Electrode kinetics: The hydrogen overpotential of metals

Related concepts
Electrode kinetics, polarization, overpotential, irreversible processes, the electrode-electrolyte interface, voltammetry and current-potential curves, relevance to electrolysis, fuel cells, corrosion, polarography.

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 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 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.

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

Equipment
- Cobra3 Basic-Unit 12150.00 1
- Power supply 12 V/2 A 12151.99 1
- Data cable, RS232 14602.00 1
- Software Cobra3 Universal writer 14504.61 1
- Current probe 6 A 12126.00 1
- Power supply, universal 13500.93 1
- Retort stand, h = 750 mm 37694.00 1
- Right angle clamp 37697.00 1
- Holder for 2 electrodes 45284.01 1
- Connecting cord, l = 500 mm, red 07361.01 2
- Connecting cord, l = 750 mm, red 07362.01 1
- Connecting cord, l = 750 mm, blue 07362.04 1
- Beaker, 150 ml, short 36012.00 6
- Laboratory thermometer, -10... +50°C 38034.00 1
- Carbon electrodes, d = 7 mm, l = 150 mm 44512.00 1
- Copper electrode, d = 8 mm, l = 150 mm 45201.00 1
- Iron electrode, d = 8 mm, l = 150 mm 45204.00 1
- Lead electrode, d = 8 mm, l = 150 mm 45203.00 1

Fig. 1. Experimental set-up.
Nickel electrode, \( d = 8 \, \text{mm}, \ l = 150 \, \text{mm} \)  
Zinc electrode, \( d = 8 \, \text{mm}, \ l = 150 \, \text{mm} \)  
Stopwatch, digital, \( 1/100 \, \text{s} \)  
Hydrochloric acid, \( 1 \, \text{M}, 1000 \, \text{ml} \)  
Water, distilled, \( 5 \, \text{l} \)  
PC, Windows® 95 or higher  
Millimeter paper  
Pencil

**Set-up and procedure**

The experimental set-up is shown in Figs. 1 and 2.

Connect the current probe to S2 and the two electrodes to Analog IN 1 of the Cobra3 Basic-Unit.

Call up the ‘Measure’ programme in Windows and enter <Universal writer> as measuring instrument. Set the measurement parameters as shown in Fig. 3. Under <Diagram> select <Current (S2)> and a range of 0 – 1 A. For <X bounds> choose a range of 0 – 4 V and <no auto range>. After having made these settings, press <Continue> to reach the field for the recording of measured values. Arrange the displays as you want them.

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. Record the first point measured by pressing <Save value>. 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 and save the data with <File> <Save the measurement as...>.

Fig. 4 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: \( d = 7 \, \text{mm} \); Cu, Fe, Ni, Pb, Zn: \( d = 8 \, \text{mm} \)) 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. To have the plot of each two of the metals shown in one diagram, use the menu prompt <Measurement> with <Assume channel...> (Figs. 5 and 6).

**Theory and evaluation**

Current-potential curves, such as in Fig. 4, provide a useful means to discuss the physico-chemical processes occurring at electrodes. The most obvious feature of Fig. 4 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.

---

**Fig. 2: Circuit diagram**

**Fig. 3: Measurement parameters**
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.

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

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

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

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

\[
E = E^\circ_{\text{Cl}_2, \text{Cl}^-} + \frac{RT}{2F} \ln \left[ \frac{a^2_{\text{H}^+ \text{HCl}}}{f_{\text{H}_2} \cdot f_{\text{Cl}_2}} \right]
\]

(1)

where
- \(E^\circ_{\text{Cl}_2, \text{Cl}^-}\): 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 (= 2)
- \(a_{\text{H}^+ \text{HCl}}\): Mean activity of solute \(\text{H}^+ \text{HCl}\)
- \(f_i\): Fugacity of gas \(i\)

Fig. 4: Current-potential curve for the electrolysis of 1 M HCl solution using graphite rod electrodes.

Fig. 5: Current-potential curve for the electrolysis of 1 M HCl solution using a graphite rod anode and Ni resp. Pb cathodes.

Fig. 6: Current-potential curve for the electrolysis of 1 M HCl solution using a graphite rod anode and Fe resp. Cu cathodes.

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. 4) 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 polarization, the e.m.f. reaches its maximum value. The threshold voltage above which the electrolysis reaction

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

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. 2 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

\[ V_d = E + \eta_A + h_C + IR \]  

(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 Fig. 5 and 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:

\[ \text{Ni} \approx \text{Fe} < \text{Cu} < \text{Zn} < \text{Pb} \]