Heterogeneous Catalysis of Multiple-Electron-Transfer Reactions at Nanoparticle-Modified Electrodes

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In some important electrochemical systems, the degree of electro-reduction (or electro-oxidation) of the reactant at the electrode surface depends on the extent of a surface-catalysed reaction that involves intermediates formed by electron transfer. The catalytic properties of the electrode surface towards this heterogeneous reaction, therefore, can control the final product of important processes, such as the electro-reduction of oxygen and some organic compounds. The modelling of this heterogeneous reaction, therefore, can control the final reaction and E<sub>fd</sub> indicates that the second electron transfer is fully driven. The results enable us to propose procedures for the identification and characterisation of the surface-catalysed process and for the optimisation of electrode modifications.

1. Introduction

The EC<sub>het</sub>E<sub>fd</sub> mechanism (where C<sub>het</sub> is a heterogeneous chemical reaction and E<sub>fd</sub> indicates that the second electron transfer is fully driven), given in Equations (1)–(3), is thought to underpin a variety of important electrode processes, in which the reactant molecule transfers a different number of electrons depending on the nature of the electrode material, for example in the electro-reduction of oxygen<sup>[1, 2]</sup> or nitromethane.<sup>[3, 4]</sup>

\[
\begin{align*}
A + e^- &\rightleftharpoons B \left(k_{B1}, \alpha_1, E_{B1}^0\right) \quad (1) \\
B &\rightarrow C \quad (2) \\
C + e^- &\rightarrow D \quad \text{fully driven} \quad (3)
\end{align*}
\]

in which \(k_{B1}\), \(\alpha_1\), and \(E_{B1}^0\) are the standard electrochemical rate constant, transfer coefficient and formal potential of the first electron transfer, respectively, and \(k_{het}\) is the heterogeneous chemical rate constant of Equation (2).

Species C is only generated at the electrode surface and is immediately reduced after its formation, that is, the second electron transfer occurs under limiting current conditions at the potential range where the voltammetric signal develops.

As a result, the concentration of species C in the system is effectively nil.

As a first approach, the above reaction mechanism can help us to understand and analyse processes in which partial or total electro-oxidation/reduction happens, depending on the characteristics of the working electrode. Thus, simple qualitative analysis of the mechanism suggests that the effective number of electrons transferred by species A will range from 1 (in the case of very slow \(k_{het}\) values) to 2 (for very fast chemical kinetics), corresponding to a switch of product from species B to D. Given that the chemical reaction [Eq. (2)] is surface-catalysed, the transition between these two limits will depend on the characteristics of the electrode material. This, for example, can be the case for the oxygen reduction reaction, in which a transition from the partial reduction of \(O_2\) (to form hydrogen peroxide) to its full reduction (to water) is observed in aqueous solution, depending on the characteristics of the cathode.<sup>[1, 2]</sup>

In previous work, the EC<sub>het</sub>E<sub>fd</sub> scheme has been investigated within the context of controlled convective voltammetry<sup>[3–5]</sup> at electrodes with a homogeneous surface. In view of the increasing interest in the use of electrodes modified by catalytic nanoparticles, this paper aims to extend the study to heterogeneous surfaces by making use of the theory developed in our group.<sup>[3, 6]</sup> The case of unmodified stationary macroelectrodes will also be considered.

First, the features of the cyclic voltammetry of the EC<sub>het</sub>E<sub>fd</sub> mechanism are discussed for different nanoparticle coverages and heterogeneous (electro)chemical kinetics. Next, criteria and working curves are given for the characterisation of the heterogeneous processes. These also enable us to analyse the effect of increasing the coverage of a certain nanosized material on the efficiency of the multiple electron transfers. This chal-
The initial, bulk and surface conditions reflect the reactivity of the species at the electrode surface, as demonstrated in Equations (5) and (6):

\[ t < 0, x > 0 \quad c_A = c_{A,bulk}, \quad c_B = 0 \text{mM} \]

\[ t > 0, x = 0 \]

\[ \begin{aligned}
  D_A \left( \frac{\partial}{\partial r} \right)_{r=0} = k_{A,ads} c_A(0) - k_{A,des} c_A(0) \\
  D_B \left( \frac{\partial}{\partial r} \right)_{r=0} = -k_{B,ads} c_B(0) + k_{B,des} c_B(0) + k_{B,oxid} c_B(0)
\end{aligned} \]

in which the electrochemical rate constants are given by:

\[ k_{A,ads} = k_{B,ads} = \frac{1}{N} \times \exp \left( \frac{-\Delta G_{A,B}}{RT} \right) \quad \text{and} \quad k_{B,des} = k_{A,des} \times \exp \left( \frac{-\Delta G_{A,B}}{RT} \right), \]

according to the Butler–Volmer model for electrode kinetics, and \( F \) is the Faraday constant.\(^{(7, 8)}\) Note that the heterogeneous chemical reaction is modelled as being rate-limited by the adsorption of species B, according to the Henry isotherm, which enables a simple description of the system with only one additional unknown variable: \( k_{B,ads} \) (m s\(^{-1}\)).

Finally, taking into account that species C is immediately transformed into species D through a one-electron transfer, the total current, \( i \), is calculated from Equation (7):

\[ i = -2D_A \left( \frac{\partial c_A}{\partial x} \right)_{x=0} + D_B \left( \frac{\partial c_B}{\partial x} \right)_{x=0} \]

in which \( A \) is the electrode area.

Nanoparticle-Modified Electrodes

In this section, the case of a substrate decorated with catalytic nanoparticles will be considered. The simulation of cyclic voltammetry is carried out with home-written programs, following the methods developed in the Compton group for an array of electroactive spherical particles on an electroinactive substrate.\(^{(9)}\) Further details of the simulation procedure can be found elsewhere\(^{(10)}\) although, the most important aspects are discussed below.

In order to obtain accurate results without prohibitive computing complexity and calculation time, some simplifications are employed. First, the modified electrode is modelled as an array of spherical nanoparticles of the same size that are evenly distributed on the surface.\(^{(11)}\) The conductive substrate is assumed to be large enough such that the contribution of particles situated at the edge is negligible. As a result, the problem is reduced to \( N \) identical independent problems (with \( N \) being the number of particles of the array) associated with each nanoparticle and its own diffusion space, which is approximated as cylindrical (see Figure 1). Therefore, the system can be represented in a two-dimensional cylindrical polar coordinate system [Eq. (8)],

\[ \frac{\partial c_i}{\partial t} = D_i \left( \frac{\partial^2 c_i}{\partial r^2} + \frac{1}{r} \frac{\partial c_i}{\partial r} + \frac{\partial^2 c_i}{\partial z^2} \right) (i \equiv A, B) \]

Regarding the boundary value problem, the initial and bulk conditions in the \( z \) direction are given by Equation (9):

\[ t = 0 \]

\[ t > 0, z \to \infty \quad c_A = c_{A,bulk}, \quad c_B = 0 \text{mM} \]

At the nanoparticle surface, the conditions related to the heterogeneous electrochemical and chemical processes apply [Eq. (10)],

\[ \left( \frac{\partial c_i}{\partial n} \right)_{r=r_i} = -2i A \]
\[
\begin{cases}
D_t \left( \frac{\partial c}{\partial t} \right) = k_{\text{het}}^{(1)} c_A - k_{\text{het}}^{(1)} c_B \\
D_t \left( \frac{\partial c}{\partial t} \right) = -k_{\text{het}}^{(1)} c_A + k_{\text{het}}^{(1)} c_B + k_{\text{het}} c_B
\end{cases}
\]  
(10)

in which \( n \) is the spatial coordinate normal to the particle surface. Note that the substrate is assumed to be inert and then zero flux condition is applied at its surface for all the species, \( \partial c_n / \partial z \big|_{r=0} = 0 \). Likewise, attending to the symmetry of the diffusion domain, no material flux takes place through the boundaries \( r = 0 \) and \( r = r_{\text{domain}} \) such that \( \partial c_n / \partial r \big|_{r=r_{\text{domain}}} = 0 \).

The resolution of the above problem is carried out by means of finite difference methods. Thus, Fick’s second law for each species is discretised by using the well-known alternating direction implicit method.\(^{[12]}\) Once the concentration profiles are calculated, the current of a single unit cell, \( I_{\text{NP}} \), is obtained from Equation (11):

\[
I_{\text{NP}} = -F 2\pi r_{\text{NP}}^{2} \int_{0}^{\pi/2} 2D_A \left( \frac{\partial c_A}{\partial r} \cos \phi + \frac{\partial c_A}{\partial z} \sin \phi \right) \cos \phi \, d\phi
\]

\[
-2F 2\pi r_{\text{NP}}^{2} \int_{0}^{\pi/2} D_B \left( \frac{\partial c_B}{\partial r} \cos \phi + \frac{\partial c_B}{\partial z} \sin \phi \right) \cos \phi \, d\phi
\]

in which \( \phi \) is the angle in radians measured from the \( r \)-axis in the \((r,z)\) plane, \( \tan \phi = \frac{z}{r} \). After scaling the result by the number of particles \( N \), the total current, \( I \), is obtained.

2. Results and Discussion

2.1. Homogeneous (Unmodified) Electrodes

In this section, a study of the mechanism at unmodified macroelectrodes with a homogeneous surface will be carried out in order to illustrate the voltammetry of the EC hematite mechanism as a function of the interplay between mass transport and the kinetics of the surface-catalysed process and the first electron transfer. Figures 2–4 show the voltammograms for three different degrees of reversibility of the first step [Eq. (1)] and different chemical kinetics.

First, we consider the case in which the first electron transfer is fully reversible, such that the analysis of the effect of the chemical kinetics is easier. As can be seen in Figure 2, the peak current, \( \psi_{\text{app}} = I_{\text{peak}} / \sqrt{\pi v} \), increases monotonously as \( k_{\text{het}} \) is faster and then more of species B are transformed into C (and then immediately electro-reduced to D) instead of diffusing away from the electrode surface. A limiting value is observed for \( \psi_{\text{app}} \) that corresponds to the two-electron transformation of species A into D, whereas the peak potential shifts continuously to more positive values. Given that the second electron transfer is supposed to be fully driven, the anodic peak in the backward scan disappears as the transformation of species B into C is faster.

The limiting \( \psi_{\text{app}} \) value is 2.2 times larger than that of the one-electron transfer (\( k_{\text{het}} = 0 \)). Thus, the first electron transfer is so fast that Nernstian equilibrium conditions between the surface concentrations of species A and B is always fulfilled [i.e. \( c_A(0) = \exp \left( \frac{-E_{\text{Dox}} - E_{\text{Dox}}}{RT} \right) \)].

\[ c_A(0) = \exp \left( \frac{-E_{\text{Dox}} - E_{\text{Dox}}}{RT} \right) c_A(0) \]  
and the conversion of B to C is rate determining, with the first step constituting a pre-equilibrium [Eq. (12)]:

Figure 2. A) Cyclic voltammetry of the \( E_{\text{Dox}}C_{\text{Nat}}E_{\text{Dox}} \) mechanism at macroelectrodes with homogeneous surface. B) Variation of the apparent number of electrons transferred defined as \( \psi_{\text{app}} = I_{\text{peak}} / \sqrt{\pi v} \) with the kinetics of the first step [Eq. (1)] and different chemical kinetics. C) Variation of the peak potential with \( \log \left( k_{\text{het}} \right) \).
Considering the above situation, we can infer that the potential dependence of the current in the $E_{\text{revChetEfd}}$ case is equivalent to that of a fully irreversible $E$ mechanism, with an apparent $\alpha$ value of 1, such that the peak current is twice that of an $E_{\text{irrev}}$ process with $\alpha = 1$ [Eq. (13)]:

$$I = -2k_{\text{het}}c_A(0) = -2k_{\text{het}} \exp \left( \frac{-F(E - E_0)}{RT} \right) c_A(0)$$

(12)

and the peak potential is given by Equation (14) [7,8]:

$$E_{\text{peak, rev, het}} = E_{\text{rev, het}}^0 - \frac{RT}{F} \left( 0.7780 - \ln(k_{\text{het}}) + \ln \left( \frac{FDv}{RT} \right) \right)$$

(14)

Therefore, as the surface-catalysed process is faster, the peak current transits from the value corresponding to a reversible $E$ mechanism, $\psi_{\text{rev, peak, het}} = 0.446$, to 0.992. If we analyse the apparent number of electrons transferred, per molecule of $A$, as the ratio between the peak currents in cyclic voltammetry in the limits of very slow and fast $k_{\text{het}}$ ($n_{\text{app}} = \psi_{\text{peak, rev, het}} / \psi_{\text{peak, irrev}}$), a meaningless value of 2.2 is obtained. This indicates that caution is
required in the analysis of the number of electrons transferred from the peak current of cyclic voltammograms, given that these are the result of a complex competition between mass transport and (electro)chemical kinetics.

The case of an irreversible first electron transfer is considered in Figure 3. The main effects of the chemical kinetics on the cyclic voltammetry are the enhancement of the cathodic signal and the disappearance of the anodic one as $k_{\text{nat}}$ increases. In the limit of very fast chemical kinetics, the peak current in the $E_{\text{p}}C_{\text{nat}}E_{\text{f}}$ scheme is twice that of a fully irreversible one-electron process, $I_{\text{p,peak}} = 2 \times (0.496/\alpha) = 0.701$. Thus, unlike in the $E_{\text{p}}C_{\text{nat}}E_{\text{f}}$ case, the $n_{\text{app}}$ value varies from 1 to 2, without exceeding the latter value.

The shape and location of the cathodic peak do not change significantly with $k_{\text{nat}}$. Thus, the potential dependence of the voltammetric response is determined by the first electron-transfer step and the Tafel slope yields a transfer coefficient equal to $\alpha_i$. With regard to the peak position, this is found to be equal to that of totally irreversible processes [Eq. (15)] in the limits $k_{\text{nat}} = 0$ and $k_{\text{nat}} \gg 1$:

$$E_{\text{inv, peak}} = E_{\text{f,1}} - \frac{RT}{aF} \left( 0.780 - \ln k_{\text{1,1}} + \ln \left( \frac{\alpha_i F DV}{RT} \right) \right)$$

(15)

For intermediate $k_{\text{nat}}$ values, the peak position slightly deviates from the value predicted by Equation (15); however, the divergence is smaller than 10 mV.

Another interesting feature of the $E_{\text{p, nat}}C_{\text{nat}}E_{\text{f}}$ mechanism is the crossing in the voltammograms, which is predicted for intermediate $k_{\text{nat}}$ values. This is attributed to the accumulation of species B around the electrode surface that can be transformed into C, and thus electro-reduced more easily than the original reactant A, at the initial potentials of the forward scan. Therefore, at these potentials, the current in the backward scan is higher than that obtained when only species A is present in solution. Note that the crossing does not appear when the concentration of species B in the reverse scan is not large, either because it is not produced fast enough (slow chemical kinetics) or because it is immediately transformed into C (fast chemical kinetics). A similar behaviour has been described for ECE mechanisms, with step C taking place in solution instead of at the electrode surface.[15]

The case in which the first electron transfer is quasi-reversible ($E_{\text{p, nat}}C_{\text{nat}}E_{\text{f}}$) is more complicated and difficult to generalise, because the response will depend on the particular ratio between the electrochemical ($k_{\text{nat}}, \alpha_i$) and chemical ($k_{\text{nat}}$) kinetics. Figure 4 shows the results obtained for $k_{\text{nat}} = 0.05 \text{ cm}^2 \text{s}^{-1}$, which illustrates the main features of the signal. As can be observed, the variation of the peak current with $k_{\text{nat}}$ shows a maximum and the peak potential shifts to a limited value. Further increase in $k_{\text{nat}}$ does not lead to any change in the cyclic voltammograms. In this situation, the first step is chemically irreversible, given that species B is consumed by the chemical process as soon as it is electrogenerated. Therefore, the potential dependence of the electrochemical response when $k_{\text{nat}} \gg 1$ is equivalent to that of fully irreversible processes [Eq. (16)]:

$$I = 2k_{\text{q,1}} \exp \left( \frac{-\alpha_i F (E - E_{\text{f,1}})}{RT} \right) c_A(0)$$

(16)

Thus, the Tafel analysis of the voltammogram within this limit yields $\alpha_i$, and the peak position can be calculated from Equation (15) [$E_{\text{p, peak}} - E_{\text{f,1}} = +84.6 \text{ mV}$ for the conditions in Figure 4] and the peak current from $I_{\text{quasi, peak}} = 2 \times (0.496/\sqrt{\alpha}) = 0.701$.

### 2.2. Nanoparticle-Modified Electrodes

As described in the Theory section, modified electrodes are simulated in this work as an array of electroactive particles of radius $r_{\text{np}}$ and spherical shape. Thus, the surface coverage by the particles, $\theta$, can be defined by Equation (17):

$$\theta = \frac{N \pi r_{\text{np}}^2}{A} \times 100$$

(17)

in which $A$ is the area of the modified substrate. As mentioned in Section 2.1 of the Results and Discussion, the electrochemical response of the $E_{\text{p, nat}}E_{\text{f}}$ mechanism reflects the competition between the diffusion of species B towards the electrolyte solution and its transformation at the electrode surface. Therefore, the characteristics of the diffusion field around the modified electrode are a key question. According to the categories defined by Davies et al.,[43] the response at a substrate partially covered with electroactive material can be analysed in terms of the magnitude of the overlapping of the diffusion domains of adjacent nanoparticles. Thus, at short time scales and/or long particle interdistance (i.e. low coverage), the overlap is negligible and the response is the sum of $N$ independent particles (which are termed cases 1 and 2). As experiments are longer and/or the nanoparticle coverage is higher, the overlapping of diffusion domains starts being significant (which is called case 3) and then the diffusion of electroactive species towards/from the electrode surface is less effective. Finally, when the overlapping is very strong (known as case 4), the diffusion is essentially linear.

Taking into account the above discussion, Figure 5 shows that, similar to the simple E mechanism,[10] the apparent kinetics of the heterogeneous chemical reaction increase as the electroactive area on the substrate increases, that is, as the nanoparticle coverage is higher. As a result, the peak current increases with $\theta$ and the peak position shifts towards more positive values; the voltammogram tends to that described for homogeneous surfaces (dashed line in Figure 5).

In order to simplify the analysis and to make our results as general as possible, it is convenient to consider conditions within or close to case 4. In this situation, the response is mainly defined by the nanoparticle coverage and not by the particle size. This is illustrated in Figure 6, which shows the variation in the peak current with $\theta$ for a typical scan rate (100 mVs$^{-1}$) and two very different particle sizes, that is, 20 and 200 nm in diameter. As can be seen, provided that $\theta > 5%$,
the variation in the peak current with the nanoparticle size is less than 2% in the range of chemical kinetics. This also enables us to minimise uncertainties related to the dispersity in the particle size. Moreover, this is an interesting situation, in practice, for promoting the full reduction/oxidation of the reactant and to minimise the escape of intermediates towards the bulk solution.

Based on the above conclusions, working curves are given in Figures 7–9 for the analysis and determination of the kinetics of the heterogeneous processes from the peak current of the forward scan. In all cases, $\theta > 5\%$ is considered such that the results are not affected by the actual nanoparticle size. Figure 7 and Figure 8 correspond to the cases in which the first electron transfer is fully reversible and fully irreversible, respectively. As discussed above, under these conditions, the peak current will be determined by the kinetics of the heterogeneous processes, and its influence is generalised through the dimensionless parameter $K_{\text{het}} = k_{\text{het}} \sqrt{\frac{RT}{FvD}}$. Thus, provided that the nanoparticle coverage is known from electrochemical or imaging techniques, the analysis of the peak current at different scan rates is a simple procedure for the determination of consistent $k_{\text{het}}$ values. Once $k_{\text{het}}$ is known for a certain nanosized material, these curves enable us to also analyse the effect of increasing the surface coverage and then the determination of the optimum coverage that balances between transformation efficiency and production cost.

In the case of fully irreversible first electron transfers, the electrochemical kinetics can be estimated from the peak position that is given by Equation (18) in the limits of very fast and very slow chemical kinetics:

$$E_{\text{irrev, peak}} = E^0_{f,1} - \frac{RT}{\alpha F} \left( 0.780 - \ln \left( \frac{4\theta}{100k_{0,1}} \right) + \ln \left( \sqrt{\frac{\alpha FDv}{RT}} \right) \right)$$ (18)

As in the case of homogeneous surface electrodes, at intermediate $k_{\text{het}}$ values, the deviation observed from Equation (18) is smaller than 10 mV. Likewise, for fully reversible first electron

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**Figure 5.** Variation of the forward scan of the cyclic voltammetry of A) $E_{\text{rev, C, E \_1}}$, B) $E_{\text{rev, C, E \_2}}$, and C) $E_{\text{irrev, C, E \_1}}$ mechanisms with the nanoparticle coverage (indicated on the graphs) at an electrode modified with spherical nanoparticles; $k_{0,1} = 10^{-3} \text{ cm s}^{-1}$, $\alpha_1 = 0.5$, $\nu = 0.1 \text{ V s}^{-1}$.

**Figure 6.** Variation of the peak current of the forward scan of the $E_{\text{irrev, C, E \_1}}$ mechanism with the nanoparticle coverage at an electrode modified with spherical nanoparticles of two different diameter: 20 nm (solid line) and 200 nm (dashed line), $\nu = 0.1 \text{ V s}^{-1}$.
transfer, the peak potential in the limit of very fast chemical kinetics can be calculated by Equation (19):

\[
E_{\text{revChetFd}}^\text{peak} = E_0^{\text{rev}} - \frac{RT}{F} \left( 0.780 - \ln \left( \frac{4 \theta}{100} k_{\text{het}} \right) + \ln \left( \frac{\sqrt{FDV}}{RT} \right) \right)
\]  

The case in which the first electron transfer is quasireversible is much more complex and difficult to generalise. In this situation, the voltammetry will be a function of both the electrochemical and chemical kinetics, which can be parameterised by means of \( K_{\text{net}} = k_{\text{net}} \sqrt{\frac{RT}{F}} \) and the ratio \( k_{0}/k_{\text{net}} \). Working curves for different \( k_{0}/k_{\text{net}} \) values are given in Figure 9. Again, once the surface coverage is known, these curves can assist the simultaneous estimation of the chemical and electrochemical kinetics from the variation in the peak current with the scan rate and the nanoparticle coverage.

### 3. Conclusions

The cyclic voltammetry of the EC hetE mechanism, in which the chemical step occurs at the electrode surface, has been studied both at nanoparticle-modified substrates and homogeneous surface macroelectrodes. This reaction scheme considers that the second electron transfer is subject to the kinetics of the heterogeneous chemical process (Chet step) and the mass transport of the intermediate towards the bulk solution. Indeed, the results obtained show that the behaviour of multi-step electrode reactions occurring, according to the EC hetE scheme, are sensitive to both the coverage of the nanoparticles and the rate of surface reaction relative to that of mass transport to and from the nanoparticles.

Working curves and analytical expressions for the quantitative analysis of experimental data have also been deduced, guiding experimentalists in their interpretation of experiments and design of electrode modifications.

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Figure 9. Variation of the dimensionless peak current, \( \Psi_{\text{peak}} = \frac{I_{\text{peak}}}{FAc} \sqrt{\frac{RT}{C_{\text{diff}}}} \), with the dimensionless chemical rate constant, \( K_{\text{het}} = k_{\text{het}} \sqrt{\frac{RT}{F}} \) for the \( E_{\text{peak,m}} \) at an electrode modified with spherical nanoparticles with different coverage degrees and \( k_{0,1}/k_{\text{het}} = \) A) 10, B) 1, C) 0.1 and D) 0.01; \( \alpha_1 = 0.5 \).

Keywords: electrode modification • fuel cells • multiple electron transfers • nanoparticles • surface-catalysed reactions

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