Institute of Mathematics, Physics and Chemistry

Department of Chemistry

Technical chemistry laboratory

Laboratory exercise

Corrosion – causes and prevention

Elaborated by:
dr inż. Andrzej Kozłowski
dr inż. Agnieszka Kalbarczyk-Jedynak
dr Magdalena Ślączka-Wilk
dr inż. Konrad Ćwirko
mgr inż. Czesław Wiznerowicz
Grażyna Gorzycka

KIEROWNIK
Zakładu Chemii
Kalbarczyk-Jedynak
dr inż. Agnieszka Kalbarczyk-Jedynak

Szczecin 2022

EXERCISE SHEET

<table>
<tr><td rowspan="5">1</td><td colspan="3">**Relation to subjects:** ESO/25, 27 DiRMiUO/25, 27 EOUNiE/25, 27</td></tr>
<tr><td>**Specialty/Subject**</td><td>**Learning outcomes for the subject**</td><td>**Detailed learning outcomes for the subject**</td></tr>
<tr><td>ESO/26 Chemistry of water, fuels and lubricants</td><td>EKP3
K_U014, K_U015, K_U016.</td><td>SEKP3 – Water quality indicators;
SEKP6 – Determination of selected indicators of technical water quality;</td></tr>
<tr><td>DiRMiUO/26 Chemistry of water, fuels and lubricants</td><td>EKP3
K_U014, K_U015, K_U016.</td><td>SEKP3 – Water quality indicators;
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<tr><td>EOUNiE/26 Chemistry of water, fuels and lubricants</td><td>EKP3
K_U014, K_U015, K_U016.</td><td>SEKP3 – Water quality indicators;
SEKP6 – Determination of selected indicators of technical water quality;</td></tr>
<tr><td>2.</td><td colspan="3">**Purpose of the exercise:**
mastering the basic chemical concepts of corrosion and acquiring practical knowledge in the field:
– galvanic cells and processes taking place in the cell,
– a series of (voltage) activities of metals,
– mechanism of electrochemical corrosion,
– anodic protection,
– processes taking place in the cell.</td></tr>
<tr><td>3.</td><td colspan="3">**Prerequisites:**
general knowledge of oxidation and reduction processes, properties and corrosion of metals, knowledge of the principles of work in a chemical laboratory.</td></tr>
<tr><td>4.</td><td colspan="3">**Description of the laboratory workplace:**
laboratory glassware kit, multimedia projector, metal sample kit, electrochemical corrosion reagent kit, phenolphthalein, ferroxide indicator.</td></tr>
<tr><td>5.</td><td colspan="3">**Risk assessment:**
the likelihood of chemical burns from exposure to 0.2 M sulphuric acid is very small, and the effects are minimal.
Final assessment – **VERY SMALL THREAT**
Safety measures required:
1. Lab coats, gloves and safety glasses.
2. Health and safety cleaning products, paper towels.</td></tr>
<tr><td>6.</td><td colspan="3">**The course of the exercise:**
1. Getting to know the workplace manual (appendix 1) and familiarizing with the kit for testing electrochemical corrosion,
2. Carrying out chemical reactions.</td></tr>
<tr><td>7.</td><td colspan="3">**Exercise report:**
1. Develop an exercise in accordance with the instructions contained in the workplace manual.
2. Solve the given tasks and/or answer the questions included in the set of tasks and questions to be completed by the student.</td></tr>
<tr><td>8.</td><td colspan="3">**Archiving of research results:**
a report on exercises, prepared in accordance with the rules in force in the lab, should be submitted in writing to the academic teacher during the next classes.</td></tr>
</table>

9.	**Assessment method and criteria:** a) EKP1, EKP2 – checking the knowledge of basic chemical concepts of corrosion in class, b) SEKP4 – the detailed effect of the student's learning will be assessed on the basis of the observations, conclusions and solutions to tasks and problems presented in the report, given for independent solution/development: – **mark 2,0** – the student does not have basic knowledge of metals and their corrosion, or is unable to use it in practice to solve the problems of protecting structures and devices against corrosion; – **mark 3,0** – has basic chemical knowledge of the activity of metals, the mechanism of electrochemical corrosion and protection against corrosion, and can use it to a small extent to solve potential problems in his specialty; – **mark 3,5 – 4,0** – has extensive chemical knowledge of corrosion and its mechanisms, methods of protection against corrosion, operation of electrochemical cells and is able to use it in a wide range in his profession; – **mark 4,5 – 5,0** – has complete chemical knowledge of corrosion and electrochemical cells, their mechanisms and is able to use complex chemical knowledge to identify the mechanism of electrochemical corrosion and select the best protection method in complex corrosion cases.
10.	**Literature:** 1. Kozłowski A., Gabriel-Półrolniczak U., Instrukcja stanowiskowa do ćwiczeń laboratoryjnych *Korozja i ochrona przed korozją,* AM Szczecin, 2014. 2. Stundis H., Trześniowski W., Żmijewska S.: *Ćwiczenia laboratoryjne z chemii nieorganicznej*. WSM, Szczecin 1995. 3. Jones L., Atkins P., *Chemia ogólna. Cząsteczki, materia reakcje*, WN PWN, Warsaw, 2004. 4. Baszkiewicz J., *Podstawy korozji materiałów*, Oficyna Wydawnicza PW, Warsaw, 1997. 5. Bielański A., *Chemia ogólna i nieorgan*iczna, PWN, Warsaw, 1996. 6. Śliwa A., Obliczenia chemiczne, PWN, Warszawa 1987 Wranglén G., *Podstawy korozji i ochrony metali*, WNT, Warsaw 1985 7. Wranglén G., *Podstawy korozji i ochrony metali*, WNT, Warsaw 1985 8. Kozłowski A., *Materiały dydaktyczne z chemii technicznej*, 2013 (not published), available on the website of the Maritime University of Szczecin. 9. Borzdyński J., Elektronik, Online edition: 412. Batteries. A revolution on the market? 10. Chemistry. Virtual textbook. *Ogniwa w zastosowaniu praktycznym*, http://www.chemia.dami.pl/liceum/liceum12/elektrochemia5.htm 11. Multimedia presentation „*Korozja elektrochemiczna*” from the resources of the AGH e-learning center in Krakow: http://zasoby1.open.agh.edu.pl/dydaktyka/chemia/a_e_chemia/filmy/wmv/
11.	Notes

APPENDIX 1 – MANUAL

1. SCOPE OF THE EXERCISE:

Issues and keywords:

- electrochemical cells (defining cathode and anode, standard potential of a cell, Nernst equation);
- types of cells;
- corrosion (definition, mechanism, types);
- ways to prevent corrosion, anodic protection.

2. THEORETICAL INTRODUCTION TO THE EXERCISE

2.1. Galvanic cells

Galvanic cells are chemical systems from which electricity can be derived. These cells are commonly used in everyday devices. They consist of two electrodes (metallic conductors) in contact with an electrolyte (ionic conductor), which may be a solution, liquid or solid.

The metal electrode and the electrolyte in which it is immersed constitute a half-cell. Two such half-cells, if we connect them with an electrolytic key, give us a cell. The first useful cell was constructed by the Italian physicist Alessandro Volta in 1800 (hence cells of this type are called Volta cells). The name „galvanic" comes from the name of Luigi Galvani, who in the 18th century described the effect of electric current on animal tissue. Examples of cells are the so-called Sticks batteries, wrongly called batteries, because the name battery means many cells connected in series or in parallel. This is the case with a 4.5 V flat battery and also in rechargeable batteries.

In the simplest case, the cell consists of two electrodes (pieces of metal), immersed in an electrolyte solution, connected to each other by a metallic conductor.

If one of the metals is e.g. zinc (Zn), which easily sends its Zn^{2+} cations into the solution, then this metal charges negatively at the surface (at low electrolyte concentration). On the other hand, there are other metals, such as copper (Cu), which by accepting Cu^{2+} cations from the solution on its surface, charging positively (the process takes place at a high concentration of electrolyte, or when the metal shows low chemical activity – it is noble), see the Fig.1.

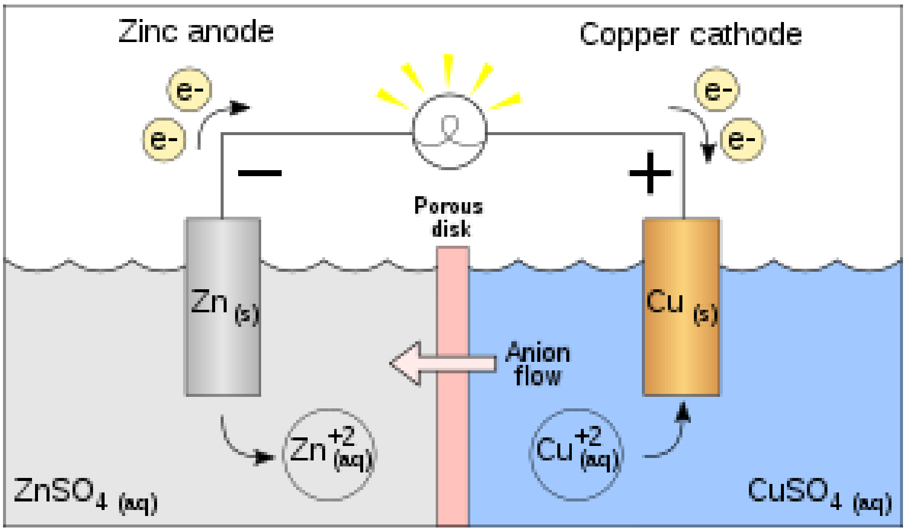


Fig. 1. Galvanic cell
source: https://en.wikipedia.org/wiki/Galvanic_cell
(accessed January, 14, 2022)

In both cases, the electrode acquires a certain electrical potential (negative or positive) and an electrical double layer is formed at the metal/solution interface due to the opposite charge ions surrounding the electrode, which depend on the type of metal, type of electrolyte and ion concentrations in the solution. Quantitatively, the potential of a metallic electrode is given by the Nernst formula (given later in this manual).

2.1.1. Daniell cell

After connecting with an electrolytic key both electrodes (zinc and copper) shown in Figures 1, immersed in their ion solution, we obtain a Daniell cell. The diagram of the created cell can be written as follows:

$$(–)\ \mathrm{Zn}\ |\ \mathrm{ZnSO_4}\ (c_1)\ ||\ \mathrm{CuSO_4}\ (c_2)\ |\ \mathrm{Cu}(+)$$

In order for the cell to work, the electrodes must be additionally connected with a metallic conductor, which allows the flow of electrons. The SEM of a Daniella cell is equal to 1.1 V.

The electrolytic key may be a U-shaped tube, filled with a salt saturated gel with good conductivity, e.g. NaCl, KCl, closed on both sides with plugs made of semi-permeable material, which allows the flow of ions to equalize the charges. In the Daniell cell, the electrodes are in separate solutions, which prevents ions from mixing.

2.1.2. Volta cell

An example of a different type of cell is the Volta cell (Fig. 2) in which both electrodes (zinc and copper) are immersed in the same electrolyte. The EMF of a Volta cell is equal to 1.1 V.

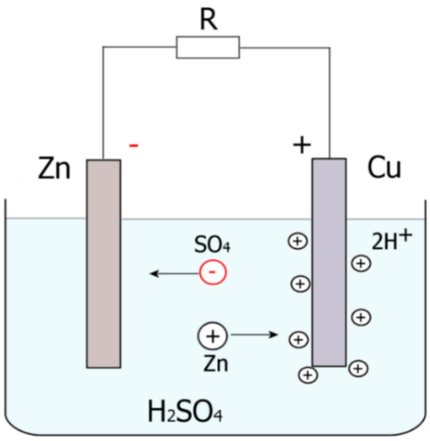
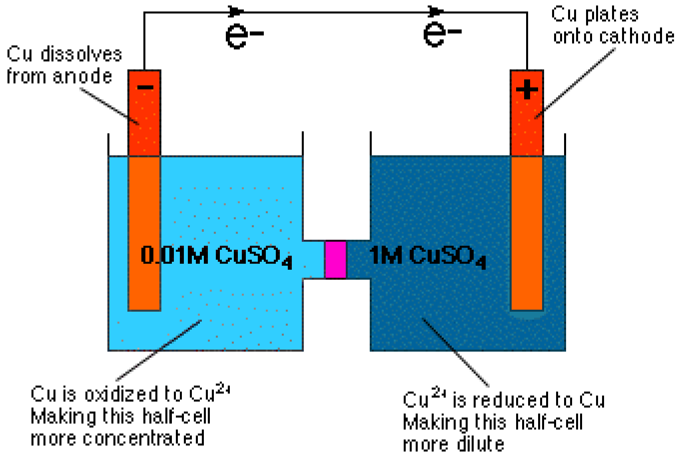


Fig. 2. Diagram of the Volta cell
source: https://pl.m.wikipedia.org/wiki/Plik:Voltaic_cell_diagram.png
(accessed December, 15, 2021)

2.1.3. Concentration cell

Yet another type is the concentration cell, a diagram of which is shown in Fig. 3.



lower concentration
$Cu^0 \longrightarrow Cu^{2+} + 2e^-$

higher concentration
$Cu^{2+} + 2e^- \longrightarrow Cu^0$

Fig. 3. Diagram of a concentration cell
source: https://socratic.org/questions/what-are-concentration-cells
(accessed December, 15, 2021)

2.1.4. Other types of cells and half-cells

In addition to the above-mentioned, there are other types of half-cells and cells, which are presented in Table 1.

Table 1

Types of half-cells

Types of electrodes	Types of half-cell	Half Reaction
metallic metal plate in a solution of its ions	metal/metal ion $Me\|Me^{n+}$	$Me \longrightarrow Me^{n+} + ne^{-}$
gas noble metal (platinum) immersed in a solution of specific ions, saturated with gas	$Pt, Cl_2 \mid Cl^{-}$	$Cl_2 + 2e^{-} \longrightarrow 2Cl^{-}$
oxidizing-reducing noble metal (e.g. platinum) immersed in a solution containing ions of a given metal with various charges	$Pt \mid Fe^{2+}, Fe^{3+}$	$Fe^{2+} \longrightarrow Fe^{3+} + e^{-}$ Fe^{2+} – reduced form Fe^{3+} – oxidized form

If the half-cell includes a noble metal (electrode), it acts as a source or receiver of electrons without taking direct participation in the reaction.

Redox electrodes are defined as electrodes made of a chemically inert metal that is immersed in a solution of a substance present both in the oxidized form (this form is marked as **ox** in the text) and reduced (denoted as **red**). The reaction that occurs on this electrode can be written as follows:

$$\text{red} \longrightarrow \text{ox} + ne^{-}$$

An inert metal (e.g. platinum, gold) is an electron carrier between the two forms. The potential of this redox electrode is expressed by the equation:

$$E = E_0 + \frac{RT}{nF} \ln \frac{c_{oks}}{c_{red}}$$

where:

E_0 – normal redox potential.

As it can be seen from the above equation, the normal potential is equal to the electrode potential, in which the activities of the oxidized (ox) and reduced (red) forms are equal to each other,

n – is the number of electrons involved in the redox reaction.

It should be noted that a metal electrode is a special example of a redox electrode, where the oxidized form is the metal cation (Me^{n+}) and the reduced metal (Me).

The oxidation and reduction reactions in the cells take place on separate electrodes, in different parts of the cell, as a result of which we can observe the flow of electrons between the electrodes. When assembling the cell, both solutions are connected by means of an electrolytic key, i.e. a U-tube filled with a gel, with a concentrated aqueous salt solution (usually KCl), enabling the connection of half-cells and exchange of ions between the solutions.

An anode is an electrode to which electrons are released as a result of oxidation, while a cathode is an electrode on which, as a result of taking electrons by ions, reduction takes place, i.e. in galvanic cells we deal with anodic oxidation and cathode reduction.

When specifying galvanic cells, an abbreviated notation is used, in which the substrate | product order is valid for each half-reaction.

In the diagram of the cell, the negative electrode (anode) is placed on the left and the positive electrode (cathode) on the right. The contact of the phases (metal solid and ion solution) is marked by a vertical line |. In the case of cells in which the half-cell chambers contain different solutions, an electrolytic key (usually a glass U-tube filled with a gel with a salt solution) is used to close the circuit, marked in the cell's record with the symbol ‖.

2.2. The electromotive force of a cell

When a metal is immersed in a solution of its ions, an electric potential difference is created at the metal / solution interface, known as the electrode potential. The difference in potentials of the electrodes making up the cell, which is also a measure of the cell's ability to generate the flow of electrons through the circuit, is called the electromotive force of the EMF cell.

$$\mathrm{SEM} = \Delta E = E_1 - E_2$$

where:

E_1 – positive electrode potential,
E_2 – negative electrode potential.

The electrode potential, determined for standard states (gas under pressure of 1 atm, electrolyte solution with a concentration of 1mol/dm^3) is called the standard electrode potential E^0, and the EMF determined for these conditions is called the standard electromotive force. Standard electrode potential values are determined in relation to the hydrogen electrode, the potential of which is assumed to be equal to zero.

The Nernst equation is used to calculate the electromotive force of a cell at any concentration of substrates and products:

$$E = E^0 + \frac{RT}{nF} \ln \frac{c_{utl}}{c_{red}}$$

where:

E^0 – standard EMF cells [V],
R – universal gas constant [J/mol·K],
T – temperature [K],
n – the number of electrons involved in the electrode reaction,
F – Faraday's constant [C/mol],
c_{utl} – molar concentration of the oxidized form [mol/dm^3],
c_{red} – molar concentration of the reduced form [mol/dm^3].

2.3. Practical use of cells

Everyday use galvanic cells are batteries (marked with symbols R3/AAA, R6/AA (so-called stick), R10, R14, R20 (with a voltage of 1.5 V) or flat batteries with a voltage of 4.5 V – three cells connected in series) and various types of batteries. The first battery cells were built at the beginning of the 19th century and the principle of their operation has not changed much since then. The electrolyte and electrodes are still used. For years, acid and alkaline cells have been available on the market.

2.3.1. The cell in the acid version

The Leclanché cell (Fig. 4) consists of a zinc cup which is also the negative pole. Inside the cup there is an electrolyte in the form of a paste composed of ammonium chloride, a small amount of zinc chloride, water and diatomaceous earth or other filler. The paste contains a carbon (graphite) rod surrounded by a bag containing finely powdered manganese(IV) oxide. The carbon rod is fitted with a brass cap at the end for better contact with the carbon rod.

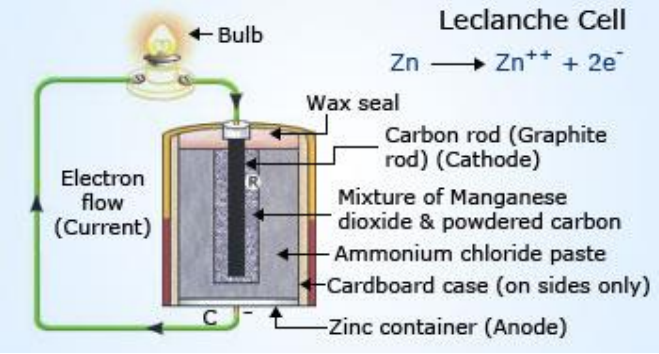


Fig. 4. The Leclanché cell
source: https://www.upsbatterycenter.com/blog/what-is-a-leclanche-cell/
(accessed December, 15, 2021)

In this cell, manganese(IV) oxide plays the role of a depolarizer. Diagram of this cell:

$$Zn(s)|ZnCl_2(aq), NH_4Cl(aq)|MnO(OH)(s)|MnO_2(s)|C, 1.5\ V$$

The following electrode reactions take place during the operation of the cell:

- on the anode $Zn \longrightarrow Zn^{2+} + 2e^-$
- on the cathode (the process is more complicated and complex):

$$MnO_2(s) + H_2O(c) + e^- \longrightarrow MnO(OH)(s) + OH^-(aq)$$
$$NH_4(aq)^+ + OH^-(aq) \longrightarrow 2NH_3(g) + H_2O(c)$$

generally

$$2NH_4(aq) + 2e^- \longrightarrow 2NH_3(g) + H_2(g)$$

The released hydrogen reacts with the MnO_2

$$H_2 + 2MnO_2 \longrightarrow Mn_2O_3 + H_2O$$

Manganese is reduced from Mn^{4+} to Mn^{3+}. The water produced provides the necessary moisture to allow the migration of ions, and the resulting ammonia is bound by zinc ions into complex amino-zinc ions:

$$4NH_3 + Zn^{2+} \longrightarrow [Zn(NH_3)_4]^{2+}$$

2.3.2. Dry alkaline cells

Alkaline cells are a bit more expensive but last longer. Engineers are constantly looking for new chemicals and technologies to achieve the highest possible energy density. One of the more interesting battery manufacturing technologies is **thin-film technology**. Contrary to traditional batteries, it takes any shape, so it can be perfectly adapted to the requirements of the device housing. Another advantage is the ability to work in a wide temperature range from –20°C to +140°C. Such a battery can withstand a temporary temperature of +280°C, which allows it to be soldered in the reflow process and reduces assembly costs. In the case of the cells used so far, it was necessary to place them in the device only at the final stage of production, often by hand. However, thin-film batteries have some limitations. First, they require a heat treatment of 700°C or even more. Another limitation is capacity. At present, 110 – 130 µAh can be obtained for each cm^2 of the cathode area. Unfortunately, this value also depends on the housing, which forces the size of the battery to be reduced and the final capacity drops by about 50%. Keep in mind that thin-film solutions are more expensive than traditional cells of resistive capacity. Charging thin film cells requires a constant voltage of 4.2 V for lithium batteries or 3.95 V for lithium-ion batteries. By applying a current of 0.4 mA to each cm^2 of the cathode surface, it is possible to charge the battery to 80% of its capacity in 15 minutes.

2.3.3. Nanobattery (Always Ready Smart Battery)

The nanobattery developed by mPhase fulfils a different role than the batteries discussed so far. It was intended to work as a backup power supply. The chemical reactions responsible for generating energy are inactive until it is needed. The technology based on nanotubes allows to separate the electrolyte from the anode and cathode, and if necessary, an electric field can be applied, the action of which will change the surface tension and allow the electrolyte to flow. When it reaches the cathode and anode, it produces a voltage. A typical area of application will be cellular connectivity for critical missions. After discharging the battery that is the primary power source, it will be possible to activate the backup nanobattery, which will allow you to talk for another 10 minutes.

2.3.4. Lithium batteries

The constant pressure to supply lithium batteries with ever greater capacity and greater safety of use forces manufacturers to constantly search for new chemicals. Examples include lithium-manganese dioxide ($Li\text{-}MnO_2$) cells containing a metallic lithium anode and a solid manganese dioxide cathode. The electrodes are immersed in an organic, non-corrosive and non-toxic electrolyte. They provide a voltage of 2.8 V.

Another example is lithium thionyl chloride ($Li\text{-}SOCl_2$) batteries. The active material of the cathode is thionyl chloride ($SOCl_2$) and the anode is made of lithium. The initial voltage is 3.6 V, the loss of capacity due to self-discharge is 1% per year, and the useful life can be from 10 to 20 years.

2.3.5. Alternative solutions

According to the assurances of ZPower, the first rechargeable silver oxide cells intended for commercial applications are to be sold. The first cells are expected to be used primarily in laptops and mobile phones. According to ZPower, they will be 40% more efficient than traditional lithium-ion cells. Moreover, they will be more environmentally friendly and safer. It is worth noting that more than 95% of the original battery components can be recycled, which also provides financial benefits to those who recycle the battery. The absence of lithium increases safety. The anode made of composite polymer is resistant to deformation and the formation of dendrites. Thanks to this, two basic disadvantages of traditional batteries have been eliminated: the risk of explosion and slow degradation of the electrode. The ZPower company has developed a highly effective separation material that slows down the growth of dendrites, but also allows the smooth flow of ions from the cathode to the anode, which contributes to reducing the internal resistance of the cell. As a result, a battery with a long service life and short charging time was obtained. The starting voltage is about 0.4 V higher than for NiCd cells, typically 1.74 V. This makes it possible to use fewer cells to achieve the required voltage, and consequently to reduce the dimensions and weight of the devices. The use of a patented electrolyte allowed to reduce the problem of the formation of dendrites, which were responsible for the „memory effect” of NiCd batteries. The research conducted by PowerGenix enabled the elimination of heavy metal elements. The batteries offered are AAA, AA and D. They are designed for more demanding applications.

Last year, PowerGenix introduced D-size batteries for hybrid vehicles. Toyota Prius was equipped with this type of batteries. According to the assurances of PowerGenix, these cells have a 30% greater energy density and greater capacity compared to solutions based on NiCd cells of the same size.

In many cases, the choice of a specific phone or laptop model is determined by the battery life. In order to remain competitive, producers must follow changes taking place on the market and adapt their products to new opportunities. Consumers can expect much longer breaks between battery charges and a reduction in the weight of the devices they buy.

2.3.6. Secondary cells

Secondary cells are current sources that enable them to be recharged multiple times. **The lead-acid battery** (Fig. 5) used in cars is one of the best-known acid batteries. It comprises a series of plates (electrodes) made of a hard lead-antimony alloy coated with a paste of lead(II) sulphate. The electrolyte is 20% sulphuric (VI) acid with a density of 1.15 g/cm^3.

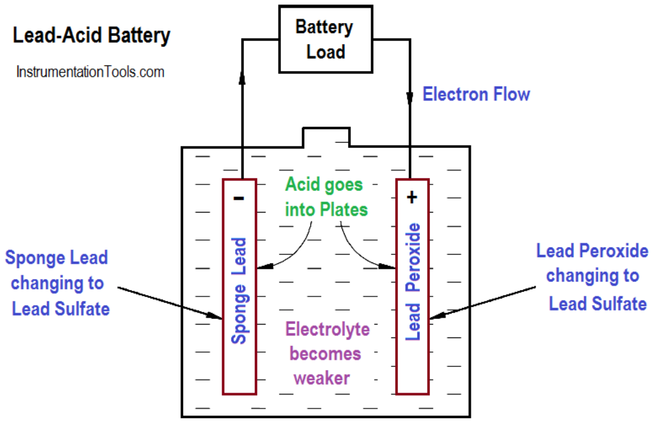


Fig. 5. Diagram of a lead battery
source: https://instrumentationtools.com/discharge-and-charging-of-lead-acid-battery/
(accessed December, 15, 2021)

During charging, part of the lead(II) sulphate(VI) on one electrode is reduced to lead (this electrode will be the anode during discharge). At the same time, on the second electrode (which is later the cathode), lead(II) sulphate(VI) is oxidized to lead(IV) oxide. In the discharging process, sulphuric(VI) acid is consumed. During subsequent recharging, the external power source forces the reaction to run in the opposite direction and regenerates the sulphuric acid. The concentration of sulphuric acid in the battery can therefore be an indicator of its charge.

Charging the battery causes differentiation of the electrodes. Charging is electrolysis of the sulfuric acid of the battery. A chain process runs on an electrode connected to the positive outer pole of the power source.

$$SO_4(c)^{2-} + PbSO_4(s) \longrightarrow Pb(SO_4)_2(c) + 2e^-$$

Lead (IV) sulphate undergoes reversible hydrolysis:

$$Pb(SO_4)_2(s) + 2H_2O(c) \longrightarrow PbO_2(s) + H_2SO_4(c)$$

and in parallel dissolved lead (IV) sulphate partially dissociates into ions

$$Pb(SO_4)_2(c) \longrightarrow Pb(c)^{4+} + 2SO_4(c)^{2-}$$

The following processes take place on the electrode connected to the negative pole of an external current source;

$$2H(c)^+ + 2e^- \longrightarrow 2H(ads)$$

$$2H(ads) + PbSO_4(s) \longrightarrow Pb(s) + H_2SO_4(c)$$

Ultimately, charging produces lead on the negative electrode, and lead(IV) oxide on the positive electrode, which is the main component deposited on lead.

A cell is created with the following diagram:

$$Pb(s)|PbSO_4(s)|H+(aq), HSO_4^-(aq)|PbO_2(s)|PbSO_4(s)|Pb(s), \qquad 2\ V$$

The substances deposited on the lead electrodes are spongy. In all cells used as current sources, the aim is to create a large active surface of electrochemical reactants. This increases the speed of the electrode processes. The positive lead battery electrode is a redox electrode in which the metallic lead acts as an electron exchanger. The negative electrode is of the first type. The following electrode processes run during battery operation:

on the negative electrode (anode):

$$Pb(s) + HSO_4^-(aq) \longrightarrow PbSO_4(s) + H^+(aq) + 2e^-$$

on the positive electrode (cathode):

$$PbO_2(s) + 3H^+(aq) + HSO_4^-(aq) + 2e^- \longrightarrow PbSO_4(s) + 2H_2O(c)$$

The overall process in the cell is as follows:

$$2PbSO_4(s) + 2H_2O(c) \longrightarrow PbO_2(s) + Pb(s) + 2H_2SO_4(c)$$

When charging the battery, the reaction is to the right, while it is running – to the left. The electromotive force of a lead battery is 2.2 V and is slightly dependent on temperature. In order to obtain a higher value of supply voltages, individual cells are connected in series into a battery of accumulators.

During battery operation, the electromotive force on a single cell should not drop below 1.8 V. Then irreversible processes take place on the electrodes. Among other things, PbS (lead(II) sulphide) is formed. We say then that the battery has been sulphated.

The lead battery is sensitive to shock, which causes the porous mass of the plates that contain the lower parts of the plates to fall off. The result is self-discharge of the battery and consequent sulphation. Requires constant maintenance, has a low capacity and is only suitable for short-term processes, e.g. when starting a car.

The nickel-iron (Edison) battery shown in Fig. 6 belongs to the alkaline type batteries. This battery is less shock-sensitive and requires no maintenance. The electrolyte is a 21 wt% KOH solution with a small addition of a lithium salt. Lithium ions adsorb to solid phases and act catalytically. The negative electrode is the iron electrode and the positive electrode is the nickel electrode.

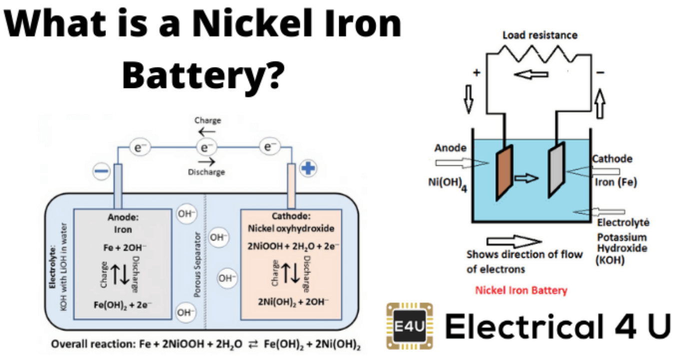


Fig. 6. The nickel-iron battery
source: https://www.electrical4u.com/nickel-iron-batteries-or-edison-batteries/Diagram of the basic battery (accessed December, 15, 2021)

Practically the nickel electrode is a mixture of NiO_2, Ni_2O_3 or Ni_3O_4 oxides

This cell can be represented by a diagram:

$$(–)\ Fe(s)\ |\ KOH_{aq}\ |\ NiOOH(s),\ NiO_2(s)\ |\ Ni(s)\ (+)$$

This cell can be represented by a scheme:

- on a negative electrode:

$$Fe(s) + 3OH(c)^- \longrightarrow FeO_2H(c)^- + H_2O(c) + 2e^-$$
$$FeO_2H(c)^- + H_2O(c) \longrightarrow Fe(OH)_2(s) + OH(c)^-$$

- on a positive electrode:

$$NiOOH(s) + H_2O(c) + e^- \longrightarrow Ni(OH)_2(s) + OH(c)^-$$
$$NiO_2(s) + H_2O(c) + e^- \longrightarrow NiOOH(s) + OH(c)^-$$

The above reactions run to the right while the cell is working, and to the left – while charging, in total, the process can be written as follows:

$$Fe(s) + 2NiOOH(s) + 2H_2O(c) \longrightarrow Fe(OH)_2(s) + 2Ni(OH)_2(s)$$

The battery shown is capable of operating until the voltage is completely lost, producing high currents. The electromotive force of such a battery is 1.4 – 1.2 V. It is used, among others, in various types of radio stations due to its large capacity. Although the nickel-iron cell has a lower voltage, it has an advantage over the lead cell, because the OH – ions produced at the cathode are consumed at the anode, so there is no change in the concentration of the electrolyte during battery operation.

The silver zinc battery was developed in 1941. The cell can be represented by a scheme:

$$(-)\mathrm{Zn(s)|KOH(aq)(30–40\%)|Ag2O(s)|Ag}(+)$$

The relevant electrode processes during operation are as follows:

$$(-)\mathrm{Zn(s)} + \mathrm{4OH^{-}(aq)} \longrightarrow \mathrm{[Zn(OH)_4]_2(aq)} + \mathrm{2e^{-}}$$
$$(+)\mathrm{Ag_2O(s)} + \mathrm{H_2O(c)} + \mathrm{2e^{-}} \longrightarrow \mathrm{2Ag(s)} + \mathrm{2OH^{-}(aq)}$$

The source of the work is therefore the summary process:

$$\mathrm{Zn(s)} + \mathrm{Ag_2O(s)} + \mathrm{2KOH(aq)} \longrightarrow \mathrm{2Ag(s)} + \mathrm{K_2[Zn(OH)_4](aq)}$$

The EMF of such a cell is equal to 1.86 V. Since this type of cell is characterized by high stability of parameters during discharge, it has been used in the military sector, space technology and to supply utility microelectronics.

2.3.7. Fuel cells

Each redox reaction can be separated into half reactions and used to form a galvanic cell. And since every combustion process is such a reaction, attempts have been made to use the energy of the combustion reaction to generate electricity. Hydrogen and methane (CH_4) have been found to be perfectly suited for this purpose. The combustion of hydrogen can be written by the reaction:

$$\mathrm{4H_2(g)} + \mathrm{O_2(g)} \longrightarrow \mathrm{2H_2O(c)},$$

which can be divided into half reactions. In an acidic solution, they are as follows:

anode: $\mathrm{2H(g)} + \mathrm{4OH^{-}(aq)} \longrightarrow \mathrm{2H_2O(c)} + \mathrm{4e^{-}}$

cathode: $\mathrm{O_2(g)} + \mathrm{4e^{-}} + \mathrm{2H_2O(c)} \longrightarrow \mathrm{4OH^{-}}$

The hydrogen fuel cell (Fig. 7) is a device that converts the chemical energy stored in the fuel into electricity. It is essentially a simple device consisting of two electrodes (anode and cathode) separated by a polymer electrolyte that allows ions to pass through but blocks the flow of electrons. The hydrogen flows to the anode, where the electrons are released, forming positive hydrogen ions. The electrons flow through the outer circuit, and the ions diffuse through the electrolyte. At the cathode, the electrons recombine with hydrogen ions and in reaction with oxygen taken from the environment, water is produced, which is a by-product. A quiet and ecologically clean conversion of chemical energy into electricity takes place in the cell. But the real advantage of fuel cells is their amazing ability to extract electricity from hydrogen atoms.

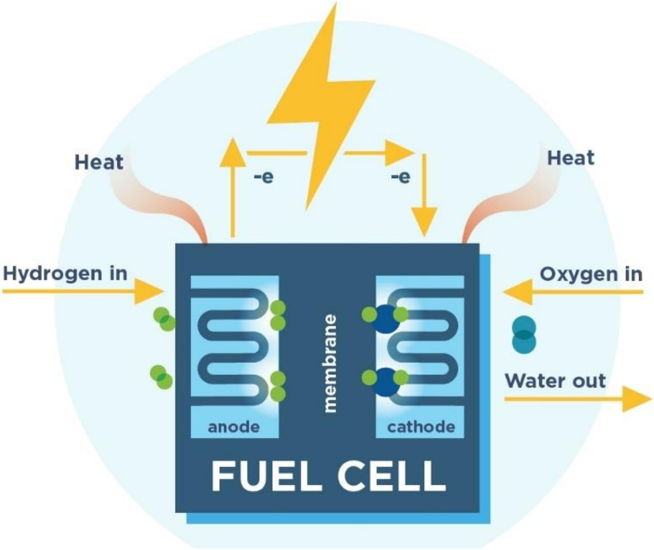


Fig. 7. Diagram of a fuel cell
source: https://www.fchea.org/h2-day-2019-events-activities/2019/8/1/fuel-cell-amp-hydrogen-energy-basics
(accessed December, 15, 2021)

Fuel cells, similar in size to traditional nickel-cadmium batteries, but lighter and cheaper, can work up to 20 times longer. Another advantage is the lack of a long-term charging process: the cells can be quickly and easily regenerated by refilling the fuel. Many companies have already presented advanced results of work on miniature fuel cells, and an experimental series of notebooks, palmtops and handhelds powered in this way should debut in the near future. It was estimated that in 2012, fuel cells will power nearly 15% of laptops working around the world. Different types of fuel cells are possible. Other promising fuel cells are those where the fuel is methanol, which, unlike hydrogen, is non-explosive and has a higher energy density than hydrogen. Table 2 summarizes the physical and chemical properties of the most popular cells.

Table 2

Selected physical and chemical properties of the most popular cells

Type of cell	Anode	Cathode	Reaction	Voltage V	Theor. cap. Ah/g	Theor. power Wh/g	Pract. power Wh/g
Leclanché (zinc-carbon)	Zn	MnO_2	$Zn + 2MnO_2 + 2H^+ \rightarrow Zn^{2+} + H_2O + Mn_2O_3$	1.6	0.224	0.358	0.085
$MnO_{2\ alkaline}$ (zinc manganese)	Zn	MnO_2	$Zn + 2MnO_2 + H_2O \rightarrow ZnO + 2MnO(OH)$	1.5	0.224	0.358	0.145
Mercury	Zn	HgO	$Zn + HgO \rightarrow ZnO + Hg$	1.34	0.190	0.255	0.100
Silver	Zn	Ag_2O	$Zn + Ag_2O + H_2O \rightarrow Zn(OH)_2 + 2Ag$	1.6	0.180	0.288	0.135
Lead acid	Pb	PbO_2	$Pb + PbO_2 + 2H_2SO_4 \rightleftarrows 2PbSO_4 + 2H_2O$	2.1	0.120	0.252	0.035
Nickel cadmium	Cd	NiOOH	$Cd + 2NiOOH + 2H_2O \rightleftarrows 2Ni(OH)_2 + Cd(OH)_2$	1.35	0.181	0.244	0.035
Nickel hydride	MH	NiOOH	$MH + NiOOH \rightleftarrows M + Ni(OH)_2$	1.35	0.178	0.240	0.075
Lithium Ion	Li_xC_6	among others $Li_{(1x)}CoO_2$	$Li_xC_6 + Li_{(1-x)}CoO_2 \rightleftarrows LiCoO_2 + C_6$	4.1	100	410	150
Fuel, hydrogen-oxygen	H_2	O_2	$H_2 + 1O_2 \rightarrow H_2O$	1.23	2.975	3.660	

Fig. 8. shows a comparison of the energy density available in popular battery production. technologies.

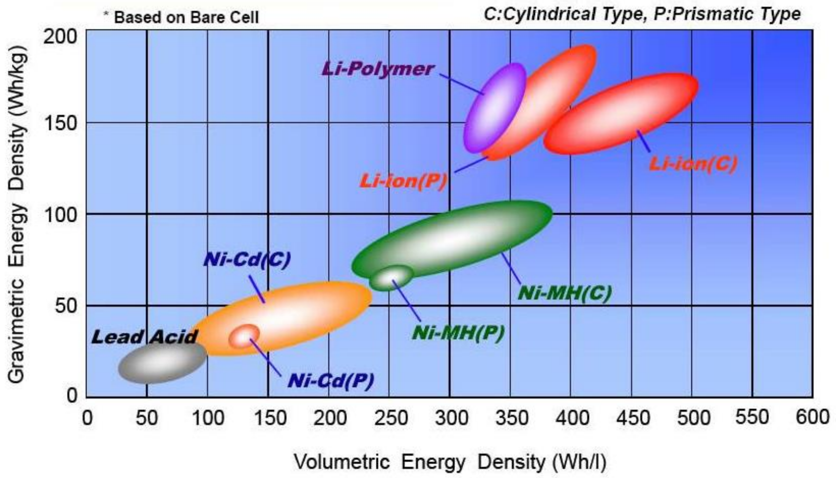


Fig. 8. Comparison of the energy density available in popular technologies of battery production
source: https://www.epectec.com/batteries/cell-comparison.html
(accessed December, 15, 2021)

2.4. Corrosion

The term corrosion (Latin *corrosio* – biting, eating) is defined as the destruction of materials under the influence of the surrounding environment (atmosphere, soil, water, precipitation), as well as technological factors released into the atmosphere as a result of human activity. Such dangerous factors are: sulphur and nitrogen oxides, carbon dioxide, dust, etc. and all kinds of chemicals. Most commonly, the term corrosion refers to metals and their alloys, although it also applies to non-metallic materials such as concrete, plastics, composites and ceramics.

Depending on the corrosion mechanism, electrochemical corrosion occurs in the presence of an electrolyte or chemical corrosion occurs in dry gases or non-electrolytes.

Electrochemical corrosion can occur in various environments such as: atmosphere (humid air), water (sea water, fresh water), soil (soil) and depends on many factors, e.g. temperature, humidity, pH, chloride content, solid or gaseous pollutants.

The corrosion process can occur in a metal or metal alloy. From the point of view of materials that are subject to corrosion, we can deal with general corrosion (uniform or uneven) or local corrosion (spot, point, pitting, intercrystalline or crevice). If corrosion occurs at the junction of two metals, then it is contact corrosion.

2.4.1. Corrosion mechanism

Electrochemical corrosion is mediated by electrode processes. In the anode areas.

(Fig. 9), the metal donates electrons and goes in the form of an ion into solution according to the reaction:

$$\mathrm{Me} \longrightarrow \mathrm{Me}^{n+} + \mathrm{ne}^{-}$$

Due to the good conductivity of the metal, the electrons migrate to the cathode regions, where the reduction takes place with the participation of the depolarizer, most often according to one of the following reactions:

a) $2H^+ + 2e^- \longrightarrow H_2$
(in acidic environments – hydrogen depolarization)

b) $O_2 + 2H_2O + 4e^- \longrightarrow 4OH^-$
(in neutral and alkaline environments – oxygen depolarization)

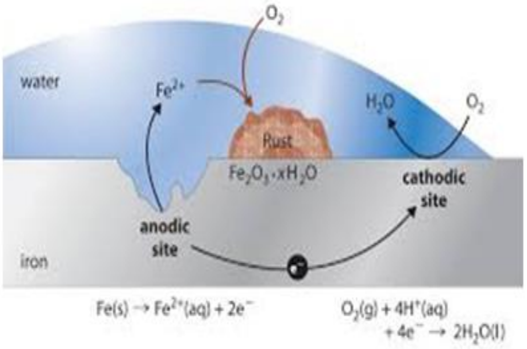


Fig. 9. Anode and cathode area of a cell
source: https://chem.libretexts.org/Bookshelves/General_Chemistry/Map%3A_Chemistry_-_The_Central_Science_(Brown_et_al.)/20%3A_Electrochemistry/20.8%3A_Corrosion
(accessed December, 15, 2021)

The formation of local corrosion cells may be caused by the heterogeneity of the metal composition or the heterogeneity of the electrolyte (e.g. different degree of air entrainment). A drop of water, containing various dissolved components from the surrounding environment, acts on the metal surface as an electrolyte in a small electrochemical cell (Fig. 10).

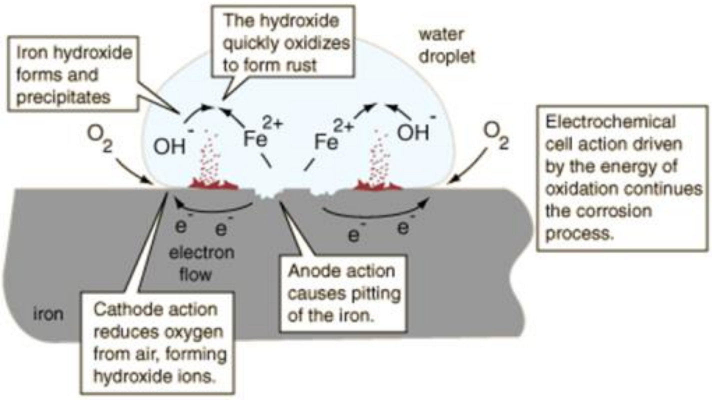


Fig. 10. Diagram of water droplet corrosion
source: https://daveh88.wordpress.com/2015/01/03/corrosion-laboratory/
(accessed December, 15, 2021)

At the edges of the drop, cathode regions are formed on which the oxygen depolarization reaction takes place. In the centre of the drop, an anode area is formed, where the iron donates electrons to form Fe^{2+} ions, which are then oxidized to Fe^{3+}. Rust is deposited in the electrolyte in the form of hydrated iron(III) oxides, $Fe_2O_3 \cdot H_2O$.

$$Fe \longrightarrow Fe^{2+} + 2e^-$$

$$Fe^{2+} + 2OH^- \longrightarrow Fe(OH)_2$$

$$2Fe(OH)_2 + \tfrac{1}{2}O_2 + H_2O \longrightarrow 2Fe(OH)_3$$

In the case of iron alloys, the cathode and anode regions are detected by a ferroxyl indicator. In the cathode areas there is a pink colour due to an increase in the concentration of OH^- ions, while in the anode areas there is a blue colour as a result of the formation of Turnbull's blue in reaction with Fe^{2+} ions.

Water conducts electricity better when salts are dissolved in it, hence corrosion is more intense in marine waters. Fig. 11 shows a diagram of electrochemical corrosion.

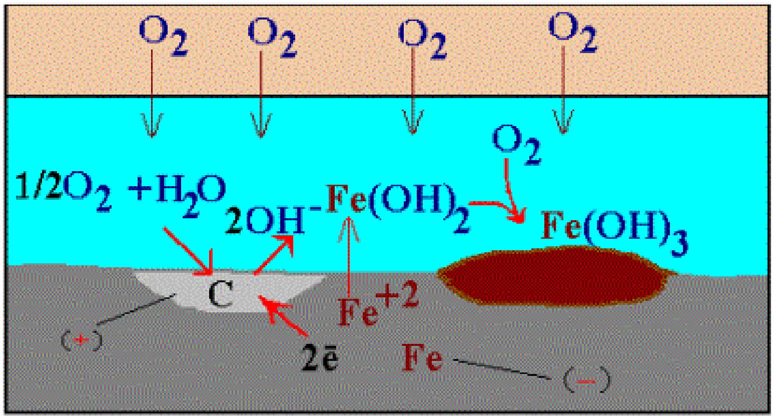


Fig. 11. Diagram of electrochemical corrosion

2.4.2. Corrosion protection

Ordinary carbon steels, which are the basic construction material, are durable, but not very resistant to corrosion. Steel becomes corrosion resistant if it contains more than 12% of hromium. Such steels are called stainless. Corrosion resistance can be additionally increased by adding other components (nickel, molybdenum, titanium) and can be obtained, the so-called acid-resistant steels. In conditions exposed to strong corrosion, including in an aggressive marine environment, austenitic steels are used, **the so-called duplexes**.

If the structure is made of carbon steel, a simple way to prevent corrosion is to isolate the metal surface from the electrolyte solution. So metals can be covered with paints, greases or other protective coatings. A common method of protection against corrosion is the application of a coating of another metal. When a metal coating with a higher potential (more resistant to corrosion) is made, we refer to the cathode coating (e.g. chrome or nickel coatings on steel). Such coatings are effective when they are non-porous and tightly cover the protected metal. In the event of their damage, a micro-cell is created in which the protected metal becomes an anode and is subject to accelerated corrosion. Anodic coatings, on the other hand, are made of metal with a lower potential, which means that in the event of damage to the coating and the formation of a cell, the protective coating material is oxidized, and the protected material acts as a cathode (it does not corrode).

2.4.3. Anodic protection

Anodic protection is a type of corrosion protection in which the protected metal acts as a **cathode**. We can distinguish cathodic, galvanic and electrolytic protection. Galvanic cathodic protection consists in attaching to the structure of a metal block with stronger reducing abilities (**metal with a lower standard potential**), which undergoes oxidation and constitutes the **anode** of the corrosion cell. Such a block of metal is called a **sacrificial anode**. Sacrificial protection is used to protect underground pipelines, tanks or hulls of ships and other large objects. Anodes are sheets or bars made of active metals: magnesium, aluminium or zinc, electrically connected to the protected object, in the vicinity of places particularly exposed to corrosion. The negative electrode created in this way is a protector and it, not the protected object, is subject to corrosion. When worn, the protectors are replaced with new ones. Therefore, anodic protection is sometimes called **sacrifice protection**. Anodes are intentionally sacrificed to protect the structure from corrosion.

Galvanic anodes must have a sufficiently low potential and no polarization tendency (small potential changes during operation, e.g. due to oxide deposition). In shipbuilding, magnesium, zinc and aluminum anodes are used. Alloy additives are introduced to pure metals, reducing the tendency to passivation and the rate of self-corrosion, and increasing the uniformity of digestion. For example, manganese is added to magnesium, which lowers the electrode potential.

Sacrificial magnesium anodes (commonly used in soil, contain additives 5 – 7% Al, 2 – 4% Zn, minimum 0.15% Mn; they have low potential, but their efficiency is low (approx. 55%).

Zinc anodes (most commonly used in seawater) are pure 99.99% or an alloy containing < 0.1 – 0.15% Hg, 0.12 – 0.15% Al, 0.05 – 0.1% Cd; they are cheaper than the magnesium ones, they belong to the group of low-potential protectors with high (90%) efficiency.

Aluminium anodes are used only in the form of alloys with Zn (up to 6%), Sn (0.1 – 1%) and In, Hg, Sn; are low-potential protectors with an efficiency of approx. 80%.

Magnesium anodes can be used to protect aluminium structures, and carbon steel protectors are used for installations made of copper alloys.

Electrolytic cathodic protection consists of a cathode made of a protected metal (object), with the use of a power supply that draws energy from an external current source.

Various types of metallic protective coatings (galvanizing, aluminizing, cadmium plating, chrome plating) are also used to protect metal elements of machines and structures.

Other popular methods of protection against corrosion are the use of corrosion inhibitors in water circuits, i.e. substances delaying corrosion processes, or the use of organic coatings (painting, polymer coatings).

3. PERFORMING THE EXERCISE

Experiment 1 – Corrosion cell

Materials and reagents:

Steel plate, sandpaper, acetone (CH_3COCH_3), ferroxide indicator (mixture: 1% potassium ferricyanate(III) solution – $K_3[Fe(CN)_6]$, 1% phenolphthalein solution, 3% sodium chloride solution – NaCl).

Performance:

On the surface of the steel plate, cleaned with sandpaper and degreased with acetone (CH_3COCH_3), place a large drop of ferroxyl indicator. Observe the sample for 30 minutes.

Elaboration of the results:

1. Illustrate graphically and write appropriate reactions to justify the appearance of coloured areas on the metal surface.
2. Explain the mechanism of electrochemical corrosion of iron, write down the reactions characterizing the anodic and cathodic processes with hydrogen depolarization (corrosion in an acidic environment) and oxygen (corrosion in an inert environment).
3. Explain the corrosion mechanism of the ship's waterline. What kind of depolarization is occurring at the cathode and why?

Experiment 2 – Iron sacrifice protection

Materials and reagents:

Rack with test tubes, sulphuric(VI) acid (H_2SO_4) (1 : 3), potassium ferricyanate(III) solution – $K_3[Fe(CN)_6]$, sandpaper, steel nails (Fe), aluminium foil (Al), copper foil (Cu), lead foil (Pb)

Performance:

Fill three test tubes half of their volume with distilled water. Each acidify with 2 – 3 drops of sulphuric acid(VI) solution (H_2SO_4 1 : 3) and add a few drops of potassium hexacyanoferrate(III) (1% $K_3[Fe(CN)_6]$). This salt is a very sensitive reagent indicating the presence of iron(II) (Fe^{2+}) ions with which it gives an intense blue color (Turnbull's blue). Mix the contents of the test tubes. Clean three steel nails with sandpaper (fine grain). Wrap one of them as tightly as possible with aluminium foil, the other with copper foil, and the third with lead foil. Throw the wrapped nails into the next test tubes with the prepared solutions. After 60 minutes, remove the nails, rinse in a stream of running water, remove the covering foil and record the results of the experiment in Table 1.

Table 1

Summary of the results of the experiment 2

Tube number	Iron / metal foil	Colour of the solution	The redox reaction taking place at the anode of the cell	Potential E^0, V
1.	Fe/Al			Al^{+3}/Al
2.	Fe/Cu			Cu^{+2}/Cu
3.	Fe/Pb			Pb^{+2}/Pb

For a half-cell Fe^{+2}/Fe $E^0 = -0.44$ V (electrochemical series).

Elaboration of the results:

1. Record the observation results in Table 1.
2. Explain the mechanism of iron sacrificial protection, write down the equations of reactions running at the anode for the tested metals, explain why not all tested metals can be an iron corrosion protector.
3. Explain where and why metal ingots are installed to protect the ship's plating from corrosion.

4. DEVELOPMENT OF THE EXERCISE

1. Prepare the report according to the guidelines in the experimental section.
2. Place the cover sheet as the first page of the report.
3. After the theoretical part has been briefly developed, include the development of individual experiments and the solved task/additional tasks given by the teacher.

5. THE FORM AND CONDITIONS FOR PASSING THE LABORATORY EXERCISE

1. Passing the so-called „entry test” before starting the exercise.
2. Submission of a correct written laboratory report on the performed exercise in accordance with the guidelines for the preparation of the laboratory report, please see the link below: https://www.am.szczecin.pl/en/facilities/institute-of-mathematics-physics-and-chemistry/department-of-chemistry/technical-chemistry/tech-chemistry-lab-manuals/

I. Sample tasks with a solution

Example 1

Record the diagram of a Daniell cell made of a zinc electrode immersed in a $ZnSO_4$ zinc sulphate(VI) solution and a copper electrode immersed in a $CuSO_4$ copper sulphate(VI) solution, in which the half-cells are connected with an electrolytic key.

Solution

There is a reaction in the cell:

$$Zn(s) + Cu^{2+}(aq) \longrightarrow Zn^{2+}(aq) + Cu(s)$$

Zinc is oxidized (gives away electrons), and copper is reduced (takes electrons), therefore zinc is the anode (negative electrode), and copper is the cathode (positive electrode). We start writing the scheme with a description of the reactants and products of the anode reaction (left side of the scheme): $Zn(s)|Zn^{2+}(aq)$. Then we write down the substrates and the products of the reaction taking place at the cathode: $Cu^{2+}(aq)|Cu(s)$. Since the solutions in which the electrodes are immersed do not touch each other, we take into account the presence of an electrolytic key marked with the symbol „‖" in the diagram of the cell.

The full record of the cell has the form:

$$Zn(s)|Zn^{2+}(aq) \parallel Cu^{2+}(aq)|Cu(s)$$

Example 2

Calculate the electromotive force of the Daniell cell at a temperature of 25°C, where the concentration of Zn^{2+} ions is 0.1 mol/dm^3, and the concentration of Cu^{2+} ions is 0.001 mol/dm^3.

Solution

The reaction in the Daniell cell follows the equation:

$$Cu^{2+}(aq) + Zn(s) \longrightarrow Zn^{2+}(aq) + Cu(s)$$

The value of E^0 calculated from the difference of the standard potentials of zinc and copper is 1.1 ($E^0 = 0.34V - (-0.76V)$). The number of electrons n participating in the electrode reaction is 2. The value of the expression RT/F at 25ºC is 0.0257V.

$$c_{utl}/c_{red} = 0.1/0.001 = 100$$

Substitute the data into the Nernst equation:

$$E = 1.1\ V - (0.0257\ V/2) \cdot \ln 100 = 1.1\ V - 0.059\ V = 1.04\ V$$

II. Tasks and questions to be completed by the student

1. Calculate the EMF of a cell composed of an iron electrode immersed in a 1-molar $FeSO_4$ solution and a lead electrode immersed in a 1-molar $Pb(NO_3)_2$ solution.
2. The standard potential of the Zn^{2+}/Zn electrode is –0.76V, and the standard electromotive force of the cell

   $$Zn(s)\,|Zn^{2+}(aq)\,\|Cu^{2+}(aq)\,|Cu(s)$$

   is 1.10V. What is the standard potential of the Cu^{2+}/Cu electrode?
3. List two metals that could be used for cathodic protection of a titanium pipe; b) what factors, apart from the relative position in the voltage series, should be taken into account in practice; c) in domestic installations, copper pipes are often connected to iron pipes, what is the effect of copper on iron pipes?
4. Under standard conditions, the SEM of a metal cell in which one of the half-cells is a copper half-cell is 0,48 V. Using a series of electrochemical metals, find what metal is the second half-cell used in this cell and determine whether it serves as a cathode or an anode.
5. From the set of half-cells shown below:

   $$Fe/Fe^{2+},\ Hg/Hg^{2+},\ Pb/Pb^{2+}, Al/Al^{3+}, Cu/Cu^{2+}$$

   select the pair for which the value of the standard electromotive force of the created cell will be the highest.
6. Which of the following metals cannot act as an iron corrosion protector, and which is the best protection for iron:

   a) Zn,
   b) Sn,
   c) Pb.
   Explain why.

7. Can potassium manganate(VII) be used to oxidize iron(II) to iron(III) under standard conditions in an acidic solution?
8. What are the methods of electrochemical protection of metals? Discuss cathodic and anodic protection using any examples.
9. List the factors influencing the rate of corrosion.
10. Why does the zinc coating protect steel products from corrosion?
11. List other modern methods of corrosion protection used in shipbuilding and other industries.