Problem VI.S ... electrochemistry 6 — migration, voltammetry and pH
10 points

1. *Using the Drude model, determine the distance traveled by an electron in copper between two collisions; the electric field intensity in the conductor equals* $E = 1.0\,\mathrm{V{\cdot}m^{-1}}$*. After doing so, compare the calculated value to the mean free path of electrons in copper and discuss why there is such a difference between these two values. Consider* $\sigma = 5.95\cdot 10^{7}\,\Omega^{-1}{\cdot}\mathrm{m^{-1}}$ *as the electrical conductivity of copper. – 3 points*

2. *In figure 1, a graph shows a part of a cyclic voltammetry measurement of the adsorption of hydrogen on platinum. Determine the electrochemically active surface area of the platinum. A platinum monocrystal has a charge density of* $240\,\mathrm{\mu C{\cdot}cm^{-2}}$*. Furthermore, calculate the areal capacity and compare it to a value obtained by the Helmhlotz model introduced in the first subtask of the 4th part of the series. The scanning speed is equal to* $v = 15\,\mathrm{mV{\cdot}s^{-1}}$*. – 4 points*

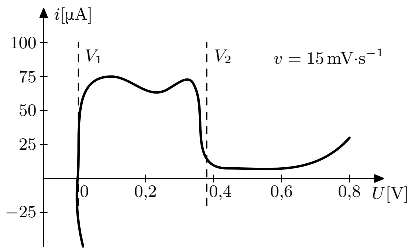

Figure 1: Graph of a cyclic voltammetry

3. *Draw a Pourbaix diagram of fykosium, a hypothetic metallic element, under standard conditions. There are three important reactions for this element:*

$$\mathrm{Fk^{0}(s) \longleftrightarrow Fk^{3+}(aq) + 3\,e^{-}}$$

with a standard reduction potential of $1.63\,\mathrm{V}$*,*

$$\mathrm{Fk(OH)_3(s) + 3\,H^{+} + 3\,e^{-} \longleftrightarrow Fk^{0}(s) + 3\,H_2O}$$

with a standard reduction potential of $2.04\,\mathrm{V}$*,*

$$\mathrm{Fk(OH)_3(s) + 3\,H^{+} \longleftrightarrow Fk^{3+}(aq) + 3\,H_2O(l)}\,.$$

– 3 points

Bonus: *Determine whether fykosium could be used as a material on an anode in a water proton exchange electrolyzer (PEM-WE). The environment has to be stable; remember that fykosium is a metallic element.*

Jarda left a few notes for the end.

Subtask 1

Let us consider the situation that forms the basis of the Drude model. The average velocity of electrons in a metal is

$$\mathbf{v} = \mu\mathbf{E} = \frac{\tau e}{m_\mathrm{e}}\mathbf{E}\,,$$

and the average time between collisions is τ. During this time, the electron travels a distance given by

$$\lambda = |\mathbf{v}|\,\tau = \frac{\tau^2 e}{m_\mathrm{e}}\,|\mathbf{E}|\;.$$

The magnitude of the field is known from the problem statement; the charge and mass of the electron are known constants. Thus, to determine λ, we only need to calculate τ. Thanks to the known specific conductivity of copper $\sigma = 5.95\cdot 10^7\,\Omega^{-1}\cdot\mathrm{m}^{-1}$, we can determine the average time between collisions as

$$\sigma = \frac{n\tau e^2}{m_\mathrm{e}} \Rightarrow \tau = \frac{\sigma m_\mathrm{e}}{ne^2}\;.$$

Substituting into the equation for λ, we get

$$\lambda_D = \frac{\sigma^2 m_\mathrm{e}}{n^2 e^3}\,|\mathbf{E}|\;.$$

Here, we need to determine the concentration of free electrons in copper n. In copper, there is 1 free electron per atom. Therefore, we need to calculate the concentration of atoms as

$$n = N_\mathrm{A}\frac{\rho}{M_\mathrm{Cu}} \doteq 850\cdot 10^{26}\,\mathrm{m}^{-3}\,,$$

where we used the Avogadro constant N_A, the density of copper $\rho = 8\,940\,\mathrm{kg}\cdot\mathrm{m}^{-3}$, and its atomic mass $M_\mathrm{Cu} \doteq 63.5\,\mathrm{g}\cdot\mathrm{mol}^{-1}$.

Numerically, the mean time τ has the value

$$\tau = \frac{\sigma m_\mathrm{e}}{ne^2} \doteq 2.5\cdot 10^{-14}\,\mathrm{s}\,.$$

and the mean free path is

$$\lambda_D \doteq 1\cdot 10^{-16}\,\mathrm{m} = 0.1\,\mathrm{fm}\,,$$

which is smaller than the radius of an atomic nucleus; the distance between atoms is five orders of magnitude larger. Let us also compare the result with values that can be found online for this quantity.

The mean free path of an electron in copper is, according to online sources[1], about $\lambda_i = 40\,\mathrm{nm}$, which is eight orders of magnitude greater than what we calculated!

Our value λ_D is the distance that indicates how far the average electron shifts before experiencing two collisions, because we used its average velocity due to the electric field for the calculation. However, as mentioned in the series, the motion of electrons is chaotic, driven by temperature, and occurs in all directions. The electron moves in one direction, travels some distance, then scatters in another direction, and so on. But if there is an electric field in the conductor, then the average position of the electron shifts in the direction of the acting force. This average motion is much slower than its thermal motion. Between collisions, the electron

[1] For example, in this article `https://pubs.aip.org/aip/jap/article/119/8/085101/143910/Electron-mean-free-path-in-elemental-metals`, but similar values can be found in Czech sources or forum discussions.

travels a distance $\lambda_i \gg \lambda_\mathrm{D}$, but this motion averages to zero, while the motion due to the electric force remains.

We stated that according to the Drude model, electrons behave like particles of an ideal gas. For an order-of-magnitude estimate of the mean free path, we can calculate their root mean square velocity using the known relation

$$v_T = \sqrt{\frac{3kT}{m_\mathrm{e}}} \doteq 120\,\mathrm{km{\cdot}s^{-1}}$$

and multiply it by the average time τ

$$\lambda_\mathrm{D} = v_T \tau \doteq 3\,\mathrm{nm}\,,$$

which is much closer to the value we can find online. However, there is still an order-of-magnitude discrepancy, which was a major shortcoming of the Drude theory, and, together with other inconsistencies with experimental data, forced scientists to develop more complex theories (e.g., the nearly-free electron model), which are based on the quantum nature of particles in metals.

Subtask 2

From the graph, we must numerically determine the area under the curve between voltages V_1 and V_2 so that we can use the relations from the series to convert it into charge that passed through the electrode during this voltage interval. However, we must not forget the influence of the electrode's capacitance, which is visible in the graph between voltages 0.4 V and 0.6 V as a constant, voltage-independent current given by the relation $i_\mathrm{cap} = Cv$.

We download the image and insert it into some graphical software where we can perform basic geometric analysis, such as *Geogebra*. Using lines and segments overlaid on the graph image, we determine the value $i_\mathrm{cap} \doteq 7\,\mathrm{\mu A}$. From this, we can immediately say that the capacitance of the electrode is

$$C = \frac{i_\mathrm{cap}}{v} \doteq 480\,\mathrm{\mu F}\,.$$

Let us proceed to determine the charge between voltages V_1 and V_2. We must obtain the area under the curve, but above the line representing the capacitive current. We enclose this area as precisely as possible with a polygon and let the program calculate its area just as in figure 2. We get approximately $S = 22 \cdot 10^{-6}\,\mathrm{V{\cdot}A}$. This value is converted into charge

$$Q = \frac{S}{v} \doteq 1\,500\,\mathrm{\mu C}\,,$$

so we can consider the electrochemically active surface area of the electrode as

$$A = \frac{Q}{\sigma_\mathrm{Pt}} = 6.1\,\mathrm{cm^2}\,,$$

where we substituted $\sigma_\mathrm{Pt} = 240\,\mathrm{\mu C{\cdot}cm^{-2}}$ as given.

Next, we determine the areal capacitance density of the electrode

$$c = \frac{C}{A} \doteq 80\,\mathrm{\mu F{\cdot}cm^{-2}}\,.$$

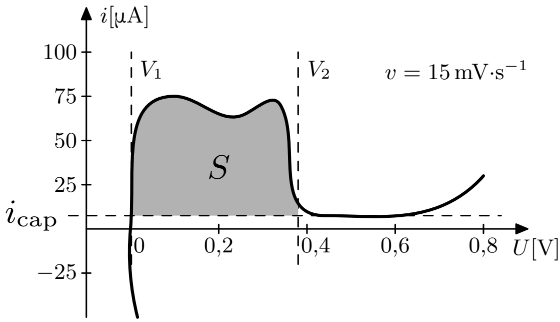

Figure 2: A cyclic voltammetry graph with depicted capacitive current and the area under the curve corresponding to the charge of adsorbed hydrogen atoms.

In the fourth part of the series, we estimated the areal capacitance density as

$$c = \frac{\varepsilon_0 \varepsilon_r}{d} \doteq 70\,\mathrm{\mu F\cdot cm^{-2}}\,,$$

which is in good agreement with the experimental result. The distance $d = 1\,\mathrm{nm}$ of the adsorbed ions was therefore estimated well.

Subtask 3

For each reaction, determine whether it depends on pH and, if so, write the Nernst equation as we did in the series. In the first reaction in the assignment, H^+ does not appear as a reactant or product, so the potential of this reaction does not depend on pH. The boundary between phases Fk^0(s) and Fk^{3+}(aq) is therefore a horizontal line in the Pourbaix diagram with a constant voltage value of 1.63 V.

In the second reaction, we see that protons in the solution act as reactants, so the reduction potential depends on their concentration, and thus on pH. Let's write the reaction in the direction of reduction:

$$\mathrm{Fk^{3+}(OH)_3(s) + 3\,H^+(aq) + 3\,e^- \longrightarrow Fk^0(s) + 3\,H_2O(l)}\,,$$

so we already know what will be in the numerator and denominator of Q. Let's write the Nernst equation:

$$E_{\text{reac}} = E^\circ_{\text{reac}} - \frac{RT}{zF} \ln \frac{[\mathrm{Fk^0(s)}][\mathrm{H_2O(l)}]^3}{[\mathrm{Fk(OH)_3(s)}][\mathrm{H^+}]^3}\,,$$

but since the concentrations of liquids and solids are conventionally taken as unity, the equation simplifies to:

$$E_{\text{reac}} = E^\circ_{\text{reac}} - \frac{RT}{zF} \ln \frac{1}{[\mathrm{H^+}]^3} \doteq E^\circ_{\text{reac}} + 3\frac{2.3RT}{zF} \log[\mathrm{H^+}] = 2.04\,\mathrm{V} - \frac{2.3RT}{F}\mathrm{pH}\,,$$

where we used $z = 3$ and $E^\circ_{\text{reac}} = 2.04\,\mathrm{V}$ in the last equality.

Let's now calculate the intersection of both found lines:

$$1.63\,\mathrm{V} = 2.04\,\mathrm{V} - 59\,\mathrm{mV}\cdot \mathrm{pH_i} \Rightarrow \mathrm{pH_i} \doteq 6.9\,.$$

In the third equation, there is no change in the oxidation state of any atoms, so the voltage value for this reaction can be arbitrary. Because this equation defines the boundary between the two phases we considered in previous equations, its pH value must again be $pH_i \doteq 6.9$. In figure 3, the Pourbaix diagram depicting all three reactions from the assignment is shown.

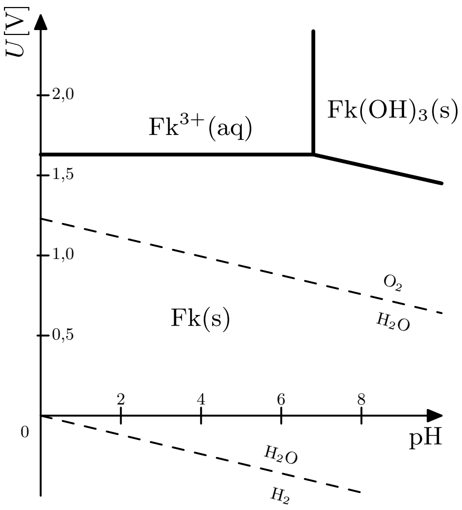

Figure 3: Pourbaix diagram for the given reactions of phycosium. The stability region of water is also shown, which is important for solving the bonus task.

Bonus solution

We must determine the conditions in terms of potential and pH at the anode of a water electrolyzer with a proton exchange membrane (PEM-WE). In this year's series, we already mentioned that the minimum voltage for electrolysis between the anode and cathode at room temperature is 1.23 V. Since hydrogen is produced at the cathode (often on platinum, which is used as a catalyst), we can assume that its potential is close to zero, similarly to the standard hydrogen electrode. The remaining 1.23 V is thus at the anode.

However, we also know that in order for current to flow and the reaction to proceed, some overpotential is needed. The total voltage across the electrolyzer must therefore be much higher, and the anode is particularly problematic, because the oxygen evolution reaction is much more complex than the hydrogen evolution reaction. On the English Wikipedia[2], we can read that the typical voltage across the entire electrolyzer must be 1.75 V to 2.2 V for hydrogen production to proceed fast enough. This gives us a fairly clear idea of the region on the Pourbaix diagram where we are.

In the solution, we found that for an anode voltage higher than 1.63 V, fykosium dissolves. This holds until $pH \doteq 6.9$, then fykosium is in the hydroxide form. However, according to the problem statement, we need metallic fykosium, so the anode should be at less than the

[2] `https://en.wikipedia.org/wiki/Proton_exchange_membrane_electrolysis`

mentioned 1.63 V. At high pH, the value would be even lower, but in PEM-WE the anode environment is acidic, and thus the pH is low.

Because the operating voltage of the electrolyzer is higher than the voltage at which phycosium is stable in metallic form, and at the same time the overvoltage at the cathode is low, we can state that phycosium is not a suitable element for use at the anode in PEM-WE. However, if development were to advance to the point where we could achieve high currents at voltages lower than 1.63 V, the use of phycosium could at least be considered.

Notes on Submitted Solutions

Almost all participants managed to solve the calculation in the first subproblem, but the issue was in interpreting the order-of-magnitude difference. The mean free path represents the average distance an electron travels between two collisions: aside from its directed drift motion, the electron also moves chaotically due to thermal motion, so it travels the mean free path equally in all directions. However, between two such collisions, it moves on average with the drift velocity and (on average) covers the tiny distance that was the subject of the calculation.

In the second problem, most participants forgot to subtract the influence of the capacitive current on the resulting charge, which originated from adsorbed hydrogen. Numerically, this was not a significant error, but if the scan rate had been set higher, the capacitive current would have played a more important role. Some of you also didn't use it in the calculation of the electrode's capacitance, even though it is a very advantageous experimental approach.

The third problem was solved without major issues. Only a few participants successfully solved the bonus task—congratulations to them!

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