



# The impedance spectroscopy response for a reversible electrode reaction based on diffusion limited chronoamperometry at an inlaid disk electrode



C. Montella \*

Univ. Grenoble Alpes, LEPMI, F-38000 Grenoble, France  
CNRS, LEPMI, F-38000 Grenoble, France

## ARTICLE INFO

### Article history:

Received 26 May 2016

Received in revised form 1 July 2016

Accepted 2 July 2016

Available online 7 July 2016

### Keywords:

Electrochemical impedance spectroscopy (EIS)

Potential step chronoamperometry (PSCA)

Microdisk electrode

Laplace transformation

Spheroidal wave functions

## ABSTRACT

First, a simple relationship is derived between the diffusion-controlled current transient resulting from application of a large potential step (PSCA method) and the diffusion impedance (EIS method) calculated at the equilibrium potential of a uniformly accessible electrode when a one-step redox reaction takes place at the electrode surface. The derivation is valid under one-dimensional (1D) diffusion conditions in the electrolyte, assuming in addition the same diffusion coefficient for both redox species involved in the electrochemical reaction. The theoretical relationship also applies to 2D diffusion from/towards an inlaid (micro)disk electrode provided the electron transfer reaction displays reversible kinetics at the electrode surface. Accurate values for the diffusion impedance at the equilibrium potential of (micro)disk electrode are obtained starting from the explicit formulation of the diffusion-controlled current transient in the article by L.K. Bieniasz, *Electrochim. Acta* 199 (2016) 1–11. These values can be used as benchmark data for checking the accuracy of numerical methods, e.g. finite element methods, employed for solving the initial boundary value problem under consideration. Finally, approximation formulae are derived for the diffusion impedance either in closed form or using a representation model together with a complex nonlinear least squares procedure.

© 2016 Published by Elsevier B.V.

## 1. Introduction

An extensive literature is devoted to theoretical modelling of electrochemical experiments on (micro)disk electrodes embedded in an insulating surface, e.g. in the textbooks [1–5].<sup>1</sup> In this article, we focus on simple (one-step) electrochemical reactions investigated on such electrodes by potential step chronoamperometry (PSCA) which is a large signal method in the time domain, and by electrochemical impedance spectroscopy (EIS) which is a small signal method in the frequency domain, and, more especially, on the theoretical relationship between the PSCA and EIS responses of such electrodes.

Modelling of the diffusion-controlled faradaic current,  $I_d(t)$ , resulting from application of a large potential step to an inlaid disk electrode, has received much attention in the electrochemical literature. Several approximations for the faradaic current transient were derived in previous works by Phillips and Jansons [6], Aoki and Osteryoung [7], Shoup and Szabo [8], Rajendran and Sangaranarayanan [9] and

Mahon and Oldham [10,11], among other authors. Britz et al. [12,13] employed conformal mapping computation procedures for checking the prediction accuracy from the above approximations.

Recently, Bieniasz [14] derived an explicit formulation for the dimensionless current,  $\psi_d(t) = I_d(t)/I_d(\infty)$ , as a function of the dimensionless time,  $T = Dt/r_e^2$ , in terms of inverse Laplace transform of an infinite series involving spheroidal wave functions [15]. Here  $D$  is the diffusion coefficient of redox species,  $r_e$  is the disk radius, and  $I_d(\infty)$  denotes the steady-state current observed at long times. This author obtained highly accurate values of  $\psi_d(T)$  using a *Mathematica* “Spheroidal” package developed by Graham [16], together with the Gaver-Wynn-rho algorithm proposed by Valkó and Abate [17] for numerical inversion of Laplace transforms. Such values should provide benchmark data for checking the computation accuracy of numerical methods, e.g. finite difference and finite element methods employed to solve the initial boundary value problem for diffusion of redox species from/towards an inlaid (micro)disk electrode.

On the other hand, only a few articles dealt with the impedance of a (micro)disk electrode inlaid in an insulating surface, when a redox reaction takes place at the electrode surface together with semi-infinite diffusion of electroactive species in the electrolyte. The analysis presented by Fleischmann and Pons [18] opened up the use of microelectrodes in impedance measurements. They presented their numerical data in the

\* Laboratoire d'Électrochimie et de Physico-chimie des Matériaux et des Interfaces (UMR 5279), Bâtiment Recherche Phelma Campus, 1130 rue de la Piscine, Domaine Universitaire BP 75, 38402 Saint Martin d'Hères Cedex, France.

E-mail address: [Claude.Montella@lepmi.grenoble-inp.fr](mailto:Claude.Montella@lepmi.grenoble-inp.fr).

<sup>1</sup> The list of quoted textbooks is far from being exhaustive.

form of tabulated functions. Some additional information is available from the work by Navarro-Laboulais et al. [19]. An algorithm for calculation of the (micro)disk impedance was outlined by these authors for its implementation in complex nonlinear least squares fitting (CNLS-Fit) programs.

An alternative approach for computing the impedance of (micro)disk electrodes is based on finite element analysis. The pioneering work on this subject was that of Ferrigno and Girault [20], which was focused on the axisymmetric recessed microdisk geometry. Gabrielli et al. [21,22] used COMSOL Multiphysics (formerly FEMLAB) software for numerical simulation of the impedance of an inlaid disk electrode. These authors investigated the influence of the disk radius and the total electrode radius (electroactive disk + insulating sheath) on the impedance diagram. More recently, Michel et al. [23] computed the impedance of (micro)disk electrode using a finite element method (FEM) together with a self-adaptive anisotropic mesh refinement strategy [24,25].

The first aim of the present work is to derive the theoretical relationship between the diffusion-controlled faradaic current  $I_d(t)$  (PSCA method) and the diffusion impedance  $Z_d(\omega)$  (EIS method) calculated at the equilibrium potential of a uniformly accessible electrode when a one-step redox reaction takes place at the electrode surface. The derivation is reported in Section 2 under the assumption of one-dimensional (1D) mass transport conditions in the electrolyte.

The theoretical relationship derived under 1D conditions also applies to 2D diffusion from/towards an inlaid (micro)disk electrode provided the electron transfer reaction displays reversible kinetics at the electrode surface. Accurate computation of the diffusion impedance for a (micro)disk electrode from its PSCA response is presented in Section 3 as an application example. Finally, Section 4 deals with the derivation of approximate formulae for the diffusion impedance of (micro)disk electrode either in closed form or using a representation model (modified Voigt circuit) together with a complex nonlinear least squares procedure.

## 2. Derivation under 1D mass transport conditions

Starting from the general formalism for linear systems developed years ago by Rangarajan [26], but using different notation, the *mass transfer function* relative to a soluble species X involved in an electrochemical reaction is defined by the ratio of Laplace transforms [27]:

$$M_X(p) = \frac{\mathcal{L}[\Delta c_X^s(t)]}{\mathcal{L}[\Delta J_X^s(t)]} = \frac{\overline{\Delta c_X^s(p)}}{\overline{\Delta J_X^s(p)}} \quad (1)$$

where  $\mathcal{L}$  is the Laplace operator, the symbol ‘upper-bar’ denotes Laplace transformed quantities with the complex variable  $p$ , and the symbol  $\Delta$  stands for deviation from the initial value, e.g.  $\Delta c_X^s(t) = c_X^s(t) - c_X^*$  for the interfacial concentration. Mathematically speaking,  $M_X(p)$  is the concentration-flux transfer function evaluated at the electrode surface (superscript ‘s’). Using Eq. (1), we tacitly assume uniform accessibility of the electrode, and therefore 1D mass transport conditions for species X. A lot of closed-form expressions for the mass transfer function  $M_X(p)$  are available from the electrochemical literature [26–35].<sup>2</sup>

Let us consider the electrochemical reaction,  $X - ze \leftrightarrow$  products, involving the soluble species X. The stoichiometric number  $z$  is positive/negative for oxidation/reduction of species X in the forward direction. A large potential step is applied to the electrode at  $t=0$ , so that the interfacial concentration of species X drops from its initial value  $c_X^*$  to zero

at  $t=0^+$ . The diffusion-controlled faradaic current transient (subscript ‘d’) can be derived as a function of time from [33]:

$$I_d(t) = zFAc_X^* \mathcal{L}^{-1} \frac{1}{pM_X(p)} \quad (2)$$

where  $A$  is the electrode area,  $F$  is Faraday’s constant, and  $\mathcal{L}^{-1}$  denotes the inverse Laplace transformation.

In the special case where the limit,  $\lim_{p \rightarrow 0} M_X(p) = m_X^{-1}$ , is real, which corresponds to non-blocking mass transport conditions, application of the final value theorem to Eq. (2) yields the steady-state current which is observed at long times:

$$I_d(\infty) = zFAm_X c_X^* \quad (3)$$

For example, the above equation applies to a hemispherical electrode with radius  $r_e$  and mass transport constant  $m_X = D_X/r_e$ , as well as to a rotating disk electrode with  $m_X = D_X/\delta_X$ , and  $\delta_X$  being the characteristic length for diffusion-convection taken from Levich theory [36].

Setting  $\psi_d(t) = I_d(t)/I_d(\infty)$  and  $M_X^*(p) = m_X M_X(p)$ , one obtains the normalized relationship from Eqs. (2) and (3):

$$\psi_d(t) = \mathcal{L}^{-1} \frac{1}{pM_X^*(p)} \quad (4)$$

In a previous work [28], we showed that the dimensionless mass transfer function is equal to the dimensionless concentration impedance:

$$M_X^*(p) = Z_X^*(p) = \frac{Z_X(p)}{R_X} \quad (5)$$

where  $Z_X(p)$  is the concentration impedance pertaining to species X, and  $R_X = \lim_{p \rightarrow 0} Z_X(p)$  is the associated resistance. From Eqs. (4) and (5), it follows that:

$$\psi_d(t) = \mathcal{L}^{-1} \frac{1}{pZ_X^*(p)} \quad (6)$$

Now, let us consider the so-called E reaction [1],  $A \leftrightarrow B + ze$ , involving two soluble species A and B. The faradaic impedance relative to this reaction is the sum of the electron transfer resistance and the concentration impedances  $Z_A(p)$  and  $Z_B(p)$ , with the diffusion impedance being the sum,  $Z_d(p) = Z_A(p) + Z_B(p)$ . Further simplification is possible when the faradaic impedance is computed at the equilibrium potential of the electrode (subscript ‘eq’), because of [37]:

$$Z_{X,\text{eq}}(p) = \frac{M_X(p)}{z^2 f F c_X^*} \quad (7)$$

where  $f = F/(RT_K)$  is Nernst constant,  $F$  and  $R$  have their usual meaning, and  $T_K$  denotes the absolute temperature. In the same way, the concentration resistance at equilibrium is given by:

$$R_{X,\text{eq}} = \frac{1}{z^2 f F m_X c_X^*} \quad (8)$$

The diffusion impedance pertaining to E reaction at the equilibrium potential is:

$$Z_{d,\text{eq}}(p) = \frac{1}{z^2 f F} \left( \frac{M_A(p)}{c_A^*} + \frac{M_B(p)}{c_B^*} \right) \quad (9)$$

<sup>2</sup> Note that the symbol  $\Delta$  means a small deviation in the context of EIS method. Nevertheless, Eq. (1) should also apply to large signal methods, e.g. PSCA, when mass transport of species X is modelled by linear equations, mathematically speaking.

Download English Version:

<https://daneshyari.com/en/article/217786>

Download Persian Version:

<https://daneshyari.com/article/217786>

[Daneshyari.com](https://daneshyari.com)