

"abc" Course CHEMICAL POWER SOURCES

Summary

The first part of this course includes the theoretical base, kinetics of the processes in the chemical energy sources and some of the main parameters of the chemical power sources. The theoretical base consists of the principles of the chemical energy sources. The role of the active compounds, the electrolyte, and the separator is also discussed. Main reaction and other possible processes in the energy sources are numbered. Thermodynamics base of the electrochemical system, relation between theoretical (thermodynamic) potential difference of the electrochemical system and energy sources' OCV, based on the same system and the dependence of the OCV from other thermodynamic parameters is also discussed.

Energy sources kinetics discusses electrode polarization, types of electrode's reaction overvoltage, ohmic polarization, net polarization of the energy sources.

The theoretical characteristic electrochemical capacity and energy capacity are defined. Material balance of the energy sources.

CHEMICAL POWER SOURCES – An "abc" Course

Part I

The energy consumption in the 20th Century has dramatically increased which is particularly true for the electric energy demand. The chemical power sources (CPS) perform a direct transformation of the potential chemical energy into electricity and this is a process distinguished by its higher efficiency than the one involving a thermal cycle of the chemical reaction (burning).

It should be noted that the exact definition of these devices would be “chemical energy sources”, however in this discussion we will stick to the more common one, namely “chemical power sources” (CPS). Some of the fundamental properties of the CPS are their autonomy and possible miniaturisation. The rapid progress of electronics together with the above-mentioned CPS advantages have led to their rapid advancement and improvement. Another major characteristic of the CPS is that their energy may be utilised whenever needed thus enabling their application as emergency power sources.

The diverse CPS are based on different electrochemical systems resulting to their disparate specific characteristics. This enables CPS to be exploited in various operating conditions, which determines their wide practical applications.

CPS

A CPS is a device, which transforms directly the potential chemical energy of an oxidation-reduction process into electric energy. In addition, the CPS is an energy reformer with a construction convenient for practical use.

In general every oxy-red reaction can be electrochemically realised. In order to achieve this

aim three conditions have to be fulfilled. They are schematically illustrated in Fig.1.

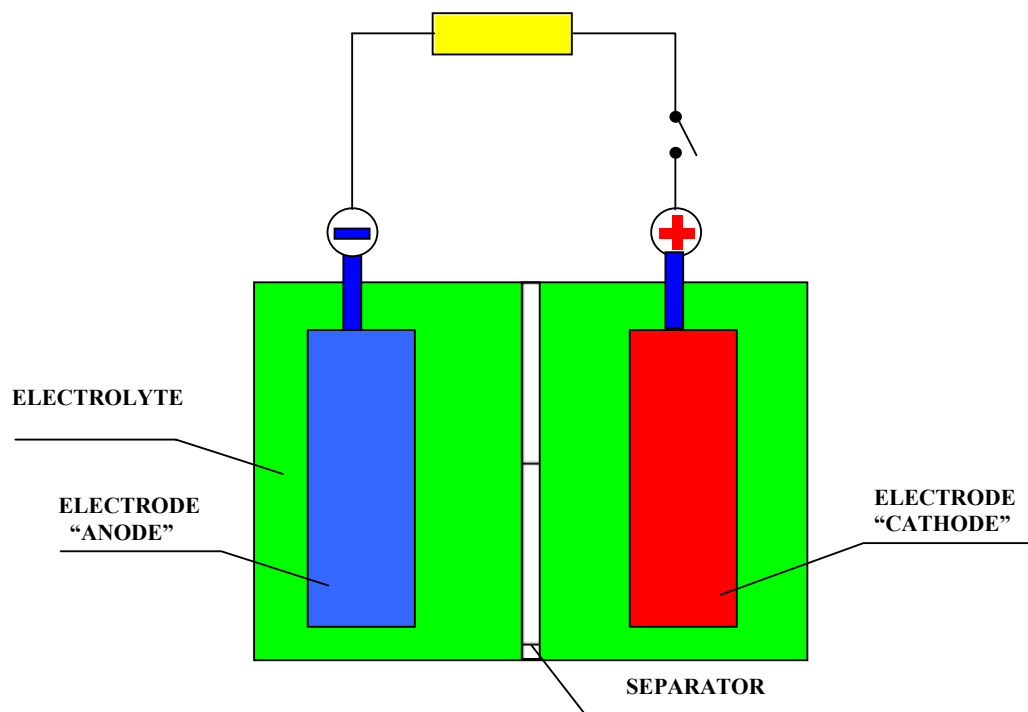


Fig. 1. A Chemical Power Source diagram

1. The reacting compounds must be separated in space, i.e. the oxidation (the reducer supplying electrons) and the reduction (the oxidiser accepting electrons) have to be carried out on the surfaces of two separate electrodes. The definition “electrode” determines the place where the oxidation or reduction process occurs.

2. The two electrodes must be in contact via an ionic conductor (electrolyte), which enables the transport of ions. The latter carry electrical charges and mass transfer from the one electrode to the other.

3. The two electrodes are connected with an electronic conductor, too. This part of the electrical circuit is “external” to the electrochemical system. The disconnection of the external electrical circuit halts the electrochemical reaction.

The combination of compounds participating in the electrochemical reaction will be defined as “an electrochemical system” (ES). At least one of the compounds included in the ES must be an electrolyte, which alongside with the ionic conductivity must be a non-electronic conductor. If the electrochemical reaction runs spontaneously, the free energy of the system decreases and the ES becomes a source of electric energy. This electrochemical

reaction is labelled as “current generating reaction” of the ES. Generally, in one ES a number of such electrochemical reactions can take place. In some ESs the electrolyte would be a composition of two constituents with different content, separated by a semi-permeable membrane preventing their mixture. One of the constituents is called “anolyte”, the other one – “catholyte”. At the same time in every electrochemical system there are at least two electronic conducting bodies called electrodes. The electrical charge exchange and the ongoing electrode electrochemical reactions occur at the electrode-electrolyte interface. The electrode, at which surface the oxidation process takes place, is identified as an “anode”. The anode carries the electrons, separated during the oxidation of the reducer, the anode active compound, towards the external part of the circuit. This is the reason why, when the electrochemical reaction runs spontaneously, the anode acts like a negative pole of the respective electrochemical (Galvani) cell. The other electrode, at which surface a reduction process takes place, is identified as a “cathode”. It supplies electrons to the cathode active compound - oxidiser - and is positively charged. As a result the cathode becomes the positive pole of the electrochemical cell. In some cases, the cathode or anode active compounds can simultaneously play the role of an electrode, too. In other cases, one of the active compounds can be dissolved into the electrolyte or can act as an electrolyte at the same time.

The definitions “negative electrode” and “positive electrode” are used in the reversible ES instead of the terms - anode and cathode. That is based on the fact that at discharge an anodic process occurs on the negative electrode, while during charge a cathodic one takes place on the same electrode.

The electrochemical literature accepts the electrochemical systems symbolic designation in a strictly defined manner. The chemical symbols of the electrodes, of the active compounds and of the electrolyte are presented in the note. Vertical lines separate the interfaces, where the electrochemical processes occur. The ES of the “dry” element of Leclanche, for example, is denoted in the following manner:



A vertical line is not used at the interface where only an electron transfer takes place. Instead, the two phases are separated by a comma, as it has been done to the right of the

above note. (The cathode active compound is manganese dioxide and the carbon rod together with the dispersed graphite and/or carbon black in the active mass serves as a current collector of the positive electrode.). Some insignificant salts in the electrolyte, as well as the electrolyte solvent (water) are not denoted. In rare cases the concentration of the solution is also mentioned. For non-aqueous electrolytes the solvent is specified. The content and the temperature of the molten or solid electrolytes are also defined. In cases of anolyte or catholyte, the membrane is denoted by a vertical dotted line.

In the ES note the anode is written to the left, and the cathode – to the right. According to the Stockholm Convention (1953) the open circuit voltage (OCV) of an electrochemical cell is represented as the algebraic potential difference between the right and left electrodes:

$$E_{\text{right}} - E_{\text{left}} = E_{\text{cell}} [\text{V}]$$

When denoted correctly, the OCV of the spontaneous electrochemical reaction will have a positive value.

Every electrochemical cell can be formally separated into two half-elements, and the electrochemical reaction can be viewed as the sum of two reciprocal, simultaneously occurring electrode reactions. The half-element consists of the electrode, the active compound and the electrolyte, and its potential is simply defined by the respective electrode reaction. That is why the broader sense of the definition “electrode” can include what has already been labelled a half-element.

From a scientific point of view the analysis of the half-element as an independent object of investigation is reasonable, since every electrode reaction has specific thermodynamic and kinetic characteristics and investigating it separately in the frames of the half-element gives the necessary scientific information for its optimisation.

The electrochemical cell forms the base of CPS but the two definitions do not fully overlap. The CPS will be considered as an electrochemical cell designed for production

with a suitable for practical application construction. The CPS may include one or more electrochemical cells.

The relative independence of the half-elements enables the construction of a great number of electrochemical cells by the combination of a limited number of half-elements. Sometimes the same half-element can play the role of both cathode or anode depending on the other half-element it is combined with.

The number of possible oxy-red reactions spontaneously occurring with the energy generation is excessively large. Since each of these reactions can be generally carried out in an electrochemical way, the number of ES, which could serve as base for the construction of CPS, should also be expected to be large. In reality however the practical possibilities for ES application are very limited. Only a small part of the large number of the possible ES can be regarded as applicable or prospective for CPS.

In order to be used in CPS, the electrochemical systems have to satisfy a number of important requirements. Some of the major ones include:

1. The randomly occurring current supplying reaction should provide for a sufficiently high OCV. If the OCV is lower than 1V, the supplied system energy will be too low, and if the OCV is below 0,5V it will be pointless to apply the system in CPS.
2. The current supplying reactions of both electrodes have to proceed at a sufficiently high rate. This will provide for a low electrode polarisation and high power of the corresponding CPS.
3. The ES has to be stable enough. The active compounds should not interact arbitrarily with the electrolyte and should not self-decompose. Every ES for which $OCV \neq 0$ in reality is far from the thermodynamic equilibrium, hence absolutely stable systems cannot exist. However, the sufficient condition is that the lateral corrosion reactions in the ES occur at a very low rate. If this condition is not fulfilled, the respective CPS will have high self-discharge and will be unstable.
4. When constructing CPS for mass consumption, all CPS components must not pose danger to humans; for example they must not be either toxic or explosive.

It is difficult to find an ES, which satisfies all of the above-mentioned requirements. Consequently some compromises have to be made. There are CPSs which do not possess good storage characteristics. They are however stored in an inactive state and are easily activated in case of emergency. The activated lead-acid battery has a long operational life when it is kept in a charged state. Another frequently compromise made is the use of toxic materials in CPS. Very often compounds of heavy metals, which are toxic, are used but the production hazards could be minimised. A couple of years ago the requirements for ecologically cleaner production lead to the termination of CPS based on the electrochemical system **Zn|KOH|HgO**.

Quantities and units of measurement used in CPS

Energy:

$$\mathbf{G = U \cdot Q}$$

“G” is the accomplished electrical work for the transfer of a charge in coulombs “Q” between two points with electrical potential difference “U”. According to the SI system the unit for energy is Jaul [J], the unit for electric potential difference is Volt [V], and the measuring unit for “Q” is the Coulomb [C].

The "Q" can be denoted with the equation:

$$\mathbf{Q = I \cdot t}$$

where **I** is the current expressed as the charge for a given unit of time:

$$\mathbf{I = \frac{Q}{t}}$$

The measurement unit is Ampere [A] and is defined as [A] = [C]/[s].

Up till now, the non-system unit for "Q", designated Ampere-hour [Ah], has been used in

relation to CPS. It is defined as the charge in coulombs that has flown for one hour.

According to the Faraday's Law the charge **Q** depends on the compound mass. From this Law the following equation can be derived:

$$\mathbf{Q = n \cdot z \cdot F}$$

where "**n**" is the number of reacting compound moles, "**z**" is the number of exchanged electrons for a single reacting molecule and **F** is the Faraday's constant.

$$\mathbf{F = 96491 [C/ mole] \quad or \quad F = 26,805 [Ah/ mole]}$$

The CPS power is defined as:

$$\mathbf{P = \frac{G}{t}}$$

or from the second equation in this paragraph it can also be denoted as:

$$\mathbf{P = U \cdot I}$$

The unit for power is Watt [W], and it could be denoted as:

$$\mathbf{[W] = \frac{[J]}{[s]} \quad or \quad [W] = [U] \cdot [A]}$$

The electric work (energy) can be expressed with the equation:

The non-system unit Watt-hour [Wh] or its larger multiple kilowatt-hour [kWh] is more frequently used for electric energy expression.

Thermodynamic voltage

During a chemical reaction the energy of the thermodynamic system changes. The liberated heat is equal to the decrease of the enthalpy of the system ($-\Delta H$) for an isobar process, or to the decrease of the internal energy ($-\Delta U$) for an isochore process.

If the reaction goes thermodynamically reversibly, the maximum work (W), which can be gained, is going to be equal to the decrease of the system's free energy. For an isothermal isochore process the work is:

$$W_{\max} = -\Delta F$$

and for an isothermal isobar process it is:

$$W_{\max} = -\Delta G$$

The sign “-“ means that the free energy is decreasing, i.e. the reaction is spontaneous.

The electric work expressed in the following equation can be derived from the occurring in an electrochemical system reaction:

$$W_{\max} = n \cdot z \cdot F \cdot E$$

Here the symbol E , with the significance of U , is a theoretical quantity, which will be labelled the thermodynamic voltage (ThV).

The ThV could exist only when the system is in a thermodynamic equilibrium:

$$G = U I t$$

$$E = \frac{-\Delta G}{n \cdot z \cdot F}$$

E of a CPS has to be a positive quantity, since electrochemical reactions can be only those red-ox processes, that result in a decrease of the free energy of ES, i.e. when ΔF or ΔG have negative values.

Dependence of ThV on the thermodynamic parameters

Knowing the standard ThV of the spontaneous electrochemical reaction of a given ES it is easy to determine the ThV of the reaction for other conditions, if the dependence of the ThV on the thermodynamic parameters of the condition is known.

Dependence on the concentration

The ThV can depend on the concentrations of the components participating in the electrochemical reaction. For the ThV of the electrochemical reaction, E, by analogy to the Nernst equation for the electrode potential, the following can be denoted:

$$E = E^0 + \frac{RT}{zF} \sum -\alpha_i \nu_i \ln a_i$$

Where a_i are the activities of the components participating in the reaction. Recalling that the activity is $a_i = f_i \cdot c_i$ (f_i – activity coefficient; c_i – concentration), it becomes apparent that ThV depends on the concentration. It has to be pointed out that the activities of the initial compounds are always in the numerator, and the activities of the products are in the denominator, which is determined by the coefficient α (sign “+” or “-”).

Dependence on the pressure

By analogy to the equation for the dependence on the activities, replacing the activity with the volatility $f \cdot p$, the following can be written down:

$$E = E^0 + \frac{RT}{zF} \sum -\alpha_i \nu_i \ln f_i p_i$$

This dependence is used mostly in cases where at least one of the components is a gaseous compound. The dependence of ThV on pressure in condensed systems is insignificant and is often neglected.

Dependence on the temperature

The Gibbs–Helmholmc equation can define the temperature dependence in the following manner:

$$E_T \approx E_{T^0}^0 + (T - T^0) \left(\frac{\partial E}{\partial T} \right)_p$$

For precise calculations ΔH and $(\partial E / \partial t)_p$, which are temperature functions, have to be found in advance, and than the equation applied.

In a narrow temperature range this equation can be used without knowing the ΔH and $(\partial E / \partial t)_p$ temperature dependence. It is noticeable that these calculations are complicated enough in a thermodynamic way. This is the reason for the frequent utilisation of the following equation with empirical coefficients:

$$E_T = E_{T^0} + \alpha(T - T^0) + \beta(T - T^0)^2 + \gamma(T - T^0)^3$$

where “ α ”, “ β ” and “ γ ” are specific for every electrochemical reaction coefficients. The temperature dependence of ThV is especially crucial for some fuel cells with operating temperatures above 150°C.

Voltage and polarisation of the electrochemical cell

If the electrochemical reaction is carried out in an irreversible thermodynamic way, the acquired electrical work will be less than the maximum one and $U < E$. In order to avoid

confusion the measured real potential difference between the electrodes of an actual electrochemical cell will be labelled as “voltage” and will be denoted by U . At the same time the symbol E and the corresponding term “Thermodynamic voltage” will be reserved only for idealised systems that are in a thermodynamic equilibrium. For them E can be thermodynamically calculated if the respective functions for the corresponding electrochemical reactions are known.

A departure from the ES's equilibrium state will be observed in all cases where some non-equilibrium and irreversible processes, with a rate other than zero, take place. Generally this is valid for all real processes. The departure from the equilibrium state, as well as the quantity that characterises it:

$$\Delta U = E - U$$

is termed polarisation and since E is defined for a strictly determined reaction, the difference $E - U$ can also be termed reaction overvoltage.

Polarisation occurs, most of all, when the current rate in the system is other than zero. Polarisation can also occur when the electric circuit is open, i.e. there is no load current at all. Then the state of equilibrium could be a disrupting one due to other lateral processes, for example due to certain corrosion reactions. In the presence of such lateral processes, even at an open circuit, the electrochemical cell voltage could be different from the ThV.

$$U^0 \neq E$$

(U^0 will be used to denote an “open circuit voltage”).

The fact that the thermodynamic and the open circuit voltages do not coincide could be due to one of the following reasons:

1. The system is not in equilibrium although current is not flowing through the circuit. At one of the electrodes, or simultaneously at both electrodes, irreversible processes take place.
2. The assumed current supplying reaction does not occur at all (for e.g. due to kinetic hindrances), and the ThV is determined by an entirely different reaction, which presence has not been assumed.
3. The electrochemical reaction mechanism is not known. The reaction most probably takes place in a number of consecutive stages and the stage determining E is unknown or is purposefully neglected.
4. Some of the system's parameters do not correspond to the hypothetical ones or are unknown (for e.g. the activities of ES components).
5. There are some "active" admixtures in the reacting compounds. They can be quickly exhausted after switching on the electric circuit and may not take part in the main current supplying reaction. However for an open circuit they can predetermine the value of the measured U^0 .

The clarification of the electrochemical reaction mechanism is one of the major objects of the scientific research work in the CPS field. This activity pursues, besides the theoretical objectives, purely practical ones. The knowledge revealing the processes mechanisms may successfully help to resolve the issues concerning novel CPS development and enhancement of existing ones.

Kinetics of the electrochemical reaction

Every electrochemical reaction is in fact the sum of two electrodes ones. Generally speaking the electrode reactions are relatively independent and their kinetics can be studied separately, which is investigated by one of the theoretical electrochemistry's disciplines. Within the CPS itself the current is the same for both electrode reactions and as a result the rate of the complete reaction is determined by the slower electrode reaction.

It is well known that the rate of an electrochemical reaction is represented by the current density (i). If the electrodes' surface is invariable, the reaction rate can also be denoted by the magnitude of the current I . Hence, the description of the reaction kinetics in essence is

reduced to describing the reasons, factors and dependencies which determine the current magnitude.

A simple electric circuit with a CPS included is presented in Fig 2. The CPS itself is depicted schematically. It consists of a constant voltage source U^0 and a variable internal resistance R' .

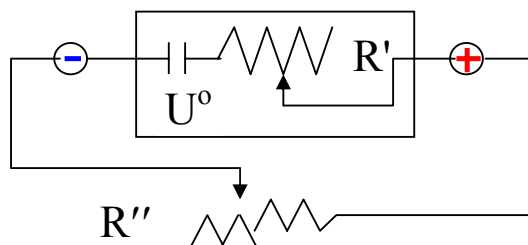


Fig. 2. CPS circuit diagram

According to the Ohm's Law, the magnitude of the current will be determined by the total resistance of the circuit:

$$I = \frac{U^0}{R' + R''}$$

Voltage U^0 will be established between the terminals (+) and (-) for an open circuit, however when the circuit is closed and a current flow is induced, the poles voltage U will decrease,

$$U = U^0 - I \cdot R'$$

and will depend on the ratio of the internal (R') and external (R'') resistances:

$$U = U^0 \frac{R'}{R' + R''}$$

The external resistance R'' and the current magnitudes can be changed arbitrarily within a wide range, too. In that manner by means of the external resistance alteration the current rate of the electrochemical reaction could be altered. This reaction is related to the

occurrence of a number of other physico-chemical processes (new phases' formation, diffusion, etc.) and all these processes are interrelated and finally influence the current rate. Generally, an expression of this influence is the internal resistance \mathbf{R}' . \mathbf{R}' depends on the nature of the electrochemical system (an uncontrolled factor) as well as on the CPS technology and design. Naturally, the particular operating conditions such as temperature, pressure, etc., can additionally affect it. During operation the internal resistance is a function of the current rate and the working time. The dependence $\mathbf{R}' = \mathbf{f}(\mathbf{I}, \mathbf{t})$ is too much complicated for accurate mathematical description.

Current rate limits

If the external resistance is increased in such an way that $\mathbf{R}'' \rightarrow \infty$, the current magnitude will tend towards zero and the terminal voltage will tend to the open circuit voltage:

$$\mathbf{R}'' \rightarrow \infty, \mathbf{I} \rightarrow \mathbf{0}, \mathbf{U} \rightarrow \mathbf{U}^0$$

The techniques for \mathbf{U}^0 measurement are based on this condition and are implemented by devices with high input resistance, $10^{10} - 10^{14}$ [Ω], thus the current flowing into the measuring circuit is 10^{-10} to 10^{-14} [A], respectively.

Conversely, if the external resistance tends to zero, according to the scheme on Fig. 2, in the case of a short circuit, the terminal voltage will also tend to zero. The current will increase, however not to infinity but to a final quantity labelled a "short circuit current", which will be solely determined by the internal resistance, i.e. for $\mathbf{R}'' \rightarrow \mathbf{0} \Rightarrow \mathbf{U} \rightarrow \mathbf{0}$ and $\mathbf{I} \rightarrow \mathbf{I}_{\text{shc}}$.

$$\mathbf{I}_{\text{shc}} = \frac{\mathbf{U}^0}{\mathbf{R}'_{\text{shc}}}$$

The measured \mathbf{I}_{shc} gives some information about \mathbf{R}' of the CPS, however it should be remembered that $\mathbf{R}'(\mathbf{I}_{\text{shc}}) \neq \mathbf{R}'(\mathbf{I})$, where $\mathbf{I} < \mathbf{I}_{\text{shc}}$.

The short circuit current I_{shc} depends on the CPS type and its value can vary at large – from microamperes to kiloamperes. The possibility to control the current I by means of R'' , i.e. the current change in the range from $I = 0$ to $I = I_{shc}$, actually means that the electrochemical reaction rate can be controlled in that interval.

Current-voltage characteristic

The electrochemical kinetics object is to study the relation between the reaction conditions and the current rate. One basic technique for electrochemical kinetics studies is the polarisation measurement and polarisation curves plotting.

The object of the electrochemical cell polarisation study is the change of the cell voltage as a function of the current rate, $U = f(I)$. It does not mean in any way that the opportunity to investigate the individual electrode polarisation $\varphi(i)$ has to be neglected, since this is even necessary when exploring the electrochemical reactions mechanisms.

The dependence $U = f(I)$ is named a "current-voltage characteristic" of the CPS. A typical curve representing such a dependence is shown in Fig. 3. The curve starts from a point for which $I = 0$ and $U = U^0$ and ends at the maximum possible current, the short circuit one, for which $I = I_{shc}$ and $U = 0$.

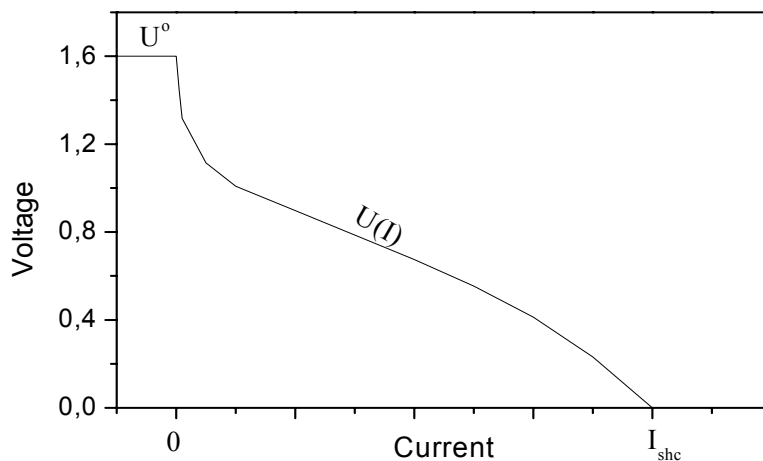


Fig. 3. Typical current-voltage characteristic of CPS

The current-voltage plot is practically a sum of three other plots expressing the dependence of both electrode potentials on the current and the voltage drop in the

electrolyte, due to its Ohmic resistance:

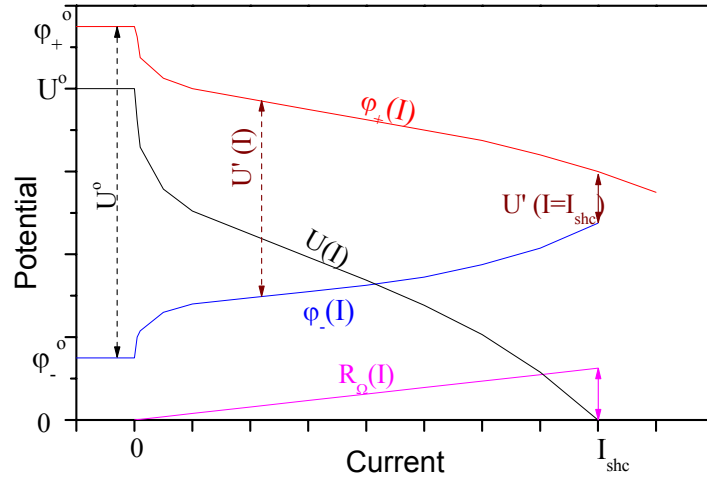


Fig. 4. Current rate electrode polarisation and Ohmic voltage drop

The total polarisation of the CPS will be the algebraic sum of the two electrodes' polarisation and the Ohmic polarisation:

$$U(\mathbf{I}) = \varphi_+(\mathbf{I}) - |\varphi_-(\mathbf{I})| - \mathbf{R}_\Omega \cdot \mathbf{I}$$

The $\mathbf{I} \cdot \mathbf{R}_\Omega$ term is accounted for with the assumption that the Ohmic resistance of the electrolyte does not depend on the current, $\mathbf{R}_\Omega = \mathbf{const}$. The potential difference \mathbf{U}' differs from the poles voltage \mathbf{U} with the quantity $\mathbf{I} \cdot \mathbf{R}_\Omega$.

$$U(\mathbf{I}) = U'(\mathbf{I}) - \mathbf{I} \cdot \mathbf{R}_\Omega$$

CPS polarisation

The current-voltage characteristic supplies exact information on the operational potential of the CPS. The smaller the slope of the current-voltage characteristic in the working current range, the better the CPS performance. The current-voltage characteristic is the combined result of a number of polarisation phenomena – of reversible and irreversible

changes in the content and concentration of the active compounds and the electrolyte.

In theoretical electrochemistry kinetic processes can be studied separately and the different types of polarisation phenomena are divided into four groups:

- Charge transfer overvoltage
- Phase polarisation
- Chemical reaction overvoltage
- Concentration (diffusion) polarisation.

The electrode reaction rate is determined by the slowest step and the electrode polarisation will be determined by one type electrochemical polarisation only.

The tendency of the electrode polarisation can be defined as "polarisability" by the equation given below:

$$\frac{\partial \Delta \varphi (\mathbf{i})}{\partial \mathbf{i}} = \frac{\partial \varphi (\mathbf{i})}{\partial \mathbf{i}}$$

The polarisability is dependent on the current rate.

In contrast to the electrode polarisation, the Ohmic polarisation is a linear function of the current and the corresponding polarisability is a constant equal to the CPS Ohmic resistance.

$$\frac{\partial (\mathbf{I} \cdot \mathbf{R}_{\Omega})}{\partial \mathbf{I}} = \mathbf{R}_{\Omega}$$

If we differentiate the current-voltage characteristic we will get the differential internal resistance of CPS:

$$\mathbf{R}_d = \frac{\partial U(\mathbf{I})}{\partial \mathbf{I}}$$

If the electrodes surface is a invariable:

$$\mathbf{R}_d = \frac{\partial \varphi_a(\mathbf{i})}{\partial \mathbf{i}} - \frac{\partial \varphi_c(\mathbf{i})}{\partial \mathbf{i}} + \mathbf{R}_\Omega$$

The polarisability $\mathbf{R}_d(\mathbf{I})$ graphically can be represented by the slope of the tangent, drawn up at a point of the current-voltage characteristic for a fixed value of \mathbf{I} .

Electrochemical and energy capacity of ES

These characteristics calculations are based on the electrochemical equivalent of the active compounds participating in the electrochemical reaction. The Faraday's law enables the calculation of the electrochemical capacity of the oxidation and the respective reducing active compounds:

$$\mathbf{Q} = \mathbf{n} \cdot \mathbf{z} \cdot \mathbf{F}; \quad \mathbf{n} = \frac{\mathbf{m}}{\mathbf{M}} \Rightarrow \mathbf{Q} = \left(\frac{\mathbf{z} \cdot \mathbf{F}}{\mathbf{M}} \right) \cdot \mathbf{m}$$

where " \mathbf{n} " is the mole number of the corresponding active compound, " \mathbf{m} " – its weight, \mathbf{M} – the molar or atomic weight, and \mathbf{F} – the Faraday's constant.

The last equation could be rewritten in the following way:

$$\mathbf{Q} = \mathbf{q} \cdot \mathbf{m}, \quad \text{where} \quad \mathbf{q} = \frac{\mathbf{z} \cdot \mathbf{F}}{\mathbf{M}}$$

The coefficient " \mathbf{q} " is labelled as an "electrochemical equivalent". It is more frequently used for CPS than in other branches of the electrochemistry. It is apparent that \mathbf{q} is proportional to the number of exchanged electrons of a single molecule and inversely

proportional to the molecular mass of the active compound. It has to be emphasised that depending on the actual reaction conditions z may prove not to be a whole number after the calculations are performed. The electrochemical equivalents of different active compounds participating in a given electrochemical reaction can also be found in various handbooks on electrochemistry.

The electrochemical equivalent is the base for the calculation of the CPS theoretical electrochemical capacity. There are at least two active compounds in the CPS and the theoretical electrochemical capacity is calculated by the formula:

$$q = \frac{z \cdot F}{\sum \nu_i M_i}$$

where “ ν_i ” are the stoichiometric coefficients of all participating constituents and M_i are their corresponding molecular (atomic) weights. Thus the calculated q concerns only the participating active compounds, since the equation does not include the electrolyte and the solvent weights of when they do not participate in the reaction process. In this case, the electrolyte and the solvent will be included in the formula denominator by their weight, which leads to a decrease of q . The quantity of the electrolyte and the solvent can be different which is the reason for the “ q ” to be customarily calculated only from the active compounds. It should be noted however that this value is unattainable in practice.

If there is only one anodic and one cathodic compound in the system, the following can be written:

$$\frac{1}{q} = \frac{1}{q_a} + \frac{1}{q_c} \quad \Rightarrow \quad q = \frac{q_a \cdot q_c}{q_a + q_c}$$

The theoretical electrochemical capacity Q for a CPS with weight m can be calculated by the formula:

$$\mathbf{Q} = \mathbf{q} \cdot \mathbf{m}$$

It is important here to point out that when applying these formulae the participating active compounds have to be taken in their stoichiometric ratio depending on the proceeding electrochemical reaction.

The theoretical specific energy capacity for a unit weight is given by the equation:

$$\mathbf{w} = \mathbf{q} \cdot \mathbf{E}$$

where **E** is the thermodynamic voltage of the reaction.

For a system with an unspecified weight **m**, the calculation is executed by the equation:

$$\mathbf{W} = \mathbf{m} \cdot \mathbf{w}$$