Supplementary Information

Cyclic Voltammetry Modeling of Proton Transport Effects on Redox Charge Storage in Conductive Material. Application to a TiO_2 Mesoporous Film.

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1. Experimental Details

1-μm thick amorphous TiO_2 films were prepared on a conductive planar ITO substrate by glancing angle deposition (GLAD) with a deposition angle of 72° as described elsewhere.[S1] These films are characterized by a surface area enhancement of 540 μm^{-1} (determined by BET analysis), a volumic density of 2.3 g cm^{-3}, and a porosity of ~40%. For electrochemistry, a geometric electrode area S of 0.3 cm^2 was delimited by nail varnish. Mesoporous GLAD TiO_2 electrodes were characterized by cyclic voltammetry in a three-electrode cell using an Autolab PGSTAT-12 potentiostat controlled by a GPES-4 software. The reference electrode was a Ag/AgCl/0.3 M KCl electrode (DriRef from WPI) and the counter electrode a platinum wire. Experiments were conducted at pH 7.0 in Hepes buffer solutions (concentrations ranging from 0 to 860 mM) containing 0.3 M KCl. The cell was flushed with argon during the entire experiment and thermostated to 25°C. A ohmic drop compensation of 50 Ω was used during the measurement.

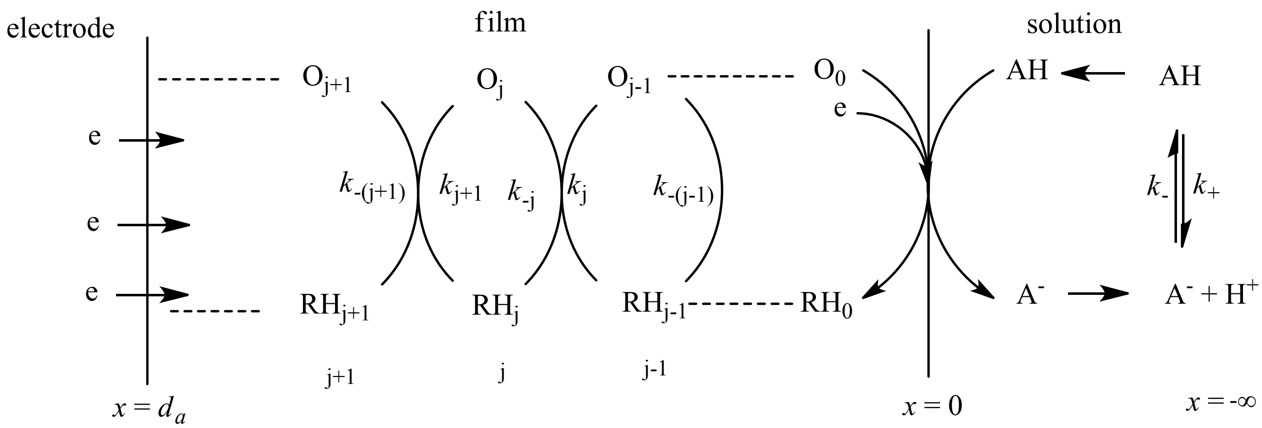
2. Derivation of cyclic voltammogram equation

Glossary of symbols

Latin lower case d_a:film thickness d_r: distance between adjacent redox centers in the film i : current $j = C_J / C_{\mathrm{AH}}^s$ k_{index} : rate constants k_S : standard rate constant $l = d_a / \sqrt{D_{\mathrm{H}} RT / Fv}$ s: Laplace variable t: time t_i: time where the scan is inverted u_{i}, u_f : dimensionless initial and inversion potentials v: scan rate x: distance to the (planar) electrode surface $y = x / \sqrt{D_{\mathrm{A}} RT / Fv}$:dimensionless distance to electrode surface ***Capital Latin*** $C_{\mathrm{SUBSCRIPT}}$: volume concentration of the subscript species $C_{\mathrm{SUBSCRIPT}}^s$: bulk solution volume concentration of the subscript species $C_{\mathrm{SUBSCRIPT}}^0$: bulk material volume concentration of the subscript species $D_{\mathrm{SUBSCRIPT}}$:diffusion coefficient of the subscript species E : potential of the electrode E_i : initial potential E_f : potential at scan inversion E^0 standard potential F: Faraday constant K_A : proton transfer equilibrium constant I_ψ : dimensionless convolution integral J_ψ : dimensionless integral L^{-1}: inverse Laplace transform R: gas constant S: geometrical electrode surface area S_a: apparent electrode surface area T: absolute temperature	***Greek lower case*** α :transfer coefficient τ: dimensionless time: $\tau = t / \left(Fv / RT\right)$; $\gamma = \dfrac{C_{\mathrm{O}}^0}{C_{\mathrm{AH}}^s} \dfrac{S_a}{S} \sqrt{\dfrac{D_{\mathrm{H}}}{D_{\mathrm{ext}}}}$ $\lambda_+ = k_+ C_{\mathrm{AH}}^s / \left(Fv / RT\right)$ $\lambda_- = k_- / \left(Fv / RT\right)$ $\psi = i / \left(FSC_{\mathrm{AH}}^s \sqrt{D_{\mathrm{ext}} Fv / RT}\right)$ $\xi = -\left(F / RT\right)\left(E - E^0\right)$ ***Capital Greek*** $\Lambda = k_S C_{\mathrm{AH}}^s / \sqrt{D_{\mathrm{H}} Fv / RT}$:

Proton hopping transport in the film

As depicted in scheme S1, the formation of RH species throughout the film can occur through proton hopping between adjacent sites together with electron localization.



Scheme S1. Schematic representation of proton transport

$$\frac{dC_{\mathrm{O}_j}}{dt} = -k_j C_{\mathrm{RH}_{j-1}} C_{\mathrm{O}_j} + k_{-j} C_{\mathrm{RH}_j} C_{\mathrm{O}_{j-1}} + k_{(j+1)} C_{\mathrm{RH}_j} C_{\mathrm{O}_{j+1}} - k_{-(j+1)} C_{\mathrm{RH}_{j+1}} C_{\mathrm{O}_j}$$

We introduce the self exchange rate constant:

$$k_0 = k_j = k_{-j} = k_{(j-1)} = k_{-(j-1)}$$

$$\frac{dC_{\mathrm{O}_j}}{dt} = k_0 \left[-C_{\mathrm{RH}_{j-1}} C_{\mathrm{O}_j} + C_{\mathrm{RH}_j} C_{\mathrm{O}_{j-1}} + C_{\mathrm{RH}_j} C_{\mathrm{O}_{j+1}} - C_{\mathrm{RH}_{j+1}} C_{\mathrm{O}_j} \right] \approx k_0 C_{\mathrm{O}}^0 \left[C_{\mathrm{O}_{j-1}} - 2C_{\mathrm{O}_j} + C_{\mathrm{O}_{j+1}} \right]$$

Replacing finite difference expression by the corresponding differential expression :

$\frac{\partial C_{\mathrm{O}}}{\partial t} = D_{\mathrm{H}} \frac{\partial^2 C_{\mathrm{O}}}{\partial x^2}$ with $D_{\mathrm{H}} = k_0 C_{\mathrm{O}}^0 d_r{}^2$ (d_r is the averaged distance between two sites).

Similarly, $\frac{\partial C_{\mathrm{RH}}}{\partial t} = D_{\mathrm{H}} \frac{\partial^2 C_{\mathrm{RH}}}{\partial x^2}$

Cyclic voltammetry conditions

$0 < t < t_i : E = E_i - vt$

$t_i < t < 2t_i : E = E_f + vt$

Diffusion reactions equations

$0 < x < d_a$:

$$\frac{\partial C_{\mathrm{O}}}{\partial t} = D_{\mathrm{H}} \frac{\partial^2 C_{\mathrm{O}}}{\partial x^2} \text{ and } \frac{\partial C_{\mathrm{RH}}}{\partial t} = D_{\mathrm{H}} \frac{\partial^2 C_{\mathrm{RH}}}{\partial x^2} \tag{S1}$$

$x < 0$

$$\mathrm{AH} \underset{k_-}{\overset{k_+}{\rightleftarrows}} \mathrm{A}^- + \mathrm{H}^+$$

$$\frac{\partial C_{\mathrm{AH}}}{\partial t} = D_{\mathrm{AH,ext}} \frac{\partial^2 C_{\mathrm{AH}}}{\partial x^2} + k_+ C_{\mathrm{A}^-} C_{\mathrm{H}^+} - k_- C_{\mathrm{AH}} \tag{S2}$$

$$\frac{\partial C_{\mathrm{A}^-}}{\partial t} = D_{\mathrm{A}^-,\mathrm{ext}} \frac{\partial^2 C_{\mathrm{A}^-}}{\partial x^2} - k_+ C_{\mathrm{A}^-} C_{\mathrm{H}^+} + k_- C_{\mathrm{AH}} \tag{S3}$$

$$\frac{\partial C_{\mathrm{H}^+}}{\partial t} = D_{\mathrm{H}^+,\mathrm{ext}} \frac{\partial^2 C_{\mathrm{H}^+}}{\partial x^2} - k_+ C_{\mathrm{A}^-} C_{\mathrm{H}^+} + k_- C_{\mathrm{AH}} \tag{S4}$$

and $K_A = \dfrac{k_+}{k_-} = \dfrac{C_{\mathrm{A}^-} C_{\mathrm{H}^+}}{C_{\mathrm{AH}}} = 10^{-pH} \dfrac{C^s_{\mathrm{A}^-}}{C^s_{\mathrm{AH}}}$

Initial and boundary conditions

$t = 0,\ 0 < x < d_a:\ C_{\mathrm{O}} = C^0_{\mathrm{O}}$ and $C_{\mathrm{RH}} = 0$

$t = 0,\ x < 0$ and $x = \infty,\ \forall t:\ C_{\mathrm{A}^-} = C^s_{\mathrm{A}^-}$ and $C_{\mathrm{AH}} = C^s_{\mathrm{AH}}$ and $C_{\mathrm{H}^+} = K_A \dfrac{C^s_{\mathrm{AH}}}{C^s_{\mathrm{A}^-}}$

$t > 0,\ x = 0:$

$$D_{\mathrm{H}} \left(\frac{\partial C_{\mathrm{O}}}{\partial x} \right)_{x=0} = k_S \exp\left[-\frac{\alpha F \left(E - E^0 \right)}{RT} \right] \left\{ \begin{array}{l} \left(C_{\mathrm{O}} \right)_{x=0} \left(C_{\mathrm{AH}} \right)_{x=0} \\ -\left(C_{\mathrm{RH}} \right)_{x=0} \left(C_{\mathrm{A}^-} \right)_{x=0} \exp\left[\dfrac{F \left(E - E^0 \right)}{RT} \right] \end{array} \right\} \tag{S5}$$

$$S_a D_{\mathrm{H}} \left(\frac{\partial C_{\mathrm{O}}}{\partial x} \right)_{x=0} = S D_{\mathrm{ext}} \left(\frac{\partial C_{\mathrm{AH}}}{\partial x} \right)_{x=0} = -S D_{\mathrm{ext}} \left(\frac{\partial C_{\mathrm{A}^-}}{\partial x} \right)_{x=0} \tag{S6}$$

where $D_{\mathrm{ext}} = D_{\mathrm{AH,ext}} = D_{\mathrm{A}^-,\mathrm{ext}}$

$t > 0,\ x = d_a$:

$$\left(\frac{\partial C_{\mathrm{O}}}{\partial x}\right)_{x=d_a} = 0$$

Expression of the current

The current (noted *i*) is evaluated as being proportional to the sum of all oxidized species in the film being reduced by unit of time:

$$\frac{i}{FS_a} = -\int_0^{d_a} \frac{\partial C_{\mathrm{O}}}{\partial t} dx \tag{S7}$$

Dimensionless formulation

We introduce the following dimensionless variables:

$$\xi = -\frac{F}{RT}\left(E - E^0\right);\ \tau = \frac{t}{RT/Fv};\ y = \frac{x}{\sqrt{D_{\mathrm{ext}}RT/Fv}};\ \psi = \frac{i}{FSC_{\mathrm{AH}}^s\sqrt{D_{\mathrm{ext}}Fv/RT}};\ ah = \frac{C_{\mathrm{AH}}}{C_{\mathrm{AH}}^s};\ a = \frac{C_{\mathrm{A^-}}}{C_{\mathrm{AH}}^s}$$

$$h = \frac{C_{\mathrm{H^+}}}{C_{\mathrm{AH}}^s};\ o = \frac{C_{\mathrm{O}}}{C_{\mathrm{O}}^0};\ rh = \frac{C_{\mathrm{RH}}}{C_{\mathrm{O}}^0};\ \lambda_+ = \frac{k_+C_{\mathrm{AH}}^s}{Fv/RT};\ \lambda_- = \frac{k_-}{Fv/RT}$$

and the following dimensionless parameters:

$$l = \frac{d_a}{\sqrt{D_{\mathrm{H}}RT/Fv}},\ \gamma = \frac{C_{\mathrm{O}}^0}{C_{\mathrm{AH}}^s}\frac{S_a}{S}\sqrt{\frac{D_{\mathrm{H}}}{D_{\mathrm{ext}}}}\ \text{and}\ \Lambda = \frac{k_S C_{\mathrm{AH}}^s}{\sqrt{D_{\mathrm{H}}Fv/RT}}$$

Formulation of the problem can thus be rewritten:

Cyclic voltammetry conditions:

$0 < \tau < \tau_i : \xi = u_i + \tau$ with $u_i << 0$

$\tau_i < \tau < 2\tau_i : \xi = u_f - \tau$

Diffusion reactions equations:

$0 < y < l$:

$$\frac{\partial o}{\partial \tau} = \frac{D_{\mathrm{H}}}{D_{\mathrm{ext}}} \frac{\partial^2 o}{\partial y^2} \text{ and } \frac{\partial rh}{\partial \tau} = \frac{D_{\mathrm{H}}}{D_{\mathrm{ext}}} \frac{\partial^2 rh}{\partial y^2} \tag{S1'}$$

$y < 0$

$$\frac{\partial ah}{\partial \tau} = \frac{\partial^2 ah}{\partial y^2} + \lambda_+ a \times h - \lambda\_ah \tag{S2'}$$

$$\frac{\partial a}{\partial \tau} = \frac{\partial^2 a}{\partial y^2} - \lambda_+ a \times h + \lambda\_ah \tag{S3'}$$

$$\frac{\partial h}{\partial \tau} = \frac{\partial^2 h}{\partial y^2} - \lambda_+ a \times h + \lambda\_ah \tag{S4'}$$

and $\frac{K_A}{C^s_{\mathrm{AH}}} = \frac{a \times h}{ah}$

Initial and boundary conditions:

$\tau = 0,\ 0 < y < l:\ (o)_{\tau=0} = \frac{C^0_{\mathrm{O}}}{C^s_{\mathrm{AH}}}$ and $(rh)_{\tau=0} = 0$

$\tau = 0,\ y < 0$ and $y = -\infty,\ \forall \tau: a = a^0$ and $ah = 1$ and $h = \frac{K_A}{C^s_{\mathrm{A^-}}}$

$\tau > 0,\ y = 0:$

$$\sqrt{\frac{D_{\mathrm{H}}}{D_{\mathrm{ext}}}} \left(\frac{\partial o}{\partial y}\right)_{y=0} = \Lambda \exp(\alpha\xi)\left[o_{y=0} \times ah_{y=0} - rh_{y=0} \times a_{y=0} \exp(-\xi)\right] \tag{S5'}$$

$$\gamma \sqrt{\frac{D_{\mathrm{H}}}{D_{\mathrm{ext}}}} \left(\frac{\partial o}{\partial y}\right)_{y=0} = \left(\frac{\partial ah}{\partial y}\right)_{y=0} = -\left(\frac{\partial a}{\partial x}\right)_{y=0} \tag{S6'}$$

$\tau > 0, y = l:$

$$\left(\frac{\partial o}{\partial y}\right)_{y=l} = 0$$

Expression of the current:

$$\psi = -\gamma\sqrt{\frac{D_{\mathrm{ext}}}{D_{\mathrm{H}}}}\int_0^l \frac{\partial o}{\partial \tau}dy \tag{S7'}$$

Resolution

Combining (S7') and (S1'), integrating and taking into account boundary condition, we have:

$\psi = \gamma\sqrt{\frac{D_{\mathrm{H}}}{D_{\mathrm{ext}}}}\left(\frac{\partial o}{\partial y}\right)_{y=0}$ and thus (S5') gives:

$$\frac{\psi}{\Lambda \exp(\alpha\xi)} = \gamma\left[o_{y=0} \times ah_{y=0} - rh_{y=0} \times a_{y=0}\exp(-\xi)\right] \tag{S8'}$$

Integration of equations (S1') in the Laplace plane and taking into account boundary conditions and coming back in the real plane leads to:

$$rh_{y=0} = \frac{1}{\gamma}\int_0^\tau \psi \times L^{-1}\left[\frac{1}{\sqrt{s}\tanh\left(l\sqrt{s}\right)}\right]_{\tau-\eta} d\eta = \frac{J_\psi^l}{\gamma}$$

$$o_{y=0} = 1 - \frac{1}{\gamma}\int_0^\tau \psi \times L^{-1}\left[\frac{1}{\sqrt{s}\tanh\left(l\sqrt{s}\right)}\right]_{\tau-\eta} d\eta = 1 - \frac{J_\psi^l}{\gamma}$$

in which $L^{-1}\left[f(s)\right]_{\tau-\eta}$ represents the inverse Laplace transform of function $f(s)$ at $\tau-\eta$ value.

Then equation (S8') becomes:

$$\frac{\psi}{\Lambda \exp(\alpha\xi)} = \left(\gamma - J_\psi^l\right) \times ah_{y=0} - J_\psi^l \times a_{y=0}\exp(-\xi) \tag{S9'}$$

Combining equations (S2') to (S4') leads to:

$$\frac{\partial(a+ah)}{\partial \tau}=\frac{\partial^2(a+ah)}{\partial y^2} \tag{S10'}$$

$$\frac{\partial(ah-h)}{\partial \tau}=\frac{\partial^2(ah-h)}{\partial y^2} \tag{S11'}$$

Integration of (S10') in the Laplace plane taking into account boundary conditions and coming back in the real plane leads to:

$a+ah=a^0+1$ and hence: $(a)_{y=0}+(ah)_{y=0}=a^0+1$

Integration of (S11') in the Laplace plane taking into account boundary conditions and coming back in the real plane leads to:

$$(ah-h)_{y=0}=\left(1-h^0\right)-\gamma\sqrt{\frac{D_{\mathrm{H}}}{D_{\mathrm{ext}}}}\frac{1}{\sqrt{\pi}}\int_0^{\tau}\frac{1}{\sqrt{\tau-\eta}}\left(\frac{\partial o}{\partial y}\right)_{y=0}d\eta$$

Recalling that: $\psi=\gamma\sqrt{\frac{D_{\mathrm{H}}}{D_{\mathrm{ext}}}}\left(\frac{\partial o}{\partial y}\right)_{y=0}$, we have:

$$(ah)_{y=0}-(h)_{y=0}=\left(1-h^0\right)+\frac{1}{\sqrt{\pi}}\int_0^{\tau}\frac{\psi}{\sqrt{\tau-\eta}}d\eta=\left(1-h^0\right)-I_{\psi}\approx 1-I_{\psi}$$

We also assume that in most cases, $(ah)_{y=0}>>(h)_{y=0}$, thus:

$(ah)_{y=0}\approx 1-I_{\psi}$ and $(a)_{y=0}\approx a^0+I_{\psi}$

Then equation (S10') becomes, the general equation of the cyclic voltammogram:

$$\frac{\psi}{\Lambda \exp(\alpha\xi)} = \left(\gamma - J_{\psi}^{l}\right) \times \left(1 - I_{\psi}\right) - J_{\psi}^{l} \times \left(\frac{C_{\mathrm{A^-}}^{s}}{C_{\mathrm{AH}}^{s}} + I_{\psi} \right) \exp(-\xi) \tag{S9'}$$

3. Procedure for numerical calculation

The general equation of the cyclic voltammogram to be computed is:

$$\frac{\psi}{\Lambda \exp(\alpha\xi)} = \left(\gamma - J_{\psi}\right)\left(1 - I_{\psi}\right) - J_{\psi} \left(\frac{C_{\mathrm{A^-}}^{s}}{C_{\mathrm{AH}}^{s}} + I_{\psi} \right) \exp(-\xi)$$

with $J_{\psi} = \int_{0}^{\tau} \psi L^{-1} \left(\frac{1}{\sqrt{s}\tanh\left(\sqrt{sl^2}\right)} \right)_{(\tau-\eta)} d\eta$ and $I_{\psi} = \frac{1}{\sqrt{\pi}} \int_{0}^{\tau} \frac{\psi}{\sqrt{\tau-\eta}} d\eta$

a. Calculation of $I_{\psi} = \frac{1}{\sqrt{\pi}} \int_{0}^{\tau} \frac{\psi}{\sqrt{\tau-\eta}} d\eta$

The integration domain is divided into small intervals within which the current is approximated by a linear function between the values at the ends of the interval. τ is divided into p divisions with width h:
$\tau = ph$

$$I_{\psi} = \frac{1}{\sqrt{\pi}} \int_{0}^{\tau} \frac{\psi}{\sqrt{\tau-\eta}} d\eta = I_{p} = \frac{1}{\sqrt{\pi}h} \sum_{j=1}^{p} \int_{\tau_{j-1}}^{\tau_{j}} \frac{\psi_{j} \times \left(\eta - \tau_{j-1}\right) + \psi_{j-1} \times \left(\tau_{j} - \eta\right)}{\sqrt{\tau_{p} - \eta}} d\eta$$

thus:

$$I_{p} = \left(I_{p-1} + \frac{2}{3}\sqrt{\frac{h}{\pi}} \psi_{p-1} \right) + \frac{4}{3}\sqrt{\frac{h}{\pi}} \psi_{p} = I'_{p-1} + \frac{4}{3}\sqrt{\frac{h}{\pi}} \psi_{p}$$

and

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

b. Calculation of $J_\psi = \int_0^\tau \psi L^{-1}\left(\frac{1}{\sqrt{s}\tanh\left(\sqrt{sl^2}\right)}\right)_{(\tau-\eta)} d\eta$

The Laplace inverse transform is calculated numerically using the Stehfest method:[S2]

$$L^{-1}\left(\frac{1}{\sqrt{s}\tanh\left(\sqrt{sl^2}\right)}\right)_{(\tau-\eta)} = \frac{\ln 2}{(\tau-\eta)}\sum_{k=1}^{N} V_k \frac{1}{\sqrt{\frac{k\ln 2}{\tau-\eta}}\tanh\left(\sqrt{\frac{k\ln 2}{\tau-\eta}l^2}\right)}$$

$$L^{-1}\left(\frac{1}{\sqrt{s}\tanh\left(\sqrt{sl^2}\right)}\right)_{(\tau-\eta)} = \frac{\ln 2}{\sqrt{\tau-\eta}}\sum_{k=1}^{N} V_k \frac{1}{\sqrt{k\ln 2}\tanh\left(\sqrt{\frac{k\ln 2}{\tau-\eta}l^2}\right)}$$

in which we consider $N = 20$ and V_k 's are constants given by:

$$V_k = (-1)^{\frac{N}{2}+k}\sum_{m=Int\left(\frac{k+1}{2}\right)}^{\min(k,N/2)} \frac{m^{N/2}(2m)!}{(N/2-m)!\,m!\,(m-1)!\,(k-m)!\,(2m-k)!}$$

Hence:

$$J_\psi = \int_0^\tau \frac{\psi}{\sqrt{\tau-\eta}}\sum_{k=1}^{N} V_k \frac{\sqrt{\ln 2}}{\sqrt{k}\tanh\left(\sqrt{\frac{k\ln 2}{\tau-\eta}l^2}\right)} d\eta$$

The integration domain is divided into p small intervals with width h within which the current is approximated by a linear function between the values at the ends of the interval. In each interval, the exponential term is approximated by a constant corresponding to the value at the center of the interval:

$$\tanh\left(l\sqrt{\frac{k\ln 2}{\tau-\eta}}\right) \approx \tanh\left(l\sqrt{\frac{k\ln 2}{\tau_p-\left(\tau_{j-1}+\frac{h}{2}\right)}}\right).$$

Hence :

$$J_\psi = J_p = \frac{1}{h}\sum_{j=1}^{p}\left[\sum_{k=1}^{N} V_k \frac{\sqrt{\ln 2}}{\sqrt{k}\tanh\left(l\sqrt{\frac{k\ln 2}{(p-j)h+h/2}}\right)}\right] \times \int_{\tau_{j-1}}^{\tau_j} \frac{\psi_j \times (\eta-\tau_{j-1}) + \psi_{j-1}\times(\tau_j-\eta)}{\sqrt{\tau_p-\eta}} d\eta$$

$$J_p = J_{p-1} + \left[\sum_{k=1}^{N} V_k \frac{\sqrt{\ln 2}}{\sqrt{k}\,\tanh\left(l\sqrt{\frac{k \ln 2}{h/2}} \right)} \right] \times \int_{\tau_{p-1}}^{\tau_p} \frac{\psi_p \times (\eta - \tau_{p-1}) + \psi_{p-1} \times (\tau_p - \eta)}{\sqrt{\tau_p - \eta}} d\eta$$

with :

$$\int_{\tau_{p-1}}^{\tau_p} \frac{\psi_p \times (\eta - \tau_{p-1}) + \psi_{p-1} \times (\tau_p - \eta)}{\sqrt{\tau_p - \eta}} d\eta = \frac{2}{3}\sqrt{h}\psi_{p-1} + \frac{4}{3}\sqrt{h}\psi_p$$

Consequently :

$$J_p = J_{p-1} + \left[\sum_{k=1}^{N} V_k \frac{\sqrt{\ln 2}}{\sqrt{k}\,\tanh\left(l\sqrt{\frac{k \ln 2}{h/2}} \right)} \right] \times \left(\frac{2}{3}\sqrt{h}\psi_{p-1} + \frac{4}{3}\sqrt{h}\psi_p \right) = J'_{p-1} + \left[\sum_{k=1}^{N} V_k \frac{\sqrt{\ln 2}}{\sqrt{k}\,\tanh\left(l\sqrt{\frac{k \ln 2}{h/2}} \right)} \right] \frac{4}{3}\sqrt{h}\psi_p$$

with

$$J'_{p-1} = J_{p-1} + \left[\sum_{k=1}^{N} V_k \frac{\sqrt{\ln 2}}{\sqrt{k}\,\tanh\left(l\sqrt{\frac{k \ln 2}{h/2}} \right)} \right] \times \frac{2}{3}\sqrt{h}\psi_{p-1}$$

and

$$J_{p-1} = \sqrt{h} \sum_{j=1}^{p-1} \left[\sum_{k=1}^{N} V_k \frac{\sqrt{\ln 2}}{\sqrt{k}\,\tanh\left(l\sqrt{\frac{k \ln 2}{(p-j)h + h/2}} \right)} \right] \times$$
$$\left[\frac{2}{3}(\psi_{j-1} - \psi_j)\left[(p-j+1)^{3/2} - (p-j)^{3/2} \right] + 2\left[\psi_j \times (p-j+1) - \psi_{j-1} \times (p-j) \right]\left[\sqrt{p-j+1} - \sqrt{p-j} \right] \right]$$

c. Discretization of the integral equation:

The integration domain is divided into p intervals within which integrals are calculated as detailed above. Hence:

$$\frac{\psi_p}{\Lambda \exp(\alpha\xi)} = (\gamma - J_p)(1 - I_p) - J_p \left(\frac{C^s_{\mathrm{A}^-}}{C^s_{\mathrm{AH}}} + I_p \right) \exp(-\xi)$$

with:

$$I_p = \left(I_{p-1} + \frac{2}{3}\sqrt{\frac{h}{\pi}}\psi_{p-1} \right) + \frac{4}{3}\sqrt{\frac{h}{\pi}}\psi_p = I'_{p-1} + \frac{4}{3}\sqrt{\frac{h}{\pi}}\psi_p$$

$$J_p = J'_{p-1} + \left[\sum_{k=1}^{N} V_k \frac{\sqrt{\ln 2}}{\sqrt{k}\tanh\left(l\sqrt{\frac{k\ln 2}{h/2}} \right)} \right] \frac{4}{3}\sqrt{\frac{h}{\pi}}\psi_p$$

Thus, we have:

$$\frac{\psi_p}{\Lambda\exp(\alpha\xi)} = \left(\gamma - J'_{p-1} - \left[\sum_{k=1}^{N} V_k \frac{\sqrt{\ln 2}}{\sqrt{k}\tanh\left(l\sqrt{\frac{k\ln 2}{h/2}} \right)} \right] \frac{4}{3}\sqrt{\frac{h}{\pi}}\psi_p \right) \left(1 - I'_{p-1} - \frac{4}{3}\sqrt{\frac{h}{\pi}}\psi_p \right)$$
$$- \left(J'_{p-1} + \left[\sum_{k=1}^{N} V_k \frac{\sqrt{\ln 2}}{\sqrt{k}\tanh\left(l\sqrt{\frac{k\ln 2}{h/2}} \right)} \right] \frac{4}{3}\sqrt{\frac{h}{\pi}}\psi_p \right) \left(\frac{C^s_{\mathrm{A}}}{C^s_{\mathrm{AH}}} + I'_{p-1} + \frac{4}{3}\sqrt{\frac{h}{\pi}}\psi_p \right) \exp(-\xi)$$

leading to a second order equation on ψ_p

$$A\psi_p^2 + B\psi_p + C = 0$$

i.e. $\psi_p = \dfrac{-B \pm \sqrt{B^2 - 4A \times C}}{2A}$

with:

$$A = \left[\sum_{k=1}^{N} V_k \frac{\sqrt{\ln 2}}{\sqrt{k}\tanh\left(l\sqrt{\frac{k\ln 2}{h/2}} \right)} \right] \left(\frac{4}{3}\sqrt{\frac{h}{\pi}} \right)^2 \left(1 - \exp(-\xi) \right)$$

$$C = \left(\gamma - J'_{p-1} \right)\left(1 - I'_{p-1} \right) - J'_{p-1} \left(\frac{C^s_{\mathrm{A}^-}}{C^s_{\mathrm{AH}}} + I'_{p-1} \right) \exp(-\xi)$$

$$B = -\frac{4}{3}\sqrt{\frac{h}{\pi}}\left\{\begin{array}{l}\left[\left(\gamma - J'_{p-1}\right) + J'_{p-1}\exp\left(-\xi\right)\right] \\ + \left[\sum_{k=1}^{N} V_k \frac{\sqrt{\ln 2}}{\sqrt{k}\tanh\left(l\sqrt{\frac{k\ln 2}{h/2}}\right)}\right]\left[\left(1 - I'_{p-1}\right) + \left(\frac{C_{\mathrm{A}}^{s}}{C_{\mathrm{AH}}^{s}} + I'_{p-1}\right)\exp\left(-\xi\right)\right]\end{array}\right\} - \frac{1}{\Lambda\exp\left(\alpha\xi\right)}$$

When $\xi = 0$, then $A = 0$ and $\psi_p = -\frac{C}{B}$

4. References

S1. K.M. Krause, M.T. Taschuk, K.D. Harris, D.A. Rider, N.G. Wakefield, J.C. Sit, J.M. Buriak, M. Thommes, M.J. Brett, *Langmuir*, 2010, **26**, 4368.

S2. H. Stehfest, *Commun. ACM*, 1970, **13**, 47.