

Simulations of Scanning Electrochemical Microscopy Experiments in Pure Negative and Positive Feedback Mode with Ring Microelectrodes

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Introduction

Scanning electrochemical microscopy (SECM) is a powerful tool recently developed for studying structures and processes in micrometer- and submicrometer-sized systems. It can probe electron, ion, and molecule transfers,¹ and other reactions at solid-liquid, and liquid-liquid, interfaces. This versatility allows for the investigation of a wide variety of processes, from metal corrosion to metabolism in single living cells. The SECM technique consists in approaching a microelectrode (diameter of 10 μm or less) near a conductive, semiconductive or insulating substrate immersed in a solution that contains a redox mediator (Figure 1). The microelectrode is connected to a bipotentiostat, that controls the applied potentials at the tip and substrate versus the reference electrode and that measures the tip and substrate currents. The microelectrode can be moved normal to the surface to probe the diffusion layer, or the microelectrode can be rastered across the surface to acquire reactive imaging. In all cases, the monitored microelectrode current obtained depends on the geometry of the microelectrode to substrate distance.

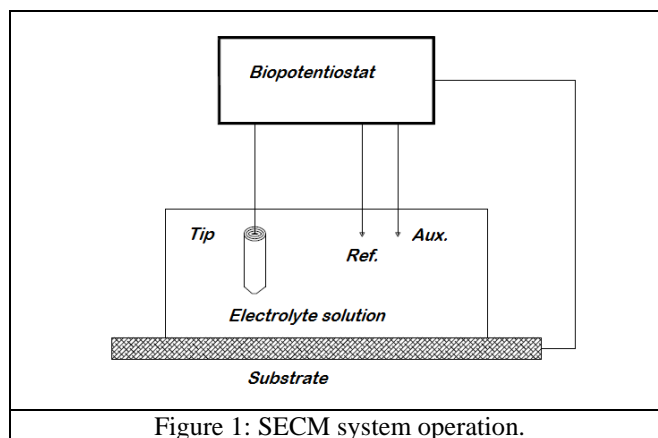
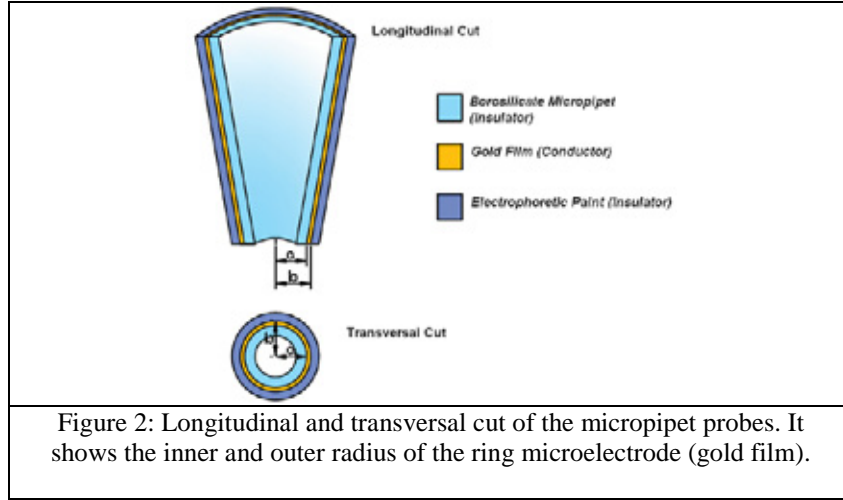


Figure 1: SECM system operation.

In most situations encountered in SECM, analytical expressions are not available and the use of numerical solutions are necessary. We are interested in simulating the SECM behaviour of a ring shaped micropipet because of its special attributes as a sensor. Ring shaped microelectrodes (Figure 2) have a characteristic perimeter-to-area ratio (PAR) that makes them ideal to monitor kinetic processes²⁻³, since it improves the temporal resolution achieved during the study of reactions with fast chemical and electrochemical kinetics. Finally, they present improved signal-to-background and signal-to-noise ratios for many forms of transient voltammetry.²⁻⁴

The theoretical treatments of classical SECM approach curves in feedback modes for a micro-ring are very limited.³ In the original study, Lee *et al.*⁵ showed that during positive feedback the effect of the characteristic dimension of the ring microelectrode is more important than that of the insulating sheath thickness, enabling them to determine the geometry of the ring electrodes using SECM approach curves. The simulated data points were however not reported and this renders future validation of new simulations difficult. We therefore use COMSOL to simulate the pure positive and negative feedback of the ring microelectrode. The main difficulty is adequately defining the meshing of the simulated domain at the interface of the active area of the tip and the insulator material. Also, since our sensors consist of ring

micropipets, it is important to adequately simulate of the contribution of the internal void of the pipet to the observed current. The study requires a two dimensional simulation to solve the diffusion equation.



Herein, we report an extensive data set from numerical simulations of the ring microelectrode for pure positive and negative feedback mode approach curves. The dependence of the resulting simulated approach curves with characteristic dimensions of the ring microelectrode is also given. The simulations were validated based on comparison to the results of a disk microelectrode, a limiting form of the ring microelectrode, because experimental and theoretical values were available. Finally, the impact of the internal void of the pipet on the current distribution is considered. In a first case, the micro-ring current is simulated considering that the air filling the void of the pipet is an insulator. In a second case, the internal void of the pipet is filled with a column of redox solution to evaluate the potential loss of sensitivity based on the diffusion of the redox generated species inside the now permeable pipet void.

Mathematical Formulation

In this article, we will focus on the case of a ring microelectrode imbedded in an insulator (Figure 2). The current and concentration profiles of the ring microelectrode are simulated using characteristics dimensions of the sensor as defined by an inner radius, a , and an outer radius, b (Figure 2). The microelectrode is immersed in an electrolyte solution that contains a concentration, c_O , of an oxidized (O) chemical species. The reduction reaction that occurs at the electrode surface generates the reduced specie (R). This reaction is described by:



Where n is the number of electrons transferred during the reduction reaction. Only diffusional mass transfer is considered, convection and migrational effects are neglected. In the bulk solution, when the microelectrode to surface distance exceeds 20 times the dimensions of the tip diameter, the most accurate steady-state diffusion controlled current, $i_{T,\infty}$, for the ring microelectrode is given by Smythe's expression⁶:

$$i_{T,\infty} = nFD_Oc_OI_O \quad [2]$$

Where D_O , represents the diffusion coefficient of the redox species, F is the Faraday's constant and:

$$I_O = \frac{\pi^2(a+b)}{\ln\left[16\left(\frac{b+a}{b-a}\right)\right]} \quad [3]$$

Applicable for a ring obeying:

$$\frac{b-a}{b} \ll 1 \quad [4]$$

Practically, equ. 3 describes a thin ring having a characteristic dimension ratio, $a/b > 0.91$. For all other dimensions, Szabo⁷ predicts the steady-state current as a function of ring thickness. Equation [7] predicts the current across the whole range of a/b , from micro-disk:

$$\frac{a}{b} = 0 \quad [5]$$

To thin ring:

$$\frac{a}{b} \rightarrow 1 \quad [6]$$

Given by:

$$I_O = \frac{\pi^2(a+b)}{\ln\left[\frac{32a}{(b-a)} + \exp\left(\frac{\pi^2}{4}\right)\right]} \quad [7]$$

Importantly, equations [3] and [7] predicts that the observed flux is spatially uniform over the surface of the electrode.⁷

The dimensionless parameters used to define the simulation space represented in Figure 2 are:

Radial distance (R)

$$R = \frac{r}{b} \quad [12]$$

Normal distance (Z)

$$Z = \frac{z}{b} \quad [13]$$

Concentration of O (C_o)

$$C_O = \frac{c_O(r,z,t)}{c_O^o} \quad [14]$$

Time (T)

$$T = t \frac{D_O}{b^2} \quad [15]$$

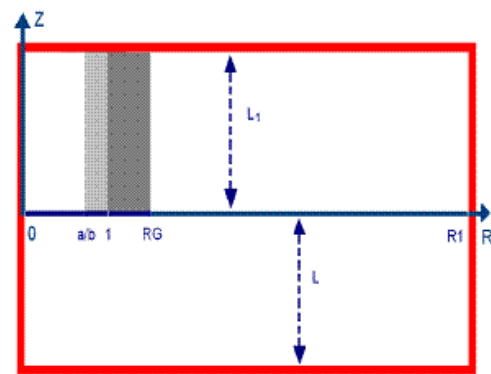


Figure 3. Normalized simulation domain used to solve the diffusion problem of a ring microelectrode. R and Z are the dimensionless cylindrical coordinates.

The current I_T is usually normalized by $I_{T,\infty}$ in such way that $\frac{I_T}{I_{T,\infty}} \rightarrow I$ when $L \rightarrow \infty$, then:

$$\frac{I_T}{I_{T,\infty}} = \frac{\int_0^{2\pi} \int_{\frac{a}{b}}^1 J(R,0,L) \cdot dS}{\int_0^{2\pi} \int_{\frac{a}{b}}^1 J(R,0,100) \cdot dS} \quad [16]$$

where $J(R,Z,L)$ is the normal flux of the species O integrated along the microelectrode boundary, with a substrate at a distance of L , $J(R,Z,100)$ is considered as the infinite distance flux, dS is the surface element

$$dS = R \cdot dR \cdot d\theta \quad [17]$$

COMSOL Simulation

To numerically solve the above SECM problem, COMSOL Multiphysics version 3.4 has been used in conjunction with MATLAB version 7.0. The model used was the steady-state diffusion application mode specific to Laplace equation resolution. It defines the concentration of species O at all points of the cell. Typically, the $b-a$ distances used were in the range of 50 to 500nm, RG was 5 (Figure 3).

Simulated domain

An important aspect in the simulation is the size of the simulated domain because it greatly influences the simulated microelectrode current.⁸ Our simulated domain is defined with L_1 and R_1 respectively fixed to 20 and 100, (Figure 3) which is large enough to accurately simulate diffusion and ensure a relative error less than 1% that is agree with the experimental results. Indeed, if $RG < 10$, satisfactory simulation accuracy can only be achieved by taking into account the mediator diffusion from behind the insulating sheath.

Meshing and resolution

Meshing is an important simulation parameter. To accurately evaluate the diffusive flux normal to the microelectrode surface where the electrochemical reaction occurs, the boundary condition discontinuities at the edge of the ring must be considered. In order to evaluate the flux at both edges, a fine exponential distributed mesh with 5000 edge elements (Figure 4) is used. Finally, we could convert the calculated COMSOL flux into a current value expressed in Amperes, multiplying the simulated flux by:

$$bnFDc_O^o \quad [18]$$

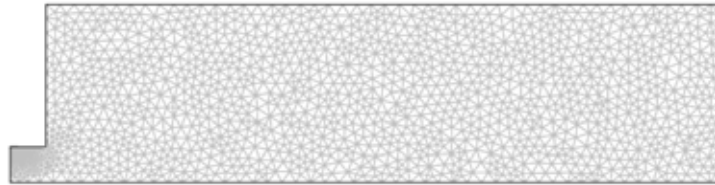


Figure 4. Mesh of the simulated domain. Here a fine exponential distributed meshing is used.

Use of results

Under the presented simulation conditions, the dimensionless time-independent SECM approach curves in positive and negative feedback mode for a reversible electrochemical reaction were obtained for a ring microelectrode. The ratios of the calculated ring current for varying a/b with the left limit current (a/b is 0) corresponding to the disk geometry microelectrode with a fixed RG of 5 and infinite limit tip to substrate distance were compared with that reported by Lee *et al.*⁵ For the a/b range of 0.5 to 0.9, the calculated ratios agree within 1% of those reported by Lee *et al.*

The present ring micropipet has an internal void that can be filled with a solution. In the first simulation, it was assumed that if it is filled with air, the internal void behaves as an insulator. To ensure that the simulation results are also valid for a void filled with fluid, the observed current variations for a $RG=2$, $a/b=0.5$ and $L=0.5$ with increasing solution column height in the void was simulated in both feedback modes (Figure 5). The relative errors observed for a similar simulation in positive feedback present current deviations inferior to 1%. Consequently, the presence of the solution column in the internal void leads to simulated current variations normally within the expected experimental error of an SECM approach curve (less than 1% of deviation). There is therefore no difference in the expected response of a solution filled and air filled micropipet. This will be important in future biological applications when the internal void of the ring microelectrode will be filled with a solution that will be ejected in close proximity to the substrate.

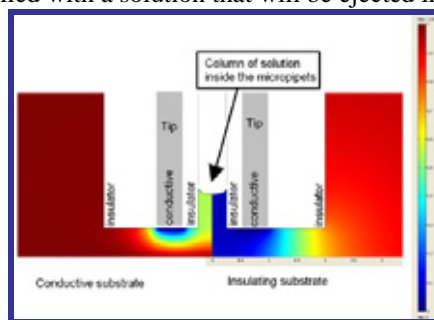


Figure 5. Comsol representation of the effect of a column of solution inside the ring microelectrode.

Conclusion

Micro-ring-injector sensors have been developed and our interest is to further apply them to biological studies where the electrochemical detection and injection time drugs in the vicinity of adhering cells are simultaneously controlled at the probe. Hence, it is important to understand their electrochemical behaviour as they approach different surfaces. Theoretical treatments of classical SECM approach curves in feedback modes for a ring microelectrode are very limited. Then the simulation becomes the tool to characterize them. COMSOL has demonstrated to be able to simulate the system with great accuracy since their results show an agreement of 1% with the experimental and theoretical results in the left geometry limit (a/b is 0). Then the simulation is well behaved for a/b ratios ranging from 0.5 to 0.9 and at the left limit. An extensive data set from numerical simulations of the ring microelectrode for pure positive and negative feedback mode approach curves is obtained. The dependence of the resulting simulated approach curves with characteristic dimensions of the ring microelectrode is also given. Finally an analysis of the impact of the internal void of the pipet over the current distribution is made.

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