

Electrolytic polarisation with the electrochemistry demo unit

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 unpolarisable electrolysis cells.
- To understand overvoltage in practice.

Principles

In electrolysis, chemical compounds are split 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 current that flows only begins to increase at a specific voltage. This value is called the decomposition or precipitation voltage and is determined by the respective redox pairs at the anode and cathode. In electrolysis, the anode and cathode form a galvanic cell and represent a DC source. From the respective potentials of the two half cells, the electromotive force (EMF, ΔE) of the galvanic cell can be calculated.

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

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.

The polarisation voltage theoretically calculated in this way is usually below the actual required voltage to achieve electrolysis, however. 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. Therefore:

$$\text{decomposition voltage} = \text{polarisation voltage} + \text{overvoltage}$$

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 this case, it is only the Ohmic resistance that must be overcome, which is independent of the flowing current, the applied voltage and the frequency. If a current/voltage curve is plotted, a line of origin can be seen.

In this experiment, current/voltage curves will be plotted. On the one hand, the polarisation voltages of three electrode materials will be compared in the electrolysis of water. On the other hand, the difference between a polarisable and a non-polarisable cell will be investigated through 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 may the solution be poured down the laboratory drain since it is very environmentally hazardous.

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



Fig. 1: Set-up of the experiment.

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

1	Electrochemistry demonstration unit	664 4071
2	Electrolysis cells	from 664 401
2	Carbon electrodes	from 664 401
2	Copper electrodes	from 664 401
2	Platinum mesh electrodes	from 664 401
2	Connecting leads, 25 cm	from 664 401
2	Crocodile clips	from 664 401
1	Sodium hydroxide, 0.1 mol/l, 500 ml	673 8410
1	Copper sulfate solution, 1 M (= 15 %)	672 9660

Set-up and preparation of the experiment

Set-up of the apparatus

- The apparatus is set up as can be seen in Fig. 1.
- Place the electrochemistry demonstration unit into the CPS frame.
- Now, the demonstration unit must be powered up.
- Combine two half cells into one electrolysis cell and screw them into place.
- Put the electrodes into the second outermost grooves, beginning with the platinum mesh electrodes. This corresponds to a separation of 7 cm.
- Insert the two connecting leads into the output of the power supply (5) (See Fig. 2).

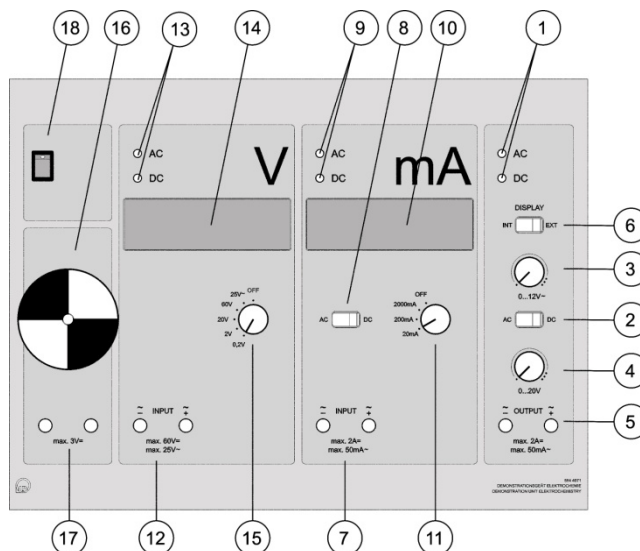


Fig. 2 Electrochemistry demonstration unit

- Connect the electrodes to the electrochemistry demonstration unit using the two crocodile clips at the other end of the connecting leads.
- Turn on the measurement display of the power supply using the selector switch (6).
- Set the changeover switches (2) and (8) and the rotary controller (15) to DC voltage (*direct current*, DC).

Electrolysis of water (0.1 M sodium hydroxide solution)

- Fill the electrolysis cell about 4 cm high with 0.1 mol/l sodium hydroxide solution.
- Carefully adjust a DC voltage of about 0.2 V at the rotary controller (4). Record the precise value of the voltage setting (U) and the current that is flowing at that setting (display (10)).
- Increase the voltage (U) further by increments of about 0.2 V and each time record the precise value of the voltage (U) and the current (I).
- Increase the voltage (U) until a final value of 3 V is reached.
- Proceed in the same manner with the copper and carbon electrodes. In the process only replace the electrodes.

Electrolysis of copper sulfate solution

- In the electrolysis of copper sulfate solution, the process is exactly the same as in the electrolysis of water.
- In this case, fill the electrolysis cell to about 4 cm high with the 1M copper sulfate solution.
- The experiment is carried out with the copper electrodes first. These are then exchanged with the carbon electrodes.
- Record the values for voltage (U) and current (I) here as well.

Observation

Electrolysis of water (0.1 M sodium hydroxide solution)

At the beginning of the experiment, there is hardly any current to be seen at any of the electrodes. 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 rising 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. For the carbon electrodes, a higher voltage is needed for 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 clearly increases in a linear fashion, the polarisation voltage and overvoltage have been exceeded. This is equal to the decomposition voltage.

Electrolysis of water (0.1 M sodium hydroxide solution)

Table 1 lists the measurements for the electrolysis of water and dilute sodium hydroxide solution for all three electrode pairs. Current/voltage curves for the electrode pairs were generated using the results; the current is plotted against the applied voltage in these curves (see Fig. 3).

The polarisation voltage is most pronounced with platinum electrodes. The value at which the polarisation voltage and overvoltage is overcome is greatest for these. 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 voltages as low as less than one volt, the current flow increase begins.

Tab. 1 Results for voltage (U) and current (I) for the electrolysis of water.

Pt		Cu		C	
U (V)	I (mA)	U (V)	I (mA)	U (V)	I (mA)
0.34	0	0.22	0.2	0.18	0.6
0.4	0.1	0.44	0.5	0.42	1.5
0.59	0.1	0.64	0.8	0.59	2.6
0.8	0.1	0.85	1	0.85	4.9
1.01	0.2	1	1.9	1.01	6
1.22	0.2	1.19	2.1	1.26	7.8
1.46	0.2	1.4	2.8	1.43	9
1.64	0.3	1.63	4	1.6	10.7
1.8	0.4	1.84	5.8	1.8	13.6
2	0.4	2.03	8.3	2.05	16.8
2.22	1	2.29	9.2	2.25	19.7
2.49	1.9	2.39	12.5	2.4	21.1
2.68	2.8	2.62	19.1	2.61	23.5
2.81	3.2	2.85	26.4	2.8	26
3.03	4	3.02	31.8	3.02	32.4

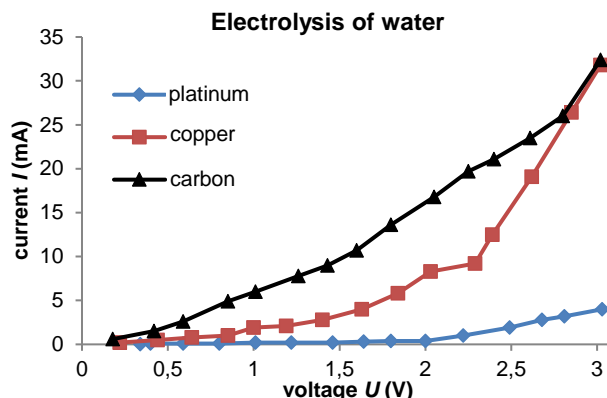


Fig. 3 Current/voltage curves for the electrolysis of water.

Electrolysis of copper sulfate solution

Table 2 lists the results for the electrolysis of a copper sulfate solution, first with carbon and then with copper electrodes. The results were converted to current/voltage curves (see Fig. 4).

Tab. 2 Results for voltage (U) and current (I) for the electrolysis of a copper sulfate solution.

C		Cu	
U (V)	I (mA)	U (V)	I (mA)
0.28	0.8	0.22	15.8
0.43	1.4	0.42	34.4
0.62	1.64	0.67	58.2
0.84	3.08	0.80	73.5
1.05	5.21	1.04	94.0
1.23	7.53	1.27	116.2
1.41	12.3	1.46	134.6
1.66	20.1	1.61	150.2
1.83	30.3	1.81	169.6
2.05	44.5	2.02	189.2
2.25	58.5	2.29	215.0
2.40	68.7	2.39	225.0
2.62	86.4	2.61	247.0
2.80	99.2	2.86	270.0
3.06	121.6	3.01	284.0

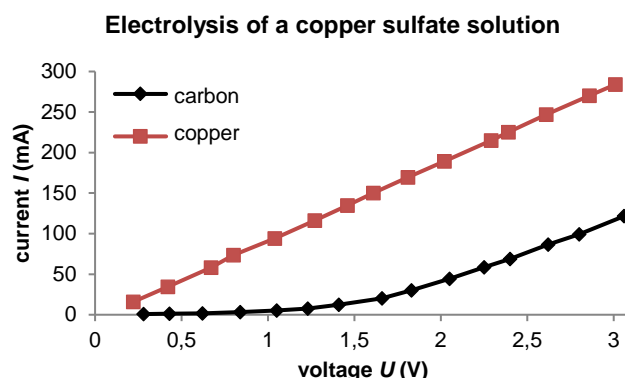


Fig. 4 Current/voltage curves for the electrolysis of copper sulfate solution.

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 an unpolarisable 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 voltage.

Due to the unpolarisable 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.

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 0.5 V, whereas for copper it is approx. 0.8 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. 1.5 V is needed.

Cleaning and disposal

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