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*Performance criteria and nomenclature in electrochemical engineering**†

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This paper is a recommendation of the Working Party on Electrochemical Engineering of the European Federation of Chemical Engineering. It was prepared by a sub-committee composed of:

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1. Introduction

Electrochemical engineering as a relatively young discipline has some important inter-relationships with both chemical engineering and electrochemistry.

One of the present needs in electrochemical engineering is a set of performance criteria (figures of merit) which allows a comparable characterization of different electrochemical cells and reactions with respect both to technical and economic points of view. Due to the interdisciplinary character of electrochemical engineering new definitions of performance criteria have been proposed in the varied literature which are not consistent in every case, and up to the present no general nomenclature has been established.

A similar situation to that currently encountered in electrochemical engineering could be observed some years ago in chemical reaction engineering. Therefore, starting in 1976 the Working Party on Chemical Reaction Engineering of the European Federation of Chemical Engineering prepared a proposal for unifying the nomenclature and symbols used in chemical reaction engineering [1, 2].

The Working Party on Electrochemical Engineering founded in 1979 as a part of the same Federation decided in November 1981 to prepare a recommendation for use of definitions and symbols characterizing the performance of electrochemical reactions and reactors. The present proposal for Electrochemical Engineering is strictly oriented around this ECRE Convention [1] in so far as definitions of this convention are only repeated if it seemed necessary, and no definitions are made contrary to this convention. However, due to the fact that some very common symbols in electrochemistry are used in the ECRE Convention with another meaning a compromise was made with these particular symbols.

The present proposals are also based strongly on the electrochemical symbols and definitions of the IUPAC recommendations [3, 4] and also the recommendations on physicochemical quantities and units of the Royal Institute of Chemistry [5].

The following paper consists of two parts: one part contains definitions which should be used for characterizing the performance of electrochemical reactions and reactors; another part gives some important symbols used in electrochemical engineering. All units are given using the SI system.

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2. Performance criteria

The meaning of symbols which are not explained explicitly can be found in the nomenclature. In general, if a quantity B depends on time and space various definitions of B are possible:

differential or point value (time and space dependent)

$$B' = B(t, x) \quad (1)$$

temporal value (time dependent, space averaged)

$$B_t = \frac{1}{A(V)} \int_{A(V)} B(t, \mathrm{x})\, \mathrm{d}A(\mathrm{d}V) \quad (2)$$

local value (time averaged, space dependent)

$$B_x = \frac{1}{t} \int_0^t B(t, \mathrm{x})\, \mathrm{d}t \quad (3)$$

overall value (time and space averaged)

$$B = \frac{1}{A(V)} \frac{1}{t} \int_{A(V)} \int_0^t B(t, \mathrm{x})\, \mathrm{d}A(\mathrm{d}V)\, \mathrm{d}t \quad (4)$$

2.1. *Performance criteria*

The following performance criteria are recommended for the characterization of electrochemical cells and processes.

2.1.1. X – fractional conversion. If a reactant A undergoes an electrochemical reaction

$$\mathrm{A} + \nu_e e \rightarrow \nu_\mathrm{P} \mathrm{P} \quad (5)$$

the fractional conversion is defined as

$$X_\mathrm{A} = 1 - \frac{n_\mathrm{A}}{n_\mathrm{A}^0} \quad (6)$$

where n_A^0 is the starting molar amount of substrate and n_A is final molar amount of substrate. In the case of multiple reactants indices, e.g. X_A, may be used to sign the key reactant. Because the number of electrons involved in an electrochemical reaction represents a stoichiometric coefficient the symbol ν_e is used according to the ECRE Convention recommmending ν_i for stoichiometric coefficients.

2.1.2. Q_r – relative amount of charge.

$$Q_\mathrm{r} = Q/Q_\mathrm{th} \quad (7)$$

Relative amount of charge is the actual charge Q passed, related to the theoretical amount of charge Q_th, which is needed for a complete conversion of the substrate assuming a current efficiency of 1. In the case of multiple reactants indices, e.g. $Q_{\mathrm{r,A}}$, may be used to sign the key reactant.

2.1.3. θ_P – overall operational yield.

$$\theta_\mathrm{P} = \frac{n_\mathrm{P}}{\nu_\mathrm{P} n_\mathrm{A}^0} \quad (8)$$

θ_P is the maximum obtainable amount of the wanted product P, in moles, from one mole of initial reactant A taking into account stoichiometric constraints.

2.1.4. ϕ_P – overall conversion related yield.

$$\phi_\mathrm{P} = \frac{n_\mathrm{P}}{\nu_\mathrm{P}(n_\mathrm{A}^0 - n_\mathrm{A})} = \frac{\theta_\mathrm{P}}{X_\mathrm{A}} \quad (9)$$

2.1.5. ϕ'_P – point conversion related yield.

$$\phi'_\mathrm{P} = -\frac{r_\mathrm{P}}{\nu_\mathrm{P} r_\mathrm{A}} \quad (10)$$

2.1.6. Current efficiency. The classical definition of current efficiency by Faraday's law is

$$\beta = \frac{mzF}{MIt} \quad (11)$$

where m is mass of product, M is molar weight, and z is the charge number of the reaction.

However, the current efficiency bears a strong analogy to any other kind of yield, e.g. to the conversion related yield.

$$\text{conversion related yield} = \frac{\text{stoichiometric amount of product}}{\text{converted amount of reactant}} \quad (12)$$

$$\text{current efficiency} = \frac{\text{stoichiometric charge consumption of the product}}{\text{consumed amount of charge}} \quad (13)$$

2.2. *Current efficiency*

The current efficiency is a 'yield of charge' and the following definitions are recommended.

2.2.1. ϕ_{P}^{e} *– overall current efficiency.*

$$\phi_{\mathrm{P}}^{e} = \frac{n_{\mathrm{P}}|\nu_e|F}{|\nu_{\mathrm{P}}|Q} \quad (14a) \qquad Q = \int_0^t I(t)\,\mathrm{d}t \quad (14b)$$

2.2.2. $\phi_{\mathrm{P}}^{e\prime}$ *– point current efficiency.*

$$\phi_{\mathrm{P}}^{e\prime} = \frac{r_{\mathrm{P}}|\nu_e|FV}{|\nu_{\mathrm{P}}|iA_{\mathrm{e}}} \tag{15}$$

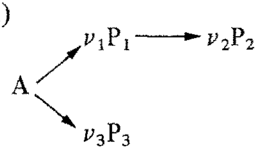
V is the volume of the reactants and not of the reactor, therefore the ratio A_{e}/V cannot be replaced by a_{e}. In the IUPAC nomenclature the c.e. has the symbol Θ (= overall yield in the ECRE Convention).

2.3. *Yield data*

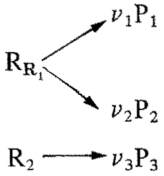
In publications concerning electrochemical reactions it is advisable to give not only current effiency data, but also yield data.

2.3.1. Characterization of reaction specificity. The reaction specificy considers both consecutive and parallel reactions.

(a)



(b)



2.3.2. S_{P_1} *– overall selectivity.*

$$S_{\mathrm{P}_1} = \frac{n_{\mathrm{P}_1}/\nu_1}{\sum\limits_i n_{\mathrm{P}_i}/\nu_i} \tag{16}$$

In the case of reaction scheme (a) the selectivity of P_1 has the same value as the conversion related yield. In case (b), however, the conversion related yield is not identical with the selectivity.

$$S_{\mathrm{P}_1} = \frac{n_{\mathrm{P}_1}/\nu_1}{\sum\limits_{i=1}^{3} n_{\mathrm{P}_i}/\nu_i} \tag{17}$$

$$\phi_{\mathrm{P}_1} = \frac{n_{\mathrm{P}_1}/\nu_1}{\sum\limits_{i=1}^{2} n_{\mathrm{P}_i}/\nu_i} \tag{18}$$

2.3.3. S'_{P_1} *– point selectivity.*

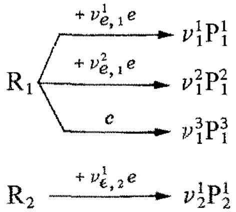
$$S'_{\mathrm{P}_1} = \frac{r_{\mathrm{P}_1}/\nu_1}{\sum\limits_i r_{\mathrm{P}_i}/\nu_i} \tag{19}$$

In electrochemical reaction engineering there is no criterion which differentiates between electrochemical side and parallel reactions. For this purpose two further quantities are introduced.

2.3.4. $\phi_{\mathrm{R}_1}^{e}$ *– reactant current efficiency.*

$$\phi_{\mathrm{R}_1}^{e} = \sum_j \phi_{\mathrm{P}_1}^{ej} \tag{20}$$

The reactant current efficiency gives the portion of a certain reactant which undergoes electrochemical reactions.



P_i^j [j is product index; i is reactant index]
$\phi_{\mathrm{R}_1}^{e} = 1$ means that only electrochemical side reactions take place forming the products P_1^1, P_1^2, etc. $\phi_{\mathrm{R}_1}^{e} < 1$ means that parallel to the electrochemical conversion of the key reactant further reactants R_2, etc. are also involved in electrochemical reactions.

2.3.5. S_e *– integral electrochemical selectivity.*

$$S_e = \frac{\sum\limits_j \sum\limits_i (1 - \delta_{0,\nu_{e,i}^j}) n_{\mathrm{P}_i^j}/\nu_i^j}{\sum\limits_j \sum\limits_i n_{\mathrm{P}_i^j}/\nu_i^j} \tag{21}$$

The integral electrochemical selectivity represents the fraction of all products which are formed electrochemically (δ is the Kronecker symbol – $\delta_{0,0} = 0; \delta_{0,n} = 1$).

2.4. *Parameters for energy considerations*

The energy costs of an electrochemical process are closely correlated to the energy efficiency. For characterizing this quantity the following definitions are recommended.

2.4.1. γ_G – *energy yield.*

$$\gamma_G = \frac{\Delta G \phi^e}{U_c \nu_e F} = \frac{U_0 \phi^e}{U_c} \qquad (22)$$

2.4.2. γ_H – *enthalpy related (thermal) energy yield.*

$$\gamma_H = \frac{\Delta H \phi^e}{U_c \nu_e F} = \frac{U_{tn} \phi^e}{U_c} \qquad (23)$$

$$U_{tn} = \Delta H / \nu_e F \qquad (24)$$

where U_{tn} is the thermoneutral cell voltage.

2.4.3. E_S – *specific electric energy consumption ($J\,kg^{-1}$, $J\,m^{-3}$).*

This is mass related for solid or liquid products

$$E_{S(m)} = \frac{U_c \nu_e F}{M \phi^e} \quad (\mathrm{J\,kg^{-1}}) \qquad (25)$$

volume related for gaseous products

$$E_{S(V)} = \frac{U_c \nu_e F}{V_M^0 \phi^e} \quad (\mathrm{J\,m^{-3}}) \qquad (26)$$

where V_M^0 is the molar volume under standard conditions. The second subscripts m or V may be omitted if in context with E_S, its dimension is mentioned.

2.5. *Investment cost*

The investment costs of an electrochemical process are related to the following quantities.

2.5.1. ρ – *overall space–time yield ($kg\,m^{-3}\,s^{-1}$).*

$$\rho = \frac{n_P M_P}{V_R t} \qquad (27)$$

where t is the reaction time (batch reactor) or the residence time (tube reactor). In the ECRE Convention the symbol ρ is also used for the mass density.

2.5.2. ρ' – *point space–time yield ($kg\,m^{-3}\,s^{-1}$).*

$$\rho' = a_e \frac{i M_P \phi_P^{e'}}{\nu_e F} \qquad (28)$$

2.5.3. i^* – *current concentration ($A\,m^{-3}$).*

$$i^* = a_e i = \frac{I}{V} \qquad (29)$$

2.5.4. τ – *space–time (s).*

$$\tau = V_R / Q \qquad (30)$$

This definition is used in the ECRE Convention and proper modifications are explained there. Q means the volumetric flow rate.

2.5.5. s – *space velocity (s^{-1}).*

$$s = \frac{\dot{V}}{V_R} = \frac{1}{\tau} \qquad (31)$$

Space velocity as well as space–time yield are conversion dependent quantities and therefore a normalization of these quantities with respect to the conversion is advisable.

2.5.6. s_n – *normalized space velocity (s^{-1}).*

$$s_n = \frac{I \phi^e}{(c_0 - c_1) V_R \nu_e F} \log\left(\frac{c_0}{c_1}\right) = \frac{a_e k}{\ln 10} \qquad (32)$$

s_n means the volume of reactant mixture (including solvents) in m^3 for which the concentration of the key reactant can be reduced by a factor of 10 during 1 s in a reactor volume of 1 m^3.

2.5.7. ρ_n – *normalized space–time yield ($kg\,m^{-3}\,s^{-1}$).*

$$\rho_n = \frac{I \phi^e M}{V_R \nu_e F} \frac{0.9}{X} \log\left(\frac{c_0}{c_1}\right) \qquad (33)$$

ρ_n means the amount of the key reactant A which can undergo a conversion of 90% during 1 s in a reactor volume of 1 m^3.

s_n and ρ_n are very convenient quantities for comparison of various experiments carried out with different fractional conversions because space-velocity and space–time yield are functions of the fractional conversion [6].

2.5.8. γ – *effectiveness factor.*

$$\gamma = \frac{\text{observed current density}}{\text{c.d. under diffusion limited conditions}} \qquad (34)$$

For the effectiveness factor of a catalytic reaction the ECRE Convention uses the symbol η which should be avoided in electrochemical engineering in order to prevent confusion with overvoltage. The effectiveness factor is especially useful for characterizing the performance of three-dimensional electrodes.

3. General nomenclature

The structure of the list follows the nomenclature in chemical reaction engineering and contains only such quantities which are used additionally in electrochemical engineering. Not all duplication in symbols can be avoided, but misunderstandings can be eliminated by the context of the use of these symbols.

3.1. *Dimensions, quantities, concentrations*

A_e	electrode area (m^2)
a_e	specific electrode area (A_e/V_R) (m^{-1})
F	Faraday number (96 487 $C\,mol^{-1}$)

3.2. *Thermodynamical parameters*

U_0	reversible cell voltage (V)
U_0^0	reversible cell voltage under standard conditions (V)
E_0	reversible electrode potential (V)
E_0^0	reversible electrode potential under standard conditions (V)

3.3. *Electrochemical and electric properties (quantities)*

χ	conductivity ($S\,m^{-1}$)
ρ	resistivity ($1/\chi$) ($\Omega\,m$)
U	voltage (V)
U_c	cell voltage (V)
Q	electric charge (A s)
E	electrode potential with respect to any reference electrode. The type of reference electrode should be signed by proper subscripts (V)
η	overvoltage (V)
R	electric resistance (Ω)
R_c	cell area resistance ($\Omega\,m^2$)
ϕ	electric potential (V)
G	conductance ($1/R$) (S)

3.4. *Parameters for flow, heat and mass transfer*

δ	thickness of diffusion layer (m)
t_A	transport number of species A (i_A/i)

3.5. *Parameters for reaction rates and conversion*

ν_e	charge number of the electrode reaction
z_i	charge number of species i
i_0	exchange current density ($A\,m^{-2}$)
i_d	diffusion limit current density ($A\,m^{-2}$)
i_r	reaction limit current density ($A\,m^{-2}$)
α	degree of dissociation
α_c	charge transfer coefficient
β	symmetry factor

3.6. *Dimensionless numbers*

Wa Wagner number of current distribution

$$Wa = \frac{\chi(d\eta/di)}{L}$$

3.7. *Subscripts*

e	electrochemical, electrode
c	cell
SHE	standard hydrogen electrode
HESS	hydrogen electrode in the same solution
SCE	saturated calomel electrode
a	anodic
c	cathodic
m	metallic phase (electrode phase)
s	electrolytic phase (solution phase)

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