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Equivalent circuits for electrochemical reaction involving consecutive charge transfer steps

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Two different equivalent circuits can be derived from kinetic equations obtained for consecutive charge transfer with the formation of soluble intermediate. Their description codes are: $R_\infty(R_1W_1)(C_2W_2)$ and $([R_3W_3][R_4W_4])$ (elements in series are given in square brackets, and elements in parallel are enclosed in parentheses). Both circuits are indistinguishable, if and only if a certain interrelation between R_1,W_1, W_2 and C_2 is satisfied. Then, upon a proper choice of parameters, both EC display the same impedance spectrum at all frequencies. All faradaic elements are interrelated and each of them depends on the characteristics of the overall process. Neither of EC elements can be attributed to the separate charge transfer step. Though the EIS data obtained for the Cu|Cu(II) system can be described by either of the two EC, the second EC is preferred due to its simplicity and more clear physical sense.

Keywords: Electrochemical impedance spectroscopy, consecutive charge transfer, equivalent circuit, copper(II) reduction.

INTRODUCTION

Consecutive charge transfer steps are typical of the most electrochemical processes including deposition and dissolution of metals. To study processes of this kind, different transient techniques were applied, including the electrochemical impedance spectroscopy (EIS). A proper analysis of impedance spectra makes it possible to determine the kinetic parameters simultaneously with the characteristics of the double electric layer. In so doing, the adequate equivalent circuits (EC), comprising characteristic features of the system, are commonly employed. However, sometimes they lack substantiation and, as a consequence, the physical meaning of EC elements is treated at random. Recently the utility and limitations of using equivalent circuits to analyse EIS data for electrochemical reaction mechanisms have been reviewed [1]. We sustain the position [1, 2] that the preferable circuits should follow from the mathematical expressions derived for the appropriate theoretical models.

In this communication, we focus on the case of step-wise charge transfer processes involving the formation of stable, solution-soluble intermediate that is capable of diffusing from/towards the bulk of solution.

The consecutive charge transfer involving adsorption steps has been considered by Grafov [3] and a rather complicated EC containing 11 elements was obtained. More simple cases arise when the elctrochemical process is controlled by charge transfer and diffusion and adsorption steps are ignored. In previous studies, a theoretical analysis of the faradaic impedance has been performed provided that the final product is also soluble [4-6]. Next, the relationships obtained in Ref. [4] have been extended for the case when an insoluble final product (e.g., metal deposit) is formed [7]. No EC was proposed in the previous investigations [4, 5] until it was found [6] that the general impedance expression corresponds to an equivalent circuit consisting of five elements that, according to the authors, “have no sensible physical meaning”. At the same time, we proposed another EC [8], which rigorously followed from analytical expressions and contained less sub-circuits. So, two different EC have been proposed for description of the same mechanism.

To avoid confusion in this situation, we made an attempt to analyze both EC so as to clarify their possible interrelation. Theoretical regularities are compared with EIS data obtained for real Cu|Cu(II) system capable of generating stable intermediate Cu^+ ions. Surfactant-free Cu(II) solutions were selected in an effort to minimize adsorption effects. EIS characteristics of the processes involving adsorption of intermediates are available elsewhere [9].

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EXPERIMENTAL

Solutions were prepared using thrice-distilled water, $CuSO_4 \cdot 5H_2O$ (Mallinckrodt, USA, chlorides less than 0.005%), and H_2SO_4 (high purity, Reakhim Russia) as a supporting electrolyte. They were deaerated before experiments with argon stream over 0.5 h. To prepare the working electrodes, a Pt wire of 0.36 cm^2 surface area was coated with 5–7 µm thick copper in the solution containing (g dm^{-3}): $Cu_2SO_4 \cdot 5\ H_2O$ – 250, H_2SO_4 – 50. Polycrystalline layer with well-exhibited crystallographic edges and faces was formed. Copper crystallites as large as 1–4 µm imparted a particular roughness of the surface.

Impedance measurements were carried out under potentiostatic conditions at the open-circuit potential within the frequency (f) range from 0.05 to 5×10^4 Hz, using a Zahner Elektrik (Germany) IM6 impedance spectrum analyzer. The amplitude of the imposed sinusoidal perturbation of the electrode potential was 5 mV. Computer programs elaborated by Boukamp [10] were used for analyzing impedance spectra.

The electrode potential E was measured in reference to the Ag | AgCl | KCl(sat) electrode and was converted to the standard hydrogen scale. All experiments were performed at 20 °C.

RESULTS AND DISCUSSION

As has been reported [6], the faradaic admittance, derived by Armstrong and Firman [5] for the mechanism $O + e \rightleftarrows Y$, $Y + e \rightleftarrows R$, can be expressed as

$$Y_F = Z_F^{-1} = R_\infty^{-1}\left(1 + b/\sqrt{s}\right)/\left(1 + c/\sqrt{s} + d/s\right), \quad (1)$$

where the complex variable $s = i\omega$; i and ω stand for the imaginary unit and angular frequency, respectively. Notice that the general relationship obtained by Despić et al [4] also takes this form.

Generally, equivalent circuits contain constant phase elements (CPE) with the admittance $Y = Y_0 s^n$. The CPE transforms into resistance (R), Warburg impedance (W), capacitance (C), or inductance (L), when the exponent n takes the value of 0, 0.5, 1 or -1 respectively [9]. Accordingly, the admittance of the specified circuit elements may be written as $1/R$, $Y_0\sqrt{s}$ Cs or $1/Ls$. When analogous terms are found in the impedance expression, there is no difficulty in understanding the structure of the adequate EC. Hence, to discover the EC compatible with Eq. (1), the certain its rearrangements should be made.

The analysis performed shows (for details see Appendix) that two different EC follow from Eq. (1). The faradaic subcircuit of the first EC was composed by Rueda et al [6]. Upon supplementing with non-faradaic elements, this EC N1 takes form shown in the upper part of Fig. 1. According to Boukamp [10], its description code may be written as: $R_\Omega([R_\infty(R_1W_1)(C_2W_2)]Z_{dl})$. Here, elements in series are given in square brackets, and elements in parallel are enclosed in parentheses.

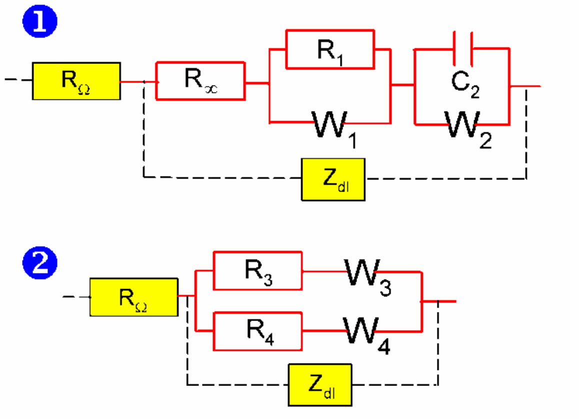

Fig. 1. Two equivalent circuits for consecutive transfer of two electrons. Faradaic elements are connected with solid lines. The ohmic resistance of the solution, R_Ω, and the double-layer impedance, Z_{dl}, are the non-faradaic elements

Though the magnitude and the frequency dependence of Y_F are essentially controlled by four parameters (see Eq. (1)), the faradaic subcircuit contains more (five) elements. For this reason, the specific link between faradaic EC elements occurs:

$$C_2 = R_1 Y_{01} Y_{02}, \quad (2)$$

where Y_{01} and Y_{02} are constants of the respective Warburg admittances (see above).

The faradaic circuit of another alternative EC N2 (lower part of Fig. 1) contains less (four) elements displaced in two parallel [RW] subcircuits. Both foregoing EC yield the same impedance spectra, if and only if the condition (2) is satisfied. As this takes place, the interrelation between elements of the two EC is given by equations (A.4)-(A.8). Besides, as the analysis shows, both circuits follow from Grafov's EC [3], when the adsorption states are neglected,

The ambiguity of EC is well known in the EIS theory. For instance, two different EC are also possible in the case of two sequential one-electron reaction steps with an adsorbed intermediate, in the absence of mass transport control [11]. They are completely interchangeable and can be transformed into each other. However, the case discussed in the present article is somewhat different owing to the constraint given by Eq. (2).

We made use of both EC in fitting experimental impedance spectra, obtained for Cu|Cu(II) system, where quite stable intermediate Cu^+ ions are formed. Considering the non-ideality of the working electrode, the CPE Q_{dl} was applied for representing the properties of the double layer. At the same time, to employ Eqns. (A.4)-(A.8),we tried to retain ideal faradaic elements W and C. Typical experimental result is shown in Fig. 2. The most part of Nyquist plot presents an arc centred below abscissa axis. On the elimination of non-faradaic elements, this arc constitutes a quarter of circle.

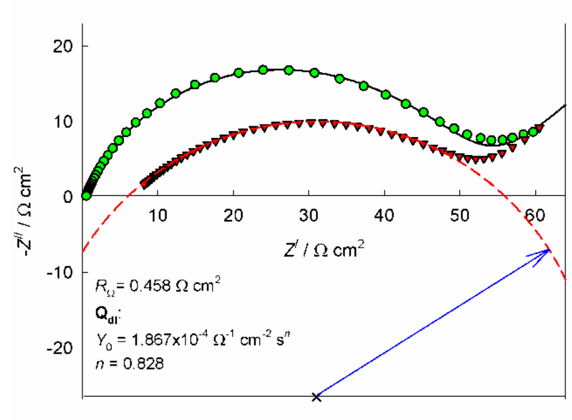

Fig. 2. Nyquist plots of total impedance (circles) obtained for 0.01 M $CuSO_4$ and 0.6 M H_2SO_4 solution at the open-circuit potential equal to 0.245 V vs. SHE. The residual plot (triangles) was obtained on the elimination of displayed non-faradaic elements

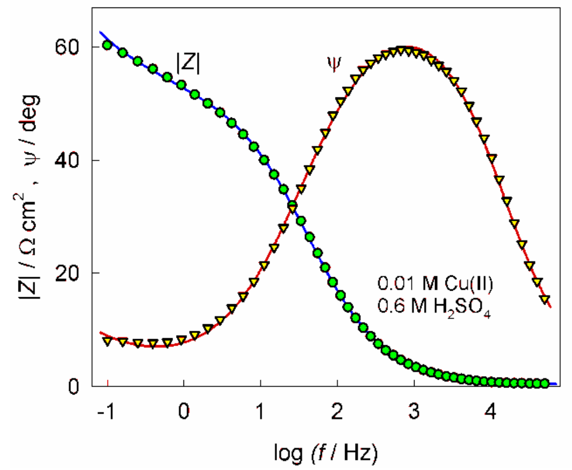

Fig. 3. Experimental (symbols) and simulated (lines) spectra of the impedance modulus, |Z|, and the phase shift, ψ

Fitting procedures performed with EC N2 show rather rapid convergences. When containing Warburg elements, this EC describe experimental spectra with error ~ 2% (Fig. 3).Even better results (~1% error) are obtained on substitution of Q for W. Non-faradaic elements are given in Fig. 2; the faradaic ones are as follows: $R_3 = 53.6$ Ω cm², $R_4 = 7.22$ Ω cm², $Y_{03} = 0.106$ Ω^{-1} cm^{-2} s$^{0.5}$, $Y_{04} = 5.5\times10^{-4}$ Ω^{-1} cm^{-2} s$^{0.5}$. The same results of simulation are obtained with EC N1 and faradaic elements recalculated with Eqns. (A.4)-(A.8): $R_0 = 6.36$ Ω cm², $R_1 = 47.0$ Ω cm², $Y_{01} = 7.08\times10^{-4}$ Ω^{-1} cm^{-2} s$^{0.5}$, $Y_{02} = 0.107$ Ω^{-1} cm^{-2} s$^{0.5}$, $C_2 = 3.55$ mF cm^{-2}.

Fitting with EC N1 operated less successful and did not improve the results obtained with EC N2. The main weakness consists in the elevated uncertainty in determination of some elements, especially of C_2. This supposedly arises from the restriction given by Eq. (2). Besides, the EC N2 is preferable due to more clear physical sense. For instance, in the case of metal deposition, the following relationships are valid under the equilibrium (open circuit) conditions [7,8]:

$$j_{01} + j_{02} = (RT/F)(1/R_3 + 1/R_4), \quad (3)$$

$$1/j_{01} + 1/j_{02} = (R_3 + R_4)(1/c_O + 4/c_Y)/\left[(\sigma_3 + \sigma_4)F\sqrt{D}\right], \quad (4)$$

where j_{01} and j_{01} are the exchange current densities of charge transfer steps, c_O and c_Y are the equilibrium concentrations of O and Y species (of Cu^{2+} and Cu^+ ions). Warburg coefficients (σ) have their common meaning with $\sigma = 1/\sqrt{2}\,Y_0$. With $D = 5\times10^{-6}$cm² s^{-1} and [Cu^+] = 77 μmol dm^{-3} [12], these relationships yield $j_{01} = 0.09$ mA cm^{-2} and $j_{02} = 3.8$ mA cm^{-2}. Since Eqns. (3) and (4) are symmetric with respect to R and σ, the established j values may be counterchanged. Therefore, to determine the rate-determining step, extra data should be invoked.

It can be seen from Eqns. (3) and (4) that R_1 and R_2 represent the charge transfer kinetics, whereas W_1 and W_2 is characterized by both the charge transfer and the semi-infinite diffusion. We wish to emphasize particularly that all faradaic elements are interrelated and each of them depends on the characteristics of both steps. Close inspection of mathematics regarding similar but adsorption-complicated processes [13] shows that this conclusion is more general and might be extended to more complex mechanisms. Otherwise, the attempts to construct EC with elements attributed to separate charge transfer steps, as is done in [14], seem to be questionable. The second EC was successfully, to our opinion, employed in the investigation of Cu(II) systems containing such surfactants as oligomers of ethylene glycol [12] and other polyethers [15].

CONCLUSIONS

Two different faradaic equivalent circuits, $R_\infty(R_1W_1)(C_2W_2)$ and $([R_3W_3][R_4W_4])$,can be derived from kinetic equations obtained for consecutive charge transfer with the formation of soluble intermediate. Both circuits follow from Grafov's EC, when the adsorption states are neglected,

The aforementioned circuits are indistinguishable, if and only if a certain interrelation between R_1, W_1, W_2 and C_2 is satisfied. Then, upon a proper choice of parameters, both EC display the same impedance spectrum at all frequencies.

All faradaic elements are interrelated and each of them depends on the characteristics of the overall process. Neither of EC elements can be attributed to the separate charge transfer step.

Though the EIS data obtained for the Cu|Cu(II) system can be described by either of the two EC, the second EC is preferred due to its simplicity and more clear physical sense.

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APPENDIX

It follows from Eq. (1) that

$$\begin{aligned} Z_F &= R_\infty + \left(1/R_1 + Y_{01}\sqrt{s}\right)^{-1} \\ &+ \left(C_2 s + Y_{02}\sqrt{s}\right)^{-1} \end{aligned}, \quad \text{(A.1)}$$

where $R_1 = R_\infty(c-b)/b$, $Y_{01} = 1/R_\infty(c-b)$,

$$C_2 = 1/R_\infty d\ ,\ Y_{02} = b/R_\infty d\ .$$

Eq. (A.1) shows that the faradaic circuit should include the resistance R_∞ that is in series with two other subcircuits whose admittances are given by two respective denominators in this equation. The terms $1 / R_1$ and $Y_{01}\sqrt{s}$ testify that the first subcircuit contains $R_1$and W_1 in parallel. Similarly, another term in the parenthesis suggests the parallel connection of C_2 and W_2 in the second subcircuit.

At the same time, another form of Eq. (1) is possible:

$$\begin{aligned} Y_F &= \left(R_3 + 1/Y_{03}\sqrt{s}\right)^{-1} \\ &+ \left(R_4 + 1/Y_{04}\sqrt{s}\right)^{-1} \end{aligned}. \quad \text{(A.2)}$$

It follows from the identity of Eqns. (1) and (A.2) that

$$b = (1 / Y_{03} + 1 / Y_{04}) / (R_3 + R_4),$$

$$c = 1 / R_3Y_{03} + 1 / R_4Y_{04}\ ,$$

$$d = 1 / R_3 R_4Y_{03} Y_{04}\ . \quad \text{(A.3)}$$

Eq. (A.2) shows that alternative faradaic EC, namely $([R_3W_3][R_4W_4])$, is possible. It contains two parallel [*RW*] subcircuits. Both EC yield the same impedance spectra, when their elements are chosen according to the following equations:

$$R_1 = R_\infty\left(R_3^2Y_{03} + R_4^2Y_{04}\right)/\left[R_3R_4\left(Y_{03} + Y_{04}\right)\right], \quad \text{(A.4)}$$

$$Y_{01} = R_3R_4\left(R_3 + R_4\right)Y_{03}Y_{04}/\left[\left(R_3^2Y_{03} + R_4^2Y_{04}\right)R_\infty\right], \quad \text{(A.5)}$$

$$Y_{02} = R_3R_4\left(Y_{03} + Y_{04}\right)/\left[\left(R_3 + R_4\right)R_\infty\right], \quad \text{(A.6)}$$

$$C_2 = R_3R_4Y_{03}Y_{04} / R_\infty\ , \qquad \text{(A.7)}$$

$$1 / R_3 + 1 / R_4 = 1 / R_\infty \qquad \text{(A.8)}$$

The latter relationship also follows from EC structures, as the limiting case when ω→∞.

ЕКВИВАЛЕНТНИ СХЕМИ НА ЕЛЕКТРОХИМИЧНА РЕАКЦИЯ ВКЛЮЧВАЩА ПОСЛЕДОВАТЕЛНИ СТЪПКИ ПРИ ПРЕНОСА НА ЗАРЯД

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(Резюме)

Две различни еквивалентни схеми могат да бъдат получени от кинетичните уравнения, описващи последователен пренос на зарядуспоредно с образуването на разтворимо междинно съединение. Схемите са описани с кодове: R_∞ (R_1W_1) (C_2W_2) и ([R_3W_3] [R_4W_4]) (сериините елементиса представени в квадратни скоби, а успоредните елементи са заградени в обикновени скоби). И двете схеми са неразличими, ако и само ако е осъществена определена взаимовръзка между R_1, W_1, W_2 и C_2. След това, при подходящ избор на параметри и двете ЕС показват същияимпедансен спектър при всички честоти. Всички „фарадееви" елементи са взаимно свързани и всеки един от тях зависи от характеристиките на цялостния процес. Нито един от елементите на ЕС не може да бъде приписан на отделнатастъпка при преноса на заряд. Въпреки, че данните получени благодарение на еквивалентната импедансна спектроскопия (ЕИС) за системата Cu | Cu (II) могат да бъдат описани от коя да е от двете ЕС. Втората ЕС е предпочетена, поради нейната простота и по-ясен физичен смисъл.