Additional exercises for Lab 2

This section contains exercises for Chapters 10, 11, and 12, complementing the practical exercises for Lab 2.

2.1 Exercise for Chapter 10 Electrode polarisation

Introduction and overview: In this exercise, we will build a cell corresponding to that in Figure 10-14 of the textbook. (It shall not correspond to Figure 10-13, and not to 10-15.) We shall use data for various parameters and construct and evaluate *I-E* (or *i-E*) polarisation plots for a working electrode under study. We shall do this by building up expected polarisation curves for the ohmic, kinetic, and transport contributions to the polarisation, cf. Fig. 10-10.

Report: Make a drawing of how the cell might look in a real setup in the lab, using a beaker with a supporting electrolyte and the reactant and products of the reaction to be studied (R(aq) and O(aq)) and real, physical electrodes in there. Make the WE and CE square planar electrodes and suggest a shape and location for the RE that makes it correspond to Fig. 10-14.

2.1.1 Ohmic polarisation

Assume that the WE and CE forms a **trough cell** with area 19 x 19 mm^2, and a distance between WE and CE electrodes also of 19 mm. Assume that the cell is filled with 11 mM $Cu(NO_3)_2$(aq). Use info around Fig. 10-5, in particular footnote 1007 and web resource Web#1007.

Report: What is the ohmic electrolyte conductivity and resistivity and the corresponding cell resistance?

Let's add 1 M KNO_3(aq) as supporting electrolyte.

Report: Use charge mobilities of ions from the textbook, and calculate the new electrolyte conductivity, resistivity, and corresponding cell resistance.

Report: Make an *I-E* plot for this polarisation between -1 and +1 V.

2.1.2 Kinetic polarisation

Assume that the reactants and products of reduction are R(aq) and O(aq), irrespective of the example of $Cu(NO_3)_2$ above.

Report: Construct a solely kinetic polarization curve for the WE electrode reaction assuming $c_R^b = 1.50$ mM, $c_O^b = 0.50$ mM, $E^{o'} = 0.0500$ V, $k^{o'} = 4.0\times10^{-6}$ m/s, $\alpha = 0.60$, $T = 280$ K. These are the same parameters as in footnote 1016, allowing you to consult Web#1016.

You may for instance make the curve between potentials of -1 and +1 V in e.g. Excel by generating a list of potentials of step 0.1 V and calculating *i* or *I* by the appropriate Butler-Volmer reaction.

Report: What is the charge transfer resistance in absolute and area-specific units?

2.1.3 Transport polarisation

Read about transport polarisation up to and including Eq. 10:19.

Report: Use the equations there to understand and calculate what is the open circuit potential (null potential)? What is the transport overpotential at a current where the difference between bulk and electrode surface concentrations vary by 10% for both R and O. Consult footnote 1019 and Web#1019.

Read on about limiting current densities.

Take your voltammogram for kinetic polarisation, select the currents (or current densities) you have at ±1 V and assume them to be the limiting anodic and cathodic current densities.

Report: Specify the values you chose. Now, make a plot of solely the transport polarisation curve using Eqs. 10:26 and 10:27.

2.1.4 Multiple polarisations

Report: Make plots of combined polarisations ohmic+kinetic and ohmic+transport. Comment.

Report: Make a similar combination for all three polarisations. Comment. Why is it not correct?

2.2 Exercise for Chapter 11 Corrosion

Read about corrosion and its significance in the textbook Chapter 11. This exercise intends to give a glimpse into two of the most important parameters when one studies corrosion of a material. These parameters are the corrosion potential (E_{corr}) and the corrosion current (I_{corr}) and one should go through pages 217-221 of the textbook.

Raw data we will use are available via the semester page. They are recorded in the Group for Electrochemistry and correspond to three sample types. The samples are based on a NiTi alloy (known also as nitinol) and sample number 1 is the pure alloy, while samples number 2 and 3 are nitinols that were surface treated with two types of compounds that might have corrosion resistance characteristics. Your job is to assess whether the coated samples have better anti-corrosion resistance than the pure alloy, by evaluating their E_{corr} and I_{corr}.

Then, and after you study Figure 11-8 and the corresponding text, you should indicate, which one of the three samples has the widest corrosion resistance potential window.

For the Report

2.2.1 Plot the three data sets[2] for sample 1, sample 2 and sample 3 the same way as the data in Figure 11-4[3] in the textbook and extract the corrosion potential and corrosion current for each sample, i.e. nitinol-based material.

2.2.2 Show the linear fits you used in your tafel analysis and draw dashed lines towards the potential axis and logI axis.

2.2.3 Assess which sample has the best anti corrosion characteristics based on the extracted parameters.

2.2.4 Which one of the three materials has the widest passive region?

2.2.5 Can you guess a possible application and research area of these materials? Where did our collaborator and his samples come from?

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[2] The current is given in A and the potential in V.

[3] As the curves you received are from a real system, do not expect them to look like the ones in this figure. On the other hand you need to identify those regions that look like the ideal curves in Figure 11-4 and extract your parameters.

2.3 Exercise for Chapter 12 Steady-state voltammetry

Read page 249-253 in Chapter 12 – steady-state voltammetry, in this session we will go through a few of the derivations and discuss a bit further.

Alternative to Equation 12:22 in the textbook, the current for reaction R*(soln)* ⇌ ne$^-$ + O*(soln)* can also be expressed as:

$$I = 2nFc_R^b k_f r_{hemi} / [((k_f/D_R) + (\pi/r_{hemi}) + (k_b/D_O)] \quad 1$$

where k_f and k_b are the forward and backward rate constants, respectively. From Butler-Volmer equations, we can have:

$$k_f = k^0 \exp[-\alpha nF(E - E^0)/RT] \quad 2$$

$$k_b = k^0 \exp[(1-\alpha)nF(E - E^0)/RT] \quad 3$$

2.3.1: Check the denominator of the right-hand side of equation 1, identify the term that corresponds to I_{kin}, I_{rem} and I_{lim}.

2.3.2: Use equation 1-3, equation 12:23 in the text book, and your answer from Exercise 1 to drive the expression for each current component I_{kin}, I_{rem} and I_{lim}, compare your results with the textbook.

2.3.3: From Exercise 2, explain why two current components have Nernstian expressions, while the other one does not.

2.3.4: Use either your results from Exercise 2 or the extended equation 12:23 in the textbook to express the current in reversible and irreversible conditions.

2.3.5: Check the simulated curve for:

Reversible:
https://demonstrations.wolfram.com/ReversibleSteadyStateVoltammogramsAtMicroelectrodes/

Quasi-reversible or irreversible:
https://demonstrations.wolfram.com/QuasiReversibleAndIrreversibleVoltammogramsAtMicroelectrodes/

Vary the parameters, plot simulated steady-state voltammograms. Describe and explain the difference between reversible, quasi-reversible and/or irreversible SSV.