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Influence of Geometry-Induced Frequency Dispersion on the Impedance of Ring Electrodes

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ABSTRACT

Finite-element simulations for the impedance response of ring electrodes were used to identify the characteristic frequency associated with the influence of electrode geometry on impedance response. An approximate expression for the characteristic ring-electrode dimension was found to be adequate for a wide ring, and have an error of 20 percent for a thin ring. A refined expression for the characteristic dimension is presented. The characteristic frequency associated with the influence of ring-electrode geometry is always larger than that associated with the geometry of a disk. These results guide the design of ring-shaped sensors that employ impedance measurements.

1. Introduction

The ring-electrode geometry has been widely used in electrochemical systems with electrochemical impedance spectroscopy (EIS) as an analysis technique. Hsieh et al. [1] conducted impedance measurements on ring-shaped interdigitated electrodes to characterize the concentration change of glycated hemoglobin. Besio and Prasad [2] used a concentric ring electrode to analyze the skin–electrode impedance. They performed single-frequency impedance measurements at 1 kHz and concluded that copper is the best material among several metals for their biosensor. Li et al. [3] conducted impedance measurements on a rotating ring electrode to determine the mechanism of the chlorine evolution reaction. Their work suggested that, on a Pt surface, the rate of chloride discharge and simultaneous chlorine adsorption is first order with respect to chloride concentration; whereas, the rate of the adsorption and desorption process is second order with respect to chloride concentration.

The current and potential distribution for the ring electrode geometry has been widely studied. The primary current distribution associated with the ring electrode geometry is nonuniform. Pierini and Newman [4] presented an analytic solution for the primary and secondary current distribution on ring electrodes. Datta et al. [5] used the finite-element method to calculate the steady-state current and potential distribution for concentric ring-ring electrodes and double concentric (ring-ring-ring) electrodes used for transcranial current stimulation. Their work showed that the electric field on a ring electrode decreases rapidly in the radial direction. Mansor and Ibrahim [6] also performed simulations indicating that the electric field on a ring interdigitated electrode reaches a maximum at the ring edges and a minimum at the center of the rings.

The term frequency or time-constant dispersion is used to describe the broadening of the impedance response associated with a distribution of time constants. Frequency dispersion associated with an electrode geometry originates from the nonuniform current and potential distribution, which changes as a function of frequency. Newman [7] showed, by solution of Laplace's equation, that frequency dispersion is observed for disk electrodes for frequencies larger than a characteristic value. A dimensionless frequency may be expressed as [7–11]

$$K = \frac{\omega C_0 \ell_{c,\mathrm{disk}}}{\kappa}. \tag{1}$$

where ω is the angular frequency, κ is the electrolyte conductivity, C_0 is the capacitance of the disk electrode, and $\ell_{c,\mathrm{disk}}$ is the characteristic length for a disk electrode. Huang et al. [8] showed that, for

$$\ell_{c,\mathrm{disk}} = r_0 \tag{2}$$

the characteristic frequency for a disk electrode occurs near $K = 1$; thus, the associated characteristic dimension for the disk electrode is the radius of the disk.

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Alexander et al. [11] showed that the characteristic dimension for a rough disk is given by

$$\ell_{c,\mathrm{rough\ \ disk}} = f_r r_0 \tag{3}$$

where f_r is the rugosity or roughness factor defined to be the ratio of the actual surface area to the superficial surface area of the disk. Alexander et al. [11] showed further that the characteristic dimension for roughness is

$$\ell_{c,\mathrm{roughness}} = f_r^2 P \tag{4}$$

where P is the period associated with roughness.

Equation (1) facilitates estimation of the characteristic frequency at which dispersion influences the impedance response for a given electrode. For $K > 1$, frequency dispersion is associated with the nonuniform current distribution. Therefore, frequency dispersion may be eliminated in a desired frequency range by choosing the appropriate parameters ℓ_c and κ to ensure that $K < 1$. The objective of this work is to find the characteristic dimension associated with the impedance response of a ring electrode.

2. Mathematical Development

The ring serves as the working electrode, which is embedded in an infinite, insulated plane with a hemispherical counterelectrode located at infinity. For the present work, the geometric parameters r_1 and r_2 represent the inner and outer radii of the ring electrode, respectively. The potential distribution for an electrolyte with uniform conductivity is governed by Laplace's equation, which may be expressed in cylindrical coordinates as

$$\frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial \Phi}{\partial r}\right) + \frac{\partial^2 \Phi}{\partial y^2} = 0 \tag{5}$$

where axial symmetry was assumed.

The potential can be expressed in terms of steady-state $\bar{\Phi}$ and oscillating $\tilde{\Phi}$ components as

$$\Phi = \bar{\Phi} + \mathrm{Re}\{\tilde{\Phi}\mathrm{e}^{\mathrm{j}\omega t}\} \tag{6}$$

Similarly, the potential applied at the electrode surface can be expressed as

$$V = \bar{V} + \mathrm{Re}\{\tilde{V}\mathrm{e}^{\mathrm{j}\omega t}\} \tag{7}$$

where $\bar{V}$ is the steady-state value and $\tilde{V}$ is the oscillating value.

The steady-state solution for the current distribution at a blocking electrode shows that the potential is uniform and the current is equal to zero. As the problem is linear, solution for the oscillating variables does not require a solution for the steady-state equation. [9] The impedance response of the ring requires solution of

$$\frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial \tilde{\Phi}}{\partial r}\right) + \frac{\partial^2 \tilde{\Phi}}{\partial y^2} = 0 \tag{8}$$

subject to boundary conditions that the oscillating potential is equal to zero for distances far away from the disk, i.e.,

$$\tilde{\Phi} \to 0 \quad \text{as} \quad r^2 + y^2 \to \infty \tag{9}$$

and that, on the insulating plane surrounding the ring,

$$\frac{\partial \tilde{\Phi}}{\partial y}\bigg|_{y=0} = 0 \quad \text{for} \quad r < r_1 \quad \text{and} \quad r > r_2 \tag{10}$$

For a blocking electrode, Huang et al. [8] showed that the flux condition at the surface of a disk electrode can be expressed as

$$C_0 \frac{\partial (V - \Phi(0))}{\partial t} = -\kappa \frac{\partial \Phi}{\partial y}\bigg|_{y=0} \tag{11}$$

where $\Phi(0)$ is the potential outside the diffuse part of the double layer. The corresponding expression in terms of oscillating variables is given by

$$\mathrm{j}\omega C_0 \left(\tilde{V} - \tilde{\Phi}(0)\right) = -\kappa \frac{\partial \tilde{\Phi}}{\partial y}\bigg|_{y=0} \tag{12}$$

The impedance was calculated as

$$Z(\omega) = \frac{\tilde{V}}{\tilde{I}} \tag{13}$$

for a specified range of frequencies, where $\tilde{I}$ is the oscillating current at the working electrode obtained by integrating the local current density over the surface of the electrode.

3. Numerical Method

The finite-element-analysis solver and simulation software COMSOL Multiphysics® was used to solve Laplace's equation in cylindrical coordinates for the ring electrode. Triangular elements were employed with quadratic interpolation. Due to the singularities that arise near the edge of the ring electrode, a nonuniform meshing scheme was implemented near the surface of the ring electrode. A direct linear solver was used. The meshing was refined manually to ensure that the impedance response of a disk electrode yielded the correct high-frequency primary resistance, i.e., $R_e \kappa r_0 = 1/4$.[12] Similar mesh sizes were then used for the ring electrodes. In contrast to the frequency-dependent adaptive mesh algorithm employed by Michel et al., [13] the same meshing was then employed for all frequencies. Calculation of 80 frequencies (10 points per decade from 10^{-2} Hz to 10^{9} Hz) required less than 30 min on a 64-bit Dell Precision T7400 workstation with dual Xeon E5410 2.33 GHz processors and 32G Byte of RAM.

A schematic representation of the finite element mesh used for the ring electrode simulations is provided in Fig. 1 detailing: a) the

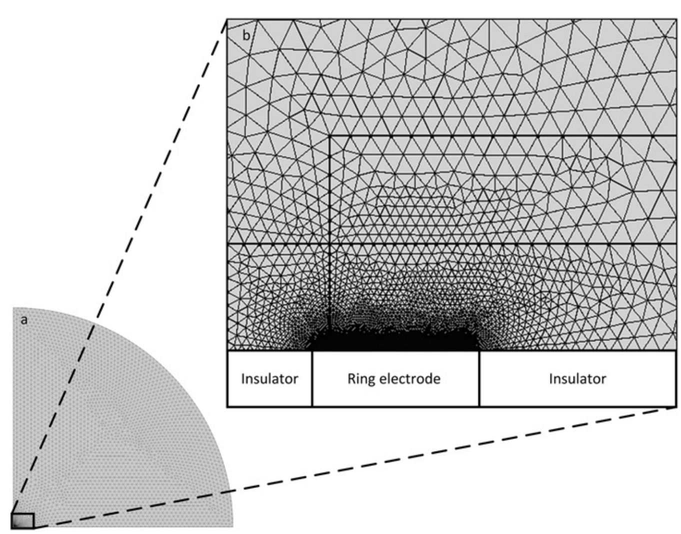

Fig. 1. Schematic representation of a sample finite element mesh used for ring electrode simulations: a) entire domain and b) an enlarged region showing the two insulating surfaces and the ring electrode.