Supporting Information

Cyclic voltammetry of electrocatalytic films. Fast conducting films.

Cyrille Costentin and Jean-Michel Savéant**

1. Formulation

The mechanism considered is:

$$\mathrm{P} + \mathrm{e}^- = \mathrm{Q}$$

$$\mathrm{Q} + \mathrm{A} \xrightarrow{k} \mathrm{P} + \textit{products}$$

Electron transport through the film (thickness: d_f) is fast, thus Q and P profiles in the film are uniform. The system can then be expressed by means of the following set of derivative equations and boundary conditions.

The electrode potential E is swept linearly between two values E_i and E_f :

$0 \le t \le t_R : E = E_i - vt$, $t_R \le t \le 2t_R : E = E_f - v(t - t_R)$ (t_R is the time at which the linear potential is reversed)

At $t = 0$:

$$\forall x,\ C_\mathrm{A} = C_\mathrm{A}^0;\ x > d_f,\ C_\mathrm{P} = 0,\ C_\mathrm{Q} = 0;\ 0 \le x \le d_f,\ C_\mathrm{P} = C_\mathrm{P}^0,\ C_\mathrm{Q} = 0$$

At $t > 0$:

In the film, $0 < x < d_f$:

$$\frac{\partial C_\mathrm{A}}{\partial t} = D_S \frac{\partial^2 C_\mathrm{A}}{\partial x^2} - kC_\mathrm{A}C_\mathrm{Q}\ ;\ d_f \frac{dC_\mathrm{Q}}{dt} = \frac{I}{F} - kC_\mathrm{Q}\int_0^{d_f} C_\mathrm{A}dx\ ;\ \frac{dC_\mathrm{P}}{dt} = -\frac{dC_\mathrm{Q}}{dt}\ ;\ \frac{C_\mathrm{Q}}{C_\mathrm{P}} = \exp\left[-\frac{F}{RT}\left(E - E_{\mathrm{P/Q}}^0\right)\right]$$

In the solution: $C_\mathrm{P} = 0,\ C_\mathrm{Q} = 0\ ;\ (C_\mathrm{A})_{x=\infty} = C_\mathrm{A}^0\ ;\ \dfrac{\partial C_\mathrm{A}}{\partial t} = D\dfrac{\partial^2 C_\mathrm{A}}{\partial x^2}$

At the electrode surface, $x=0$: $\left(\dfrac{\partial C_\mathrm{A}}{\partial x}\right)_{x=0} = 0$

At the film/ diffusion layer interface, $x=d_f$: $D\left(\dfrac{\partial C_\mathrm{A}}{\partial x}\right)_{x=d_{f+}} = D_S\left(\dfrac{\partial C_\mathrm{A}}{\partial x}\right)_{x=d_{f-}}\ ;\ (C_\mathrm{A})_{x=d_{f-}} = \kappa_\mathrm{A}(C_\mathrm{A})_{x=d_{f+}}$

2. Resolution:

In the solution, integration of $\dfrac{\partial C_\mathrm{A}}{\partial t} = D\dfrac{\partial^2 C_\mathrm{A}}{\partial x^2}$ taking onto account the boundary conditions leads to:

$$\frac{(C_\mathrm{A})_{x=d_{f-}}}{\kappa_\mathrm{A}C_\mathrm{A}^0} = 1 - \frac{1}{\sqrt{\pi}}\int_0^{\frac{Fvt}{RT}} \frac{FD_S\left[\frac{\partial (C_\mathrm{A})}{\partial x}\right]_{x=d_{f-}}}{I_\mathrm{A}} \frac{1}{\sqrt{\frac{Fvt}{RT} - \eta}}d\eta$$

(convolution of the current density with the function $1/\sqrt{\pi t}$) with introduction of $I_\mathrm{A} = FC_\mathrm{A}^0\sqrt{D}\sqrt{\dfrac{Fv}{RT}}$.

In the film, $0 < x < d_f$:

$\dfrac{d\left(C_\mathrm{P} + C_\mathrm{Q}\right)}{dt} = 0$ which integration leads to $C_\mathrm{P} + C_\mathrm{Q} = C_\mathrm{P}^0$ hence: $C_\mathrm{Q} = \dfrac{C_\mathrm{P}^0}{1 + \exp\left[\frac{F}{RT}\left(E - E^0\right)\right]}$

then: $$\frac{dC_\mathrm{Q}}{dt} = \frac{Fv}{RT}C_\mathrm{P}^0 \frac{\exp\left[\frac{F}{RT}\left(E - E^0\right)\right]}{\left\{1 + \exp\left[\frac{F}{RT}\left(E - E^0\right)\right]\right\}^2}$$

We restrict our analysis to pure kinetics conditions in the film for both A and Q:

$$D_S \frac{\partial^2 C_\mathrm{A}}{\partial x^2} = kC_\mathrm{A}C_\mathrm{Q} \text{ and } d_f \frac{dC_\mathrm{Q}}{dt} = \frac{I}{F} - kC_\mathrm{Q}\int_0^{d_f} C_\mathrm{A}dx \approx 0 \, .$$

Noting that $\frac{dC_\mathrm{Q}}{dt} = \frac{Fv}{RT} C_\mathrm{P}^0 \frac{\exp\left[\frac{F}{RT}\left(E-E^0\right)\right]}{\left\{1+\exp\left[\frac{F}{RT}\left(E-E^0\right)\right]\right\}^2}$, we can define a non-catalytic current component: $\frac{I_{NC}}{F} = d_f \frac{dC_\mathrm{Q}}{dt}$. Pure kinetics conditions implies that catalysis is strong enough so that $\frac{I}{F} = \frac{I_{NC}}{F} + kC_\mathrm{Q}\int_0^{d_f} C_\mathrm{A}dx \approx kC_\mathrm{Q}\int_0^{d_f} C_\mathrm{A}dx$, i.e. $I >> I_{NC}$.

We now introduce ***normalized variables and functions*** so as to obtain a dimensionless formulation of the diffusion-reaction problem:

time: $\tau = \frac{Fv}{RT}t$; Potential: $\xi = -\frac{F}{RT}\left(E - E^0_{\mathrm{P/Q}}\right)$, $u_i = \frac{F}{RT}\left(E_i - E^0_{\mathrm{P/Q}}\right)$, $u_f = \frac{F}{RT}\left(E_f - E^0_{\mathrm{P/Q}}\right)$, in practice $u_i >> 0$ and $u_f << 0$; space: $y = x/d_f$; concentrations: $j = \frac{C_\mathrm{J}}{C_\mathrm{P}^0}$, J being one of the species : P, Q, A. We obtain:

At $\tau = 0$: $\forall y,\ a = \gamma$; $y > 1,\ p = 0,\ q = 0$; $0 \le y \le 1,\ p = 1,\ q = 0$

At $\tau > 0$:

At the film/ diffusion layer interface, y=1 :

$$\left(\frac{\partial a}{\partial y}\right)_{y=1^-} = \frac{D}{D_S}\left(\frac{\partial a}{\partial y}\right)_{y=1^+} \ ; \ (a)_{y=1^-} = \kappa_\mathrm{A}(a)_{y=1^+} \ ; \ (a)_{y=1^-} = \frac{\kappa_\mathrm{A}C_\mathrm{A}^0}{C_\mathrm{P}^0} - \frac{1}{\sqrt{\pi}}\int_0^\tau \frac{I_S}{I_\mathrm{A}}\left(\frac{\partial a}{\partial y}\right)_{y=1^-}\frac{1}{\sqrt{\tau-\eta}}d\eta$$

$$\frac{C_\mathrm{P}^0}{\kappa_\mathrm{A}C_\mathrm{A}^0}(a)_{y=1^-} = 1 - \frac{1}{\sqrt{\pi}}\int_0^\tau \frac{C_\mathrm{P}^0}{\kappa_\mathrm{A}C_\mathrm{A}^0}\frac{I_S}{I_\mathrm{A}}\left(\frac{\partial a}{\partial y}\right)_{y=1^-}\frac{1}{\sqrt{\tau-\eta}}d\eta$$

We introduce: $a^* = \frac{C_\mathrm{P}^0}{\kappa_\mathrm{A}C_\mathrm{A}^0}a$ then: $\left(a^*\right)_{y=1^-} = 1 - \frac{1}{\sqrt{\pi}}\int_0^\tau \frac{I_S}{I_\mathrm{A}}\left(\frac{\partial a^*}{\partial y}\right)_{y=1^-}\frac{1}{\sqrt{\tau-\eta}}d\eta$

At the electrode surface, y=0 : $\left(\frac{\partial a^*}{\partial y}\right)_{y=0} = 0$

In the film, 0 <y< 1 :

$$\frac{I}{I_k} = q\int_0^1 a^* dy$$

$$\frac{\partial^2 a^*}{\partial y^2} = \left(\frac{I_k}{I_S}q\right)a^*$$

after introducing $I_k = FkC_\mathrm{P}^0\kappa_\mathrm{A}C_\mathrm{A}^0 d_f$ and $I_S = \frac{FD_S\kappa_\mathrm{A}C_\mathrm{A}^0}{d_f}$

Resolution leads to:

$$a^* = \frac{\exp\left(y\sqrt{\frac{I_k}{I_S}q}\right) + \exp\left(-y\sqrt{\frac{I_k}{I_S}q}\right)}{\exp\left(\sqrt{\frac{I_k}{I_S}q}\right) + \exp\left(-\sqrt{\frac{I_k}{I_S}q}\right)}\left[1 - \frac{1}{\sqrt{\pi}}\int_0^\tau \frac{I_S}{I_\mathrm{A}}\left(\frac{\partial a^*}{\partial y}\right)_{y=1^-}\frac{1}{\sqrt{\tau-\eta}}d\eta\right]$$

Then, it can be shown that:

$$q\int_0^1 a^* dy = \frac{I_S}{I_k}\left(\frac{\partial a^*}{\partial y}\right)_{y=1^-}$$

Leading to:

$$\frac{I}{I_S}=\left(\frac{\partial a^*}{\partial y}\right)_{y=1^-}\text{, hence: } a^*=\frac{\exp\left(y\sqrt{\frac{I_k}{I_S}}q\right)+\exp\left(-y\sqrt{\frac{I_k}{I_S}}q\right)}{\exp\left(\sqrt{\frac{I_k}{I_S}}q\right)+\exp\left(-\sqrt{\frac{I_k}{I_S}}q\right)}\left[1-\frac{1}{\sqrt{\pi}}\int_0^{\tau}\frac{I}{I_\mathrm{A}}\frac{1}{\sqrt{\tau-\eta}}d\eta\right]$$

We finally obtain:

$$\frac{I/I_\mathrm{A}}{\frac{\sqrt{I_kI_S}}{I_\mathrm{A}}\sqrt{\frac{1}{1+\exp(-\xi)}}\tanh\left(\sqrt{\frac{I_k}{I_S}\frac{1}{1+\exp(-\xi)}}\right)}=\left[1-\frac{1}{\sqrt{\pi}}\int_0^{\tau}\frac{I}{I_\mathrm{A}}\frac{1}{\sqrt{\tau-\eta}}d\eta\right]$$

The behavior in pure kinetics conditions can be described by two parameters: $\frac{I_k}{I_S}=\frac{kC_\mathrm{P}^0{d_f}^2}{D_S}$ and $\frac{I_\mathrm{A}}{I_S}=\frac{\sqrt{D}\sqrt{Fv/RT}d_f}{D_S}$ or a combination of both such as $\frac{I_kI_S}{{I_\mathrm{A}}^2}=\frac{D_S}{D}\frac{kC_\mathrm{P}^0}{Fv/RT}$.

2. Numerical calculations of voltammograms

We note $\psi=\frac{I}{I_A}$ and $I_\psi=I_{conv}^{difA}=\frac{1}{\sqrt{\pi}}\int_0^{\tau}\frac{I}{I_\mathrm{A}}\frac{1}{\sqrt{\tau-\eta}}d\eta$. The expression of CVs under pure kinetics conditions can be written as:

$$\psi=\frac{\sigma\tanh\left(\frac{\sqrt{\lambda}}{\sqrt{1+\exp(-\xi)}}\right)}{\sqrt{1+\exp(-\xi)}}\left(1-I_\psi\right)\text{ with }\lambda=\frac{I_k}{I_S}\text{ and }\sigma=\frac{\sqrt{I_kI_S}}{I_A}$$

Numerical resolution requires evaluation of I_ψ.

Procedure for numerical calculation:

The integral domain is divided into small divisions within which the current is expressed approximately as a linear function between the value of the border of the division. θ is divided into *p* divisions with width *h*: $\theta=ph$

$$\frac{1}{\sqrt{\pi}}\int_0^{\theta}\frac{\psi(\eta)}{\sqrt{\theta-\eta}}d\eta=\frac{1}{\sqrt{\pi}h}\sum_{j=1}^{p}\int_{\theta_{j-1}}^{\theta_j}\frac{\psi_j\left(\eta-\theta_{j-1}\right)+\psi_{j-1}\left(\theta_j-\eta\right)}{\sqrt{\theta_p-\eta}}d\eta$$

$$I_p=\frac{1}{\sqrt{\pi}}\int_0^{\theta}\frac{\psi(\eta)}{\sqrt{\theta-\eta}}d\eta=I_{p-1}+\frac{1}{\sqrt{\pi}h}\int_{\theta_{p-1}}^{\theta_p}\frac{\psi_p\left(\eta-\theta_{p-1}\right)+\psi_{j-1}\left(\theta_p-\eta\right)}{\sqrt{\theta_p-\eta}}d\eta=I_{p-1}+\frac{2}{3}\sqrt{\frac{h}{\pi}}\psi_{p-1}+\frac{4}{3}\sqrt{\frac{h}{\pi}}\psi_p$$

and

$$I_{p-1}=\sqrt{\frac{h}{\pi}}\sum_{j=1}^{p-1}\frac{2}{3}\left(\psi_{j-1}-\psi_j\right)\left[(p-j+1)^{\frac{3}{2}}-(p-j)^{\frac{3}{2}}\right]+2\left[\psi_j(p-j+1)-\psi_{j-1}(p-j)\right]\left(\sqrt{p-j+1}-\sqrt{p-j}\right)$$

Indeed:

$$\frac{1}{h}\int_{\theta_{p-1}}^{\theta_p}\frac{\psi_p\left(\eta-\theta_{p-1}\right)+\psi_{j-1}\left(\theta_p-\eta\right)}{\sqrt{\theta_p-\eta}}d\eta=\frac{1}{h}\int_{\theta_{p-1}}^{\theta_p}\frac{\psi_p\left(\eta-\theta_p\right)}{\sqrt{\theta_p-\eta}}d\eta+\frac{1}{h}\int_{\theta_{p-1}}^{\theta_p}\frac{\psi_p\left(\theta_p-\theta_{p-1}\right)}{\sqrt{\theta_p-\eta}}d\eta+\frac{1}{h}\int_{\theta_{p-1}}^{\theta_p}\psi_{j-1}\sqrt{\theta_p-\eta}d\eta$$

and

$$\frac{1}{h}\int_{\theta_{p-1}}^{\theta_p}\frac{\psi_p\left(\eta-\theta_p\right)}{\sqrt{\theta_p-\eta}}d\eta=-\frac{\psi_p}{h}\int_{\theta_{p-1}}^{\theta_p}\sqrt{\theta_p-\eta}d\eta=\frac{2\psi_p}{3h}\left[\left(\theta_p-\eta\right)^{\frac{3}{2}}\right]_{\theta_{p-1}}^{\theta_p}=-\frac{2\psi_p}{3h}\left(\theta_p-\theta_{p-1}\right)^{\frac{3}{2}}=-\frac{2}{3}\psi_p\sqrt{h}$$

$$\frac{1}{h}\int_{\theta_{p-1}}^{\theta_p}\frac{\psi_p\left(\theta_p-\theta_{p-1}\right)}{\sqrt{\theta_p-\eta}}d\eta=\psi_p\int_{\theta_{p-1}}^{\theta_p}\frac{1}{\sqrt{\theta_p-\eta}}d\eta=-2\psi_p\left[\sqrt{\theta_p-\eta}\right]_{\theta_{p-1}}^{\theta_p}=2\psi_p h$$

$$\frac{1}{h}\int_{\theta_{p-1}}^{\theta_p}\psi_{j-1}\sqrt{\theta_p-\eta}d\eta=\frac{\psi_{j-1}}{h}\int_{\theta_{p-1}}^{\theta_p}\sqrt{\theta_p-\eta}d\eta=-\frac{2\psi_{j-1}}{3h}\left[\left(\theta_p-\eta\right)^{\frac{3}{2}}\right]_{\theta_{p-1}}^{\theta_p}=\frac{2}{3}\psi_{j-1}\sqrt{h}$$

Integral equation calculation:

Since the integral domain is divided into small divisions within which the current is expressed approximately as a linear function between the value of the border of the division. θ is divided into *p* divisions with width *h*:

$$\psi_p = \frac{\sigma \tanh\left(\frac{\sqrt{\lambda}}{\sqrt{1+\exp(-\xi)}}\right)}{\sqrt{1+\exp(-\xi)}}\left(1 - I_p\right) \text{ with } I_p = I_{p-1} + \frac{2}{3}\sqrt{\frac{h}{\pi}}\psi_{p-1} + \frac{4}{3}\sqrt{\frac{h}{\pi}}\psi_p$$

Thus: $$\psi_p = \frac{\frac{\sigma \tanh\left(\frac{\sqrt{\lambda}}{\sqrt{1+\exp(-\xi)}}\right)}{\sqrt{1+\exp(-\xi)}}}{\left(1 + \frac{4}{3}\sqrt{\frac{h}{\pi}}\frac{\sigma \tanh\left(\frac{\sqrt{\lambda}}{\sqrt{1+\exp(-\xi)}}\right)}{\sqrt{1+\exp(-\xi)}}\right)}\left(1 - I'_{p-1}\right) \text{ with } I'_{p-1} = I_{p-1} + \frac{2}{3}\sqrt{\frac{h}{\pi}}\psi_{p-1}$$