Thin-layer voltammetry of soluble species on screen-printed electrodes: Proof of concept

Electronic Supplementary Material

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List of symbols

A: working electrode area (cm²)

- C^{o} : bulk concentration of the electroactive specie (mol cm⁻³)
- C_{ox}^{o} : concentration of the oxidized specie (mol cm⁻³)
- C_{red}^o : concentration of the reduced specie (mol cm⁻³)
- *D*: diffusion coefficient of the electroactive specie ($\text{cm}^2 \text{ s}^{-1}$)
- $E_{\rm P}$: peak potential (V)
- $E_{\rm P/2}$: potential where the current is at half the peak value (V)
- *E^o*: standard electrode potential (V)
- *F*: Faraday constant (96485 C mol⁻¹)
- $i_{\rm P}$: peak current (A)
- k^{o} : heterogeneous standard rate constant (cm s⁻¹)
- *I*: thin layer thickness (cm)
- *n*: number of electrons exchanged
- R: gas constant (8.314 J mol⁻¹ K⁻¹)
- SEM: scanning electron microscopy
- T: absolute temperature (K)
- v: voltage scan rate (V s⁻¹)
- αn_o : transfer coefficient

Voltammetry under semi-infinite linear diffusion regime

The theory of voltammetry under semi-infinite linear diffusion has been developed by Nicholson and Shain in 1964. $^{\rm 1}$

Reversible case

Peak current are linearly related with the square root of the voltage scan rate ($v^{1/2}$), and the equation for this relationship is usually employed to determine the electroactive area of the electrode (A) or the diffusion coefficient of the electroactive specie (D)

$$i_{\rm P} = 0.4463 n FAC_o^* \left(\frac{n FD v}{RT}\right)^{1/2}$$
 Eq. 1

Peak potentials are independent of v, with a peak potential difference of 57 mV at 25 °C:

$$E_{\rm Pc/a} = E^o \mp 1.109 \frac{RT}{nF}$$
 Eq. 2

Quasi-reversible case

The quasi-reversible case is considered for peak potential difference below 220 mV, and still holds a linear relationship with $v^{1/2}$. From the peak potential difference, the Matsuda parameter can be obtained from tabulated data, which is used to calculate the heterogeneous rate constant k^o (see for example Ref.²).

Totally irreversible case

In the totally irreversible case, one of the contributions is absent. The current peak is linearly related to $v^{1/2}$.

$$i_{\rm P} = 0.4958nFAC_o^* \left(\frac{\alpha n_o FDv}{RT}\right)^{1/2}$$
 Eq. 3

The equation depends on *D*, *A*, and the transfer coefficient (α). For this reason, it is usually employed for analytical purposes through the calibration curve $i_{\rm P}$ vs. $v^{1/2}$.

Peak potentials are related in a complex way to k^{o} , and α , and it is very difficult to obtain both kinetic parameters.

$$E_{\rm P} = E^{o} + \frac{RT}{nF} \left[0.780 + ln \left(\frac{D^{1/2}}{k^{o}} \right) + ln \left(\frac{\alpha n_{o} F v}{RT} \right)^{1/2} \right]$$
 Eq. 4

One approach is to measure the potential at half peak ($E_{P/2}$) to obtain α and then calculate k^o .

$$\left| E_{\rm P} - E_{\rm P/2} \right| = \frac{1.857RT}{(\alpha n_o)F}$$
 Eq. 5

Nevertheless, the diffusion coefficient should be known for the calculation.

Voltammetry under thin-layer diffusion regime

Equations for thin-layer diffusion regime were developed by A.T. Hubbard in his PhD thesis, and published in Ref.³ The following equations involve a general reaction between the oxidized and reduced species exchanging *n* electrons.

Reversible case

The reversible (ideal) case consider that under thin-layer diffusion, the reactant concentration at the electrode surface is nearly the same to that of the bulk solution. The Nernst equation holds for this situation:

$$E = E^{o} + \frac{RT}{nF} ln \frac{C_{ox}}{C_{red}}$$
 Eq. 6

and there is a complete consumption of the species involved in each scan. A symmetrical output is obtained in the current-potential graph, with the following peak parameters:

$$i_P = \frac{n^2 F^2 l A v C^o}{4 R T}$$
 Eq. 7

which defines a linear relationship between the current peak i_P and the voltge scan rate v. In relation with the potential:

$$E_P = E^o$$
 Eq. 8

Quasi-reversible case

The mathematical expression for the anodic and cathodic current – potential curves are:³

$$i_{a} = nFAk^{o}C_{ox}^{o}exp\left\{\frac{\alpha n_{o}F}{RT}(E - E^{o}) - \frac{ARTk^{o}}{\alpha n_{o}FVv}exp\left[\frac{\alpha n_{o}F}{RT}(E - E^{o})\right]\right\}$$
Eq. 9

$$i_c = -nFAk^o C_{red}^o exp\left\{\frac{(1-\alpha)n_o F}{RT}(E-E^o) - \frac{ARTk^o}{(1-\alpha)n_o FVv}exp\left[\frac{(1-\alpha)n_o F}{RT}(E-E^o)\right]\right\}$$
Eq. 10

where the subscripts *a* and *c* stands for anodic and cathodic, respectively. The shape of both curves depends on k^o and αn_o .

The thickness of the thin-layer solution can be introduced from:

$$V = lA$$
 Eq. 11

and the corresponding currents are expressed as:

$$i_a = nFAk^o C_{red}^o exp\left\{\frac{\alpha n_o F}{RT}(E - E^o) - \frac{RTk^o}{\alpha n_o Flv}exp\left[\frac{\alpha n_o F}{RT}(E - E^o)\right]\right\}$$
Eq. 12

$$i_{c} = -nFAk^{o}C_{ox}^{o}exp\left\{\frac{(1-\alpha)n_{o}F}{RT}(E-E^{o}) - \frac{RTk^{o}}{(1-\alpha)n_{o}Flv}exp\left[\frac{(1-\alpha)n_{o}F}{RT}(E-E^{o})\right]\right\}$$
Eq. 13

As a consequence, the thickness of the thin layer also affects the current-potential outputs.

From these equations, a set of equations for the peak parameters can be obtained:³

$$E_{P,a} = E^o + \frac{RT}{\alpha n_o F} ln \frac{\alpha n_o F v l}{RT k^o}$$
 Eq. 14

$$i_{P,a} = \frac{\alpha n_o n F^2 l A v C_{red}^o}{2.718 RT}$$
 Eq. 15

$$E_{P,c} = E^o - \frac{RT}{(1-\alpha)n_o F} ln \frac{(1-\alpha)n_o F v l}{RT k^o}$$
Eq. 16

$$i_{P,c} = -\frac{(1-\alpha)n_o n F^2 l A v C_{ox}^0}{2.718 R T}$$
 Eq. 17

Peak currents are linearly related to the voltage scan rate v.

It should be noted that the diffusion coefficient is not needed in the equations, which represents and advantage in comparison to the semi-infinite linear diffusion.

The kinetic parameter αn_o (or $(1 - \alpha)n_o$) could be obtained from the current peaks, but the thickness of the thin layer should be known. However, Hubbard³ demonstrated that in the case of a quasi-reversible case (or whenever both oxidation and reduction peaks are seen in the cyclic voltammogram), the transfer coefficient α can be easily obtained from:

$$\alpha = \frac{i_{P,a}}{i_{P,a} + |i_{P,c}|}$$
 Eq. 18

$$(1 - \alpha) = \frac{|i_{P,c}|}{i_{P,a} + |i_{P,c}|}$$
 Eq. 19

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and once α is known, the thickness layer can be obtained from the peak current equations, and k^o from the peak potential equations. However, in the latter case, the standard potential E^o should be known, but as demonstrated by Hubbard, this may not be necessary, as:

$$k^{o} = \left\{ \frac{2.718i_{P,a}}{nFAC^{o}} \left(\frac{2.718|i_{P,c}|}{nFAC^{o}} \right)^{\left| \frac{i_{P,a}}{i_{P,c}} \right|} exp\left[-\frac{2.718i_{P,a}}{nFlAvC^{o}} (E_{P,a} - E_{P,c}) \right] \right\}^{\frac{|i_{P,c}|}{i_{P,a} + |i_{P,c}|}}$$
Eq. 20

Hence, all the main kinetic parameters can be obtained just from the knowledge of the experimental peak parameters.

When $\alpha n_o \approx 0.5$ and $i_{P,a} \approx |i_{P,c}|$, k^o can be calculated from:

$$logk^{o} = -\left(\frac{1260}{T}\right)\left(E_{P,a} - E_{P,c}\right) + log\left(\frac{Fvl}{2RT}\right)$$
 Eq. 21

Totally irreversible case

In the case of a totally irreversible case, only one the reactions is observed: cathodic or anodic. This situation is obtained when $\Delta E_P > 200$ mV, that is, $E_P - E^o > 100$ mV. In this case, equations representing the observed process are Eqs. (14) and (15) or (16) and (17).

To those equations, the total charge involved in the electrochemical process can be introduced. As the electrolysis is complete, the following relationship based on Faraday's law holds:

$$Q = nFVC$$
 Eq. 22

which allows to calculate the volume of the thin layer, as defined in Eq. 11.

Examples

Thin-layer voltammetry for 1 mM HCF at v = 0.004 V s⁻¹.

Experimental results: $i_{P,a}$ = 8.8 x 10⁻⁷ A, $i_{P,c}$ = -9.30 x 10⁻⁷ A, $E_{P,a}$ = 0.144 V, $E_{P,c}$ = 0.081 V.

From Eq. 18, α = 0.486. As n_o = 1, from Eq. 15, l = 2.6 x 10⁻³ cm, i.e. 26 µm. Finally, as $\alpha \approx 0.5$, from Eq. 21 $k^o = 1.1 \times 10^{-4} \text{ cm s}^{-1}$.

Thin-layer voltammetry for 5 mM AA at v = 0.008 V s⁻¹.

Experimental results: i_P = 27.22 μ A, E_P = 0.316 V_{spre}, Q = 627 μ C. From Eq. 15, αn_o = 0.38, and from Eq. 22, $V = 6.5 \times 10^{-4} \text{ cm}^3$, and $I = 5.2 \times 10^{-3} \text{ cm} (52 \,\mu\text{m})$ (Eq. 11). Then, from Eq. 14, $k^o =$ $2.9 \times 10^{-5} \text{ cm s}^{-1}$.

1,5 $I = 35 \ \mu m; m = 126,7 \ mg$ 1,0 *l* = 29 μm; *m* = 973,5 mg 0,5 Current (µA) 0,0 -0,5 -1,0 -1,5 -0,3 -0,2 -0,1 0,0 0,1 0,2 0,3 0,4 Potential (V_{spre})

Figure S1: Cyclic voltammetry for HCF redox couple at a concentration 1 mM in NaNO₃ 0.1 M, under the indicated weights and cell thickness calculated according the Eq. (15).

Influence of coverslip weight

Calculation of the value of V_{spre}

The material employed for the reference potential of the screen-printed electrodes from DropSens[®] is under proprietary secret, but announced as a "quasi-reference silver electrode".

The redox couple $[Fe(CN)_6]^{-3}/[Fe(CN)_6]^{-4}$ is a surface sensitive probe towards electron transfer, though not dependent on the presence of oxides. It is widely used in the characterization of screen-printed surfaces,² and it is also used as a secondary reference electrode to measure the redox potential of quasi-reference electrodes.⁴

The measured redox potential for $[Fe(CN)_6]^{-3}/[Fe(CN)_6]^{-4}$ in 0.1 M NaNO₃ is 0.120 V, and taking into account that for the same redox couple in the SHE scale the value is 0.356 V, the measured potential for the V_{spre} = 0.236 V_{SHE}.

Screen-printed electrode features

In order to address the real electrode area, a Scanning Electron Microscopy (SEM) analysis was carried out. The SEM image (Figure S2) shows that the thickness of the printed layer was around ca. 10 μ m, therefore the outer ring area represents only 1 % of the total exposed electrode area. In other words this lateral area is disregarded.



Figure S2: SEM image focused on the lateral view of the screen-printed graphite (working) electrode, showing the electrode thickness of ca. 10 µm.

Another point of concern is the wettability of the electrode surface. For commercial screen-printed electrodes, some components added to the ink formulation turns the electrodic surface from hydrophilic to hydrophobic. Some examples reported in the literature agree with a contact angle above 90°. ⁵⁻⁷

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