



The impedance response of rotating disk electrodes



Shao-Ling Wu^a, Mark E. Orazem^{a,*}, Bernard Tribollet^b, Vincent Vivier^b

^a Department of Chemical Engineering, University of Florida, Gainesville, FL 32611, USA

^b LISE, UPR 15 du CNRS, Université P. et M. Curie, CP 133, 4 Place Jussieu, 75252 Paris cedex 05, France

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ABSTRACT

Classifications and recent findings are reviewed for numerical simulations describing the impedance response of rotating disk electrodes. The disk geometry is shown to cause a complex character to the ohmic contribution to the impedance response. For reactions that do not involve formation of adsorbed intermediates, the frequency dispersion associated with the disk geometry occurs above a characteristic frequency. Such dispersion may be avoided by selecting a disk of sufficiently small dimension. For reactions that do involve formation of adsorbed intermediates, a low-frequency dispersion is also seen. Models including the influence of mass transfer show that the coupling of faradaic and charging currents induces frequency dispersion at frequencies associated with the faradaic reaction.

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1. Introduction

The disk electrode, consisting of a circular electrode embedded in an insulating plane, is commonly used in electrochemical measurements. The disk geometry may be associated with rotating or stationary electrodes. Newman showed, in 1966, that electrode-insulator interface gives rise to nonuniform current and potential distributions for currents below the mass-transfer limited current [1,2]. The geometry-induced nonuniform current and potential distributions influences the transient response of the disk electrode. Nisancioglu and Newman [3,4] developed a solution for the transient response of a faradaic reaction on a non-polarizable disk electrode to step changes in current. The solution to Laplace's equation was performed using a transformation to rotational elliptic coordinates and a series expansion in terms of Legendre polynomials. Antohi and Scherson have recently expanded the solution to the transient problem by expanding the number of terms used in the series expansion [5].

Newman also provided a treatment for the impedance response of a disk electrode which showed that the capacity and ohmic resistance were functions of frequency above a critical value of frequency [6]. More recently, the present authors embarked on a comprehensive numerical and experimental study of the impedance response of the disk electrode, including the response of ideally polarized electrodes [7], electrodes showing local CPE behavior [8], electrodes with faradaic reactions [9], electrodes with reactions involving adsorbed intermediates [10,11], and electrodes

subject to reactions influenced by mass transfer [12]. The authors also explored the origin of the complex ohmic impedance [13,14] and provided experimental verification of the phenomena predicted by the simulations [15,16]. The objective of this work is to provide an overview of the impedance of a disk electrode.

2. Mathematical development

Deterministic impedance models for a disk electrode may be divided into two categories. The models presented in Section 2.1 consider that mass transfer is unimportant. The potential and current is either controlled by the ohmic resistance of the electrolyte, i.e., a primary distribution, or a combination of ohmic resistance and kinetic effects at the electrode, a secondary distribution. The models presented in Section 2.2 pertain to systems where mass transfer plays a significant role.

2.1. Influence of ohmic and kinetic phenomena

Under the assumption that mass-transfer may be neglected, the electrical potential in the electrolyte is governed by Laplace's equation

$$\nabla^2 \phi = 0 \quad (1)$$

The system may be assumed to have cylindrical symmetry such that the potential in solution is dependent only on the radial position r along the electrode surface and the normal position y . In response to an alternating current with a particular angular frequency $\omega = 2\pi f$, the potential can be separated into steady and time-dependent parts as

* Corresponding author. Tel.: +1 (352) 392 6207; fax: +1 (352) 392 9513.

E-mail address: meo@che.ufl.edu (M.E. Orazem).

$$\Phi = \bar{\Phi} + \text{Re}\{\tilde{\Phi} \exp(j\omega t)\} \quad (2)$$

where $\bar{\Phi}$ is the steady-state solution for potential and $\tilde{\Phi}$ is the complex oscillating component which is a function of position only. Similarly, the applied potential can be expressed as

$$V = \bar{V} + \text{Re}\{\tilde{V} \exp(j\omega t)\} \quad (3)$$

Therefore, the form of Laplace's equation to be solved, subject to appropriate boundary conditions, is

$$\frac{1}{r} \frac{\partial}{\partial r} \left(r \frac{\partial \tilde{\Phi}}{\partial r} \right) + \frac{\partial^2 \tilde{\Phi}}{\partial y^2} = 0 \quad (4)$$

Eq. (4) can be solved using numerical methods.

The boundary condition for potential at $r \rightarrow \infty$ is that $\tilde{\Phi} \rightarrow 0$, and the boundary condition on the insulating surface is that $\partial \tilde{\Phi} / \partial y = 0$. The distinction between different conditions simulated is seen in the boundary condition for the electrode surface.

2.1.1. Blocking electrode

For a blocking electrode [7],

$$jK(\tilde{V} - \tilde{\Phi}_0) = -r_0 \frac{\partial \tilde{\Phi}}{\partial y} \Big|_{y=0} \quad (5)$$

where Φ_0 is the potential in the solution adjacent to the electrode and K is the dimensionless frequency

$$K = \frac{\omega C_0 r_0}{\kappa} \quad (6)$$

where C_0 is the double layer capacitance and κ is the electrolyte conductivity. The current is only that required to charge or discharge the electrode.

2.1.2. Blocking electrode with CPE behavior

For a blocking electrode with CPE behavior [8], the interfacial impedance is given as

$$Z_{\text{CPE}} = \frac{\tilde{V} - \tilde{\Phi}}{\tilde{i}} = \frac{1}{(j\omega)^\alpha} Q \quad (7)$$

On application of the Euler identity,

$$j = \cos\left(\frac{\pi}{2}\right) + j \sin\left(\frac{\pi}{2}\right) \quad (8)$$

Thus

$$K(\tilde{V} - \tilde{\Phi}_0) \left(\cos\left(\frac{\alpha\pi}{2}\right) + j \sin\left(\frac{\alpha\pi}{2}\right) \right) = -r_0 \frac{\partial \tilde{\Phi}}{\partial y} \Big|_{y=0} \quad (9)$$

where K is the dimensionless frequency defined for a system with CPE behavior to be

$$K = \frac{Q\omega^\alpha r_0}{\kappa} \quad (10)$$

The definition of the dimensionless frequency presented in Eq. (10) differs from the definition expressed in Eq. (6).

2.1.3. Electrode with faradaic reactions

For an electrode with faradaic reaction [9], the boundary condition at the electrode is expressed in frequency domain as

$$jK(\tilde{V} - \tilde{\Phi}_0) + J(\tilde{V} - \tilde{\Phi}_0) = -r_0 \frac{\partial \tilde{\Phi}}{\partial y} \Big|_{y=0} \quad (11)$$

where \tilde{V} represents the imposed perturbation in electrode potential referenced to an electrode at infinity and K is defined by Eq. (6) under the assumption of pure capacitive behavior for the double

layer. Under the assumption of linear kinetics, valid for $\bar{i} \ll i_0$, the parameter J is defined to be

$$J = \frac{(\alpha_a + \alpha_c) F i_0 r_0}{RT\kappa} \quad (12)$$

For Tafel kinetics, valid for $\bar{i} \gg i_0$, the parameter J is defined to be

$$J(\bar{V} - \bar{\Phi}_0) = \frac{\alpha_c F \left| \bar{i}(\bar{V} - \bar{\Phi}_0) \right| r_0}{RT\kappa} \quad (13)$$

As $\bar{\Phi}_0$ depends on radial position, the value of J expressed in Eq. (13) is a function of radial position.

The charge-transfer resistance for linear kinetics can be expressed in terms of parameters used in Eq. (12) as

$$R_t = \frac{RT}{i_0 F (\alpha_a + \alpha_c)} \quad (14)$$

and, in terms of parameters used in Eq. (13),

$$R_t = \frac{RT}{\left| \bar{i}(\bar{V} - \bar{\Phi}_0) \right| \alpha_c F} \quad (15)$$

For linear kinetics, R_t is independent of radial position, but, under Tafel kinetics, as shown in Eq. (15), R_t depends on radial position. From a mathematical perspective, the principal difference between the linear and Tafel cases is that J and R_t are held constant for the linear polarization; whereas, for the Tafel kinetics, J and R_t are functions of radial position determined by solution of the nonlinear steady-state problem.

Huang et al. [9] provide a relationship between the parameter J and the charge-transfer and ohmic resistances as

$$J = \frac{4 R_c}{\pi R_t} \quad (16)$$

Large values of J are seen when the ohmic resistance is much larger than the charge-transfer resistance, and small values of J are seen when the charge-transfer resistance dominates. The definition of parameter J in Eq. (16) is the reciprocal of the Wagner number [17], which is a dimensionless quantity that measures the uniformity of the current distribution in an electrolytic cell.

2.1.4. Electrode with faradaic reactions coupled by adsorbed intermediate

As the reaction sequences become more complicated, it becomes difficult to express the model results in a general manner. Wu et al. [10] analyzed the impedance response associated with two successive charge-transfer steps involving an intermediate species adsorbed on the electrode surface, i.e.,



and



The reactant could be a metal M which dissolves to form an adsorbed intermediate X_{ads}^+ , which then reacts to form the final product P^{2+} . The reactions were assumed to be irreversible, and diffusion processes were considered negligible. Similar mechanisms were proposed by Epelboin and Keddam [18] for calculating the impedance of iron dissolution through two steps involving an adsorbed FeOH intermediate, and by Péter et al. [19] for the impedance model of the dissolution of aluminum in three consecutive steps with two adsorbed intermediates.

Under the assumption of Tafel kinetics, the steady-state current densities for reactions (17) and (18) may be expressed by

$$\bar{i}_M = K_M (1 - \bar{\gamma}) \exp[b_M(\bar{V} - \bar{\Phi}_0)] \quad (19)$$

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