Conversion of electrical energy into chemical energy

Conversions of electrical energy into chemical form are performed through the conversion systems, which can be divided into:

- ***electrolyzers*** – conversion electro-chemical
- ***galvanic cells*** – conversion chemical-electrical

Electrical accumulator is reversible source of direct current. What is the regime of accumulator (as a conversion element) it depends on current flow direction, that flows in closed electrical circuit (Fig. 1)

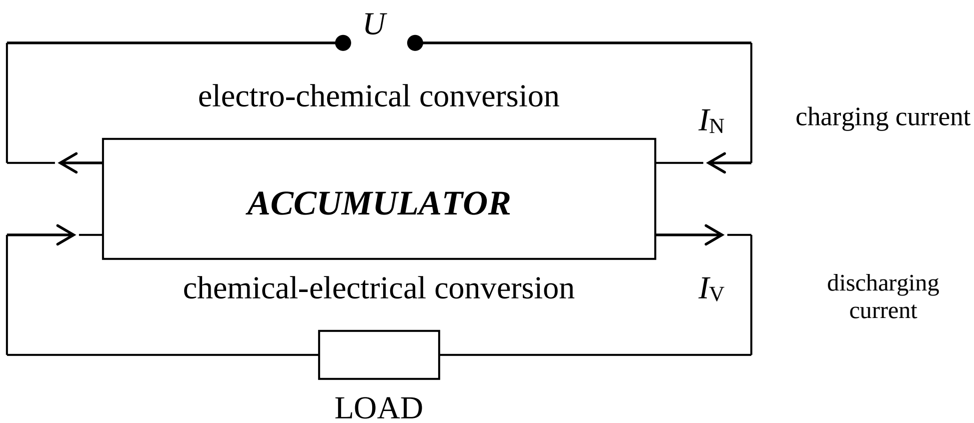

Fig. 1 Working regimes of accumulator

Discoveries of principles of electro-chemical phenomena belong the oldest ones and they date back to the late of the 18th century and the first half of the 19th century (Galvani, Volta, Faraday).

1.1 Basic terms

Electrolytes are conductors of the 2nd class, where the current flow change the physical properties and the chemical composition (some acid solutions, bases and metal salts).

Dissociation – is the process of degradation of the electrolyte molecules (molecules in a liquid solvent of the electrolyte are split into positive and negative ions).

If such an electrolyte solution through the system of electrodes is connected to a source of direct current, by the influence of created electric field the particular ions begin to move to the electrodes of opposite polarity and to separate on their surfaces.

Electrolysis – is the electrochemical process in which by the influence of an electric field (a system of electrodes connected to a direct current source) will start to move each of the ions of the electrolyte solution to the electrodes of opposite polarity and begin to secrete on their surface. It takes place in the electrolyser, electrolytic bath with at least two electrodes, an ***anode*** and a ***cathode***. The electrodes are usually from metal or carbon.

Electrolyser – a device in which is performed process of electrolysis.

Among the electrolytes belong also some solid substances that are by melting converted into a liquid state. If melting of the substance is carried out in order to change the chemical quality, the process is called ***thermal electrolysis*** or electrolysis by melting. The principle of electrolysis, respectively. thermal electrolysis is indicated in Fig. 2.

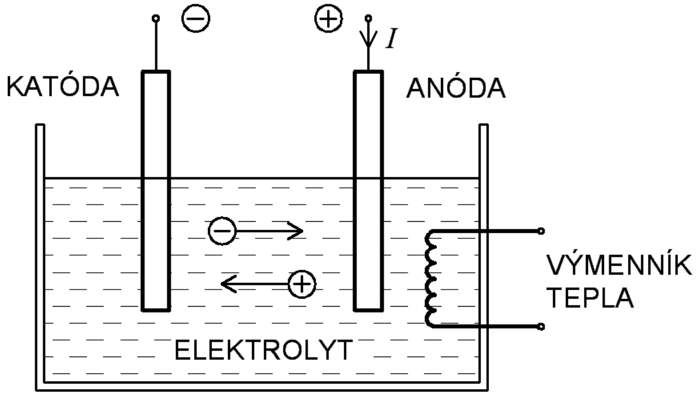

Fig. 2 Principle of electrolysis

The ***electrolytic dissociation*** or dissociation of the electrolyte in solution is the process of formation of free ions in the electrolyte solution, able to convey the current conduction in the solution.

The conduction of current through the solution or electrolyte melt is mediated by the directed migration of positive and negative ions in the present electric field. The ion carrying a positive charge is called the ***cation***, i.e. in the direct-current field it will move to the electrode of negative potential, e.g. ***cathode***. Conversely, ion, which is a carrier of negative charge is called ***anion***. In the same field it moves to the electrode of positive potential, e.g. ***anode***.

The charge of cation, respectively of anion is always an integer multiple of the elementary charge, which also indicates its valence. The ***ion valence*** is a positive or negative number expressed by portion of ion charge and the elementary charge $e = +1{,}602.10^{-19}$ C. It expresses the relationship

$$z = \frac{q}{e} \tag{1}$$

where q is the ion charge. The ions hence can be the positive monovalent ($q = e$), positive divalent ($q = 2 \cdot e$), negative monovalent ($q = -e$), negative divalent ($q = -2 \cdot e$) atc.

1.2 Faraday laws of electrolysis

The essential throughout in electrochemistry have the laws formulated by M. Faraday already in the 1st half of the 19th century. They express the quantitative relationship between the electric charge passing through the electrolyte and chemical effects, which it activated.

For repetition:

- ***amount of substance*** – is a standards-defined quantity that measures the size of an ensemble of elementary entities, such as atoms, molecules, electrons, and other particles. It is sometimes referred to as chemical amount. The unit of substance amount is mol – what is amount of substance, which contain as much elementary entities as atoms in 0,012 kg of C (12). The amount of substance is determined from portion of mass [kg] and molar mass of the substance [kg·mol^{-1}].

$$n = \frac{m}{M} \qquad [\text{mol}] \qquad (2)$$

- ***molar mass M*** – is a physical property defined as the mass of a given substance (chemical element or chemical compound) divided by the amount of substance. The base SI unit for molar mass is kg/mol. However, for historical reasons, molar masses are almost always expressed in g/mol.

$$M = \frac{m}{n} \qquad [\text{kg}\cdot\text{mol}^{-1}] \qquad (3)$$

Faraday's laws of electrolysis are quantitative relationships based on the electrochemical researches published by Michael Faraday in 1834. They were discovered by experiment and they belong to some empirical laws that are valid exactly.

1. Faraday law – the amount of the compound m [kg] that is eliminated or chemically modified on the electrode is proportional to the charge transferred by ions in electrolytic process, e.g. mathematically

$$m = A \cdot Q = A \cdot \int_0^t I \cdot \mathrm{d}t \qquad [\text{kg}] \qquad (4)$$

where Q is charge, which passed through the electrolyte solution [C]
A is a constant which is numerically equal to the amount of the substance to be eliminated, when through the electrolyte solution flows charge of 1 C. It is called the ***electrochemical weight equivalent*** [kg.C^{-1}]

Freely interpreted, according to the first Faraday's law, the same ***electric charge will exclude or chemically change on the electrode always the same amount of the same substance***.

2. Faraday law – the same electric charge will exclude from the solution of various substances such amounts that are proportional to their molecular weights. If the size of the charge is 1 C, then according to the first law, the amount of the excluded substance is equal to its electrochemical equivalent A

$$A = k \cdot M \qquad [\text{kg}\cdot\text{C}^{-1}] \qquad (5)$$

where k is constant of proportionality [mol·C^{-1}]

By substitution (5) into (4) we get the general (unified) Faraday law

$$m = k \cdot M \cdot Q \qquad (6)$$

which it shows that the elimination of any molecular weight compound ($m = M$) consumes always the same amount of charge $Q_0 = 1/k$. This amount of electrical charge is known as the Faraday charge or Faraday constant F. From the equation (6) and using of (3) there can be calculated the size of Faraday charge

$$Q_0 = \frac{1}{k} = F = \frac{Q}{\frac{m}{M}} = \frac{Q}{n} = 96490\ \mathrm{C \cdot mol^{-1}} \quad (7)$$

By substitution (7) into (6) we get another expression of general Faraday law

$$m = M \cdot \frac{Q}{F} = M \cdot \frac{I \cdot t}{F} \quad (8)$$

at a constant intensity of the electric current *I*.

Example 1

How much of the electric charge is needed to lead through the solution of CuSO4, to secrete the 3,32 g of Cu?

Solution:

According to Faraday laws, the charge of 96490 C can secrete in the case of divalent copper ½ 63,5 g.

Thus:

63,5 g Cu .... 2 · 96490 C
3,32 g Cu x

$$x = \frac{2 \cdot 96490 \cdot 3{,}32}{63{,}5} = 10089{,}7\ \mathrm{C}$$

Example 2

How many grams of Cu we can obtain from the solution of CuSO4, when through it there flows the current of 5 A during the 20 minutes?

Solution:

The charge is

$$Q = I \cdot t$$

If

$$I = 5\ \mathrm{A}$$

$$t = 20\ \mathrm{min} = 1200\ \mathrm{s}$$

we get

$$Q = I \cdot t = 5 \cdot 1200 = 6000\ \mathrm{C}$$

By the charge of 96490 C it can be obtained 31,75 g of Cu (see ***Example 1***).

$$m = \frac{31{,}75 \cdot 6000}{96490} = 1{,}97\ \mathrm{g\ Cu}$$

Example 3

By the current flowing through the solution of silver salt there is secreted on the cathode during the 10 minutes 1 g of Ag. Calculate the amperage intensity.

Solution:

On the cathode there takes place the reaction:

$$\mathrm{Ag^+} + e^- \rightarrow \mathrm{Ag^0}$$

$$t = 10\ \mathrm{minutes} = 600\ \mathrm{s}$$

$$m_{\mathrm{Ag}} = 1\ \mathrm{g}$$

$M_{Ag} = 107{,}87 \text{ g.mol}^{-1}$

$F = 96490 \text{ C.mol}^{-1}$

Then:

$$m_{Ag} = \frac{M_{Ag} \cdot I \cdot t}{F}$$

we express the intensity and substitute the values:

$$I = \frac{m_{Ag} \cdot F}{M_{Ag} \cdot t} = \frac{1\,\text{g} \cdot 96490}{107{,}87 \cdot 600} = 1{,}49 \text{ A}$$

Example 4

By the solution of NiCl2 passed current of 2 A for 3 hours. Calculate the mass of metal which was secreted an the cathode, and the excluded volume of gas (in normal conditions), produced at the anode.

Solution:

Reactions that run over at particular electrodes we can write by equations:

on cathode: $Ni^{2+} + 2e^- \rightarrow Ni^0$ cathodic reduction

on anode: $2Cl^- + 2e^- \rightarrow Cl_2^0$ anodic oxidation

According to the united Faraday's law, $m = \frac{A \cdot I \cdot t}{n \cdot F}$, where $t = 3\,\text{hours} = 10800\,\text{s}$

$$m_{Ni} = \frac{58{,}71 \cdot 2 \cdot 10800}{2 \cdot 96490} = 6{,}571\,\text{g Ni}$$

$$m_{Cl_2} = \frac{(2 \cdot 35{,}45) \cdot 2 \cdot 10800}{2 \cdot 96490} = 7{,}936\,\text{g Cl}_2$$

The weight of chlorine corresponds to the volume of

$$V = \frac{V_0 \cdot m_{Cl_2}}{M_{Cl_2}} = \frac{22{,}42 \cdot 7{,}936}{70{,}9} = 2{,}51\,\text{dm}^3$$

Example 5

How many mg of $AgNO_3$ is decomposed by electric charge of 1 Coulomb? [1,76 mg of $AgNO_3$]

Example 6

During the electrolysis process of solution of $CuSO_4$ there were secreted at anode the 448 ml of oxygen under the normal conditions. How many of $CuSO_4$ were decomposed? [6,384 g of $CuSO_4$]

Example 7

How many of Coulomb should be conducted through a solution of a silver salt to excrete from a solution of 1 gram of silver? [894,59 C]

Example 8

How many grams of nickel is excreted in galvanic electroplating, when through the plating bath pass of 1,600 coulombs? [0,4867 g of Ni]