Supporting Information

Conductive Mesoporous Catalytic Films. Current Distortion and Performance Degradation by Dual-Phase Ohmic Drop Effects. Analysis and Remedies.

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Experimental Details

Electrochemical measurements

The potentiostat used for linear scan voltammetry was a home-build potentiostat equipped with positive feedback for ohmic drop compensation.[1] The working electrode was polished and cleaned glassy carbon surface of a rotating disk electrode (5 mm diameter, Pine Research Intrumentation). The counter–electrode was a platinum wire and the reference electrode an aqueous calomel electrode. All experiments were carried out under argon at 20 °C. The electrolyte solutions were prepared from KNO_3 (Sigma-Aldrich, ≥ 99 %) or HNO_3 (Prolabo) with deionized water (0.06 µS at room temperature).

Electrode preparation

From a mixture of carbon Vulcan XC72R (Cabot), Nafion (250 µL, perfluorosulfonic acid-PTFE copolymer, 5% w/w solution, Alfa Aesar) and water (250 µL, deionized water, 0.06 µS at room temperature) sonicated for 10 minutes, 8.8 µL of this suspension were deposited on the electrode surface, which was then dried in air for 15 min and left for 30 min at 100 °C in an oven to form a homogeneous thin film.

Microscopy

SEM images were obtained with a Zeiss Supra 40 scanning electron microscope. The images were taken at different magnifications using an In lens detector at a low voltage (5 kV) and in a small working distance (5 mm). After the electrochemical measurements the electrode was rinsed twice in deionized water to remove residual acid traces and plunged into a three-electrode cell using Pt as counter electrode, SCE as reference electrode and a 0.1 M solution of KNO_3 as electrolyte. A positive feedback iR overcompensation was applied to generate a few hydrogen bubbles on the electrode surface and detach the catalytic film. The thin film was included in an epoxy resin (Spurr) and then aged at 60 °C for 2 days. The resin was then cut with a microtome (Reichert Jung) with a diamond knive and the SEM images have been obtained directly on the surface of the cut resin after metallation (3 nm of platinum using cathodic arc deposition).

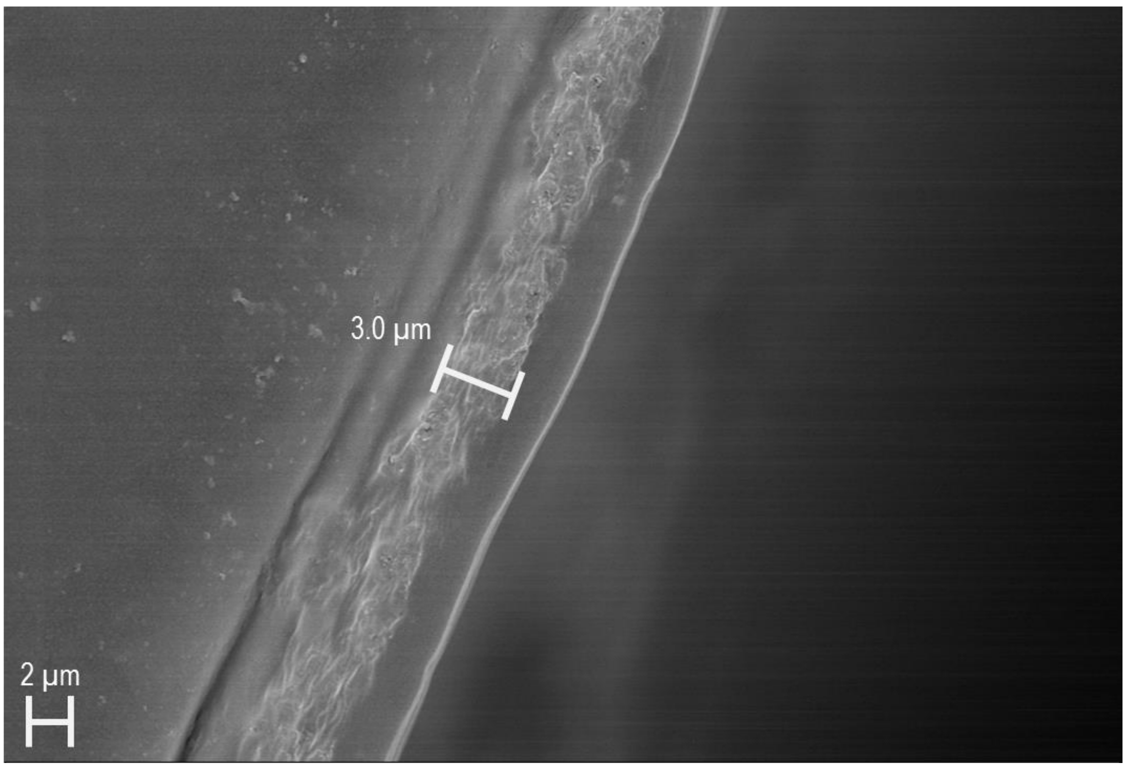

Fig 1S. SEM image of the thin film embedded in the epoxy resin.

Correction of experimental data

A linear drift of the plateau capacitive current is observed on each measurement (this linear drift is also observed on the freshly polihed glassy carbon electrode without deposited film and it is observed whatever the range of potential accessible without contribution of a significant faradaic current). Therefore, experimental data have been corrected by substration of an affine contribution as shown on figure 2S as an example so as to obtain an horizontal plateau.

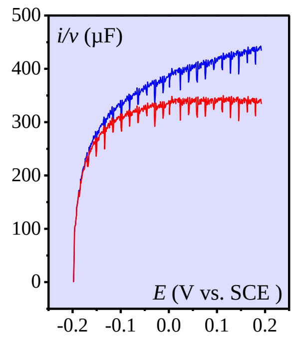

Fig 2S. Linear sweep voltammograms of a 5 mg Vulcan®+Nafion® film on a 5 mm diameter glassy carbon electrode from -0.2 to 0.2 V vs. SCE in presence of 0.1 M KNO_3. v = 20 V/s. blue: raw data. red: corrected data.

Determination of *L* using a dummy cell

L is a self-inductance related to the instrument bandpass characteristics. [1S] It has been evaluated using a dummy cell (Autolab Dummy Cell 2) corresponding to a RC circuit with C = 1 µF and R = 100 Ω. Charging currents are recorded with the home-build potentiostat using the same gain as the one used for the experiments. Ohmic drop compensation was achieved with the positive feedback device of the potentiostat up to observation of damped oscillations (figure 3S). This situation corresponds to 98% compensation. The oscillations frequency, $\omega = \frac{2\pi}{T}$, was measured leading to the self-inductance : $L = \frac{1}{C\omega^2}$ = 1.66 10^{-5} H.

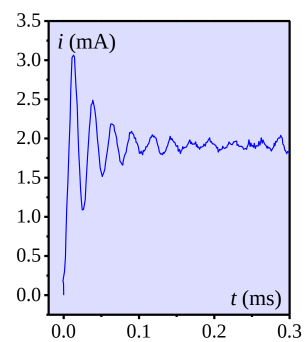

Fig. 3S. Linear scan voltammetry on a dummy cell (C = 1 µF and R = 100 Ω.) at 2000 V/s with 98% ohmic drop compensation.

Derivations and Relationships

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.

k_{cat} : first-order catalytic rate constant.

r_B, r_P : distributed resistances of the bulk of the film and pores per unit of thickness of the film and for unit of surface area of the electrode, respectively.

($r_B = \gamma_B \rho_B, r_P = \gamma_P \rho_P$, with $\gamma_B + \gamma_P = 1$)

$t_f = {d_f}^2 (r_B + r_P) c$: film time constant.

x: distance from the (planar) base electrode.

$C_f = Scd_f$: film capacitance.

E^0 : standard potential of the catalyst couple.

F: Faraday.

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

$I_F^0 = \dfrac{F \Gamma^0 k_{cat}}{d_f} \exp\left(\mp F \dfrac{E^0}{RT} \right)$: catalytic current density at $E = 0$.

L: instrument equivalent self-inductance.

R: perfect gas constant

$R_f = d_f (\rho_B + \rho_P) / S$: film resistance

R_u^{max} : maximal absolute value of the positive feedback compensable resistance.

R_u: resistance between the working and reference electrodes that remains uncompensated by the positive feedback compensation device.

R_S: solution resistance.

S: surface area of the base electrode.

T: absolute temperature.

v: scan rate

γ_B and γ_P: fractions of the base electrode surface that are covered by the bulk of the film and the pores, respectively ($\gamma_B + \gamma_P = 1$).

ρ_P, ρ_B: resistivities of the pores and the bulk, respectively.

Γ^0: total surface concentration of catalyst.

$\phi_{WE,\ RE,\ B\ and\ P}$: 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

$$y = \frac{x}{d_f}$$

$$\beta_u = \frac{SR_u}{d_f\,(\rho_B + \rho_P)}\ ,\ \beta_u^{max} = \frac{SR_u^{max}}{d_f\,(r_B + r_P)}$$

$$\lambda = (F\,/\,RT)\,d_f\,(r_P + r_B)\,I_F^0$$

$$\sigma = \frac{SL}{d_f{}^3\,(r_B + r_P)^2\,c}$$

$$\tau = \frac{t}{t_f}$$

$$\varphi_B = \frac{\phi_B}{d_f{}^2 cv(r_B + r_P)}, \varphi_P = \frac{\phi_P}{d_f{}^2 cv(r_B + r_P)}$$

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

1. Predicted cyclic voltammetric behavior in the absence of faradaic reactions

1.1 Recalling the model

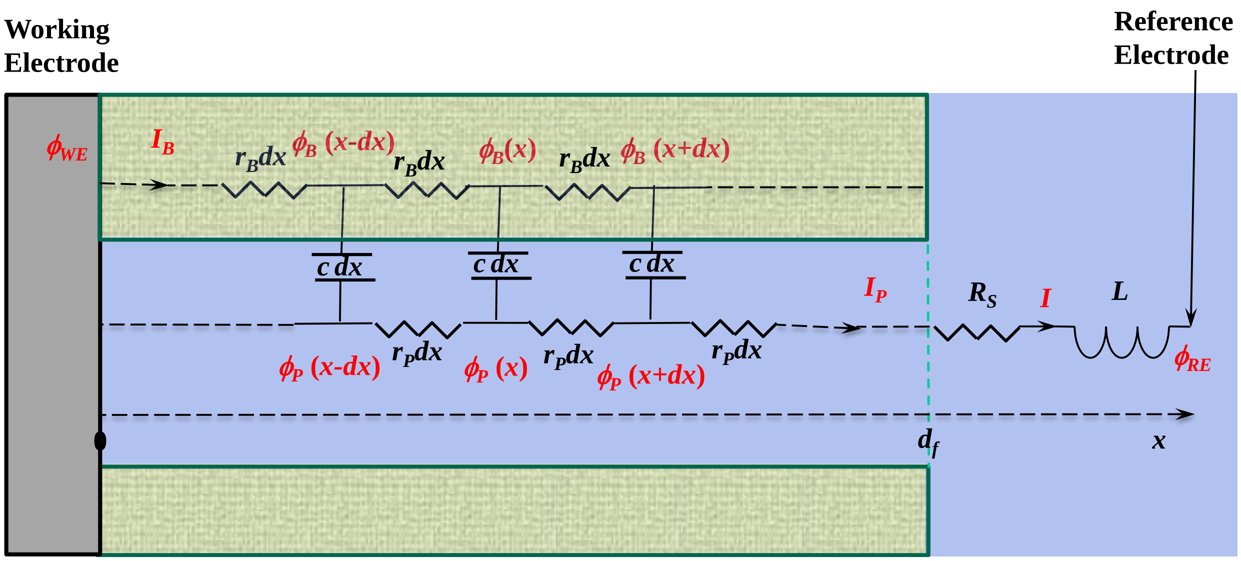

Fig. 4S. Schematic representation of the mesoporous films. The pores and the solution are in blue and the solid parts are in green. In red: potentials ($\phi_{WE,\ RE,\ B\ and\ P}$: potential at the working electrode, the reference electrode, in the bulk solid parts of the film and in the pores, respectively) and current densities (currents per working electrode unit surface area), $I_{B,}$ $I_{P,}$ and I in solid parts of the film, pores and solution, respectively. In black, the resistance and capacitance parameters of the equivalent transmission line: $r_{B\ and\ P}$: distributed resistances of the bulk of the film and pores per unit of thickness of the film and for unit of surface area of the electrode, respectively. 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. R_S is the solution resistance between the working and reference electrodes. L is a self-inductance related to the instrument bandpass characteristics.

1.2. Governing equations

We are looking for the time-dependence of the current density when the potential difference between the working and reference electrode is varied linearly, recalling that the potential across the film

$\phi_B(0,t)-\phi_P\left(d_f,t\right)$ is related to the potential difference between working electrode and reference electrode, $\phi_{WE}-\phi_{RE}$ according to:

$$\phi_B(0,t)=\phi_{WE} \text{ and } \phi_P\left(x=d_f,t\right)=\phi_{RE}+SR_u I(t)+SL\frac{dI(t)}{dt}$$

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 at the risk of perturbing oscillations depending of the band pass performances of the instrument (represented by the self-inductance L). R_u may even become negative depending on the dual-phase ohmic drop situation in the film.

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 ($x=d_f$).

Ohmic drop in the solid parts of the film: $\frac{\partial \phi_B}{\partial x}+r_B I_B=0$ (1S)

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

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

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

Initial conditions:

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

Boundary conditions:

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

$x=d_f: \phi_P\left(d_f,t\right)-\phi_{RE}=R_u i+L\frac{di}{dt}=\left(SR_u\right)I+(SL)\frac{dI}{dt}$, $\frac{\partial \phi_B}{\partial x}\left(d_f,t\right)=0$, $I_B\left(d_f,t\right)=0$, $I_P\left(d_f,t\right)=I$

(S is the electrode surface area).

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:

$$\phi_B(0,t) - \phi_p\left(d_f, t\right) = \phi_{WE} - \phi_{RE} - (SR_u)I - (SL)\frac{dI}{dt} = E_i + vt - (SR_u)I - (SL)\frac{dI}{dt}$$

and therefore:

$$\frac{\partial\left[\phi_B(0,t) - \phi_p\left(d_f, t\right)\right]}{\partial t} + (SR_u)\frac{\partial I}{\partial t} + (SL)\frac{\partial^2 I}{\partial t^2} = \frac{d\left(\phi_{WE} - \phi_{RE}\right)}{dt} = v \qquad \text{(5S)}$$

1.3. 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 $t_f = d_f{}^2\left(r_B + r_P\right)c$ is the time constant of the film.

Potentials: $\varphi_B = \frac{\phi_B}{d_f{}^2 cv\left(r_B + r_P\right)}, \varphi_P = \frac{\phi_P}{d_f{}^2 cv\left(r_B + r_P\right)}$

Currents densities:

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

Uncompensated solution resistance: $\beta_u = \frac{SR_u}{d_f\left(r_B + r_P\right)}$

Instrument bandpass characteristic: $\sigma = \frac{SL}{d_f{}^3\left(r_B + r_P\right)^2 c}$

Thus, in dimensionless terms:

$$\frac{\partial\varphi_B}{\partial y} + \frac{\left(r_B / r_P\right)}{1 + \left(r_B / r_P\right)}\psi_B = 0 \qquad \text{(1'S)}$$

$$\frac{\partial\varphi_P}{\partial y} + \frac{\left(r_P / r_B\right)}{1 + \left(r_P / r_B\right)}\psi_P = 0 \qquad \text{(2'S)}$$

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

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

Initial conditions:

$$\tau = 0 : \varphi_P(y,0) = \varphi_{RE} \,,\; \varphi_B(y,0) = \varphi_{WE} \,,\; \psi_B(y,0) = \psi_P(y,0) = \psi(0) = 0$$

Boundary conditions:

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

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

Potential scanning (from (5S)): $\frac{\partial\left[\varphi_B(0,\tau) - \varphi_P(1,\tau)\right]}{\partial \tau} + \beta_u \frac{\partial \psi}{\partial \tau} + \sigma \frac{\partial^2 \psi}{\partial t^2} = 1$

It follows that, in dimensionless terms, the system depends on only three dimensionless parameters, *viz*. r_B / r_P, β_u and σ.

1.4. 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:

$$\varphi_B^{m,j} = \varphi_B^{m-1,j} - \Delta y \frac{1}{1 + r_P / r_B} \psi_B^{m,j} \qquad \text{(1S'')}$$

$$\varphi_P^{m,j} = \varphi_P^{m-1,j} - \Delta y \frac{1}{1 + r_B / r_P} \psi_P^{m,j} \qquad \text{(2S'')}$$

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

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

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

$$
\begin{pmatrix}
1\ 0\ \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 0 \\
0\ 0\ 0\ 1\ \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 0 \\
\ldots\ldots \\
0\ldots\ldots\text{-}1\ 0\ 0\ 0\ 1\ 0\ \Delta y \dfrac{1}{1+r_P/r_B}\ 0\ldots\ldots 0 \\
0\ldots\ldots 0\ \text{-}1\ 0\ 0\ 0\ 1\ 0\ \Delta y \dfrac{1}{1+r_B/r_P}\ \ldots\ldots 0 \\
0\ldots\ldots 0\ 0\ \text{-}1\ 0\ \dfrac{\Delta y}{\Delta\tau}\ \text{-}\dfrac{\Delta y}{\Delta\tau}\ 1\ 0\ \ldots\ldots 0 \\
0\ldots\ldots 0\ 0\ 0\ \text{-}1\ \text{-}\dfrac{\Delta y}{\Delta\tau}\ \dfrac{\Delta y}{\Delta\tau}\ 0\ 1\ \ldots\ldots 0 \\
\ldots\ldots \\
0\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 0\ 0\ \psi_B^{l,j}\ 0 \\
0\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 0\ 1\ 0\ \text{-}\left(\beta_u+\dfrac{\sigma}{\Delta\tau}\right)
\end{pmatrix}
\times
\begin{pmatrix}
\begin{Bmatrix} \varphi_B^{0,j} \\ \varphi_P^{0,j} \\ \psi_B^{0,j} \\ \psi_P^{0,j} \end{Bmatrix} \\[2ex]
\begin{Bmatrix} \varphi_B^{k,j} \\ \varphi_P^{k,j} \\ \psi_B^{k,j} \\ \psi_P^{k,j} \end{Bmatrix} \text{(}k\text{=1 to }l\text{ - 1)} \\[2ex]
\begin{Bmatrix} \varphi_B^{l,j} \\ \varphi_P^{l,j} \\ \psi_B^{l,j} \\ \psi_P^{l,j} \end{Bmatrix}
\end{pmatrix}
=
\begin{pmatrix}
\begin{Bmatrix} \tau \\ 0 \end{Bmatrix} \text{ 2 lines (lines \# 1 and 2)} \\[2ex]
\begin{Bmatrix} 0 \\ 0 \\ \dfrac{\Delta y}{\Delta\tau}\left(\varphi_B^{m,j-1}-\varphi_P^{m,j-1}\right) \\ -\dfrac{\Delta y}{\Delta\tau}\left(\varphi_B^{m,j-1}-\varphi_P^{m,j-1}\right) \end{Bmatrix} \begin{array}{c} 4l \text{ lines (}m\text{=1 to l)} \\ \text{(lines \# 3} \\ \text{to } 4l+2\text{)} \end{array} \\[2ex]
\begin{Bmatrix} 0 \\ -\dfrac{\sigma}{\Delta\tau}\psi_P^{l,j-1} \end{Bmatrix} \begin{array}{c} \text{2 lines} \\ \text{(lines \# } 4l\text{+3 and } 4l+4\text{)} \end{array}
\end{pmatrix}
$$

Inversion of the square matrix provides the values of ψ we are looking for.

1.5. Laplace Transform approach

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:

$\bar{f}(s)=\int_0^\infty f(\tau)\exp(-s\tau)\,d\tau$, where s is the Laplace variable corresponding to the dimensionless time variable τ. 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') – (4S') equations thus become (1S''') – (4S''') in the Laplace space.

$$\frac{\partial\bar{\varphi}_B}{\partial y}+\frac{\bar{\psi}_B}{1+\left(r_P/r_B\right)}=0 \qquad \text{(1S''')}$$

$$\frac{\partial\bar{\varphi}_P}{\partial y}+\frac{\left(r_P/r_B\right)\bar{\psi}_P}{1+\left(r_P/r_B\right)}=0 \qquad \text{(2S''')}$$

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

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

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

$$\frac{\partial^2 \bar{\varphi}_B}{\partial y^2} + \frac{1}{1+\left(r_P / r_B\right)} \frac{\partial \bar{\psi}_B}{\partial y} = 0, \text{ and from (3S'''): } \frac{\partial^2 \bar{\varphi}_B}{\partial y^2} - \frac{1}{1+\left(r_P / r_B\right)} s\left(\bar{\varphi}_B - \bar{\varphi}_P\right) = 0$$

$$\frac{\partial^2 \bar{\varphi}_P}{\partial y^2} + \frac{r_P / r_B}{1+\left(r_P / r_B\right)} \frac{\partial \bar{\psi}_P}{\partial y} = 0 \text{, and from (2S'''): } \frac{\partial^2 \bar{\varphi}_P}{\partial y^2} + \frac{r_P / r_B}{1+\left(r_P / r_B\right)} s\left(\bar{\varphi}_B - \bar{\varphi}_P\right) = 0$$

leading by subtraction to:

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

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

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

and thus, in particular, to:

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

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

We are looking for the dimensionless current-time response:

$$\frac{\partial\left[\varphi_B(0,\tau) - \varphi_P(1,\tau)\right]}{\partial \tau} + \beta_u \frac{\partial \psi}{\partial \tau} + \sigma \frac{\partial^2 \psi}{\partial t^2} = 1 \qquad \text{(9S''')}$$

In the Laplace space:

$$s\left[\bar{\varphi}_B(0,\mathrm{s}) - \bar{\varphi}_P(0,\mathrm{s})\right] + s\beta_u \bar{\psi} + s^2 \sigma \bar{\psi} = \frac{1}{s}$$

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

after introduction of the Laplace dimensionless impedance of the film

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

This is not a Laplace transform, of any function of τ, 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 in the Appendix.

$$z(s)=\frac{(r_P/r_B)}{\left[1+(r_P/r_B)\right]^2}+\frac{2(r_P/r_B)}{\left[1+(r_P/r_B)\right]^2}\frac{1}{\sqrt{s}\sinh\left(\sqrt{s}\right)}+\frac{1+(r_P/r_B)^2}{\left[1+(r_P/r_B)\right]^2}\frac{1}{\sqrt{s}}\frac{\cosh\left(\sqrt{s}\right)}{\sinh\left(\sqrt{s}\right)}$$

or: $$z(s)=\frac{r_B r_P}{(r_B+r_P)^2}+\frac{2r_B r_P}{(r_B+r_P)^2}\frac{1}{\sqrt{s}\sinh\left(\sqrt{s}\right)}+\frac{r_B^2+r_P^2}{(r_B+r_P)^2}\frac{1}{\sqrt{s}}\frac{\cosh\left(\sqrt{s}\right)}{\sinh\left(\sqrt{s}\right)},$$

showing that the dimensionless Laplace impedance and the ensuing dimensionless current response, are

$$\bar{\psi}=\frac{1}{s\left\{s\left[\frac{r_B r_P}{(r_B+r_P)^2}+\frac{2r_B r_P}{(r_B+r_P)^2}\frac{1}{\sqrt{s}\sinh\left(\sqrt{s}\right)}+\frac{r_B^2+r_P^2}{(r_B+r_P)^2}\frac{1}{\sqrt{s}}\frac{\cosh\left(\sqrt{s}\right)}{\sinh\left(\sqrt{s}\right)}+\beta_u\right]+s^2\sigma\right\}}$$

perfectly symmetrical toward r_B and r_P.

The following limiting situations of interest are reached when:

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

since, $\sinh\left(\sqrt{s}\right)\xrightarrow{s\to 0}\sqrt{s}$ and $\frac{\cosh\left(\sqrt{s}\right)}{\sinh\left(\sqrt{s}\right)}\xrightarrow{s\to 0}\frac{1}{\sqrt{s}}$:

$z(s)\xrightarrow{s\to 0}\frac{1}{s}$, and therefore:

$$\bar{\psi}\xrightarrow{s\to 0}\frac{1}{s}$$

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:

$$z(s) \xrightarrow{s\to\infty} \frac{r_B r_P}{(r_B+r_P)^2} + \frac{r_B{}^2 + r_P{}^2}{(r_B+r_P)^2}\frac{1}{\sqrt{s}} \xrightarrow{s\to\infty} \frac{2r_B r_P}{(r_B+r_P)^2}$$

The Laplace dimensionless current then becomes:

$$\bar{\psi} = \frac{1}{s\left\{s\left[z(s)+\beta_u\right]+s^2\sigma\right\}} \xrightarrow{s\to\infty} \frac{1}{s\left\{s\left[\frac{r_B r_P}{(r_B+r_P)^2} + \frac{r_B{}^2 + r_P{}^2}{(r_B+r_P)^2}\frac{1}{\sqrt{s}} + \beta_u\right] + s^2\sigma\right\}}$$

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:

$$\bar{\psi} \xrightarrow[\beta_u\to 0,\ \sigma\to 0]{s\to\infty} \frac{1}{s\left\{\left[\frac{r_B r_P}{(r_B+r_P)^2}s + \frac{r_B{}^2 + r_P{}^2}{(r_B+r_P)^2}\sqrt{s}\right]\right\}}$$

It is itself comprised between two limiting cases. One in which $r_B / r_P \to 0$ or vice-versa $r_P / r_B \to 0$ and the other in which $\rho_B / \rho_P \to 1$.

In the $r_B / r_P \to 0$ or $r_P / r_B \to 0$ case:

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

In the $r_B / r_P \to 1$ case:

$$\bar{\psi} \xrightarrow[\substack{\beta_u\to 0,\ \sigma\to 0 \\ r_B/r_P \text{ or } r_P/r_B\to 0}]{s\to\infty} \frac{1}{s\left(0.25s+0.5\sqrt{s}\right)}.$$

It follows that, in the original place, the tangent at the origin of the $\psi(\tau)$ is $\psi = 4\times\tau$.

1.6. Appendix

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

$$\frac{\partial\bar{\varphi}_B}{\partial y}+\frac{\bar{\psi}_B}{1+(r_P\,/\,\mathrm{r}_B)}=0,\frac{\partial\bar{\varphi}_P}{\partial y}+\frac{(r_P\,/\,r_B)\bar{\psi}_P}{1+(r_P\,/\,\mathrm{r}_B)}=0,$$

$$\frac{\partial(\bar{\varphi}_B-\bar{\varphi}_P)}{\partial y}+\frac{\bar{\psi}_B}{1+(r_P\,/\,\mathrm{r}_B)}-\frac{(r_P\,/\,r_B)\bar{\psi}_P}{1+(r_P\,/\,\mathrm{r}_B)}=0$$

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

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

$$\frac{\partial(\bar{\varphi}_B-\bar{\varphi}_P)}{\partial y}+\frac{\bar{\psi}_B}{1+(r_P\,/\,r_B)}-\frac{(r_P\,/\,r_B)\bar{\psi}_P}{1+(r_P\,/\,r_B)}=0$$

It follows that:

$$\sqrt{s}\left(A\exp\left(y\sqrt{s}\right)-B\exp\left(-y\sqrt{s}\right)\right)+\frac{\bar{\psi}_B}{1+(r_P\,/\,r_B)}-\frac{(r_P\,/\,r_B)\bar{\psi}_P}{1+(r_P\,/\,r_B)}=0$$

This equation is applied at each film boundaries:

$$y=0:\sqrt{s}\,(A-B)+\frac{\bar{\psi}}{1+(r_P\,/\,r_B)}=0,$$

$$y=1:\sqrt{s}\left(A\exp\left(\sqrt{s}\right)-B\exp\left(-\sqrt{s}\right)\right)-\frac{(r_P\,/\,r_B)\bar{\psi}}{1+(r_P\,/\,r_B)}=0$$

from which:

$$A=-\frac{\bar{\psi}}{\sqrt{s}}\frac{\dfrac{(r_P\,/\,r_B)}{1+(r_P\,/\,r_B)}+\dfrac{\exp\left(-\sqrt{s}\right)}{1+(r_P\,/\,r_B)}}{\exp\left(-\sqrt{s}\right)-\exp\left(\sqrt{s}\right)}\;,\;B=-\frac{\bar{\psi}}{\sqrt{s}}\frac{\dfrac{(r_P\,/\,r_B)}{1+(r_P\,/\,r_B)}+\dfrac{\exp\left(\sqrt{s}\right)}{1+(r_P\,/\,r_B)}}{\exp\left(-\sqrt{s}\right)-\exp\left(\sqrt{s}\right)} \qquad \text{(13S''')}$$

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

From (3S''') and (6S'''):

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

$$\bar{\psi}_B(y) = -\sqrt{s}\left[A\exp\left(y\sqrt{s}\right) - B\exp\left(-y\sqrt{s}\right)\right] + C$$

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

$$\bar{\psi}_B(y) = -\sqrt{s}\left[A\exp\left(y\sqrt{s}\right) - B\exp\left(-y\sqrt{s}\right)\right] + \sqrt{s}\left[A\exp\left(\sqrt{s}\right) - B\exp\left(-\sqrt{s}\right)\right]$$

$$\frac{\partial\bar{\varphi}_B}{\partial y} + \frac{\bar{\psi}_B}{1+\left(r_P / r_B\right)} = 0, \frac{\partial\bar{\varphi}_B}{\partial y} = -\frac{\bar{\psi}_B}{1+\left(r_P / r_B\right)}$$

$$\frac{\partial\bar{\varphi}_B}{\partial y} = \frac{\sqrt{s}}{1+\left(\rho_P / \rho_B\right)}\left\{\left[A\exp\left(y\sqrt{s}\right) - B\exp\left(-y\sqrt{s}\right)\right] - \left[A\exp\left(\sqrt{s}\right) - B\exp\left(-\sqrt{s}\right)\right]\right\} \quad \text{(14S''')}$$

Integration of equation (14S''') leads to:

$$\left[\bar{\varphi}_B\right]_0^1 = \frac{1}{1+\left(r_P / r_B\right)}\left[A\exp\left(y\sqrt{s}\right) + B\exp\left(-y\sqrt{s}\right)\right]_0^1 - \frac{\sqrt{s}}{1+\left(r_P / r_B\right)}\left[A\exp\left(\sqrt{s}\right) - B\exp\left(-\sqrt{s}\right)\right] \times \left[y\right]_0^1, \text{ i.e.:}$$

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

Similarly from:

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

$$\bar{\psi}_P(y) = \sqrt{s}\left[A\exp\left(y\sqrt{s}\right) - B\exp\left(-y\sqrt{s}\right)\right] + C',$$

$$\bar{\psi}_P(0) = \sqrt{s}\left[A - B\right] + C' = 0, C' = -\sqrt{s}\left[A - B\right]$$

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

$$\frac{\partial\bar{\varphi}_P}{\partial y} + \frac{\left(r_P / r_B\right)\bar{\psi}_P}{1+\left(r_P / r_B\right)} = 0, \frac{\partial\bar{\varphi}_P}{\partial y} = -\frac{\left(r_P / r_B\right)\bar{\psi}_P}{1+\left(r_P / r_B\right)}$$

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

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

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

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

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

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

Recalling that:

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

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

It follows that, according *e.g.* to the first option:

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

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

taking into account that:

$$A+B=\frac{\frac{\bar{\psi}}{\sqrt{s}}}{\exp\left(\sqrt{s}\right)-\exp\left(-\sqrt{s}\right)}\left[2\frac{(r_P/r_B)}{1+(r_P/r_B)}+\frac{\exp\left(\sqrt{s}\right)+\exp\left(-\sqrt{s}\right)}{1+(r_P/r_B)}\right]$$
$$A-B=-\frac{\bar{\psi}}{\sqrt{s}}\frac{1}{1+(r_P/r_B)}$$
$$A\exp\left(\sqrt{s}\right)+B\exp\left(-\sqrt{s}\right)=\frac{\frac{\bar{\psi}}{\sqrt{s}}}{\exp\left(\sqrt{s}\right)-\exp\left(-\sqrt{s}\right)}\left\{\frac{2}{1+(r_P/r_B)}+\frac{(r_P/r_B)}{1+(r_P/r_B)}\left[\exp\left(\sqrt{s}\right)+\exp\left(-\sqrt{s}\right)\right]\right\}$$

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

Finally: $\dfrac{\bar{\varphi}_B(0,s)-\bar{\varphi}_P(1,s)}{\bar{\psi}}=z(s)=\dfrac{2r_Pr_B}{(r_B+r_P)^2}+\dfrac{2r_Pr_B}{(r_B+r_P)^2}\dfrac{1}{\sqrt{s}\sinh\left(\sqrt{s}\right)}+\dfrac{r_B{}^2+r_P{}^2}{(r_B+r_P)^2}\dfrac{1}{\sqrt{s}}\dfrac{\cosh\left(\sqrt{s}\right)}{\sinh\left(\sqrt{s}\right)}$

2. Dual-phase ohmic drop effects in linear sweep voltammetric and prep-scale electrolysis on catalytic currents responses in Tafel conditions

2.1 Recalling the model

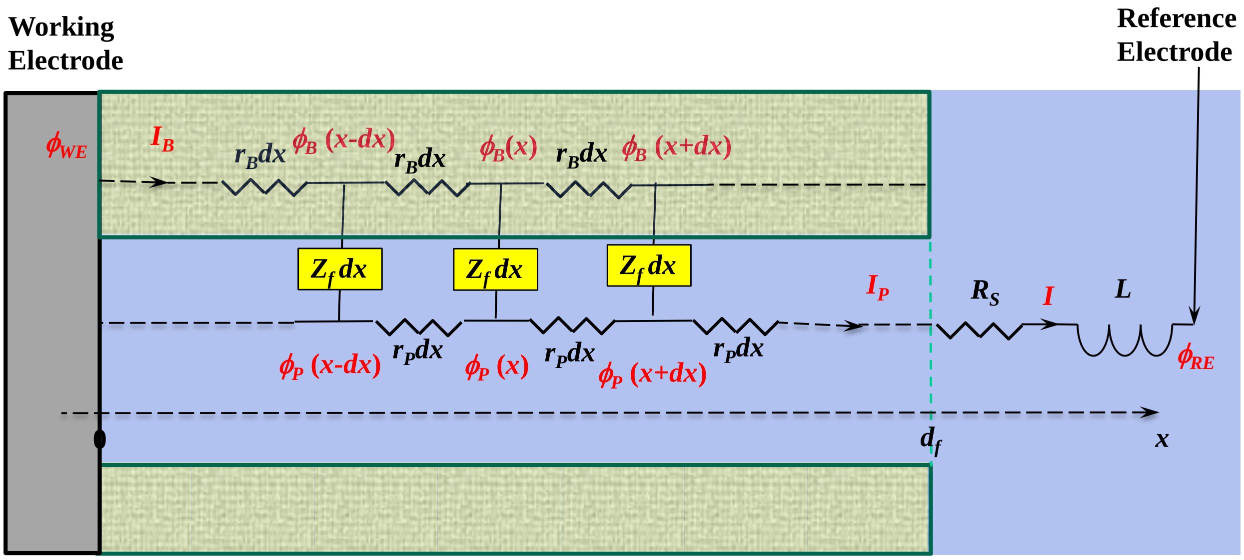

Fig. 5S. Schematic representation of the mesoporous films with a catalytic reaction represented by a the distributed faradaic impedance, Z_f . Same symbolism as in figure 4S.

2.2. Governing equations

Ohmic drop in the bulk of the film: $\dfrac{\partial \phi_B}{\partial x} + r_B I_B = 0$ (10S)

Ohmic drop in the pores: $\dfrac{\partial \phi_P}{\partial x} + r_P I_P = 0$ (11S)

Catalysis at the pore s' walls: $\dfrac{\partial I_P}{\partial x} = -\dfrac{\partial I_B}{\partial x} = \dfrac{F\Gamma^0 k_{cat}}{d_f} \exp\left(-F\dfrac{(\phi_B - \phi_P)^0}{RT}\right) \exp\left(F\dfrac{(\phi_B - \phi_P)}{RT}\right)$ (12S)

$= \dfrac{I_F^0}{d_f} \exp\left(F\dfrac{(\phi_B - \phi_P)}{RT}\right)$ with: $I_F^0 = F\Gamma^0 k_{cat} \exp\left(-F\dfrac{(\phi_B - \phi_P)^0}{RT}\right)$

Equation (12S) expresses a steady-state situation ($\partial(\phi_B - \phi_P)/\partial t = 0$) in which the capacitance is charged and the instrument is hypothetically perfect.

Conservation of fluxes throughout the system: $I_P(x,t) + I_B(x,t) = I(t)$ (13S)

Boundary conditions:

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

$$x = d_f: \phi_P(d_f) - \phi_{RE} = R_u i = (SR_u)I, \ \frac{\partial \phi_B}{\partial x}(d_f) = 0, \ I_B(d_f) = 0, \ I_P(d_f) = I$$

The potential difference $\phi_{WE} - \phi_{RE}$ is imposed by the instrument, and:

$$\phi_B(0) - \phi_p(d_f) = \phi_{WE} - \phi_{RE} - (SR_u)I$$

2.3. *Dimensionless formulation*

Because the discussion encompass here cases where there is no capacitive current (or where it is negligible) and because we focus on a faradaic catalytic current, the definition of the dimensionless current densities had to be changed:

$\psi_P^{cat} = \frac{I_P}{I_F^0}, \psi_B^{cat} = \frac{I_B}{I_F^0}, \psi^{cat} = \psi_B^{cat} + \psi_P^{cat} = \frac{I}{I_F^0}$ (but for the sake of simplicity, in the following we note $\psi_P^{cat} = \psi_P, \psi_B^{cat} = \psi_B, \psi^{cat} = \psi$)

and a new dimensionless parameter had to be introduced:

$$\lambda = \frac{F}{RT} d_f (r_P + r_B) I_F^0$$

defines the competition between two types of current-controlling factors, the catalytic reaction on the one hand and the effect of various resistances (or resistivities) on the other.

Thus:

$$\frac{\partial \varphi_B}{\partial y} + \frac{r_B}{r_P + r_B} \lambda \psi_B = 0 \quad (10S')$$

$$\frac{\partial \varphi_P}{\partial y} + \frac{r_P}{r_P + r_B} \lambda \psi_P = 0 \quad (11S')$$

$$\frac{\partial \psi_P}{\partial y} = -\frac{\partial \psi_B}{\partial y} = \exp(\varphi_B - \varphi_P) \quad (12S')$$

$$\psi_B(y) + \psi_P(y) = \psi \quad (13S')$$

Boundary conditions:

y=0: $\varphi_B(0) = \varphi_{WE}$, $\dfrac{\partial \varphi_P}{\partial y}(0) = 0$, $\psi_P(0) = 0$, $\psi_B(0) = \psi$

$y = 1$: $\dfrac{\partial \varphi_B}{\partial y}(1) = 0$, $\psi_B(1) = 0$, $\psi_P(1) = \psi$

Potential: $\varphi_B(0) - \varphi_p(1) = \dfrac{F(\phi_{WE} - \phi_{RE})}{RT} - \beta_u \lambda \psi$

The system thus depends upon three dimensionless parameters, which can be conveniently chosen as:

λ , r_P / r_B and β_u .

2.4. ***Semi-analytical resolution***

From (10S' – 12S'):

$$\frac{\partial^2 (\varphi_B - \varphi_P)}{\partial y^2} = \lambda \exp(\varphi_B - \varphi_P)$$

and after integration,

$$\frac{1}{2}\left[\frac{\partial(\varphi_B - \varphi_P)}{\partial y}\right]^2 = \lambda \exp(\varphi_B - \varphi_P) + A \qquad \text{(14S')}$$

$$\frac{1}{2}\left(\frac{\partial \varphi_B}{\partial y}\right)^2_{y=0} = \lambda \exp(\varphi_{B,0} - \varphi_{P,0}) + A \qquad \text{(15S')}$$

$$\frac{1}{2}\left(\frac{\partial \varphi_P}{\partial y}\right)^2_{y=1} = \lambda \exp(\varphi_{B,1} - \varphi_{P,1}) + A \qquad \text{(16S')}$$

It follows that:

$$\varphi_{B,0} - \varphi_{P,0} = \ln\left[\frac{\left(\dfrac{r_B}{r_P + r_B}\right)^2 \lambda^2 \psi^2 - 2A}{2\lambda}\right] \qquad \text{(17S')}$$

$$\varphi_{B,1} - \varphi_{P,1} = \ln\left[\frac{\left(\frac{r_P}{r_P + r_B}\right)^2 \lambda^2\psi^2 - 2A}{2\lambda}\right] \qquad (18S')$$

From (10S') and (11S'):

$$\frac{r_P + r_B}{r_B}\frac{\partial\varphi_B}{\partial y} + \frac{r_P + r_B}{r_P}\frac{\partial\varphi_P}{\partial y} + \lambda\psi = 0$$

By integration, taking the boundary conditions into account:

$$\frac{r_P + r_B}{r_B}\left(\varphi_{B,1} - \varphi_{B,0}\right) + \frac{r_P + r_B}{r_P}\left(\varphi_{P,1} - \varphi_{P,0}\right) = -\lambda\psi$$

To obtain the expression of the dimensionless catalytic current-potential response, it remains to introduce the potential difference between the working and the reference electrode as:

$$\varphi_{B,0} - \varphi_{p,1} = \frac{F\left(\phi_{WE} - \phi_{RE}\right)}{RT} - \lambda\beta_u\psi$$

Defining $E = \phi_{WE} - \phi_{RE}$ and using (17S') and (18S'):

$$\ln\left\{\left[\frac{\lambda^2\left(\frac{r_P}{r_P + r_B}\right)^2\psi^2 - 2A}{2\lambda}\right]^{\frac{r_P}{r_P+r_B}}\left[\frac{\lambda^2\left(\frac{r_B}{r_P + r_B}\right)^2\psi^2 - 2A}{2\lambda}\right]^{\frac{r_B}{r_P+r_B}}\right\} = \pm\frac{FE}{RT} - \lambda\beta_u\psi \qquad (19S')$$

(+ for oxidations, - for reductions)

A remains to be determined. We start from the variation of $\varphi_B - \varphi_P$ with the dimensionless distance, *y*, given by equation (14S'). We assume that, starting from the electrode surface, $\partial\left(\varphi_B - \varphi_P\right)/\partial y$ is first negative and changes sign at $y = y_{tr}$ $(0 < y_{tr} < 1)$ before reaching the film's end (in a second stage, the validity of these starting assumptions will be checked later on by *reductio ad absurdum*). Thus:

$$\int_{\varphi_{B,0}-\varphi_{P,0}}^{\varphi_{B,tr}-\varphi_{P,tr}} \frac{d\left(\varphi_B-\varphi_P\right)}{\sqrt{2\lambda\exp\left(\varphi_B-\varphi_P\right)+2A}} = -y_{tr} \text{ and:}$$

$$0=\lambda\exp\left(\varphi_{B,tr}-\varphi_{P,tr}\right)+A \quad \text{(showing that } A<0\text{)}$$

Integration, taking the latter equation into account leads to:

$$y_{tr}=\frac{2}{\sqrt{-2A}}\arctan\sqrt{\frac{\lambda\exp\left(\varphi_{B,0}-\varphi_{P,0}\right)+A}{-A}}$$

Taking into account that, from (17S'), $2\lambda\exp\left(\varphi_{B,0}-\varphi_{P,0}\right)+2A=\lambda\left(\frac{r_B}{r_B+r_P}\right)^2\psi^2$:

$$y_{tr}==\frac{2}{\sqrt{-2A}}\arctan\left[\sqrt{\frac{\lambda^2\left(\frac{\rho_B}{\rho_B+\rho_P}\right)^2\psi^2}{-2A}}\right]$$

Similarly:

$$1-y_{tr}=\frac{2}{\sqrt{-2A}}\arctan\left[\sqrt{\frac{\lambda^2\left(\frac{r_P}{r_B+r_P}\right)^2\psi^2}{-2A}}\right]$$

An implicit expression for A as a function of ψ,λ and r_P/r_B is finally obtained:

$$\sqrt{-\frac{A}{2}}=\arctan\left[\sqrt{\frac{\lambda^2\left(\frac{r_P}{r_B+r_P}\right)^2\psi^2}{-2A}}\right]+\arctan\left[\sqrt{\frac{\lambda^2\left(\frac{r_B}{r_B+r_P}\right)^2\psi^2}{-2A}}\right] \qquad \text{(20S')}$$

The dimensionless catalytic current-potential curve, $\psi\left(FE/RT\right)$, thus results from the elimination of A between equations (19S') and (20S') not leading to a close-form expression. Numerical resolution may thus be called for to obtain the $\psi(FE/RT)$ relationship. An alternative to this approach is to numerically resolve the problem by direct finite difference resolution of the derivative equation system as described in the next section. Before we come to this point, we may use equations (19S') and (20S') to obtain the asymptotic behavior of the $\psi(FE/RT)$ response when $E \to \pm\infty$ (for oxidations) or $E \to -\infty$ (for reductions)

In order to validate the assumption that that, starting from the electrode surface, $\partial(\varphi_B - \varphi_P)/\partial y$ is first negative, we make the assumption that $\partial(\varphi_B - \varphi_P)/\partial y$ is positive. We then obtain:

$$\int_{\varphi_{B,0}-\varphi_{P,0}}^{\varphi_{B,tr}-\varphi_{P,tr}} \frac{d(\varphi_B - \varphi_P)}{\sqrt{2\lambda \exp(\varphi_B - \varphi_P) + 2A}} = y_{tr} \text{ and } 0 = \lambda \exp(\varphi_{B,tr} - \varphi_{P,tr}) + A \text{ (showing that } A < 0\text{)}$$

Integration, taking the latter equation into account leads to:

$$y_{tr} = -\frac{2}{\sqrt{-2A}} \arctan\sqrt{\frac{\lambda \exp(\varphi_{B,0} - \varphi_{P,0}) + A}{-A}} \text{ leading to } y_{tr} < 0 \text{ which is absurd.}$$

2.5. *Asymptotes of the catalytic Tafel plots for* $E \to \pm\infty$

If compensation has been adjusted to its maximal value, equation (19S') becomes:

$$\ln\left\{\left[\frac{\lambda^2\left(\frac{r_P}{r_P + r_B}\right)^2 \psi^2 - 2A}{2\lambda}\right]^{\frac{r_P}{r_P+r_B}} \left[\frac{\lambda^2\left(\frac{r_B}{r_P + r_B}\right)^2 \psi^2 - 2A}{2\lambda}\right]^{\frac{r_B}{r_P+r_B}}\right\} = \pm\frac{FE}{RT}$$

Then, when $E \to \pm\infty$, $\psi \to \infty$ but A remains finite because the function $\tan^{-1}$ is limited to $[0,\pi/2]$ for a positive argument. It follows that:

$$\ln\left\{\left[\frac{\lambda\left(\frac{r_P}{r_P+r_B}\right)^2\psi^2}{2}\right]^{\frac{r_P}{r_P+r_B}}\left[\frac{\lambda\left(\frac{r_B}{r_P+r_B}\right)^2\psi^2}{2}\right]^{\frac{r_B}{r_P+r_B}}\right\}=\pm\frac{FE}{RT}$$

$$\ln\psi\rightarrow\pm\frac{FE}{2RT}-\ln\left[\frac{\lambda}{2}\left(\frac{r_P}{r_P+r_B}\right)^{\frac{2r_P}{r_P+r_B}}\left(\frac{r_B}{r_P+r_B}\right)^{\frac{2r_B}{r_P+r_B}}\right] \qquad \text{(21S')}$$

2.6. Finite difference resolution

The finite difference method is applied to the set of equations (10S') – (14S') and attending boundary conditions in the same way as in section 1.4.

Equations (10S') to (13S') become:

$$\varphi_B^{m,j}=\varphi_B^{m-1,j}-\Delta y\frac{\lambda}{(1+r_P/r_B)}\psi_M^{m,j} \qquad \text{(22S')}$$

$$\varphi_P^{m,j}=\varphi_P^{m-1,j}-\Delta y\frac{r_P/r_B}{(1+r_P/r_B)}\lambda\psi_P^{m,j} \qquad \text{(23S')}$$

$$\psi_B^{m,j}-\psi_B^{m-1,j}+\Delta y\exp\left(\varphi_B^{m,j}-\varphi_P^{m,j}\right)=0 \qquad \text{(24S')}$$

$$\psi_B^{m,j}-\psi_B^{m-1,j}=-\left(\psi_P^{m,j}-\psi_P^{m-1,j}\right) \qquad \text{(25S')}$$

We now have to linearize $\exp\left(\varphi_B^{m,j}-\varphi_P^{m,j}\right)$

We can use the value obtained at the previous potential (or time) in the framework of a linear scan:

$$\begin{aligned}
\exp\left(\varphi_B^{m,j}-\varphi_P^{m,j}\right)&=\exp\left[\left(\varphi_B^{m,j-1}-\varphi_P^{m,j-1}\right)+\left[\left(\varphi_B^{m,j}-\varphi_P^{m,j}\right)-\left(\varphi_B^{m,j-1}-\varphi_P^{m,j-1}\right)\right]\right]\\
&=\exp\left(\varphi_B^{m,j-1}-\varphi_P^{m,j-1}\right)\exp\left[\left(\varphi_B^{m,j}-\varphi_P^{m,j}\right)-\left(\varphi_B^{m,j-1}-\varphi_P^{m,j-1}\right)\right]\\
&\approx\exp\left(\varphi_B^{m,j-1}-\varphi_P^{m,j-1}\right)\left\{1+\left[\left(\varphi_B^{m,j}-\varphi_P^{m,j}\right)-\left(\varphi_B^{m,j-1}-\varphi_P^{m,j-1}\right)\right]\right\}
\end{aligned}$$

Equation (24S') becomes:

$$\psi_B^{m,j} - \psi_B^{m-1,j} + \left(\varphi_B^{m,j} - \varphi_P^{m,j}\right)\left\{\mathit{\Delta} y \exp\left[\left(\varphi_B^{m,j-1} - \varphi_P^{m,j-1}\right)\right]\right\}$$
$$= \left\{\left(\varphi_B^{m,j-1} - \varphi_P^{m,j-1}\right) - 1\right\}\mathit{\Delta} y \exp\left[\left(\varphi_B^{m,j-1} - \varphi_P^{m,j-1}\right)\right]$$

At each j, we have $4l$+4 variables: for m = 0 to l: $\psi_B^{m,j}$, $\psi_P^{m,j}$, $\varphi_B^{m,j}$, $\varphi_P^{m,j}$ and $4l$+4 equations linking these $4l$+4 variables and the previous values (at j-1) thus leading to the equation (DC)(D)=(P)

This can be written as a matrix equation (DC)(D)=(P): (DC) being a square matrix of dimension $4l$+4 and (D) and (P) are column matrix with $4l$+4 lines, see below). Inversion of matrix (DC) allows getting each variable (in (D)) at each time corresponding to j knowing the values at j-1 (P).

$$(DC)\times\begin{pmatrix} \begin{cases} \varphi_B^{0,j} \\ \varphi_P^{0,j} \\ \psi_B^{0,j} \\ \psi_P^{0,j} \end{cases} \\ \\ \begin{cases} \varphi_B^{k,j} \\ \varphi_P^{k,j} \\ \psi_B^{k,j} \\ \psi_P^{k,j} \end{cases} (k\text{=1 to } l\text{ -1}) \\ \\ \begin{cases} \varphi_B^{l,j} \\ \varphi_P^{l,j} \\ \psi_B^{l,j} \\ \psi_P^{l,j} \end{cases} \end{pmatrix} = \begin{pmatrix} \left.\begin{cases} \pm FE/RT \\ 0 \end{cases}\right\} \text{2 lines (lines \# 1 and 2)} \\ \left.\begin{cases} 0 \\ 0 \\ \left\{\left(\varphi_B^{m,j-1} - \varphi_P^{m,j-1}\right) - 1\right\}\mathit{\Delta} y \exp\left[\left(\varphi_B^{m,j-1} - \varphi_P^{m,j-1}\right)\right] \\ 0 \end{cases}\right\} 4l \text{ lines } (m\text{=1 to l) (lines \# 3 to } 4l+2) \\ \left.\begin{cases} 0 \\ 0 \end{cases}\right\} \text{2 lines (lines \# } 4l\text{+3 and } 4l+4) \end{pmatrix}$$

This allows filling the column matrix (P). Taking into account the initial conditions, the initial (P) matrix is nil. Then, at the beginning of each j calculation filling of column matrix (P) is as follows from previous values being in (D).

$$
\left(DC\right)=\left(\begin{array}{l}
1\ 0\ \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 0\\
0\ 0\ 0\ 1\ \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 0\\
\ldots\ldots\\
0\ldots\ldots -1\ 0\ 0\ 0\ 1\ 0\ \Delta y\dfrac{\lambda}{1+r_P/r_B}\ 0\ldots\ldots\ldots\ldots\ldots\ldots 0\\
0\ldots\ldots 0\ -1\ 0\ 0\ 0\ 1\ 0\ \Delta y\dfrac{\lambda}{1+r_B/r_P}\ \ldots\ldots\ldots\ldots\ldots\ldots 0\\
0\ldots\ldots 0\ 0\ -1\ 0\ \left\{\Delta y\exp\left[\varphi_B^{m,j-1}-\varphi_P^{m,j-1}\right]\right\}\ -\left\{\Delta y\exp\left[\varphi_B^{m,j-1}-\varphi_P^{m,j-1}\right]\right\}\ 1\ 0\ \ldots\ldots 0\\
0\ldots\ldots 0\ 0\ -1\ -1\ 0\ 0\ 1\ 1\ \ldots\ldots\ldots\ldots\ldots\ldots\ldots 0\\
\ldots\ldots\\
0\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 0\ 0\ 1\ 0\\
0\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 0\ 1\ 0\ -\beta_u
\end{array}\right)
$$

REFERENCES and NOTES

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