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ARTICLE *in* JOURNAL OF THE AMERICAN CHEMICAL SOCIETY · SEPTEMBER 2015

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Supporting Information

Molecular Catalysis of O₂ Reduction by Iron Porphyrins in Water.

Heterogeneous vs. Homogeneous Pathways.

Cyrille Costentin*, Hachem Dridi and Jean-Michel Savéant*

1. Experimental details

Chemicals

Iron (III) meso-tetrakis (N-methyl-4-pyridyl) porphyrin (abbreviated; FeTMPyP) was purchased from Frontier Scientific and used without further purification. Hydrochloric acid (37 %), potassium hydroxide (> 85 %) and acetic acid (100 %) were purchased from Prolabo. Potassium nitrate (> 99.0 %) was from Merck, boric acid (≥ 99.8 %) was from Sigma-Aldrich and hydrogen peroxide (35 wt. %) was purchased from Acros-Organic. All these chemical reagents were analytical grade and were used as received.

Supporting electrolyte and buffer solutions were prepared with ultrapure water (TKA Micro-pure, conductivity 0.055 $\mu\text{S}\cdot\text{cm}^{-1}$).

Electrochemistry

All electrochemical measurements were made either on a CH Instruments bipotentiostat (model 750E) or a Metrohm AUTOLAB potentiostat (model PGSTAT12). The supporting electrolyte and buffer solutions utilized in this study are listed in table (S1). No significant effect of the buffer or anions concentrations on the redox potential of the Fe^{III/II} TMPyP were observed. A Hanna instrument *pH*-meter (model HI221) equipped with a Fisherbrand combined glass/AgCl electrode (model 11769798) was used to determine the solution *pH* values.

Table S1. Supporting electrolyte and buffer solutions

<i>pH</i> range	Supporting electrolyte	Buffer solutions
1.15	0.1 M KNO ₃	0.4 M phosphate buffer
3.8	0.1 M KNO ₃	0.4 M acetate buffer
1.5-13.5	0.1 M KNO ₃	0.04 M Britton-Robinson buffer

The “universal” Britton-Robinson buffer is a mixture of 0.04 M H₃BO₃, 0.04 M H₃PO₄ and 0.04 M CH₃COOH that has been titrated to the desired *pH* with 0.2 M NaOH.^{S1}

Cyclic voltammetry

For mechanistic investigations purposes and in order to select the adequate *pH* of the solution that avoids dimerization of the FeTMPyP molecule, cyclic voltammetry experiments were carried out under argon using a standard three-compartment electrochemical cell with a platinum wire counter electrode and a saturated calomel reference electrode (SCE, Radiometer Analytical XR110). The working electrode was either a 3 mm or a 5.61 mm diameter glassy carbon disk (Tokai Ltd.) carefully polished on a polishing cloth with an aqueous suspension of 0.05 μm alumina. The residual alumina particles were removed by sonication in distilled water for 30 s. Then, the electrodes were air-dried before use. The water jacketed cell was thermostated at 22 ± 1 °C.

Rotating Disk Electrode Voltammetry (RDEV) and Rotating Ring Disk Electrode Voltammetry (RRDEV)

RRDEV and RDEV experiments were conducted in a home-built 100 mL Pyrex cell using a Pine Instrument rotator (model: AFMSRCE) connected to a CH Instruments bipotentiostat (model 750E). A solution volume of 20 mL was used to ensure both sufficient depth of the electrode into the solution and distance from the cell bottom to avoid turbulence. The counter electrode was a Pt wire, the reference electrode (same electrode used in the CV experiments) was isolated from the main cell compartment by immersion in a glass tube terminated by a sintered glass frit.

The working electrode was obtained from Pine Instrument (model: AFE7R9GCPT). It is composed of a glassy carbon disk (5.61 mm diameter) surrounded by a platinum ring. To ensure reproducibility, the ring-disk electrode was repolished between scans for several minutes in a similar manner as above, and voltammograms for each experimental conditions were repeated until a reasonably consistent voltammogram was achieved (usually 2-5 scans). The collection coefficient of the working electrode was determined to be 0.4 using the ferrocyanide/ferriocyanide redox couple. This was in good agreement with the value calculated from the electrode geometry ($N=0.37$). Ohmic drop was compensated using the positive feedback compensation implemented in the instrument. Experiments were made at room temperature (at 22 ± 2 °C) either under argon, pure oxygen or air, in the 100-2500 rpm range, although most of the RRDEV data were obtained at 2500 rpm.

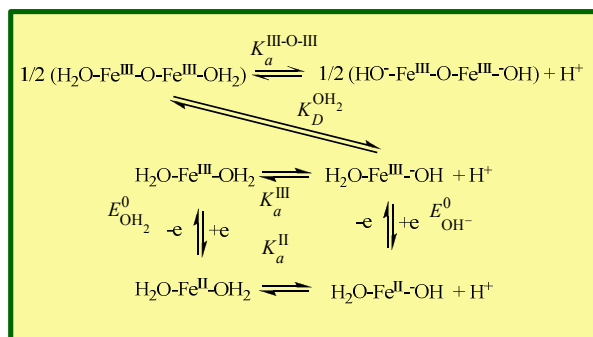
H_2O_2/H_2O selectivity measurements were carried out at $pH=3.8$ (0.1 M KNO_3 + 0.4 M acetate buffer) and $pH=1.15$ (0.1 M KNO_3 + 0.4 M phosphate buffer), respectively, under 1 atm. pure oxygen (or air), generated from a constant stream bubbling in the cell solution. The reported data were performed at a rotation rate of 2500 rpm with the disk swept cathodically at a scan rate of 50 mV/s while the ring electrode potential was held at 1.04 or 1.19 V vs. SHE (with respect to the pH value).

To perform heterogeneous catalysis experiments, the ring-disk electrode was dipped in solutions of FeTMPyP during 15-20 minutes in order to reach the saturation adsorption corresponding to the solution concentration, then pulled out, washed with the same buffer solution used to dissolve the porphyrin (at the same pH) and transferred into a fresh buffer solution of the same composition with no FeTMPyP present.

2. Pourbaix diagram

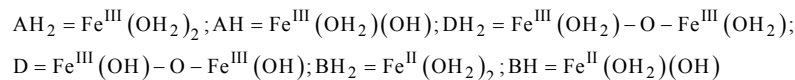
The reaction scheme corresponding to the catalyst reduction in water is recalled in scheme S1.

Scheme S1



The Pourbaix diagram is obtained from the variation of the apparent standard potential (obtained from the middle potential between the cathodic and anodic peaks). We establish below the expression of the cyclic voltammogram corresponding to the reaction scheme S1 in the framework of fast equilibria, nernstian electron transfers and same diffusion coefficient D for all species.

The various species involved in Scheme 1 are noted as follows :



Equilibrium being fast, at any time and distance from the electrode we have:

$$K_a^{III} = \frac{k_{III,1}}{k_{III,2}} = \frac{[AH][H^+]}{[AH_2]}, K_a^{II} = \frac{k_{II,1}}{k_{II,2}} = \frac{[BH][H^+]}{[BH_2]}, K_D^{OH_2} = \frac{k_{d,1}}{k_{d,2}} = \frac{[DH_2]}{[AH]^2}, (K_a^{III-O-III})^2 = \frac{k_{III,1}}{k_{III,2}} = \frac{[D][H^+]^2}{[DH_2]}$$

The electrode potential is swept linearly from front to back between two values E_i and E_f :

$$0 \leq t \leq t_R : E = E_i - vt$$

$$t_R \leq t \leq 2t_R : E = E_f - v(t - t_R)$$

(t_R is the time where the linear potential is reversed)

For the oxidized species we can write the following reaction-diffusion equations (x is the distance from the electrode surface) :

$$\frac{\partial [\text{AH}_2]}{\partial t} = D \frac{\partial^2 [\text{AH}_2]}{\partial x^2} - k_{\text{III},1} [\text{AH}_2] + k_{\text{III},2} [\text{H}^+] [\text{AH}]$$

$$\frac{\partial [\text{AH}]}{\partial t} = D \frac{\partial^2 [\text{AH}]}{\partial x^2} + k_{\text{III},1} [\text{AH}_2] - k_{\text{III},2} [\text{H}^+] [\text{AH}] - 2k_{d,1} [\text{AH}]^2 + 2k_{d,2} [\text{DH}_2]$$

$$\frac{\partial [\text{DH}_2]}{\partial t} = D \frac{\partial^2 [\text{DH}_2]}{\partial x^2} - k_{ad,1} [\text{DH}_2] + k_{ad,2} [\text{H}^+]^2 [\text{D}] + k_{d,1} [\text{AH}]^2 - k_{d,2} [\text{DH}_2]$$

$$\frac{\partial [\text{D}]}{\partial t} = D \frac{\partial^2 [\text{D}]}{\partial x^2} + k_{ad,1} [\text{DH}_2] - k_{ad,2} [\text{H}^+]^2 [\text{D}]$$

Boundary conditions :

At $t = 0, x > 0$ and $t > 0, x = \infty$: the total concentration of the substrate is the same from the electrode to the bulk of the solution and equal to C^0 .

At $t > 0, x = 0$:

$$i = FSD \left(\frac{\partial [\text{AH}_2] + [\text{AH}]}{\partial x} \right)_{x=0} = -FSD \left(\frac{\partial [\text{BH}_2] + [\text{BH}]}{\partial x} \right)_{x=0}, \text{ } i \text{ is the current, } S \text{ is the electrode surface and } F \text{ the Faraday.}$$

$$\left(\frac{\partial [\text{DH}_2]}{\partial x} \right)_{x=0} = 0 \text{ and } \left(\frac{\partial [\text{D}]}{\partial x} \right)_{x=0} = 0$$

$$E = E_{\text{OH}_2}^0 + \frac{RT \ln 10}{F} \log \left(\frac{[\text{AH}_2]_{x=0}}{[\text{BH}]_{x=0}} \right)$$

Combination of the reaction-diffusion equations gives :

$$\frac{\partial [\text{AH}_2] + [\text{AH}] + 2[\text{DH}_2] + 2[\text{D}]}{\partial t} = D \frac{\partial^2 [\text{AH}_2] + [\text{AH}] + 2[\text{DH}_2] + 2[\text{D}]}{\partial x^2}$$

which integration taking into account boundary conditions leads to :

$$([\text{AH}_2] + [\text{AH}] + 2[\text{DH}_2] + 2[\text{D}])_{x=0} = C^0 (1 - I_\psi)$$

where I_ψ is the dimensionless convolution integral.

Taking into account equilibrium relationships :

$$[\text{AH}_2]_{x=0} \left(1 + \frac{K_a^{\text{III}}}{[\text{H}^+]} \right)_{x=0} + 2K_D \frac{(K_a^{\text{III}})^2}{[\text{H}^+]^2} \left(1 + \frac{(K_a^{\text{III-O-III}})^2}{[\text{H}^+]^2} \right) [\text{AH}_2]_{x=0}^2 = C^0 (1 - I_\psi)$$

$$\text{leading to : } [\text{AH}_2]_{x=0} = \frac{-\left(1 + \frac{K_a^{\text{III}}}{[\text{H}^+]}\right) + \sqrt{\left(1 + \frac{K_a^{\text{III}}}{[\text{H}^+]}\right)^2 + 8K_D^{\text{OH}_2} \left(\frac{K_a^{\text{III}}}{[\text{H}^+]}\right)^2 \left(1 + \frac{(K_a^{\text{III-O-III}})^2}{[\text{H}^+]^2}\right) C^0 (1 - I_\psi)}}{4K_D \left(\frac{K_a^{\text{III}}}{[\text{H}^+]}\right)^2 \left(1 + \frac{(K_a^{\text{III-O-III}})^2}{[\text{H}^+]^2}\right)}$$

For the reduced species we can write the following reaction-diffusion equations

$$\frac{\partial [\text{BH}_2]}{\partial t} = D \frac{\partial^2 [\text{BH}_2]}{\partial x^2} - k_{\text{II},1} [\text{BH}_2] + k_{\text{II},2} [\text{H}^+] [\text{BH}]$$

$$\frac{\partial [\text{BH}]}{\partial t} = D \frac{\partial^2 [\text{BH}]}{\partial x^2} + k_{\text{II},1} [\text{BH}_2] - k_{\text{II},2} [\text{H}^+] [\text{BH}]$$

$$\text{We obtain : } \frac{\partial [\text{BH}_2] + [\text{BH}]}{\partial t} = D \frac{\partial^2 [\text{BH}_2] + [\text{BH}]}{\partial x^2}$$

The integration of which, taking into account the boundary conditions, leads to :

$$([\text{BH}_2] + [\text{BH}])_{x=0} = C^0 I_\psi$$

Taking into account equilibrium relationships :

$$[\text{BH}_2]_{x=0} = \frac{I_\psi}{\left(1 + \frac{K_a^{\text{II}}}{[\text{H}^+]}\right)}$$

Application of Nernst relationship to AH_2/BH_2 couple leads to the equation of the voltammogram in conditions of fast equilibriums:

$$E_{ap}^0 = E_{\text{OH}_2}^0 + \frac{RT \ln 10}{F} \log \left[\frac{\frac{-\left(1 + \frac{K_a^{\text{III}}}{[\text{H}^+]}\right) + \sqrt{\left(1 + \frac{K_a^{\text{III}}}{[\text{H}^+]}\right)^2 + 8K_D^{\text{OH}_2} \left(\frac{K_a^{\text{III}}}{[\text{H}^+]}\right)^2 \left(1 + \frac{(K_a^{\text{III-O-III}})^2}{[\text{H}^+]^2}\right) C^0 (1 - I_\psi)}}{4K_D \left(\frac{K_a^{\text{III}}}{[\text{H}^+]}\right)^2 \left(1 + \frac{(K_a^{\text{III-O-III}})^2}{[\text{H}^+]^2}\right)}}{\frac{C^0 I_\psi}{\left(1 + \frac{K_a^{\text{II}}}{[\text{H}^+]}\right)}} \right]$$

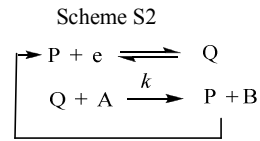
Variations of the apparent standard potential with pH can finally be obtained from the following equation :

$$E_{ap}^0 \approx E_{OH_2}^0 + \frac{RT \ln 10}{F} \log \left[\frac{- \left(1 + \frac{K_a^{III}}{[H^+]} \right) + \sqrt{\left(1 + \frac{K_a^{III}}{[H^+]} \right)^2 + 8K_D^{OH_2} \left(\frac{K_a^{III}}{[H^+]} \right)^2 \left(1 + \frac{(K_a^{III-O-III})^2}{[H^+]^2} \right) C^0}}{4K_D \left(\frac{K_a^{III}}{[H^+]} \right)^2 \left(1 + \frac{(K_a^{III-O-III})^2}{[H^+]^2} \right) C^0} \right]$$

$$\left[\frac{1}{1 + \frac{K_a^{II}}{[H^+]}} \right]$$

3. Analysis of the RDE voltammetry of catalytic systems

In order to illustrate the interplay between catalytic reaction and mass transport in RDEV of catalytic systems, we consider the simple one electron transfer process sketched in Scheme S2.



In the following, k is an apparent rate constant.

In steady-state conditions corresponding to the rotating-disc electrode voltammetry, the following reaction-diffusion equation can be written in the diffusion layer ($0 < x < \delta$ where δ is the thickness of the diffusion layer related to the rotation rate ω):

$$0 = D_P \frac{d^2[P]}{dx^2} + k[Q] \times [A]$$

$$0 = D_P \frac{d^2[Q]}{dx^2} - k[Q] \times [A]$$

$$0 = D \frac{d^2[A]}{dx^2} - k[Q] \times [A]$$

With the boundary conditions:

$x = 0$:

$$\frac{i}{FS} = D_P \left(\frac{d[P]}{dx} \right)_{x=0} = -D_P \left(\frac{d[Q]}{dx} \right)_{x=0}$$

$$\left(\frac{d[A]}{dx} \right)_{x=0} = 0$$

$$\frac{[P]_0}{[Q]_0} = \exp \left[\frac{F(E - E^0)}{RT} \right]$$

$x = \delta$:

$$[P]_\delta = C_P^0, [Q]_\delta = 0, [A]_\delta = C_A^0$$

We now introduce dimensionless parameters:

$$y = \frac{x}{\delta}; j = \frac{[J]}{C_P^0}; \gamma = \frac{C_A^0}{C_P^0}; \lambda = \frac{kC_P^0}{D/\delta^2}; \psi = \frac{i}{FSDC_P^0/\delta} = \frac{i}{i_D} \text{ with } i_D = \frac{FSDC_P^0}{\delta} = 0.62FSC_P^0D^{2/3}\nu^{-1/6}\omega^{1/2}; \xi = -\frac{F}{RT}(E - E^0)$$

We obtain for $0 < y < 1$:

$$0 = \frac{D_P}{D} \frac{d^2 p}{dy^2} + \lambda q \times a$$

$$0 = \frac{D_P}{D} \frac{d^2 q}{dy^2} - \lambda q \times a$$

$$0 = \frac{d^2 a}{dy^2} - \lambda q \times a$$

For $y = 0$:

$$\frac{p_0}{q_0} = \exp(-\xi)$$

$$\psi = \frac{D_P}{D} \left(\frac{dp}{dy} \right)_0 = - \frac{D_P}{D} \left(\frac{dq}{dy} \right)_0$$

$$\left(\frac{da}{dy} \right)_0 = 0$$

For $y = 1$:

$$p_1 = 1; \quad q_1 = 0; \quad a_1 = \gamma$$

The system depends on two parameters λ and $\gamma = \frac{C_A^0}{C_P^0}$. A zone diagram could be drawn as in cyclic voltammetry.^{S2} We will here only

describe two limiting cases within the framework of fast catalysis:

Case 1: Large substrate excess (no substrate diffusion) then: $a = \gamma$

The equations to be solved in the diffusion layer are:

$$\frac{d^2 q}{dy^2} = \lambda \gamma \frac{D}{D_P} q$$

$$0 = \frac{D_P}{D} \frac{d^2 (p+q)}{dy^2}$$

which resolution taking into account boundary conditions leads to:

$$p_0 + q_0 = 1$$

and

$$q_0 = \frac{\psi \frac{D}{D_P}}{\sqrt{\lambda \gamma \frac{D}{D_P}}} \tanh \left(\sqrt{\lambda \gamma \frac{D}{D_P}} \delta \right)$$

Considering fast catalysis, $\sqrt{\lambda \gamma \frac{D}{D_P}} \delta \rightarrow \infty$ (catalysis takes place in a reaction layer close to the electrode surface) and we obtain:

$$q_0 = \frac{\psi}{\sqrt{\lambda \gamma \frac{D_P}{D}}}$$

$$\text{thus: } \frac{\psi}{\sqrt{\lambda \gamma \frac{D_P}{D}}} = \frac{1}{1 + \exp(-\xi)}$$

An S-shaped wave is obtained with a plateau current given by $\psi_{pl} = \sqrt{\lambda \gamma \frac{D_P}{D}}$, i.e. $\frac{i_{pl}}{FS} = C_P^0 \sqrt{D_P k C_A^0}$ independent of rotation rate and identical to the catalytic plateau current obtained in cyclic voltammetry.²

Case 2: Small substrate concentration implying that its diffusion should be taken into account.

a is assumed to be constant in the reaction layer close to the electrode and equal to a_0

The equations to be solved in the diffusion layer are:

$$\frac{d^2 q}{dy^2} = \lambda a_0 \frac{D}{D_P} q$$

$$0 = \frac{D_P}{D} \frac{d^2 (p+q)}{dy^2}$$

which resolution, taking into account boundary and fast catalysis conditions, leads to:

$$p_0 + q_0 = 1$$

$$q_0 = \frac{\psi}{\sqrt{\lambda \frac{D_P}{D} a_0}}$$

We also have:

$$\frac{d^2 \left(a - \frac{D_P}{D} q \right)}{dy^2} = 0$$

Which resolution taking into account boundary conditions leads to:

$$a_0 = \gamma + \frac{D_P}{D} \frac{1}{1 + \exp(-\xi)} - \psi$$

Finally we obtain the following voltammogram equation:

$$\frac{\psi}{\gamma} = \frac{-\frac{\lambda}{\gamma} \frac{D_P}{D} + \sqrt{\left(\frac{\lambda}{\gamma} \frac{D_P}{D} \right)^2 + 4[1 + \exp(-\xi)]^2 \frac{\lambda}{\gamma} \frac{D_P}{D} \left(1 + \frac{D_P}{D} \frac{1}{\gamma[1 + \exp(-\xi)]} \right)}}{2[1 + \exp(-\xi)]^2}$$

At large overpotentials, i.e., when $\exp(-\xi) \rightarrow 0$, a plateau current is obtained:

$$\frac{\psi_{pl}}{\gamma} = \frac{\lambda}{2\gamma} \frac{D_P}{D} \left\{ \sqrt{1 + 4 \frac{\gamma}{\lambda} \frac{D}{D_P} \left(1 + \frac{D_P}{D} \frac{1}{\gamma} \right)} - 1 \right\}$$

indicating a mixed control by the catalytic reaction and diffusion. Note that a Koutecky-Levich plot ($1/i_{pl}$ vs. $1/\sqrt{\omega}$) would not be linear in that case.

When $\frac{\lambda}{\gamma} = \frac{kC_A^0}{D/\delta^2} \rightarrow \infty$ (total catalysis): $\psi_{pl} = \gamma + \frac{D_P}{D}$ i.e. $i_{pl} = \frac{FSDC_A^0}{\delta} + \frac{FSD_P C_P^0}{\delta}$. A linear Levich plot (i_{pl} vs. $\sqrt{\omega}$) is obtained.

When $\frac{\lambda}{\gamma} = \frac{kC_A^0}{D/\delta^2} \rightarrow 0$ (canonical catalysis): $\psi_{pl} = \sqrt{\lambda \gamma \frac{D_P}{D} \left(1 + \frac{D_P}{D} \frac{1}{\gamma} \right)}$ i.e. $i_{pl} = FSC_P^0 \sqrt{D_P k C_A^0 \left(1 + \frac{D_P}{D} \frac{C_P^0}{C_A^0} \right)}$ independent from rotation rate.

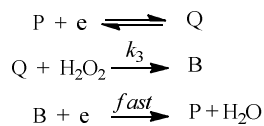
4. Estimation of H₂O₂ reduction rate constant

The RDEV plateau current for H₂O₂ reduction catalyzed by FeTMPyP assuming a simple two electron mechanism (scheme S3) controlled by the kinetics of reduction is given by :

$$\frac{i_{pl}}{FS} = 2\sqrt{D_{cat} k_3 [H_2O_2]} C_{cat}^0$$

With 1 mM catalyst, 1mM H₂O₂, 5.6 mm electrode diameter, the current observed in figure 8f leads to $k_3 = 10^4 \text{ M}^{-1}\text{s}^{-1}$.

Scheme S3



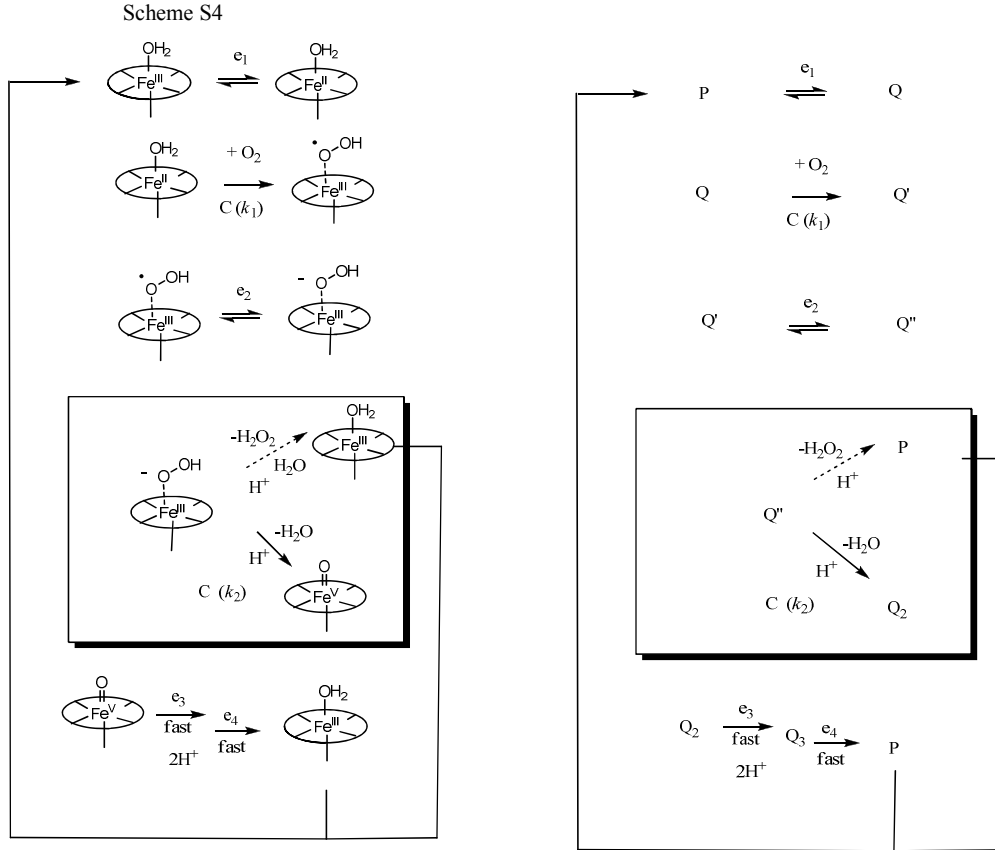
5. Proof of equations 1 to 3:

We consider the mechanism shown in Scheme S4 for a catalyst adsorbed on the electrode surface. This mechanism corresponds to the first wave of the heterogeneous catalytic process for O₂ reduction by FeTMPyP.

The total surface concentration of catalyst is Γ_0 , pure kinetic control is assumed (no interference of O₂ diffusion). All electron transfers are fast (Nernstian). Standard potential corresponding to electron transfers 2, 3 and 4 are much positive than the standard potential of the first electron transfer. All chemical rate constants are apparent first order rate constants.

The total current i is the sum of four contributions:

$$i = i_1 + i_2 + i_3 + i_4$$



The kinetic evolution of the various catalyst forms is described by :

$$\frac{d\Gamma_Q}{dt} = \frac{i_1}{FS} - k_1 \Gamma_Q$$

$$\frac{d\Gamma_{Q'}}{dt} = -\frac{i_2}{FS} + k_1 \Gamma_Q$$

$$\frac{d\Gamma_{Q''}}{dt} = \frac{i_2}{FS} - (k_{2,H_2O_2} + k_{2,H_2O}) \Gamma_{Q''}$$

$$\frac{d\Gamma_{Q_2}}{dt} = -\frac{i_3}{FS} + k_{2,H_2O} \Gamma_{Q''}$$

$$\frac{d\Gamma_{Q_3}}{dt} = \frac{i_4 - i_3}{FS}$$

with :

$$\Gamma^0 = \Gamma_P + \Gamma_Q + \Gamma_{Q'} + \Gamma_{Q''} + \Gamma_{Q_2} + \Gamma_{Q_3}$$

Application of Nernst relationships for each elementary electron transfer leads to :

$$\frac{\Gamma_P}{\Gamma_Q} = \exp\left[\frac{F}{RT}(E - E^0)\right] ; \frac{\Gamma_{Q'}}{\Gamma_{Q''}} = \exp\left[\frac{F}{RT}(E - E_2^0)\right] ; \frac{\Gamma_{Q_2}}{\Gamma_{Q_3}} = \exp\left[\frac{F}{RT}(E - E_3^0)\right] ; \frac{\Gamma_{Q_3}}{\Gamma_P} = \exp\left[\frac{F}{RT}(E - E_4^0)\right]$$

Taking account that a steady state is established in RDEV:

$$\frac{i_1}{FS} = \frac{i_2}{FS} = k_1 \Gamma_Q = (k_{2,H_2O_2} + k_{2,H_2O}) \Gamma_{Q''}$$

$$\frac{i_4}{FS} = \frac{i_3}{FS} = k_{2,H_2O} \Gamma_{Q''}$$

Therefore:

$$\frac{i}{FS} = \left(2 + 2 \frac{k_{2,H_2O}}{k_{2,H_2O_2} + k_{2,H_2O}}\right) k_1 \Gamma_Q$$

and

$$\Gamma^0 = \Gamma_Q \left[1 + \exp\left[\frac{F}{RT}(E - E^0)\right]\right] + \Gamma_{Q''} \left[1 + \exp\left[\frac{F}{RT}(E - E_2^0)\right]\right] + \Gamma_{Q_3} \left[1 + \exp\left[\frac{F}{RT}(E - E_3^0)\right]\right]$$

Because $E^0 \ll E_2^0$, $E^0 \ll E_3^0$, at the level of the catalytic wave we have : $1 \gg \exp\left[\frac{F}{RT}(E - E_2^0)\right]$ and $1 \gg \exp\left[\frac{F}{RT}(E - E_3^0)\right]$

It follows that:

$$\Gamma^0 = \Gamma_Q \left[1 + \exp\left[\frac{F}{RT}(E - E_{cat}^0)\right]\right] + \frac{k_1}{k_{2,H_2O_2} + k_{2,H_2O}}$$

Finally :

$$\frac{i}{FS} = \frac{2 \left(1 + \frac{k_{2,H_2O}}{k_{2,H_2O_2} + k_{2,H_2O}}\right) k_1 \Gamma^0}{1 + \frac{k_1}{k_{2,H_2O_2} + k_{2,H_2O}} + \exp\left[\frac{F}{RT}(E - E_{cat}^0)\right]}$$

And the plateau current is given by:

$$\frac{i_{pl}}{FS} = \frac{2 \left(1 + \frac{k_{2,H_2O}}{k_{2,H_2O_2} + k_{2,H_2O}}\right)}{\frac{1}{k_1} + \frac{1}{k_{2,H_2O_2} + k_{2,H_2O}}} \Gamma^0$$

and with introduction of

$$\left(\frac{\%H_2O_2}{100}\right) = \frac{k_{2,H_2O}}{k_{2,H_2O_2} + k_{2,H_2O}} \text{ then, } \frac{k_{2,H_2O}}{k_{2,H_2O_2} + k_{2,H_2O}} = 1 - \left(\frac{\%H_2O_2}{100}\right) :$$

$$\frac{i_{pl}}{FS} = n_{ap} \frac{\Gamma^0}{\frac{1}{k_1} + \frac{1}{k_{2,H_2O_2} + k_{2,H_2O}}} \text{ with } n_{ap} = 4 - 2 \left(\frac{\%H_2O_2}{100}\right)$$

$$i.e., \frac{i_{pl}}{FS} = n_{ap} k_{ap} \Gamma^0 \text{ with : } \frac{1}{k_{ap}} = \frac{1}{k_1} + \frac{1}{k_{2,H_2O_2} + k_{2,H_2O}}$$

The half-wave potential is thus given by :

$$E_{1/2} = E_{cat}^0 + \frac{RT}{F} \ln \left(1 + \frac{k_1}{k_{2,H_2O_2} + k_{2,H_2O}}\right)$$

If we consider that $k_1 \approx k_{2,H_2O_2} + k_{2,H_2O}$, it follows that:

$$\frac{i_{pl}}{FS} \approx \frac{n_{ap}}{2} k_1 \Gamma^0$$

6. Homogeneous catalysis of O₂ reduction by FeTMPyP with H₂O₂ reduction; proof of equations 4 and 5:

We consider the mechanism shown in scheme S5 for an homogeneous catalyst in the framework of rotating disk voltammetry. This mechanism corresponds to the first wave of the homogeneous catalytic process for O₂ reduction by FeTMPyP taking into account H₂O₂ reduction by the same catalyst. We consider no O₂ diffusion (pure kinetic control).

In steady-state conditions, as in the case in the rotating-disc electrode voltammetry, the following reaction-diffusion equations apply within the diffusion layer ($0 < x < \delta$ where δ is the thickness of the diffusion layer related to the rotation rate ω):

$$0 = D_{\text{cat}} \frac{d^2[Q]}{dx^2} - (k_1^{\text{hom}} + k_3[H_2O_2])[Q]$$

$$0 = D_{\text{cat}} \frac{d^2[Q']}{dx^2} + k_1^{\text{hom}}[Q]$$

$$0 = D_{\text{cat}} \frac{d^2[Q'']}{dx^2} - (k_{2,H_2O_2}^{\text{hom}} + k_{2,H_2O}^{\text{hom}})[Q'']$$

$$0 = D_{\text{cat}} \frac{d^2[Q_2]}{dx^2} + k_{2,H_2O}^{\text{hom}}[Q'']$$

$$0 = D_{\text{cat}} \frac{d^2[Q_3]}{dx^2}$$

$$0 = D_{\text{cat}} \frac{d^2[I]}{dx^2} + k_3[H_2O_2][Q]$$

$$0 = D \frac{d^2[H_2O_2]}{dx^2} + k_{2,H_2O_2}^{\text{hom}}[Q''] - k_3[H_2O_2][Q]$$

with the boundary conditions:

$$x = 0:$$

$$i = i_1 + i_2 + i_3 + i_4 + i_5$$

$$\frac{i_1}{FS} = -D_{\text{cat}} \left(\frac{d[Q]}{dx} \right)_{x=0}; \quad \frac{i_2}{FS} = -D_{\text{cat}} \left(\frac{d[Q']}{dx} \right)_{x=0}; \quad \frac{i_3}{FS} = -D_{\text{cat}} \left(\frac{d[Q_2]}{dx} \right)_{x=0}; \quad \frac{i_4}{FS} = D_{\text{cat}} \left(\frac{d[Q_3]}{dx} \right)_{x=0}; \quad \frac{i_5}{FS} = D_{\text{cat}} \left(\frac{d[I]}{dx} \right)_{x=0}$$

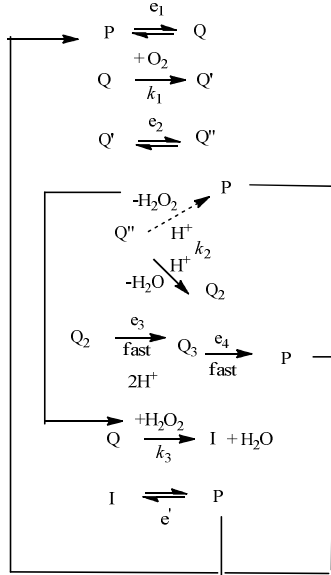
$$\left(\frac{d[H_2O_2]}{dx} \right)_{x=0} = 0$$

$$\frac{[P]_0}{[Q]_0} = \exp \left[\frac{F(E - E^0)}{RT} \right]; \quad \frac{[Q']_0}{[Q'']_0} = \exp \left[\frac{F(E - E_2^0)}{RT} \right]; \quad \frac{[Q_2]_0}{[Q_3]_0} = \exp \left[\frac{F(E - E_3^0)}{RT} \right]$$

$$x = \delta:$$

$$[P]_{\delta} = C_{\text{cat}}^0, [Q]_{\delta} = [Q']_{\delta} = [Q'']_{\delta} = [Q_2]_{\delta} = [Q_3]_{\delta} = [I]_{\delta} = 0, [H_2O_2]_{\delta} = 0$$

Scheme S5



We assume that the concentration of H_2O_2 is constant within the reaction layer, the size of which is much smaller than the diffusion layer owing to the fact that the catalytic reaction is fast. Thus:

$$0 = \frac{d^2[Q]}{dx^2} + \frac{d^2[Q']}{dx^2} + \frac{d^2[Q'']}{dx^2} + \frac{d^2[Q_2]}{dx^2} + \frac{d^2[Q_3]}{dx^2} + \frac{d^2[I]}{dx^2} + \frac{d^2[P]}{dx^2} \text{ leads to } C_{\text{cat}}^0 = [P]_0 + [Q]_0 + [Q']_0 + [Q'']_0 + [Q_2]_0 + [Q_3]_0 + [I]_0$$

$$\frac{d^2[Q]}{dx^2} = \frac{(k_1^{\text{hom}} + k_3[\text{H}_2\text{O}_2])}{D_{\text{cat}}} [Q] \text{ leads to } [Q]_0 = \frac{i_1}{FS\sqrt{D_{\text{cat}}(k_1^{\text{hom}} + k_3[\text{H}_2\text{O}_2])}}$$

$$\frac{d^2[Q'']}{dx^2} = \frac{(k_{2,\text{H}_2\text{O}_2}^{\text{hom}} + k_{2,\text{H}_2\text{O}}^{\text{hom}})}{D_{\text{cat}}} [Q''] \text{ leads to } [Q'']_0 = \frac{i_2}{FS\sqrt{D_{\text{cat}}(k_{2,\text{H}_2\text{O}_2}^{\text{hom}} + k_{2,\text{H}_2\text{O}}^{\text{hom}})}}$$

$$\frac{d^2[Q_3]}{dx^2} = 0 \text{ leads to } i_3 = i_4$$

$$\frac{d^2[Q] + [Q'] + [I]}{dx^2} = 0 \text{ leads to } i_1 = i_2 + i_5$$

$$\frac{1}{(k_{2,\text{H}_2\text{O}_2}^{\text{hom}} + k_{2,\text{H}_2\text{O}}^{\text{hom}})} \frac{d^2[Q'']}{dx^2} + \frac{1}{k_{2,\text{H}_2\text{O}}^{\text{hom}}} \frac{d^2[Q_2]}{dx^2} = 0, \text{ leading to: } i_3 = \frac{k_{2,\text{H}_2\text{O}}^{\text{hom}}}{k_{2,\text{H}_2\text{O}_2}^{\text{hom}} + k_{2,\text{H}_2\text{O}}^{\text{hom}}} i_2$$

$$\frac{1}{(k_1^{\text{hom}} + k_3[\text{H}_2\text{O}_2])} \frac{d^2[Q]}{dx^2} + \frac{1}{k_1^{\text{hom}}} \frac{d^2[Q']}{dx^2} = 0, \text{ leading to: } i_2 = \frac{k_1^{\text{hom}}}{k_1^{\text{hom}} + k_3[\text{H}_2\text{O}_2]} i_1$$

Then :

$$i = 2 \left(1 + \frac{k_{2,\text{H}_2\text{O}}^{\text{hom}}}{k_{2,\text{H}_2\text{O}_2}^{\text{hom}} + k_{2,\text{H}_2\text{O}}^{\text{hom}}} \frac{k_1^{\text{hom}}}{k_1^{\text{hom}} + k_3[\text{H}_2\text{O}_2]} \right) i_1$$

Applying then Nernst relationships:

$$C_{\text{cat}}^0 = [Q]_0 \left(1 + \exp \left[\frac{F}{RT} (E - E^0) \right] \right) + [Q'']_0 \left(1 + \exp \left[\frac{F}{RT} (E - E_2^0) \right] \right) + [Q_3]_0 \left(1 + \exp \left[\frac{F}{RT} (E - E_3^0) \right] \right) + [I]_0$$

Because $E^0 \ll E_2^0$, $E^0 \ll E_3^0$, at the level of the catalytic wave, we have :

$$1 \gg \exp \left[\frac{F}{RT} (E - E_2^0) \right] \text{ and } 1 \gg \exp \left[\frac{F}{RT} (E - E_3^0) \right] \text{ and hence :}$$

$$C_{\text{cat}}^0 = [Q]_0 \left(1 + \exp \left[\frac{F}{RT} (E - E^0) \right] \right) + [Q'']_0 + [Q_3]_0 + [I]_0 \approx [Q]_0 \left(1 + \exp \left[\frac{F}{RT} (E - E^0) \right] \right) + [Q'']_0$$

Finally :

$$C_{\text{cat}}^0 = \frac{i}{2 \left(1 + \frac{k_{2,\text{H}_2\text{O}}^{\text{hom}}}{k_{2,\text{H}_2\text{O}_2}^{\text{hom}} + k_{2,\text{H}_2\text{O}}^{\text{hom}}} \frac{k_1^{\text{hom}}}{k_1^{\text{hom}} + k_3 [\text{H}_2\text{O}_2]} \right) FS \sqrt{D_{\text{cat}} (k_1^{\text{hom}} + k_3 [\text{H}_2\text{O}_2])}} \left(1 + \exp \left[\frac{F}{RT} (E - E^0) \right] \right) + \frac{k_1^{\text{hom}}}{k_1^{\text{hom}} + k_3 [\text{H}_2\text{O}_2]} \frac{i}{2 \left(1 + \frac{k_{2,\text{H}_2\text{O}}^{\text{hom}}}{k_{2,\text{H}_2\text{O}_2}^{\text{hom}} + k_{2,\text{H}_2\text{O}}^{\text{hom}}} \frac{k_1}{k_1 + k_3 [\text{H}_2\text{O}_2]} \right) FS \sqrt{D_{\text{cat}} (k_{2,\text{H}_2\text{O}_2}^{\text{hom}} + k_{2,\text{H}_2\text{O}}^{\text{hom}})}}$$

Thus :

$$\frac{i}{FS} = \frac{2 \left(1 + \frac{k_{2,\text{H}_2\text{O}}^{\text{hom}}}{k_{2,\text{H}_2\text{O}_2}^{\text{hom}} + k_{2,\text{H}_2\text{O}}^{\text{hom}}} \frac{k_1^{\text{hom}}}{k_1^{\text{hom}} + k_3 [\text{H}_2\text{O}_2]} \right) \sqrt{D_{\text{cat}} (k_1^{\text{hom}} + k_3 [\text{H}_2\text{O}_2])} C_{\text{cat}}^0}{1 + \frac{\sqrt{k_1^{\text{hom}} + k_3 [\text{H}_2\text{O}_2]}}{\sqrt{k_{2,\text{H}_2\text{O}_2}^{\text{hom}} + k_{2,\text{H}_2\text{O}}^{\text{hom}}}} \left(\frac{k_1^{\text{hom}}}{k_1^{\text{hom}} + k_3 [\text{H}_2\text{O}_2]} \right) + \exp \left[\frac{F}{RT} (E - E^0) \right]}$$

At the plateau :

$$\frac{i_{\text{pl}}}{FS} = \frac{2 \left(1 + \frac{k_{2,\text{H}_2\text{O}}^{\text{hom}}}{k_{2,\text{H}_2\text{O}_2}^{\text{hom}} + k_{2,\text{H}_2\text{O}}^{\text{hom}}} \frac{k_1^{\text{hom}}}{k_1^{\text{hom}} + k_3 [\text{H}_2\text{O}_2]} \right) \sqrt{D_{\text{cat}} (k_1^{\text{hom}} + k_3 [\text{H}_2\text{O}_2])} C_{\text{cat}}^0}{1 + \frac{\sqrt{k_1^{\text{hom}} + k_3 [\text{H}_2\text{O}_2]}}{\sqrt{k_{2,\text{H}_2\text{O}_2}^{\text{hom}} + k_{2,\text{H}_2\text{O}}^{\text{hom}}}} \left(\frac{k_1^{\text{hom}}}{k_1^{\text{hom}} + k_3 [\text{H}_2\text{O}_2]} \right)}$$

Remark : if H_2O_2 is not reduced :

$$\frac{i}{FS} = \frac{2 \left(1 + \frac{k_{2,\text{H}_2\text{O}}^{\text{hom}}}{k_{2,\text{H}_2\text{O}_2}^{\text{hom}} + k_{2,\text{H}_2\text{O}}^{\text{hom}}} \right) \sqrt{D_{\text{cat}} k_1^{\text{hom}}} C_{\text{cat}}^0}{1 + \frac{\sqrt{k_1^{\text{hom}}}}{\sqrt{k_{2,\text{H}_2\text{O}_2}^{\text{hom}} + k_{2,\text{H}_2\text{O}}^{\text{hom}}}} + \exp \left[\frac{F}{RT} (E - E^0) \right]} = \frac{\left(4 - 2 \frac{\% \text{H}_2\text{O}_2}{100} \right) \sqrt{D_{\text{cat}} k_1^{\text{hom}}} C_{\text{cat}}^0}{1 + \frac{\sqrt{k_1^{\text{hom}}}}{\sqrt{k_{2,\text{H}_2\text{O}_2}^{\text{hom}} + k_{2,\text{H}_2\text{O}}^{\text{hom}}}} + \exp \left[\frac{F}{RT} (E - E^0) \right]} = \frac{n_{\text{ap}} \sqrt{D_{\text{cat}} k_1^{\text{hom}}} C_{\text{cat}}^0}{1 + \frac{\sqrt{k_1^{\text{hom}}}}{\sqrt{k_{2,\text{H}_2\text{O}_2}^{\text{hom}} + k_{2,\text{H}_2\text{O}}^{\text{hom}}}} + \exp \left[\frac{F}{RT} (E - E^0) \right]}$$

In the reaction layer:

$$D \frac{d^2 [\text{H}_2\text{O}_2]}{dx^2} + \frac{k_{2,\text{H}_2\text{O}}^{\text{hom}}}{(k_{2,\text{H}_2\text{O}_2}^{\text{hom}} + k_{2,\text{H}_2\text{O}}^{\text{hom}})} D_{\text{cat}} \frac{d^2 [Q'']}{dx^2} - \frac{k_3 [\text{H}_2\text{O}_2]}{(k_1^{\text{hom}} + k_3 [\text{H}_2\text{O}_2])} D_{\text{cat}} \frac{d^2 [Q]}{dx^2} = 0$$

Integration leads to:

$$D \frac{d [\text{H}_2\text{O}_2]}{dx} + \frac{k_{2,\text{H}_2\text{O}}^{\text{hom}}}{(k_{2,\text{H}_2\text{O}_2}^{\text{hom}} + k_{2,\text{H}_2\text{O}}^{\text{hom}})} D_{\text{cat}} \frac{d [Q'']}{dx} - \frac{k_3 [\text{H}_2\text{O}_2]}{(k_1^{\text{hom}} + k_3 [\text{H}_2\text{O}_2])} D_{\text{cat}} \frac{d [Q]}{dx} = \text{constant}$$

$$= - \frac{k_{2,\text{H}_2\text{O}_2}^{\text{het}}}{(k_{2,\text{H}_2\text{O}_2}^{\text{het}} + k_{2,\text{H}_2\text{O}}^{\text{het}})} \frac{i^{\text{het}}}{FS} - \frac{k_{2,\text{H}_2\text{O}_2}^{\text{hom}}}{(k_{2,\text{H}_2\text{O}_2}^{\text{hom}} + k_{2,\text{H}_2\text{O}}^{\text{hom}})} \frac{i_2}{FS} + \frac{k_3 [\text{H}_2\text{O}_2]}{(k_1^{\text{hom}} + k_3 [\text{H}_2\text{O}_2])} \frac{i_1}{FS}$$

$$\text{with } i_2 = \frac{k_1^{\text{hom}}}{k_1^{\text{hom}} + k_3 [\text{H}_2\text{O}_2]} i_1 \text{ and } i = 2 \left(1 + \frac{k_{2,\text{H}_2\text{O}}^{\text{hom}}}{k_{2,\text{H}_2\text{O}_2}^{\text{hom}} + k_{2,\text{H}_2\text{O}}^{\text{hom}}} \frac{k_1^{\text{hom}}}{k_1^{\text{hom}} + k_3 [\text{H}_2\text{O}_2]} \right) i_1$$

At the reaction layer boundary ($x = \mu$) $\frac{d[Q'']}{dx} \approx \frac{d[Q]}{dx} \approx 0$:

$$D \left(\frac{d[\text{H}_2\text{O}_2]}{dx} \right)_{\mu} = - \frac{k_{2,\text{H}_2\text{O}_2}^{\text{het}}}{k_{2,\text{H}_2\text{O}_2}^{\text{het}} + k_{2,\text{H}_2\text{O}}^{\text{het}}} \frac{i^{\text{het}}}{FS} + \left[- \frac{k_{2,\text{H}_2\text{O}_2}^{\text{hom}}}{k_{2,\text{H}_2\text{O}_2}^{\text{hom}} + k_{2,\text{H}_2\text{O}}^{\text{hom}}} \frac{k_1^{\text{hom}}}{k_1^{\text{hom}} + k_3[\text{H}_2\text{O}_2]} + \frac{k_3[\text{H}_2\text{O}_2]}{k_1^{\text{hom}} + k_3[\text{H}_2\text{O}_2]} \right] \frac{i}{2 \left(1 + \frac{k_{2,\text{H}_2\text{O}}^{\text{hom}}}{k_{2,\text{H}_2\text{O}_2}^{\text{hom}} + k_{2,\text{H}_2\text{O}}^{\text{hom}}} \frac{k_1^{\text{hom}}}{k_1^{\text{hom}} + k_3[\text{H}_2\text{O}_2]} \right) FS}$$

In the diffusion layer, the flux is constant. Thus at the diffusion layer outer boundary :

$$SD \left(\frac{d[\text{H}_2\text{O}_2]}{dx} \right)_{\delta} = - \frac{k_{2,\text{H}_2\text{O}_2}^{\text{het}}}{(k_{2,\text{H}_2\text{O}_2}^{\text{het}} + k_{2,\text{H}_2\text{O}}^{\text{het}})} \frac{i^{\text{het}}}{F} + \left[\frac{k_3[\text{H}_2\text{O}_2] - k_1^{\text{hom}} \frac{k_{2,\text{H}_2\text{O}_2}^{\text{hom}}}{k_{2,\text{H}_2\text{O}_2}^{\text{hom}} + k_{2,\text{H}_2\text{O}}^{\text{hom}}}}{k_1^{\text{hom}} + k_3[\text{H}_2\text{O}_2]} \right] \frac{i}{2 \left(1 + \frac{k_{2,\text{H}_2\text{O}}^{\text{hom}}}{k_{2,\text{H}_2\text{O}_2}^{\text{hom}} + k_{2,\text{H}_2\text{O}}^{\text{hom}}} \frac{k_1^{\text{hom}}}{k_1^{\text{hom}} + k_3[\text{H}_2\text{O}_2]} \right) F}$$

And, noting that : $-SD \left(\frac{d[\text{H}_2\text{O}_2]}{dx} \right)_{\delta} = \frac{dn_{\text{H}_2\text{O}_2}}{dt} = \frac{i_{\text{ring}}}{2FN_{\text{eff}}}$, we obtain :

$$\frac{i_{\text{ring}}}{2FN_{\text{eff}}} = \frac{i_{\text{ring}}^{\text{het}}}{2FN_{\text{eff}}} + \left[\frac{k_1^{\text{hom}} \frac{k_{2,\text{H}_2\text{O}_2}^{\text{hom}}}{k_{2,\text{H}_2\text{O}_2}^{\text{hom}} + k_{2,\text{H}_2\text{O}}^{\text{hom}}} - k_3[\text{H}_2\text{O}_2] \right] \frac{i}{2 \left(1 + \frac{k_{2,\text{H}_2\text{O}}^{\text{hom}}}{k_{2,\text{H}_2\text{O}_2}^{\text{hom}} + k_{2,\text{H}_2\text{O}}^{\text{hom}}} \frac{k_1^{\text{hom}}}{k_1^{\text{hom}} + k_3[\text{H}_2\text{O}_2]} \right) F} \quad \text{with } i = i_{\text{disk}}^{\text{hom}}$$

Then:

$$\frac{i_{\text{ring}}^{\text{hom}}}{2FN_{\text{eff}}} = \left[\frac{\frac{k_{2,\text{H}_2\text{O}_2}^{\text{hom}}}{k_{2,\text{H}_2\text{O}_2}^{\text{hom}} + k_{2,\text{H}_2\text{O}}^{\text{hom}}} - \frac{k_3[\text{H}_2\text{O}_2]}{k_1^{\text{hom}}}}{1 + \frac{k_3[\text{H}_2\text{O}_2]}{k_1^{\text{hom}}}} \right] \frac{i_{\text{disk}}^{\text{hom}}}{2 \left(1 + \frac{k_{2,\text{H}_2\text{O}}^{\text{hom}}}{k_{2,\text{H}_2\text{O}_2}^{\text{hom}} + k_{2,\text{H}_2\text{O}}^{\text{hom}}} \frac{1}{1 + \frac{k_3[\text{H}_2\text{O}_2]}{k_1^{\text{hom}}}} \right) F}$$

Remark : if H_2O_2 is not reduced, we are back to the classical relationship: $\frac{i_{\text{ring}}^{\text{hom}} / N_{\text{eff}}}{2i_{\text{disk}}^{\text{hom}}} = \frac{k_{2,\text{H}_2\text{O}_2}^{\text{hom}}}{2k_{2,\text{H}_2\text{O}_2}^{\text{hom}} + 4k_{2,\text{H}_2\text{O}}^{\text{hom}}}$

7. References:

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