Simulation of the chronoamperometric response of a regular array of micro-disc electrodes

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Abstract

Simulation based on finite element resolution has been carried out to study the diffusion process to a regular array of micro-disc electrodes. The effect of the centre to centre distance between inlaid micro-disc electrodes has been investigated for chronoamperometry. The chronoamperometric response of an array of micro-discs in a thin layer cell and of an array of recessed micro-discs has also been investigated. © 2000 Elsevier Science S.A. All rights reserved.

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1. Introduction

Microelectrodes are now used widely [1–4] and the theory of mass transport to a single micro-hemisphere [5], micro-disc [6–11] or micro-ring [12–15] electrode is now well established, with precise analytical expressions available. The current measured is usually very small and in order to increase the measured signal, arrays of micro-electrodes are often used. Many types of micro-electrode arrays have been studied for the design of sensors: micro-discs, bands, squares, interdigitated electrodes... The electrochemical response depends on the shape of the electrodes and the pattern of the array. Several models based on analytical and numerical solutions have also been published to analyse the diffusion process occurring at a regular ensemble of micro-disc electrodes [16–24]. In the case of a regular array of micro-disc electrodes, the general trend of the chronoamperometric response is now well known. At short times, a regular array of micro-discs behaves as the individual electrodes, and therefore the current response to a potential step, well past the formal potential value, fits the relationship developed by Aoki et al. [6] where:

\[ f(t) = \frac{1}{4zFDc_0} \left( \sqrt{\frac{\pi}{4\tau}} + \frac{\pi}{4} + 0.094\tau^{1/2} \right) \]

for small values of \( \tau = \frac{4Dt}{\tau^2} \) (1)

with \( z \) the number of electrons, \( F \) the Faraday constant, \( D \) the diffusion coefficient, \( c_0 \) the bulk concentration of the reactant and \( r \) the radius of the micro-disc. The current is proportional to \( t^{-1.2} \), the slope being the same as in the Cottrell expression for linear diffusion to a single micro-disc. However, the intercept is not zero and is equal to a current \( I = \pi zFDC_0r \). Towards long times, when the non linear diffusion fields of the individual electrodes overlap, the array behaves like a macroelectrode with an area equal to the total geometric area of the array. Between these two limits, there is a mixed mass transport regime.

Gueshi et al. [16] and Lindemann et al. [17] have developed an analytical expression to fit the chronoamperograms of micro-disc arrays. The expressions obtained were not precise due to the simplifying assumptions. Reller et al. [18] solved the model proposed by Gueshi et al. numerically by an explicit finite difference technique taking into consideration the transient character of the radial diffusion. The analytical
Scharfker [21] has developed a rather simple analytical approach to calculate the time dependent diffusion current to square, hexagonal and random arrays considering the overlap of the diffusion zones. To this purpose, an equivalent area of the plane surface towards which the same amount of material diffuses through linear diffusion is defined as the amount that diffuses through radial diffusion. The analytical expressions obtained were found to be in fairly good agreement with the theoretical results of Shoup and Szabo for \( \theta = 0.53 \) and 0.58. All these results relate to an infinite number of micro-disc interfaces. In more recent papers, the diffusion processes for finite number of micro-interfaces have been investigated [24–27]. Kolev et al. [24] gave a 3D mathematical approach to solve the diffusion process for an array of micro-disc electrodes with an arbitrary distribution.

Our main interest is to study the behaviour of arrays of micro-disc interfaces in chronoamperometric mode, as we have developed various electrochemical systems based on arrays of micro-holes filled with an organic electrolyte gel phase [28–30] or arrays of liquid | liquid interfaces for the extraction of ionic species [31] in flow conditions. This paper deals with the 3D simulation of the chronoamperometric response for an array of inlaid micro-discs. Then, thin layer cells and arrays of recessed micro-disc electrodes are considered.

\[ f(\tau, \theta) = \frac{1}{4D\pi x^2}c_0 \]
\[ = \frac{\sqrt{\pi}}{2\sqrt{\tau}} + \frac{\pi}{4} + \left(1 - \frac{\pi}{4}\right) \exp \left[\frac{-B\theta^2(3 - 2\theta)}{\sqrt{\tau}}\right] \]
\[ \exp \left[-\frac{\sqrt{\pi}}{2(1 - \theta)} + B\left(1 - \frac{\pi}{4}\right)\theta^2(3 - 2\theta)\right] \]
\[ = \frac{1 + 3\sqrt{\pi}}{2\tau}(1 - \theta) \]
\[ \text{with } B = 0.7823; \tau = \frac{4Dt}{r^2} \text{ and } \theta = 1 - \left(\frac{r}{L}\right)^2 \]  

\[ \frac{\partial c}{\partial t} = D \left(\frac{\partial^2 c}{\partial x^2} + \frac{\partial^2 c}{\partial y^2} + \frac{\partial^2 c}{\partial z^2}\right) \]  

The 3D geometry was made of a 2D mesh on the plane \( x, y \) containing the micro-discs of radius \( r \) separated from each other by a distance \( d = 2L \) as shown in Fig. 1. The problem has been simplified by taking into consideration the axes of symmetry, which reduces the 2D geometry to the hatched unit cell shown in Fig. 1. This 2D plane was then elevated on the z-axis to a height \( (H) \) to create the 3D geometry required.

The following boundary conditions have been used for the concentration:

\[ c(x, y, z, 0) = c_0 = 1 \text{ mol m}^{-3} \]
\[ c(x, y, 0, t) = 0 \quad x^2 + y^2 \leq r^2 \]
\[ \lim_{z \to \infty} \frac{\partial c}{\partial z} = 0 \quad x^2 + y^2 > r^2 \]

All the simulations have been carried out with dimensional mass transport parameters. The accuracy on the current obtained has been checked by comparison with analytical expressions whenever possible. Triangular finite elements were used in the plane of the electrode, with a finer mesh around its edge as shown in Fig. 2. The mesh away from the electrode was, however, kept as fine as possible considering the limitation imposed by the computer memory available. Similarly on the z-axis, the geometry was elevated with closer packed layers near the electrode as follow:

- \( z = 0 - 10 \mu m \) 10 \mu m divided in six layers
- \( z = 10 - 110 \mu m \) 100 \mu m divided in six layers
- \( z = 110 - 500 \mu m \) 390 \mu m divided in four layers
- \( z = 500 - 750 \mu m \) 250 \mu m divided in two layers

These conditions led to a 3D geometry containing between 10 000 and 20 000 nodes for the geometry (a) and (b) of Fig. 1 corresponding to an infinite number of micro-interfaces and between 20 000 and 30 000 nodes for the geometry (c) of Fig. 1 corresponding to four micro-interfaces. Finer meshes did not improve the accuracy and no divergence has been observed with the type of mesh used. In fact, the most important deter-
Fig. 1. Bottom view of the 3D geometry used to simulate (a) an infinite number of discs in a hexagonal lattice; (b) infinite number of discs in a square lattice; and (c) four discs in a square lattice. $L$, centre to centre distance between the discs of radii $r$. The hatched part corresponds to the simplified unit cells used for the simulation.

Fig. 2. Type of mesh used for the resolution of an infinite number of interfaces in a square lattice with $r = 10 \mu m$; $L = 50 \mu m$.

mining factors for the type of mesh used were the stepping time and the thickness of the first layer. The shorter the stepping time, the more accurate was the resolution. An error lower than 2% was obtained in the following simulations for an infinite number of micro-interfaces.

3. Results and discussion

The chronoamperograms have been calculated for various cases: (i) an infinite number of micro-discs in a hexagonal lattice; (ii) an infinite number of micro-discs in a square lattice; and (iii) four micro-discs in a square lattice using the unit cells defined in Fig. 1. Our simulated results were first compared to Eq. (2) obtained from fitting simulation results [20] and to the analytical expression proposed by Scharifker [21].

3.1. Infinite number of micro-interfaces

It is now well known that for an array of micro-disc interfaces, the deviation from the response obtained for a single micro-disc interface increases as the centre to centre distance $2L$ decreases. Fig. 3 shows a plot of the normalised current as a function of the inverse of the square root of time for an array of micro-discs positioned in a hexagonal lattice showing a trend similar to what has been already published. As we are mainly interested in the region where the diffusion fields overlap, we have sacrificed the accuracy at very short times to decrease the computational time. Therefore, as seen in Fig. 3, our results deviate slightly from the analytical expression (Eq. (1)) [6] as shown by curve (c). At short times, the current is proportional to the inverse of the square root of time leading to a straight line (dashed line in Fig. 3) parallel to that obtained from the Cottrell expression for linear diffusion to the area of that of a single micro-disc (curve b). For long times ($L = 20 \mu m$), the diffusion process does not reach a steady state but follows a semi-infinite linear diffusion process due to the overlap of the diffusion fields. The curve tends to the Cottrell expression for linear diffusion to the total geometric surface area (curve a). It deviates from the behaviour of a single micro-disc electrode, which can be approximated by Eq. (4) [6]:

$$f(\tau) = \frac{1}{4zFDc_0\tau} = (1 + 0.71835\tau^{-1/2} + 0.05626\tau^{-3/2} - 0.00646\tau^{-5/2}) \text{ for large values of } \tau$$  (4)
Curve (c) in Fig. 3 represents the combination of expressions (1) and (4). In the case of an array, the decrease in current at longer times depends on the micro-interface radius, the centre to centre distance between the micro-interfaces and the diffusion coefficient. The greater the diffusion coefficient, the faster the diffusion fields will overlap. For micro-electrodes separated by a long distance ($L = 200 \, \mu m$), the current at long times tends to the steady state limiting current according to Aoki's relationship (Eq. (4)) [6].

Fig. 4 shows a plot of the dimensionless current $f(t, \theta)$ as a function of the inverse of the square root of time.
Fig. 5. Plots of the dimensionless current according to Scharifker’s representation with $u = nr/(\pi Dt)^{1/2}$ (○) Simulated results; (a) single micro-disc [6]; (b) Cottrell for the total area; (c) Eqs. (5)–(7); and (d) Eq. (2) for $\theta = 0.75$, $r = 10 \mu m$ and $d = 40 \mu m$. Light line: extrapolation of Eq. (5) to the long time domain.

The analytical expressions developed by Scharifker were obtained from the two limiting cases (i) parallel to the Cottrell plot for semi-infinite linear diffusion for the electroactive area which intercepts at a current $I = \pi nr z F D c_0$ (light line in Fig. 5 covered by curve c at short times) and the Cottrell plot for semi-infinite linear diffusion for the total surface of the array (curve b in Fig. 5). In the mixed region where the diffusion fields overlap, the analytical expression was deduced from the two limiting cases Eqs. (5) and (7).

The dimensionless time $\tau$ defined above in Eq. (2). For low coverage ($\theta > 0.9$), our simulated results fit Eq. (2) fairly well but deviate slightly as the centre to centre distance between the micro-interfaces is reduced. This difference is probably related to the assumption made by Shoup and Szabo who considered the micro-disc surrounded by a circle rather than by a hexagon corresponding to the non-electroactive part (see Fig. 1). The contribution of this dead volume, which is not taken into account, becomes more and more important compared to the total non-electroactive surface as the centre to centre distance between the micro-interfaces decreases. As a consequence, for closed packed arrays ($\theta < 0.9$), the chronoamperometric current defined by Eq. (2) decreases at an earlier time in comparison to our simulated results.

The analytical expressions developed by Scharifker were obtained from the two limiting cases (i) parallel to the Cottrell plot for semi-infinite linear diffusion for the electroactive area which intercepts at a current $I = \pi nr z F D c_0$ (light line in Fig. 5 covered by curve c at short times) and the Cottrell plot for semi-infinite linear diffusion for the total surface of the array (curve b in Fig. 5). In the mixed region where the diffusion fields overlap, the analytical expression was deduced from the two limiting cases Eqs. (5) and (7).

For arrays of micro-discs separated by long distances, the inaccuracy of Eq. (6) is significant and can be as

$$I = \pi n r z F D c_0 \sqrt{\frac{3}{\pi u}} \left\{ \left(2\sqrt{3}(u + nr^2) - 1\right)^{1/2} + 2\sqrt{3}(u + nr^2) \left[ \frac{\pi}{6} \arctan(2\sqrt{3}(u + nr^2) - 1) \right]^{1/2} \right\}$$

for: $u < 1/(2\sqrt{3}) - nr^2$

$$\frac{I}{\pi n r z F D c_0} = 1 + \frac{nr^2}{u}$$

(5)

for: $1/(2\sqrt{3}) - nr^2 \leq u \leq 2/(3\sqrt{3}) - nr^2$

$$\frac{I}{\pi n r z F D c_0} = 1 - \frac{nr^2}{u}$$

(6)

for: $u > 2/(3\sqrt{3}) - nr^2$

$$\frac{I}{\pi n r z F D c_0} = \frac{1}{\pi u}$$

(7)

where $u$ is the adimensional time $nr \sqrt{\pi Dt}$ and where $n$ is the number density of microelectrodes $2/(\sqrt{3}d^2)$ for a hexagonal lattice. At short times not simulated here, Eq. (2) and Eq. (5) merge. Fig. 5 compares our simulated curves with the ones resulting from Eqs. (5)–(7) and Eqs. (2) and (4). At very short times not shown in Fig. 5 and at very long times illustrated in Fig. 5, it is clear that the Scharifker relationships (Eqs. (5) and (7)) fit the present simulated results as well as Eq. (2). However, in the region where the diffusion fields overlap, expression (6) deviates significantly. This is due to the fact that in the case of a micro-disc electrode the steady state current is equal to $4z F D c_0$ which is higher by a factor $4/\pi$ than the intercept of Eq. (5) illustrated by the light line in Fig. 5. Consequently, towards the region where the diffusion fields overlap the two curves (c) and (d) are significantly separated. Fig. 6 compares the present simulation to Scharifker’s model for various centre to centre distances between the micro-interfaces. For arrays of micro-discs separated by long distances, the inaccuracy of Eq. (6) is significant and can be as
much as $\pi/4$. However, for very close packed arrays ($\theta \approx 0.55$), Eqs. (5)–(7) seem to fit reasonably well.

All in all, the present study shows that Eq. (2) is good for large values of $\theta$ ($\theta > 0.9$), whereas Eq. (6) is valid only for smaller values of $\theta$ ($\theta < 0.6$).

Another important parameter when working with arrays of microelectrodes is the time for which the current decreases due to the overlap of the diffusion fields which corresponds to the transition from spherical to semi-infinite linear diffusion. Scharifker defined the transition time as the intercept between the two asymptotes relatives to the two limiting cases defined by Eqs. (5) and (7)

$$t_{\theta \to p} = \frac{(1 - \pi nr^2)^2}{\pi D (\pi nr)^2}$$

whilst Shoup and Szabo gave the following expression:

$$t^* = \frac{(1 - \pi nr^2)^2}{\pi D (\pi nr)^2}$$

Fig. 6. Plots of the dimensionless current according to Scharifker's representation with $u = nr(\pi Dt)^{1/2}$: (▲) $L = 15 \mu m$, $\theta = 0.555$; (■) $L = 20 \mu m$, $\theta = 0.75$; (□) $L = 50 \mu m$, $\theta = 0.96$; (●) $L = 100 \mu m$, $\theta = 0.99$; — fitting with Scharifker's relationships (Eqs. (5)–(7)); $r = 10 \mu m$.

Fig. 7. Plot of the time corresponding to the decrease of the current due to the merging of the diffusion fields as a function of the inverse of the diffusion coefficient; $L = 20 \mu m$; $r = 10 \mu m$ and $\theta = 0.75$. (a) Scharifker's relationship $t^* = \frac{(1 - \pi nr^2)^2}{\pi D (\pi nr)^2}$ with $n = 2/\sqrt{3}d^2$; (b) Shoup and Szabo's relationship $t^* = \frac{(L - r)^2}{6D}$ and simulated results for various percentages.
Fig. 8. Comparison between an infinite number of micro-interfaces and a finite number of four micro-interfaces. $D = 5 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$; $L = 20 \mu\text{m}$; $r = 10 \mu\text{m}$. (a) Four micro-interfaces $H = 750 \mu\text{m}$; (b) infinite number of micro-interfaces; (c) calculated curve with Eq. (10); (d) single micro-disc [6].

Fig. 9. Illustration of Eq. (10) for a $3 \times 3$ array.

\[ t_{s-p} = \frac{(L - r)^2}{6D} \]  

which corresponds to the diffusion time inside the disc of radius $L$. Fig. 7 shows a plot of this transition time as a function of the reciprocal of the diffusion coefficient for the relationships (8) and (9) and results correspond to a decrease from 3 to 50% of the calculated current from the steady state current, taken as the current provided by the array with the longest $L$ value which therefore should include the error coming from our simulation conditions. According to our results, the current starts to decrease as soon as the diffusion fields overlap. With Eq. (8), the current has decreased by more than 50%, whereas Eq. (9) seems to correspond to the beginning of the overlap of the diffusion fields.

A similar study was carried out for an array of micro-discs positioned in a square lattice. No noticeable differences were obtained between the square and the hexagonal arrangement with the same number density $n$. The transition time from spherical to semi-infinite linear diffusion was also exactly the same as the one calculated for an array of micro-discs in a hexagonal lattice as shown in previous publications [18,21].

3.2. Four micro-interfaces

In the case of an array with a finite number of micro-electrodes, the chronoamperograms depend obviously on the number of micro-interfaces located on the edge of the array. Fig. 8 shows the difference under the same conditions between four micro-interfaces (curve a) and an infinite number of micro-interfaces (curve b). As expected, at short times the responses are nearly identical, the difference being due to the fact that the simulation for a four micro-electrode system requires a coarser grid able to cover the larger space domain. Towards longer times, the contribution from spherical diffusion is greater for four micro-interfaces, as the diffusion fields overlap only in the centre of the square defined by the four electrodes. As shown in Fig. 8, the chronoamperogram for a given number of micro-interfaces can be calculated from the chronoamperogram of a single micro-disc interface and the response for a micro-disc interface located within an infinite number of micro-interfaces. Curve c, shown in Fig. 8, has been calculated for the array of four micro-discs in a square lattice taking the contribution for each micro-disc electrode equal to three times the quarter of the current corresponding to the diffusion to a single stand-alone micro-disc electrode plus a quarter of the contribution of a micro-disc electrode located within an infinite number of micro-discs.

In other words for a square lattice, the current to a finite number of micro-interfaces $N$ with $N_e$ the total number of micro-discs on the four edges is equal to:
\[ I_{\text{finite square}} = \left[ 1 + \frac{N_E}{2} \right] I_{\text{Single}} + \left[ N - \frac{N_E}{2} - 1 \right] I_\infty \] (10)

where \( I_{\text{Single}} \) and \( I_\infty \) represent the current to a single isolated micro-electrode and to a micro-electrode in an infinite array, respectively. This is illustrated in Fig. 9 where the parts of the electrodes working as isolated micro-electrodes are lightly shaded and those working as micro-electrodes in an infinite array are heavily shaded.

The transition time occurs at the same time as the diffusion fields will still overlap at the same time.

3.3. Finite height cell

A cell configuration with a finite height can be interesting for the development of electrochemical detectors especially in flow conditions. Fig. 9 shows the effect of

![Graph](image1)

**Fig. 10.** Plot of the normalised current as a function of the inverse of the square root of time for an infinite number of micro-discs positioned in a square lattice with \( d = 40 \, \mu m \); \( D = 1 \times 10^{-10} \, m^2 \, s^{-1} \) and \( r = 10 \, \mu m \). \( H = 20; 50; 110; 500; 750 \, \mu m \).

![Graph](image2)

**Fig. 11.** Plot of the current as a function of the inverse of the square root of time for an infinite number of micro-discs in a square lattice with a centre to centre distance of \( d = 40 \, \mu m \); \( r = 10 \, \mu m \); \( D = 1 \times 10^{-10} \, m^2 \, s^{-1} \); \( H = 750 \, \mu m \). (▲) Recess = 10 \, \mu m; (△) Recess = 5 \, \mu m; (●) Recess = 1 \, \mu m; (○) Recess = 0 \, \mu m.
the thickness of the cell in the z dimension on the chronoamperogram. As the thickness of the cell is reduced, the current decreases at earlier times due to the depletion of the electroactive species in the cell. This result shows that it is important to consider the height of the cell only if \( H < d \).

3.4. Recessed micro-disc

Fig. 10 shows the chronoamperometric responses for recessed micro-disc interfaces. The presence of a slight recess affects essentially the response at short times. The response tends to a straight line obtained for semi-infinite linear diffusion according to Cottrell and not to its parallel as shown previously. The deeper the recess, the more important the linear diffusion effect and consequently the plot will follow Cottrell behaviour towards longer times. Towards very long times, the current will again drop as previously, however, the overlap of the diffusion fields will occur at longer times for a deep recess. It is therefore essential when comparing theoretical and experimental results to be sure that the electrode is not slightly recessed as even for a recess of 1 \( \mu m \) for an electrode radius of 10 \( \mu m \) the effect is not negligible as is shown in Figs. 10 and 11.

4. Conclusions

The simulated results obtained for the response to a potential step for an array of micro-discs fit the analytical expression of Shoup and Szabo fairly well for \( \theta > 0.9 \) [20]. A small deviation was observed for micro-discs separated by small distances due to the assumption made by Shoup and Szabo which uses a circle rather than a hexagon to map the non-electroactive area. The expression developed by Scharifker [21] can be used only for close packed arrays of micro-discs (\( \theta < 0.6 \)) as it is considered that for all times, the limit towards short time tends to the Cottrell behaviour obtained for semi-infinite linear diffusion. For arrays of micro-discs separated by a large distance, the overlap of the diffusion fields occurs at a time when the difference between the Cottrell behaviour obtained for short times which intercepts at a current \( I = \pi z F D C_0 r \) and the current for longer time scales which intercepts at \( 4z F D C_0 r \) deviates significantly.

Arrays of recessed micro-electrodes behave quite differently from arrays of inlaid electrodes in the short and medium time domains.

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