

POTENTIAL OF ELECTROCHEMICAL DEPOSITION OF HYDROGEN

INTRODUCTION

The Galvanic cell consists of two half-cells connected with an electrolyte solution. The connection of the electrodes results in the flow of the electric current. This current flow is caused by chemical processes occurring at the electrode/electrolyte interface.

Electrochemical processes at electrodes can be also forced by the external power supply. Such a process is called **electrolysis**. The electrolysis process is possible only when the potentials of the electrodes exceed the stationary potentials that can be described by the **Nernst equations**.

During the electrolysis of water or water solutions, a cathodic process can occur with hydrogen deposition.

The reduction of the hydrogen can be described by the equation:



In the case of hydrogen electrode, when the electrode stays in contact with hydrogen ions and gas hydrogen particles as well, potential can be described by the equation:

$$E = \frac{RT}{nF} \ln[H^+] \quad (2)$$

The potential at which the deposition process starts is called **deposition potential** E_p :

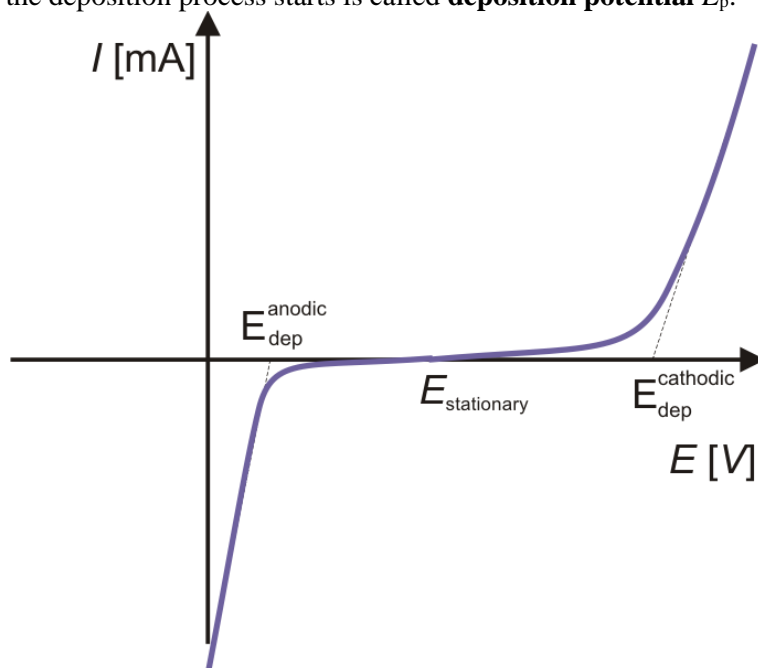


Figure 1. Potential – Current characteristics.

A value of the additional potential at which the electrode process occurs is called **overpotential** η (Greek symbol: eta).

$$E_{dep} = E_{stat} + \eta \quad (3)$$

Where $E_{stationary}$ – stationary potential described by the Nernst equation.

Curves of the current – potential can be measured by two methods: potentiostatic or galvanostatic.

The galvanostatic method consists of measuring the potential of the electrode versus the reference electrode (i.e. calomel electrode) at constant values of the current signal flowing between the measured electrode and the counter electrode

The potentiostatic method is based on the constant values of potential and measures the current flowing through the working electrode.

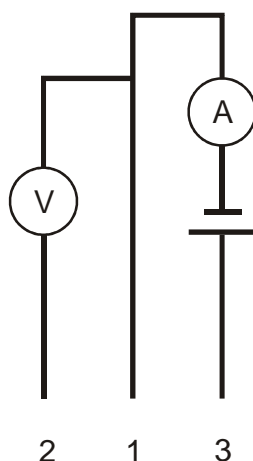


Fig.2. Scheme of the circuit used during the galvanostatic method;

1 – Working (measured) electrode, 2 – reference electrode, 3 – counter electrode, V – voltmeter, A – power supply.

EXERCISE PURPOSE

The aim of this exercise is to draw a curve of the current–potential (by the galvanostatic methods) for the hydrogen deposition process at the platinum and copper electrodes as well determination of the overpotential of the hydrogen deposition.

APPARATUS

- DC power supply.
- Multimeter.
- Magnetic stirrer.
- Electrode holder and stand.
- Counter electrode - Platinum electrode.
- Measured electrodes - platinum and copper electrodes.
- Reference electrode – saturated calomel electrode (SCE)
- Connecting wires

LAB GLASS

- Beaker - 100 ml.
- Volumetric flask - 100 ml.



- Pipettes - 10 ml.

CHEMICALS

- Solution of the H_2SO_4 - 0.1 N.
- Solutions of the NaOH - 0.1 N.

EXPERIMENT PROCEDURES

1. Connect the circuit according to information from Fig 2. Place the electrodes in the solution of the 0.1 N H_2SO_4
2. Set the value of the current on 0.2 mA and measure the potential values of the copper electrode as a working electrode versus the calomel electrode.
3. Repeat measurements in the range of 0.2 to 5.0 mA, every 0.2 mA. Repeat the measurements for the platinum electrode.
4. Repeat the measurements for solutions of 0.01N H_2SO_4 , 0.1N NaOH and 0.01 NaOH . Obtained data let you draw eight curves.

CALCULATIONS

1. Place all measured and calculated values in the table form.
2. Draw the current–potential curves for all particular solutions of hydrogen ion concentrations and electrodes
3. Draw the tangents of the curves at regions of chemical reactions (see an example in Fig 1). Read the values of the hydrogen deposition potentials from the figures (E_{dep})
4. Calculate values of the deposition potentials in the hydrogen scale. Values of the calomel electrode potential +0.274V in hydrogen scale:

$$E_{\text{dep}} (\text{vs. hydrogen electrode}) = E_{\text{dep}} (\text{vs. calomel electrode}) + 0.274\text{V}$$

5. Calculate the overpotential of the hydrogen depositions by the use of Equation (3). Stationary potential can be calculated from Nernst equation (Eq. (2)) taking into account appropriate concentration of the hydrogen ions (i.e. for H_2SO_4 0.1 N concentration of $[\text{H}^+]$ is 0.1 mol dm^{-3}) In case of sodium hydroxide solutions, concentration of the hydrogen ions can be calculated assuming self-ionization of water and ionic product of water ($[\text{H}^+][\text{OH}^-] = 10^{-14} \text{ mol}^2 \text{ dm}^{-6}$)
6. Calculate the mean value of the overpotentials for platinum and copper.



Template of the table and draft of the study

..... <i>Faculty</i> <i>Field of study</i> <i>Full-time/ part-time studies</i> <i>Name and surname</i> <i>Date:</i>
<i>Group no.:</i> <i>Team no.:</i> <i>Exercise no.:</i> <i>Instructor:</i>

..... <i>Wydział</i> <i>Kierunek</i> <i>Studia stacjonarne/niestacjonarne</i> <i>Imię i Nazwisko studenta</i> <i>Data wykonywania ćwiczenia:</i>
<i>Nr grupy:</i> <i>Nr zespołu:</i> <i>Nr ćwiczenia:</i> <i>Nazwisko Prowadzącego:</i>

1. Temat ćwiczenia
2. Cel ćwiczenia:
3. Wstęp teoretyczny:
4. Pomiar:
5. Obliczenia:
6. Wykresy:
7. Wnioski

1. Exercise title:
2. The aim of the exercise:
3. Theoretical introduction:
4. Results:
5. Calculations:
6. Graphs:
7. Conclusions: