Please, note the following error in the notes "lecture19+20" (Hydrodynamic electrodes and Microelectrodes): on page two, 3rd line, the correct expression for the exchange current density should be

$$j^0 = Fk^0 c_{red}^{b\,(1-a)} c_{ox}^{b\,a}$$

as defined before (in the part on electrode kinetics).

Electrochemical Impedance Spectroscopy (EIS)

The purpose of this techniques is the same as for Cyclic Voltammetry:

- characterization of electrochemical systems
- understanding the interplay of relevant physical and chemical processes which may occur on widely different time scales, i.e. with widely varying rate constants (consider for instance the range over which the kineric rate constant of charge transfer processes, k^0, could vary!!!)
- determine relevant parameters.

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

- Double layer charging ® C_{dl}
- Charge transfer ® k^0, a, j^0
- Mass transport ® D, d
- Adsorption, desorption ® q, k_{ad}, k_{des}

All these processes and parameters are coupled to each other in a complex way. There are two ways to disentangle this "mess":

- **Use selective experimental techniques, which single out and probe one particular process in the system (e.g. use supporting electrolyte to eliminate migration in solution, use rotating disc electrode to eliminate diffusion limitations, etc.). However, such techniques are usually only applicable to simple structures (e.g. planar, smooth electrodes, semi-infinite diffusion), under well-defined conditions, with controlled parameters (uniform concentrations in bulk solution, fixed temperature). These are studies on model systems or ex-situ studies.**
- **Use cumulative methods, like CV and EIS, which can probe the dynamic behaviour of a system over a broad range of scales and contain information on the full coupling between different processes. Such techniques can be used to study real systems under realistic conditions, i.e. in-situ, e.g. an operating fuel cell, corrosion processes, etc. However, we need simple analogues (like for instance equivalent circuits) or physical models to discriminate the processes and to be able to extract particular parameters.**

Impedance Spectroscopy

In impedance spectroscopy, a sinusoidally varying potential dE is applied to the electrochemical interface or to the complete electrochemical cell. As we will see below, this signal could be applied in addition to a steady state potential. This potential variation can be written as (in complex notation)

$$dE(t) = E_0 \exp(iwt),$$

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

It is completely defined through its amplitude E_0 and the angular frequency w. The response of current (AC current) to this potential perturbation is measured. When the amplitude E_0 is small, i.e. $E_0 << \frac{RT}{F} \approx 25.7$ mV, the response in AC current density will be linear, i.e.

$$dj(t) = j_0 \exp(iwt).$$

The amplitude j_0 of this current density is generally complex. Overall, we, thus, have to consider the phase and the amplitude of $dj(t)$ relative to $dE(t)$. The well-known concept of electrical resistance has to be extended. The complex impedance is defined as

$$\boxed{Z = \frac{dE(t)}{dj(t)} = \frac{E_0}{j_0}}.$$

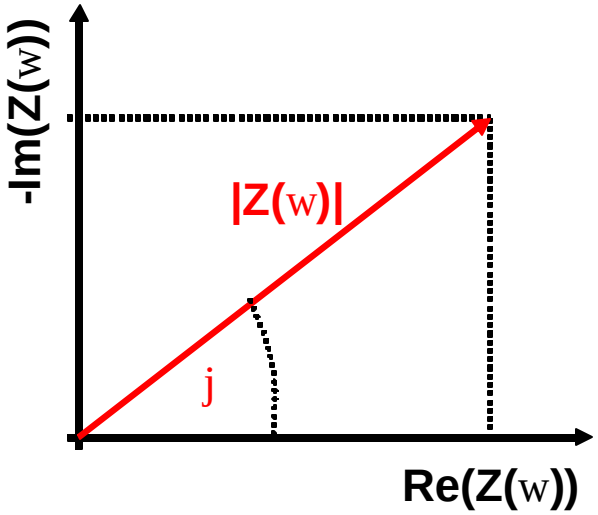
The impedance is a function of the frequency w. Since $Z(w)$ is a complex quantity, it can be decomposed into real and imaginary part,

$$Z(w) = \mathrm{Re}(Z(w)) + i\,\mathrm{Im}(Z(w)) = |Z(w)| \exp(ij)$$

or alternatively into absolute value and phase angle

$$|Z(w)| = \left(\mathrm{Re}(Z(w))^2 + \mathrm{Im}(Z(w))^2\right)^{1/2} \text{ and } j = \arctan\left(-\frac{\mathrm{Im}(Z(w))}{\mathrm{Re}(Z(w))}\right).$$

The complex plane representation displays these pieces of information



Impedance measurement

In practice, the impedance measurement is performed in the following way:

- **The working point is fixed. This is a point of stationary operation of the considered electrochemical system, i.e. fixed point on the steady state current voltage curve:** j_s, E_s
- **Using a frequency response analyzer, a small-signal harmonic variation,** $dE(t) = E_0 \exp(iwt)$, **is added to the steady state potential. The resulting electrode or cell potential is, thus,**

$$E(t) = E_s + dE(t) = E_s + E_0 \exp(iwt)$$

- **Measure the resulting current signal,**

$$j(t) = j_s + dj(t) = j_s + j_0 \exp(iwt),$$

extract the AC part

$$dj(t) = j_0 \exp(iwt)$$

- **The impedance can be determined as** $Z = \frac{E_0}{j_0}$
- **Frequencies are sampled over the relevant range, determined by the limitations of the equipment and the range of characteristic**

frequencies in the system. The typical range of feasible frequencies for recording impedance spectra is:

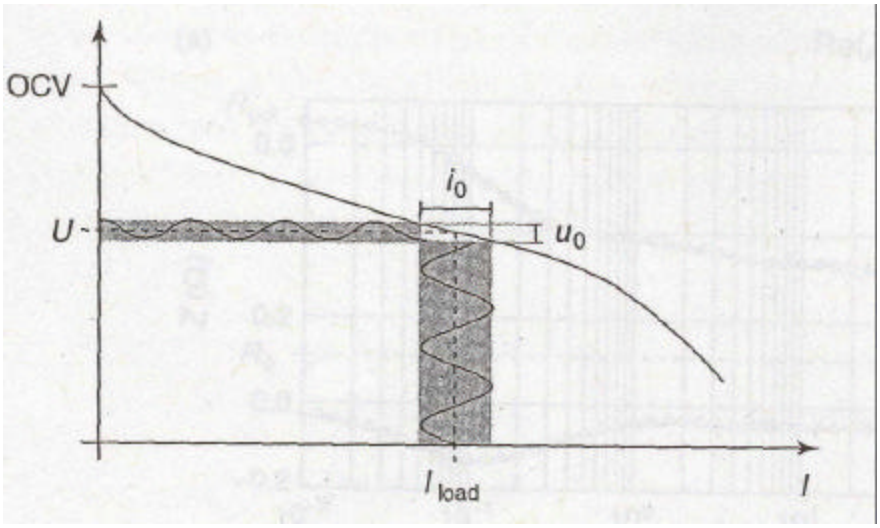
$$10^{-3}\,s^{-1} < w < 10^{6}\,s^{-1}$$

Stability of the system determines the lower limit. At 10^{-3} s^{-1}, one cycle corresponds to 17 min. It is difficult to provide stable conditions for such long times, i.e. low frequencies. At the large frequency limit, the electrical wiring of the equipment interferes with the measurement. Unwanted inductivities become important.

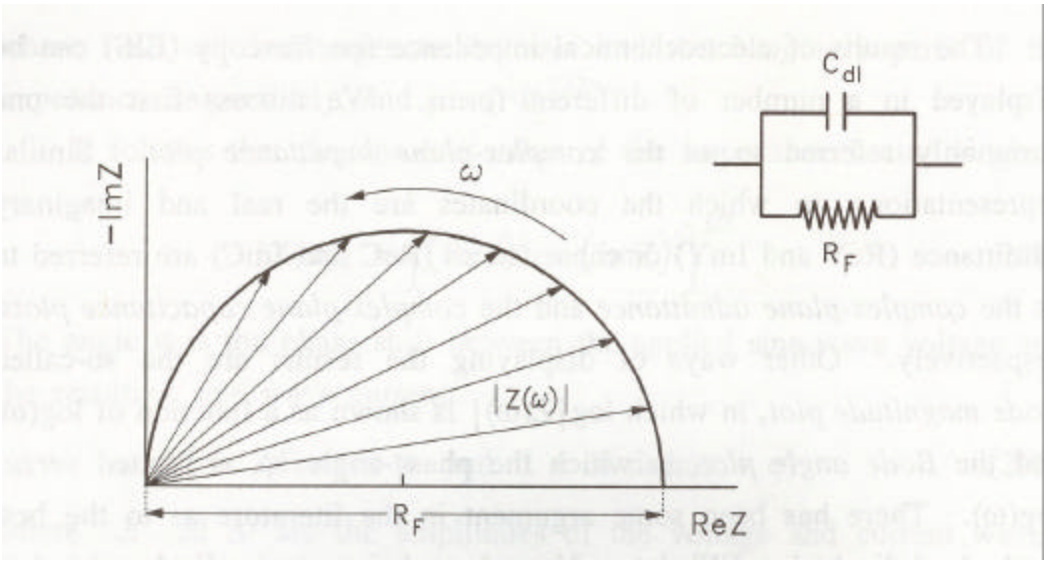
- **Usually, the sample interval is determined on a logarithmic scale by the number N of sample points, and the minimum and maximum frequencies:**

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

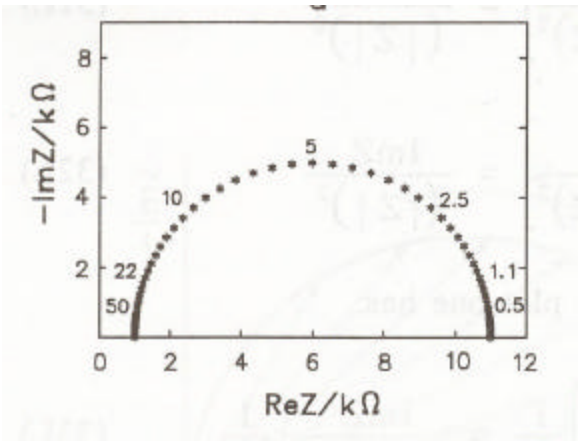
The following picture illustrates the sinusoidal perturbation of potential and the corresponding AC current response at a fixed working point of the electrochemical cell.



After recording impedances at various frequencies, the following picture is obtained. This picture shows as an example the impedance spectrum for a parallel equivalent circuit of faradaic resistance and double layer capacitance. As discussed below, this circuit can represent a simple charge transfer process at a planar electrode.



Connecting the points at different frequencies results in the so-called impedance spectrum. There are different ways to display the information in impedance spectra.

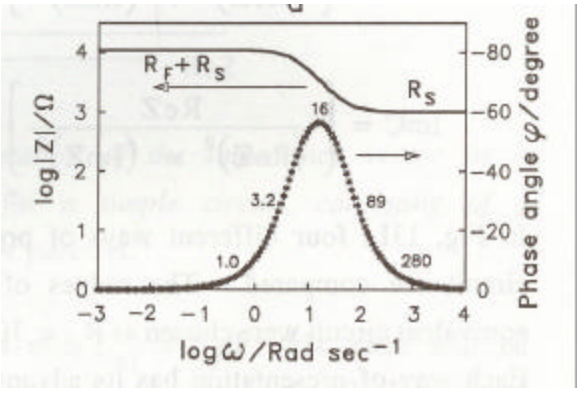


NYQUIST-plot (Cole-Cole plot):

In this representation, $-\mathrm{Im}(Z(w))$ is plotted over $\mathrm{Re}(Z(w))$. The advantage is that characteristic responses of typical elements can be immediately identified. The disadvantage is that the frequency information is usually not explicitly given. In this example, some frequencies are indicated on the graph. But usually they are not shown. This could give rise to misinterpretation of Nyquist-plots.

The frequency information is important!!!!

In any impedance spectrum, at least the frequency at the maximum should be shown. As we will see, in most cases, electrochemical systems have impedance spectra with $\mathrm{Im}(Z) < 0$. Therefore, the negative imaginary part is plotted on the ordinate.



BODE-plot:

$\log(|Z(w)|)$ and phase angle $j(w)$ are plotted over $\log(w)$. A phase angle $j \approx 0$ indicates that real resistances dominates. The maximum in j corresponds to a large capacitive current, approaching 90° ($=\frac{p}{4}$) for a pure capacitance.

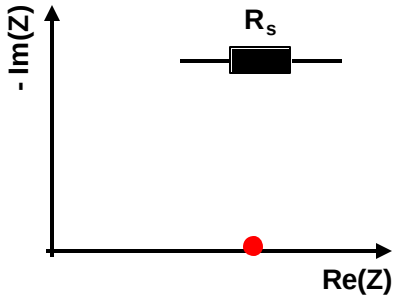
Elements of an Electrochemical Cell

In this section, the elements of an electrochemical cell will be discussed, and their representations in Nyquist plots will be depicted (from simple to complex).

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

1. Simple resistance

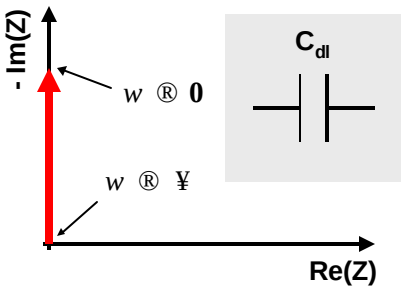
(e.g. solution resistance or ideally non-polarizable electrode with $C_{dl} = 0$)



$\boxed{Z = R_s}$ **(only real part)**

2. Simple capacitance

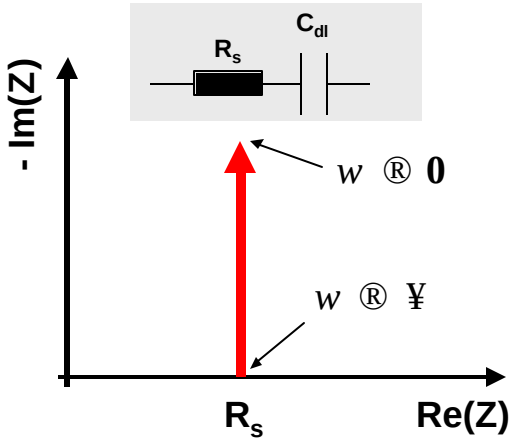
(e.g. ideally polarizable electrode, $R_F \to \infty$)



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

3. Series of resistance and capacitance

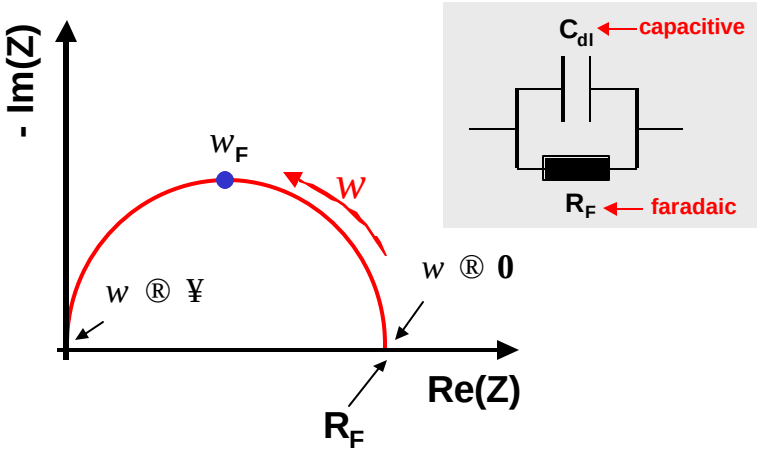
(e.g. charging of ideal capacitor: solution resistance and capacitance)



$$Z = R_s - \frac{i}{wC_{dl}}$$

4. Capacitor and resistor in parallel

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



$$Z = \left(\frac{1}{R_F} + iwC_{dl}\right)^{-1} = R_F \frac{1 - iw/w_F}{1 + (w/w_F)^2}$$

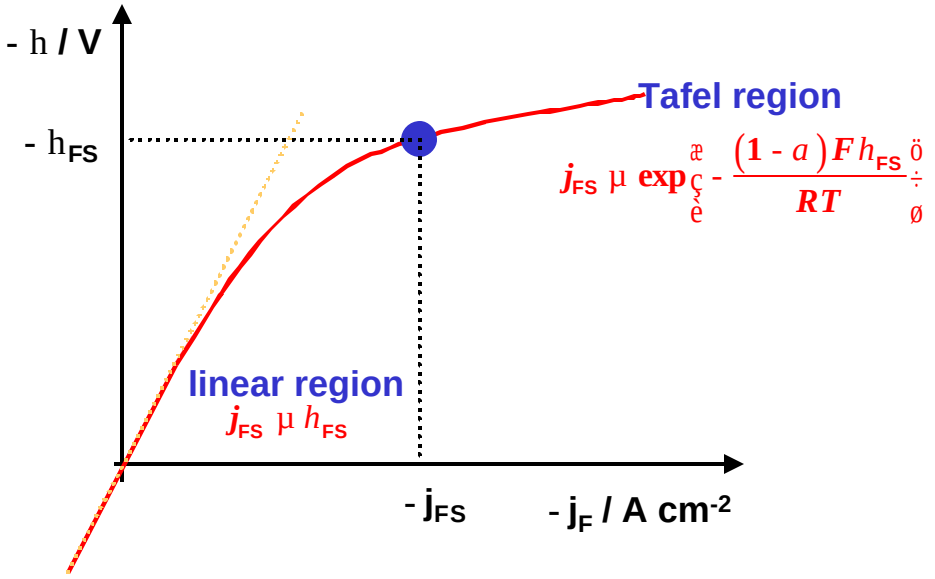
Response is semicircle with diameter R_F

Frequency at maximum:

$$w_F = \frac{1}{R_F C_{dl}}$$

Now, let's consider the previous case 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 h_{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:

$$dE = E_0 \exp(iwt) \quad \overset{\text{linear}}{\underset{\text{response}}{\Longleftrightarrow}} \quad dj = j_0 \exp(iwt)$$

Let's derive the relation between dE and dj, first in the linear region and then in the Tafel-region:

(1.) Linear region

$$dj = dj_F + dj_C$$

$$= \frac{dE}{R_{CT}} + \frac{d(dQ)}{dt}$$

$$dQ = C_{dl} dE \Rightarrow = \frac{dE}{R_{CT}} + C_{dl}\frac{d(dE)}{dt}$$

$$\frac{d(dE)}{dt} = iw\,dE \Rightarrow = \left(\frac{1}{R_{CT}} + iwC_{dl}\right) dE$$

$$j_0 \exp(iwt) = \left(\frac{1}{R_{CT}} + iwC_{dl}\right) E_0 \exp(iwt)$$

$$\Rightarrow \boxed{Z(w) = \frac{dE}{dj} = \frac{E_0}{j_0} = \frac{1}{\frac{1}{R_{CT}} + iwC_{dl}}}$$

Electrode impedance in linear region:

$$\boxed{Z = R_{CT}\frac{1 - iw/w_{CT}}{1 + (w/w_{CT})^2}}$$

with

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

In other words: the response is determined by the double layer capacitance, C_{dl}, and by the exchange current density, j^0. It is independent of the working point.

(2.) <u>Tafel region</u>

again: $dj = dj_F + dj_C,\ j = j_S + dj,\ E = E_S + dE$

Faradaic current (cathodic reaction):

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

<u>Can this be written as</u> $-j_F = -j_{FS} + dj_F$ **?**

Insert $E = E_S + dE$

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

$$\approx -j_{FS} \times \left[1-\frac{(1-a)F}{RT}dE\right]$$

A Taylor expansion was used on the second line. For that the perturbation has to be small,

$$dE << \frac{RT}{(1-a)F},$$

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

Then, we finally get

$$-j_F = -j_{FS} + \frac{(1-a)F}{RT} j_{FS} dE$$

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

$$d\,j = \frac{(1 - a)F}{RT}\, j_{FS}\, d\,E$$

or

$$d\,E = R_F d\,j \text{ with } R_F = \frac{RT}{(1 - a)F}\frac{1}{j_{FS}}$$

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

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

Overall, impedance responses of simple electrode processes involve faradaic and capacitive currents. The impedance is given by

$$Z = R_F \frac{1 - i\,w/w_F}{1 + (w/w_F)^2}$$

The resulting Nyquist-plot is a semicircle. The diameter is

$$R_F = \frac{RT}{(1 - a)F}\frac{1}{j_{FS}}$$

and the characteristic frequency (maximum of semicircle) is

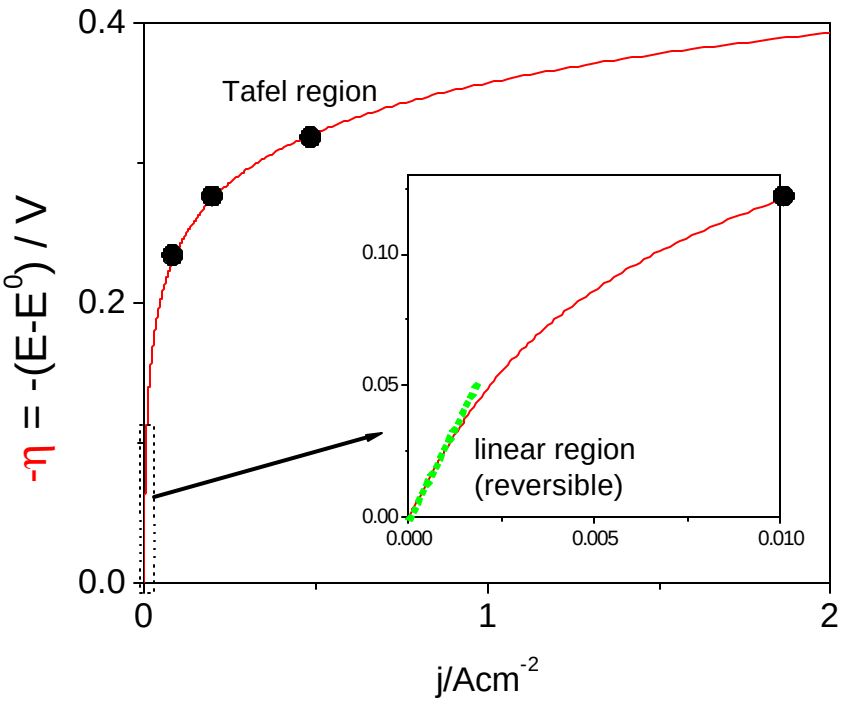
$$w_F = \frac{(1 - a)F}{RTC_{dl}} j_{FS}$$

In summary: analysis of impedance response of planar electrode gives

- **<u>… in the linear case</u>: j^0, i.e. k^0, and C_{dl}**
- **<u>… in the Tafel case</u>: a and C_{dl}**

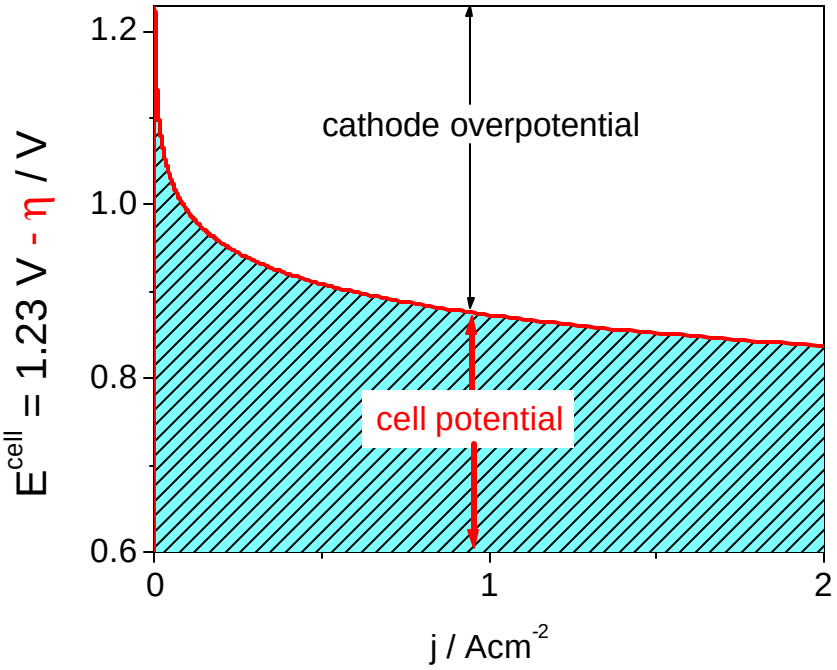
Let's look at some results in the context of electrode overpotential. Consider the following case of a cathode reaction. The rate constant is $k^0 = 10^{-3}\,\frac{\text{cm}}{\text{s}}$. For such an intermediate rate constant, the reaction could exhibit reversible or irreversible characteristics, depending on the working point. Assume that concentrations of oxidized and reduced species in the bulk are equal, $c_{ox}^{b} = c_{red}^{b} = 10^{-2}\,\text{mol/l} = 10^{-5}\,\text{mol/cm}^3$. (What does this mean for the equilibrium potential?) The exchange current density is $j^0 = nFk^0 c_{ox}^{b} = 0.965 \times 10^{-3}\,\text{A/cm}^2$ (with $n = 1$). The charge transfer resistance (in the linear region) is $R_{CT} = \frac{RT}{F}\frac{1}{j^0} = \frac{b}{j^0} = 26.63\,\Omega\text{cm}^2$. The transfer coefficient is $a = 0.5$. The following plot shows the overpotential vs. current density relation for a cathode reaction.

<u>Overpotential vs. current density plot</u>



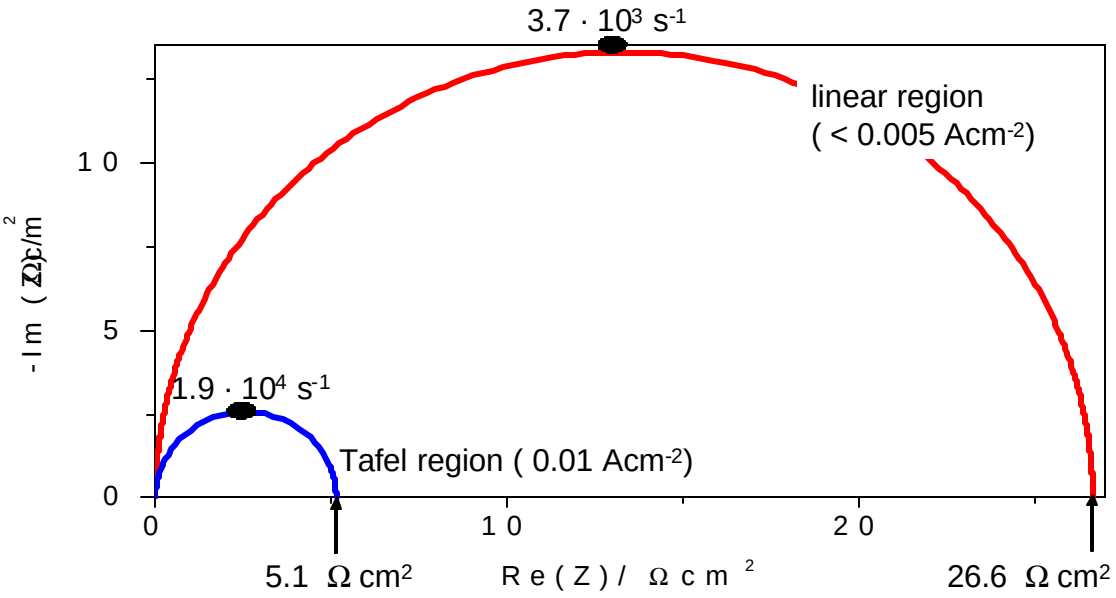
The inset zooms into the region of small current densities where the linear behaviour can be observed. The following plot shows the cell potential, i.e. the difference of equilibrium potential and cathode overpotential (if all other overpotentials are negligible).

Cell potential vs. current density plot

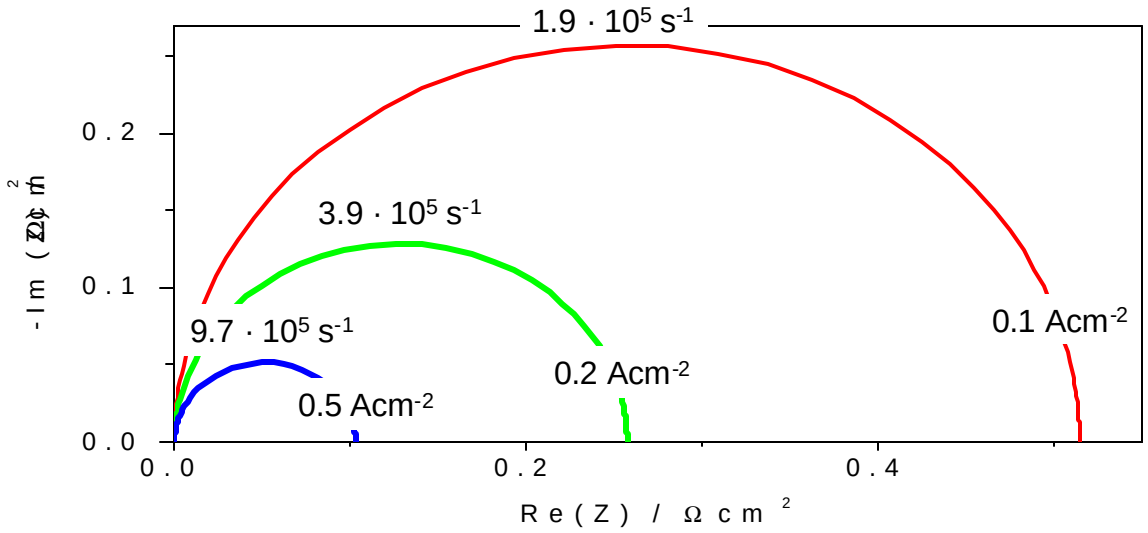


Overall, 4 points in the Tafel region are indicated in the overpotential vs. current density plot. Below, impedance spectra will be shown in the linear region and at these four working points.

Impedance spectra: linear and Tafel region



Impedance spectra: Tafel region at different working points



The impedance spectrum in the linear region is independent of the working point. It is only determined by the exchange current density. In the Tafel region, the radius of the semicircle decreases with increasing current density, whereas the characteristic frequency increases. Measuring at even larger current densities would not make sense, since the characteristic frequency would exceed the upper limit of feasibility of impedance spectroscopy, which was specified before as $10^6\,s^{-1}$. Only part of the semicircle would be measurable.

The decrease of faradaic resistance R_F (= diameter of semicircle) with increasing j_{FS} seems counterintuitive at first sight, right? How can we rationalize that? R_F corresponds to the slope of the overpotential vs. current density relation at the working point. Due to the exponential dependence between current density and overpotential, this slope decreases with increasing j_{FS}. The effect is obvious in the corresponding figure above.

… to be continued!!