Synthesis of equivalent electrical circuits based on electrochemical impedance data

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One of the main tasks of electrochemical impedance spectroscopy (EIS) is a synthesis of the equivalent electrical circuit based on experimental data in the broad range of frequencies. This problem, in principle, should be solved without recourse to a priori model of the impedance of the electrode process.

In electrical engineering, the synthesis problem is solved by means of representing the impedance either using Cauer canonical forms [1] or Foster canonical forms [2]. In electrochemistry, the forms of Foster are more commonly used for the synthesis of an equivalent electrical circuit.

According to the first Foster form, the impedance of the electrochemical system is represented as a series connection of several elements that constitute the parallel connection of resistor and capacitor [2]. For the second Foster form, the admittance of the system is given as a parallel connection of several elements that include a series connection of resistor and capacitor. Both forms are the result of the expansion of the function of the input resistance (conductance) of the circuit to a sum of single fractions. Denominators of these fractions are the roots of the numerator and denominator of the rational fraction with respect to $j\omega$.

In electrochemistry, there are models of admittances of electrochemical systems whose input functions include polynomials with respect to $(j\omega)^{1/2}$. For example, the admittance of hydrogen evolution, when the part of the adsorbed hydrogen atoms diffuses along the surface to the reaction center, where formation of molecular hydrogen takes place (equation 7 in [3]) has the following form:

$$Y = \frac{-\omega^2\alpha_1 + (j-1)\omega^{3/2}\beta_1 + j\omega\gamma_1 + (1+j)\omega^{1/2}\rho_1 + \kappa_1}{-\omega^2\alpha_2 + (j-1)\omega^{3/2}\beta_2 + j\omega\gamma_2 + (1+j)\omega^{1/2}\rho_2 + \kappa_2} \quad (1)$$

where $\alpha_1, \beta_1, \ldots, \kappa_2$ are coefficients, expressed through the parameters of the electrode process.

In the model of the admittance of the corrosion process that takes into account the adsorption of participants of coupled reactions and diffusion-controlled anodic process, the function of the input admittance (equation 29 in [4]) has the form:

$$Y = \frac{-j\omega^3 n\alpha_1 - (j+1)\omega^{5/2} n\beta_1 - \omega^2\gamma_1 + (j-1)\omega^{3/2}\delta_1 + j\omega\kappa_1 + (1+j)\omega^{1/2}\mu_1 + \nu_1}{-j\omega^3\alpha_1 - (j+1)\omega^{5/2}\beta_1 - \omega^2\gamma_2 + (j-1)\omega^{3/2}\delta_2 + j\omega\kappa_2 + (1+j)\omega^{1/2}\mu_2 + \nu_2} \quad (2)$$

In this paper, we propose to represent the input admittance functions of type (1) and (2) using the second form of Foster and as a sum of terms of $\left(R_i + (1-j)\omega^{-1/2}A_i\right)^{-1}$. Here the second term is the Warburg impedance. All of the expression as a whole is an impedance of Ershler-Randles. Expansion of the input admittances (1) and (2) consist of the 4 and 6 terms, respectively. If in (1) and (2) there are the same roots, the number of terms is reduced, however the new members appear. Therefore, if there are two identical roots, we obtain a member:

$$\left(R_i + (1-j)\omega^{-1/2}A_i\right)^{-2} = \left(R_i' + (1-j)\omega^{-1/2}A_i' + \left(j\omega C_i'\right)^{-1}\right)^{-1} \quad (3)$$

In equation (3) the right-hand side represents the impedance of Frumkin-Melik-Gaykazyan.

The proposed method was used for the synthesis of an equivalent electrical circuit based on the results of EIS of polycrystalline Pt in 0.5 M H_2SO_4 in the presence of Cl^- ions in the region of cathodic hydrogen evolution and in the hydrogen adsorption-desorption region (-100 – 25 mV vs. RHE). Satisfactory agreement between experiment and calculation is obtained for the electrical circuit, containing, in addition to the resistance of the solution and the electric double layer capacitance, the parallel connection that includes three branches. One branch represented by a resistor. The second branch represents the impedance of the Ershler-Randles. The third branch is the impedance of the Frumkin-Melik-Gaykazyan.

References

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