*Supporting Information*

# Electrochemical Capacitive Charging in Porous Materials. Discriminating between Ohmic Potential Drop and Counter-Ion Diffusion.

*Cyrille Costentin* and Jean-Michel Savéant**

*[1] Université Paris Diderot, Sorbonne Paris Cité, Laboratoire d'Electrochimie Moléculaire, Unité Mixte de Recherche Université - CNRS N° 7591, Bâtiment Lavoisier, 15 rue Jean de Baïf, 75205 Paris Cedex 13, France.*

*[2] Present address: Department of Chemistry and Chemical Biology, Harvard University, 12 Oxford Street, Cambridge, Massachusetts 02138, United States.*

Cyrille Costentin : cyrille.costentin@univ-paris-diderot.fr, Jean-Michel Savéant : saveant@univ-paris-diderot.fr

**1. Capacitance of RC circuit in cyclic voltammetry:**

We consider the RC circuit shown in figure 2 that includes a potentiostat able to maintain an applied linear potential ramp. During the first CV scan between $E_i$ and $E_f$, at a scan rate *v*, the current is:

$$i = C_f v\left[1-\exp\left(-\frac{t}{R_u C_f}\right)\right] = C_f v\left[1-\exp\left(-\frac{E-E_i}{vR_u C_f}\right)\right],$$ [1]

and the capacitance $C$, calculated according to $\left(\int_{E_i}^{E_f} \frac{i}{v} dE\right)/\Delta E$ :

$$C = \left(\int_{E_i}^{E_f} \frac{i}{v} dE\right)/\left(E_f - E_i\right) = \left(\int_{E_i}^{E_f} C_f\left[1-\exp\left(-\frac{E-E_i}{vR_u C_f}\right)\right]dE\right)/\left(E_f - E_i\right)$$

Hence:

$$\frac{C}{C_{max}} = 1-\frac{v}{v_{RC}}\left[1-\exp\left(-\frac{v_{RC}}{v}\right)\right] \text{ with } v_{RC} = \left(E_f - E_i\right)/R_u C_f \text{ and } C_{\max} = C_f$$

What is now the expression of the capacitance for successive CVs? We first derive the expression of the current at the scan limits (*i.e.*: at $E = E_f$ and $E = E_i$, or equivalently at $t = (2n+1)t_f$ and $t = (2n+2)t_f$ (with $n > 0$), where $t_f$ is the time corresponding to a forward or reverse scan, *i.e.* : $t_f = \left(E_f - E_i\right)/v$ for successive CVs. We use here a recurrence reasoning which consists in establishing expressions at cycle #*n*+1 from expression of cycle #*n* also showing that the considered expressions are valid at the initial cycle considered, here CV #2.

***At CV #1***

we have shown that the current of the forward scan is:

$i = C_f v\left[1-\exp\left(-\frac{t}{R_u C_f}\right)\right]$ and thus the current at the end of the forward scan is: $i_1 = C_f v\left[1-\exp\left(-\frac{t_f}{R_u C_f}\right)\right]$.

On the reverse scan, the applied potential is $E = v\left(2t_f - t\right)$, and we have: $E = R_u i + \frac{q}{C_f}$, $i = \frac{dq}{dt}$, thus $\frac{di}{dt} + \frac{i}{R_u C_f} = -\frac{v}{R_u}$

The solution of this differential equation is: $i = -C_f v + A\exp\left(-\frac{t}{R_u C_f}\right)$ with $A$ a constant and at $t = t_f$, we have:

$i_1 = -C_f v + A\exp\left(-\frac{t_f}{R_u C_f}\right) = C_f v\left[1-\exp\left(-\frac{t_f}{R_u C_f}\right)\right]$, then: $A = 2C_f v\exp\left(\frac{t_f}{R_u C_f}\right) - C_f v$. Hence, the current at the end of the first cycle is: $i_2 = -Cv\left[1-2\exp\left(-\frac{t_f}{R_u C_f}\right)+\exp\left(-\frac{2t_f}{R_u C_f}\right)\right]$

We now assume that the current at the end of the forward scan and at the end of the CV #$n$ ($n$>1) are:

$$i_{2n-1} = C_f v - 2C_f v\left[\sum_{j=1}^{2n-2}(-1)^{j-1}\exp\left(\frac{-jt_f}{R_u C_f}\right)\right] \qquad \text{(S1)}$$

$$i_{2n} = -C_f v + 2C_f v\left[\sum_{j=1}^{2n-1}(-1)^{j-1}\exp\left(\frac{-jt_f}{R_u C_f}\right)\right] \qquad \text{(S2)}$$

***At CV # 2***

During the forward scan, the potential is $E = v\left(t-2t_f\right)$ and we have $E = R_u i + \frac{q}{C_f}$; $i = \frac{dq}{dt}$ hence: $\frac{di}{dt} + \frac{i}{R_u C_f} = \frac{v}{R_u}$

We obtain: $i = C_f v + B\exp\left(-\frac{t}{R_u C_f}\right)$ with $B$ a constant.

At $t=2t_f$, we have:

$$i_2 = -Cv\left[1-2\exp\left(-\frac{t_f}{R_u C_f}\right)+\exp\left(-\frac{2t_f}{R_u C_f}\right)\right] = C_f v + B\exp\left(-\frac{2t_f}{R_u C_f}\right) \text{ hence: } B = -2C_f v\left[\exp\left(\frac{2t_f}{R_u C_f}\right)-\exp\left(\frac{t_f}{R_u C_f}\right)\right]$$

Thus, $t=3t_f$: $i_3 = C_f v - 2C_f v\left[\exp\left(-\frac{t_f}{R_u C_f}\right)-\exp\left(-\frac{2t_f}{R_u C_f}\right)\right]$ which verifies equation (S1) with $n = 2$

On the reverse scan, the potential is: $E = v\left(4t_f - t\right)$ and we have: $E = R_u i + \frac{q}{C_f}$ and $i = \frac{dq}{dt}$,

thus $\frac{di}{dt} + \frac{i}{R_u C_f} = -\frac{v}{R_u}$

We obtain: $i=-C_f v+H\exp\left(-\frac{t}{R_u C_f}\right)$ with $H$ a constant.

At $t=3t_f$, we have:

$$i_3=C_f v-2C_f v\left[\exp\left(-\frac{t_f}{R_u C_f}\right)-\exp\left(-\frac{2t_f}{R_u C_f}\right)\right]=-C_f v+H\exp\left(-\frac{3t_f}{R_u C_f}\right)\text{, hence:}$$

$$H=2C_f v\left[\exp\left(\frac{3t_f}{R_u C_f}\right)+\exp\left(\frac{t_f}{R_u C_f}\right)-\exp\left(\frac{2t_f}{R_u C_f}\right)\right]$$ and therefore, at $t=4t_f$, we have:

$$i_4=-C_f v+2C_f v\left[\exp\left(-\frac{t_f}{R_u C_f}\right)-\exp\left(-\frac{2t_f}{R_u C_f}\right)+\exp\left(-\frac{3t_f}{R_u C_f}\right)\right]$$ which verifies equation (S2) with $n = 2$

***At CV # n+1***

We now show expressions (S1) and (S2) are valid at CV #$n$+1.

During the forward scan, the potential is: $E=v\left(t-2nt_f\right)$ and we have $E=R_u i+\frac{q}{C_f}$ and $i=\frac{dq}{dt}$ hence:

$$\frac{di}{dt}+\frac{i}{R_u C_f}=\frac{v}{R_u}$$

Resolution of this differential equation leads to:

$i=C_f v+D\exp\left(-\frac{t}{R_u C_f}\right)$ with $D$ a constant.

At $t=2nt_f$, we have:

$i_{2n}=C_f v+D\exp\left(-\frac{2nt_f}{R_u C_f}\right)$ hence: $D=\left(i_{2n}-C_f v\right)\exp\left(\frac{2nt_f}{R_u C_f}\right)$

At $t=(2n+1)t_f$, we have:

$i_{2n+1}=C_f v+D\exp\left(-\frac{(2n+1)t_f}{R_u C_f}\right)$, thus $i_{2n+1}=C_f v+\left(i_{2n}-C_f v\right)\exp\left(-\frac{t_f}{R_u C_f}\right)$. Therefore introducing equation (S2):

$$i_{2n+1}=C_f v-2C_f v\left(\exp\left(-\frac{t_f}{R_u C_f}\right)-\sum_{j=1}^{2n-1}(-1)^j\exp\left(\frac{-(j+1)t_f}{R_u C_f}\right)\right)=C_f v-2C_f v\left[\sum_{j=1}^{2n}(-1)^{j-1}\exp\left(\frac{-jt_f}{R_u C_f}\right)\right]$$

This shows that the expression of $i_{2n+1}$ is valid for any integer value of $n$ >1.

On the reverse scan, the potential is: $E=v\left(2nt_f-t\right)$ and we have $E=R_u i+\frac{q}{C_f}$ and $i=\frac{dq}{dt}$, thus $\frac{di}{dt}+\frac{i}{R_u C_f}=-\frac{v}{R_u}$.

Resolution of this differential equation leads to: $i=-C_f v+G\exp\left(-\frac{t}{R_u C_f}\right)$ with $G$ a constant.

At $t=(2n+1)t_f$, we have: $i_{2n+1}=-C_f v+G\exp\left(-\frac{(2n+1)t_f}{R_u C_f}\right)$, thus: $G=\left(C_f v+i_{2n+1}\right)\exp\left(\frac{(2n+1)t_f}{R_u C_f}\right)$

At $t=(2n+2)t_f$, we have: $i_{2n+2}=-C_f v+G\exp\left(-\frac{(2n+2)t_f}{R_u C_f}\right)$

thus $i_{2n+2}=-C_f v+\left(C_f v+i_{2n+1}\right)\exp\left(\frac{(2n+1)t_f}{R_u C_f}\right)\exp\left(-\frac{(2n+2)t_f}{R_u C_f}\right)=-C_f v+\left(C_f v+i_{2n+1}\right)\exp\left(-\frac{t_f}{R_u C_f}\right)$

Thus, introducing equation (S1):

$$i_{2n+2}=-C_f v+2C_f v\left(\exp\left(-\frac{t}{R_u C_f}\right)+\left[\sum_{j=1}^{2n}(-1)^j\exp\left(\frac{-(j+1)t_f}{R_u C_f}\right)\right]\right)=-C_f v+2C_f v\left[\sum_{j=1}^{2n+1}(-1)^{j-1}\exp\left(\frac{-jt_f}{R_u C_f}\right)\right]$$

This shows that the expression of $i_{2n+2}$ is valid for any integer value of $n>1$.

We can now calculate the capacitance for any cycle taking into account the expression of the forward current at the corresponding cycle #*n+1, n>1*:

$i(t)=C_f v+\left(i_{2n}-C_f v\right)\exp\left(\frac{2nt_f}{R_u C_f}\right)\exp\left(-\frac{t}{R_u C_f}\right)$ with $i_{2n}=-C_f v+2C_f v\left[\sum_{j=1}^{2n-1}(-1)^{j-1}\exp\left(\frac{-jt_f}{R_u C_f}\right)\right]$, hence:

$$i(t)=C_f v-2C_f v\left(1-\left[\sum_{j=1}^{2n-1}(-1)^{j-1}\exp\left(\frac{-jt_f}{R_u C_f}\right)\right]\right)\exp\left(\frac{2nt_f}{R_u C_f}\right)\exp\left(-\frac{t}{R_u C_f}\right)$$

Therefore:

$$\frac{C_{n+1}}{C_f}=\frac{\left(\int_{E_i}^{E_f}\frac{i}{C_f v}dE\right)}{\left(E_f-E_i\right)}=\frac{\left(\int_{E_i}^{E_f}1-2\left(1-\left[\sum_{j=1}^{2n-1}(-1)^{j-1}\exp\left(\frac{-jt_f}{R_f C_u}\right)\right]\right)\exp\left(\frac{2nt_f}{R_u C_f}\right)\exp\left(-\frac{t}{R_u C_f}\right)dE\right)}{\left(E_f-E_i\right)}$$

leading to: $\frac{C_{n+1}}{C_f}=1-2\left(1-\left[\sum_{j=1}^{2n-1}(-1)^{j-1}\exp\left(\frac{-jt_f}{R_f C_u}\right)\right]\right)\frac{R_u C_f v\left[1-\exp\left(-\frac{t_f}{R_u C_f}\right)\right]}{\left(E_f-E_i\right)}$

and thus: $\frac{C_{n+1}}{C_f}=1-2\frac{v}{v_{RC}}\left[1-\exp\left(-\frac{v_{RC}}{v}\right)\right]\left[\sum_{j=0}^{2n-1}(-1)^j\exp\left(-j\frac{v_{RC}}{v}\right)\right]$

When $n\to\infty$: $\frac{C_\infty}{C_f}=1-2\frac{v}{v_{RC}}\left[1-\exp\left(-\frac{v_{RC}}{v}\right)\right]\left[\sum_{j=0}^{\infty}(-1)^j\exp\left(-j\frac{v_{RC}}{v}\right)\right]$

taking into account: $\sum_{j=0}^{\infty}(-1)^j\exp\left(-j\frac{v_{RC}}{v}\right)=\frac{1}{1+\exp\left(-\frac{v_{RC}}{v}\right)}$

we finally obtain: $\frac{C_\infty}{C_{\max}} = 1 - 2\frac{\nu}{\nu_{RC}}\left[\frac{1-\exp\left(-\frac{\nu_{RC}}{\nu}\right)}{1+\exp\left(-\frac{\nu_{RC}}{\nu}\right)}\right] = 1 - \frac{2\nu}{\nu_{RC}}\tanh\left(\frac{\nu_{RC}}{2\nu}\right)$, with $C_{\max} = C_f$

**2. Capacitive charge storage in nanopores and diffuse layer**

We consider the porous structure shown in figure S1.

The conductive material has an homogeneous Galvani potential $\Phi_M$. At a given position in the macropore (from the underlying electrode), the potential in the nanopores is assumed to be constant ($\Phi_{np}$) while the potential in the macropore is not constant due to the development of a diffuse layer.

The accumulated charge in the conductive material $\sigma_M$ is equal to the sum of the charge accumulated in the nanopores and in the diffuse layer in the macropore:

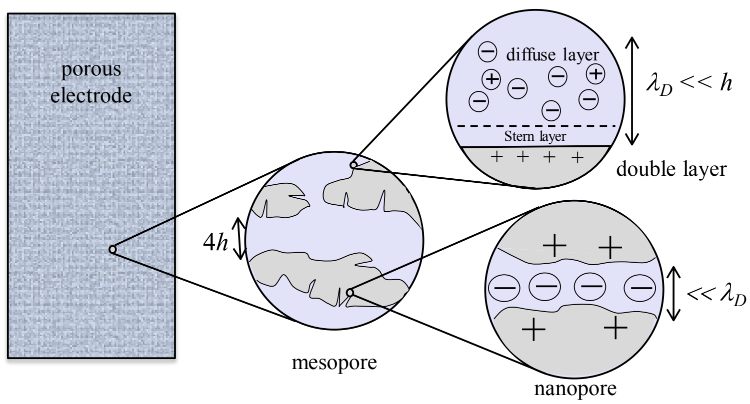


Fig. S1. Schematic representation of the bi-hierarchical structure with macropores and nanopores.

$\sigma_M = \sigma_{nano} + \sigma_{dif}$ Hence the differential capacitance:

$$C_d = \frac{d\sigma_M}{d\Phi_M} = \frac{d\sigma_{nano}}{d\Phi_M} + \frac{d\sigma_{dif}}{d\Phi_M}$$

and, from the Gouy-Chapman model of the diffuse layer: $\frac{d\sigma_{dif}}{d\Phi_M} \approx C_{dl}$

Thus: $C_d = \frac{d\sigma_{nano}}{d\Phi_M} + C_{dl}$

Then, considering $C_{nano} \approx \frac{d\sigma_{nano}}{d\Phi_M}$: $C_d = C_{nano} + C_{dl}$, showing that the differential capacitance is equivalent to two capacitances in parallel, one describing the nanopores and the other the double layer in the macropores.

**3. Transmission line model**

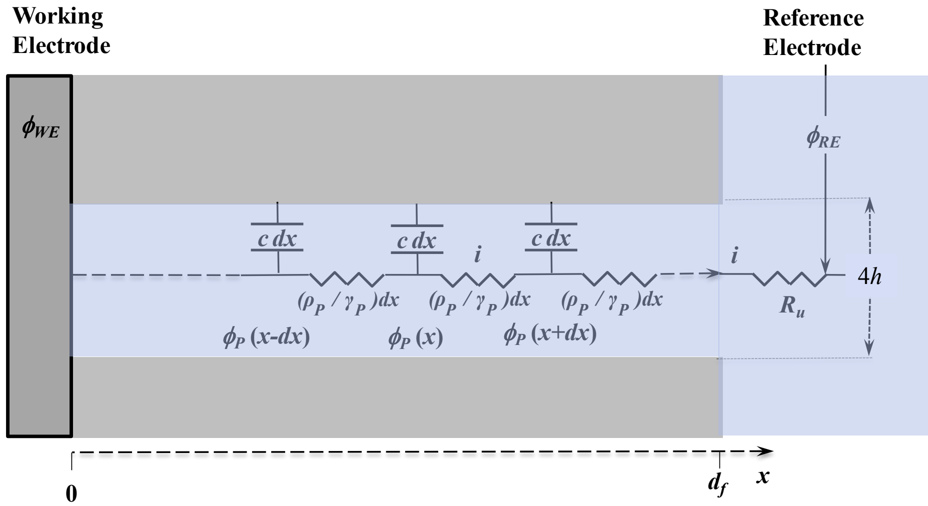


Fig.S2. Transmission line model.

**Glossary of symbols**

$c$: distributed capacitance per unit of surface area of the electrode and unit of thickness of the film, *i.e.*, a capacitance per unit of volume of the film.

$d_f$ : thickness of the film.

$i$: current.

$r$ : radius of a pore.

$t$: time.

$t_f = d_f^{\,2}\left(\rho_P / \gamma_P\right)c$ : film time constant.

$x$: distance from the (planar) base electrode.

$C_f = S_{geom} c d_f$ : film capacitance.

$E_i, E_f$ : initial and final potentials in cyclic voltammetry.

$F$: Faraday.

$I_B$, $I_P$, and $I$ : current densities (currents per working electrode unit surface area $S_{geom}$) in solid parts of the film, pores and solution, respectively.

$R$: radius of the electrode

$R_f = \dfrac{\rho_P d_f}{\gamma_P S_{geom}}$ : film resistance.

$R_S$ : solution resistance between the working electrode and the reference electrode.

$R_u$ : uncompensated solution resistance between the working electrode and the reference electrode.

$S_{geom}$ : surface area of the base electrode.

$T$: absolute temperature.

$v$: scan rate.

$\gamma_P$ : fraction of the base electrode surface that are covered by the pores.

$\rho_P$ : resistivity of the solution in the pores.

$\phi_{WE,\ RE,\ B \text{ and } P}$ : potential at the working electrode, the reference electrode, in the bulk solid parts of the film and in the pores, respectively.

**Definition of the dimensionless variables and parameters**

$y=\frac{x}{d_f}$; $\tau=\frac{t}{t_f}$; $\psi_P=\frac{I_P}{I}$; $\psi_B=\frac{I_B}{I}$; $\psi=\psi_B+\psi_P=\frac{I}{I}$; $\varphi_B=\frac{\phi_B}{IS_{geom}\times t_f/C_f}=\frac{\phi_B}{i\times R_f}$;

$\varphi_P=\frac{\phi_P}{IS_{geom}\times t_f/C_f}=\frac{\phi_P}{i\times R_f}$; $\beta_u=\frac{R_u}{d_f\frac{\rho_P}{\gamma_P S_{geom}}}$

**Governing equations**

We are looking for the time-dependence of the potential between the working and reference electrode when a constant current is applied from $t$=0, recalling that the potential across the film $\phi_B(0,t)-\phi_P(d_f,t)$ is equal to the potential difference between working electrode and reference electrode, $\phi_{WE}-\phi_{RE}$ according to (assuming an ideal potentiostat):

$\phi_B(0,t)=\phi_{WE}$ and $\phi_P(x=d_f,t)=\phi_{RE}+S_{geom}R_uI(t)$.

The definition of $R_u$ deserves a particular attention. With no attempt to compensate ohmic drop effect by means of positive feedback, $R_u=R_S$. When positive feedback is activated, part or total of $R_S$ may be compensated.

The potential differences and the current densities obey the following set of partial derivative equation accompanied by a series of initial and boundary conditions, at the two boundaries of the film, *i.e.*, at the electrode ($x=0$) and at the film solution interface ($x=d_f$).

No ohmic drop in the bulk material: $\phi_B(x,t)=\phi_B(0,t)=\phi_{WE}$ (1S)

Ohmic drop in the pores: $\frac{\partial\phi_P}{\partial x}+\frac{\rho_P}{\gamma_P}I_P=0$ (2S)

Capacitance charging at the pores' walls $\frac{\partial I_P}{\partial x}=-\frac{\partial I_B}{\partial x}=c\frac{\partial(\phi_B-\phi_P)}{\partial t}$ (3S)

Conservation of fluxes throughout the system: $I_P(x,t)+I_B(x,t)=I(t)$ (4S)

The potential difference $\phi_{WE}-\phi_{RE}$ is imposed by the instrument. In case of, e.g., an oxidation the linear potential scanning: $\phi_{WE}-\phi_{RE}=E=E_i+vt$, $E_i$ being the starting potential and $v$ the scan rate, leads to:

$\phi_B(0,t)-\phi_p(d_f,t)=\phi_{WE}-\phi_{RE}-(S_{geom}R_u)I=E_i+vt-(S_{geom}R_u)I$

and therefore:

$$\frac{\partial\left[\phi_B(0,t)-\phi_p(d_f,t)\right]}{\partial t}+(SR_u)\frac{\partial I}{\partial t}=\frac{d(\phi_{WE}-\phi_{RE})}{dt}=v \quad (5S)$$

Initial conditions:

$t=0:\phi_P(x,0)=\phi_{RE}$, $\phi_B(x,0)=\phi_{RE}$, $I_B(x,t)+I_P(x,t)=I$

Boundary conditions:

$x=0$: $\phi_B(0,t)=\phi_{WE}$, $\frac{\partial\phi_P}{\partial x}(0,t)=0$, $I_P(0,t)=0$, $I_B(0,t)=I$

$x=d_f:\phi_P(d_f,t)-\phi_{RE}=R_ui=(S_{geom}R_u)I$, $\frac{\partial\phi_B}{\partial x}(d_f,t)=0$, $I_B(d_f,t)=0$, $I_P(d_f,t)=I$

**Dimensionless formulation**

The advantage of a dimensionless formulation of the problem is that it minimizes the number of effective parameters from which the system depends, as these effective parameters are each a combination of several experimental parameters.

Space: $y=\frac{x}{d_f}$, time: $\tau=\frac{t}{t_f}$ where $t_f=d_f^2\left(\frac{\rho_P}{\gamma_P}\right)c=R_fC_f$ is the time constant of the film.

Potentials: $\varphi_B=\frac{\phi_B}{IS_{geom}\times t_f/C_f}=\frac{\phi_B}{i\times R_f}$; $\varphi_P=\frac{\phi_P}{IS_{geom}\times t_f/C_f}=\frac{\phi_P}{i\times R_f}$

Currents densities:

$$\psi_P = \frac{I_P}{I},\ \psi_B = \frac{I_B}{I},\ \psi = \psi_B + \psi_P = 1$$

Uncompensated solution resistance: $\beta_u = \dfrac{R_u}{d_f \dfrac{\rho_P}{\gamma_P S_{geom}}}$

Thus, in dimensionless terms:

$$\frac{\partial \varphi_B}{\partial y} = 0 \qquad (1\text{'S})$$

$$\frac{\partial \varphi_P}{\partial y} + \psi_P = 0 \qquad (2\text{'S})$$

$$\frac{\partial \psi_P}{\partial y} = -\frac{\partial \psi_B}{\partial y} = \frac{\partial\left(\varphi_B - \varphi_P\right)}{\partial \tau} \qquad (3\text{'S})$$

$$\psi_B(y,\tau) + \psi_P(y,\tau) = \psi(\tau) \qquad (4\text{'S})$$

Initial conditions:

$$\tau = 0:\ \varphi_P\left(y,0\right) = \varphi_{RE}\ ,\ \varphi_B\left(y,0\right) = \varphi_{WE}\ ,\ \psi_B(y,\tau) = 1$$

Boundary conditions:

$$y\text{=}0:\ \varphi_B\left(0,\tau\right) = \varphi_{WE}\ ,\ \frac{\partial \varphi_P}{\partial y}\left(0,\tau\right) = 0\ ,\ \psi_P\left(0,\tau\right) = 0\ ,\ \psi_B\left(0,\tau\right) = \psi$$

$$y = 1:\ \frac{\partial \varphi_B}{\partial y}\left(1,\tau\right) = 0\ ,\ \psi_B\left(1,\tau\right) = 0\ ,\ \psi_P\left(1,\tau\right) = \psi$$

Potential scanning: $\dfrac{\partial\left[\varphi_B\left(0,\tau\right) - \varphi_p\left(1,\tau\right)\right]}{\partial \tau} + \beta_u \dfrac{\partial \psi}{\partial \tau} = 1$

**Resolution:**

Derivation of limiting behaviors of interest is greatly eased by the passage into the Laplace transform space as it is the case for all problems relative to electrical circuit and electronic devices. Any function $f(\tau)$ is thus replaced by its Laplace transform:

$\bar{f}(s) = \displaystyle\int_0^\infty f(\tau)\exp\left(-s\tau\right)d\tau$ , where $s$ is the Laplace variable corresponding to the dimensionless time variable $\tau$. The main interest of Laplace transformation is that differentiation and integration are replaced by multiplication and division by the Laplace variable, $s$, respectively. The set of the (1S') – (5S') equations thus become (1S''') – (5S''') in the Laplace space.

$$\frac{\partial \bar{\varphi}_B}{\partial y} = 0 \qquad (1\text{S'''})$$

$$\frac{\partial \bar{\varphi}_P}{\partial y} + \bar{\psi}_P = 0 \qquad (2\text{S'''})$$

$$-\frac{\partial \bar{\psi}_B}{\partial y} = \frac{\partial \bar{\psi}_P}{\partial y} = s\left(\bar{\varphi}_B - \bar{\varphi}_P\right) \qquad (3\text{S'''})$$

$$\bar{\psi}_B(y,s) + \bar{\psi}_P(y,s) = \bar{\psi}(s) = \frac{1}{s} \qquad (4\text{S'''})$$

Differentiation of equations (1S''') and (2S''') leads to:

$$\frac{\partial^2 \bar{\varphi}_B}{\partial y^2} = 0,$$

$\dfrac{\partial^2 \bar{\varphi}_P}{\partial y^2} + \dfrac{\partial \bar{\psi}_P}{\partial y} = 0$, and from (2S'''): $\dfrac{\partial^2 \bar{\varphi}_P}{\partial y^2} + s\left(\bar{\varphi}_B - \bar{\varphi}_P\right) = 0$

leading by subtraction to:

$$\frac{\partial^2\left(\bar{\varphi}_B - \bar{\varphi}_P\right)}{\partial y^2} - s\left(\bar{\varphi}_B - \bar{\varphi}_P\right) = 0 \qquad (5S''')$$

Integration of equation (5S''') leads to:

$$\bar{\varphi}_B - \bar{\varphi}_P = A\exp\left(y\sqrt{s}\right) + B\exp\left(-y\sqrt{s}\right) \qquad (6S''')$$

and thus, in particular, to:

$$\left(\bar{\varphi}_B - \bar{\varphi}_P\right)(0,s) = A + B \text{, i.e., } \bar{\varphi}_B(0,s) - \bar{\varphi}_P(0,s) = A + B \qquad (7S''')$$

$$\left(\bar{\varphi}_B - \bar{\varphi}_P\right)(1,s) = A\exp\left(\sqrt{s}\right) + B\exp\left(-\sqrt{s}\right)\text{, i.e. } \bar{\varphi}_B(1,s) - \bar{\varphi}_P(1,s) = A\exp\left(\sqrt{s}\right) + B\exp\left(-\sqrt{s}\right) \qquad (8S''')$$

We are looking for the dimensionless current-time response:

$$\frac{\partial\left[\varphi_B(0,\tau) - \varphi_p(1,\tau)\right]}{\partial\tau} + \beta_u\frac{\partial\psi}{\partial\tau} = 1 \qquad (9S''')$$

In the Laplace space:

$$s\left[\bar{\varphi}_B(0,\mathrm{s}) - \bar{\varphi}_P(0,\mathrm{s})\right] + s\beta_u\bar{\psi} = \frac{1}{s}$$

$$\bar{\psi} = \frac{1}{s^2\left[z(s) + \beta_u\right]} \qquad (10S''')$$

after introduction of the Laplace dimensionless impedance of the film

$$z(s) = \frac{\bar{\varphi}_B(0,\mathrm{s}) - \bar{\varphi}_P(0,\mathrm{s})}{\bar{\psi}} \qquad (11S''')$$

This is not a Laplace transform, of any function of $\tau$, unlike the $\bar{\varphi}$ s and the $\bar{\psi}$ s. It is simply a function of $s$. The expression of $z$(s) as a function of the various parameters is derived at the end of this section.:

$$z(s) = \frac{1}{\sqrt{s}}\frac{1}{\tanh\left(\sqrt{s}\right)}$$

showing that the ensuing dimensionless current response, is:

$$\bar{\psi} = \frac{1}{s^2\left[\dfrac{1}{\sqrt{s}}\dfrac{1}{\tanh\left(\sqrt{s}\right)} + \beta_u\right]}$$

The following limiting situations of interest are reached when:

a) $s \to 0$, corresponding to asymptotic behavior at large values of $\tau$. Then:

$\dfrac{1}{\tanh\left(\sqrt{s}\right)} \xrightarrow{s\to 0} \dfrac{1}{\sqrt{s}}$ therefore: $\bar{\psi} \xrightarrow{s\to 0} \dfrac{1}{s}$ *i.e.*, in the original space: $\psi \xrightarrow{\tau\to\infty} 1$

i.e., a plateau of unity height is asymptotically reached at long times.

b) $s \to \infty$, $\tau \to 0$ in the original space, embodies the limiting behavior prevailing at the initial stages of the current-time responses

Then: $z(s) \xrightarrow{s\to\infty} \dfrac{1}{\sqrt{s}}$

The Laplace dimensionless current then becomes: $\bar{\psi} = \dfrac{1}{s^2\left[z(s) + \beta_u\right]} \xrightarrow{s\to\infty} \dfrac{1}{s^2\left[\dfrac{1}{\sqrt{s}} + \beta_u\right]}$

The intrinsic properties of the film may be obtained from a situation where the resistance of the solution outside the film would be totally compensated by means of a hypothetically perfect positive feedback resistance compensation. Then, in the Laplace plane, this characteristic dimensionless current-time response is:

$\bar{\psi} \xrightarrow[\beta_u \to 0]{s\to\infty} \frac{1}{s\sqrt{s}}$ i.e., in the original place $\psi \xrightarrow[\beta_u \to 0]{s\to\infty} \frac{2}{\sqrt{\pi}}\sqrt{\tau}$

***Determination of A and B*** **,** i.e. of a $z(s)=\frac{(\bar{\varphi}_B-\bar{\varphi}_P)(1,\mathrm{s})}{\bar{\psi}}$

Determination of $A$ and $B$ as a function of $\bar{\psi}(s)$ from equations (1S''') and (2S'''):

$$\frac{\partial\bar{\varphi}_B}{\partial y}=0,\ \frac{\partial\bar{\varphi}_P}{\partial y}+\bar{\psi}_P=0$$

$$\frac{\partial\left(\bar{\varphi}_B-\bar{\varphi}_P\right)}{\partial y}-\bar{\psi}_P=0$$

We already know from equation (5S''') that:

$$\bar{\varphi}_B-\bar{\varphi}_P=A\exp\left(y\sqrt{s}\right)+B\exp\left(-y\sqrt{s}\right)$$

It follows that:

$$\sqrt{s}\left(A\exp\left(y\sqrt{s}\right)-B\exp\left(-y\sqrt{s}\right)\right)-\bar{\psi}_P=0$$

This equation is applied at each film boundaries:

$$y=0:\sqrt{s}\left(A-B\right)=0,$$

$$y=1:\sqrt{s}\left(A\exp\left(\sqrt{s}\right)-B\exp\left(-\sqrt{s}\right)\right)-\bar{\psi}=0$$

from which:

$$A=B=-\frac{\bar{\psi}}{\sqrt{s}}\frac{1}{\exp\left(-\sqrt{s}\right)-\exp\left(\sqrt{s}\right)} \qquad \text{(13S''')}$$

The next step consists in the derivation of $\bar{\varphi}_B\left(0,\mathrm{s}\right)-\bar{\varphi}_P\left(0,\mathrm{s}\right)$ as a function of $A$ and $B$ so to obtain $z(s)$ according to equation (11S''').

We have:

$$\bar{\varphi}_B\left(1,s\right)-\bar{\varphi}_B\left(0,s\right)=0$$

We also have: $\bar{\psi}_P\left(y\right)=\sqrt{s}\left[A\exp\left(y\sqrt{s}\right)-B\exp\left(-y\sqrt{s}\right)\right]$

$$\frac{\partial\bar{\varphi}_P}{\partial y}+\bar{\psi}_P=0,$$

$$\frac{\partial\bar{\varphi}_P}{\partial y}=-\bar{\psi}_P\left\{\sqrt{s}\left[A\exp\left(y\sqrt{s}\right)-B\exp\left(-y\sqrt{s}\right)\right]\right\}$$

$$[\bar{\varphi}_P]_0^1=-\bar{\psi}_P\left\{\left[A\exp\left(y\sqrt{s}\right)+B\exp\left(-y\sqrt{s}\right)\right]_0^1\right\}$$

$$\bar{\varphi}_P\left(1,\mathrm{s}\right)-\bar{\varphi}_P\left(0,s\right)=-\frac{\left(r_P/r_B\right)}{1+\left(r_P/r_B\right)}\left\{\left[A\exp\left(\sqrt{s}\right)+B\exp\left(-\sqrt{s}\right)-\left(A+B\right)\right]\right\}$$

We are looking now for an expression of the potential difference $\bar{\varphi}_B\left(0,s\right)-\bar{\varphi}_P\left(1,s\right)$ in the dimensionless Laplace space that is going to serve in the expression of the dimensionless Laplace impedance of equation (8S'''). We have::

$$\bar{\varphi}_B\left(0,s\right)-\bar{\varphi}_P\left(1,s\right)=\bar{\varphi}_B\left(0,s\right)-\bar{\varphi}_P\left(0,s\right)+\bar{\varphi}_P\left(0,s\right)-\bar{\varphi}_P\left(1,s\right)$$

Recalling that:

$$\bar{\varphi}_B(1,s)-\bar{\varphi}_B(0,s)=0$$

$$\bar{\varphi}_P(1,\mathrm{s})-\bar{\varphi}_P(0,s)=-\left\{\left[A\exp\left(\sqrt{s}\right)+B\exp\left(-\sqrt{s}\right)-(A+B)\right]\right\}$$

$$\bar{\varphi}_B(0,s)-\bar{\varphi}_P(0,s)=A+B$$

$$\bar{\varphi}_B(1,s)-\bar{\varphi}_P(1,s)=A\exp\left(\sqrt{s}\right)+B\exp\left(-\sqrt{s}\right)$$

It follows that:

$$\bar{\varphi}_B(0,s)-\bar{\varphi}_P(1,s)=\bar{\varphi}_B(0,s)-\bar{\varphi}_P(0,s)+\bar{\varphi}_P(0,s)-\bar{\varphi}_P(1,s),$$

$$\bar{\varphi}_B(0,s)-\bar{\varphi}_P(1,s)=A+B+\left\{\left[A\exp\left(\sqrt{s}\right)+B\exp\left(-\sqrt{s}\right)-(A+B)\right]\right\}$$

taking into account that:

$$A=B=-\frac{\bar{\psi}}{\sqrt{s}}\frac{1}{\exp\left(-\sqrt{s}\right)-\exp\left(\sqrt{s}\right)}$$

$$\bar{\varphi}_B(0,s)-\bar{\varphi}_P(1,s)=A\exp\left(\sqrt{s}\right)+B\exp\left(-\sqrt{s}\right).$$

Finally: $\dfrac{\bar{\varphi}_B(0,s)-\bar{\varphi}_P(1,s)}{\bar{\psi}}=z(s)=\dfrac{1}{\sqrt{s}}\dfrac{1}{\tanh\left(\sqrt{s}\right)}$

**Finite difference resolution**

The dimensionless film thickness is divided into $l$ intervals: $1=l\times\Delta y$ and thus $y=m\times\Delta y$ with $m=0,1,....,l$. The dimensionless time is divided into $n$ intervals: $\tau_f=n\times\Delta\tau$ and thus $\tau=j\times\Delta\tau$ with $j=0,1,....,n$. Equations (1S') to (4S') then become:

$$\varphi_B^{m,j}=\varphi_B^{m-1,j} \qquad \text{(1S'')}$$

$$\varphi_P^{m,j}=\varphi_P^{m-1,j}-\Delta y\times\psi_P^{m,j} \qquad \text{(2S'')}$$

$$\psi_B^{m,j}-\psi_B^{m-1,j}+\frac{\Delta y}{\Delta\tau}\left[\left(\varphi_B^{m,j}-\varphi_P^{m,j}\right)-\left(\varphi_B^{m,j-1}-\varphi_P^{m,j-1}\right)\right]=0 \qquad \text{(3S'')}$$

$$\psi_B^{m,j}-\psi_B^{m-1,j}=-\left(\psi_P^{m,j}-\psi_P^{m-1,j}\right) \qquad \text{(4S'')}$$

At each $j$, $4l+4$ variables: for $m=0$ to $l$, $\psi_B^{m,j}$, $\psi_P^{m,j}$, $\varphi_B^{m,j}$, $\varphi_P^{m,j}$ and the previous values (at $j$-1) are related $4l+4$ equations thus leading to the following matrix equation:

$$
\begin{pmatrix}
1\ 0\ \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots 0 \\
0\ 0\ 0\ 1\ \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots 0 \\
\dots\dots \\
0\dots\dots\dots -1\ 0\ 0\ 0\ 1\ 0\ 0\ 0\dots\dots\dots 0 \\
0\dots\dots\dots 0\ -1\ 0\ 0\ 0\ 1\ 0\ \Delta y\ \dots\dots\dots 0 \\
0\dots\dots\dots 0\ 0\ -1\ 0\ \dfrac{\Delta y}{\Delta\tau}\ -\dfrac{\Delta y}{\Delta\tau}\ 1\ 0\ \dots\dots\dots 0 \\
0\dots\dots\dots 0\ 0\ 0\ -1\ -\dfrac{\Delta y}{\Delta\tau}\ \dfrac{\Delta y}{\Delta\tau}\ 0\ 1\ \dots\dots\dots 0 \\
\dots\dots \\
0\dots\dots\dots\dots\dots\dots\dots\dots\dots 0\ 0\ \psi_B^{l,j}\ 0 \\
0\dots\dots\dots\dots\dots\dots\dots\dots\dots 0\ 1\ 0\ -\beta_u
\end{pmatrix}
\times
\begin{pmatrix}
\begin{Bmatrix} \varphi_B^{0,j} \\ \varphi_P^{0,j} \\ \psi_B^{0,j} \\ \psi_P^{0,j} \end{Bmatrix} \\
\begin{Bmatrix} \varphi_B^{k,j} \\ \varphi_P^{k,j} \\ \psi_B^{k,j} \\ \psi_P^{k,j} \end{Bmatrix} (k=1 \text{ to } l-1) \\
\begin{Bmatrix} \varphi_B^{l,j} \\ \varphi_P^{l,j} \\ \psi_B^{l,j} \\ \psi_P^{l,j} \end{Bmatrix}
\end{pmatrix}
=
\begin{pmatrix}
\begin{Bmatrix} \tau \\ 0 \end{Bmatrix} \text{ 2 lines (lines \# 1 and 2)} \\
\left.\begin{Bmatrix} 0 \\ 0 \\ \dfrac{\Delta y}{\Delta\tau}\left(\varphi_B^{m,j-1}-\varphi_P^{m,j-1}\right) \\ -\dfrac{\Delta y}{\Delta\tau}\left(\varphi_B^{m,j-1}-\varphi_P^{m,j-1}\right) \end{Bmatrix}\right\} \begin{matrix} 4l \text{ lines } (m=1 \text{ to } l) \\ \text{(lines \# 3} \\ \text{to } 4l+2) \end{matrix} \\
\begin{Bmatrix} 0 \\ 0 \end{Bmatrix} \begin{matrix} \text{2 lines} \\ \text{(lines \# } 4l+3 \text{ and } 4l+4) \end{matrix}
\end{pmatrix}
$$

Inversion of the square matrix provides the values of $\psi$ we are looking for.

**4. Cyclic voltammograms for a transmission line with a series resistance:**

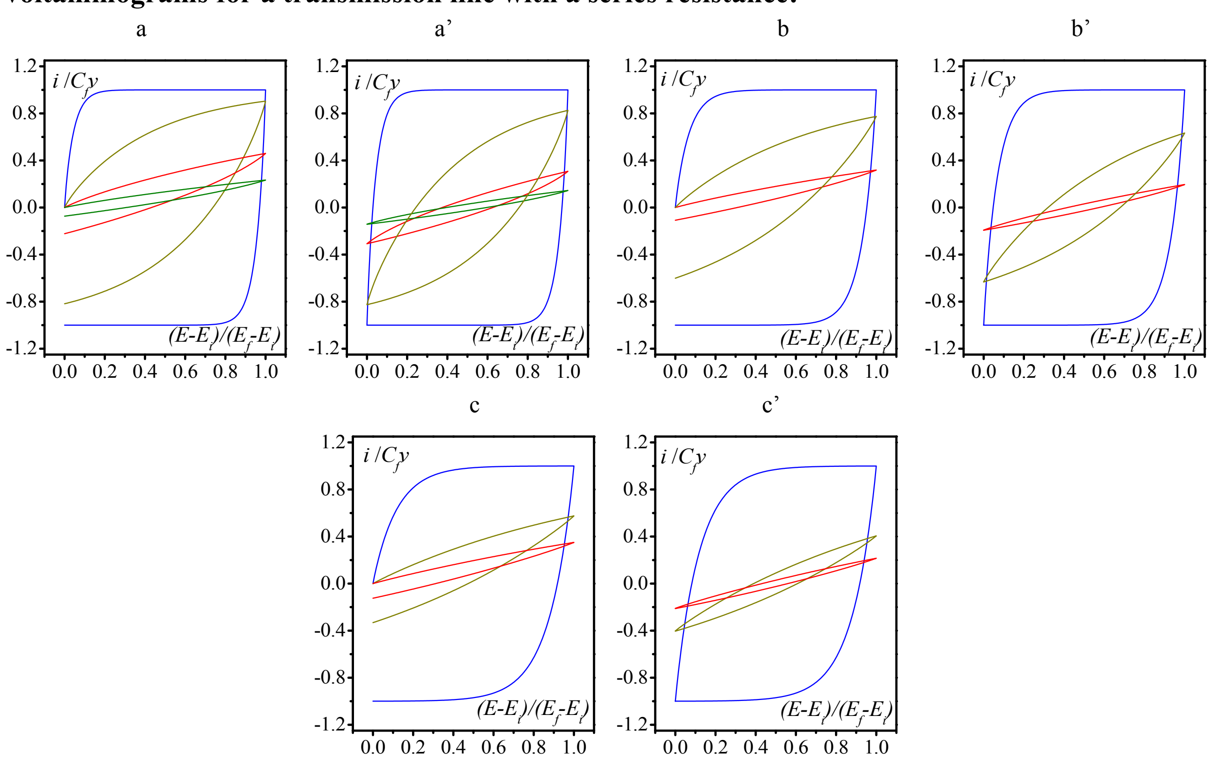

Fig.S3. Variation of the dimensionless current function with the dimensionless potential $\left(E-E_i\right)/\left(E_f-E_i\right)$ using the transmission line model with $\beta_u = 0.5$ (a, a'), 1 (b, b'), 2 (c, c'). (a, a') $t_f / t_v = v / v_0 =$ 0.05 (blue); 0.5 (dark yellow), 2 (red), 5 (green). (b, b') $t_f / t_v = v / v_0 =$ 0.05 (blue); 0.5 (dark yellow), 2 (red). (c, c') $t_f / t_v = v / v_0 =$ 0.05 (blue); 0.5 (dark yellow), 1 (red). Curves on (a), (b), (c) correspond to the first scan and curves on (a'), (b'), (c') correspond the steady-state cycle.

**Reference**


1. Savéant, J-M. Elements of Molecular and Biomolecular Electrochemistry. Wiley, 2006, p14.