Electrode kinetics: The hydrogen overpotential of metals with CobraSMARTsense

Chemistry › Physical chemistry › Electrochemistry › pH & potential measurement

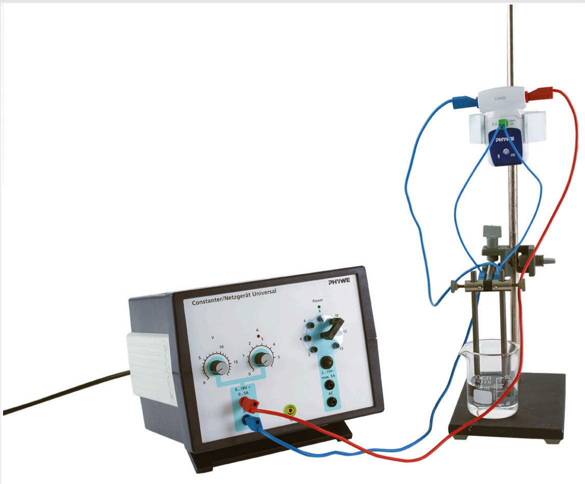
Difficulty level	Group size	Preparation time	Execution time
medium	2	10 minutes	20 minutes

This content can also be found online at:

http://localhost:1337/c/6092f0ca965cc500035e5ba7

General information

Application



Experimental setup

Electrode polarisation and the presence of overpotentials are important concepts in understanding electrode processes.

In this experiment, a special focus is placed on overvoltage, which affects the behavior of redox systems during electrolysis and will halt the processes, until a certain voltage is given.

More specifically we will determine how the hydrogen overvoltage is related to the metals used as electrodes and what conclusions can be drawn from this.

Other information (1/2)

Prior knowledge

The students should be familiar with the concept of electrolysis and its relation to the electric potential.

Scientific principle

This experiment is based on the principle of electrolysis and demonstrates the varying hydrogen overpotentials of different metals.

For this purpose, the electrical quantities voltage and current are recorded during electrolysis and their relationship is analyzed.

Other information (2/2)

Learning objective

The students learn how hydrogen overvoltages explain the course of an electrolysis and how this circumstance is related to the metals used as electrodes.

Tasks

1. Record the current-potential curve for the electrolysis of a 1 M hydrochloric acid solution using graphite rod electrodes and determine the decomposition voltage. Discuss the physical processes determining the form of this curve.

2. By replacing the graphite rod cathode with a series of different metal rod electrodes, compare the overpotential for hydrogen evolution at these metals.

Safety instructions

For this experiment the general instructions for safe experimentation in science lessons apply.

For H- and P-phrases please consult the safety data sheet of the respective chemical.

Theory (1/2)

If the oxidation and reduction steps of an electrode reaction are rapid (high exchange current densities) then the passage of charge across the electrode-solution interface will barely displace the reaction equilibrium. Such an electrode is said to be non-polarizable in the sense that its potential, for small currents, is stable and equal to the equilibrium electrode potential.

If, on the other hand, reaction equilibrium is established only slowly due to the kinetic inhibition of a step involved in the electrode reaction, then the electrode is said to be polarizable. To induce the reaction to proceed in a given direction the kinetic inhibition of the reaction must be overcome by applying a high overpotential.

Electrode polarization and the presence of overpotentials are important concepts in understanding electrode processes. They underlie the fact that galvanic cells always deliver current at less than the equilibrium electromotive force (emf) and that an applied potential greater than the equilibrium emf is required in order to drive a reaction in an electrolytic cell.

Theory (2/2)

Furthermore, a number of important electrochemical devices (e.g. the lead-acid accumulator) and electroanalytical techniques (e.g. polarography) make use of the inhibition (high overpotential) of certain electrode reactions.

Current-potential curves provide a useful means to discuss the physico-chemical processes occurring at electrodes. The most obvious feature establishing and observing these curves is that there is a threshold to electrolysis. Above the threshold voltage the cell current increases rapidly and is accompanied, in the present case, by the evolution of gas bubbles at the electrode surfaces. Below the threshold there is a small, but nevertheless observable, cell current which rises only very slowly with increasing applied voltage.

Equipment

Position	Material	Item No.	Quantity
1	Cobra SMARTsense Energy (Bluetooth + USB)	12919-00	1
2	measureLAB, multi-user license	14580-61	1
3	PHYWE Power supply, universal DC: 0...18 V, 0...5 A / AC: 2/4/6/8/10/12/15 V, 5 A	13504-93	1
4	Connecting cord, 32 A, 500 mm, red	07361-01	1
5	Connecting cord, 32 A, 500 mm, blue	07361-04	2
6	Retort stand, h = 750 mm	37694-00	1
7	Right angle boss-head clamp	37697-00	1
8	Holder for two electrodes	45284-01	1
9	Graphite electrode,d=7,l=150,6pc	44512-00	1
10	Copper electrode, d=8mm, l=15cm	45201-00	1
11	Iron electrode, d 8mm	45204-00	1
12	Lead electrode, d 8mm, l 110mm	45203-01	1
13	Nickel electrode, d 8mm	45205-00	1
14	Bar electrode, Zinc, d = 6 mm, l = 140 mm	45288-03	1
15	Thermometer -10...+50 °C	38034-00	1
16	Digital stopwatch, 24 h, 1/100 s and 1 s	24025-00	1
17	Beaker, 150ml, low-form	46060-00	6
18	Hydrochloric acid, 1.0 mol/l, 1000 ml	48454-70	1
19	Water, distilled 5 l	31246-81	1
20	Holder for Cobra SMARTsense	12960-00	1

PHYWE

Setup and procedure

Setup (1/2)

PHYWE

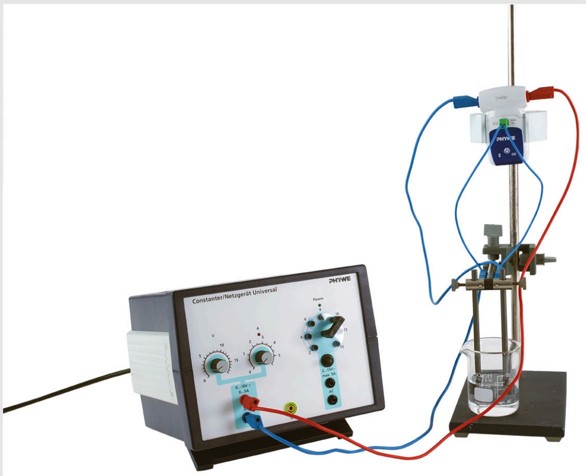


Fig. 1

Before you start with the experiment, make yourself familiar with the PHYWE measureLab software, using the manual. Progress with the experimental setup:

1. The experimental setup is shown in Fig. 1.

2. Attach the Cobra SmartSense Energy to the support rod with the holder for SmartSense sensors.

3. Attach the electrode holder to the support stand using a right angle clamp.

4. Connect the “+” socket of the power supply to the “+” socket of the SmartSense Sensor Unit Energy using a red cable.

Setup (2/2)

5. Connect the “-” socket of the Cobra SmartSense Energy to the electrode holder. The other socket of the electrode holder has to be connected to the “-” socket of the power supply via a blue cable.

6. Plug the green cables into the Cobra SmartSense Energy Exterior socket and connect them to the sockets of the electrode holder.

7. Fit two graphite electrodes in the holes of the electrode holder.

8. Start the PC and call up the "measureLAB" m program and boot the experiment P3061867: "Electrode kinetics: The hydrogen overpotential of metals with SmartSense". The measurement parameters for this experiment are loaded now. The data acquisition mode is preset to "Single measurement".

9. Place a 150 ml glass beaker containing approximately 80 ml of the 1 M HCl solution underneath the graphite rod electrodes and lower the electrodes into the solution to an equal depth of about 2 cm. The voltage regulator on the power supply unit should be set to zero.

Procedure (1/2)

1. Start the measurement with the "start" button ○. Record the first point measured by pressing the "record" button (next to the start button, looking like the symbol for "play" ▶).

2. Now carefully raise the applied potential difference in steps of 0.2 V up to a maximum of 4.0 V. After each voltage increase, wait one minute before acquiring the value by again pressing the ▶ button. During this time the electrode surfaces should be monitored for evidence of gas evolution.

3. Note the temperature of the acid electrolyte at intervals throughout the electrolysis.

4. Stop the measurement by pressing the "stop" button ■.

Procedure (2/2)

5. Remove the graphite rod cathode and replace it with one of the cleaned metal electrodes.

Since the electrodes have differing diameters (C: d = 7 mm; Cu, Fe, Ni, Zn: d = 8 mm) it is necessary to immerse them to different depths into the acid solution to ensure equal current densities at the anode and cathode surfaces.

The following immersion dephts are required for an electrode area of 5 cm^2: C: 21 mm and Cu, Fe, Ni, Zn: 18 mm.

6. Using this mark for guidance, lower each of the electrodes into a fresh 80 ml sample of acid solution.

7. Carefully increase the applied voltage to record the voltages required to induce electrolysis currents of 120 mA, 180 mA, 240 mA, 300 mA and finally 360 mA.

8. Measure each metal electrode in this way.

Evaluation (1/10)

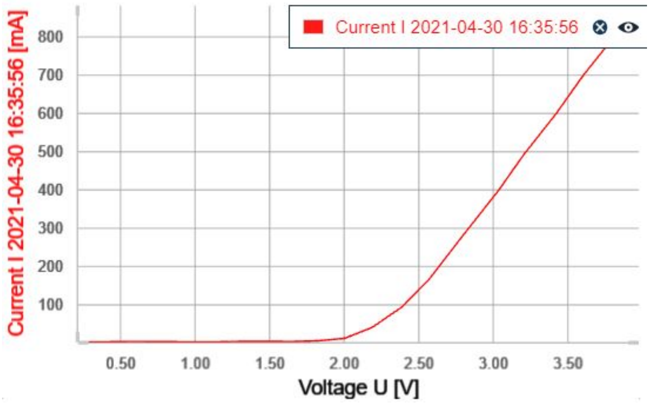


Fig. 2: **Example** for a current-potential curve for the electrolysis of 1.0 M HCl solution using graphite rod electrodes (example only, results may vary).

Evaluation (2/10)

Current-potential curves, such as in Fig. 2, provide a useful means to discuss the physico-chemical processes occurring at electrodes. The most obvious feature of Fig. 2 is that there is a threshold to electrolysis.

Above the threshold voltage the cell current increases rapidly and is accompanied, in the present case, by the evolution of gas bubbles at the electrode surfaces.

Below the threshold there is a small, but nevertheless observable, cell current which rises only very slowly with increasing applied voltage.

Evaluation (3/10)

As soon as there is a voltage between the electrodes, hydrogen is deposited at the negatively charged cathode and chlorine at the positively charged anode.

$$2\ \mathrm{H}^+_{(\mathrm{aq})} + 2\ \mathrm{e}^- \rightarrow \mathrm{H}_{2(\mathrm{g})}$$

$$2\ \mathrm{Cl}^-_{(\mathrm{aq})} \rightarrow \mathrm{Cl}_{2(\mathrm{g})} + 2\ \mathrm{e}^-$$

The gases are, however, unable to escape from solution as their partial pressures are still below atmospheric pressure. They remain adsorbed at the graphite electrodes, which may be now regarded as hydrogen and chlorine electrodes. Together they form the galvanic cell

$$\mathrm{C} \mid \mathrm{H}_2, \mathrm{H}^+, \mathrm{Cl}^-, \mathrm{Cl}_2 \mid \mathrm{C}$$

whose emf opposes the externally applied voltage.

Evaluation (4/10)

The magnitude of this opposing voltage E is given by the following Nernst equation

$$E = E^{\ominus}_{\mathrm{Cl_2,Cl^-}} - \frac{RT}{2F}\ln\left(\frac{a^2_{\pm,\mathrm{HCl}}}{f_{\mathrm{H_2}}\cdot f_{\mathrm{Cl_2}}}\right) \quad (1)$$

where

$E^{\ominus}_{\mathrm{Cl_2,Cl^-}}$ Standard $\mathrm{Cl_2|Cl^-}$ half cell potential = 1.36 V, R Universal gas constant, T Temperature

F Faraday constant, n Number of electrons participating in the electrode reation (n=2), $a_{\pm,\mathrm{I}}$ Mean activity of the solute I and f_i Fugacity of gas I

Evaluation (5/10)

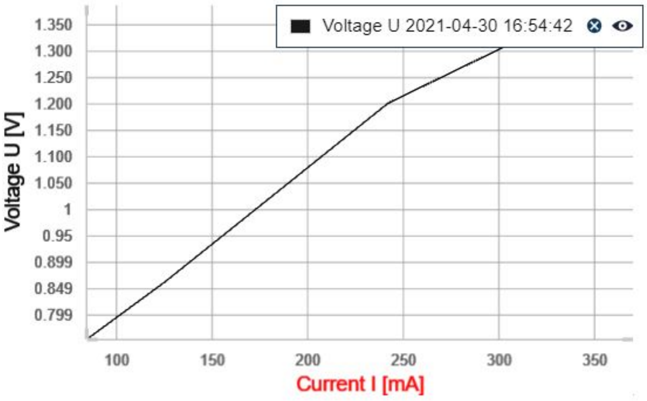


Fig. 3: **Example** for a current-potential curve for a electrolysis of 1.0 M HCl solution using a graphite rod anode and an iron rod cathode (example only, results may vary).

Evaluation (6/10)

As long as the emf (Eq. (1)) just compensates the applied voltage no current flows through the cell (in case of removing the applied voltage the emf of the galvanic cell could be measured). In fact a small current can be measured (see Fig. 3) because small amounts of hydrogen and chlorine gas desorb and diffuse away from the electrodes allowing equivalent amounts to be electrolytically deposited – thus leading to a small cell current.

As the externally applied voltage is increased, the partial pressures of the adsorbed gases will continue to rise until eventually atmospheric pressure is attained. At that point hydrogen or chlorine gas can escape from the solution and, as a result of chemical polarisation, the emf reaches its maximum value. The threshold voltage above which the electrolysis reaction

$$2\,H^+_{(aq)} + 2\,Cl^-_{(aq)} \rightarrow H_{2(g)} + Cl_{2(g)}$$

occurs to an appreciable extent is the so-called decomposition voltage V_d.

Evaluation (7/10)

It will be equal in magnitude but opposite in sign to the emf of the galvanic cell formed by the electrolysis products. For a 1 M HCl solution, the mean ionic activity is a = 0.810. By assuming the gases to behave perfectly the fugacities may be replaced by pressures and a value for V_d of –1.41 V is calculated from Eq. (1).

However, the approximate value of the decomposition voltage of –1.8 V, determined from Fig. 3 by extrapolating the initial part of the steeply rising portion of the current potential curve to zero current, is considerably greater than the theoretical equilibrium value. The difference between the two values is called the cell overpotential.

The cell overpotential is considered to be composed of a number of independent contributions:

1. Resistance overpotential arising from the ohmic drop (IR) between the electrodes due to the fact that the electrolyte solution is not of infinite conductivity but exhibits a resistance R.

Evaluation (8/10)

2. Activation overpotential at one or both electrodes arising from kinetic inhibition of one of the steps involved in the electrode reaction. Examples might be the desolvation of the reactive ion prior to migration through the electric double layer, or the chemisorption of the reaction product at a suitable site on the electrode surface.

3. Concentration or diffusion overpotential at one or both electrodes due to the presence of concentration gradients in the vicinity of the electrode surface. As a result of electrochemical reaction, the concentrations at the electrode surface no longer have their equilibrium values. If migration through the electric double-layer is very rapid then, at high cell currents, diffusion from the bulk of the solution towards the electrode will be unable to replenish the ions at the double-layer quickly enough and a concentration gradient will result.

Evaluation (9/10)

The decomposition voltage measured here has no easily defined theoretical significance since it consists of two individual electrode potentials and the ohmic (IR) drop between them.

Each electrode will also exhibit an overpotential which depends upon temperature, concentration, electrode current density and the physical and chemical nature of the electrode surface. Thus

$$\mathrm{V}_d = E + \eta_A + \eta_C + IR \ \ (2)$$

where E is the magnitude of the back emf of the galvanic cell formed (see Eq. (1)) and η_A and η_C are the overpotentials at the anode and cathode respectively.

Evaluation (10/10)

By keeping the anode (graphite) and the electrolyte solution (1 M HCl) constant, the variation of the decomposition voltage with cathode material may be used to provide an approximate indication of the relative sizes of the cathodic overpotential η_C required to generate hydrogen.

Since the gradients are all similar, one may immediately arrange the order of the hydrogen overpotentials in the electrolysis of 1 M hydrochloric acid as follows:

$\mathrm{Ni} \approx \mathrm{Fe} < \mathrm{Cu} < \mathrm{Zn}$