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NOMENCLATURE, SYMBOLS AND DEFINITIONS IN ELECTROCHEMICAL ENGINEERING

(IUPAC Recommendations 1993)

Prepared for publication by

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Nomenclature, symbols and definitions in electrochemical engineering (IUPAC Recommendations 1993)

Abstract - This document treats performance parameters in electrochemical engineering. Nomenclature and definitions for electrochemical engineering together with the respective symbols are given. Parameters to account for electrochemical reactions in electrolysis as well as for electrochemical power sources (electrochemical energy generators) are included in this document.

1. INTRODUCTION

Electrochemical engineering has strong interrelations to chemical engineering, to electrochemistry and to physical chemistry as well as to heat and mass transfer phenomena. It covers both processes where electrical energy is applied in electrolysis to form products and to the electrochemical generation of electrical energy. However, uniform nomenclature and terminology in many areas of electrochemical engineering are presently not available. Individual proposals in the literature are inconsistent and often not in agreement with recommendations by the International Union of Pure and Applied Chemistry (IUPAC) and the International Electrotechnical Commission (IEC). This report supplies definitions of quantities important to electrochemical engineering and recommends the respective symbols. The recommended parameters allow the characterization of electrochemical processes on both a technical and an economical scale independent of the nature of the electrochemical reactor. IUPAC recommendations in the area of electrochemistry (refs. 1 - 3), in physical chemistry (ref. 4), IEC publication (ref. 5) relevant to electrochemical engineering as well as recommendations by the European Federation of Chemical Engineering (ref. 6) were taken into account. Current usage in the area of electrochemical engineering as given in publications and in textbooks was also considered during the preparation of this document to assure that the recommendations in this paper will agree with common practice whenever possible. Great care was taken to avoid conflicting notations with other disciplines, which overlap with electrochemical engineering.

The definitions are written in a manner to assist engineers, who are not expert electrochemists, in getting an understanding of electrochemical engineering. This document includes both terms for electrolytic processes and for electrochemical power sources (electrochemical energy sources).

A list of symbols, defined in this document, their names and SI units as well as other symbols important to electrochemical engineering are listed at the end of this document. Whenever convenient multiples and submultiples of SI units may be used.

2. GENERAL REMARKS

Due to the interrelations of electrochemical engineering with other fields of engineering, several of the symbols preferred in electrochemistry had to be substituted. The symbol U is used for the cell voltage, the symbol W for work and energies, while E is reserved for thermodynamic potentials of electrochemical cell reactions. ν_e is employed for the stoichiometric number of the electrochemical cell reactions and the half-cell reactions instead of n , to distinguish it from the amount of substance, which also has the symbol n , since both quantities frequently appear in the same equations.

The expression "amount of substance", abbreviated amount, is used throughout the text to describe what is usually referred to as "number of moles", following IUPAC recommendations (ref. 4). The practice of calling the amount of substance "number of moles" should be abandoned, since number of moles refers to the unit, not to the physical quantity.

Following IUPAC recommendations a clear distinction is made between quantities divided by mass, which are called specific and quantities divided by volume, which are called densities. Lower case letters of the symbols are used for specific quantities (ref. 4).

Quantities used in electrochemical engineering generally depend on both time and space. If a quantity Y is a function of time and space, various definitions of Y are possible, depending on whether time or space or both are averaged. The space dependency in electrochemical engineering is either referenced to the electrode area (A) or to the volume of the electrochemical reactor (V). The temporal value of Y is obtained by averaging over space, time being a variable.

$$\langle Y \rangle_A(t) = \frac{1}{A} \int_0^A Y(t, A) dA \quad (1)$$

and

$$\langle Y \rangle_V(t) = \frac{1}{V} \int_0^V Y(t, V) dV \quad (2)$$

The local value of Y is time-averaged, space being a variable.

$$\langle Y \rangle_t(A) = \frac{1}{t} \int_0^t Y(t, A) dt \quad (3)$$

$$\langle Y \rangle_t(V) = \frac{1}{t} \int_0^t Y(t, V) dt \quad (4)$$

The overall value of Y is both time and space averaged.

$$\langle Y \rangle_{A,t} = \frac{1}{A,t} \int_0^A \int_0^t Y(t, A) dt dA \quad (5)$$

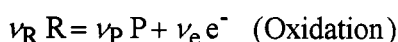
$$\langle Y \rangle_{V,t} = \frac{1}{V,t} \int_0^V \int_0^t Y(t, V) dt dV \quad (6)$$

The two quantities usually measured in electrolysis as well as for electrochemical power sources are the cell voltage (U) and the current (I) flowing through the electrochemical cell.

The current is usually referenced to the electrode area and reported as current density (j). Both cell voltage and current density were previously defined by IUPAC (refs. 1 - 3). An abbreviated form of these definitions is repeated in this document.

2.1 Electrochemical Cell Reactions

In electrochemistry the overall cell reactions can be separated into the half-cell reactions of the processes, which take place at the cathode and at the anode. When discussing properties in electrochemical engineering the individual equations for the half-cell reactions and the overall cell reaction should always be specified, since the stoichiometric numbers (stoichiometric coefficients) are defined by the way the equations are written. Examples for half-cell reactions are given below:



ν_R is the stoichiometric number for the reactant (educt) R and ν_P is the stoichiometric number of product P for the cell reactions given above. Possible charges on R and P are omitted for the sake of clarity.

2.2 Current Density j SI unit: $A\ m^{-2}$

The current density was defined in Ref. 3. A distinction was made between the local current density (j_x) and the average current density (j). The average current density is defined as:

$$j = \frac{1}{A} \int_0^A j_x dA \quad (8)$$

where A is the electrode area and dA is an infinitesimal electrode surface element. In electrochemical engineering the geometric (projected) electrode area is generally used and the current density is calculated by dividing the total current flowing through an electrochemical cell by the geometric electrode area. The geometric electrode area, however, generally differs from the true electrode area, since the effects of surface roughness are not taken into account. The estimation of the true electrode area for solid electrodes is usually difficult. If quantities in electrochemical engineering are referred to the true electrode area, it is essential to give a precise statement describing how the true surface area was measured (ref. 7).

2.3 Cell Voltage U SI unit: V

The cell voltage, as defined in Ref. 1, is the potential difference between two identical metallic terminals attached to the anode and to the cathode. When a current is flowing through an electrochemical reactor, the cell voltage can be considered to comprise of several components, such as the potential differences associated with the electrochemical processes occurring on the cathode and the anode, the potential drop due to the bulk resistivity of the electrolyte and the potential drop due to the resistivity of the leads. Theoretical interpretations of the potential differences at the anode and the cathode are given in Ref. 1.

In electrolysis the cell voltage increases with increasing current density. During discharging of electrochemical power sources (primary and secondary batteries) the cell voltage decreases with increasing current densities.

While both electrolysis and electrochemical power sources are part of electrochemical engineering, different nomenclature has been established for these two areas. Therefore, definitions, symbols and units are listed separately for electrolysis and for electrochemical power sources.

3. ELECTROLYSIS

For electrolytic processes investment costs for the electrochemical reactors and operating costs, expressed as the energy necessary to make the product, are usually the main factors in evaluating the economy of the overall process. The following definitions pertain to quantities, which relate the actual performance of an electrochemical process to the theoretical values obtained from thermodynamic considerations. These quantities are thus a measure of how efficiently a given electrochemical process is carried out in the electrochemical reactor.

3.1 Current Efficiency (Charge Yield) Φ^e (ε)

The current efficiency is the ratio of the theoretical charge required for the amount of product obtained (Q_P) to the total charge (Q) passed through the electrolytic cell during the duration of the electrolysis:

$$\Phi_P^e = \left| \frac{Q_P}{Q} \right| \quad (9)$$

This value is frequently multiplied by 100 to yield the current efficiency in percent. The theoretical amount of charge necessary for the amount of product P obtained (Q_P) is calculated from the stoichiometry of the respective half-cell reaction employing Faraday's law:

$$Q_P = \left| \frac{m_P v_e F}{v_P M_P} \right| = \left| \frac{n_P v_e F}{v_P} \right| \quad (10)$$

Where m_P is the mass and n_P the amount of the product P formed during the electrolysis, M_P is the molar mass of P, F is the Faraday constant. v_e represents the stoichiometric number of electrons for the electrode reaction yielding P.

The total amount of charge passed through an electrochemical cell is obtained from the integral:

$$Q = \int_0^t I(t) dt \quad (11)$$

Industrial electrochemical processes are often performed at constant current. In such cases the total charge Q can be obtained by multiplying the current (I) with the duration (t) of the electrolysis.

A value of one (100 %) for the current efficiency means that the total amount of charge passed through the cell resulted in the formation of the desired amount of product P. It must be noted at this point that in electrochemistry different products will be formed at the anode and at the cathode. Current efficiencies can thus be calculated for the products formed at the anode and for the products formed at the cathode for such cases where both the anode and the cathode products are of interest (e. g. in the electrolysis of aqueous sodium chloride solutions to produce hydrogen, sodium hydroxide and chlorine). Current efficiencies for products formed at the cathode can be different from current efficiencies for products formed at the anode in the same electrochemical reactor.

A value less than one (less than 100 %) indicates that additional electrochemical reactions are occurring at the respective electrode. Such reactions can either be parallel reactions at the electrode leading to the production of other substances (e. g. the simultaneous discharge of hydrogen in the electrowinning of metals) or consecutive reactions of the desired product (e. g. the reaction of chlorine with water in the chlorine alkali electrolysis). For products which are soluble in the electrolyte, oxidation of the cathode products at the anode or reduction of the anode products at the cathode will decrease the current efficiency.

Current efficiencies apparently greater than one (greater than 100 %) can also be observed for certain processes. For instance, values greater than one may be observed, when a chemical reaction of the electrolyte with the anode material occurs in parallel to the anodic dissolution process of this material.

Although not apparent from the definition of the current efficiency, it is worthwhile to note that current efficiencies generally depend on the current densities.

In industrial electrochemistry current efficiencies are often based on the overall loss of the product in the whole production process, sometimes even including losses during purification steps. Therefore the conditions for calculating current efficiencies should always be specified.

3.2 Theoretical Mass Yield $\Phi_{P,th}$

The theoretical mass yield is the mass of product P, which can be obtained from one kg of the reactant (educt) R based on the electrochemical cell reaction (7) for a current efficiency

Φ_P^e of one.

$$\Phi_{P,th} = \left| \frac{\nu_P M_P}{\nu_R M_R} \right| \quad (12)$$

3.3 Practical Mass Yield Φ_P

The practical mass yield for product P is the theoretical mass yield times the current efficiency

$$\Phi_P = \Phi_{P,th} \Phi_P^e \quad (13)$$

3.4 Fractional Conversion X

If a reactant (educt) R undergoes an electrochemical reaction, the fractional conversion of R is defined as:

$$X_R = 1 - \frac{n_R}{n_R^0} = 1 - \frac{m_R}{m_R^0} \quad (14)$$

where n_R^0 is the starting amount of reactant (educt) R and n_R is the final amount of reactant R. The fractional conversion per pass through an electrochemical reactor is an important parameter in electrochemical engineering, since in industrial cells complete conversion of the educt in one pass is generally not economical.

3.5 Gibbs Energy Yield (Energy Efficiency) Φ_G

The energy yield describes the ratio of the theoretical Gibbs energy change (ΔG) to the electrical energy W_P actually required for the production of one mole of substance P. The required electrical energy is:

$$W_P = \left| \frac{U \nu_e F}{\nu_P \Phi_P^e} \right| \quad (15)$$

The theoretical Gibbs energy change (ΔG) for one mole of product P is calculated from the complete cell reaction at the temperature of the electrolysis, assuming that no side reactions occur. The energy yield is then calculated by:

$$\Phi_G = \left| \frac{\nu_P \Delta G \Phi_P^e}{U \nu_e F} \right| = \left| \frac{\Delta G}{W_P} \right| \quad (16)$$

3.6 Enthalpy (Thermal Energy) Yield Φ_H

The enthalpy yield is the ratio of the enthalpy change (ΔH) of the cell reaction at the temperature of the electrolysis to the electrical energy actually needed to form one mole of product P.

$$\Phi_H = \left| \frac{\nu_P \Delta H \Phi_P^e}{U \nu_e F} \right| = \left| \frac{\Delta H}{W_P} \right| \quad (17)$$

3.7 Thermoneutral Cell Voltage U_{tn} SI unit: V

The thermoneutral cell voltage is the voltage, at which no heat exchange with the surrounding occurs. The thermoneutral cell voltage is defined as:

$$U_{tn} = \left| \frac{\nu_P \Delta H}{\nu_e F} \right| \quad (18)$$

ΔH for the electrochemical cell reaction(s) must be calculated for the temperature of the surrounding and for one mole of P.

A cell operated at the thermoneutral cell voltage remains at the temperature of the surroundings by consumption or production of (electrical) energy not used for electrochemical reactions.

3.8 Heat Flow Rate of an Electrochemical Cell ϕ SI unit: W

The heat flow rate is the thermal energy exchanged between an electrochemical reactor and the surroundings per time.

$$\phi = I(U_{\text{tn}} - U) \quad (19)$$

The heat flow has a negative sign for a heat-producing cell and a positive sign for a heat-consuming cell.

3.9 Specific Electric Energy Consumption w SI unit: J kg⁻¹

The specific energy consumption (work) is the electrical energy necessary to form one kg of the desired product P in a given electrochemical cell.

$$w = \left| \frac{U v_e F}{M_P \Phi_P^e v_P} \right| \quad (20)$$

The specific energy consumption is frequently given in kWh kg⁻¹.

3.10 Space Time Yield σ SI unit: kg m⁻³ s⁻¹

The space time yield represents the mass of a product P formed per volume of the reactor and time.

$$\sigma_P = \frac{m_P}{V t} \quad (21)$$

3.11 Space Velocity s SI unit: s⁻¹

Residence Time τ SI unit: s

The space velocity is the ratio of the volume flow rate of the electrolyte divided by the volume of the electrochemical reactor.

The reciprocal of the space velocity is called residence time (τ).

$$s = \frac{1}{\tau} \quad (22)$$

4. ELECTROCHEMICAL POWER SOURCES (ELECTROCHEMICAL ENERGY GENERATORS)

For several of the performance criteria of electrochemical power sources (primary and secondary batteries) a distinction must be made between the theoretical values and the practical values. Theoretical values are calculated from the thermodynamics of the electrochemical cell reaction and are thus independent of a particular cell design. Practical values are related to the total mass of the complete battery, including the mass of the electrolyte, the separators, the current collectors, the terminals and the cell housing. They depend strongly on the cell design and on the conditions of discharge. Several parameters for rechargeable batteries depend also on the conditions for recharging.

4.1 Charge Capacity Q SI unit: C

The charge capacity is the total amount of charge obtainable from a practical cell. The charge capacity is frequently given in A h.

4.2 Theoretical Specific Charge q_{th} SI unit: C kg⁻¹

The theoretical specific charge is the amount of charge per kg of reactants, which can be calculated from the stoichiometry of the overall cell reaction assuming complete conversion of the reactands *via* Faraday's law.

The theoretical specific charge is often incorrectly called theoretical charge density. The expression theoretical charge density for this property should be abandoned, since it leads to confusion with the quantity: charge divided by volume, which is correctly called charge density.

4.3 (Practical) Specific Charge q SI unit C kg⁻¹

The (practical) specific charge is the total charge obtainable under specified discharge conditions from a practical cell in one discharge cycle divided by the total mass of the cell (m_b).

$$q = \left| \frac{Q}{m_b} \right| \quad (23)$$

The (practical) specific charge is often incorrectly called charge density.

While the proper SI unit for the specific charge is C kg⁻¹, it is common to use also A h kg⁻¹.

4.4 Charge Density Q_V SI unit: C m⁻³

The charge density represents the total charge obtainable from a practical cell divided by the volume of the cell. The charge density is frequently given in A h dm⁻³.

4.5 Energy Capacity W SI unit: J

The energy capacity is the total energy (work) obtainable from a practical cell upon discharge under specified conditions.

4.6 Theoretical Specific Energy w_{th} SI unit: J kg⁻¹

The theoretical specific energy can be calculated from the Gibbs energy change (ΔG) of the electrochemical cell reaction divided by the sum of the stoichiometric masses of the reactants. The theoretical specific energy is often incorrectly called theoretical energy density. Quite often the units W h kg⁻¹ are used. Whenever possible J kg⁻¹ should be used.

$$w_{th} = \left| \frac{\Delta G}{\sum_i m_{R,i}} \right| \quad (24)$$

4.7 (Practical) Specific Energy w SI unit: J kg⁻¹

The (practical) specific energy is the total electrical energy (W_c) obtainable from a practical cell in one discharge cycle divided by the mass of the respective cell (m_b). This quantity is often incorrectly called (practical) energy density. The specific energy is frequently given in W h kg⁻¹.

$$w = \frac{W_c}{m_b} \quad W_c = \int_0^t U(t)I(t) dt \quad (25)$$

4.8 Energy Density W_V SI unit: J m⁻³

The energy density is the total electrical energy obtainable from a practical cell under specified discharge conditions divided by the volume of the cell.

Frequently the energy density is given in W h dm⁻³.

4.9 Specific Power p SI unit: W kg⁻¹

The specific power, often incorrectly called power density, is the capability to deliver power per mass of a primary or secondary battery. The specific power of a cell depends on the discharge current and decreases during discharge. The specific power is often incorrectly called power density.

4.10 Power Density P_V SI unit: W m⁻³

The power density is the power divided by the volume of the cell. This property is frequently given in W dm⁻³.

4.11 Coulomb Efficiency Φ_Q

For secondary cells the Coulomb efficiency represents the ratio of charge released during the discharge (Q_{dis}) to the charge necessary for charging the battery (Q_{ch}).

$$\Phi_Q = \frac{Q_{\text{dis}}}{Q_{\text{ch}}} \quad (26)$$

Both Q_{dis} and Q_{ch} are obtained by integrating the respective currents over the charging and discharging time, respectively. They depend on the conditions for charging and discharge.

4.12 Energy Efficiency Φ_W

The energy efficiency of a secondary cell is the ratio of the output of electrical energy during discharge of the cell (W_{dis}) to the input (W_{ch}) of electrical energy during the charge cycle.

$$\Phi_W = \left| \frac{W_{\text{dis}}}{W_{\text{ch}}} \right| \quad (27)$$

Both W_{dis} and W_{ch} are obtained by integrating the cell voltages and the currents over the time for discharge and charging, respectively. They depend on the conditions for charging and discharge.

5. INDEX OF SYMBOLS

Symbol	Name	SI unit
A	electrode area	m^2
E°	standard potential of the electrochemical cell reaction, (standard electrode potential)	V
F	Faraday constant	C mol^{-1}
I	electric current	A
j	(electric) current density	A m^{-2}
j_x	local current density	A m^{-2}
m_b	mass of a battery	kg
m_p	mass of product P	kg
m_R	mass of reactant (educt) R	kg
M_p	molar mass of product P	kg mol^{-1}
M_R	molar mass of reactant R	kg mol^{-1}
n	amount of substance	mol
n_p	amount of product P	mol
n_R	amount of reactant R	mol
p	specific power	W kg^{-1}
P_V	power density	W m^{-3}
q	specific charge	C kg^{-1}
q_{th}	theoretical specific charge	C kg^{-1}
Q	electric charge	C
Q_{ch}	charge required to load a secondary cell	C
Q_{dis}	charge released upon discharge	C
Q_p	charge necessary to form product P	C
Q_R	amount of charge necessary for reactant R	C
Q_{th}	theoretical amount of charge	C
Q_V	charge density	C m^{-3}
R	electrical resistance	Ω
s	space velocity	s^{-1}
t	time	s
U	potential difference between anode and cathode (cell voltage)	V
U_{tn}	thermoneutral cell voltage	V
V	volume of the electrochemical reactor	m^3
w	specific energy (work)	J kg^{-1}
W	energy (work)	J
W_c	electrical energy of a cell	J
W_{ch}	work (energy) required to charge a secondary cell	J
W_{dis}	work (energy) released upon discharge	J

Symbol	Name	SI unit
W_V	energy density	J m^{-3}
X	conversion	1
X_R	fractional conversion of reactant R	1
κ	conductivity	S m^{-1}
ν_e	stoichiometric number of the electrons	1
ν_P	stoichiometric number of product P	1
ν_R	stoichiometric number of reactant R	1
σ	space-time yield	$\text{kg m}^{-3} \text{s}^{-1}$
σ_P	space-time yield of product P	$\text{kg m}^{-3} \text{s}^{-1}$
τ	residence time	s
ϕ	heat flow	J s^{-1}
Φ^e	current efficiency (charge yield)	1
Φ_P^e	current efficiency (charge yield) of product P	1
Φ_G	energy yield	1
Φ_H	enthalpy yield	1
Φ_P	(practical) mass yield of product P	1
Φ_Q	Coulomb efficiency of a battery	1
Φ_W	energy efficiency of a battery	1

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