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Numerical simulation of the far-field boundaries onto a microdisc electrode by using the infinite element

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ABSTRACT

The numerical simulation of the diffusion problem onto a microdisc electrode is made difficult by the presence of a boundary singularity at the electrode edge (edge effect) and the truncated far-field boundary conditions. In general, the far-field distance is several orders larger than the radius of the microelectrode. Simulating in such a large domain is time-consuming so the far-field distance is often truncated. The accuracy of the simulated current depends on how far of the truncated far-field boundary conditions. An approximated function is obtained to estimate the sufficient distance for a given accuracy of the current calculation and vice-versa. We also introduce the use of infinite elements at far-field boundary which is proved as an optimal approach to deal with boundary conditions at semi-infinite distance.

1. Introduction

Microelectrodes are widely used in electroanalysis and electrochemical techniques due to the small dimension of the probe, the very low ohmic drop, the steady state measurement, and the possibility to study fast kinetics [1–4]. Among the microelectrodes, the microdisc electrode is the most popular as it is preferably used as the probe in the Scanning Electrochemical Microscopy (SECM) technique. The quantitative SECM analyses are available by using the numerical simulations. The simulation models for the simplest case of the mass transport process at a microdisc electrode and for more complex processes involving several techniques have been studied [5]. However, the simulation of the electrochemical process at the microdisc electrode is still "challenging" due to not only the boundary singularities at the electrode-insulator interface but also to the unbounded exterior problem. Several approaches such as conformal mapping [6–9], mesh refinement [10,11], local valid series [12,13] attempted to deal with the edge effect problem. Gavaghan et al. [14] provided an excellent review of these approaches. However, the far-field boundary condition in electrochemistry is not fully investigated. Several conformal mappings to a finite rectangle space which "folds" the radius axis at the electrode-insulator edge in order to remove the singularity were studied [6–9]. The transformation proposed by Amatore and Fosset [6] also allowed applying exactly the far-field boundary conditions because the infinite distance was transformed to the finite space. This transformed coordinates of the conformal mapping are more complex than those in the original cylindrical coordinates. In addition, the choice of conformal mapping is problem-dependent and it is difficult to apply conformal mapping in more complex geometries such as those in SECM technique with the presence of the substrate and sharp tip. The mesh refinement approach, in both continuous and discontinuous finite element methods with finer mesh at the boundary singularity was reviewed [14]. However, the truncated finite region with the boundary condition defined from the known analytical solution was used to validate the numerical framework in this work. But in most of the practical problems, it is difficult to obtain a closed-form analytical solution to apply on the finite boundary domain. Alternatively, a large finite domain can be selected as an approximation to infinity. This method is often "expensive" due to the expansion far away of the simulation domain from the region of interest (the microelectrode surface). For example, the region of interest in the model for microdisc electrode is few times larger than the microelectrode dimension (10 μm) but the typical electrochemical cell is about 5 cm where the far-field boundary conditions for bulk concentration are applied. This far-boundary condition is then 5000 times larger than the region of interest and simulating in such a large domain is then less effective; therefore the far-field distance is often truncated.

This work firstly studies the errors of the far-field approximation in numerical simulations of electrochemical problems on microdisc electrodes derived from the widely-used truncation of

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the bulk condition using the finite elements methods (FEM). The issue of the truncated far-field conditions in other numerical methods such as finite difference methods (FDM) and boundary elements methods (BEM) could also be considered but is beyond the scope of this article. Recently, Richard G. Compton's group [15] compared the relative error in the 1D, 2D and 3D electrochemical simulations by comparing the default predefined and user-defined FEM mesh with the well-defined FDM simulation and concluded that meshing in commercial FEM softwares should be done with caution. In this work, the appropriate FEM meshing and boundary conditions are carefully controlled to obtain a good accuracy (relative error about 0.3%). Secondly, we introduce an alternative approach to deal with the far-boundary condition in electrochemistry by using the well-established infinite elements (IE). IE are the virtual domains that scale the coordinate surrounding the region of interest toward infinity. These virtual domains can be implemented in both stationary and transient problems. The idea of the IE is instead of using a global mapping for the entire simulation domain, the local mapping for each element is used [16]. This method is used in modeling the electromagnetic field [17], structural acoustics modeling [18], infinite reservoir model [19], exterior Helmholtz problem [20], etc. Based on the *Comsol Multiphysics*© Manual Guide [21,22], the IE is then applied in this work for the simulation of electrochemical processes at microdisc in both steady-state and transient problem to deal with the far-field boundary conditions. The numerical results are then compared to the approximation results reported in the literature.

2. The model problem

We consider the simulation of the steady-state at a microdisc electrode as the test model because this problem has a closed-form analytical solution and has been widely studied by several approaches in the literature [6,11,12]. The transient problem (potential-step chronoamperometry) at a microdisc is also examined although no true exactly solution exists but only approximations derived from FDM simulations [23–25]. The simulation result of the transient problem is then compared with these well-known approximations.

The problem is briefly described below.

At the microdisc electrode surface, a simple redox reaction occurs with an infinitely fast kinetic. The mass transport is governed by the partial differential equation (PDE) diffusion equation for 2D cylindrical coordinates. For the steady-state problem:

$$\frac{\partial^2 u}{\partial r^2}+\frac{1}{r}\frac{\partial u}{\partial r}+\frac{\partial^2 u}{\partial z^2}=0 \tag{1}$$

For the transient problem:

$$\frac{\partial u}{\partial T}=\frac{\partial^2 u}{\partial r^2}+\frac{1}{r}\frac{\partial u}{\partial r}+\frac{\partial^2 u}{\partial z^2} \tag{2}$$

where $u = c/c_{bulk}$ is the dimensionless concentration, c_{bulk} is the bulk concentration at the far-boundary domain and c is the concentration of the electroactive specie. The spatial coordinates r and z are also normalized to the electrode radius a. The normalized time is given as $T=\frac{Dt}{a^2}$ where D is the diffusion coefficient of the redox species.

The boundary conditions for the steady-state problem are:

$$\frac{\partial u}{\partial r}=0 \quad at \quad r=0 \tag{3}$$

$$u=0 \quad at \quad r\leqslant 1,\ z=0 \tag{4}$$

$$\frac{\partial u}{\partial z}=0 \quad at \quad r>1,\ z=0 \tag{5}$$

$$\begin{aligned} &u=1 \quad at \quad r\to\infty,\ z\to\infty \\ &u=1 \quad at \quad r\to r_{\max},\ z\to z_{\max} \end{aligned} \tag{6}$$

For the transient problem, beside the boundary conditions given above, the initial condition is included:

$$u=1 \quad at \quad T=0, \quad all \quad r,z \tag{7}$$

The boundary condition at $r\to\infty, z\to\infty$ is the far-field boundary condition or unbounded exterior condition. This boundary condition cannot be done in an infinite domain but it has to be applied at a sufficient distance from the electrode surface. The simulation domain is then truncated at the sufficient far distance $(0, r_{\max}) \times (0, z_{\max})$ to approximate the true problem $(0,\infty)\times(0,\infty)$.

In general, the measured quantity of interest is the current at the electrode surface, which is the integration of the inhomogeneous concentration flux at the electrode. The steady state dimensionless flux J and the current I is given by:

$$J=2\pi\int_{r=0}^{r=1} r\left(\frac{\partial u}{\partial z}\right)_{z=0} dr \tag{8}$$

$$I=nFDc_{bulk}aJ \tag{9}$$

The exact solution for the steady-state problem was given by Saito [26] and Crank and Furzeland [12]. Based on this analytical solution, the analytical concentration gradient over the electrode surface is then given by:

$$\left(\frac{\partial u}{\partial z}\right)_{z=0}=\frac{2}{\pi\sqrt{1-r^2}} \tag{10}$$

By applying Eq. (10), the analytical steady-state dimensionless flux is:

$$J_{anal}=2\pi\int_{r=0}^{r=1} r\frac{2}{\pi\sqrt{1-r^2}}\ dr=4 \tag{11}$$

This value leads to the formation of the well-known Saito's equation:

$$I=4nFDc_{bulk}a \tag{12}$$

The current integration for the transient problem is:

$$J(T)=2\pi\int_{r=0}^{r=1} r\left(\frac{\partial u(T)}{\partial z}\right)_{z=0} dr \tag{13}$$

No exact analytical solution of the transient problem exists, but several approximation functions were proposed in literature [23]. Using the FDM simulation, Shoup and Szabo [25] proposed the approximation guaranteeing a maximum relative error of 0.6% in a range of $0.002\leqslant T\leqslant 10$.

$$J_{Shoup-Szabo}(T)=4\left(0.7854+\frac{0.4431}{\sqrt{T}}+0.2146\times\exp\left(\frac{-0.3912}{\sqrt{T}}\right)\right) \tag{14}$$

The more accurate approximation was proposed by Mahon and Oldham [24] in short-time and long-time forms with 0.1% error in the range of $0\leqslant T\leqslant 1$ and $0.4\leqslant T$, respectively:

$$J_{Oldham-short}(T)=\pi\left(\frac{1}{\sqrt{\pi T}}+1+\frac{\sqrt{T}}{2\sqrt{\pi}}-0.12003\ \ T+0.013273\ \ \sqrt{T^3}\right) \tag{15}$$

$$J_{Oldham-long}(T)=4+\pi\begin{pmatrix} 8\pi^{-5/2}T^{-1/2}+8.9542\times10^{-3}T^{-3/2} \\ -2.5664\times10^{-4}T^{-5/2} \\ -2.2312\times10^{-4}T^{-7/2} \\ +2.7628\times10^{-5}T^{-9/2} \end{pmatrix} \tag{16}$$