

# On the understanding and design of bidirectional and reversible catalysts of multielectron, multistep reactions

## Supplementary material

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### S1 Procedure for computing the currents

In the following, we consider that only the concentration of the catalytic intermediates vary; the concentration of the substrates is assumed to be constant, so that all reactions follow pseudo first-order kinetics. We assume linear semi-infinite diffusion, with the electrode sitting at  $x = 0$ .

We will use vector space algebra for the derivation of the currents. The vector of the concentrations of the catalytic intermediates is denoted  $\mathbf{c}(x)$ , it is of size  $m$ , the number of different species in the catalytic cycle. We assume that all the catalytic intermediates diffuse with the same diffusion coefficient,  $D$ .

Since all the chemical reactions are first order, the change in concentration that results from the chemical reactions can be put under the form:

$$\left. \frac{\partial \mathbf{c}}{\partial t} \right|_{\text{chemistry}} = \check{\mathbf{K}} \mathbf{c} \quad (\text{S1})$$

in which  $\check{\mathbf{K}}$  is a  $m \times m$  matrix. The reaction-diffusion equation governing the concentration vector  $\mathbf{c}$  is written thus:

$$\frac{\partial \mathbf{c}}{\partial t} = D \frac{\partial^2 \mathbf{c}}{\partial x^2} + \left. \frac{\partial \mathbf{c}}{\partial t} \right|_{\text{chemistry}} \quad (\text{S2})$$

The stationary solution is therefore obtained by solving the equation:

$$D \frac{d^2 \mathbf{c}}{dx^2} = -\check{\mathbf{K}} \mathbf{c} \quad (\text{S3})$$

The boundary conditions for the diffusion/reaction problem are given by the electrode reactions at  $x = 0$ , governed by another  $m \times m$  matrix,  $k_0 \times \check{\mathbf{B}}$ :

$$D \left. \frac{\partial \mathbf{c}}{\partial x} \right|_{x=0} = k_0 \times \check{\mathbf{B}} \mathbf{c} \quad (\text{S4})$$

and at  $x = \infty$ , a null flux:

$$D \left. \frac{\partial \mathbf{c}}{\partial x} \right|_{x \rightarrow \infty} = \mathbf{0} \quad (\text{S5})$$

Assuming that the kinetic matrices  $\check{\mathbf{K}}$  are diagonalizable with real eigenvalues that are negative or null<sup>1</sup>, a general solution that satisfies equations (S3) and (S5) is:

$$\mathbf{c}(x) = \sum_i \alpha_i \mathbf{k}_i \exp -\frac{x}{\lambda_i} \quad (\text{S6})$$

in which  $\alpha_i$  is an integration coefficient determined below,  $\mathbf{k}_i$  is the  $i$ -th eigenvector of  $\check{\mathbf{K}}$ , and  $\lambda_i$  is defined by:

$$\lambda_i = \sqrt{-\frac{D}{\kappa_i}} \quad (\text{S7})$$

where  $\kappa_i$  is the  $i$ -th eigenvalue of  $\check{\mathbf{K}}$ .

Injecting equation (S6) into equation (S4) gives the following condition for the values of  $\alpha_i$ :

$$D \sum_i \frac{\alpha_i}{\lambda_i} \mathbf{k}_i - k_0 \times \check{\mathbf{B}} \sum_i \alpha_i \mathbf{k}_i = \mathbf{0} \quad (\text{S8})$$

Let us note  $\boldsymbol{\alpha}$  the coefficients  $\alpha_i$  ( $\boldsymbol{\alpha}$  is of dimension  $m$ , like  $\check{\mathbf{K}}$ ) and  $\check{\mathbf{k}}$  the matrix of eigenvectors, so that, by definition of  $\boldsymbol{\alpha}$  and  $\check{\mathbf{k}}$ :

$$\mathbf{c} = \check{\mathbf{k}} \boldsymbol{\alpha} \quad (\text{S9})$$

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<sup>1</sup>This assumption is verified for all matrices used herein.

Equation (S8) can therefore be written as:

$$\left(D \check{\mathbf{K}} \text{Diag } 1/\lambda_i - k_0 \check{\mathbf{B}} \check{\mathbf{K}}\right) \boldsymbol{\alpha} = 0 \quad (\text{S10})$$

Determining  $\boldsymbol{\alpha}$  is just a matter of solving equation (S10) with the additional constraint:

$$\sum_i c_i = c \quad (\text{S11})$$

in which  $c$  is the total concentration of catalyst.

To determine the flux of electrons reaching the electrode, one attributes a redox number to each species, in a vector  $\mathbf{q}$  (only the relative differences in oxidation number matter for the computation of the current). Using this vector, the flux of charges  $J$  is given by:

$$J = D \mathbf{q} \cdot \frac{d\mathbf{c}}{dx}(x=0) = D \sum_i \frac{\alpha_i}{\lambda_i} \mathbf{q} \cdot \mathbf{k}_i = \sum_i \alpha_i \sqrt{-\kappa_i} D \mathbf{q} \cdot \mathbf{k}_i \quad (\text{S12})$$

The value of the current is obtained in the limiting case of  $k_0 \rightarrow \infty$ .

For all the models below, we determine the current  $i = AFJ$  (where  $F$  is the Faraday constant) and express it under the following form:

$$i = \frac{i_{\text{lim}}^{\text{ox}} e_1^c e_2^c - i_{\text{lim}}^{\text{red}}}{1 + e_2^c + e_1^c e_2^c} \quad (\text{S13})$$

in which:

$$e_1^c = \exp \frac{F(E - E_{\text{cat}}^{n=1, \text{ox}})}{RT} \quad e_2^c = \exp \frac{F(E - E_{\text{cat}}^{n=1, \text{red}})}{RT} \quad (\text{S14})$$

We shall express  $e_1^c$  and  $e_2^c$  as a function of the following quantities

$$e_1 = \exp \frac{F(E - E_1^\circ)}{RT} \quad e_2 = \exp \frac{F(E - E_2^\circ)}{RT} \quad (\text{S15})$$

## S2 Demonstration that all ordered schemes give equation (1)

In this section, we demonstrate that, for all the ordered kinetic schemes that contain exactly two electron transfer steps, the current can be put under the form of equation (1).

Under the assumption of two distinct electron transfers, the only terms that depend on potential in the  $\check{\mathbf{B}}$  matrix are  $e_1^{1/2}$ ,  $e_1^{-1/2}$ ,  $e_2^{1/2}$  and  $e_2^{-1/2}$ , and only one of each. Therefore, the  $(D \check{\mathbf{K}} \text{Diag } 1/\lambda_i - k_0 \check{\mathbf{B}} \check{\mathbf{K}})$  matrix also contains terms that are linear combinations of these terms. As a consequence, the inverse of that matrix contains rational fractions of these terms, and only one of each. As a consequence, the maximal order of  $\exp F E / RT$  in these expressions is 2. Therefore, all the results can be put under the forms of equation (1).

## S3 EEC<sub>r</sub>



We define the concentration and the charge vectors as:

$$\mathbf{c} = ([\text{O}], [\text{I}], [\text{R}])^T \quad \mathbf{q} = (2, 1, 0)^T \quad (\text{S17})$$

The system matrices are given by:

$$\check{\mathbf{K}} = \begin{bmatrix} -k_{-2} & 0 & k_2 \\ 0 & 0 & 0 \\ k_{-2} & 0 & -k_2 \end{bmatrix} \quad \check{\mathbf{B}} = \begin{bmatrix} -e_1^{-1/2} & e_1^{1/2} & 0 \\ e_1^{-1/2} & -e_1^{1/2} - e_2^{-1/2} & e_2^{1/2} \\ 0 & e_2^{-1/2} & -e_2^{1/2} \end{bmatrix} \quad (\text{S18})$$

Solving for the current gives:

$$e_1^c = e_1 \quad e_2^c = e_2 \quad \frac{i_{\text{lim}}^{\text{red}}}{i_{\text{lim}}^{\text{ox}}} = \frac{k_2}{k_{-2}} \quad i_{\text{lim}}^{\text{red}} = 2 F A k_2 c \sqrt{\frac{D}{k_2 + k_{-2}}} \quad (\text{S19})$$

## S4 EC<sub>r</sub>EC<sub>r</sub>



We define the concentration and the charge vectors as:

$$\mathbf{c} = ([\text{O}], [\text{I}], [\text{X}], [\text{R}])^T \quad \mathbf{q} = (2, 1, 1, 0)^T \quad (\text{S21})$$

The system matrices are given by:

$$\check{\mathbf{K}} = \begin{bmatrix} -k_{-2} & 0 & 0 & k_2 \\ 0 & -k_1 & k_{-1} & 0 \\ 0 & k_1 & -k_{-1} & 0 \\ k_{-2} & 0 & 0 & -k_2 \end{bmatrix} \quad \check{\mathbf{B}} = \begin{bmatrix} -e_1^{-1/2} & e_1^{1/2} & 0 & 0 \\ e_1^{-1/2} & -e_1^{1/2} & 0 & 0 \\ 0 & 0 & -e_2^{-1/2} & e_2^{1/2} \\ 0 & 0 & e_2^{-1/2} & -e_2^{1/2} \end{bmatrix} \quad (\text{S22})$$

Solving for the current gives:

$$\frac{i_{\text{lim}}^{\text{red}}}{i_{\text{lim}}^{\text{ox}}} = \frac{\kappa_1 \kappa_2 (\kappa_{-1} + \kappa_{-2})}{\kappa_{-1} \kappa_{-2} (\kappa_1 + \kappa_2)} \quad i_{\text{lim}}^{\text{red}} = 2 F A \sqrt{D} \frac{\kappa_1 \kappa_2}{\kappa_1 + \kappa_2} \quad (\text{S23})$$

$$e_1^c = \frac{e_1 e_2 (\kappa_{-2} + \kappa_{-1})}{\kappa_1 e_2 + e_1 \kappa_2 + \kappa_{-2} e_1 + \kappa_{-1} e_2} \quad e_2^c = \frac{(\kappa_1 + \kappa_{-1}) e_2 + (\kappa_2 + \kappa_{-2}) e_1}{\kappa_1 + \kappa_2} \quad (\text{S24})$$

in which we have defined:

$$\kappa_1 = \frac{k_1}{\sqrt{k_1 + k_{-1}}} \quad \kappa_{-1} = \frac{k_{-1}}{\sqrt{k_1 + k_{-1}}} \quad \kappa_2 = \frac{k_2}{\sqrt{k_2 + k_{-2}}} \quad \kappa_{-2} = \frac{k_{-2}}{\sqrt{k_2 + k_{-2}}} \quad (\text{S25})$$

## S5 EEC<sub>r</sub>C<sub>r</sub>



We define the concentration and the charge vectors as:

$$\mathbf{c} = ([\text{O}], [\text{I}], [\text{R}], [\text{X}])^T \quad \mathbf{q} = (2, 1, 0, 0)^T \quad (\text{S27})$$

The system matrices are given by:

$$\check{\mathbf{K}} = \begin{bmatrix} -k_{-2} & 0 & 0 & k_2 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & -k_1 & k_{-1} \\ k_{-2} & 0 & k_1 & -k_2 - k_{-1} \end{bmatrix} \quad \check{\mathbf{B}} = \begin{bmatrix} -e_1^{-1/2} & e_1^{1/2} & 0 & 0 \\ e_1^{-1/2} & -e_1^{1/2} - e_2^{-1/2} & e_2^{1/2} & 0 \\ 0 & e_2^{-1/2} & -e_2^{1/2} & 0 \\ 0 & 0 & 0 & 0 \end{bmatrix} \quad (\text{S28})$$

Solving for the current gives:

$$\frac{i_{\text{lim}}^{\text{red}}}{i_{\text{lim}}^{\text{ox}}} = \frac{k_1 k_2}{k_{-1} k_{-2}} \times \frac{k_2 + k_{-2} + k_{-1} + \sqrt{\kappa}}{k_2 + k_1 + k_{-1} + \sqrt{\kappa}} \quad (\text{S29})$$

$$e_1^c = e_1 \times \frac{\sqrt{\kappa} \times (k_{-1} + k_{-2} + k_2 + \sqrt{\kappa})}{(k_2 + k_{-1}) \sqrt{\kappa} + k_2 k_1 + k_{-2} k_{-1}} \quad e_2^c = e_2 \times \frac{(k_2 + k_{-1}) \sqrt{\kappa} + k_2 k_1 + k_{-2} k_{-1}}{\sqrt{\kappa} \times (k_2 + k_1 + k_{-1} + \sqrt{\kappa})} \quad (\text{S30})$$

$$i_{\text{lim}}^{\text{red}} = \left\{ \frac{1}{2} F A \sqrt{D} k_2 k_1 [\alpha_1 (\beta_1 + \alpha_3 \beta_2) + \alpha_2 (\beta_1 - \alpha_3 \beta_2)] \right\} / \left\{ (-k_1 + k_{-2}) (k_2 k_1 + k_{-2} k_{-1} + k_{-2} k_1) \sqrt{\kappa} \right. \\ \left. + k_{-1} k_{-2} (k_1 + k_2 + k_{-1})^2 + k_1 k_2 (k_2 + k_{-2})^2 + k_{-1} k_2 (k_{-2}^2 + 2 k_2 k_1 + k_1 k_{-1} + k_1^2) \right\} \quad (\text{S31})$$

in which we have defined:

$$\kappa = k_2 k_1 + k_1 k_{-2} + k_{-1} k_{-2} \quad (\text{S32})$$

$$\alpha_1^2 = 2 [(k_1 + k_2 + k_{-1} + k_{-2}) - \alpha_3] \quad (\text{S33})$$

$$\alpha_2^2 = 2 [(k_1 + k_2 + k_{-1} + k_{-2}) + \alpha_3] \quad (\text{S34})$$

$$\alpha_3^2 = (k_1 + k_2 + k_{-1} + k_{-2})^2 - 4 \kappa \quad (\text{S35})$$

$$\beta_1 = (k_{-1} + k_2)^2 - k_2 k_1 + k_1 k_{-1} + k_{-2}^2 + 2 k_{-2} k_2 - k_{-2} k_1 \quad (\text{S36})$$

$$\beta_2 = k_{-1} + k_2 + k_{-2} \quad (\text{S37})$$

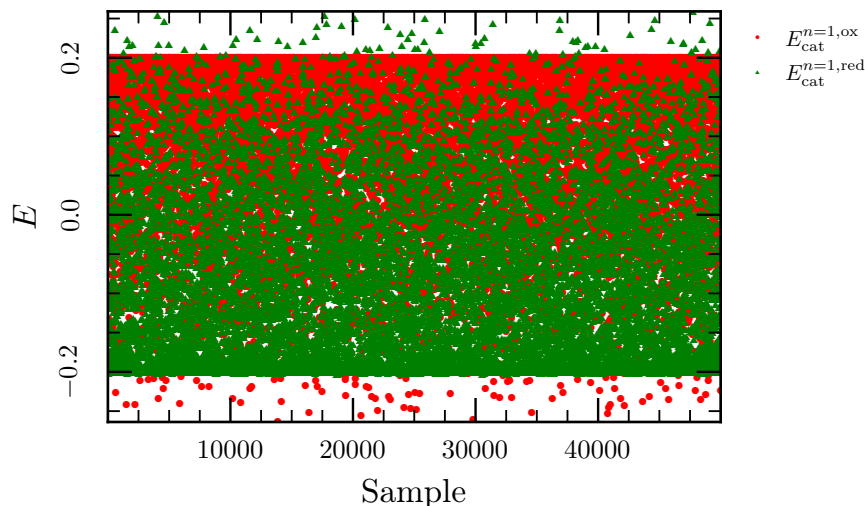


Figure S1: Catalytic potentials determined from simulations of 50000 random selection of parameters

The limiting case  $k_{-1} = k_{-2} = 0$ , (corresponding to an  $\text{EEC}_i\text{C}_i$  reaction) was treated by Costentin and coworkers [1]. In that limit, we obtain from equation (S30):

$$\frac{e_2}{e_2^c} = 1 + \sqrt{\frac{k_1}{k_2}} \times \frac{1}{1 + \sqrt{\frac{k_2}{k_1}}} \quad (\text{S38})$$

which is equivalent to the expression of  $E_{1/2}$  in table 2 of ref 1, and equation (S31) simplifies into:

$$i_{\text{lim}}^{\text{red}} = 2 F A \sqrt{D} \frac{\sqrt{k_1} k_2 (k_2 - k_1)}{k_2^2 - k_1 \sqrt{k_1} k_2} \quad (\text{S39})$$

Further rearrangements yield the expression of  $i_{pl}$  in table 2 of ref 1.

## S6 $\text{EEC}_r\text{C}_r\text{C}_r$

We did not attempt to derive the full equation for the  $\text{EEC}_r\text{C}_r\text{C}_r$  model. We rather simulated a series of (adsorbed) voltammograms using an  $\text{EEC}_r\text{C}_r\text{C}_r$  kinetic scheme, with chemical rate constants randomly selected with a log uniform distribution between  $10^{-4}$  and  $10^4$ , and fitted each resulting voltammogram using an  $\text{EEC}_r$  model, and plotted the resulting values of the fitted catalytic potentials in figure S1. Clearly, no value of  $E_{\text{cat}}^{n=1,\text{ox}}$  is above  $E_1^\circ = 0.2$  V, while no value of  $E_{\text{cat}}^{n=1,\text{red}}$  is below  $E_2^\circ = -0.2$  V, which demonstrate that the conclusion that in the  $\text{EEC}_r\text{C}_r$  model, the catalytic potentials are moved towards lower driving force still holds for the  $\text{EEC}_r\text{C}_r\text{C}_r$  model.

## S7 Monte-carlo simulations for detemining the correlation between reversibility and equilibrium constants in the $\text{EC}_r\text{EC}_r$

To study the correlation between the equilibrium rate constants and the difference in the catalytic potentials in the case of the  $\text{EC}_r\text{EC}_r$  model, we have run a Monte-Carlo simulation in which we drew randomly a million different sets of the four rate constants  $k_1$ ,  $k_{-1}$ ,  $k_2$  and  $k_{-2}$ , and calculated the difference in the catalytic potentials, assuming  $E_1^\circ = 0.2$  V and  $E_2^\circ = -0.2$  V, and using the formulas for the adsorbed model. Out of these, we selected the sets that gave a bias close to one, i.e.  $\left| \log_{10} \left( i_{\text{red}}^{\text{lim}} / i_{\text{ox}}^{\text{lim}} \right) \right| < 0.3$ , and plotted the difference between the catalytic potentials as a function of the values of the equilibrium constants  $K_1$  and  $K_2$  (figure S2). The results show no correlation between the difference in the catalytic potentials and  $K_2$  (figure S2, right panel), and correlation between the difference in the catalytic potentials and  $K_1$  only in the case of crossed catalytic potentials  $E_{\text{cat}}^{n=1,\text{ox}} - E_{\text{cat}}^{n=1,\text{red}} < 30$  mV.

## References

- [1] C. Costentin and J.-M. Savéant. Multielectron, multistep molecular catalysis of electrochemical reactions: Benchmarking of homogeneous catalysts. *ChemElectroChem*, **1** (7), 1226–1236, July 2014. doi: [10.1002/celec.201300263](https://doi.org/10.1002/celec.201300263).

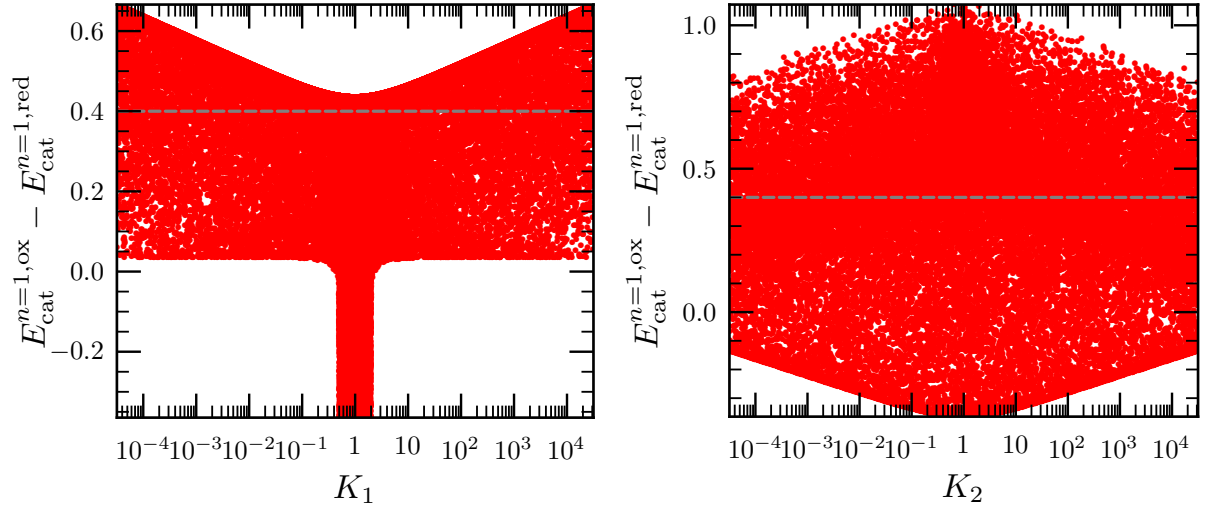


Figure S2: Plot of the difference in the catalytic potentials as a function of  $K_1$  and  $K_2$  for selected simulations with a bias close to unity. The horizontal gray line marks  $E_1^o - E_2^o$ , so that anything below that line corresponds to an increase in the reversibility with respect to the non-catalytic potentials.

	$E_1^o$	$k_{01}$	$E_2^o$	$k_{02}$	$k_1$	$k_{-1}$	$k_2$	$k_{-2}$
Fig. 4A (EEC <sub>r</sub> )	0.2	1	-0.2	1			40	40
Fig. 4B (EEC <sub>r</sub> )	-0.2	10 <sup>3</sup>	0.2	10 <sup>3</sup>			40	40
Fig. 4C (EEC <sub>r</sub> C <sub>r</sub> )	0.2	10 <sup>9</sup>	-0.2	10 <sup>9</sup>	10 <sup>7</sup>	10 <sup>5</sup>	10 <sup>5</sup>	10 <sup>7</sup>
Fig. 4D (EC <sub>r</sub> EC <sub>r</sub> )	0.2	10 <sup>3</sup>	-0.2	10 <sup>3</sup>	10 <sup>7</sup>	10 <sup>5</sup>	10 <sup>2</sup>	10 <sup>2</sup>
Fig. 5A (EEC <sub>r</sub> C <sub>r</sub> )	0.125	10 <sup>5</sup>	-0.125	10 <sup>5</sup>	10 <sup>10</sup>	10 <sup>6</sup>	10 <sup>6</sup>	10 <sup>10</sup>
Fig. 5B (EEC <sub>r</sub> C <sub>r</sub> )	0.125	10 <sup>5</sup>	-0.125	10 <sup>5</sup>	10 <sup>6</sup>	10 <sup>6</sup>	10 <sup>6</sup>	10 <sup>6</sup>
Fig. 5C (EEC <sub>r</sub> C <sub>r</sub> )	-0.3	10 <sup>5</sup>	0.3	10 <sup>5</sup>	10 <sup>6</sup>	10 <sup>6</sup>	10 <sup>6</sup>	10 <sup>6</sup>
Fig. 6A (EC <sub>r</sub> EC <sub>r</sub> )	0.2	10 <sup>5</sup>	-0.2	10 <sup>5</sup>	10 <sup>6</sup>	10 <sup>6</sup>	10 <sup>11</sup>	10 <sup>11</sup>
Fig. 6B (EC <sub>r</sub> EC <sub>r</sub> )	0.2	10 <sup>5</sup>	-0.2	10 <sup>5</sup>	10 <sup>6</sup>	10 <sup>6</sup>	10 <sup>6</sup>	10 <sup>6</sup>
Fig. 6C (EC <sub>r</sub> EC <sub>r</sub> )	0.2	10 <sup>5</sup>	-0.2	10 <sup>5</sup>	10	10	10 <sup>6</sup>	10 <sup>6</sup>

Table S1: Parameters of the simulations