

# State variable approach to electrochemical dynamics

A. Sadkowski \*

*Institute of Physical Chemistry of the Polish Academy of Sciences, Kasprzaka 44/52, 01-224 Warsaw, Poland*

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## Abstract

Advantages of the state variable approach in the formulation of evolution equations of complex electrochemical processes are presented. This approach allows one to deal with electrochemical dynamics according to the uniform approach of process dynamics of deterministic systems with all specificity of the systems' evolution reduced to the mathematical properties of the governing differential equations. Recommendations are formulated as to the judicious choice of the state variables based on the conservation laws. The distinction between state variables and kinetic variables is noted. The specificity of steady-states and, particularly, of the states of equilibrium is outlined. Definitions of equivalent capacities and resistances of partial processes in linear approximation are restricted to steady-states only. Electrochemical examples are presented which can be looked at as building blocks for more complex systems obtained by combination of their evolution equations. © 1998 Elsevier Science S.A. All rights reserved.

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## 1. Introduction

Complex electrode processes are usually analyzed by electrochemical kinetics involving, from the very beginning, kinetic equations of elementary steps making up the entire process: heterogeneous charge transfers, surface or bulk chemical reactions and transport processes [1–5]. The variables in these equations are the electrode potential ( $E$ ) and the concentrations of reagents, including intermediates in the bulk phases ( $c$ ) and at the surface ( $\Gamma$ ). The rates of individual steps ( $v_i$ ) are related to partial current densities ( $j_i = Fz_i v_i$ ) which sum up to the overall Faradaic current density  $j = \sum_i j_i$  and this may be compared with the experimental  $j$ – $E$  relation after proper allowance for the non-Faradaic current of the double layer charging and the voltage drop in the electrolyte. Successive elimination of variables (concentrations of intermediates) from separate equations allows step-by-step reduction of their number and for a complex, multi-step reaction it is often possible to

derive the unique kinetic equation as an current density versus potential ( $j$ – $E$ ) relation. This procedure of step-by-step elimination of variables constitutes the core of formal electrode kinetics. In most cases it is feasible only with simplifying assumptions such as the time invariance (steady-state approximation) and virtual equilibrium of some partial reactions or, on the contrary, their complete irreversibility (linear Tafel approximation). The validity of these simplifying assumptions may be difficult to verify experimentally other than by comparing the final, kinetic formulae with experiments on which they were initially based and such verification is often far from conclusive. Even with these simplifying assumptions the kinetic formulae obtained may be quite complex, as can be proved by the mere inspection of references [1–4] in chapters devoted e.g. to hydrogen or oxygen reactions, not even mentioning the more complex electrocatalytic reactions of organic reagents. The complexity of kinetic formulae obscures the physical significance of the relations analyzed and behind bulky formalism of algebraic transformations may be hidden more important problems of electrode kinetics.

\* Fax: +48 22 6325276; e-mail: ansad@ichf.edu.pl

Analysis of complex electrode reactions in transient conditions, i.e. out of their steady-state, using this standard apparatus of formal electrode kinetics, may be even more perplexing. It is therefore understandable that sometimes it is reasonable to abandon the ambitious task of formulating complex kinetic equation in its final explicit form, impaired by simplifying assumptions, and to resort rather to a numerical solution of complete kinetic equations in the time domain [6]. For this the approach may be recommended which has been well established for a long time in system dynamics and process control [7–12]. It consists in selecting several variables characterizing the state of the system followed by subsequent analysis of their evolution, i.e. their time variation governed by differential equations of the system's dynamics. The variables in question, called state (or system) variables, must be independent, their number has to be a minimum, yet sufficient to define at every instant the system as a whole both in steady-state and in transient conditions. The time variation of these state variables (system variables) is identified with the evolution of the system itself. The determination of the number of state variables and their appropriate selection is not a trivial problem [10] and it is related to finding the number of degrees of freedom of the system. The state variable approach is particularly useful when dealing with global dynamic properties such as the system's stability, controllability, oscillatory and/or chaotic regime etc., at the expense of less important local details. Global analysis of a multivariate systems' dynamics can be done efficiently when based on geometrical (topological) analogs [9,14] due to the correspondence between dynamic characteristics and the topological properties of trajectories on the (so called) phase portrait of the dynamic system. The form of these trajectories displays the system's dynamics in the most concise and illustrative way showing the regions of asymptotic stability, instability, multiple steady-states, oscillatory and chaotic behavior [9,12,13,15].

The state variable approach was applied successfully in the past to electrochemical problems (see reviews in Refs [7,15]) but there are also examples of its electrochemical applications [16] with incorrect selection of state variables leading to erroneous conclusions.

It is the aim of this paper to present simple recommendations regarding the selection of state variables and the formulation of evolution equations based on experience gathered in the field of system dynamics and process control. Several examples are given of the formulation of evolution equations applicable in electrochemistry in a form suitable for integration. For the sake of conciseness only autonomous systems (without explicit time dependence) and only those with lumped elements are presented and, consequently, only ordinary differential equations are considered [9,14]. The first limitation is not very restrictive because the proper

transformation of state variables in the time-dependent (non-autonomous) system restores the time-invariance and makes its equation tractable exactly like the normal, autonomous systems [9]. More restrictive is the second limitation because, in general, no distributed system, such as the one involving infinite or limited diffusion can be reduced to the system with lumped parameters or, in mathematical terms, no partial differential equation can be substituted by the ordinary one. In terms of electrochemical experiment this means that systems with distributed parameters, such as a simple charge transfer reaction on a plane electrode with infinite diffusion of reagent have, in principle, the steady-state only at equilibrium, i.e. at open circuit potential. Any change of the state (e.g. by a potential step) out of these equilibrium conditions requires infinite charge and infinite time to attain the new steady-state. Incidentally, the same irrelevance of the steady-state is also true for solid electrodes which display frequency dispersion of interfacial capacitance of the constant phase type [17]. Therefore we have restricted our treatment of diffusion processes to the diffusion layer (Nernst) approximation [3,5]. The rationale of this restriction is to present first of all the general structure of evolution equations showing their interdependence by balance equations representing conservation laws.

The formulation of electrochemical dynamics in terms of state variable analysis allows moreover the rigorous formulation of small signal (local, differential) parameters such as capacitance, resistance or local time constant of crucial importance for the interpretation of small signal (electrochemical immittance) data and for the analysis of a system's stability.

For the system dynamic approach to be applied successfully one has to make the important assumption that the system in question is deterministic. All the systems governed by differential equations in the time domain are deterministic, i.e. strictly reproducible in the same values of state and input variables. This is in contrast to stochastic systems which do not obey the rules of dynamics in a strictly reproducible way but abide by the rules of statistics [18]. In this paper we assume that the electrical and electrochemical systems considered are deterministic which is generally true for sufficiently large systems.

## 2. State equations

Let the evolution of the system be governed by the set of  $n$  ordinary differential equations of first order, generally nonlinear [7–10,19,20]:

$$\dot{x} = f(x, y) \quad (1)$$

where  $x = \{x_1, x_2, \dots, x_n\}$  is the vector of state (system) variables;  $\dot{x} = \{\dot{x}_1, \dot{x}_2, \dots, \dot{x}_n\}$  is the vector of their time

derivatives:  $\dot{x}_i = \partial x_i / \partial t$ ;  $y = \{y_1, y_2, \dots, y_m\}$  is the vector of input (control, perturbation) variables. This equation, which is the axiom of the deterministic system, asserts simply that the system's evolution is determined by the values its state variables have in any instant taken as initial and by the input variables which are functions of time. Integration of the set of ordinary differential equations for  $t \geq 0$  with initial values  $x_0 = x(t=0)$  and with input signal specified as the time function  $y = y(t)$  equips us with the complete knowledge of the system's states in the future:  $x = x(t)$  for  $t \geq 0$ . The same is true also for the knowledge (implicit) of the past of the deterministic system which is assured whenever the state of the system is known in the instant taken as the time zero:  $x_0 = x(t=0)$  and the 'history' of the input signal is known  $y = y(t)$  for  $t \leq 0$ .

The system is called  $n$ -dimensional, when its state is determined by  $n$  state variables.

Another vector defined as:

$$z = z(x, y) \quad (2)$$

is the vector of the output variables  $z$ , dependent on state variables  $x$  and inputs  $y$ . In the simplest case, components of the output vector  $z$  may be merely components of the state vector  $x$  or their simple functions. In the special case of a linear system or a nonlinear system in the small signal (local, incremental) regime, the Eqs. (1) and (2) simplify to:

$$\dot{x} = Ax + By \quad (3)$$

$$z = Cx + Dy \quad (4)$$

where  $A$ ,  $B$ ,  $C$  and  $D$  are matrices of linear transformations.

The steady-state (zero state, time invariant state [9]) is at  $\dot{x} = 0$ . At  $y = 0$  there is zero input (free) response. Application of the input signal  $y$  at the steady-state usually causes the transient attainment of a new steady-state. In some cases however this new steady-state may have the form of sustained oscillations (harmonic oscillations, limiting cycles for system of two or more dimensions) or chaotic oscillations (systems of three or more dimensions) [9,12–15].

Linear systems are analyzed by well established linear theory and their solutions (trajectories) are available in explicit form [9]. They constitute the domain of small signal, i.e. immittance analysis not to be dealt with here in detail.

Solutions of non-linear equations typical for electrochemical kinetics (exponents!) are available in most cases only in numerical form and proper selection of state variables is crucial for the successful numerical analysis of a system's evolution.

### 3. Selection of state variables

Recommendations for the proper selection of the state variables follow the vast experience of system dynamics and process control [8–11]. First of all, state variables should be independent and constitute the minimum set adequate for determination of the state of the system. Next, they should allow for structural interlinking of individual steps constituting the complex process and therefore they should account for accumulation restricted by the conservation laws for the mass, substance, charge, energy etc. In the steady-state there is no accumulation of variable  $x_i$  but in non-steady (transient) conditions this accumulation may occur as the result of the net input:  $F_i = (\text{in-flow})_i - (\text{out-flow})_i$  and the presence of the sources  $G_i$  where both  $F_i$  and  $G_i$  are functions of state ( $x_j$ ) and inputs ( $y_k$ ):

$$\partial x_i / \partial t = F_i(x_j, y_k) + G_i(x_j, y_k) \quad (5)$$

It is recommended therefore that the variable chosen as the state variable be extensive in the sense of thermodynamics [21] or intensive but specific (concentration, density etc.), i.e. directly derived from the extensive one by division by the mass, volume, surface area, etc.

We do not recommend, for example, selecting voltage or temperature, not governed by conservation laws, as the state variables but rather their conjugates (in thermodynamic sense [21]), that is charge (or charge density) and energy (or its density). These conjugates are conservative variables, i.e. their sum is invariant in closed systems and hence they can be used in balance equations.

It has to be noted that conservation (accumulation, balance) equations are either global or local (macroscopic or microscopic) [10]. In the first case they are related to the system as a whole and expressed by ordinary differential equations, in the second case they are related to the infinitesimal parts of the volume or surface area (interface) and expressed by partial differential equations of the Laplace type such as Fick's diffusion equation. Systems of the first class are referred to as those with lumped parameters; the second class comprises systems with distributed parameters. Only the first class will be considered here, yet it has to be noted, that ordinary differential equations applicable to the first class of the systems are often used as a first approximation before applying the complete but more complex models with partial differential equations. This is the case when the Nernst layer model involving only lumped parameters is applied as the first approximation to diffusion problems before in the general case the second Fick's law of diffusion is applied with distributed parameters and much greater mathematical problems.

Below we shall present several examples of electrical models and electrochemical systems with ordinary dif-

ferential equations governing evolution of state variables such as the charge or its close equivalent-concentration.

#### 4. Electrical models

Electrical equivalent circuits are commonly used as models of electrochemical dynamics [22–24], i.e. as the substitute (graphical representation) of the governing differential equations. For complex systems the use of electrical models in place of differential equations suffers from structural (related to the structure of the equivalent circuit) and parametric (values of its parameters) uncertainty intrinsic to all problems of electrical circuit synthesis [25]. This uncertainty is well known in electrical engineering but seems to have been apprehended only quite recently by electrochemists [26,27] but it is always worthwhile to remember it.

This shortcoming of electrical models is, at least partly, compensated by their quality of showing clearly the reversible and irreversible constituents of the overall process. The reactive elements (capacitors) in the electric model represent reversible process while active elements (resistors) represent irreversibility of kinetic processes. All energy dissipation (entropy generation) which is the measure of a process's irreversibility is represented by Joule's heat dissipated in resistors of the electrical model while the energy accumulated and delivered by the model's capacitors is transferred reversibly. Unfortunately, hardly ever the individual elements of the electrical model be associated with individual steps of the complex process [28] or with separate elementary processes (charge transfer, transport, chemical reaction etc.). Usually each element of the electrical model combines the contribution of various physical phenomena or various steps of the complex process.

Electrical models can be used not only in local, linear analysis (electrochemical immittance) but also in the global, non-linear one. In the linear case the parameters of the equivalent circuit are constant, the mathematics is reduced to operational calculus (Laplace transformation) using the rich arsenal of linear circuit theory [11,25,29,30] and explicit expressions are obtained for the time evolution or frequency dependence of the state variables. In the non-linear case elements of the equivalent circuit are no longer constant but they are parametrized with respect to the voltage, the current or the charge and therefore generally one has to rely on the numerical analysis [9,30,31].

Presenting the state variable approach first for simple electrical models should also help to identify the concepts crucial for rational analysis of electrochemical systems such as the equilibrium, steady-state and transient conditions.

The delicate difference between the state of equilibrium and the steady-state has to be noted here. In electrochemistry, as in chemistry in general, the equilibrium is understood in the thermodynamic sense (thermodynamic equilibrium) while in system dynamics it is usually defined in a less specific but more formal way as the steady-state, i.e. the one for which Eq. (1) equals zero. In the system dynamics there is often no clear distinction between the time invariant steady-state and the thermodynamic equilibrium. The comment on this difference in the footnote on page 67 of Ref. [7] may be recommended to the reader. In this paper we will adhere to the chemical approach and we will emphasize the difference, if they exist, between equilibria and steady-states.

The order of the system defined as the number of state variables can be also identified as the number of capacitors in the electrical model, the number of distinct time constants in the time domain relaxation or the number of poles (complex frequencies zeroing the denominator) of the immittance function.

No restrictions are imposed on the signs of individual elements of the models presented below, i.e. they may be either positive or negative.

##### 4.1. R-C circuit

The circuit in Fig. 1a is the simplest one applied in electrochemistry. It is commonly used as the model of double layer charging of a polarizable electrode through the electrolyte (ohmic) resistance [24]. It is also used to model the time and frequency responses of the electrochemical adsorption reaction [32–35]. The state variable chosen judiciously according to recommendations in part 3 is the charge  $Q$  on the condenser  $C$  with voltage  $V$  over the whole circuit taken as the input variable. The evolution equation has the simple form:

$$I = dQ/dt = -Q/(RC) + V/R \quad (6)$$

In view of the proportionality  $E = Q/C$  ( $E = V - IR$  is the capacitor voltage or voltage across the double layer in electrochemistry), this voltage may be used also as the state variable. However we do not recommend this because the voltage  $E$  variable is not directly affected by the conservation law, contrary to the charge, its conjugate, which obviously is conserved. As this is quite unacceptable we consider the choice of the voltage  $V$  as the state variable as was done in [16].

Incidentally, in Ref. [16] the selection of state variables is inconsistent in that either it violates the principles of their minimum number and independence by selecting in this role the voltage  $V$  and charge, i.e. the variable conjugated with voltage, represented there as  $X$  or by referring the term state variables to kinetic variables in rate equations which are not constrained by the principles specified for state variables.

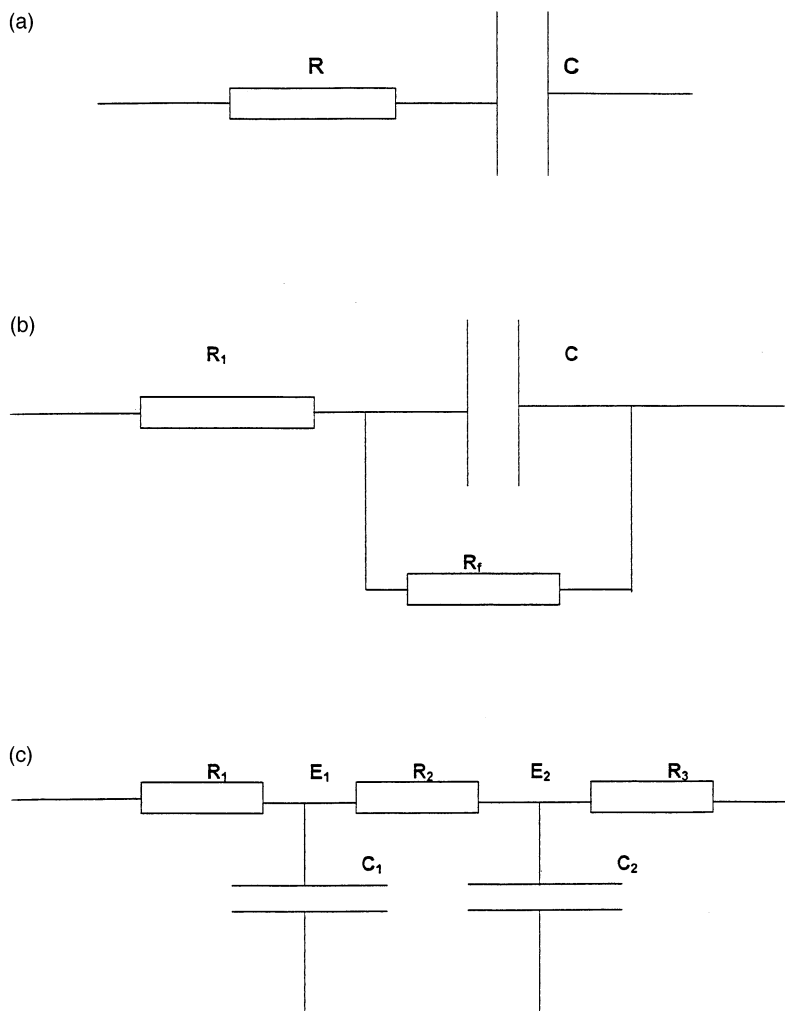


Fig. 1. Electrical equivalent circuits: (a) simple RC circuit; (b) R(CR) circuit; (c) second order RC circuit.

The state of the circuit in Fig. 1a like that of any real dynamic system of the 1st order modelled by this simple equivalent circuit is determined by the charge  $Q$  and the evolution of the circuit is determined by the evolution Eq. (6) with input signal (control variable) specified as the time function  $V = V(t)$  and the current  $I$  as the output variable. The evolution Eq. (6) defined in this way conforms entirely to the general scheme of Eqs. (1) and (2).

The steady-state defined by  $dQ/dt = 0$  is also the state of equilibrium because there are no fluxes (currents) in the circuit. Equilibrium is described by the functional correspondence between the control variable ( $V$ ) and the state variable at equilibrium ( $Q_{eq}$ ):  $Q_{eq} = VC$  which is in fact a definition of the capacitance because in equilibrium  $V = E$ .

The RC circuit is the first order dynamic model of various processes from diverse branches of science and engineering with no steady-state fluxes (batch processes). Its admittance in the complex frequency

(Laplace) domain is:

$$Y(s) = (1/R) s / (s - p) \quad (7)$$

where  $s$  is the complex frequency or Laplace operator;  $p = -1/(RC)$  (minus the reciprocal of the time constant) is the single pole of the admittance function. Under potential control the circuit is stable for  $RC > 0$  (positive time constant). It is always stable for current control.

The immittance Eq. (7) implies that  $Y(s \rightarrow \infty) = 1/R$  and  $Y_{dc} = Y(s \rightarrow 0) = 0$  and this last equation is another form of the assertion that the steady-state is also the state of equilibrium (no fluxes) formulated already for the time domain representation Eq. (6).

The concepts of Laplace transformation, poles and zeros of immittance functions used in this paper were also used earlier in a similar context by other authors, see, e.g. [36] and this reference with back-references therein may be consulted for explanation of these terms which may be uncommon for electrochemists.

#### 4.2. $R(CR)$ circuit

Fig. 1b shows a somewhat more complex circuit which the models electrochemical interface (double layer) as a locus of the charge transfer reaction whose kinetics are represented by the resistor  $R_f$ . The same circuit can also be applied as the model of simple electrocatalytic reaction, i.e. the charge transfer reaction with adsorption of the intermediate [28].

Again, the charge  $Q$  on the capacitor  $C$  has to be taken as the state variable according to recommendations in part 3. The evolution equation is:

$$dQ/dt = -Q/(R_1 C) - I_f(Q) + V/R_1 \quad (8)$$

The term  $I_f(Q)$  represents characteristics of the (possibly non-linear) resistor  $R_f$ . By definition, the resistor is the passive element having the current-voltage characteristic  $I(E)$ . Due to the functional dependence  $Q = Q(E)$  the characteristic defining the resistor  $I(E)$  may be equally well represented by  $I(Q)$  as in Eq. (8).

For linear approximation of  $I_f(E) = E/R_f$  the evolution equation is:

$$dQ/dt = -Q/(R_1 C) - Q/(R_f C) + V/R_1 \quad (9)$$

and this varies from Eq. (6) by an additional term  $Q/(R_f C)$  representing another way of charging the capacitor  $C$ .

The steady-state (index ss) is the one for which  $dQ/dt = 0$  and it is no longer the state of equilibrium if a non-zero flux (current) is present:

$$I_{ss} = I_f(Q_{ss}) = (V - Q_{ss}/C)/R_1 = V/(R_1 + R_f) \quad (10)$$

In the steady-state the functional relation exists between the state variable ( $Q_{ss}$ ) and the control variable ( $V$ ) similarly to that for the RC circuit in equilibrium. For the non-linear function  $I_f(E)$  this relation is given by the implicit function  $Q_{ss}(V)$ :

$$Q_{ss}(V) = CV - R_1 C I_f \quad (11)$$

and for the linear characteristic  $E/I_f = R_f$  it reduces to:

$$Q_{ss} = V C R_f / (R_1 + R_f) \quad (12)$$

The  $R_1(CR_f)$  circuit is the model of dynamics of various first order processes allowing for the steady-state flux in diverse branches of science and engineering. Its admittance function in the complex frequency (Laplace) domain is:

$$Y(s) = (1/R_1)(s - z)/(s - p) \quad (13)$$

where  $z = -1/(CR_f)$  is the single zero;  $p = -(R_1 + R_f)/(R_1 R_f)$  is the single pole. They have to be negative for the circuit to be stable under potential control and current control respectively. Extrapolation of the admittance function to zero and infinite frequency gives:  $Y_{DC} = Y(s \rightarrow 0) = 1/(R_1 + R_2)$  and  $Y(s \rightarrow \infty) = 1/R_1$ , respectively.

#### 4.3. Second order RC circuit

Finally, let us consider shortly an even more complex, second order electrical model shown in Fig. 1c. This circuit can be used as the model of the electrochemical interface with electrolyte resistance represented by  $R_1$ , double layer represented by  $C_1$  and with a simple electrocatalytic reaction, i.e. the charge transfer with adsorption of intermediate product represented by elements  $R_2$ ,  $C_2$  and  $R_3$ .

There are now two independent state variables and our recommendations in part 3 imply taking charges  $Q_1$  and  $Q_2$  of condensers  $C_1$  and  $C_2$  as these variables. The system's evolution is then governed by the set of two differential equations:

$$dQ_1/dt = -[1/(C_1 R_1) + 1/(C_1 R_2)]Q_1 + Q_2/(C_2 R_2) + V/R_1 \quad (14)$$

$$dQ_2/dt = Q_1/(C_1 R_2) - Q_2[1/(C_2 R_2) + 1/(C_2 R_3)] \quad (15)$$

The pair of first order differential equations with appropriate initial conditions  $Q_1(t=0)$ ,  $Q_2(t=0)$  may be substituted by a single differential equation of the second order for  $Q_1$ :

$$\begin{aligned} \frac{d^2 Q_1}{dt^2} + \left( \frac{1}{C_1 R_1} + \frac{1}{C_1 R_2} + \frac{1}{C_2 R_2} + \frac{1}{C_2 R_3} \right) \frac{dQ_1}{dt} \\ + \frac{1}{C_1 C_2} \left( \frac{1}{R_1 R_2} + \frac{1}{R_1 R_3} + \frac{1}{R_2 R_3} \right) Q_1 \\ = \frac{1}{R_1} \frac{dV}{dt} + \left( \frac{1}{C_2 R_2} + \frac{1}{C_2 R_3} \right) \frac{V}{R_1} \end{aligned} \quad (16)$$

with initial conditions of  $Q_1(t=0)$  and  $dQ_1/dt(t=0)$ .

The steady-state occurs for  $dQ_1/dt = dQ_2/dt = 0$ . It is generally not the state of equilibrium since the steady-state flux (current) exists and has the value:

$$I_{ss} = V/(R_1 + R_2 + R_3) \quad (17)$$

State variables in the steady-state have values:

$$Q_{1ss} = V C_1 (R_2 + R_3) / (R_1 + R_2 + R_3) \quad (18)$$

$$Q_{2ss} = V C_2 R_3 / (R_1 + R_2 + R_3) \quad (19)$$

The second order RC circuit is the model of dynamics of various processes of the second order with steady-state (dc) flux from various branches of science and engineering. Its admittance function in the complex frequency (Laplace) domain is:

$$Y(s) = (1/R_1) (s - z_1)(s - z_2)/((s - p_1)(s - p_2)) \quad (20)$$

with  $z_1$ ,  $z_2$ -zeros and  $p_1$ ,  $p_2$ -poles of the admittance function with real or complex values calculable in the standard way [25,29,30].

Extrapolated values are:  $Y(s \rightarrow \infty) = 1/R_1$  and  $Y_{DC} = Y(s \rightarrow 0) = z_1 z_2 / (p_1 p_2 R_1)$ , and both have finite real values.

For potential control the steady-state is stable when the real parts of the poles  $p_1$  and  $p_2$  are negative [11,15]. The steady-state is stable under current control (galvanostatic conditions) when the real parts of the zeros  $z_1$  and  $z_2$  are negative.

## 5. Electrochemical examples

The electrochemical examples presented below belong to two groups corresponding roughly to what is known in chemical engineering as batch and flow-through reactors. The first group of the first order systems (examples (1), (2) and (3) below) comprises the cases without steady-state fluxes and hence the steady-states in these examples are equivalent to the states of thermodynamic equilibrium [21] and Eq. (5) is simplified by  $F_i(x_j, y_k) = 0$ . The remaining examples allow for such fluxes, i.e. the complete form of Eq. (5) is relevant. The electrochemical examples are presented here in the simplest diffusion layer approximation in order to remain in the domain of ordinary differential equations and lumped parameters [8–10].

With the charge  $Q$  (or its mass equivalent) chosen as the state variable, the current as the output variable and the electrode potential  $E$  as the control variable, the equivalent capacitance  $C$  is defined for steady-states, including equilibrium as the special case, as  $C = (\partial Q / \partial E)_{ss}$ .

Analogous differentiation defines the equivalent resistance  $R = (\partial I / \partial E)_{ss}^{-1}$ .

The subscript ss indicates the steady-state here and in the subsequent text. The equilibrium will be denoted with index 0 and the standard conditions (potential, concentration, charge etc.) in kinetic equations are denoted by an upper index s.

### 5.1. Electrochemical cell in the linear approximation with respect to the kinetics

This merely means that the whole kinetics of the cell's processes are substituted by the internal resistance of the cell  $R_i$  assumed constant. The reagents are in the solution, the open circuit voltage  $E_0$  is the equilibrium voltage given as the Nernst function of concentrations and the charge  $Q$  accumulated in the cell is referred to some arbitrary reference (standard) state of the cell with  $E_0 = E^s$ ,  $c = c^s$  and  $Q = Q^s$ . Open circuit characteristics of the cell  $E_0 = f(Q)$  are given by the Nernst formula (one electron reactions assumed for simplicity):

$$E_0 = E^s + RT/F \ln[c/c^s] = E^s + RT/F \ln[Q/Q^s] \quad (21)$$

where  $Q = VFc$  and analogously for  $Q^s$ . ( $c$ ,  $c^s$ -concentrations of active components;  $Q$ ,  $Q^s$ , equivalent charge;  $V$ , cell volume, other symbols as usual).

With  $Q$  taken as the state variable and the cell voltage  $E$  as the control variable, the evolution equation is:

$$dQ/dt = (E - E_0)/R_i = -f(Q)/R_i + E/R_i \quad (22)$$

where function  $f(Q)$  is the Nernst Eq. (21).

It is expedient to take the current as the output variable:

$$I = dQ/dt \quad (23)$$

In these terms the last equations conform to the scheme defined by Eqs. (1) and (2).

The steady-state with  $dQ/dt = 0$  is the state of equilibrium with  $E = E_0$  (no fluxes) and the equivalent cell capacitance at equilibrium is defined as

$$C_{cell} = (\partial Q / \partial E)_{E_0} = FQ/RT \quad (24)$$

The equivalent resistance of the cell is simply its internal resistance according to the linear approximation of the kinetics and this conforms to the result of direct substitution of Eq. (22) and Eq. (24) into the definition:

$$R_{cell} = [(\partial I / \partial E)^{-1}]_{E_0} = R_i \quad (25)$$

The rate of the cell's relaxation around the state of equilibrium is characterized by its single time constant:

$$\tau_{cell} = R_{cell} C_{cell} \quad (26)$$

### 5.2. Electrochemical half-cell with current-voltage characteristics of the Butler–Volmer type

Let us assume an oxidation/reduction reaction with one electron transferred:



on a plane electrode with cross-sectional area  $A$ , with ideal electrolyte mixing, i.e. uniform concentration of the reaction components throughout the volume  $V$  of the half-cell. The rate  $v$  is given by the Butler–Volmer kinetic equation is [3,5]:

$$v = k \{ c_R \exp[\alpha F(E - E^s)/RT] - c_{Ox} \exp[(\alpha - 1)F(E - E^s)/RT] \} \quad (28)$$

with potential  $E$  scale and rate constant  $k$  referred to the standard equilibrium potential  $E^s$ . The balance (mass conservation) condition for reagents R and Ox is:

$$c_R + c_{Ox} = c = \text{const} \quad (29)$$

and this obviously requires that a corresponding number of counter-ions has to be supplied from the other half-cell or from the auxiliary electrode compartment to meet the requirement of electrical neutrality of the half-cell as a whole.

The (relative) charge of the half-cell is defined as the charge equivalent of the reaction progress or simply, as

the charge input to the cell by the half-cell terminal. This charge equivalent we define as:

$$Q = VF(c_{\text{Ox}} - c/2) \quad (30)$$

From Eq. (29) the relation follows between actual concentrations and the relative charge defined in Eq. (30):

$$c_{\text{Ox}} = c/2 + Q/(VF) \quad (31)$$

$$c_{\text{R}} = c/2 - Q/(VF) \quad (32)$$

Zero charge is fixed arbitrarily at standard state:  $c_{\text{R}} = c_{\text{Ox}} = c/2$  and  $E = E^s$  and possible variations of this charge are limited by the condition:

$$-c/2 < Q/VF < c/2 \quad (33)$$

In Eq. (27) the anodic process consumes and the cathodic one accumulates the charge according to the equation:

$$dQ/dt = AFv \quad (34)$$

and this gives the evolution equation of the form:

$$\frac{dQ}{dt} = AFk \left\{ \left( \frac{Q}{VF} - \frac{c}{2} \right) \exp \left[ \frac{\alpha F(E - E^s)}{RT} \right] - \left( \frac{c}{2} + \frac{Q}{VF} \right) \exp \left[ \frac{(\alpha - 1)F(E - E^s)}{RT} \right] \right\} \quad (35)$$

With the relative charge taken as the state variable, potential as the control variable and the current  $I = dQ/dt$  taken as the output variable, the last equation conforms to the scheme defined by Eqs. (1) and (2). For any form of the perturbation signal  $E = E(t)$  and initial condition  $Q_{t=0} = Q_0$ , the integrated Eq. (35) gives the state evolution of the form:  $Q = Q(t)$  and the corresponding variations of concentrations of cell reagents and of the current.

Inasmuch as there are no fluxes of active components to and out of the half-cell (the flux of counter-ions is not taken into consideration here), its steady-state is again the state of equilibrium and is given by the Nernst formula:

$$E_0 = E^s + \frac{RT}{F} \ln \left[ \frac{c/2 + Q/(VF)}{c/2 - Q/(VF)} \right] \quad (36)$$

or alternatively:

$$Q = 0.5VFc \tanh [0.5(\varepsilon_0 - \varepsilon^s)] \quad (37)$$

where  $\varepsilon = EF/RT$ .

From Eq. (37) we can calculate the equivalent capacitance of the half-cell characterizing its equilibrium:

$$C_{\text{hc}} = (\partial Q / \partial E)_{E_0} = VcF^2 / (4RT) \operatorname{sech}^2 [0.5(\varepsilon_0 - \varepsilon^s)] \quad (38)$$

From Eq. (35), recognizing that it represents the current  $I = dQ/dt$  at the half-cell's terminal, we define the equivalent resistance of the half-cell characterizing

its kinetics. For a small potential perturbation about the equilibrium and for  $\alpha = 0.5$  the resistance of the half-cell has the form:

$$R_{\text{hc}} = [(\partial I / \partial E)^{-1}]_{E_0} = \{0.5AFk/c \operatorname{sech} [0.5(\varepsilon_0 - \varepsilon^s)]\}^{-1} \quad (39)$$

The single time constant  $\tau_{\text{h.c.}} = C_{\text{h.c.}}R_{\text{h.c.}}$  represents the rate of the relaxation of the half-cell after a small-signal perturbation and with Eq. (38) and Eq. (39) it is:

$$\tau_{\text{h.c.}} = C_{\text{h.c.}}R_{\text{h.c.}} = \delta F / (2RT) \operatorname{sech} [0.5(\varepsilon_0 - \varepsilon^s)] \quad (40)$$

where  $\delta = V/A$  is the thickness of the electrolyte reservoir of the half-cell.

Eq. (38), Eq. (39) and Eq. (40) present bell shaped curves with minima/maxima at  $\varepsilon_0 = \varepsilon^s$ , that is at equal concentrations of active components.

It has to be noted that the form of kinetic equation, which instead of the rate constant includes the exchange current ( $I_0$ ), concealing the concentration dependence, is quite unsuitable for the evolution equation as seen from its form:

$$I = dQ/dt = I_0 \{ \exp [\alpha F(E - E_0)/RT] - \exp [(\alpha - 1)F(E - E_0)/RT] \} \quad (41)$$

with  $I_0 = kFAc_{\text{Ox}}^\alpha c_{\text{R}}^{1-\alpha}$  as the exchange current;  $E - E_0 = \eta$  as the overvoltage.

This is related to the fact that in Eqs. (28)–(40) the reference potential  $E^s$  is constant whereas in Eq. (41) the reference potential  $E_0$  evolves in phase with varying concentration and charge. The same premise is valid in subsequent examples and therefore we use everywhere rate constants of heterogeneous reactions and not their exchange currents.

### 5.3. Electrochemical adsorption reaction

This reaction has been analyzed many times in the past [32–35,37] but it is worthwhile to invoke it here again and in examples (5) and (6) below to address again the equilibrium and steady-states and the problem of state variables and kinetic variables.



We assume the constant and uniform concentration of reagent A in the electrolyte solution and account for this concentration in the following equations only for formal completeness. The surface concentration of B is expressed as surface fractional coverage:  $\theta = \Gamma / \Gamma_{\text{m}}$ ;  $\Gamma$ , concentration of  $B_{\text{ads}}$  in  $[\text{mol m}^{-2}]$ ;  $\Gamma_{\text{m}}$ , this concentration for monolayer (saturation) coverage.

With the coverage  $\theta$  taken as the state variable, potential  $E$  as the control variable and assuming the Langmuir adsorption isotherm, the evolution equation is:



$$\begin{aligned} d\theta/dt = k \{ (c_A/c^s)(1 - \theta) \exp [\alpha F(E - E^s)/RT] \\ - \theta \exp [(\alpha - 1)F(E - E^s)/RT] \} \end{aligned} \quad (43)$$

The output variable is the current density  $j$  directly related to the time variation of the fractional coverage:

$$j = dq/dt = F d\Gamma/dt = F\Gamma_m d\theta/dt \quad (44)$$

$q$ -charge density associated with adsorption,  $E^s$ -standard value of the potential, i.e. the one of the equilibrium for  $c_A = c^s$  and standard coverage  $\theta = 1/2$ ;  $k$ -the rate constant referred to standard conditions of equilibrium with  $\theta = 0.5$ ,  $c_A = c^s$  and  $E = E^s$ .

Again, the form of Eq. (43) and Eq. (44) conforms to the scheme defined by Eq. (1) and Eq. (2) and for any form of input  $E(t)$ , it can be integrated to give the state evolution equation  $\theta = \theta(t)$  and the resulting current density  $j = j(t)$ .

As before, the steady-state in the absence of external fluxes is the state of equilibrium for which  $d\theta/dt = 0$  and from this and equation Eq. (43) the unique relation  $\theta_0 = \theta_0(E_0, c_A)$ , the Langmuir isotherm, is derived:

$$E_0 = E^s - RT/F \ln[c_A/c^s] + RT/F \ln[\theta_0/(1 - \theta_0)] \quad (45)$$

Allowing for  $q = F\Gamma_m\theta$ , the slope of this isotherm gives the adsorption capacitance which is the electrical equivalent of the equilibrium behavior of the electrochemical adsorption reaction [32]:

$$C_{\text{ads}} = F\Gamma_m/(\partial E/\partial \theta)_{\text{eq}} = RT\Gamma_m\theta_0(1 - \theta_0) \quad (46)$$

which with allowance for Eq. (45) may be expressed in terms of the equilibrium potential:

$$C_{\text{ads}} = RT\Gamma_m \frac{(c^s/c_0)\exp(\varepsilon^s - \varepsilon_0)}{[(c^s/c_0)\exp(\varepsilon^s - \varepsilon_0) + 1]^2} \quad (47)$$

where  $\varepsilon = EF/RT$ .

Analogously, the potential derivative of Eq. (43) with allowance for Eq. (44) gives the electrical equivalent of the reaction kinetics, i.e. the adsorption resistance:

$$1/R_{\text{ads}} = F^2\Gamma_m k/(RT) (1 - \theta_0)^{1-\alpha} \theta_0^\alpha (c_A/c^s)^{1-\alpha} \quad (48)$$

The time constant is obtained from Eqs. (46)–(48) as

$$\tau_{\text{ads}} = C_{\text{ads}}R_{\text{ads}}.$$

Analogous derivations to the above were made for non-ideal adsorption described by the Frumkin adsorption isotherm and the final formulae were reported, among others, in Ref. [28].

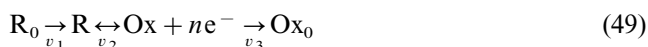
The difference between state variables and the kinetic variables in the rate equation has to be noted here. In the evolution (rate) Eq. (43) both state variables ( $c_A$  and  $\theta$ ) and control (input) variable  $E$  are used as kinetic variables. The state variables alone suffice to define the steady-state but both state and input variables are needed to define the transient state. The combination of these two concepts is involved in the electrochemical immittance [24] (this is possibly the main difficulty in its apprehension by the novice) in

which a small non-steady-state (transient) ac signal expressed by a kinetic equation [37] is superimposed on the steady-state (in terms of large signals) which is governed by the equation of state  $f(x, y) = 0$  following from zeroing the evolution Eq. (1).

We consider it as unjustified to use the term state variables for all kinetic variables as was done, e.g. in Ref. [16].

#### 5.4. Simple redox with ad- and out-transport

We consider the process of  $n$ -electron oxidation of R to Ox at the electrode with transport of R to the surface and Ox away from the surface by diffusion through diffusion layers of thickness  $\delta_R$  or  $\delta_{\text{Ox}}$ :



index 0 denotes bulk and equilibrium concentrations. The rates of individual steps are:

$$v_1 = k_{\text{DR}}(c_{\text{R}_0} - c_{\text{R}}) = -k_{\text{DR}}\Delta c_{\text{R}} \quad (50)$$

$$\begin{aligned} v_2 = k \{ c_{\text{R}}/c_{\text{R}_0} \exp [\alpha nF(E - E^s)/RT] \\ - c_{\text{Ox}}/c_{\text{Ox}_0} \exp [(\alpha - 1)nF(E - E^s)/RT] \} \end{aligned} \quad (51)$$

$$v_3 = k_{\text{DOx}}(c_{\text{Ox}} - c_{\text{Ox}_0}) = k_{\text{DOx}}\Delta c_{\text{Ox}} \quad (52)$$

Conservation laws enter here as the balance equations of R and Ox components in the diffusion layers  $\delta_R$  and  $\delta_{\text{Ox}}$ :

$$d\Delta c_{\text{R}}/dt = (v_1 - v_2)/\delta_R \quad (53)$$

$$d\Delta c_{\text{Ox}}/dt = (v_2 - v_3)/\delta_{\text{Ox}} \quad (54)$$

It is rational to select  $\Delta c_{\text{R}}$  and  $\Delta c_{\text{Ox}}$  as state variables because the conservation Eq. (53) and Eq. (54) affect them directly. For the sake of computational flexibility it is expedient however to define their dimensionless equivalents:  $x_1 = \Delta c_{\text{R}}/c_{\text{R}_0}$  and  $x_2 = \Delta c_{\text{Ox}}/c_{\text{Ox}_0}$ . With these dimensionless state variables the final form of the evolution equations is:

$$dx_1/dt = (v_1 - v_2)/(\delta_R c_{\text{R}_0}) \quad (55)$$

$$dx_2/dt = (v_2 - v_3)/(\delta_{\text{Ox}} c_{\text{Ox}_0}) \quad (56)$$

and then:

$$v_1 = -k_{\text{DR}}c_{\text{R}_0}x_1 \quad (57)$$

$$\begin{aligned} v_2 = k \{ (x_1 + 1) \exp [\alpha nF(E - E^s)/RT] \\ - (x_2 + 1) \exp [(\alpha - 1)nF(E - E^s)/RT] \} \end{aligned} \quad (58)$$

$$v_3 = k_{\text{DOx}}c_{\text{Ox}_0}x_2 \quad (59)$$

The output variable is current density:

$$j = nFv_2 \quad (60)$$

With the electrode potential  $E$  and the thickness of the diffusion layers  $\delta_R$  and  $\delta_{\text{Ox}}$  (on electrodes with controlled diffusion/convection such as a rotating disc,

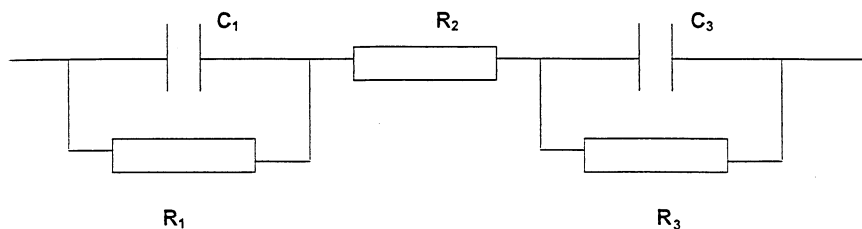


Fig. 2. Equivalent circuit of simple redox with ad and out-transport (case 4 of electrochemical examples).

impinging jet, microelectrode, etc.) taken as control variables, Eq. (55) and Eq. (56) with allowance for Eqs. (57)–(59) conform to definitions (1) and (2). For any form of input  $E(t)$ , the evolution Eqs. (55) and (56) can be integrated to give the evolution of the state represented by the functions  $x_1 = x_1(t)$  and  $x_2 = x_2(t)$ . These substituted into Eqs. (58) and (60) give the current transient  $j = j(t)$  as the output variable.

The steady-state is obtained as the one with  $dx_1/dt = dx_2/dt = 0$ . These conditions applied to Eqs. (55)–(60) give the classical polarization curve [3], i.e. the steady-state relation  $j_{ss} = j_{ss}(E)$ :

$$j_{ss} = nF(k \{ \exp[(\alpha F(E - E^s)/RT)] - \exp[(\alpha - 1)F(E - E^s)/RT] \} \times (1 + (k/k_{\text{DOx}} c_{\text{Ox}_0}) \exp[(\alpha F(E - E^s))/RT] + (k/k_{\text{DR}} c_{\text{R}_0}) \exp[(\alpha - 1)F(E - E^s)/RT])^{-1} \quad (61)$$

Dimensionless notation was abandoned here to get direct comparison with traditional formulae [1–5].

Due to the openness of the system (flow-through reactor analogy) definitions of the equivalent capacitance and resistance of the process are not so straightforward as in previous examples and require the standard procedure of small signal analysis of electrochemical systems [37].

Let us cast Eq. (58) in its most general form of kinetic equation involving as kinetic variables both state and control variables:

$$v_2 = v_2(x_1, x_2, E) \quad (62)$$

Its time derivative:

$$dv_2/dt = (\partial v_2/\partial x_1) (dx_1/dt) + (\partial v_2/\partial x_2) (dx_2/dt) + (\partial v_2/\partial E) (dE/dt) \quad (63)$$

and the Laplace transform in the steady-state:

$$\bar{s}v_2 = p_1 \bar{s}x_1 + p_2 \bar{s}x_2 + g \bar{s}E \quad (64)$$

where  $p_1 = \partial v_2/\partial x_1$ ;  $p_2 = \partial v_2/\partial x_2$ ,  $g = \partial v_2/\partial E$ ,  $s$ -complex angular frequency or Laplace operator; barred symbols are variables in the complex frequency (Laplace) domain.

Analogously for  $x_1$  and  $x_2$ :

$$s\bar{x}_1 = -\frac{k_{\text{DR}}}{\delta_{\text{R}}} \bar{x}_1 - \frac{\bar{v}_2}{\delta_{\text{R}} c_{\text{R}_0}} \quad (65)$$

$$s\bar{x}_2 = -\frac{k_{\text{DOx}}}{\delta_{\text{Ox}}} \bar{x}_2 + \frac{\bar{v}_2}{\delta_{\text{Ox}} c_{\text{Ox}_0}} \quad (66)$$

Substitution of Eq. (65) and Eq. (66) into Eq. (64) with allowance for Eq. (60) gives the operational impedance:

$$Z(s) = \bar{E}/\bar{j} = \frac{1}{nF} \left[ \frac{1}{g} + \frac{p_1/g \delta_{\text{R}} c_{\text{R}_0}}{s + k_{\text{DR}}/\delta_{\text{R}}} - \frac{p_2/g \delta_{\text{Ox}} c_{\text{Ox}_0}}{s + k_{\text{DOx}}/\delta_{\text{Ox}}} \right] \quad (67)$$

and this corresponds to the equivalent electrical circuit shown in Fig. 2. with its elements defined by:

$$1/R_2 = nFg; \quad (68)$$

$$\tau_1 = R_1 C_1 = \delta_{\text{R}}/k_{\text{DR}}; \quad C_1 = nFg \delta_{\text{R}} c_{\text{R}_0}/p_1 \quad (69)$$

$$\tau_3 = R_3 C_3 = \delta_{\text{Ox}}/k_{\text{DOx}}; \quad C_3 = -nFg \delta_{\text{Ox}} c_{\text{Ox}_0}/p_2 \quad (70)$$

The impedance Eq. (67) and its electrical model in Fig. 2 illustrate the fact that the system is of second degree since it has two ‘capacitances’ or two ways of accumulation of energy represented by state variables  $x_1$  and  $x_2$ .

It has to be noted that reaction resistance  $R_2$  and time constants  $\tau_1$  and  $\tau_3$  have simple physical significance:  $1/R_2$  is the slope of the Butler–Volmer equation;  $\tau_1$  and  $\tau_3$  are the residence times in the diffusion layers.

The minus sign in the expression for  $C_3$  is related to the negative, in general, value of the  $p_2$  parameter and consequently all elements of the equivalent circuit are usually positive, the system is stable and its relaxation is decaying.

Due to the openness of the system, i.e. the presence of fluxes (flow-through electrochemical reactor) the steady-state is now not necessarily the equilibrium state and definition of differential parameters: capacitance, resistance and time constant-their product, pertain now to the steady-state. The parameters defined by Eqs. (68)–(70) evolve together with evolution of the state defined by variations of state variables  $x_1(t)$ ,  $x_2(t)$ . We would not recommend now (in contrast to our earlier position [38,39]) considering the values defined in Eqs. (68)–(70) as resistance, capacitance or time constant proper when the system is out of the steady-state, i.e. in the course of transient evolution from one steady-state to another. When the time invariance condition is not

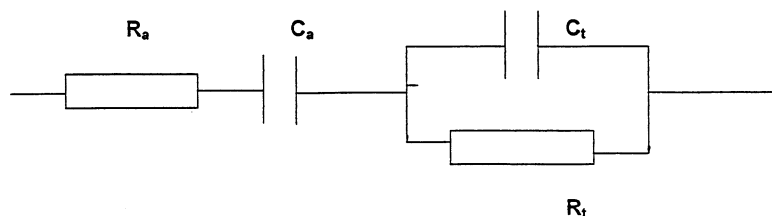


Fig. 3. Equivalent circuit of the electrochemical adsorption with transport (case 5 of electrochemical examples).

fulfilled in the time scale comparable to the steady-state values of time constants  $\tau_1$  and  $\tau_2$ , the parameters defined by Eqs. (68)–(70) should be considered merely as differential parameters. The proper significance of  $C$ ,  $R$  and  $\tau$  is regained only when the system is stabilized in the new steady-state, i.e. in time invariant conditions. This point will be further addressed in the discussion below.

The non-equilibrium character of the steady-state is reflected in dependence of  $R$  and  $C$  elements on kinetic parameters. This is in contrast to equilibrium conditions when  $C$  is purely a thermodynamic variable, dependent only on equilibrium parameters of the partial processes with all kinetic information limited to  $R$ . It is mathematically exhibited in the impedance Eq. (67) by the terms:

$$g/p_1 = (\partial v_2/\partial E)(\partial x_1/\partial v_2); g/p_2 = (\partial v_2/\partial E_2)(\partial x_2/\partial v_2) \quad (71)$$

which depend on kinetics and are involved in definitions of  $C_1$  and  $C_3$  in Eqs. (69) and (70).

Only in the equilibrium state can these last expressions Eq. (71) be transformed to purely thermodynamic variables (slopes) as:  $-\partial x_1/\partial E$  and  $-\partial x_2/\partial E$ . In the steady-states the original, kinetics-dependent forms of expressions Eq. (71) are valid. In this context we recommend the relevant comments in [40] on p. 4 concerning Eq. (25) in that reference.

### 5.5. Electrochemical adsorption reaction with ad-transport



This reaction was analyzed in part already in example (3) but here it is preceded by the ad-transport of reagent A which patterns exactly the transport steps presented in example (4) in the context of rate Eqs. (57) and (59).

The rate of the transport in diffusion layer approximation is:

$$v_t = k_D(c_{A_0} - c_A) = -k_D c_{A_0} x \quad (73)$$

where  $x = (c_A - c_{A_0})/c_{A_0}$ .

The rate of the electrode reaction proper:

$$v = k \{ c_{A_0}/c^s(x+1)(1-\theta) \exp[\alpha F(E-E^s)/RT] - \theta \exp[(\alpha-1)F(E-E^s)/RT] \} \quad (74)$$

where the standard state is the equilibrium state with  $c_{A_0} = c^s$ ;  $\theta = 0.5$  and  $E_0 = E^s$  (see example (iii)).

The state of the system is most suitably characterized by the evolution of dimensionless variables  $x$  and  $\theta$ :

$$dx/dt = (v_t - v)/(\delta c_{A_0}) = k_D x/\delta - v(x, \theta, E)/(\delta c_{A_0}) \quad (75)$$

$$d\theta/dt = v(x, \theta, E)/\Gamma_m \quad (76)$$

As usual, the output variable is current density  $j$  according to Eq. (44); the potential  $E$  and possibly the diffusion layer thickness  $\delta$  (controlled convection) are control variables. With these premises Eqs. (75) and (76) conform to the scheme defined by Eqs. (1) and (2) and for any form of  $E(t)$  input, they can be integrated to give the state evolution as a pair of functions  $\{x = x(t), \theta = \theta(t)\}$ .

The steady-state is put to zero for Eqs. (75) and (76) and this gives  $v_t - v = 0$  and hence  $v_t = 0$ ,  $v = 0$  and also  $x = 0$  and it is seen that the steady-state is here only at equilibrium and the formulae related to the equilibrium state in example (iii) are valid also here.

The linear response of the reaction is again available by Laplace transformation of the evolution equations slightly perturbed around the steady-state:

$$s\bar{x} = (k_D/\delta)\bar{x} - \bar{v} \quad (77)$$

$$sv = p\bar{s}\bar{x} + w\bar{v} + g\bar{s}\bar{E} \quad (78)$$

where the barred symbols are Laplace-transformed variables,  $s$  is the complex angular frequency.

$$p = \partial v/\partial x; w = \partial v/\partial \theta; g = \partial v/\partial E \quad (79)$$

Allowing for  $j = Fv$  we obtain from Eqs. (77) and (78) the equivalent impedance:

$$Z(s) = \frac{\bar{E}}{j} = \left( \frac{1}{g} - \frac{w}{sg} + \frac{p/g}{s - k_D/\delta} \right) / F \quad (80)$$

and this is equivalent to the impedance of the electrical analog in Fig. 3 which is intuitively acceptable considering that the series subcircuit  $R_a - C_a$  represents electrochemical adsorption and the parallel subcircuit  $R_t || C_t$  represents transport in diffusion layer.

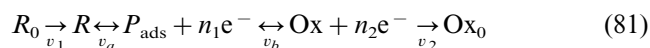
The impedance function Eq. (80) and its electrical model in Fig. 3 illustrate the fact that the system in this example has second degree, i.e. it has two 'capacitances' or two ways of accumulation represented by state variables  $x$  and  $\theta$ .

It is appropriate to note here that electrical equivalent circuits are good and intuitive models of the physical events when individual steps are separated in space such as a transport of reagents taking place in the electrolyte adjacent to the metal surface and a charge transfer occurring on the surface. The transport ( $R_t||C_t$ ) and surface process ( $R_a - C_a$ ) in Fig. 3 although separated in real conditions and in the electrical model in Fig. 3 are not independent, as being linked by the common parameter  $g$  representing the charge transfer kinetics according to Eq. (79). This linkage is effectively the same as the case of kinetic-infinite diffusion coupling discussed thoroughly by de Levie et al. [48,49] but it is easier to apprehend for 'localised' transport conditions as in the Nernst diffusion layer approximation applied here.

The elements of the equivalent circuit in Fig. 3 can be uniquely attributed to the equilibria ( $C$ ) and kinetics ( $R$ ) of individual elementary processes separated in space. Such separation of electrical elements pertaining to individual steps of the complex reaction is usually not feasible when two or more elementary processes take place on the surface as is the case with an electrocatalytic reaction, i.e. two steps of charge transfer with adsorption of the intermediate [28,37].

### 5.6. Electrocatalytic reaction with transport

This is the last and the most complex of our electrochemical examples. Its evolution equations and their consequences are only sketched here and the extensive analysis of a simple electrocatalytic reaction will be presented elsewhere [41,42].



The rate equations assuming the diffusion layer approximation and Langmuir adsorption isotherm are as follows:

$$v_1 = -k_{\text{DR}} c_{\text{R}_0} x_1 \quad (82)$$

$$v_2 = k_{\text{DOx}} c_{\text{Ox}_0} x_2 \quad (83)$$

with

$$x_1 = (c_{\text{R}} - c_{\text{R}_0})/c_{\text{R}_0}; x_2 = (c_{\text{Ox}} - c_{\text{Ox}_0})/c_{\text{Ox}_0} \quad (84)$$

$$v_a = k_a \left\{ \frac{c_{\text{R}}}{c_{\text{R}}^s} (1 - \theta) \exp[\alpha_a n_1 F(E - E_a^s)/RT] - \theta \exp[(\alpha_a - 1) n_1 F(E - E_a^s)/RT] \right\} \quad (85)$$

$$v_b = k_b \left\{ \theta \exp[\alpha_b n_2 F(E - E_b^s)/RT] - \frac{c_{\text{Ox}}}{c_{\text{Ox}}^s} (1 - \theta) \exp[(\alpha_b - 1) n_2 F(E - E_b^s)/RT] \right\} \quad (86)$$

This is the system of third order and in accordance with our practice in previous examples, we adopt  $x_1$ ,  $x_2$  and  $\theta$  as state variables. The evolution equations are:

$$\frac{dx_1}{dt} = \frac{v_1 - v_a}{\delta_{\text{R}} c_{\text{R}_0}} = -\frac{k_{\text{DR}}}{\delta_{\text{R}}} x_1 - \frac{v_a}{\delta_{\text{R}} c_{\text{R}_0}} \quad (87)$$

$$\frac{dx_2}{dt} = \frac{v_b - v_2}{\delta_{\text{Ox}} c_{\text{Ox}_0}} = -\frac{k_{\text{DOx}}}{\delta_{\text{Ox}}} x_2 - \frac{v_b}{\delta_{\text{Ox}} c_{\text{Ox}_0}} \quad (88)$$

$$d\theta/dt = (v_a - v_b)/\Gamma_m \quad (89)$$

As usually, the current density is the output variable according to:

$$j = F(n_a v_a + n_2 v_b) \quad (90)$$

The potential  $E$  and, possibly (in controlled convection experiments),  $\delta_{\text{R}}$ ,  $\delta_{\text{Ox}}$  are control variables. With these premises Eqs. (87)–(90) conform to the scheme defined by Eq. (1) and Eq. (2). For any form of the input function  $E(t)$ , they can be integrated numerically to give the state evolution represented by the vector of functions  $\{x_1 = x_1(t), x_2 = x_2(t), \theta = \theta(t)\}$ .

The steady-state is for Eqs. (87)–(89) equal to zero and this gives  $v_1 = v_a = v_b = v_2 = v_{\text{ss}}$ . Insofar as the system is open to fluxes  $v_1$  and  $v_2$ , the state variables  $x_1$ ,  $x_2$  and  $\theta$  can be eliminated from steady-state equations and the function  $v_{\text{ss}} = v_{\text{ss}}(E)$  may be obtained with numerous parameters ( $k_a$ ,  $k_b$ ,  $k_{\text{DR}}$ ,  $k_{\text{DOx}}$  etc.). The explicit form of such a function, although derivable from steady-state equations, is tedious and very lengthy and is not reported here.

A particular case of the steady-state is the equilibrium for which  $v_{\text{ss}} = 0$  and  $E_{\text{ss}} = E_0$ ,  $E_0$  being the equilibrium potential of the overall reaction of bulk components:



where  $n = n_a + n_b$ .

For the equilibrium state:

$$\frac{1 - \theta}{\theta} \frac{c_{\text{R}_0}}{c_{\text{R}}^s} \exp\left[\frac{n_a F(E_0 - E_a^s)}{RT}\right] = 1 \quad (92)$$

$$\frac{\theta}{1 - \theta} \frac{c_{\text{Ox}}^s}{c_{\text{Ox}_0}} \exp\left[\frac{n_b F(E_0 - E_b^s)}{RT}\right] = 1 \quad (93)$$

and from this follows the equilibrium potential of the overall reaction:

$$E_0 = \frac{n_a E_a^s + n_b E_b^s}{n_a + n_b} + \frac{RT}{(n_a + n_b)F} \ln \left[ \frac{c_{\text{Ox}_0} c_{\text{R}}^s}{c_{\text{Ox}}^s c_{\text{R}_0}} \right] \quad (94)$$

Consequently, the relation between the standard potential of the overall reaction (Eq. (81)) and the standard potentials of partial reactions is:

$$nE^s = n_a E_a^s + n_b E_b^s \quad (95)$$

To determine the equivalent capacitances and the time constants of the process in question one has to recourse again to the Laplace operational calculus. The final immittance formula derivable in explicit form is very lengthy and will not be presented here. Suffice it to say that it demonstrates the third order of the system as follows merely from the number of three state variables and their evolution equations Eqs. (87)–(89). We were unable to relate the immittance function directly and intuitively to any electrical model whose elements represent uniquely individual steps of the reaction. It can be obviously represented by an arbitrary electrical circuit of the third order such as the canonical Cauer circuit [25] ('ladder circuit' [24]) but its elements have no direct relevance to system parameters and such a model has to be looked at merely as a measurement model according to Ref. [43] (see also my note at the end of Section 5.5).

## 6. Discussion

The state variable approach allows comprehensive dealing with the electrochemical dynamics as a part of the uniform approach of deterministic system dynamics. All the specificity of the systems' evolution is then simplified to the mathematical properties of differential equations governing this evolution. This allows the global analysis [9,41,42] of the systems' dynamics revealing the structure of the complex process, i.e. interdependence of its individual steps of charge transfer, mass and charge fluxes, variations of intermediates' concentration, all this without going into details of the kinetics of the individual steps. In this sense, the state variable approach in time domain (global) is somewhat analogous to the common way of linear (local) analysis of electrochemical systems originated by Melik-Gaykazyan and Frumkin [44], further developed (electrochemical impedance, in the frequency domain only) by Lorenz and Moeckel [45] and many others and fully elaborated by Armstrong et al. [37]. The common feature of these approaches is that initially they do not require detailed information about kinetics of individual steps but rely on the knowledge of (or rational assumption about) the structure of the complex reaction i.e. on interdependence of concentrations of reagents and intermediates as functions of time. This includes their differentiation or integration in the time domain which for a linear approach in the complex frequency (Laplace) domain is equivalent to multiplication or division by the complex angular frequency (Laplace domain variable  $s$ ) or simply by  $s = i\omega$  in the real frequency domain. The structural analysis both in large signal (non-linear, global) and small signal (linear, local) implementation is based on conservation laws. This is the case with linear equations formulated for immittance analysis [37,44,45] where linear equations

have the form of balance equations, analogous to conservation Eq. (1) or Eq. (3) in this paper but transformed into the linear, complex frequency domain.

An additional advantage of the state variable approach is that it reveals the similarity of diverse systems having analogous forms of evolution equations and, in particular, the similarity of electrochemical systems to electric circuits which is the basis of modelling by equivalent circuits [22–24].

For closed systems, i.e. systems without steady-state fluxes (similar to batch reactors) the steady-state is the state of thermodynamic equilibrium. With the judicious choice of electrochemical state variables such as charges  $Q_i$  or their mass equivalents according to Faraday's law, coverage, concentration etc. and with the electrode potential  $E$  as the control variable, there is a direct and intuitive definition of steady-state capacitances as  $C_i = [\partial Q_i / \partial E]_{ss}$ . With the current taken as output variable there is direct definition of the equivalent steady-state resistance characterising the system's kinetics:  $R^{-1} = [\partial I / \partial E]_{ss}$ . The time constant of the relaxation of such a system when driven slightly out of its steady-state is  $\tau = RC$  and its positive value serves as the stability criterion of the system's steady-state.

Definitions of equivalent capacitances  $C_i$  and resistances  $R_i$  involve, in the general steady-state, both the thermodynamic and the kinetic parameters of the process. In the particular state of true equilibrium (no fluxes) equivalent capacitances  $C_i$  revert to purely equilibrium variables defined only in terms of thermodynamic parameters.

On the other hand, when the system is out of the steady-state and derivatives denoted as  $C_i$  and  $R_i$  above are calculated in terms of state and input variables, these values in most cases evolve together with the system. We prefer and recommend now to consider derivatives denoted as  $C_i$  and  $R_i$  out of the steady-state, i.e. in time-variant conditions, merely as differential parameters according to their definitions (for instance Eqs. (68)–(70)) and to preserve the significance of capacitances, resistances and time constants ( $C$ ,  $R$  and  $\tau$ ) to these derivatives only when they are stabilised in the new steady-state. This is contrary to our earlier understanding of concepts of equivalent capacitance and resistance in the linear approximation also under transient conditions [46]. It can be shown [47] that for many electrochemical systems the very measurement of ac immittance is not feasible in transient conditions because the time required for single ac measurement at the lowest frequency is sufficiently long for the system to evolve considerably and change its state.

Electrical examples, despite looking trivial, help to specify the concepts of steady-state and equilibrium versus transient states of the system, illustrate the judicious selection of state variables and their distinction from kinetic variables.

The electrochemical examples cover the broad range

of electrochemical systems from Sections 5.1 and 5.2 which may seem trivial to quite complex such as the case in Section 5.6 of electrocatalytic reaction of ad and out-transport of reagents which is the prototype of hydrogen evolution/oxidation with Nernst layer approximation for transport kinetics. This latter case whereas quite complex in itself, is far from the complexity of real electrocatalytic processes of organic species and its evolution equations can be solved only by numerical integration. The rational selection of state variables based on conservation laws makes such integration feasible and assures that in specifying their evolution, we specify in fact the evolution of the system as a whole.

The difference has to be noted between state variables and the kinetic variables involved in evolution equations. The state variables determine the steady-state of any system, also the electrochemical one, and together with input (control) variables they determine the system's evolution, i.e. its states in the future. Kinetic variables combining usually both state and control variables, determine the rate of the evolution. Their selection and number are not restricted by the strict rules relevant to state variables. Mistaking kinetic variables for state variables may lead to erroneous conclusions [16].

The electrochemical examples presented here can be also looked at as building blocks for more complex systems such as a complete galvanic cell combined from two half-cells from the example in Section 5.3 with a proper account for transport processes at the junction e.g. the transport of counterions.

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