

## NON-LINEAR PROPERTIES OF ELECTROCHEMICAL SYSTEMS

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### INTRODUCTION

Electrochemical processes proceeding at the interface of electrode/electrolyte involve, as a rule, several steps. The main of them are as follows: a charge transfer process, mass transport of electrically active species or products of its electrochemical transformation, chemical reactions taking place both in the bulk of solution and at the electrode surface. One of the processes is commonly a rate-determining step, while other steps may proceed under conditions approaching an equilibrium state.

Each of the processes mentioned has its own mathematical description in terms of non-linear differential equations or involving such non-linear elements as *e.g.* charge transfer resistance or frequency-dependent capacitors, *etc.* [1].

An account of non-linear properties of electrochemical systems is often rather complicated from mathematical point of view. Therefore, most of investigation methods take advantage of a low-level perturbation which allows the electrochemical characteristics to be linearized. When, *e.g.*, the system is perturbed by means of an alternating current, an amplitude of the latter is required to be significantly smaller than  $RT/F$  [1] ( $R$  is the gas constant,  $T$  is the absolute temperature and  $F$  is the faraday). This value is *ca* 25 mV at a room temperature. Alternatively, the revealing of non-linear properties is the way to characterize most adequately electrochemical processes.

The present paper deals with the analysis of some non-linear effects which are related to different steps of a net electrochemical process.

### NON-LINEARITY OF VOLTAMMOGRAM OF THE CHARGE TRANSFER PROCESS

The rate of the redox process



is characterized by the exchange current density  $i_0$  under equilibrium conditions and by the current density  $i$  at non-zero overvoltage  $\eta$ . The well-known kinetic relationship for process (1) may be written as follows [1]:

$$i = i_0 \left\{ \frac{[\text{R}]_s}{[\text{R}]_b} \exp\left(\frac{\alpha_a n F}{RT} \eta\right) - \frac{[\text{O}]_s}{[\text{O}]_b} \exp\left(-\frac{\alpha_c n F}{RT} \eta\right) \right\}, \quad (2)$$

where subscripts  $s$  and  $b$  indicate the surface and bulk concentrations of species given in square brackets,  $\alpha_a$  and  $\alpha_c$  are anodic and cathodic charge transfer coefficients, respectively. In the case of symmetric potential barrier,  $\alpha_a = \alpha_c = 0.5$ . If the mass transport phenomena are not taken into account, Eq. (2) may be rearranged to give the expression for faradaic current density  $i_F$ :

$$i_F = 2i_0 \sinh(k\eta), \quad (3)$$

where  $k = nF/2RT$ .

An equivalent circuit of the electrode may be conceived as the resistance  $R_F$  and the capacitance of double electric layer  $C_{dl}$  in parallel. The faradaic and non-faradaic currents flow along these elements, respectively. Then

$$d\eta/dt = [i - 2i_0 \sinh(k\eta)] / C_{dl}, \quad (4)$$

where  $i$  is total current density and  $t$  is time.

It is of interest to analyze such a simplified model in terms of faradaic impedance  $Z$ . The following relationship is valid in this case:

$$\square\square\square\square \quad Z(s) = \eta(s)/i(s),$$

(5)

where  $\eta(s)$  and  $i(s)$  are the Laplace transforms of  $\eta(t)$  and  $i(t)$ ,  $s$  is an imaginary part of complex variable. When the system is perturbed by the constant current pulse ( $i = \text{const}$ ) and exhibits linear properties ( $\eta \ll RT/nF$ ), it follows from the above equations that

$$Z(s) = R_0 \omega / (s + \omega), \quad (6)$$

where  $\omega = 2\pi f$  is an angular frequency of a sinusoidal oscillation and the resistance  $R_0$  is uniquely related to the exchange current density as follows:

$$R_0 = RT/nFi_0. \quad (7)$$

The above relations show that the response, as well as the perturbing signal, contains the only main harmonic of frequency  $\omega$ .

If  $\eta \gg RT/nF$ , impedance equations acquire a more complicated form [2]:

$$Z(p) = (ikp)^{-1} [F(1, p; p+1; x_1) - F(1, p; p+1; x_2)], \quad (8)$$

where

$$p = s / \sqrt{a^2 + b^2},$$

$$x_1 = a(\sqrt{a^2 + b^2} - a) / [b(\sqrt{a^2 + b^2} + b)],$$

$$x_2 = -a(\sqrt{a^2 + b^2} + a) / [b(\sqrt{a^2 + b^2} + b)],$$

$$a = ik/C_{dl},$$

$$b = 2i_0 k/C_{dl},$$

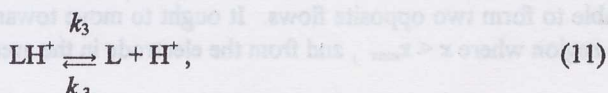
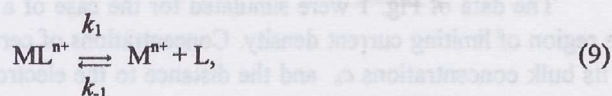
and  $F(x, y; z; u)$  refers to hypergeometric function. Its analysis seems to be a rather difficult problem in the case of complex arguments. Nevertheless, it is possible to conclude that the response would contain a number of higher harmonics, this being typical of non-linear systems.



## NON-LINEAR EFFECTS RELATED TO MASS TRANSPORT OF CHEMICALLY INTERACTING COMPONENTS

Regularities of mass transport become more complicated when chemical interactions between components are possible. Such a situation is typical of solutions involving complex compounds. The so-called CE-mechanism (chemical step + electrochemical step) must be analyzed in this case. Analytical solutions of this problem are available only in the case of chemical reactions of the first (or pseudo-first) order.

Let us consider the system involving complexes of metal,  $ML_j^{n+}$ , and some protonated forms of ligand,  $LH_m^{m+}$ . Then, the following chemical interactions are possible:



Rate constants,  $k$ , of direct and reverse processes are designated by positive and negative indexes respectively. To solve the mass transport problem, the second Fick's law supplemented by non-linear terms should be used. The latter terms reflect the formation or the decomposition rate of certain species in the course of chemical process. Such an equation written for species of  $M^{n+}$ , takes the following form:

$$\frac{\partial[M^{n+}]}{\partial t} = D \frac{\partial^2[M^{n+}]}{\partial x^2} + k_1 [ML^{n+}] - k_{-1} [M^{n+}][L]. \quad (14)$$

The term of  $k_1 [ML^{n+}]$  reflects the formation rate of  $M^{n+}$  ions according to the direct reaction (9) and is positive. Similarly, the term of  $k_{-1} [M^{n+}][L]$  reflects the exhaustion of  $M^{n+}$  ions in the reverse reaction (9) and is negative. The relationships for other species may be written in the same manner taking into account the fact that certain particles may participate in several chemical reactions:

$$\frac{\partial[ML^{n+}]}{\partial t} = D \frac{\partial^2[ML^{n+}]}{\partial x^2} + k_{-1} [M^{n+}][L] - k_1 [ML^{n+}] + k_2 [ML_2^{n+}] - k_{-2} [ML^{n+}][L], \quad (15)$$

$$\frac{\partial[ML_2^{n+}]}{\partial t} = D \frac{\partial^2[ML_2^{n+}]}{\partial x^2} + k_{-2}[ML^{n+}][L] - k_2[ML_2^{n+}], \quad (16)$$

$$\frac{\partial[L]}{\partial t} = D \frac{\partial^2[L]}{\partial x^2} + k_1[ML^{n+}] - k_{-1}[M^{n+}][L] + k_2[ML_2^{n+}] - k_{-2}[ML^{n+}][L] + k_3[LH^+] - k_{-3}[L][H^+] \quad (17)$$

and so on.

In addition, making use of material balance equations, the concentration profiles may be obtained for any species. This problem has been discussed in more detail in [3].

The data of Fig. 1 were simulated for the case of a steady-state electrolysis in the region of limiting current density. Concentrations of certain species are normalized to its bulk concentrations  $c_b$  and the distance to the electrode surface  $x$  is normalized to the thickness of diffusion layer  $\delta$ .

It must be emphasized that such profiles are possible only in the case of superposition of two processes, viz., diffusive mass transport and chemical interactions between transported particles. The profiles containing maxima are unfeasible in the absence of the latter process. It would be assumed then that a certain complex particle is able to form two opposite flows. It ought to move towards the electrode surface in the region where  $x < x_{max}$ , and from the electrode in the area where  $x > x_{max}$ .

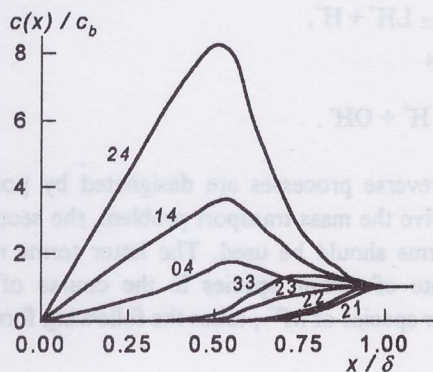


Fig. 1. Concentration profiles of Cu(II)-diethanolamine complexes  $Cu^{2+}(DEA)_p(OH)_q$ .

Bulk concentrations:

Cu(II) - 0.05 M

DEA - 0.2 M

pH = 10,

$p$  and  $q$  values are given at corresponding curves

## OSCILLATIONS IN ELECTROCHEMICAL SYSTEMS

Up to the present, the periodic phenomena involved in a variety of electrochemical systems have been the subject of many investigations. Current or potential oscillations were observed both under cathodic and anodic polarization conditions. A comprehensive review of papers in this field is given in, e.g., [4,5].

Recent mathematical models deal with a set of coupled differential equations, analyzing their stability and bifurcation properties. According to some simplified



models, two conditions should be fulfilled for oscillations to appear. The first of them requires that the voltammogram should have a section with a negative slope in a certain potential range.

The investigation of copper and tin codeposition has been carried out using sulphate solutions with Laprol 2402C as a surface-active substance [6]. The latter compound constitutes a product of copolymerization of ethylene and propene oxides, with molecular mass of ca 3200. A negative slope of voltammograms is observed at  $E \approx -0.2$  V for such solutions (Fig. 2). A negative value of polarization resistance in the above range points to a negative value of faradaic impedance ( $Z_F < 0$ ) at sufficiently low frequencies. This conclusion is confirmed by direct impedance measurements (Fig. 3). The reasons for such a behaviour are conditioned by adsorption of a surface-active substance resulting in the process inhibition.

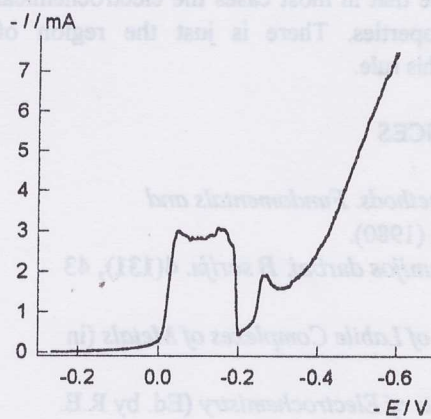


Fig. 2. Typical cathodic voltammogram of codeposition of Cu and Sn in the solutions involving Laprol 2402 C as a surface-active substance. The electrode surface area is equal to  $0.3 \text{ cm}^2$ .

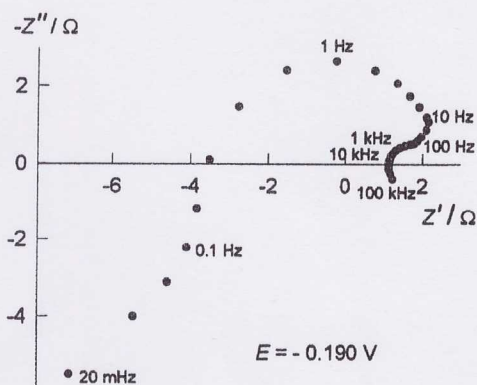


Fig. 3. Real  $Z'$  and imaginary  $Z''$  components of faradaic impedance obtained in the region of negative slope of voltammograms. The alternating current frequency is given at some points.

The second condition requires that the resistance  $R_s$  in series with faradaic impedance shunted by the double layer capacity should be higher than the absolute value of  $Z_F$  ( $R_s > |Z_F|$ ). The ohmic resistance of either the solution or the passivating layer as well as the external resistance in series with an electrochemical cell may be included in the  $R_s$  value. The  $R_s$  value in the system under investigation may be varied in several ways. One method involves the usage of an external resistance in series with the electrochemical cell. This leads to the shift of impedance plot to the right, so that this plot passes the origin at a certain frequency. Then the system exhibits current oscillations with the same frequency. The observed oscillations are rather stable and their amplitude grows continuously from zero, this being typical of supercritical Hopf bifurcation.

The above examples allow to conclude that in most cases the electrochemical systems exhibit well-defined non-linear properties. There is just the region of sufficiently low overvoltages exempted from this rule.

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