**

Further Elements in Electrochemical Systems

Solution Impedance



What about the resistance in electrolyte solution? How does it look like in impedance spectra?

Flux of electrical current through electrochemical cell:

- **electric field in solution (= - gradient of potential) is driving force for movement of ions**
- **Electrical current density is given by** $\vec{j} = -\sigma_s \nabla \varphi^s$

  σ_s **: conductivity of solution,** φ^s **: local potential**
- **Resistance of volume element in solution (surface area** A_s **and length** l **, see picture) is given by**

$$R_S = \frac{l}{\sigma_s A_s}$$

With respect to ion transport: solution behaves like an ideal (linear) resistance.

Is that all? Besides being an **ion conductor**…

- ❑ **electrolyte solution** is **dielectric medium**
- ❑ molecules possess **spatially distributed and flexible charges** and **electric dipole moments**
- ❑ **electric polarization in applied electric field** (the same field that causes ions to move)

Various mechanisms cause **displacement of electric charge** in matter and contribute to **polarizability**:

Rotations, vibrations, electronic polarizability

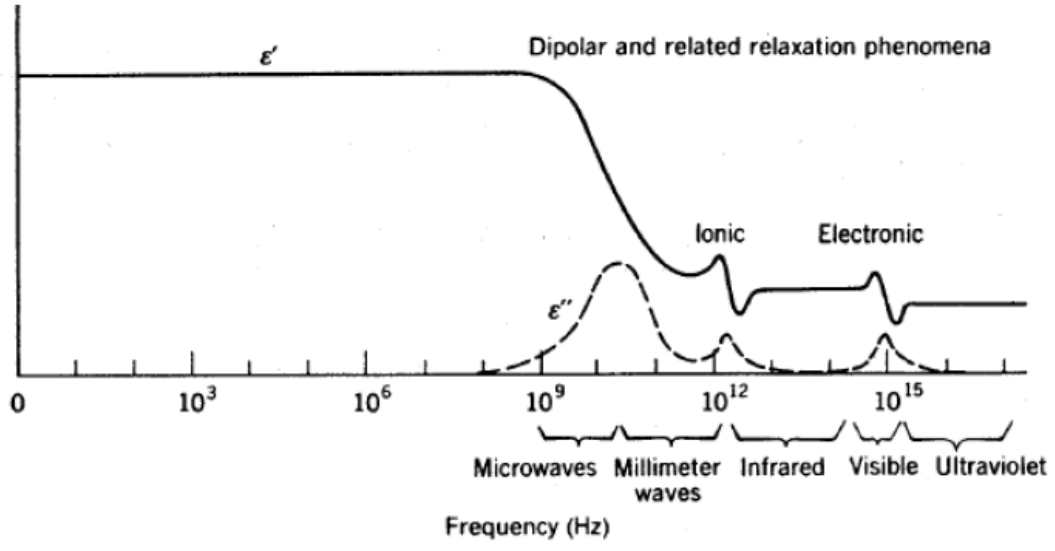
→ contribute to **dielectric constant** ε of the medium,

→ in general a **function of the frequency**:

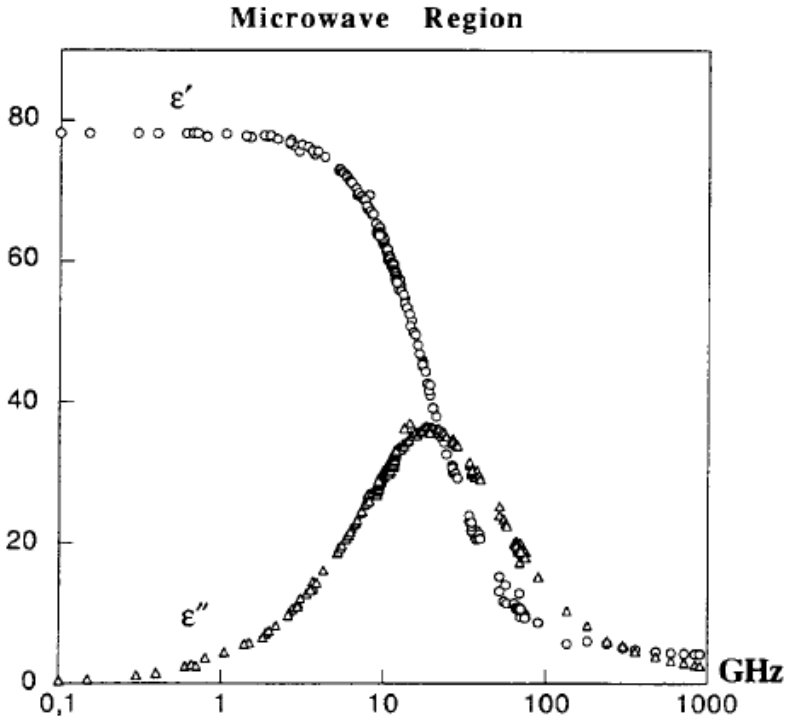
- ❑ **lowest** ω: all interactions possible, **largest** ε
- ❑ **increasing** ω: dipole reorientations too slow, cannot respond to oscillating field, ε **decreases**

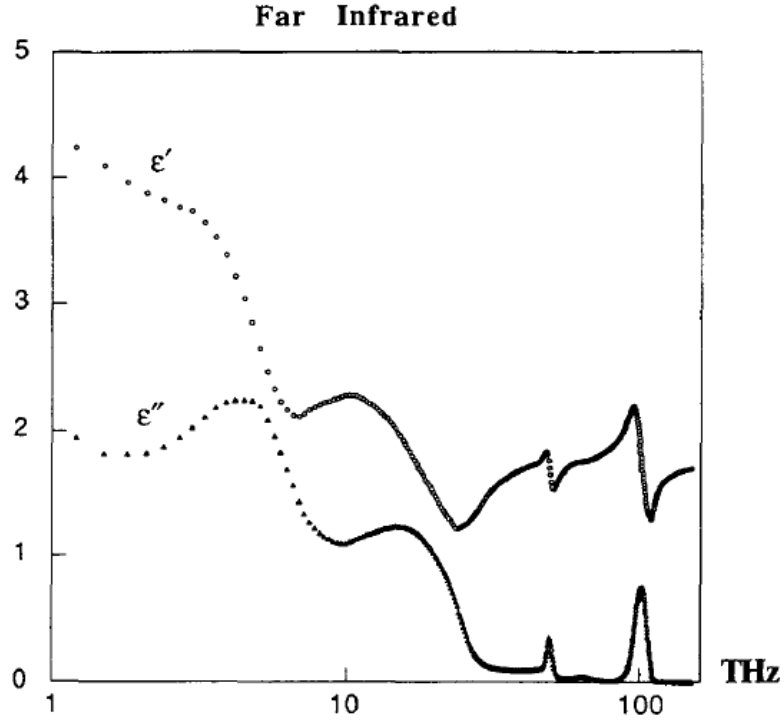
Water: all processes contribute to ε for $\omega < 10^8\,\mathrm{s}^{-1}$

→ dielectric constant is $\varepsilon \approx 80$ at such low frequencies



Dielectric permittivity of water [J.W. Ellison et al., J. Mol. Liq. 68, 171 (1996).]



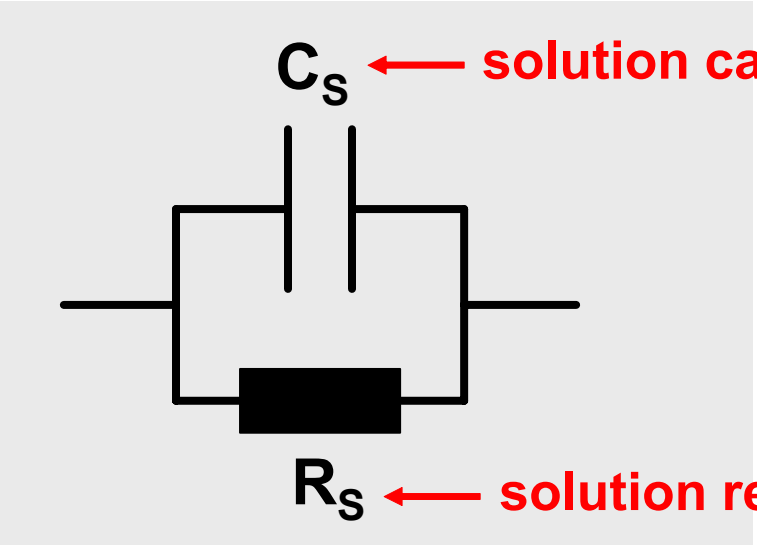


Due to polarizability: volume element in solution (surface area A_S and length l) possesses **capacitance**:

$$C_S = \varepsilon\varepsilon_0 \frac{A_S}{l}$$

where ε_0 is the **dielectric constant** of vacuum.

Equivalent circuit representing impedance of solution:



Expected response in Nyquist-plots: semicircle!

What will typically be seen of this response in IS?

Let's calculate the characteristic frequency:

$$\omega_S = \frac{1}{R_S C_S} = \frac{\sigma_S A_S}{l} \frac{l}{\varepsilon\varepsilon_0 A_S} = \frac{\sigma_S}{\varepsilon\varepsilon_0}$$

(this is the frequency at which capacitive and resistive current in the circuit have the same absolute value)

Estimate:

$\sigma_S \sim 10^{-2} - 10^{-1}$ S cm^{-1}, $\varepsilon \approx 80$, $\varepsilon_0 = 8.8542 \cdot 10^{-12}$ A s V^{-1}m^{-1}

$$\rightarrow \omega_S \approx 10^{10} \text{ s}^{-1}$$

Based on this estimate: what do you expect to see?

Usual equipment: upper limit for IS is $\omega_{max} \approx 10^6$ s^{-1}

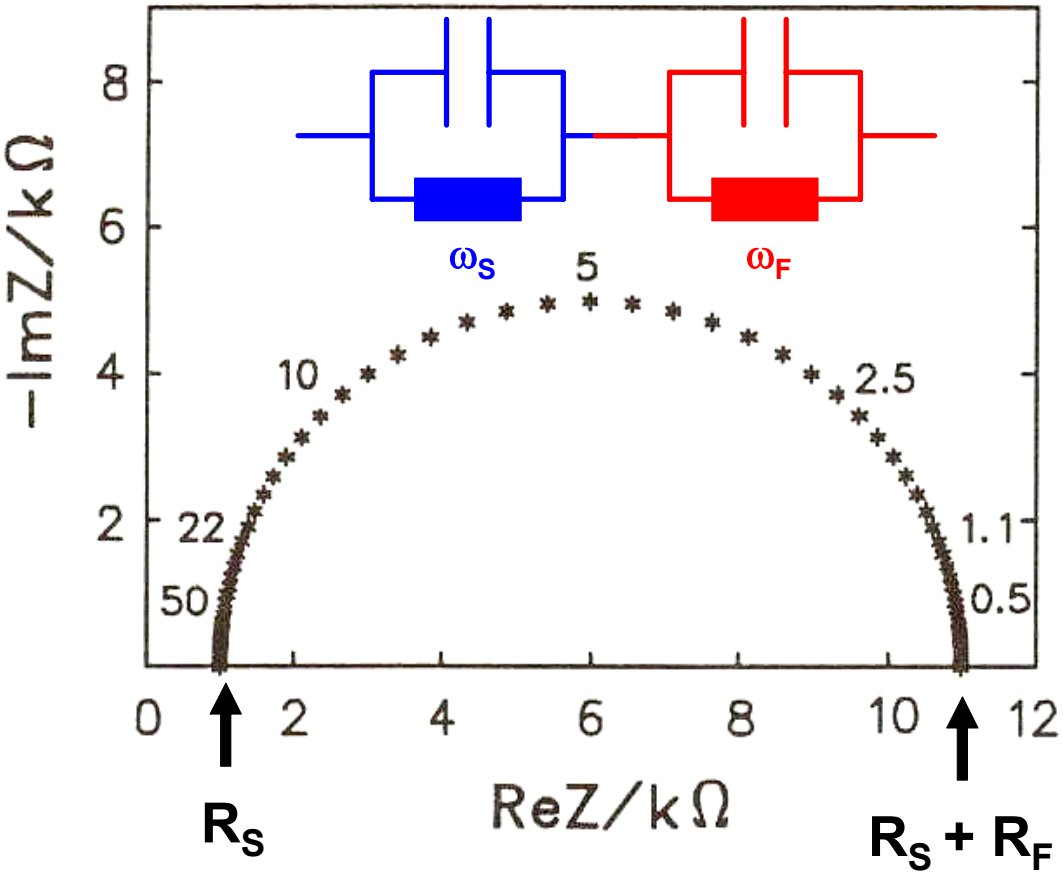
Such frequencies: capacitive current contribution negligible – one will only see a dot, representing real solution resistance in IS.

For full IS of electrolyte solutions: use frequencies in microwave region, $\omega > 10^9$ s^{-1} ($f > 10^8$ s^{-1})

Remember: we are talking about angular frequencies ω.

Related to genuine frequency, ν **or** f **[Hz], via** $\omega = 2\pi f$.

IS and equivalent circuit for system involving processes at surface of a planar electrode and processes in electrolyte solution are shown in the following figure.



Effect of Diffusion

Mass transport of reactant species in solution:

resistance to the progress of charge transfer reactions

Supply of reactant molecules not rapid enough:

diffusion is overall limiting step

How does this resistance to mass transport translate into a complex impedance?

Diffusion impedance (electrode under diffusion control):

- **diffusion equation (Fick's second law) and boundary condition (see chapter on mass transport)**
- **can be solved in complete analogy for low amplitude sine wave (AC current) superimposed on DC current**

With the semi-infinite boundary conditions, as used before, the solution gives the so-called Warburg impedance:

$$Z_W(\omega) = \frac{\sigma}{\omega^{1/2}}(1-i)$$

where

$$\sigma = \frac{RT}{(nF)^2}\frac{1}{2^{1/2}}\left\{\frac{1}{D_{ox}^{1/2}c_{ox}^{b}} + \frac{1}{D_{red}^{1/2}c_{red}^{b}}\right\}$$

Straight line with slope 1 (phase angle $\varphi = \frac{\pi}{4}$) in Nyquist plot (-Im(Z) over Re(Z)).

Impedance is proportional to $\omega^{-1/2}$.

This means: the Warburg impedance increases with decreasing ω.