Physical Chemistry

Electrochemistry
Electrolysis

Electrolytic polarisation with CASSY

Aims of the experiment

■ To perform an electrolysis.

■ To understand polarisation and decomposition voltage.

■ To compare electrolysis using various redox pairs.

■ To examine polarisable and nonpolarisable electrolysis cells.

■ To understand overvoltage in practice.

Principles

In electrolysis, chemical compounds are broken up using electrical current; or metals are dissolved or precipitated. If the voltage is increased from a value of zero in order to carry out an electrolysis, one will see that the flowing current only begins to increase at a specific voltage. This value is called the decomposition or precipitation voltage and is determined by the redox pair under investigation at the anode and cathode. In electrolysis, the anode and cathode form a galvanic element and represent a DC source. From the respective potentials of the two half cells, the electromotive force (EMF, ΔE) of the galvanic element can be calculated.

$$EMK = \Delta E = E_{Anode} - E_{Cathode}$$

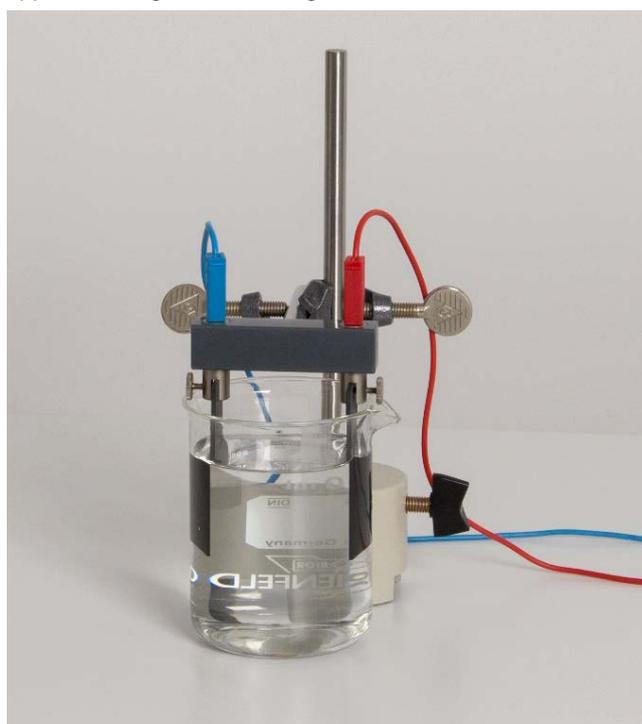The EMF that forms between two half cells acts against the applied voltage. The voltage that must be overcome is equal to the polarisation voltage.

However, the theoretically calculated polarisation voltage is usually below the actual required voltage to achieve electrolysis. As in many chemical reactions, this is a type of activation energy that must be overcome. This difference between the theoretically calculated and the practically required voltage is called overvoltage.

The overvoltage depends on the limitation of the reaction at the electrodes and on the electrolyte, its concentration, the temperature and the current density. Thus:

Decomposition voltage =

Polarisation voltage + Overvoltage

A peculiarity arises when the same redox pair is used at the anode and the cathode. In this case, no polarisation or decomposition voltage can be observed and the cell cannot be polarised. In such an electrolysis, only the Ohmic resistance must be overcome, which is independent of the flowing current, the applied voltage and the frequency. If a current/voltage curve is plotted for this, a line of origin can be observed.

In this experiment, current/voltage curves will be plotted. First, the polarisation voltages of three electrodes will be compared in the electrolysis of water. Also, the difference between a polarisable and a nonpolarisable cell will be observed in the electrolysis of a copper sulfate solution.

Risk assessment

When working with copper sulfate solution, make sure that no contact occurs with skin or eyes. Also, under no circumstances must the solution be drained down the lab drain since it is environmentally hazardous.

The sodium hydroxide solution used in the experiment is very dilute, but contact with skin and eyes must be avoided.

Fig. 1

Copper sulfate solution, approx. 1 M (=15%)	
Signal word: Caution	**Hazard warnings:** H302 Harmful if swallowed. H319 Causes serious eye irritation. H315 Causes skin irritation. H410 Very toxic to aquatic life with long-lasting effects. **Safety information:** P273 Avoid release into the environment. P302+P352 IF ON SKIN: Wash with plenty of water and soap. P305+P351+P338 IF IN EYES: Rinse continuously with water for several minutes. Remove contact lenses if present and easy to do. Continue rinsing.

Sodium hydroxide, 0.1 mol/l	
Signal word: Caution	**Hazard warnings:** H290 May be corrosive to metals. **Safety information:** P234 Keep only in original container. P390 Absorb spillage to prevent material damage.

Equipment and chemicals

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1  Power CASSY USB.................................524011USB
1  CASSY Lab 2 ..........................................524 220
1  Electrode holder .......................................664 373
2  Plate electrodes, copper, 76 x 40 mm ......591 53
2  Plate electrodes, carbon, 76 x 40 mm ......591 61
1  Mesh electrode, platinum, 55 x 40 mm.....664 420
1  Beaker, Boro 3.3, 400 ml, squat...............664 131
1  Connecting leads 19 A, 50 cm .................501 45
1  Saddle base ...........................................300 11
1  Stand rod, 25 cm, 12 mm diam. ...............300 41
1  Bosshead S.............................................301 09
1  Sodium hydroxide solution, 0.1 mol/l........673 8410
1  Copper sulfate solution, 1 M (= 15 %)......672 9660
Additionally required:
PC with Windows 7 or higher
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Set-up and preparation of the experiment

Set-up of the apparatus

1. The apparatus is set up as can be seen in Fig. 1.

2. Fix the stand rod in the saddle base.

3. Fasten the electrode holder to the stand rod using a bosshead S clamp.

4. Clamp the platinum mesh electrodes into the electrode holder.

5. Insert the two connecting leads into the outputs of the electrode holder and connect to the respective inputs at the power CASSY USB.

6. Connect the power CASSY USB to the USB port of the PC and turn on CASSY Lab 2.

7. Load the settings into CASSY Lab 2.

CASSY Lab 2 settings:
Voltage U_1 (Out) activated:
Signal form:
Parameters: 0.1 Hz, 3 Vp, 100%, 0 V=
Current I_1 activated
Representation
Select new representation, X-axis: U_1 Y-axis: I_1

Performing the experiment

Electrolysis of water (0.1 M sodium hydroxide solution)

1. Place the electrodes into the beaker and fill up with NaOH (0.1 M) for them to be about half immersed.

2. Start the measurement using the stopwatch symbol.

3. The Power CASSY will now automatically increase the voltage from 0 V to the end point setting of 3 V and measures the current *I* in mA at the same time.

4. From the values measured, a current/voltage curve is immediately obtained.

5. Then, repeat the experiment for the copper and carbon electrodes.

Electrolysis of copper sulfate solution

1. The process is exactly the same for the electrolysis of copper sulfate solution as in the electrolysis of water.

2. Place the electrodes in the beaker and fill as much copper sulfate solution (1 M) for them to be about half immersed.

3. The experiment is first carried out with the copper electrodes, which are then replaced by the carbon electrodes.

4. Start the measurement using the stopwatch symbol.

Observation

Electrolysis of water (0.1 M sodium hydroxide solution)

At the beginning of the experiment, there is hardly any current to be seen with either electrode. With the carbon electrodes, the current begins to flow right away when the voltage is increased slightly. At the moment that the current is increased, the electrolyte begins to decompose. This can be seen by the formation of gas bubbles. With the copper and platinum electrodes, the current only begins to flow at higher voltages, but then increases linearly as with the carbon electrodes.

Electrolysis of copper sulfate solution

In the electrolysis of the copper sulfate solution, the difference between the two tested electrode materials is even clearer. When using the copper electrodes, the current flow begins to increase right away at very low voltages. In the carbon electrodes, a higher voltage is needed to cause the electrolytes to decompose.

Evaluation

For the evaluation of the experiment, the measurements for current (*I*) are plotted against those for voltage (*U*). At the voltage at which the current increases linearly, the polarisation voltage and overvoltage have been exceeded. This corresponds to the decomposition voltage.

Electrolysis of water (0.1 M sodium hydroxide solution)

The current/voltage curves are plotted using CASSY Lab 2. The results can be seen in Fig. 2.
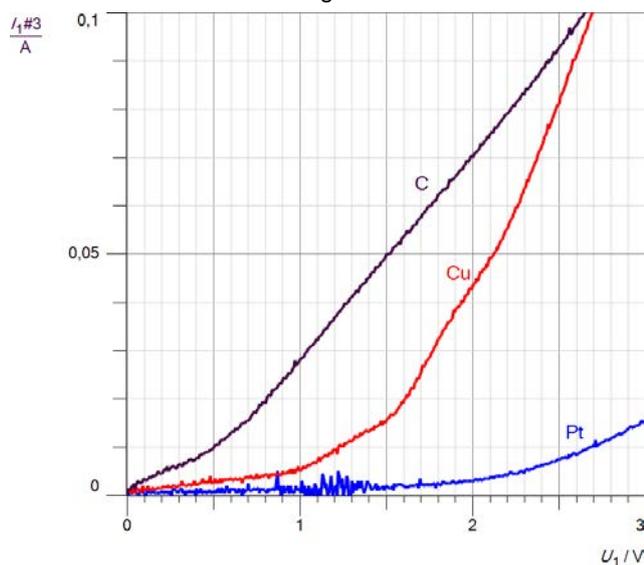

Fig. 2 Current/voltage curves for the electrolysis of water.

The polarisation voltage is most pronounced with platinum electrodes. The value at which the polarisation voltage and overvoltage are overcome has the highest value. Not until a value of 2 V does a linear current increase begin, and at this point gas generation is observed. In contrast, the carbon electrodes have the weakest polarisation. Even at low voltages of less than one volt, the current flow increase begins.

Electrolysis of copper sulfate solution

The current/voltage curves of the electrolysis of copper sulfate solution are shown in Fig. 3.

In this test section, the difference in polarisation between the various electrode materials with the same electrolytes is even clearer. With the carbon electrodes, a much higher decomposition voltage is needed for the electrolysis of copper sulfate. It increased linearly beginning at a value of about 1.5 V. No polarisation is seen during the electrolysis using copper electrodes. In this case this is a nonpolarisable cell since the same redox pair exists both at the anode and at the cathode. It must only overcome the Ohmic resistance so that the current can increase linearly relative to the voltage.

Due to the nonpolarisable nature of the cell, a line of origin is obtained. This can be useful in copper cladding or copper refining since only low voltages are needed. This in turn helps to avoid undesirable secondary reactions in such processes.
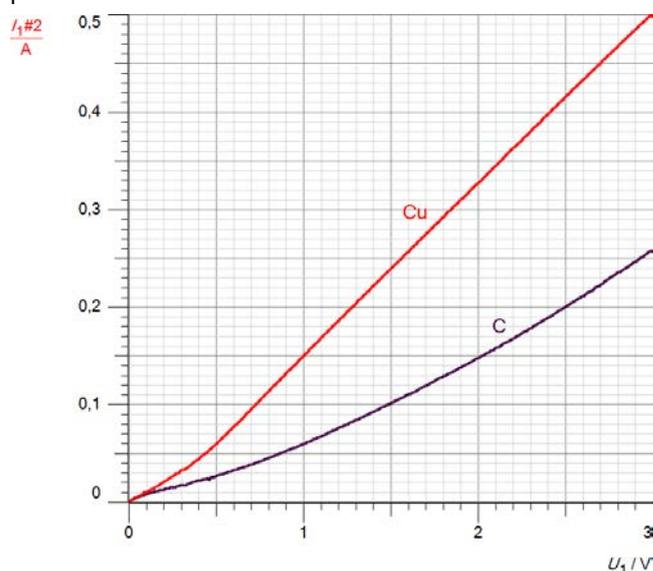

Fig. 3 Current/voltage curves for the electrolysis of copper sulfate solution.

Results

The decomposition voltage of the electrolyte depends on many factors. In addition to the electrode material, the electrolyte also plays an important role. Since concentration and temperature also have an influence, the values measured here should only be considered as tendencies. In water, the decomposition voltage is the lowest for carbon at less than 0.4 V, whereas for copper it is approx. 1 V and for platinum it is approx. 2 V.

In copper sulfate solution, on the other hand, the decomposition voltage for copper electrodes is 0 V, whereas for carbon approx. 0.5 V is needed.

Cleaning and disposal

The copper sulfate solution must be collected in the waste for inorganic salt solutions that contain heavy metals. The sodium hydroxide solution can be disposed of in the laboratory sink with plenty of water.