Exercise 1:

Consider an alkaline water electrolysis cell with a manganese (Mn) coated nickel (Ni) anode and a platinum (Pt) coated Ni cathode submerged in a KOH solution and separated by a porous diaphragm.

Assume the following values:

$R_{cat} = 0.2\ \Omega\ cm^2$ for the cathodic resistance

$R_{an} = 2\ \Omega\ cm^2$ for the anodic resistance

$R_s = 1\ \Omega\ cm^2$ for the serial resistance composed of the diaphragm and the KOH electrolyte

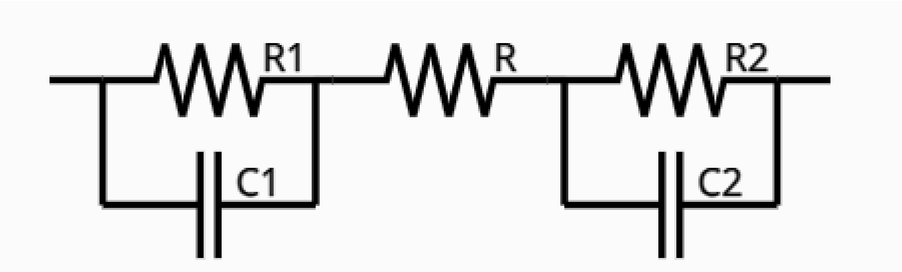
$C_{cat} = 10\ \mu F\ cm^{-2}$ for the cathodic capacitance

$C_{an} = 1\ mF\ cm^{-2}$ for the anodic capacitance

a) Construct the equivalent circuit of the electrolysis cell.
b) Using the assumed parameters, formulate the total impedance of the system Z_{tot}.
c) Using the formula developed in part b, Plot the Nyquist and Bode diagrams for the frequencies ranging from 1 MHz to 10 mHz (use Excel/MATLAB).
d) Assume the anode was replaced by a $NiFeO_x$ anode, and the anodic capacitance and resistance are now changed to $C_{an} = 100\ \mu F\ cm^{-2}$ and $R_{an} = 2\ \Omega\ cm^2$ respectively. Replot the Nyquist and Bode diagrams and conclude.

Solution:

a) The equivalent circuit is represented as 3 components in a series configuration: anode, cathode and resistance. Both electrodes are each represented as a resistor and a capacitor in parallel, while the KOH solution and the diaphragm are represented as the serial resistance as shown the figure below.



b) Let f be the frequency in Hz, then $\omega = 2\pi f$

The capacitive impedance is $Z_C = \frac{1}{i\omega C}$

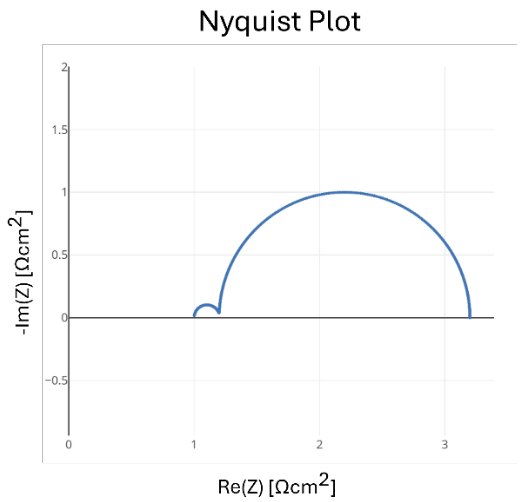
For the parallel RC circuit of each electrode, $\frac{1}{Z_{RC}} = \frac{1}{Z_C} + \frac{1}{R}$

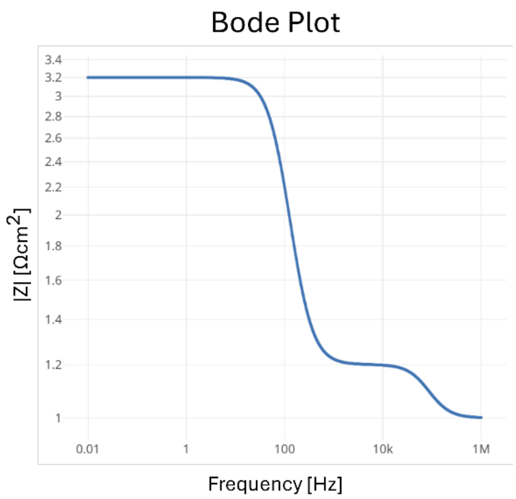
$$Z_{RC} = \frac{RZ_C}{R+Z_C} = \frac{R\,\frac{1}{i\omega C}}{R+\frac{1}{i\omega C}} = \frac{1}{\frac{1}{R}+i\omega C}$$

The total impedance of the electrolysis cell is $Z_{tot} = Z_{R_1C_1} + R_s + Z_{R_2C_2}$

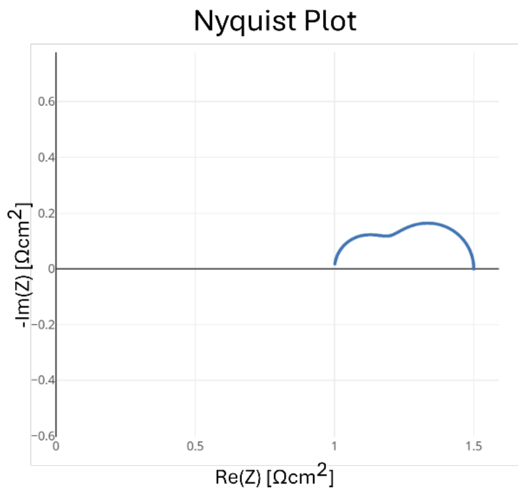
Therefore $Z_{tot} = \frac{1}{\frac{1}{R_1}+i\omega C_1} + R_s + \frac{1}{\frac{1}{R_2}+i\omega C_2}$

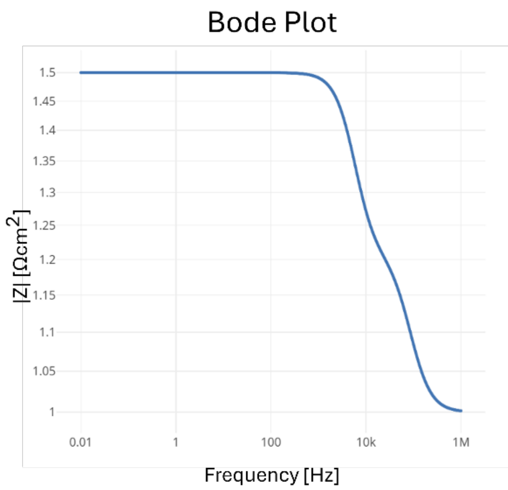
c) Calculating the impedance over a large range of frequencies, the Nyquist and Bode plots are represented as follows:





d) Changing the anode material results in changes in the anodic capacitance and resistance, therefore the new Nyquist and Bode plots are shown as:





By comparing the Nyquist plots of the two different cells, it can be concluded that when the time constants of the 2 RC circuits are different enough (case 2), the 2 semi-circles are distinct, but when the time-constants are close (case 1), the semi-circles overlap.

<u>Exercise 2:</u>

Exercise about charge/energy density, comparison fuel cell with battery.

a) Compute the energy density of a portable polymer electrolyte fuel cell (PEFC), weighing 100 g, including a 30 ml metal-hydride tank which stores 3 g of hydrogen (molar mass H2 = 2 g/mol). The working discharge voltage of the fuel cell is admitted to be constant throughout at 0.6 V.

b) Same computation as before, but this time with a 30 ml methanol storage tank instead of hydrogen (LHV MeOH = 5 kWh/L).

c) If we run a portable electronic device from this fuel cell, consuming on average 10 We, for how long can it run until full discharge from H2, respectively methanol, before a refill is necessary ?

d) compare to a 100 g battery with an energy density of 200 Wh/kg.

Solutions:

a)

3 g H_2 = 1.5 mole H_2 , 2 e^- per mole of H_2, total 3 mole e^- transferred
Capacity = 3 mole e^- × 96485 C/mole = 289455 C = 80.4 A·h

Energy = Capacity × Voltage = 80.4 A·h × 0.6 V = 48.24 W·h

Energy density = 48.24 W·h/ 100 g = 482 W·h/kg

b)

Energy = 30 ml × 5 kW·h /L = 0.15 kW·h

Energy density = 0.15 kW·h / 100 g = 1500 W·h/kg

c)

H_2 : Time = Energy/Power = 48.24 W·h / 10 W = 4.82 hours

MeOH : Time = Energy/Power = 0.15 kW·h / 10 W = 15 hours

d)

Battery:

Energy = 100 g × 200 W·h /kg = 20 W·h

Time = Energy/Power = 20 W·h/ 10 W = 2 hours