Cyclic voltammetry at a regular microdisc electrode array

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Abstract

A simulation of cyclic voltammetric responses has been performed to study the diffusion process of a regular array of microdisc interfaces by the use of finite element software. The effect of centre-to-centre distance between the active electrodes on the current response and also their voltammetric shape and characteristics have been investigated. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

Nowadays, the design of microelectrode arrays with well-defined geometries is reported mostly for electroanalytical purposes [1]. The geometries feature an assembly of parallel microbands operating at the same potential or alternatively polarised as cathodes or anodes [2,3]. This latter configuration is generally known as the interdigitated band electrode configuration. Another common geometry is the microdisc array where the electrodes are arranged in a hexagonal or a square lattice [4–7] or even in a random manner [8–10].

A theoretical analysis of ensembles of microelectrodes has been originally initiated in order to explain the effect of the partial blocking at a large electrode [11–14]. As already shown, the apparent electron transfer rate constant seems slower at a dirty (not polished) electrode than at a cleaned, freshly polished one. This phenomenon results from the partial blocking of the electrode by an insulating material leading to the formation of a random array of microelectrodes. Gueshi et al. [11,12] demonstrated theoretically and experimentally that a distortion of the cyclic voltammogram appears in this case. A mathematical treatment of this phenomenon has been reported by Amatore et al. [15] for a hexagonal assembly of microdisc and microband electrodes. They have shown that depending on the fractional coverage of the array, various voltammogram shapes are obtained. For a low coverage by inactive sites, i.e. small inter-electrode distance, a Nernstian peak-shaped voltammogram is obtained whereas a sigmoidal shape results from a large inactive site coverage. Moreover, between these two limiting cases, the increase of the peak-to-peak separation with the inter-electrode distance is also noticed even if a fast electron transfer reaction is assumed.

For arrays of microelectrodes as for the single microelectrode case, the theoretical consideration is mostly cumbersome due to the non-linear diffusion profiles at the electrodes. Analytical expressions are available for the chronoamperometric response of microdisc electrodes alone [16], in a hexagonal [17,18] or a square lattice [18]. Depending on the inter-electrode distance, the response of an array can be simply the sum of the individual responses when the inter-electrode distance is large compared to the individual diffusion layers. Otherwise, when the diffusion fields begin to overlap, a more complex behaviour is observed arising from the mixed diffusion behaviour. Finally, if the experimental time scale is sufficiently large, all the individual diffusion layers merge to form one single linear diffusion layer. A proposed condition generally reported for observing independent behaviour of the active sites and therefore avoiding a shielding effect is that [19]:

\[ R_0 r > 6, \text{ i.e. } d/r > 12 \] (1)

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where $2R_0 = d$ is the inter-electrode centre-to-centre distance and $r$ is the radius of the active site.

Condition (1) arises from the fact that 90% of the concentration lines are located within a distance of 6.3$r$ at a microdisc electrode [19]. This condition is often used for the design of a microelectrode array but does not seem to be always appropriate experimentally. For an array with nanometer-scale microdisc electrodes, a pure spherical cyclic voltammogram is not observed when $r = 50$ nm and $2R_0 = 1.3$ $\mu$m (i.e. $d/r = 26$) [20].

Cyclic voltammetry treatment at an assembly of microelectrodes is rather more complicated than chronoamperometry, as one more parameter, the potential, is introduced. But cyclic voltammetry has also proved over the years to be one of the most ubiquitous electrochemical methods. In the case of semi-infinite linear diffusion, the technique is often used to determine the reversibility of the electrode reactions. When applied to a microelectrode or a microelectrode array, cyclic voltammetry is mainly used in the steady state limit. From an electroanalytical viewpoint, the major issue is then to choose a scan rate to ensure that a steady state current can be measured. Otherwise, a peak-shaped CV will be recorded, the characterising of the diffusion processes of an assembly of microdisc electrodes is rather more complicated than in the bulk region. The mesh away from the plane of the microdisc with a finer mesh around its edge is the radius of the active site.

d

$D$ is its diffusion coefficient.

The geometries simulated in this work are the classical hexagonal and square lattices already presented in our previous paper [21]. The 3D mesh is made of a 2D plane containing the microdiscs of radius ($r$) separated from each other by a centre-to-centre distance $d = 2R_0$. The 2D mesh is then elevated on the $z$-axis in order to create the 3D geometry required.

The boundary and the initial conditions used in the simulations are:

$$c(x,y,z,0) = c_0 = 1 \text{ mol m}^{-3}$$

$$\left(\frac{\partial c}{\partial z}\right)_{z = 0} = 0, \ x^2 + y^2 > r^2$$

$$\lim_{z \to \infty} c = c_0 = 1 \text{ mol m}^{-3}$$

At the electroactive sites, due to the potential scan, a time evolution condition is defined as:

$$t < \tau \quad \frac{c}{c_0} = \Theta e^{-\gamma t}/1 + \Theta e^{-\gamma t}$$

$$\tau < t < 2\tau \quad \frac{c}{c_0} = \Theta e^{-(2\gamma t)/1} + \Theta e^{2\gamma t}$$

where the various parameters, $\tau$, $\Theta$ and $\gamma$ read:

$$\tau = \Delta E/\nu$$

$$\Theta = e^{2F/RT(E_{ox} - E^o)}$$

$$\gamma = zF\nu/RT$$

with $E$, being the initial potential, $E^o$ the formal potential, $\Delta E$ the potential window, $\nu$ the potential sweep rate, $F$ the Faraday constant, $z$ the number of exchanged electrons, $R$ the universal gas constant and $T$ the temperature.

The relationships in Eqs. (6) and (7) are valid only if the diffusing species and its product compound have the same diffusion coefficient.

The various geometrical and physical parameter values taken in this work are:

- Inter-electrode distance: $d = 2R_0 = 30, 60, 120, 400, 600, 1000, 1500$ $\mu$m.
- Microelectrode radius: $r = 10$ or 13 $\mu$m.
- Diffusion coefficient: $D = 10^{-9}$ m$^2$ s$^{-1}$.
- Bulk concentration: $c_0 = 1$ mol m$^{-3}$.
- Sweep rate: $\nu = 10, 40, 100$ mV s$^{-1}$.

All simulations are carried out with dimensional mass transport parameters and using a transient linear algorithm. Triangular finite elements are used in the plane of the microdisc with a finer mesh around its edge than in the bulk region. The mesh away from the microdisc is kept as fine as possible considering the limitation imposed by the available computer memory. Extra points are placed in both regions to impose a grid construction and the number of nodes as well as the

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

where $c$ is the concentration of the diffusing species and $D$ is its diffusion coefficient.

2. Numerical details: 3D geometries and numerical parameters

The 3D-simulation of the diffusion processes of an array of infinite and finite numbers of inlaid microdiscs is performed using a commercial finite element software package (Flux-Expert®, Simulog Grenoble, Montbonnot St. Martin) and operated on a UNIX workstation (Silicon Graphics Indigo 2 Impact 10000, 640 MB RAM). The diffusion profiles are calculated by solving Fick’s second law in Cartesian coordinates assuming a fast electron transfer at the active sites, and written as:
node repartition can be modulated on segments linking two such points. A geometrical distribution of the nodes is used near the interface edge, whereas an arithmetic distribution of the nodes is used on lines far from the interface. Similarly on the z-axis, the geometry is elevated with closer packed layers near the microinterface in the same manner as described in a previous paper [21]. The accuracy of the present simulation method is assessed using an infinite number of microdiscs spaced by a large distance \((d = 1500 \mu m)\) in a hexagonal array. A 2\% error is obtained on the steady state current value. In most cases, the potential window chosen is 1 V and the potential increment is 10 mV for all the scan rates.

3. Results and discussion

3.1. Infinite number of microdisc interfaces in a hexagonal array

3.1.1. Voltammetric responses

From the previous results obtained in the case of a hexagonal array of inlaid microdisc interfaces [21], it has been confirmed that the spacing distance between the adjacent microinterfaces strongly influences the diffusion process of the redox reactions. Thus, the effect of the inter-electrode distances in an infinite number of microdiscs \((r = 10 \mu m)\) arranged in a hexagonal lattice is here investigated by cyclic voltammetry. The voltammetric responses presented in Fig. 1 are obtained for centre-to-centre distances ranging from 30 to 1000 \(\mu m\). The scan rate used is 10 mV s\(^{-1}\) unless otherwise specified.

The smaller the centre-to-centre distances between the microdiscs, the smaller the measured current is with respect to the value obtained from Eq. (11). This equation is valid for the case of an array of inlaid solid microdiscs when no overlapping of the individual diffusion fields is noticed:

\[
I_{ss} = 4nzFDC_r \tag{11}
\]

where \(m\) is the number of microinterfaces. It can be observed that the steady state values obtained for large values of the ratio \(d/r\) exceed the theoretical values by 2\%.

This result corroborates the screening effect of the individual diffusion fields. It can be pointed out that two characteristic limiting polarisation curves are obtained as follows: (i) in the case of \(d/r > 40\), a sigmoidal shape that can be related to microdisc electrode behaviour (spherical diffusion); and (ii) in the case of \(d/r < 6\), a peak-shaped voltammogram that can correspond to reversible linear diffusion. We can already conclude here that the proposed Condition (1), \(d/r > 12\), is not satisfactory.

Significant decreases of the current at closely spaced active sites (e.g. \(d/r = 3\)) compared with those with large centre-to-centre distances can be explained by the fact that the former interfaces cannot be considered as independent of each other. The border-to-border distance is almost equal to the diameter of the microdiscs, so that the individual diffusion fields may strongly overlap. The merged diffusion fields then form an almost planar diffusion layer and the voltammetric behaviour of the microinterfaces becomes similar to a conventional macroelectrode.

This finding was investigated using various parameters such as the plot of the peak current as a function of the square root of the scan rate and also the evolution of the peak-to-peak separation with the parameter \(d/r\). The slope of the simulated peak current response vs the square root of the scan rate (0.043) is in good agreement with the Randles–Sevcik equation (0.049) (see Fig. 2) for the case \(d/r = 3\). Here the surface area used in the calculation is the sum of the active microdisc electrode and the insulating area. Further supportive evidence can be the peak-to-peak separation on the forward and reverse scans, which should be equal to \(59/z\) mV at 298 K for the case of a reversible reaction. The simulated value is close to 60 mV for the case of \(d/r = 3\) and starts deviating from \(d/r > 6\).

When the ratio of \(d/r\) is larger than 40, the shape of the voltammograms tends towards sigmoidal and a steady state current is reached. The ratio of the simulated steady state current and the theoretical value (Eq. (11)) is close to unity. This indicates typical behaviour.
3.1.2. Dimensionless analysis

The aim of this section is to provide a dimensionless diagram in order to predict the behaviour of an array of microelectrodes. The same analysis can be applied to an array of supported liquid–liquid interfaces but subject to specific conditions.

The critical parameters here are the characteristic lengths \( d, r \) and the scan rate \( v \). If the scan rate is reduced to a length \( \frac{d}{p|RTD|^n} \), the dimensionless parameters \( d/r \) and \( d/r \) can be used.

For chronoamperometry, Shoup and Szabo [17] and Scharifker [18] defined a parameter \( t_{s-p} \) expressing the transition time between spherical and planar diffusion. These equations read, respectively:

\[
\begin{align*}
\tau_{s-p} &= \frac{(R_0 - r)^2}{6D} \\
\tau_{s-p} &= \left( 1 - \frac{n\pi r^2}{\pi D} \right)^2 \left( \frac{n^2 r^2}{\pi D} \right)^2
\end{align*}
\]

where \( n = (2/\sqrt{3}d^2) \) for a hexagonal array. It is worth pointing out that Shoup and Szabo’s Eq. (14) corresponds to the beginning of the overlap of the diffusion fields, whereas in Sharifker’s Eq. (15) the current has already decreased by more than 50%. The former transition corresponds to the departure from the spherical diffusion behaviour whereas the latter corresponds to the onset of a planar diffusion regime.

From Eqs. (12) and (13) and the definition of the scan rate reduced to a length \( \frac{d}{p|RTD|^n} \), we can associate \( d/r \) values to these two transition times, and thereby define two dimensionless parameters associated with the merging of the diffusion fields:

\[
\begin{align*}
\frac{\delta_{s-p}}{r} &= \left( \frac{d}{2r} - 1 \right) \sqrt{3} \\
\frac{\delta_{s-p}}{r} &= \frac{2}{\sqrt{2\pi}} \left( \frac{\sqrt{3}d^2}{2\pi r^2} - 1 \right)
\end{align*}
\]

The plot of \( \log(d/r) \) vs \( \log(\delta/r) \) is presented in Fig. 3. Eqs. (14) and (15) define three main areas where the central area delimited by these equations can be regarded as the domain where a mixed diffusion process is encountered, i.e. where a peak-to-peak separation larger than 59 mV is obtained. In the left side a spherical process is established whereas in the right side linear diffusion prevails. For the case of a macroelectrode (i.e. \( d/r = 2 \)), only linear diffusion is exhibited and therefore Eqs. (14) and (15) tend toward an asymptotic trend. This phenomenon can be easily understood by noticing that in this case a peak-shaped voltammogram is obtained whatever the scan rate used.

The simulated results reported in Fig. 3 corroborate the analysis derived above. Spherical, mixed and linear voltammograms are located in the respective areas defined by Eqs. (14) and (15). It is also worth noticing that Fig. 3 represents only half of the real zone dia-
gram. A symmetric representation can be envisaged where a transition between spherical and linear takes place again for microelectrodes when the scan rate is increased. Fig. 3 clearly shows that the condition to fulfil for independent diffusion fields and pure spherical diffusion is given by Eq. (14), i.e. \((\delta/\rho) < [(d/2r) - 1]/\sqrt{3}\). Generally, the reported condition (1) is \(d/r > 12\). Condition (1) is really not satisfactory as it should be sweep rate dependent. Fig. 3 clearly shows that this statement is correct only for a range of scan rates. For instance, for \(r = 10 \mu m\) or \(5 \text{ nm}\) the scan rate value must be larger than 30 mV s\(^{-1}\) and 120 kV s\(^{-1}\), respectively, to remain in the spherical behaviour area if \(d/r = 12\).

3.1.3. Zone diagram

The shapes and characteristics of the voltammograms for the various distances, \(d/r\) ranging from 3 to 60 are further investigated by comparison with the analysis developed by Amatore et al. [15] for charge transfer at partially blocked surfaces. Two dimensionless parameters, \(K_l^{1/2}\) and \(A(1 - \theta)\) are considered:

\[ K_l^{1/2} = [(1 - \theta)/\theta] \]
\[ \left[ (2D/R_0^2)\theta^{-1}(1 - \theta)^{1/2}/\ln[1 + \left| z(1 - \theta)^{-1/2}\right| t_c^2 \right]^{1/2} \]
\[ A(1 - \theta) = k(t_c/D)^{1/2}(1 - \theta) \]

where \(R_0\) is the half distance between the active site, \(t_c\) is equal to \(RT/Fv\) and \(z\) is an empirical adjustable parameter that is taken as equal to 0.27 [15]. \(\theta\) represents the fractional coverage of the insulating sites, which is defined as \(\theta = S_{ins}/(S_{ins} + S_{active})\). \(S_{ins}\) and \(S_{active}\) are the insulating and electroactive surface areas, respectively, and \(k\) is the standard rate constant for the electron transfer at the active site. As a fast electron transfer reaction is assumed in our case, \(k\) must be taken large enough, e.g. \(\geq 0.1\ \text{ cm s}^{-1}\).

The graphical meaning of these dimensionless parameters is first described in Fig. 4, representing a zone diagram as reported by Amatore et al. [15]. The representation of \(\log A(1 - \theta)\) vs \(\log K_l^{1/2}\) defines four main domains where different characteristic behaviour is encountered. The vertical frontier delimits the linear and spherical diffusion fields. In the left hand side of the representation, a sigmoidal shape is obtained for the voltammogram whereas in the right hand side, a peak shape is achieved. Then, a division is also distinguished between the upper and lower sides. In the upper side, a fast electron transfer is stated whereas in the lower part, the voltammogram exhibits apparent quasi-irreversible electron transfer behaviour. The graphical evidence includes a steady state voltammogram, which is not centred on \(E^0\) and a peak-to-peak separation larger than the thermodynamic value. This representation was derived for a hexagonal array of microdisc electrodes with the assumption of disc inactive sites rather than hexagonal ones.

The values calculated for the examples shown in Fig. 1 are summarised in Table 1 and are plotted in Fig. 4. In the case of \(d/r = 40\), where the fractional coverage was close to unity (0.998), the location in the log/log plot is in the upper left side, which corresponds to a steady state reversible voltammogram (see Fig. 4). By simulation, a polarisation curve having the shape of a polarogram where the plateau height is also independent of the sweep rate (see Fig. 1) is obtained. The slope of the plot of \(\ln(I_i - I)/I\) vs potential yields 24.5 mV, which is in good agreement with the theoretical value of a reversible reaction (25 mV at 298 K). Also, the half-wave potential is simply equal to the formal potential of the reaction.

On the other hand, the case of \(d/r = 3\) where the fractional coverage is not close to unity (0.595), is represented in the upper right side of the log/log plot (see Fig. 4). The simulated voltammogram presents a peak shape with a peak-to-peak separation corresponding to the Nernstian behaviour.

![Fig. 4. Zone diagram reported from Ref. [15] representing the main characteristics of cyclic voltammograms as a function of two dimensionless parameters, \(K_l^{1/2}\) and \(A(1 - \theta)\), using Eqs. (15) and (16) taken from Ref. [15].](image)

### Table 1

<table>
<thead>
<tr>
<th>(d/r)</th>
<th>(\theta)</th>
<th>(K_l^{1/2})</th>
<th>(\log K_l^{1/2})</th>
<th>(A(1 - \theta))</th>
<th>(\log A(1 - \theta))</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>0.595</td>
<td>11.21</td>
<td>1.05</td>
<td>1839</td>
<td>2.26</td>
</tr>
<tr>
<td>6</td>
<td>0.899</td>
<td>1.14</td>
<td>0.057</td>
<td>45.9</td>
<td>1.66</td>
</tr>
<tr>
<td>12</td>
<td>0.975</td>
<td>0.20</td>
<td>-0.70</td>
<td>11.4</td>
<td>1.06</td>
</tr>
<tr>
<td>24</td>
<td>0.994</td>
<td>0.039</td>
<td>-1.42</td>
<td>2.7</td>
<td>0.43</td>
</tr>
<tr>
<td>40</td>
<td>0.998</td>
<td>0.012</td>
<td>-1.94</td>
<td>0.91</td>
<td>-0.041</td>
</tr>
<tr>
<td>60</td>
<td>0.999</td>
<td>0.00506</td>
<td>-2.30</td>
<td>0.45</td>
<td>-0.35</td>
</tr>
</tbody>
</table>
For both $d/r = 3$ and 40 cases, the present simulation data obtained for a hexagonal array corroborates the analysis [15].

Between the two limiting cases, as the inter-electrode distance is increased, the representation goes from the reversible linear diffusion voltammogram to the sigmoidal shape by increasing both the forward current value and the peak-to-peak separation. The fractional coverage strongly influences the apparent standard rate constant of the reaction.

3.2. Finite number of microdisc interfaces

An infinite number of interfaces is obviously an assumption, and experimental data are generally obtained for arrays with a finite number of microdisc interfaces. Due to the edge effect resulting from the interfaces located at the edges of the array, the amperometric response of an array of a finite number of interfaces can deviate drastically from the response of a theoretical lattice with an infinite number of electroactive sites. As demonstrated previously for chronoamperometry [21], the behaviour of an array with a finite number of interfaces can be derived by calculation from both simulated responses of a single microinterface and an array of an infinite number of interfaces. This assumption has been investigated here for the cases of square and hexagonal lattices during cyclic voltammetry experiments. The same kinds of simulations as shown in Section 3.1 have been carried out for an array of a finite number of microdisc interfaces.

3.2.1. Square lattice microdisc interfaces

Simulated current responses as a function of the applied potential at three different geometries are shown in Fig. 5 for geometries featuring an inter-electrode distance of 45 µm and a radius of 13 µm. The response of an individual interface depends on its environment as it is placed alone in a semi-infinite plane, located within an array containing a finite or an infinite number of microinterfaces.

The case of a single microelectrode was modelled by a 0.1 µm recessed microdisc resulting in a small decrease of the steady state current compared with the pure inlaid case (deviation less than 2% compared to Eq. (11)). Moreover, the semi-logarithmic representation of $(I_{\infty} - I)/I$ vs $(E - E^\circ)$ yielded a straight line with a slope of 24.5 mV per decade (1.1% error).

In the case of an infinite number of microdiscs separated by $d/r = 3.46$ (45/13 µm), a peak-shaped voltammetric response was observed at 10 mV s$^{-1}$ as has already been shown in Section 3.1 for a hexagonal array. When the finite number of electrodes (4 microdiscs, $2 \times 2$) is taken into account, a quasi-sigmoidal-shape response was obtained but with a current value lower than that for a single microdisc. This demonstrates the significant influence of the microelectrodes located at the edges of the array. This observation also allows the predict on that the condition $(\delta/r) < [(d/2r) - 1]/3$ valid for no diffusion field overlap in an array of a finite number of interfaces must be re-estimated in the case of an array of a finite number of microdisc electrodes.

A theoretical equation considering the edge effect on the square lattice array was used to fit the simulated data. In this case, the current due to a finite number of microdisc interfaces $N$ with the number of microinterfaces on the edge $N_0$ can be expressed as [21]:

$$I_{\text{finite square}}(E) = [1 + N/E/2]I_{\text{single}}(E) + [N - N_0/2 - 1]I_{\infty}(E) \tag{18}$$

where $I_{\text{single}}(E)$ and $I_{\infty}(E)$ represent the current at a single isolated microelectrode and at a microelectrode in an infinite array determined by simulation during a cyclic voltammetry experiment, respectively.

The calculated cyclic voltammogram of four microdisc interfaces in a square array (Eq. (18)) is also presented in Fig. 5. As was already reported for chronoamperometry, it can be observed that the calculated voltammetric response is in good agreement with the simulated current response (within error of 2% of the steady state current).

3.2.2. Microdisc interfaces in a hexagonal array

One direct application of the semi-analytical approach derived above is when the simulation limit is reached as in the case of a finite number of interfaces.
assembled in a hexagonal array. In this case, the present 3D-simulation approach requires a large computer memory. Therefore, the simulation of the finite case is not achieved here. To circumvent this limitation, Eq. (19) can be used to calculate the current response of a hexagonal microdisc array.

\[ I_{\text{finite hexagonal}}(E) = aI_{\text{single}}(E) + \beta I_{\alpha}(E) \]  

(19)

where \( a \) and \( \beta \) are weighting parameters representing the number of microdisc interfaces responsible for the edge and the array term in the total current, respectively.

The calculated current response for a finite number of electrodes obtained from the simulated data is shown in Fig. 6 for a hexagonal array (6 \times 11) having a centre-to-centre distance of 120 \( \mu \)m and an interface radius of 10 \( \mu \)m. The number of microelectrodes responsible for the edge and array were \( a = 50 \) and \( \beta = 16 \), respectively, in the present array.

For the case of an infinite number of microdiscs in a hexagonal array separated by \( d = 120 \) \( \mu \)m, the peak shape of the voltammetric response was observed to be similar to the case of a square array having the same inter-electrode distance. In the case of the finite number of interfaces, the calculated voltammogram shows a quasi-sigmoidal response with a current value lower than that for a single microdisc. This finding also supports the significant influence of the interfaces located at the edges of the array on the current response of the finite number of interfaces.

The comparison of the calculated voltammogram with an experimental one is also performed in Fig. 6. These experimental data were achieved for the case of the transfer of tetrarmethylammonium ions across a liquid | liquid interface featuring the geometry described above [5–7]. Liquid interfaces supported on microholes can be easily manufactured by laser ablation of polymer films. The amperometric response of an array of liquid | liquid microinterfaces supported on a microhole array can be compared to an array of solid microdisc electrodes when symmetric forward and reverse diffusion fields are assumed. It can be pointed out that the calculated voltammetric response is in good agreement with that of the experimental current response (within an error of 2%). This demonstrates the validity of the present simulation and the semi-analytical method.

The comparison of a hexagonal array with an infinite number of interfaces and a (6 \times 11) hexagonal lattice has shown that a smaller \( d/r \) condition is determined for a sigmoidal shape. In the case presented here, the limit is pushed to \( d/r > 24 \) (compared with 40 for Section 3.1). Nevertheless, even for \( d/r = 3 \) a sigmoidal shape is observed due to the large deviation of the current values between a single microdisc and an array with an infinite number of active sites.

4. Conclusions

The study of the diffusion behaviour at a regular array of microdisc interfaces showed the importance of the spacing between the adjacent active sites in optimising the interfacial geometry.

This report clearly shows that the usual condition \( d/r > 12 \) is not really satisfactory. A complete characterisation can be achieved with the log/log plot of the dimensionless parameters, \( \delta/r \) and \( d/r \). The resulting zone diagram delimits the area where spherical, mixed or linear diffusion fields prevail. This diagram emphasises that a quasi-irreversible voltammogram can be explained merely by a mixed diffusion field rather than by a slow charge transfer rate constant.

For a finite number of interfaces in an array, the optimum inter-electrode distance can be reduced significantly due to the edge effect. The validity of Eq. (18), a concept developed in a previous paper [18], is also demonstrated by both the simulated and experimental data.

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