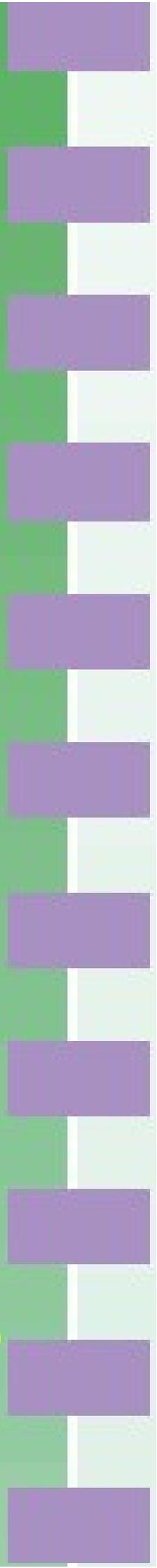# Electrochemistry

Laboratory exercises for KJM3110 at UiO

2020

Welcome to the laboratory course

KJM3110 Electrochemistry provides an introduction to electrochemistry. In the laboratory course we will illustrate and complement some parts of the curriculum, introduce some additional concepts, provide training in laboratory work, and see how research in electrochemistry are important parts of the work at IFE and SINTEF.

GENERAL INFORMATION

The laboratory exercises and excursions in KJM3110 are mandatory with respect to attendance, execution, and reports. Accepted reports are required to be admitted to the exam in KJM3110.

The only acceptable reason for absence is normally sickness with doctor's attestation. By acceptable absence, a compensating exercise can be requested, e.g. the same exercise at a later occasion, or a theoretical exercise.

Before the first exercise the students shall have taken the standard safety training at the Department of Chemistry and read its laboratory safety rules as well as the ones that follow here.

Use protective equipment, including your goggles and lab coat.

Before each lab, the student is expected to have taken part in any announced mandatory preparation lectures and colloquiums, have read the laboratory exercise instructions, made required calculations, and noted any unclear points and questions one might have.

It is important to meet at the right time, and be prepared. The practical part of the exercise is nominally maximum 5 hours including breaks for lunch etc. Students will work in small groups at different experiment stations.

Write a **journal** during the exercise, and have it signed by the supervisor. Together with the accepted **report**, it forms the documentation for having made that laboratory exercise.

The report shall be delivered by email or otherwise as instructed within one week after the laboratory. The report shall on average be less than 2 pages per experiment station, plus front page, and e.g. references. It shall for each experiment contain a short introduction of principles and theory, experimental setup, summary and/or tables or plots of results, discussion, and conclusion. It is recommended to take pictures of setups, but to draw them schematically, and in any case mark essential parts. Detailed measurements and e.g. some of the pictures or schematics can be left for the journal, and the report need not repeat unnecessary detail. The report shall not unnecessarily repeat materials from the exercise instructions, textbook, or other sources, but form an original independent document.

While students in the group may share the same data set, pictures, etc., the reports must be independent. Note that academia and the university has strict rules against improper use of text you have not written yourself.

SAFETY RULES IN THE LABORATORY

Messages and instructions from supervisors and other personnel must be observed and followed. By injury, immediately alert the staff and initiate first aid. Telephone numbers to rescue at UiO and hospital are posted in the laboratory.

In chemistry laboratory, all must wear lab coat and eye protection – goggles or lab glasses. All must know where the nearest fire extinguisher, emergency shower, eye-flush, and first aid kits are and how they are operated.

Respect all warning signs.

Be careful when operating electrical apparatus. Voltages higher than 42 V are considered potentially lethal, and must never be applied to electrodes etc., or touched. In electrochemistry, we apply only much smaller voltages – of the order of a few volts – to electrodes and solutions. They are safe to touch (connect, disconnect, etc.) but as a precaution, do *not* hold on to earthed chassis, water pipes, taps, racks, etc. with the other hand when handling electrical and electrochemical small voltage experiments in the laboratory.

Do not eat or drink in the laboratory.

Private laboratory experiments are not allowed. Presence in the laboratory outside of course hours is not allowed.

Make yourself acquainted with waste procedures. Small amounts of non-harmful chemicals may be flushed out in sinks. However, dispose of harmful chemicals only in designated containers. Ask personnel if in doubt.

By fire alarm, close/stop flames, and evacuate the building.

Do not rush. Do not run in the laboratory or just outside it.

Follow rules and keep the workspace in the laboratory tidy.

Unauthorised persons and students not registered for the course do not have access to the laboratory.

Breakage of safety rules can lead to danger for your own and others' health.

Serious breakage of rules may lead to expulsion from the laboratory course.

SIMPLE FIRST AID

Splash of chemicals in the eye: Flush with cold water from nearest tap or eye-shower or eye-washing flask. Continue till doctor takes charge. See poster "Legehjelp ved ulykker" and similar. Users of contact lenses: Flush first. Remove lenses. Continue flushing.

Splash of chemicals on the skin: Flush with ample cold water, remove stained clothes, flush the skin, wash with soap and water.

Burns: Flush burnt area with cold water from nearest source such as tap or shower. Keep the burnt area in water (15 - 20˚C). Continue treatment also while waiting for and during transport to hospital.

Cuts: Flush with cold water from the tap. Stop bleeding, put on band aid, use "enkeltmannspakke" or "blodstopper" in the first aid kit cupboard. Seek doctor for sewing if needed.

Gas poisoning: Fresh air and calm, call for doctor/ambulance.

Poison in the mouth/stomach: Drink a lot of cold water. Consult the chemicals data bank for dangers and remedies. The «Giftinformasjonssentralen», tlf. 22 59 13 00, may give additional information. Contact the hospital; Ullevål sykehus, Medisinsk avd., akuttmottaket, tlf. **02770**.

Electric shock: Remove the injured from the voltage source. By heart arrest: Start immediately first aid: artificial breathing and heart massage.

Fainting: Stable side position. Check pulse and breath.

1. Electrochemical cells

1a. The Galvanic (Daniell) cell

Chemical reactions involving the transfer of electrons from one reactant to another are called oxidation-reduction reactions or redox reactions. A piece of zinc going into a solution as zinc ions, with each Zn atom giving up 2 electrons, is an example of an oxidation half-reaction.

$$Zn(s) \rightarrow Zn^{2+} (aq) + 2e^- \tag{1}$$

Alternatively, ions gain a certain number of electrons to decrease their oxidation number, e.g. the reverse of reaction (1), is an example of reduction half-reaction. Another examples is Cu^{2+} ions receive $2e^-$ to form solid copper,

$$Cu^{2+} (aq) + 2e^- \rightarrow Cu(s) \tag{2}$$

Each half-reaction has its own chemical potential, which follows Nernst equation and is dependent on ion activities (concentrations) and temperature. In order to make things simple, at standard conditions, i.e. 25 °C and concentrations of 1.0 M for the aqueous ions, the measured voltage of the **reduction** half-reaction is defined as the standard reduction potential, $E°$, as shown in the table below.

	Reduction half-reaction	E^0 vs. SHE (V)
E^0_1	$Zn^{2+} + 2e^- \rightarrow Zn$	- 0.762
E^0_2	$Cu^{2+} + 2e^- \rightarrow Cu$	+ 0.342

Note E^0_1 is more negative than E^0_2. This means at standard conditions, Zn^{2+} is more difficult to be reduced than Cu^{2+}, in other words, Zn is more likely to be oxidized (losing electrons) forming Zn^{2+} and Cu^{2+} tends to be reduced (receiving electrons) forming Cu. If we put reactions (1) and (2) together, it leads to a full reaction.

$$Zn(s) + Cu^{2+} \rightarrow Zn^{2+} (aq) + Cu \tag{3}$$
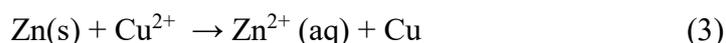
Reaction (3) indicates an electron flow from Zn to Cu^{2+}, hence can be used as a battery, of which the voltage can be written as:

$$E_{cell} = E_{red} - E_{ox} = E_{Cu^{2+}/Cu} - E_{Zn^{2+}/Zn}$$

Equipment

100 ml beakers
Filter paper (to establish the salt bridge)
Cu foil
Zn foil
LED light
Voltmeter (or multimeter)
4 wires with crocodile clips

Assemble a Daniell cell according to the figure below and the text following.
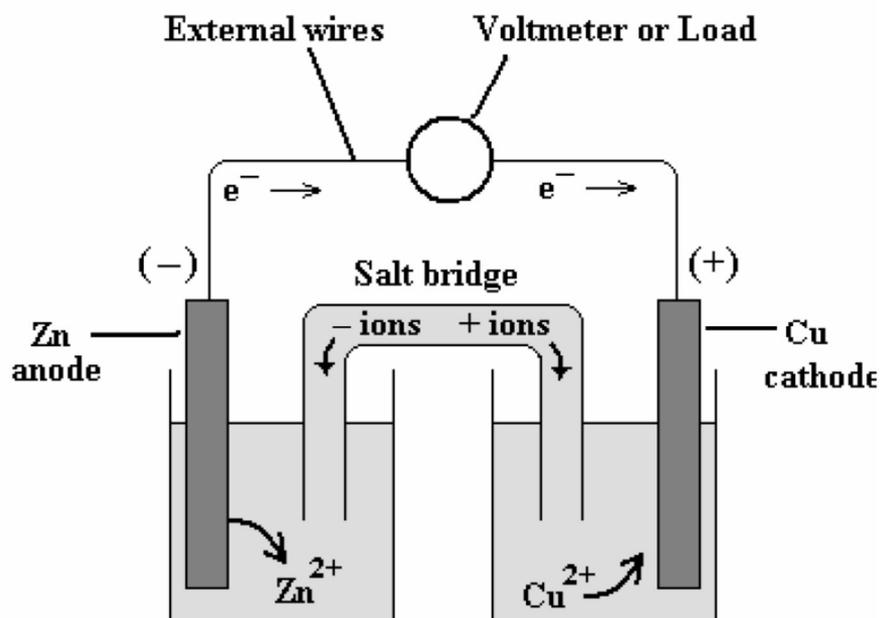
Fill the beaker having the Cu foil with copper sulphate solution in the concentration of 1M. Fill the other beaker with the Zn foil with Zn sulphate solution also in the concentration of 1M.

Soak the filter paper with 1 M KNO_3 solution and establish the salt bridge by straddling the two beakers.

Connect the positive side of the voltmeter to the Cu electrode and the negative side to the Zn electrode and measure the voltage.

Practical and report exercises

1. Use Nernst equation to express $E_{Cu^{2+}/Cu}$, $E_{Zn^{2+}/Zn}$ separately, and write the Nernst equation for the complete reaction voltage E_{cell}.

2. Use the expression of E_{cell} from Exercise 1 to explain the voltage you measured. If the 1 M Zn sulphate is replaced by 0.5 M, predict the value of E_{cell}, and confirm your prediction by experiment.

3. Replace the voltmeter with the LED provided, it needs 1.6~2.0 V to light up. Use all the materials available to construct a battery to power the LED. Hint: the longer pin of the LED needs positive potential, i.e. the current should flow into the diode thought the longer pin.

4. Select proper cathode and anode half-reactions from the standard chemical potential table (either from the book or from internet), design your own battery and predict the output voltage.

1b. Electrosynthesis – Ni electrodeposition

Read about electrosynthesis in the textbook Chapter 4, pages 71-73. In this exercise you set up an electrolysis cell, where you can deposit a metal, from a solution of its ions (plating solution), on the surface of a substrate. In this case, Ni is electrodeposited on two different substrates; i) Conducting glass and ii) Carbon-based substrate.

The electrodeposition can be carried out in a two-electrode or three-electrode electrochemical cell. Both configurations should be tested.

Equipment

100 ml beaker
Stirrer and stirring bar
Plating solution
The substrate or working electrode
The auxiliary or counter electrode (Pt or Ni foam)
The reference electrode (only for the three-electrode configuration): Standard calomel electrode (SCE).
Voltmeter (or multimeter)
Power supply
Potentiostat
3 wires with crocodile clips

Practical exercises

1. Prepare a 250 ml plating solution consisting of 0.01 M nickel sulphamate, 0.227 mM nickel chloride and 0.025 M boric acid.

2. Electrodeposition in two-electrode configuration: Set the working electrode[1] as the cathode and the Ni foam as the anode and apply a voltage of 1.45 V (use power supply) for 3 min. Test the deposition with and without stirring. How would you characterise the film?

3. Electrodeposition in three-electrode configuration: In this case the reference electrode (SCE) is measuring the voltage against the working electrode. In the same plating solution apply -1.35V vs. SCE (use a potentiostat) for 3 min. Test the deposition with and without stirring. How would you characterise the film now?

Report exercises

1. Estimate how much Ni is deposited in each case by integrating the current vs. time curve.

---

[1] Tip! The glass substrate you received is conducting from one side because it is coated by a thin layer of fluorine doped tin oxide (FTO). Use the multimeter to find which side is conducting and where to expect the Ni deposition to occur.

2. In which case does the electrodeposited Ni film appear more homogeneous? Can you explain why?

3. Find the Pourbaix diagram for Ni and point on it where the deposition was carried out. Can you estimate the pH of the plating solution before measuring it with the pH meter?

1c. H₂ evolution by H₂O electrolysis

Read the electrolysis of water part in the textbook Chapter 4, page 77-79 and the electrode potentials part in the Chapter 6, page 105-109. The Daniell cell uses the electricity "created" during the red-ox reactions, where electrons transfer from species with a higher energy state to another with lower energy state. On the other hand, electricity can be used to force electron transfer that cannot occur spontaneously, i.e., to pump the electrons from a lower energy state to higher. In a H₂ fuel cell, H₂ donates electrons to O₂ forming H₂O.

$$2H_2 + O_2 \rightarrow 2H_2O \tag{1}$$

Reaction (1) has a standard cell voltage of E^0_{cell} = *1.23 V*, and it is a spontaneous reaction since $\Delta G = -nFE^0_{cell} < 0$. In this experiment, we will use electricity to reverse reaction (1) to produce H₂ from the electrolysis of water.

$$2H_2O \rightarrow 2H_2 + O_2 \tag{2}$$

Equipment

100 ml beaker
Potentiostat
FTO glass (both clean and with Ni deposited)
Pt foil
Pt wire as counter electrode
SCE reference electrode
KNO₃

Practical exercises

1. Fill the beaker with 50 ml water.

2. Set up the three-electrode electrochemical cell: connect the counter electric wire (C) to the Pt wire, the reference electric wire (R) to the SCE reference electrode, and the working electric wire (W) to a clean FTO glass (with 2 cm² electrically active area immersed in the solution).

3. Run Linear Sweep Voltammetry (LSV) from 0 to -1.5 V vs. SCE, with scan rate of -10 mV/s.

4. Change the clean FTO glass to Ni-deposited one, with the same electrically active area immersed in the solution, repeat step 3.

5. Change the working electrode to Pt foil, note now the Pt foil is conducting on both sides, so the nominal area immersed should be half of the FTO glass electrodes. Repeat step 3.

6. Add a certain amount (ca. 5 g) of KNO_3 into the water, repeat step 2-5, and see the effect of supporting ions.

Report exercises

1. Normalize the current with respect to electrically active area, plot the j-E curves of the three electrodes in the same solution (2 plots, one with water the other with KNO_3 added).

2. Plot the j-E curves of the same electrodes but in different solutions (3 plots, each electrode in two different solutions should be plotted together).

3. Describe and explain the phenomena you witnessed in exercise 1 and 2.

4. Use Nernst equation to calculate the chemical potential of $E_{H+/H2}$ in water (pH 7). SCE has a potential of 0.241 V vs. SHE, determine the $E_{H+/H2}$ *vs. SCE (equation 6:5)* and mark it in the plots.

5. Plot *E* against *log j* for different electrodes, either in water or with salt, extract the Tafel slopes, compare and discuss the information you can get from those values.

1d. Diffusion coefficient for the oxidised species in the $[Fe(CN)_6]^{3-/4-}$ redox couple

We shall attempt a measurement of diffusivity using the setup in textbook Figure 8-7, using related theory on pages 154-157, illustrating the application of Fick's laws of diffusion and analysing the results using the Cottrell equation. In this exercise you set up an electrochemical cell with the redox couple $[Fe(CN)_6]^{3-/4-}$ in an aqueous solution containing a supporting electrolyte, KNO_3. We will reduce the $[Fe(CN)_6]^{3-}$ ion, so the reaction will be the opposite of an oxidation reaction as used in the examples in the textbook.

We use a suitable, planar WE in a geometry that resembles that in Fig. 8-7, and a suitable, reversible RE.

Equipment

100 ml beaker
Potassium ferricyanide, $K_3[Fe(CN)_6]$
Potassium nitrate KNO_3
Potentiostat or power supply
Working electrode: Pt
Reference/counter electrode: SCE, Pt, or graphite rod

Practical exercises

1. Prepare a solution of 1 M KNO_3 and 100 mM $K_3[Fe(CN)_6]$.
2. Set up the two-electrode measurement cell with a liquid volume of 70 ml.
3. What is the open circuit potential of the cell?
4. Instantly, apply 1 V more negative potential to the WE and record the current vs time till it has decayed significantly.
5. Stir, let come to rest, and repeat at the same voltage as any of the preceding ones, to check reproducibility.
6. Stir, let come to rest, and repeat at two different (still more negative than open circuit) voltages, dependent on your experience with the first one. If you have no other indications, repeat at 0.7 and 1.3 V more negative.

Report exercises

1. Plot the current vs time for all parallels. Does it seem to follow the Cottrell equation?
2. Derive a linear version of the Cottrell equation, and replot all the curves according to that. Are they linear, i.e. confirming the assumptions and behaviour expected in the experiment?
3. Find the slopes by linear regression, include standard deviation (error), and calculate the corresponding diffusion coefficients.
4. Are they independent on voltage and are they reproducible? If not, discuss possible reasons.
5. Is the diffusivity of an order of magnitude as expected for such an ion in water at ambient conditions?

6. Suggest one or two additional experiments or parallels you would think it would be useful and/or interesting to do on the same diffusivity for the same system, and argue what they would lead to of additional information and insight.

1e. Ion-selective membranes and electrodes: The pH meter

The potentiometric measurement of pH is based on an ion selective electrode (ISE) for H^+ ions, utilising a glass membrane which is permeable to H^+ (or H_3O^+) ions.

Read about ISEs on pages 119-123 in the textbook.

The galvanic cell shown in Fig. 6.10 can for instance utilise two Ag|AgCl electrodes:

$Ag \mid AgCl_{(s)} \mid HCl_{(0.1N)} \mid$ glass membrane $\mid$ unknown solution $\mid HCl_{(0.1N)} \mid AgCl_{(s)} \mid Ag$
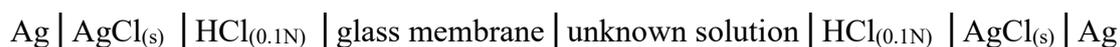
or it can utilise a calomel reference electrode:

$Ag \mid AgCl_{(s)} \mid HCl_{(0.1N)} \mid$ glass membrane $\mid$ unknown solution $\mid KCl_{(sat)} \mid Hg_2Cl_2 , Hg$

With the assumption that the diffusion potentials of this electrode are close to zero, the potential that forms is

$E = E_{ref} - E_g$

The glass electrode potential under standard conditions is

$E_g = E_g{}^o - 0.059\ pH$

So the potential of the unknown solution can be found from

$$pH = \frac{E + E_g^o - E_{ref}}{0.059}$$

Equipment

Voltmeter
pH electrode cell
pH meter
Two or three solutions of known pH
One solution of unknown pH
Beaker for flushing
Water for flushing electrodes
Paper for drying electrodes

Report and practical exercises

1. What is E_{ref} for the two cells above? Why are they constant?

2. Derive the equation for E_g and find the nominal value for $E_g{}^0$.

3. Inspect the pH meter and identify the galvanic cell given above. Provide your own schematic of the cell and label the essential components.

4. Calibrate the pH cell using two or three known solutions and draw the calibration curve.

5. Measure the voltage of the cell using an unknown solution and find its pH using the calibration curve.

6. How does it compare with the value yielded by the pH meter?