Catalytic mechanism in cyclic voltammetry at disc electrodes: an analytical solution

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The theory of cyclic voltammetry at disc electrodes and microelectrodes is developed for a system where the electroactive reactant is regenerated in solution using a catalyst. This catalytic process is of wide importance, not least in chemical sensing, and it can be characterized by the resulting peak current which is always larger than that of a simple electrochemical reaction; in contrast the reverse peak is always relatively diminished in size. From the theoretical point of view, the problem involves a complex physical situation with two-dimensional mass transport and non-uniform surface gradients. Because of this complexity, hitherto the treatment of this problem has been tackled mainly by means of numerical methods and so no analytical expression was available for the transient response of the catalytic mechanism in cyclic voltammetry when disc electrodes, the most popular practical geometry, are used. In this work, this gap is filled by presenting an analytical solution for the application of any sequence of potential pulses and, in particular, for cyclic voltammetry. The induction principle is applied to demonstrate mathematically that the superposition principle applies whatever the geometry of the electrode, which enabled us to obtain an analytical equation valid whatever the electrode size and the kinetics of the catalytic reaction. The theoretical results obtained are applied to the experimental study of the electrocatalytic Fenton reaction, determining the rate constant of the reduction of hydrogen peroxide by iron(II).

1. Introduction

The inlaid disc electrode is more widely employed in electrochemical studies in preference to other geometries due to its easier fabrication and cleaning. Therefore, the development of the theory for the electrochemical response at this kind of electrodes is of major interest.

The theoretical treatment of a physical system comprising an electrolytically active surface of disc geometry is noticeably complex since it involves a two-dimensional mass transport problem of concentration variations with non-uniform surface gradients. This is significantly more complicated than the one-dimensional problem corresponding to planar, spherical and cylindrical electrodes,1–7 and it has been mainly tackled by means of numerical simulations.8

Nevertheless, there have also been many attempts to resolve this problem by analytical methods. This fact clearly indicates the interest of having analytical solutions for the electrochemical response available in order to directly analyze the influence of the different variables of the system and to establish the conditions under which limit and particular behaviors of interest can be observed. In addition, they are usually much faster and easier to compute than numerical solutions. Because of the complexity of the problem, analytical equations for the transient response are available only for simple charge transfer processes9 and for the first-order catalytic mechanism10,11 under limiting current conditions. Very recently analytical expressions for a simple charge transfer process, applicable to any voltammetric technique and for a catalytic process in constant potential chronoamperometry, have been reported for the first time.12,13

The catalytic process can be characterized by the resulting peak current in cyclic voltammetry that always exceeds the value of a simple electrochemical reaction and it is one of the most extensively studied. Thus, the purpose of the present work is to give an analytical solution for the first-order catalytic mechanism at disc electrodes valid for an arbitrary sequence of potential pulses, and to particularize the results for cyclic voltammetry. For this, we mathematically demonstrate, by applying the induction principle, that for the first-order catalytic mechanism the superposition principle applies whatever the geometry of
the electrode. In the process, we reveal interesting physical implications pointing out that, despite the non-uniform physical gradients, the surface concentrations of the electroactive species are equal across the whole electrode surface and the total concentration of the electroactive species remains constant for any value of distance and time regardless of the geometry when the diffusion coefficients of the species are equal.

The analytical solutions presented are applicable to disc electrodes of any radius under transient and stationary conditions and they are compared with those previously obtained for spheres and microhemispheres. We have studied the effect of the kinetics of the catalytic reaction, the disc radius and the sweep rate. Moreover, the attainment of the steady state response is analyzed, establishing the conditions where a time-independent sigmoidal voltammogram is obtained. The equivalence relationships between the stationary voltammograms at discs and spheres are studied as a function of the catalytic kinetics and the electrode radius.

Finally, the characterization of the coupled catalytic reaction by means of cyclic voltammetry is considered. Simple procedures are given based on the value of the maximum current of the voltammograms (the peak current under transient conditions or the plateau current in the steady state). The results are applied to the experimental study of the electrocatalytic Fenton reaction determining the rate constant of the reduction of hydrogen peroxide by electrochemically generated iron(II). This reaction and variants involving organic peroxides are of great interest since they are a source of highly reactive radicals with application, for example, in wastewater treatment.14

2. Experimental

2.1. Chemical reagents

Hydrogen peroxide (H2O2, Sigma-Aldrich, solution 30 wt% in H2O), potassium chloride (KCl, Sigma-Aldrich, 99.0–100.5%), iron(II) chloride hexahydrate (BDH, 99%), hydrochloric acid (HCl, Fisher Scientific, 36%), ferrocene (Fe(C5H5)2, Aldrich, 98%), acetonitrile (MeCN, Fisher Scientific, dried and distilled, 99%) and tetra-n-butylammonium perchlorate (TBAP, Fluka, Puriss electrochemical grade, 99%) were all used as received without further purification.

2.2. Instrumentation

A computer-controlled µ-Autolab potentiostat Type II (Eco-Chemie, Netherlands) was used to carry out the experiments. A three-electrode set-up was employed, with gold electrodes of different sizes (A = 2.1 mm², r0 = 69.4 μm, r0 = 14.4 μm and r0 = 5.8 μm, with A being the electrode area of the macroelectrode and r0 the radii of the microelectrodes) as the working electrode, a gold wire as the counter electrode and a Saturated Calomel Electrode (SCE, Radiometer, Denmark) as the reference electrode.

The calibration of the size of the electrodes was performed electrochemically from the reduction of a 2 mM solution of ferrocene in acetonitrile containing 0.1 M TBAP, adopting a value of the diffusion coefficient of ferrocene in MeCN of \( D = 2.3 \times 10^{-9} \text{ m}^2 \text{ s}^{-1} \) at 25 °C.15

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<td>( D )</td>
<td>Diffusion coefficient</td>
</tr>
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<td>( c_i^* )</td>
<td>Equilibrium concentration of species ( i )</td>
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<td>Area of the electrode</td>
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<td>Radius of the electrode</td>
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<td>Concentration of species ( i ) at the electrode surface at the ( p )-th potential pulse</td>
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2.3. Theory

Let us consider the case of the pseudo first-order catalytic process where the electrode reaction is reversible and the reactive species O is regenerated in solution by means of a chemical reaction according to the following scheme:

\[ O + e^- \rightleftharpoons R \]

\[ R + Z \xrightleftharpoons[k_f]{k_2} O + P \] (3)

where \( Z \) and \( P \) are electroinactive species in the whole range of applied potentials and they are present in a large excess in such a way that \( k_1 = k_1' c_2^* \) and \( k_2 = k_2' c_0^* \) are both pseudo-first order rate constants of the homogeneous reaction with \( c_i^* \) being the equilibrium concentration of species \( i \),

\[ K = \frac{k_2}{k_1} = \frac{c_i^*}{c_0} \] (4)

where \( K \) is the inverse of the equilibrium constant of the catalytic reaction (see Table 1 for definitions).
In a previous paper we have shown that the solution for this mechanism corresponding to the application of a constant potential \( E_1 \) at a disc electrode when the electrode process is reversible is given by:  \(^{(1)}\)

\[
\frac{I_d}{FAD} = (c_O^* - c_O^{(1)}(\varepsilon = 0))j_d(r_d, z_1, \zeta_1)
\]

(5)

where \( A_d = \pi r_d^2 \) denotes the disc area with \( r_d \) being the disc radius. The function \( j_d'(r_d, z_1, \zeta_1) \) and \( c_O^{(1)}(\varepsilon = 0) \) are given by eqn (A43) and (A44).

Note that the surface concentrations are only dependent on the applied potential (see eqn (A7) and (A8)) and therefore independent of time at any point of the disc surface, in spite of the fact that the concentration gradient at the electrode surface \( \left( \frac{\partial c}{\partial \zeta} \right)_{\zeta = 0} \) has a different value depending on the distance of the surface point considered to the disc centre.  \(^{(1)}\)

We previously demonstrated that the superposition principle can be applied to this mechanism at spherical and planar electrodes, such that the problem corresponding to the application of \( n \) potential pulses can be treated as \( n \) independent single-pulse problems and the current is given as a sum of \( n \) responses of single potential steps. In the Appendix, we have extended the application of this principle to any electrode geometry. Thus, by following the procedure indicated in this Appendix we find the following explicit and simple expression for the current corresponding to the application of an arbitrary sequence of potentials \( E_1, E_2, \ldots, E_p \) to the catalytic mechanism at a disc electrode (d super/subscripts),

\[
\frac{I_d}{FAD} = \frac{\zeta^*}{1 + K} \sum_{m=1}^{p} Z_m j_d(r_d, \chi_m, \zeta_m)
\]

(6)

where \( Z_m, \chi_m \) and \( \zeta_m \) are defined in the Appendix by eqn (A43) and (A44).

### 3.1. Linear sweep voltammetry and cyclic voltammetry

In the case of linear sweep voltammetry (LSV) and cyclic voltammetry (CV) we consider the application of a staircase of potential steps \( E_1, E_2, \ldots, E_p \) with a pulse amplitude (\( \Delta E \)) tending to zero for a fixed scan rate \( (i.e., \Delta E < 0.01 \text{ mV}) \) in practice, see ref. 19), so the applied potential waveform behaves as a continuous function of time in the way:

\[
E(t) = E_{\text{initial}} - vt \text{ for } t \leq \lambda
\]

\[
E(t) = E_{\text{final}} + vt \text{ for } t > \lambda
\]

(7)

where \( \lambda \) is the time at which the scan is reversed and \( v \) is the scan rate defined as \( v = dE/dt \).

If we take into account the following relationship for the time elapsed between the application of the \( m \)-th and \( p \)-th potential, \( t_{mp} \), and the applied potential,

\[
t_{mp} = (p - m + 1)\tau = \frac{|E_{m-p+1} - E_{\text{initial}}|}{v}
\]

(8)

By introducing eqn (7) and (8) into (6), the following expression for the cyclic staircase or cyclic voltammetric current is obtained:

\[
\psi = \frac{I_d^d}{FAD} \frac{1}{\sqrt{DRT}} \sqrt{\lambda} \sum_{m=1}^{p} Z_m T_d(Q, \Lambda, \delta_{mp})
\]

\[
= \psi_{\text{radial}} + \psi_{\text{radial}} + \frac{1}{Q(1 + K)(1 + e^{-\beta_{\text{initial}}})}
\]

(9)

where \( \zeta^* = c_O^* + c_R^* \) (see eqn (A3)) and,

\[
T_d = T + 2.732 \sqrt{\lambda} \int_0^{\lambda} \exp \left[ \frac{-0.39115}{\mu} - \Lambda\mu \right] d\mu
\]

\[
+ 0.2732 \sqrt{\lambda} \exp \left( -\frac{\Lambda}{Q^2} \delta_{mp} - \frac{0.39115Q}{\sqrt{\delta_{mp}}} \right)
\]

(11)

\[
T = \left( \exp \left( -\frac{\Lambda}{Q^2} \delta_{mp} \right) + \text{erf} \left( \frac{\sqrt{\lambda}}{Q^2} \delta_{mp} \right) \right)
\]

(12)

\[
\delta_{mp} = \frac{F}{RT} (E_{m-p+1} - E_{\text{initial}})
\]

(13)

The parameters \( \Lambda \) and \( Q \) are given by (see also eqn (A43) in the Appendix):

\[
\Lambda = \frac{\gamma_{mp}}{\gamma_{mp}} = \frac{(k_1 + k_2)r_d^2}{D}
\]

(14)

\[
Q = \frac{\gamma_{mp}}{\gamma_{mp}} = \frac{Fv_r^2}{RTD} = \frac{Fv}{RT(k_1 + k_2)}
\]

(15)

Moreover, by introducing eqn (13) in (A44) we define now:

\[
Z_m = e^{\delta_{\text{initial}}(1 - e^{\delta_{\text{initial}}})/e^{\delta_{\text{initial}} + e^{\delta_{\text{initial}}}})
\]

(16)

\[
m = 1, 2, \ldots, p
\]

\[
\delta_{m} = \frac{F}{RT} (E_m - E_{\text{initial}})
\]

(17)

\[
\delta_{0} = F(E_{\text{eq}} - E_{\text{initial}})/(RT)
\]

(18)

where \( E_{\text{initial}} \) is the value of the potential at the beginning of the scan and \( E_{\text{eq}} \) is the equilibrium potential given by:

\[
E_{\text{eq}} = E^{0/} + RT \ln(c_O^*/c_R^*)/F.
\]

In the particular case of a spherical electrode (s super/subscripts) of radius \( r_s \), the voltammetric current can be written as:

\[
\psi = \psi_{\text{planar}} + \psi_{\text{radial}}
\]

(19)
where

$$\psi_{\text{planar}} = \frac{\sqrt{\Lambda}}{Q(1 + K)} \sum_{n=1}^{p} Z_m T(Q, \Lambda, \beta_{sp})$$  \hspace{1cm} (20)$$

and $\psi_{\text{radial}}$ is given by eqn (10).

So, in this case the current can be expressed as a sum of the solution corresponding to planar electrodes and the stationary solution for ultramicrohemispheres.

The transient current–potential relationship given by eqn (9)–(18) gives rise to three stationary limits (time-independent $\Psi$–$\eta$ curves, with $\eta = F(E - E^{0})/(RT)$ depending on the values of the parameters $Q$ and $\Lambda$. Thus for $(\Lambda \beta_{sp}/Q^2) > 1.5$, a steady state response is attained (see ref. 19). Depending on the value of $\Lambda$, kinetic ($\Lambda \gg 1$) or microgeometrical (microelectrodes, $\Lambda \to 0$) responses are obtained, the $\Psi$–$\eta$ curves being insensitive to the kinetics of the catalysis in the last case (see Section 4.1 for a deeper discussion).

4. Results and discussion

In Fig. 1 we have plotted the dimensionless cyclic voltammograms $\Psi$–$\eta$ for the pseudo-first order catalytic mechanism with $K = 0$, both at disc (solid line) and spherical (dashed line) electrodes with the same radius: $r_d = r_s$.

From these curves we can observe the evolution of the response from a transient regime to a stationary one where sigmoidal voltammograms are obtained, the current being only a function of the applied potential ($\eta$) (see Fig. 1A). For a given electrode radius, the achievement of the stationary response is promoted by fast catalytic kinetics ($i.e.$, large $\Lambda$ values) and slow scan rates ($i.e.$, small $Q$ values).

As expected, the influence of the catalytic kinetics diminishes as the scan rate increases such that the curves corresponding to different $\Lambda$ values approach (see Fig. 1B and C). For very fast scan rates ($Q \geq 50$, see Fig. 1D) a single voltammogram is obtained corresponding to a simple charge transfer process under linear diffusion since the timescale of the experiment is very short and neither the coupled catalytic reaction nor the radial diffusion have significant effects on the response.

With respect to the difference between the dimensionless voltammograms at disc and spherical electrodes, this is more apparent at small values of $Q$ and $\Lambda$, that is, for small rate constants and slow scan rates for a given electrode radius. Both give rise to the spreading of the depleted region of the solution surrounding the electrode and so the different extension of the reaction layer at discs and spheres has a more significant effect on the electrochemical response.

The influence of the electrode radius (through the parameter $Q$) on the cyclic voltammograms is analyzed in Fig. 2 for a given scan rate and two different $k_1$ values corresponding to transient conditions ($\Lambda/Q^2 = 0.04$, Fig. 2A and C) and stationary conditions ($\Lambda/Q^2 = 10$, Fig. 2B and D).

In Fig. 2A and B the same value of the electrode radius is considered for discs and spheres. As can be observed in Fig. 2A, under transient conditions the dimensionless current at disc electrodes is always greater than at spherical ones, the smaller the electrode ($i.e.$, the smaller the $Q$ value), the greater the difference. When the stationary response is attained, three different steady states can be defined depending on the value of the rate constants and the electrode radius (see Fig. 2B).13,19

![Fig. 1](image-url)
Thus, for very small electrodes ($Q = 0.01$) the large diffusion transport masks the kinetic contribution and the microgeometrical steady state is achieved. For these conditions, the response is equivalent to that of a simple charge transfer process such that the ratio between the dimensionless curves at discs and spheres is given by $\psi^d/\psi^s = 4/\pi$ (provided that $r_d = r_s$). On the other hand, for large electrodes ($Q = 5$) a “purely” kinetic steady state is reached and the dimensionless current only depends on the chemical kinetics, being independent of the electrode size and geometry (i.e., $\eta^d/\eta^s = 1$). In both figures an intermediate behaviour is found for medium-sized electrodes ($Q = 0.5$).13

Fig. 2C and D are similar to the previous ones, although in this case the values of the electrode radii have been selected such that they fulfill the following equivalence relationship: $r_d/r_s = 4/\pi$.\textsuperscript{23,24} As a consequence, equivalent cyclic voltammograms are obtained at spherical and disc electrodes under microgeometrical steady state conditions (see curves for $Q = 0.01$ in Fig. 2D). The $\Psi-\eta$ curves are also coincident in the kinetic steady state (see curves for $Q = 5$ in Fig. 2D) since, as stated above, the current density under these conditions is independent of the electrode size. In the intermediate geometric-kinetic steady state, some divergence is found although in this case the dimensionless current corresponding to spherical electrodes is greater. This is also observed under transient conditions (see Fig. 2C).

In Fig. 3 the influence of the constant $K$ of the catalytic reaction on the cyclic voltammograms at discs and spheres is shown. As expected for $K \neq 0$, at the beginning of the scan the current is not null but takes large negative values corresponding to the oxidation of species R that is initially present in solution. As the constant $K$ increases the magnitude of the anodic current increases whereas the cathodic one diminishes in accordance with the relationship of concentrations of the electroactive species established by $K$.

4.1. Determination of the catalytic rate constants from the transient and stationary CV curves

As we have pointed out in Section 3.1, the catalytic mechanism gives rise to a stationary voltammetric response for values of $(\Lambda \delta_{mp}/Q^2) > 1.5$. Thus, it is found that for $(\Lambda/Q^2) > 0.4$ at
planar electrodes and \((\Lambda/Q^2) > 0.25\) at conventional microelectrodes \((r_0 = 50 \, \mu m)\) the steady state plateau current is achieved. For \((\Lambda/Q^2)\) values smaller than these limits a transient response is obtained and the cathodic branch of the voltammogram will exhibit a well-defined peak.

In Fig. 4 we have plotted the variation of the voltammetric peak parameters \((E_p - E^0, \ \psi_p, \ \text{Fig. 4A, and } \psi_p, \ \text{Fig. 4B})\) versus \(\log Q\), corresponding to transient CV curves. All the cyclic voltamograms have been calculated from eqn (9) by fixing the value of parameter \(\Lambda\) and considering disc (solid lines) and spherical (dashed lines) electrodes of the same radius \((r_d = r_s = 0.01 \, \text{cm})\) for the most common case of \(K = 0\). From curves in Fig. 4 it can be seen that the cathodic peak potential becomes more negative and the dimensionless current decreases as \(\log Q\) (i.e., the scan rate) increases (see eqn (15)). For large \(Q\) values, both the peak potential and the peak current are independent of \(Q\) and their values coincide with those obtained for a simple fast charge transfer process at planar electrodes:\[^{22}\] \(E_{p,cath} - E^0 = -28\ \text{mV}\) and \(\psi_{p,cath} = 0.446\) (see dotted-dashed lines in Fig. 4). The limiting \(Q\) value to observe this behaviour increases with \(\Lambda\).

Note also that for small values of \(\Lambda\) (i.e., \(\log \Lambda < -2\)), no sensitivity of the response to the catalysis kinetics is observed and the differences between disc and spherical electrodes are due to geometrical reasons. In the contrary case (i.e., \(\log \Lambda > 0\)), there are no differences in the peak potential and current at discs and spheres, and therefore, although a transient behaviour is obtained, it does not depend on the particular electrode geometry but on the kinetics of the chemical step.

The dotted line in Fig. 4 marks the maximum values of the ratio \((\Lambda/Q^2)\) for which a transient behaviour is achieved, i.e., a well-defined peak is obtained in CV (with the relative difference between the peak and plateau currents being greater than 5%). From the data shown in this figure, it is concluded that values of \((\Lambda/Q^2) > 0.4\) are required to observe a transient behaviour, whatever the electrode radius.

For \((\Lambda/Q^2) > 0.5\) the stationary CV response is obtained (for example, for \(k_1 + k_2 = 10\ \text{s}^{-1}\), the stationary voltammogram corresponds to scan rates below 500 \(\text{mV s}^{-1}\)). Under these conditions, the expression of the voltammogram at disc electrodes is given by:

\[
\psi^{\text{radial}} = \psi_{ss} = \psi^{\text{radial}} \left(1 + \sqrt{\Lambda} + 0.5465\Lambda \right) \times \int_0^\infty u \exp \left( -\frac{0.39115}{\sqrt{u}} - \Lambda u^2 \right) du
\]  

and at spherical electrodes:

\[
\psi^{\text{radial}} = \psi_{ss} = \psi^{\text{radial}} \left(1 + \sqrt{\Lambda} \right)
\]

The stationary CV curve given by eqn (21) and (22) has a sigmoidal shape with the plateau currents at very positive (an) or negative (cath) potentials being given by:

\[
\psi^{\text{radial}} = \psi_{ss}^{\text{cath}} = \psi^{\text{radial}} \left(1 + \sqrt{\Lambda} + 0.5465\Lambda \right) \times \int_0^\infty u \exp \left( -\frac{0.39115}{\sqrt{u}} - \Lambda u^2 \right) du
\]

\[
\psi^{\text{radial}} = \psi_{ss}^{\text{cath}} = \psi^{\text{radial}} \left(1 + \sqrt{\Lambda} + 0.5465\Lambda \right) \times \int_0^\infty u \exp \left( -\frac{0.39115}{\sqrt{u}} - \Lambda u^2 \right) du
\]

For spherical electrodes, these current plateaus take the following expressions:

\[
\psi_{ss} = \frac{1}{1 + K Q} \left(1 + \sqrt{\Lambda} \right)
\]

\[
\psi_{ss}^{\text{cath}} = \frac{1}{1 + K Q} \left(1 + \sqrt{\Lambda} \right)
\]

in such a way that the ratio between the cathodic and anodic plateau currents is given by:

\[
\frac{|\psi_{ss}^{\text{an}}|}{|\psi_{ss}^{\text{cath}}|} = K
\]

independently of the electrode geometry.
Moreover, eqn (21) leads to two limiting cases depending on the relationship between $\sqrt{D/(k_1 + k_2)}$ and $r_0$.

- For $\sqrt{D/(k_1 + k_2)} \geq 10r_0$, the kinetics of the chemical step is masked (the catalytic process behaves as a simple charge transfer process), and the microgeometrical steady state is reached:

$$\psi_{ss}^d = \frac{4}{\pi} \psi_{radial}$$  \hspace{1cm} (26)

$$\psi_{ss}^s = \psi_{radial}$$  \hspace{1cm} (27)

- For $10\sqrt{D/(k_1 + k_2)} \leq r_0$, the kinetic steady state is attained and the resulting CV curve is independent of the electrode radius and geometry:

$$\psi_{ss} = \frac{1 - Ke^\beta e^{-\beta_{min}}}{(1 + K)(1 + e^\beta e^{-\beta_{min}})} \sqrt{\frac{RT}{F}} \frac{(k_1 + k_2)}{v}$$  \hspace{1cm} (28)

### 4.2. Experimental study of the reaction of Fe(II) with hydrogen peroxide (Fenton reaction)

The electrocatalytic Fenton reaction is an example of a catalytic mechanism where the Fe(II) electrogenerated at the electrode surface reduces the O–O bond of hydrogen peroxide, being oxidized to Fe(III) according to the following scheme:\(^{17}\)

$$\text{Fe(III)} + e^- \rightarrow \text{Fe(II)} \hspace{1cm} (E)$$

$$2\text{Fe(II)} + H_2O_2 \xrightarrow{k_1} 2\text{Fe(III)} + 2\text{OH}^- \hspace{1cm} (C')$$  \hspace{1cm} (29)

The kinetics of the reaction of Fe(II) with hydrogen peroxide has been studied under different conditions and by means of different techniques.\(^{17,25-30}\) In this paper, we employ cyclic voltammetry for the characterization of this reaction, making use of the analytical expressions presented above.

In Fig. 5 the cyclic voltammograms of the reduction of Fe(III) in the absence (dashed line) and presence (solid line) of hydrogen peroxide are shown. Gold electrodes of two different sizes are employed as the working electrode. As can be observed in Fig. 5A, the voltammogram at the macroelectrode ($A = 2.1 \text{ mm}^2$) in the absence of hydrogen peroxide is a quasi-reversible peak-shaped wave with the cathodic peak located at ca. 430 mV vs. SCE. After the addition of $H_2O_2$, the increase of the cathodic branch and the disappearance of the anodic one are very apparent, as predicted for the catalytic mechanism. In the case of the microelectrode, in the absence and presence of hydrogen peroxide a sigmoidal steady-state voltammogram is recorded with a scan rate of 10 mV s\(^{-1}\), with the plateau current notably increasing after the addition of the catalyst, $H_2O_2$.

The effect of the sweep rate on the electrocatalytic response is shown in Fig. 6. The experimental voltammograms recorded at a gold macroelectrode corresponding to a mixture of Fe(III) and $H_2O_2$ for different scan rates are plotted. We can observe the evolution of the signal from a peak-shaped response at fast scan rates ($v > 500 \text{ mV s}^{-1}$) to a sigmoidal wave for slow ones. As we discussed in previous sections, the longer the experiment, the greater the influence of the catalytic reaction such that, at scan rates slow enough, the steady state is reached and a sigmoidal response is recorded even with large electrodes (see Fig. 5A). On the other hand, at very fast scans the response tends to that corresponding to a simple E mechanism.
The quantitative determination of the rate constant of the Fenton reaction was performed by cyclic voltammetry using gold disc microelectrodes of two different sizes \((r_0 = 69.4 \, \mu m\) and \(r_0 = 5.8 \, \mu m\) in a solution of 0.236 mM Fe(III), 0.5 M KCl and 0.02 M HCl at 22°C. The \(O_2\) concentration was set at a value \([H_2 O_2] = 32 \, mM\) where pseudo-first order conditions are ensured \(([H_2 O_2]/[Fe(III)] = 135 \, mM)\) and the possible interference of hydroxyl-radical-induced decomposition of \(O_2\) is minimized.\(^{17}\)

From the value of the plateau current of the steady-state voltamogram the rate constant of the reduction of \(O_2\) by electrogenerated Fe(II) was determined by means of eqn (23), given that the electrode size and the diffusion coefficient of the electroactive species were known (see Section 2.2). The rate constant obtained was halved according to the stoichiometry of reaction (29):

\[
r_0 = 5.8 \, \mu m: \quad k'_R = 42.8 \pm 1.4 \, M^{-1} \, s^{-1} \quad (30)
\]

\[
r_0 = 69.4 \, \mu m: \quad k'_R = 37.8 \pm 1.6 \, M^{-1} \, s^{-1} \quad (31)
\]

where the error bars are calculated from the standard deviation of the values obtained at different scan rates. The values obtained compare well with those existing in the literature; \(k'_R = 38 - 42 \, M^{-1} \, s^{-1}\).\(^{17}\)

It is worth highlighting that the methodology employed for the determination of the rate constant is independent of the reversibility of the electrode process, since this is extracted from the value of the plateau current that corresponds to steady-state limiting current conditions and therefore it is not affected by the heterogeneous kinetics. Hence, this can be applied to the first-order catalytic mechanism with irreversible or quasi-reversible charge transfer processes, as indeed is the case of the Fe(III)/Fe(II) redox couple at gold electrodes.

5. Conclusions

The problem of the first-order catalytic mechanism in voltammetric electrochemical techniques at disc electrodes has been solved by means of an analytical approach. By demonstrating that the superposition principle applies whatever the electrode geometry, an analytical solution for cyclic voltammetry has been derived valid for disc electrodes of any radius and regardless of the kinetics of the catalytic reaction.

From this solution, the effect of the electrode radius and the rate constants of the chemical reaction have been examined. Moreover, the different steady-state responses attainable have been studied as a function of the electrode size and the chemical kinetics. Simple procedures for the characterization of the chemical reaction have been given based on the values of the peak current and peak potential of the peak-shaped voltammograms under transient conditions, or on the plateau current in the steady state.

Finally, the theoretical results have been applied to the experimental study of the Fenton reaction. The rate constant of the reduction of hydrogen peroxide by the iron(II) electro-generated at gold disc electrodes has been determined.

Appendix

In this Appendix we will mathematically show that, by applying the induction principle, the superposition principle is fulfilled for the catalytic mechanism, independently of the electrode geometry.

For the reaction mechanism given by eqn. (3), when a constant potential \(E_1\) is applied to an electrode of any geometry during a time \(0 \leq t_1 \leq \tau_1\), the following differential equation system must be solved:

\[
\begin{align*}
\frac{d}{dt}[c_0^{(l)}(t)] &= k_R^{(l)}[c_0^{(l)}(t)] - k_R^{(l)}[c_0^{(l)}(t)] \\
\frac{d}{dt}[c_R^{(l)}(t)] &= -k_R^{(l)}[c_0^{(l)}(t)] + k_R^{(l)}[c_R^{(l)}(t)]
\end{align*}
\quad (A1)
\]

where \(\delta_i\) (\(i\equiv O, R\)) is the operator corresponding to Fick’s second law in any geometry.

Next we introduce the function \(\xi(q,t_1)\) given by:

\[
\xi(q,t_1) = c_0^{(l)}(q,t_1) + c_R^{(l)}(q,t_1)
\quad (A2)
\]

where \(q\) refers to any geometrical coordinate.

According to eqn (A1) and that the flux is conserved at the electrode surface, the following solution is obtained for \(\xi(q,t_1)\) when the diffusion coefficients of species O and R are equal \((D_O = D_R = D)\):

\[
\xi(q,t_1) = c_0^{*} + c_R^{*} = \xi^*
\quad (A3)
\]

such that the sum of the concentrations of both species remains constant for any value of distance and time regardless of the geometry of the electrode employed.\(^{13,18,19,31-33}\)

If we assume that the charge transfer reaction is reversible, the following boundary value problem must be fulfilled:

\[
\begin{align*}
t_1 &= 0, \quad q \geq q_{\text{surface}} \quad \Rightarrow \quad c_0^{(l)}(q,t_1) = c_0^{*}, \quad c_R^{(l)}(q,t_1) = c_R^{*} \\
t_1 > 0, \quad q \rightarrow \infty \quad \Rightarrow \quad c_0^{(l)}(q,t_1) = 0
\end{align*}
\quad (A4)
\]

\[
Q_1 = \exp \left\{ \frac{F}{RT} (E_1 - E^{0R}) \right\}
\quad (A6)
\]

with \(E^{0R}\) being the formal potential of the \(O/R\) couple, \(c_0^{(l)}(q_{\text{surface}})\) the surface concentrations of the electroactive species \(i\) and \(q_{\text{surface}}\) the value of \(q\) at the electrode surface in the normal direction, that is, at \(r = r_s\) for hemispherical electrodes and at \(z = 0\) for disc electrodes, and \(c_0^{*}\) and \(c_R^{*}\) the equilibrium concentrations (see eqn (4)).

From eqn (A3) and (A5), we can immediately deduce for any electrode geometry that:

\[
\begin{align*}
&c_0^{(l)}(q_{\text{surface}}) = \frac{Q_1}{1 + Q_1} \quad (A7) \\
&c_R^{(l)}(q_{\text{surface}}) = \frac{Q_1}{1 + Q_1} \quad (A8)
\end{align*}
\]

In order to obtain the solutions for the concentration profiles of species O and R, \(c_0^{(l)}(q,t_1)\) and \(c_R^{(l)}(q,t_1)\), and for the current, it is convenient to introduce a second variable change:

\[
\phi^{(l)}(q,t_1) = (c_R^{(l)}(q,t_1) - Kc_0^{(l)}(q,t_1))e^{\varepsilon t_1}
\quad (A9)
\]
Hence, from eqn (A10)–(A14) it is obvious that we only need to deduce the complete solution for the current of the catalytic mechanism.

Taking into account that the flux of the oxidized species at the electrode surface is given by: \( D \frac{\partial\phi^{(1)}(q,t_1)}{\partial q} \)

\[ = -D \frac{e^{-q t_1}}{1+K} \frac{\partial\phi^{(1)}(q,t_1)}{\partial q} \] (A14)

where \( q \) refers to the characteristic dimensions of the electrode, and the form of function \( f^G(t_1,q_G,k_1+k_2) \) depends on the electrode geometry. For spheres the expression for \( f^G(t_1,q_G,k_1+k_2) \) has been obtained in ref. 19 and 34:

\[ F^{(r,s)}(r,s,\tau_1,\xi_1) = \frac{1}{r_s} + \sqrt{\frac{k_1 + k_2}{D}} T(\tau_1) \] (A16)

and for disc electrodes a general solution has been obtained from Danckwerts’ expression (see ref. 10, 11, and 13):

\[ F^{(d)}(r_d,\tau_1,\xi_1) = \frac{1}{r_d} + \sqrt{\frac{k_1 + k_2}{D}} D(\tau_1,\xi_1) \] (A17)

where

\[ T(\tau_1) = \frac{\exp(-\tau_1)}{\sqrt{\pi \tau_1}} + \text{erf}(\sqrt{\tau_1}) \] (A18)

and the current is given by:

\[ I_1 = \text{FAD} \frac{\partial\phi^{(1)}(q,t_1)}{\partial q} \] (A14)

\[ = -\text{FAD} \frac{e^{-q t_1}}{1+K} \frac{\partial\phi^{(1)}(q,t_1)}{\partial q} \] (A14)

Hence, from eqn (A10)–(A14) it is obvious that we only need to obtain the unknown function \( \phi^{(1)}(q,t_1) \) to deduce the complete solution for the current of the catalytic mechanism.

Taking into account that the flux of the oxidized species at the electrode surface is given by: \( D \frac{\partial\phi^{(1)}(q,t_1)}{\partial q} \)

\[ = -D \frac{e^{-q t_1}}{1+K} \frac{\partial\phi^{(1)}(q,t_1)}{\partial q} \] (A14)

the expression for the current has the following general form independently of the electrode geometry:

\[ \frac{J_1}{\text{FAD}} = \left( \frac{\partial\phi^{(1)}(q,t_1)}{\partial q} \right) \] (A14)

\[ = \left( c_0 - c^{(1)}_G(q_{\text{surface}}) \right) f^G(t_1,q_G,k_1+k_2) \]

\[ = \frac{\xi^*}{1+K} \left( \frac{1}{1+J_1} - \frac{1}{1+J_0} \right) f^G(t_1,q_G,k_1+k_2) \] (A15)
such that the surface concentrations are given by:

$$c_{O}^{(2)}(q_{\text{surface}}) = \frac{J_{2}z^*}{1 + J_{2}}$$  \hspace{1cm} (A27)  

$$c_{K}^{(2)}(q_{\text{surface}}) = \frac{z^*}{1 + J_{2}}$$  \hspace{1cm} (A28)

Analogously to the first pulse, we define the function $\phi^{(2)}(q,t)$ as:

$$\phi^{(2)}(q,t) = (c_{O}^{(2)}(q,t) - Kc_{O}^{(2)}(q,t)e^{kt}) = \phi^{(1)} + \tilde{\phi}^{(2)}$$  \hspace{1cm} (A29)

where $\phi^{(1)}$ is the solution of the first pulse and $\tilde{\phi}^{(2)}(q,t) = (c_{K}^{(2)}(q,t) - Kc_{O}^{(2)}(q,t)e^{kt})$. From eqn (A27) and (A28) we deduce that:

$$e^{-kt}\phi^{(2)}(q_{\text{surface}}) = \left(1 - \frac{1}{1 + J_{2}}\right)\frac{z^*}{1 + J_{2}}$$  \hspace{1cm} (A30)

By combining eqn (A7), (A8) and (A27)-(A29) the boundary value problem for the second potential step can be written only as a function of $\tilde{\phi}^{(2)}(q,t)$:

$$t_{2} = 0, \quad q \geq q_{\text{surface}} \hspace{1cm} \tilde{\phi}^{(2)}(q,t) = 0 \hspace{1cm} (A31)$$

$$t_{2} > 0, \quad q = q_{\text{surface}}:\n$$

$$e^{-kt}\phi^{(2)}(q_{\text{surface}}) = (1 + K)[c_{O}^{(1)}(q_{\text{surface}}) - c_{O}^{(2)}(q_{\text{surface}})]$$

$$= (1 + K)\left(1 - \frac{1}{1 + J_{2}}\right)\frac{z^*}{1 + J_{2}}$$  \hspace{1cm} (A32)

where $J_{1}$ and $J_{2}$ are given by eqn (A6) and (A26), respectively.

As can be seen, the boundary value problem for $\phi^{(2)}(q,t)$ is similar to that for $\phi^{(1)}(q,t)$ (eqn (A11) and (A12)) such that the expression for $e^{-kt}\phi^{(2)}(q,t)$ will be identical to that obtained for $e^{-kt}\phi^{(1)}(q,t)$ after changing $J_{0}$ and $J_{1}$ by $J_{1}$ and $J_{2}$, respectively (see eqn (A12) and (A32)).

Therefore, the form of $\tilde{\phi}^{(2)}(q,t)$ must be analogous to that of $\phi^{(1)}(q,t)$ and the current $I_{2}$ will be given by the following two formally identical addends (see eqn (A22), (A23) and (A27)-(A30)):

$$I_{2} = \frac{I_{p}}{FAD} \frac{\partial c_{O}^{(2)}(q,t)}{\partial q} = \frac{I_{p}}{1 + K} \sum_{m=1}^{p} Z_{m}G(t_{mp}, q_{G}, k_{1} + k_{2})$$  \hspace{1cm} (A41)

For a disc electrode, $f^{G}(t_{mp}, q_{G}, k_{1} + k_{2})$ is $f^{G}(r_{d}, l_{mp}, \xi_{mp})$ (see eqn (A17)). In this case, eqn (A41) becomes:

$$I_{p} = \frac{I_{p}}{FAD} \frac{\xi_{mp}^{*}}{1 + K} \sum_{m=1}^{p} Z_{m}^{G}(r_{d}, l_{mp}, \xi_{mp})$$  \hspace{1cm} (A42)

where

$$Z_{m} = \frac{1}{1 + J_{m} - \frac{1}{1 + J_{m-1}}}$$  \hspace{1cm} (A44)

and $J_{0}$ is given by eqn (A13).

Therefore, it has been rigorously shown that the superposition principle applies for the first-order catalytic mechanism under
voltammetric conditions whatever the geometry of the electrode, \textit{i.e.}, that this problem of \( p \) potential pulses can be treated as \( p \) independent single pulse problems. Therefore, the current (and also the concentration profiles) of the \( p \)-th pulse is given by a sum of \( p \) responses corresponding to a single potential step. Consequently, the above results can be extended to any sequence of potential pulses and the solutions for the different voltammetric techniques can be derived. Note that the validity of the superposition principle under these conditions is not trivial since the boundary value problem includes the time-dependent function \( \phi(q,t) \).

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