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Solutions to the tasks:
Chapter 7 – Electrochemical impedance spectroscopy

Task 7.1 (Charge transfer resistance)

This task closely relates to task 2.3. Similarly, the exponential functions in the Butler-Volmer equation are approximated by

$$\exp x \approx 1 + x$$

for small values of x:

$$\Delta i \approx i_0 \cdot \left(1 + \frac{(1-\alpha)nF \cdot \Delta E}{RT} - 1 - \frac{-\alpha nF \cdot \Delta E}{RT}\right) = i_0 \cdot \frac{nF}{RT} \cdot \Delta E$$

Rearrangement and considering the transition from current density to current ($\Delta I = \Delta i \cdot A$) lead to the charge transfer resistance:

$$R_{\mathrm{ct}} = \frac{\Delta E}{\Delta I} = \frac{RT}{nFAi_0}$$

Task 7.2 (Randles circuit)

The complex impedance of a Randles circuit with uncompensated resistance R_{u} in series with a parallel circuit of the charge transfer resistance R_{ct} and the double layer capacity C_{dl} is:

$$Z = R_{\mathrm{u}} + \frac{1}{\imath\omega C + \frac{1}{R}} = R_{\mathrm{u}} + \frac{1}{1 + \imath\omega R_{\mathrm{ct}} C_{\mathrm{dl}}}$$

The time constant of the system is $R_{\mathrm{ct}}C_{\mathrm{dl}}$.

Evaluating the absolute value and the phase requires splitting the impedance between the real and imaginary parts, which is often cumbersome when more than two elements are involved. A convenient approach is relying on math software capable of symbolic calculations. Here we use the Python library *SymPy* (https://www.sympy.org/) providing the real and the imaginary part separately (slightly rearranged compared to the output of the symbolic calculation in the attached Jupyter notebook):

$$Z' = R_{\mathrm{u}} + \frac{R_{\mathrm{ct}}}{\omega^2 R_{\mathrm{ct}}^2 C_{\mathrm{dl}}^2 + 1} \qquad \text{and} \qquad Z'' = -\frac{\omega R_{\mathrm{ct}}^2 C_{\mathrm{dl}}}{\omega^2 R_{\mathrm{ct}}^2 C_{\mathrm{dl}}^2 + 1}$$

This allows the calculation of the absolute value and the phase:

$$|Z| = \sqrt{Z'^2 + Z''^2} = \frac{\sqrt{\omega^2 R_{\mathrm{ct}}^4 C_{\mathrm{dl}}^2 + (R_{\mathrm{ct}} + R_{\mathrm{u}}(\omega^2 R_{\mathrm{ct}}^2 C_{\mathrm{dl}}^2 + 1))^2}}{\omega^2 R_{\mathrm{ct}}^2 C_{\mathrm{dl}}^2 + 1}$$

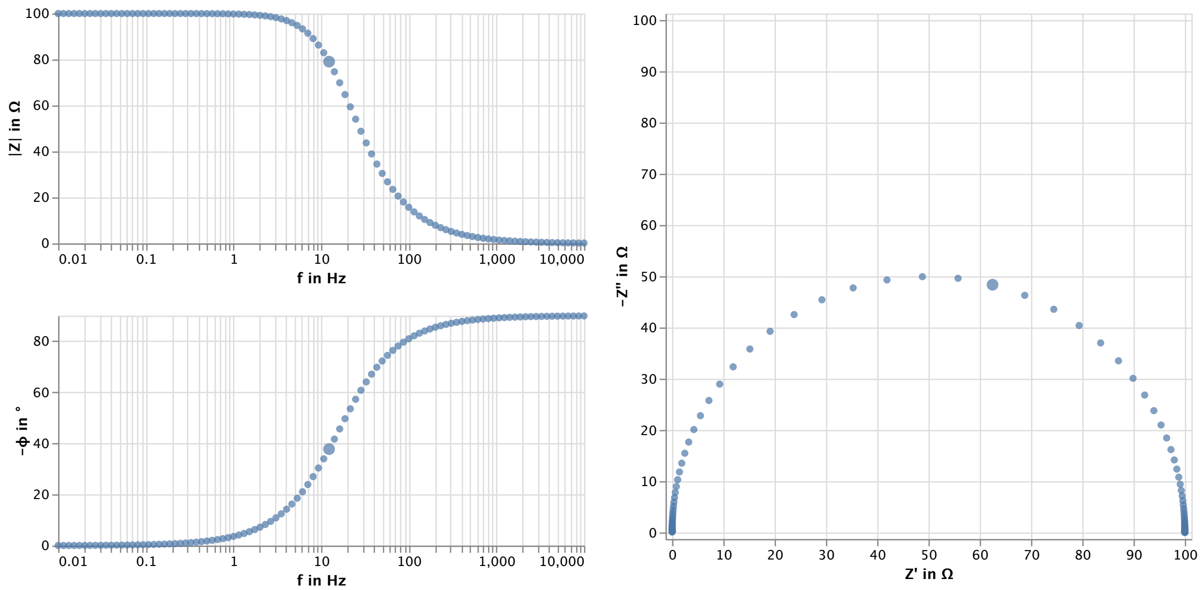
$$\phi = \arctan\left(\frac{Z''}{Z'}\right) = -\arctan\left(\frac{\omega R_{\mathrm{ct}}^2 C_{\mathrm{dl}}}{R_{\mathrm{ct}} + R_{\mathrm{u}}(\omega^2 R_{\mathrm{ct}}^2 C_{\mathrm{dl}}^2 + 1)}\right)$$

Task 7.3 (Electrochemical impedance spectroscopy – simulation)

Simulating different basic equivalent circuits and changing the parameter helps get a sound understanding of EIS models. We use the library *impedance.py* (https://doi.org/10.21105/joss), primarily designed to analyze experimental data.

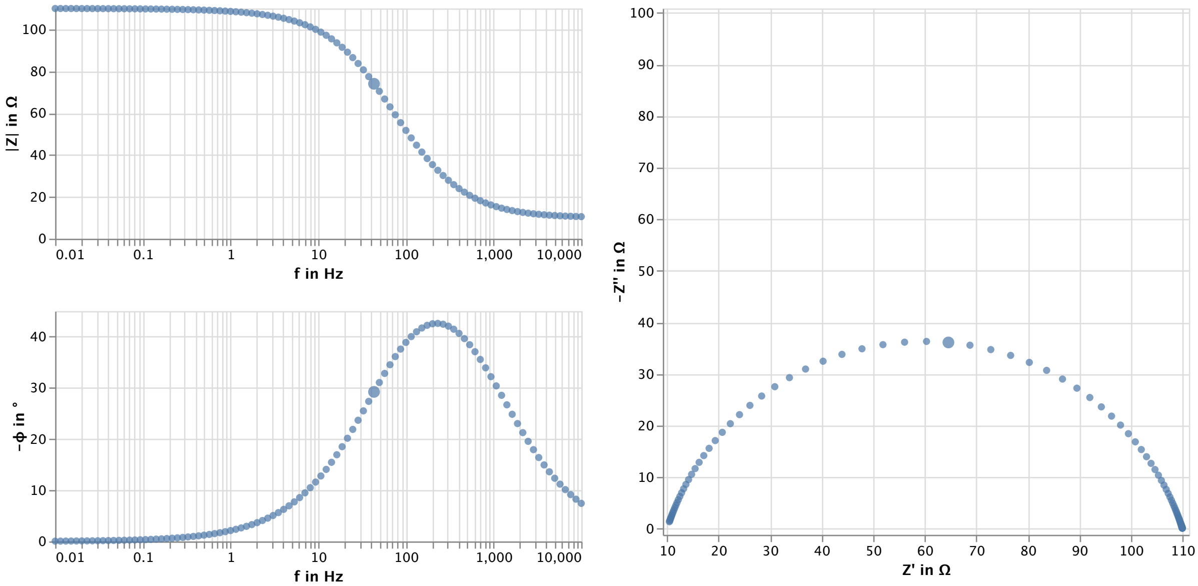
After installing the library following the description on https://github.com/ECSHackWeek/impedance.py, you can follow the examples below using the provided Jupyter notebook or explore it on your own. If you prefer plain Python, you have to use the plots based on Matplotlib instead of the default interactive plots relying on Altair. If you use a Jupyter notebook and Altair, you can choose “Open in Vega Editor” in the plot’s menu to adjust the appearance according to your preferences (e. g., in the figures below, a custom notation for the axis labeling).

1. The most simple representation of an electrode reaction is a simple RC parallel circuit representing the charge transfer resistance and double layer capacity. A good starting point for your explorations are 100 Ω for the charge transfer resistance and 100 µF for the double layer capacity (typical values for a 1 cm^2 electrode).



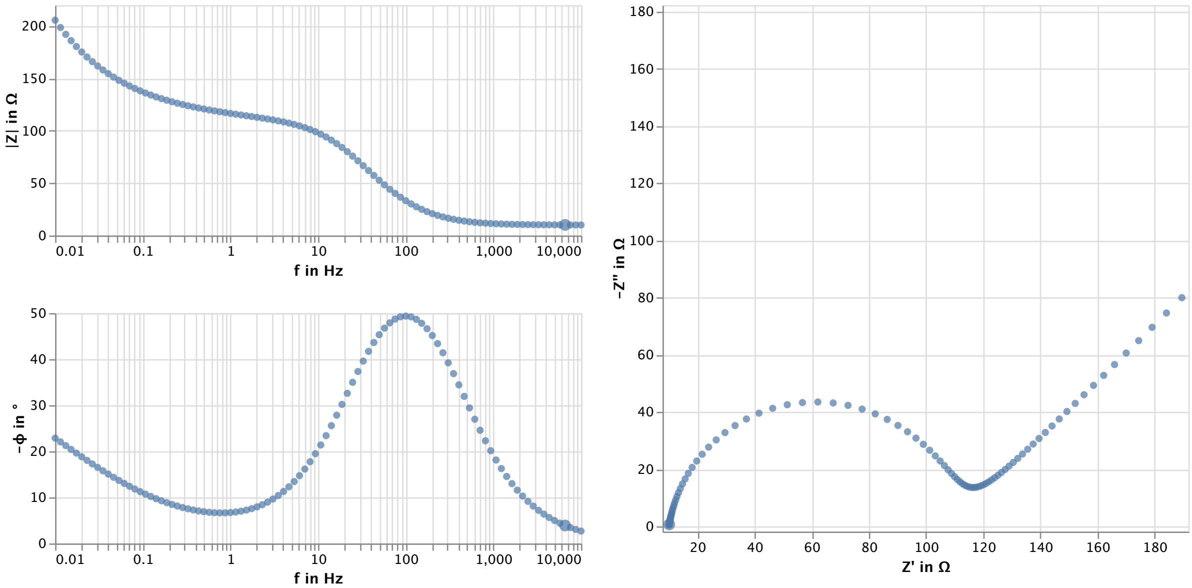
The Bode plot shows an absolute value of the impedance of 100 Ω for low frequencies when the circuit is purely resistive (phase 0). The impedance drops to zero for high frequencies, and the system is strictly capacitive (phase $-90°$). The Nyquist plot shows a semi-circle crossing the x-axis at 0 and 100 Ω.

2. A constant phase element (CPE) with an exponent less than one often models the electrical double layer better than an ideal capacitor. The typical range of the exponent is between 0.7 and 0.9. In the plot below, it is 0.8. For the serial resistor representing the uncompensated resistor, 10 Ω is a reasonable choice.



The serial resistor adds to the charge transfer resistance at low frequencies (110 Ω as the absolute value of the impedance in the Bode plot or the right crossing with the x-axis in the Nyquist plot). In contrast to the case with the ideal capacitor, the CPE causes deviation from an exact semi-circle in the Nyquist plot.

3. Finally, a Warburg element comes in series with the charge transfer resistance representing the diffusion limitation which kicks in at low frequencies. A possible value is $20\,\Omega\,s^{0.5}$.



Characteristic for a system under diffusion limitation is the 45° slope in the Nyquist plot for low frequencies (on the right).

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