Electrode kinetics: The hydrogen overpotential of metals with Cobra4 (Item No.: P3061861)

Curricular Relevance

<table>
<thead>
<tr>
<th>Area of Expertise:</th>
<th>Education Level:</th>
<th>Topic:</th>
<th>Subtopic:</th>
<th>Experiment:</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chemistry</td>
<td>University</td>
<td>Physical Chemistry</td>
<td>Electro Chemistry</td>
<td>Electrode kinetics: The hydrogen overpotential of metals with Cobra4</td>
</tr>
</tbody>
</table>

Difficulty | Preparation Time | Execution Time | Recommended Group Size |
<table>
<thead>
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<tbody>
<tr>
<td>Difficult</td>
<td>☒ ☒ ☒ ☒ ☒ ☒ ☒ ☒</td>
<td>☒ ☒ ☒ ☒ ☒ ☒ ☒ ☒</td>
<td>☒ ☒ ☒ ☒ ☒ ☒ ☒ ☒</td>
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</tbody>
</table>

Additional Requirements:
- PC with USB interface, Windows XP or higher

Experiment Variations:

Keywords:
electrode kinetics, polarisation, overpotential, irreversible processes, the electrode-electrolyte interface, voltammetry and current-potential curves, relevance to electrolysis, fuel cells, corrosion, polarography

Overview

Short description

Principle
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 polarisable. 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 polarisation 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 e.m.f. and that an applied potential greater than the equilibrium e.m.f. is required in order to drive a reaction in an electrolytic cell. 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.
Safety instructions

When handling chemicals, you should wear suitable protective gloves, safety goggles, and suitable clothing. Please refer to the appendix for detailed safety instructions.
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Disposal
The diluted and neutralised solution of the used acid can be disposed by rinsing into the drain.

Hydrochloric acid 1.0 N
H290: May be corrosive to metals.
H314: Causes severe skin burns and eye damage.
H335: May cause respiratory irritation.
P234: Keep only in original container.
P260: Do not breathe dust/fume/gas/mist/vapours/spray.
P304 +340: IF INHALED: Remove victim to fresh air and keep at rest in a position comfortable for breathing.
P303 + 361 + 353: IF ON SKIN (or hair): Remove/ Take off immediately all contaminated clothing. Rinse skin with water/shower.

Hydrogen
H220: Extremely flammable gas
P210: Keep away from heat, hot surfaces, sparks, open flames and other ignition sources. No smoking.
P381: Eliminate all ignition sources if safe to do so.

Chlorine
H270: May cause or intensify fire; oxidizer.
H319: Causes serious eye irritation.
H400: Very toxic to aquatic life.
EUH071: Corrosive to the respiratory tract
P220: Keep/Store away from clothing/.../combustible materials.

Iron chloride solution
H315: Causes skin irritation.
P280: Wear protective gloves/protective clothing/eye protection/face protection.

Zinc chloride solution
H315: Causes skin irritation
P273: Avoid release to the environment.
P280: Wear protective gloves/protective clothing/eye protection/face protection.
### Equipment

<table>
<thead>
<tr>
<th>Position No.</th>
<th>Material</th>
<th>Order No.</th>
<th>Quantity</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Cobra4 Wireless/USB-Link incl. USB cable</td>
<td>12601-10</td>
<td>2</td>
</tr>
<tr>
<td>2</td>
<td>Cobra4 Sensor-Unit Electricity, current ± 6A / voltage ± 30V</td>
<td>12644-00</td>
<td>2</td>
</tr>
<tr>
<td>3</td>
<td>curricuLAB measureLAB</td>
<td>14580-61</td>
<td>1</td>
</tr>
<tr>
<td>4</td>
<td>Holder for Cobra4 with support rod</td>
<td>12680-00</td>
<td>1</td>
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<tr>
<td>5</td>
<td>Stand for Cobra4</td>
<td>12681-00</td>
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<td>6</td>
<td>PHYWE power supply, universal DC: 0…18 V, 0…5 A / AC: 2/4/6/8/10/12/15 V, 5 A</td>
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<td>7</td>
<td>Connecting cord, 32 A, 500 mm, red</td>
<td>07361-01</td>
<td>2</td>
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<td>Connecting cord, 32 A, 500 mm, blue</td>
<td>07361-04</td>
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<td>9</td>
<td>Retort stand, h = 750 mm</td>
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<td>Right angle boss-head clamp</td>
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<td>Copper electrode, d=8mm, l=15cm</td>
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<td>Iron electrode, d 8mm</td>
<td>45204-00</td>
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<td>15</td>
<td>Nickel electrode, d 8mm</td>
<td>45205-00</td>
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<td>Bar electrode, Zinc, d=8mm, l=100mm</td>
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<td>Thermometer -10...+50 °C</td>
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<td>Stopwatch, digital, 1/100 s</td>
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<td>Beaker, low, BORO 3.3, 150ml</td>
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<td>Hydrochloric acid, 1.0 mol/l, 1000 ml</td>
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<tr>
<td>21</td>
<td>Water, distilled 5 l</td>
<td>31246-81</td>
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### 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.

### Setup and procedure

- The experimental setup is shown in Fig. 1.
- Combine the Cobra4 Sensor Units Electricity with the Cobra4 Wireless/USB-Links. Attach them to the support rod with the holders for Cobra4.
- Attach the electrode holder to the support stand using a right angle clamp.
- Connect the “+” socket of the power supply to the “+” current socket of one of the Cobra4 Sensor Units Electricity using a red cable.
- Connect the “-” socket of this Cobra4 Sensor Unit Electricity 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.
- Connect the “+” and “-” voltage sockets of the second Cobra4 Sensor Unit Electricity to the sockets of the electrode holder.
Fit two graphite electrodes in the holes of the electrode holder.

Start the PC and connect the Cobra4 Wireless/USB-Links with the computer using USB cables.

Call up the “measureLAB” programme and boot the experiment “Electrode kinetics: The hydrogen overpotential of metals with Cobra4”. The measurement parameters for this experiment are loaded now.

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.

Start the measurement with

Record the first point measured by pressing

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 saving the value. During this time the electrode surfaces should be monitored for evidence of gas evolution.

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

Stop the measurement by pressing

Fig. 2 shows the graph as it is presented by the programme when the measurement is stopped.

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, Pb, 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 depths are required for an electrode area of 5 cm²: C: 21 mm Cu, Fe, Ni, Pb, Zn: 18 mm.

Adjustment of the different immersion depths can be conveniently carried out by laying the electrodes on a sheet of millimeter ruled graph paper. It is also useful to draw the immersion mark of 21 mm on the graphite anode in pencil.

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

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.

Measure each metal electrode in this way.

Theory and evaluation

Current-potential curves, such as in Fig. 3, provide a useful means to discuss the physico-chemical processes occurring at electrodes. The most obvious feature of Fig. 3 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.

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.

\[
2H^{+\text{(aq)}} + 2e^- \rightarrow H_2(g)
\]

\[
2Cl^-\text{(aq)} \rightarrow Cl_2(g) + 2e^-
\]

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

\[ \text{C} | \text{H}_2, \text{H}^+, \text{Cl}^-, \text{Cl}_2 | \text{C} \]

whose e.m.f. opposes the externally applied voltage. The magnitude of this opposing voltage \( E \) is given by the following Nernst equation

\[
E = E_{\text{Cl}_2, \text{Cl}}^{\circ} - \frac{RT}{2F} \ln \left( \frac{a_{\text{Cl}^-}^{\text{eq}}}{a_{\text{Cl}^-}^{\text{eq}}} \right)
\]

where

- \( E_{\text{Cl}_2, \text{Cl}}^{\circ} \) Standard 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 reaction (\( n = 2 \))
- \( a_{\text{Cl}^-}^{\text{eq}} \) Mean activity of solute i
- \( f_i \) Fugacity of gas i

As long as the e.m.f. (Eq. 1) just compensates the applied voltage no current flows through the cell (in case of removing the applied voltage the e.m.f. 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 e.m.f. reaches its maximum value. The threshold voltage above which the electrolysis reaction

\[
2\text{H}_2^{\text{(aq)}} + 2\text{Cl}^{-}^{\text{(aq)}} \rightarrow \text{H}_2(\text{g}) + \text{Cl}_2(\text{g})
\]

occurs to an appreciable extent is the so-called decomposition voltage \( V_d \). It will be equal in magnitude but opposite in sign to the e.m.f. 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 -2.1 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 \( R \).

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.
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

$$V_d = E + \eta_A + \eta_C + IR \quad (2)$$

where $E$ is the magnitude of the back e.m.f. of the galvanic cell formed (see Eq. 1) and $\eta_A$ and $\eta_C$ are the overpotentials at the anode and cathode respectively. 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 $\eta_C$ required to generate hydrogen. The results are shown in Figs. 3 to 6. 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:

$$\text{Ni} \approx \text{Fe} < \text{Cu} < \text{Zn} < \text{Pb}$$

Fig. 3: Current-potential curve for a electrolysis of 1.0 M HCl solution using a graphite rod anode and a lead rod cathode.

Fig. 4: Current-potential curve for a electrolysis of 1.0 M HCl solution using a graphite rod anode and a nickel rod cathode.
Fig. 5: Current-potential curve for a electrolysis of 1.0 M HCl solution using a graphite rod anode and an iron rod cathode.

Fig. 6: Current-potential curve for a electrolysis of 1.0 M HCl solution using a graphite rod anode and a copper rod cathode.