Problem IV.S ... Electrochemistry 4 — capacitance and impedance spectroscopy

10 points; průměr 5,72; řešilo 32 studentů

1. *The geometric surface area of our platinum electrode is* $4\,\mathrm{cm}^2$*. However, its surface is very rough, so the active surface area may be higher. In an experiment, we measured the capacitance of the whole electrode to be* $700\,\mu\mathrm{F}$*. If we estimate the distance of adsorbed ions in the solution from the platinum surface to be* $1\,\mathrm{nm}$*, how many times larger is the active surface area compared to the geometric area? The experiment takes place in water with* $\varepsilon_\mathrm{r} \doteq 80$*. – 2 points*

2. *Draw the impedance spectrum in a Nyquist plot for a resistor* $R = 23\,\mathrm{m\Omega}$*, a capacitor with capacitance* $C = 0.5\,\mathrm{mF}$*, and CPE with parameters* $Q = 0.3\,\Omega^{-1}{\cdot}\mathrm{s}^{\alpha}$ *and* $\alpha = 0.6$ *for the frequencies ranging from* $f_1 = 1\,\mathrm{kHz}$ *to* $f_2 = 10\,\mathrm{kHz}$*. – 2 points*

3. *Determine all the parameters of a Randles circuit from the provided spectrum. The data points are distributed logarithmically over the frequency range from* $10\,\mathrm{Hz}$ *to* $10\,\mathrm{kHz}$*, with 5 data points per one frequency decade. – 3 points*

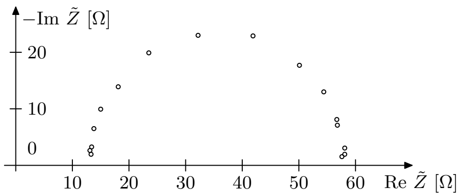

Figure 1: Measured spectrum.

4. *Impedance spectra of a simple reaction, described by a Randles circuit, were measured at a DC current* I *given in the table 1. From curve fitting the spectra, the ohmic resistance was found to be* $R_\Omega = 55\,\Omega$ *for all measured values. The charge transfer resistance* R_ct *values are listed in the table below. Assume the measurements were conducted in the Tafel regime. Determine the parameter* b *in the exponential form of the Tafel equation* $j = j_0 \exp(\eta/b)$ *derived in the third episode of the series. – 3 points*

Table 1: Values of the current and the resistance.

measuring	$\frac{I}{\mathrm{mA}}$	$\frac{R_\mathrm{ct}}{\Omega}$
1	0.13	208
2	0.24	99
3	0.57	45
4	1.11	22
5	2.04	14

Jarda devoted the whole episode to his favourite experimental method.

Problem 1

The solution is quite straightforward. From the formula for capacitance, we express the active electrode area as

$$A_{\mathrm{act}} = \frac{Cd}{\varepsilon_0 \varepsilon_{\mathrm{r}}} = 9.9\,\mathrm{cm}^2\,,$$

where $d = 1\,\mathrm{nm}$. The ratio to the value A_{geo} is thus approximately 2.5.

Problem 2

Subproblem 2a) The impedance of the resistor is simply $\tilde{Z}_R = R$, meaning it does not depend on frequency, so all points will map to a single location. Furthermore, it is a real number, so it will be on the real axis at the coordinate $R + 0i = 23\,\mathrm{m\Omega}$.

Subproblem 2b) The impedance of the capacitor according to the serial text is

$$\tilde{Z}_C = -\frac{i}{C\omega}\,,$$

which if a frequency function, so multiple points will appear in the graph. Additionally, it is purely imaginary, meaning all these points will lie on the vertical axis. For $f_1 = 1\,\mathrm{kHz}$, the impedance is $\tilde{Z}_C \doteq -318i\,\mathrm{m\Omega}$, while for frequency f_2, it is ten times smaller.

Subproblem 2c) The impedance of the constant phase element is given by the serial text as

$$\tilde{Z}_P = \frac{1}{Q\,(i\omega)^{\alpha}} = \frac{1}{Q\omega^{\alpha}} i^{-\alpha}\,.$$

The imaginary unit i can be written as

$$0 + i \cdot 1 = \cos\frac{\pi}{2} + i\ \sin\frac{\pi}{2} = \mathrm{e}^{i\frac{\pi}{2}}\,,$$

then

$$i^{-\alpha} = \left(\mathrm{e}^{i\frac{\pi}{2}}\right)^{-\alpha} = \mathrm{e}^{-i\frac{\alpha\pi}{2}} = \cos\left(-\frac{\alpha\pi}{2}\right) + i\ \sin\left(-\frac{\alpha\pi}{2}\right) = \cos\left(\frac{\alpha\pi}{2}\right) - i\ \sin\left(\frac{\alpha\pi}{2}\right)\,.$$

The ratio of the imaginary and real components is constant for all frequencies, so the impedance always lies on a line passing through the point $[0, 0]$, inclined at an angle $\alpha\pi/2$ toward the negative part of the imaginary axis.

Substituting into the definition of the impedance of this element, we obtain

$$\tilde{Z}_P = \frac{1}{Q\,(i\omega)^{\alpha}} = \frac{1}{Q\omega^{\alpha}}\left(\cos\left(\frac{\alpha\pi}{2}\right) - i\ \sin\left(\frac{\alpha\pi}{2}\right)\right)\,.$$

For f_1, the impedance is $(10\,\mathrm{m\Omega}, -14i\,\mathrm{m\Omega})$, while for f_2, it is approximately $(2.6\,\mathrm{m\Omega}, -3.6i\,\mathrm{m\Omega})$. The spectra of the individual elements are shown in graphs 2, 3, and 4.

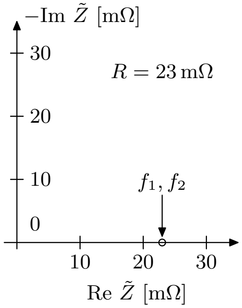

Figure 2: Graph for pure resistance.

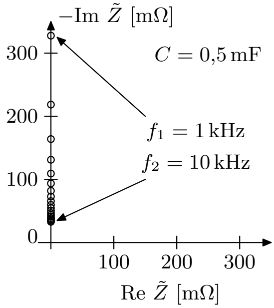

Figure 3: Graph for the capacitor.

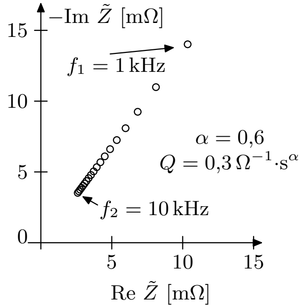

Figure 4: Graph for the constant phase element.

Problem 3

The ohmic resistance is determined from the point where the measured curve approximately intersects the real axis at higher frequencies, therefore on the left side of the graph. The intersection is closer to $10\,\Omega$ than to $20\,\Omega$ but not that close; the correct value is $R_\Omega = 13\,\Omega$.

The charge transfer resistance is given by the diameter of the circle in the graph, so we subtract the intersection at lower frequencies, which has a value of approximately $58\,\Omega$. Thus, $R_{ct} \doteq 58\,\Omega - 13\,\Omega = 45\,\Omega$.

The most challenging part here is determining the capacitance, the final characteristic of the circuit. To determine the resistances, we used intersections with the real axis, but these are not suitable for capacitance determination. Therefore, we also use the imaginary part of the complex impedance, which arises precisely due to the capacitive behavior of the reaction. From the series, we have the equation for the impedance of the Randles circuit

$$\tilde{Z}_{\mathrm{Ran}} = R_\Omega + \frac{R_{\mathrm{ct}}}{2} + \frac{R_{\mathrm{ct}}}{2} \frac{1}{1 + C^2\omega^2 R_{\mathrm{ct}}^2} \left(1 - C^2\omega^2 R_{\mathrm{ct}}^2 - 2iC\omega R_{\mathrm{ct}}\right) .$$

We have proven that the points lie on a circle; therefore, an angular frequency ω_i, at which the imaginary part equals the radius of this circle, exists; we know the radius to be equal to $R_{\mathrm{ct}}/2$. This particular point is interesting because it is at the greatest distance from the real axis. From the general equation for $\tilde{Z}_{\mathrm{Ran}}$ we can solve for the frequency ω_i by equating the imaginary parts

$$-i\frac{R_{\mathrm{ct}}}{2} = \frac{R_{\mathrm{ct}}}{2} \frac{1}{1 + C^2\omega_i^2 R_{\mathrm{ct}}^2} \left(-2iC\omega_i R_{\mathrm{ct}}\right) \quad \Rightarrow \quad 1 - 2C\omega_i R_{\mathrm{ct}} + C^2\omega_i^2 R_{\mathrm{ct}}^2 = 0 \,.$$

The solution to this equation is clearly $C\omega_i R_{\mathrm{ct}} = 1$. Thus, if we know R_{ct} and determine the angular frequency of this special point, we can easily calculate the desired capacitance. In our case, we already know $R_{\mathrm{ct}} = 45\,\Omega$.

The spectrum consists of 16 points, with 5 points per decade of frequency. Counting the frequencies from the right, the rightmost lower point should correspond to 10 Hz, the sixth point along the arc to 100 Hz, and the twelfth to 1 000 Hz. The point on the arc where our model predicts the maximum imaginary component lies somewhere between the eighth and ninth points. We estimate its frequency to be $f_i = 300\,\mathrm{Hz}$. The capacitance is then calculated simply as

$$C = \frac{1}{R_{\mathrm{ct}}\omega_i} = \frac{1}{2\pi f_i R_{\mathrm{ct}}} \doteq 1.2 \cdot 10^{-5}\,\mathrm{F}\,.$$

Problem 4

In the problem statement, we were given the dependence of current density on overvoltage η, which we derived in the third part of the series. Charge transfer resistance was defined in the fourth part as

$$R_{\mathrm{ct}} = \left(\frac{\mathrm{d}I}{\mathrm{d}\eta}\right)^{-1} = \frac{\mathrm{d}\eta}{\mathrm{d}I}\,.$$

How does this resistance specifically depend on the current or overvoltage? We express η as a function of I and substitute

$$\eta = b\ln\left(\frac{I}{I_0}\right) \quad \Rightarrow \quad R_{\mathrm{ct}} = \frac{\mathrm{d}\eta}{\mathrm{d}I} = \frac{b}{I}\,.$$

The charge transfer resistance is thus, for this model, inversely proportional to the current raised to a power, and the proportionality constant is exactly the parameter we are looking for! We just need to take a pair of $R_i I_i$, multiply them, and average them. We get the value

$$b = \frac{\sum R_i I_i}{5} = (26 \pm 1)\mathrm{mV}\,.$$

So, if we increase the overvoltage by $26\,\mathrm{mV}$, the current increases by e-times. By multiplying this value by the number $\ln 10 \doteq 2.3$, we get a value $60\,\mathrm{mV{\cdot}dec^{-1}}$, which is easier to interpret—it tells us what voltage is required to increase the current tenfold. This value is called the Tafel slope.

For comparison, let us also examine the value of b with quantities that appeared in the exponent in the third part of the series. We have

$$\frac{(1-\alpha)z\,F}{RT}\eta = \frac{\eta}{b}\,.$$

The temperature T is set for the experiment, R and F are constants, η cancels out, and b has been determined from the experiment. For a symmetric energy barrier, we have $\alpha = 1/2$, so we can determine the number of electrons per reaction z as

$$z = \frac{RT}{0,5Fb} \doteq 2\,,$$

where we substituted the standard temperature $T = 25\,^\circ\mathrm{C}$ and $b = 26\,\mathrm{mV}$. The obtained Tafel slope thus corresponds to a two-electron reaction.

Notes on the solutions sent by participants

In subproblem 2, the task was slightly unclear; to solve it correctly, it was enough to plot the graph for each of the named elements separately. However, some participants calculated the spectrum for various parallel or series combinations of the given elements. If their spectrum was correctly depicted within the chosen model, they were awarded full points.

In subproblem 3, most participants calculated the capacitance from the position of a point in the spectrum. It is necessary to choose the point with the highest imaginary part, as the points along the real axis are more densely packed and their position depends less on the frequency, which reduces the achievable accuracy.

In the final subproblem, many participants calculated the charge transfer resistance R_{ct} as

$$R_{ct} = -\frac{RT}{j_0 z\ F}\,,$$

which was given in the third part of the series. However, in its derivation, a condition was mentioned that the exponentials in the Butler-Volmer equation can be linearized, meaning that the currents and overvoltages are small. In our task, however, we were operating in the Tafel regime, where the current depends exponentially on the overvoltage. Therefore, we cannot use the definition of R_{ct} from the third part, but rather from the fourth part:

$$R_{ct} = \left(\frac{dI}{d\eta}\right)^{-1}\,,$$

where I is the current in the system and η is the overvoltage (here, we silently switched from current density to current, so we are not normalizing to the electrode surface). Therefore, for the charge transfer resistance, *Ohm's law does not apply* in general, and we calculate it only using the derivative. You can verify for yourself that when you perform the calculation of R_{ct} from the new definition in the region where the Butler-Volmer equation can be linearized, you obtain the above relation $R_{ct} = -RT/(j_0 zF)$.

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