

Supporting Information

Guidelines for the Voltammetric Study of Electrode Reactions with Coupled Chemical Kinetics at an Arbitrary Electrode Geometry

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SI-1. Boundary value problem (bvp) of a single variable for the CEC mechanism at an arbitrary electrode geometry

Let us consider the voltammetric response of a CEC mechanism as given in Scheme (I) of the main text when an electrode of any geometry is employed. The bvp under conditions where diffusion is the only mass transport mechanism of the electroactive species and they show equal diffusion coefficients (D) is given by:

$$\left. \begin{aligned} \frac{\partial c_B(q,t)}{\partial t} &= D\nabla_G^2 c_B(q,t) - k_1 c_B(q,t) + k_2 c_C(q,t) \\ \frac{\partial c_C(q,t)}{\partial t} &= D\nabla_G^2 c_C(q,t) + k_1 c_B(q,t) - k_2 c_C(q,t) \\ \frac{\partial c_D(q,t)}{\partial t} &= D\nabla_G^2 c_D(q,t) - k_3 c_D(q,t) + k_4 c_E(q,t) \\ \frac{\partial c_E(q,t)}{\partial t} &= D\nabla_G^2 c_E(q,t) + k_3 c_D(q,t) - k_4 c_E(q,t) \end{aligned} \right\} \quad (2)$$

$$\left. \begin{aligned} t=0, q \geq q_s \\ t > 0, q \rightarrow \infty \end{aligned} \right\} \quad c_B(q,t) = c_B^*; \quad c_C(q,t) = c_C^*; \quad c_D(q,t) = c_D^*; \quad c_E(q,t) = c_E^* \quad (3)$$

$$t > 0, q = q_s,$$

$$\left(\frac{\partial c_C(q,t)}{\partial q_N} \right)_{q=q_s} = - \left(\frac{\partial c_D(q,t)}{\partial q_N} \right)_{q=q_s} \quad (4)$$

$$\left(\frac{\partial c_B(q,t)}{\partial q_N} \right)_{q=q_s} = \left(\frac{\partial c_E(q,t)}{\partial q_N} \right)_{q=q_s} = 0 \quad (5)$$

$$\frac{c_C(q_s,t)}{c_D(q_s,t)} = e^{\eta(t)} \quad (6)$$

where q_N is the coordinate normal to the electrode surface, q_s are the values of the spatial coordinates (q) at the electrode surface and ∇_G^2 is the Laplacian operator for a given electrode geometry (G) (see Table S1)^a. Also, a Nernstian behaviour has been assumed for the charge transfer reaction (Eq. (6)). The above conditions are common for any electrode geometry, and they are the only ones necessary for (hemi)spherical electrodes (Figure S1A). For some

^a For example, in the case of (hemi)spherical electrodes (Fig. S1A) $q \equiv r$, $q_N \equiv r$, $q_s = r_0$ and $\nabla_{sp}^2 = \frac{\partial^2}{\partial r^2} + \frac{2}{r} \frac{\partial}{\partial r}$, whereas at discs (Fig. S1B) $q \equiv \{r, z\}$, $q_N \equiv z$, $q_s = \{0 \leq r \leq r_0, z = 0\}$ and $\nabla_{disc}^2 = \frac{\partial^2}{\partial r^2} + \frac{1}{r} \frac{\partial}{\partial r} + \frac{\partial^2}{\partial z^2}$.

geometries, additional boundary conditions are to be considered; for example, for disc electrodes (Figure S1B), Eqs. (7) and (8) hold,

Axial symmetry

$$t > 0, r = 0, z > 0, \left(\frac{\partial c_B(r, z, t)}{\partial r} \right)_{r=0} = \left(\frac{\partial c_C(r, z, t)}{\partial r} \right)_{r=0} = \left(\frac{\partial c_D(r, z, t)}{\partial r} \right)_{r=0} = \left(\frac{\partial c_E(r, z, t)}{\partial r} \right)_{r=0} = 0 \quad (7)$$

Insulating supporting surface

$$t > 0, r > r_0, z = 0, \left(\frac{\partial c_B(r, z, t)}{\partial z} \right)_{z=0} = \left(\frac{\partial c_C(r, z, t)}{\partial z} \right)_{z=0} = \left(\frac{\partial c_D(r, z, t)}{\partial z} \right)_{z=0} = \left(\frac{\partial c_E(r, z, t)}{\partial z} \right)_{z=0} = 0 \quad (8)$$

Introducing the variables,

$$c_1(q, t) = c_B(q, t) + c_C(q, t), \quad c_2(q, t) = c_D(q, t) + c_E(q, t) \quad (9)$$

$$\phi_1(q, t) = c_B(q, t) - K_1 c_C(q, t), \quad \phi_2(q, t) = c_D(q, t) - \frac{1}{K_2} c_E(q, t) \quad (10)$$

and taking into account that the total concentration remains constant over time and space^{1,2}, $c_1(q, t) + c_2(q, t) = c_T^*$, the bvp (2)-(6) becomes into the following three-variable problem:

$$\begin{aligned} \frac{\partial c_1(q, t)}{\partial t} &= D \nabla_G^2 c_1(q, t) \\ \frac{\partial \phi_i(q, t)}{\partial t} &= D \nabla_G^2 \phi_i(q, t) - \kappa_i \phi_i(q, t) \quad (i = 1, 2) \end{aligned} \quad (11)$$

$$\left. \begin{aligned} t = 0, q \geq q_s \\ t > 0, q \rightarrow \infty \end{aligned} \right\} c_1(q, t) = c_1^* = c_B^* + c_C^*, \quad \phi_1(q, t) = \phi_2(q, t) = 0 \quad (12)$$

$$t > 0, q = q_s,$$

$$\frac{1 + K_2}{K_2(1 + K_1)} \left[\left(\frac{\partial c_1(q, t)}{\partial q_N} \right)_{q=q_s} - \left(\frac{\partial \phi_1(q, t)}{\partial q_N} \right)_{q=q_s} \right] = \left(\frac{\partial c_1(q, t)}{\partial q_N} \right)_{q=q_s} - \frac{1}{K_2} \left(\frac{\partial \phi_2(q, t)}{\partial q_N} \right)_{q=q_s} \quad (13)$$

$$\left(\frac{\partial c_1(q, t)}{\partial q_N} \right)_{q=q_s} = -\frac{1}{K_1} \left(\frac{\partial \phi_1(q, t)}{\partial q_N} \right)_{q=q_s} \quad (14)$$

$$\frac{1 + K_2}{K_2(1 + K_1)} [c_1(q_s, t) - \phi_1(q_s, t)] = e^{\eta(t)} \left[\frac{1}{K_2} (c_T^* - c_1(q_s, t)) + \phi_2(q_s, t) \right] \quad (15)$$

Additionally, for disc electrodes, Eqs. (16) and (17) fulfill,

Axial symmetry

$$t > 0, r = 0, z > 0, \left(\frac{\partial c_1(r, z, t)}{\partial r} \right)_{r=0} = \left(\frac{\partial \phi_1(r, z, t)}{\partial r} \right)_{r=0} = \left(\frac{\partial \phi_2(r, z, t)}{\partial r} \right)_{r=0} = 0 \quad (16)$$

Insulating supporting surface

$$t > 0, r > r_0, z = 0, \left(\frac{\partial c_1(r, z, t)}{\partial z} \right)_{z=0} = \left(\frac{\partial \phi_1(r, z, t)}{\partial z} \right)_{z=0} = \left(\frac{\partial \phi_2(r, z, t)}{\partial z} \right)_{z=0} = 0 \quad (17)$$

SI-1.1 The kinetic steady state treatment

At this point, the introduction of the so-called kinetic steady state, kss, treatment, which assumes that the perturbation of the chemical equilibrium is independent of time (see Eq. (18)), is very convenient to further simplify the mathematical problem while warranting accurate results when the chemical kinetics is not very slow^{3,4}.

- **Spherical electrodes**

By assuming the kinetic steady state (kss) approximation for both equilibrium perturbation functions, ϕ_1 and ϕ_2 ^{3,5}, that is:

$$\frac{\partial \phi_i(r, t)}{\partial t} = 0 \quad (i=1, 2) \quad (18)$$

which implies that,

$$\phi_i(r) = \phi_i(r_0) \frac{r_0}{r} e^{-\sqrt{\kappa_i/D}(r-r_0)} \quad (i=1, 2) \quad (19)$$

then,

$$\left(\frac{\partial \phi_i}{\partial r} \right)_{r=r_0} = -\frac{\phi_i(r_0)}{\delta_{r,i}^{sp}} \quad (i=1, 2) \quad (20)$$

where the expression of $\delta_{r,i}^{sp}$ is given by Eq. (9) of the main text (see also Table S1).

- **Disc electrodes**

Provided that the average surface flux of ϕ_i ($i=1, 2$) can be expressed as the product of a function independent of the surface conditions (specifically, the inverse of the thickness of the linear reaction layer, $\delta_{r,i}^{disc}$) and a potential-dependent function (the ϕ_i -value at the electrode surface) that take an approximately uniform value across the electrode surface ($\phi_i(0 \leq r \leq r_0, z=0) \approx \langle \phi_i \rangle_{z=0}$ and $\delta_{r,i}^{disc}(0 \leq r \leq r_0) \approx \langle \delta_{r,i}^{disc} \rangle$), then it follows that:

$$t > 0, 0 \leq r \leq r_0, z = 0: \left(\frac{\partial \phi_i}{\partial z} \right)_{z=0} \approx \left\langle \left(\frac{\partial \phi_i}{\partial z} \right)_{z=0} \right\rangle \approx -\frac{\langle \phi_i \rangle_{z=0}}{\langle \delta_{r,i}^{disc} \rangle} \quad (i=1, 2) \quad (21)$$

where the $\langle \delta_{r,i}^{\text{disc}} \rangle$ -value at disc electrodes can be calculated accurately from⁶⁻⁸:

$$\langle \delta_{r,i}^{\text{disc}} \rangle = r_0 \frac{\pi}{4} \left\{ \frac{1 + 1.3650 r_0 \sqrt{\frac{\kappa_i}{D}} + 0.8826 r_0^2 \frac{\kappa_i}{D} + 0.32853 \left(r_0^2 \frac{\kappa_i}{D} \right)^{3/2} + 0.063566 \left(r_0^2 \frac{\kappa_i}{D} \right)^2}{1 + 2.0016 r_0 \sqrt{\frac{\kappa_i}{D}} + 1.8235 r_0^2 \frac{\kappa_i}{D} + 0.96367 \left(r_0^2 \frac{\kappa_i}{D} \right)^{3/2} + 0.307949 \left(r_0^2 \frac{\kappa_i}{D} \right)^2 + 0.049925 \left(r_0^2 \frac{\kappa_i}{D} \right)^{5/2}} \right\} (i=1,2) \quad (22)$$

- **Any electrode geometry**

Extending the results in Eqs. (20) and (21) for any electrode geometry, the surface gradient of the equilibrium-perturbation functions ϕ_i within the kss treatment can be written in general as^{7,8}:

$$\left(\frac{\partial \phi_i}{\partial q_N} \right)_{q=q_s} \approx \left\langle \left(\frac{\partial \phi_i}{\partial q_N} \right)_{q=q_s} \right\rangle \approx - \frac{\langle \phi_i \rangle_{q=q_s}}{\langle \delta_{r,i}^G \rangle} (i=1,2) \quad (23)$$

that is rigorously true at (hemi)spherical electrodes. Note that the expression for $\langle \delta_{r,i}^G \rangle$ can be derived for other electrode geometries from the corresponding analytical solutions for the steady state limiting current of the catalytic mechanism as discussed elsewhere⁸.

SI-1.2 Single variable bvp for any electrode geometry

Attending to (23), the bvp (11)-(15) is simplified to the following single variable problem (see Table S1),

$$\frac{\partial c_1(q,t)}{\partial t} = D \nabla_G^2 c_1(q,t) \quad (24)$$

$$\left. \begin{array}{l} t=0, q \geq q_s \\ t>0, q \rightarrow \infty \end{array} \right\} c_1(q,t) = c_1^* = c_B^* + c_C^* \quad (25)$$

$$t>0, q=q_s$$

$$\begin{aligned} \left(\frac{\partial c_1(q,t)}{\partial q_N} \right)_{q=q_s} &= \frac{1 + K_2 + (1 + K_1) e^{\eta(t)}}{\langle \delta_{r,1}^G \rangle K_1 (1 + K_2) + \langle \delta_{r,2}^G \rangle e^{\eta(t)} K_2 (1 + K_1)} \left[(c_1(q_s,t) - (c_1^* + c_2^*)) \frac{(1 + K_1) e^{\eta(t)}}{1 + K_2 + (1 + K_1) e^{\eta(t)}} \right] \\ &= \Lambda^G (A + B) [c_1(q_s,t) - c_{1,\text{eq}}^{\text{sur}}] \end{aligned} \quad (26)$$

where $c_{1,\text{eq}}^{\text{sur}}$ is given in Table S1. Additionally, in the case of disc electrodes,

Axial symmetry

$$t>0, r=0, z>0: \left(\frac{\partial c_1(r,z,t)}{\partial r} \right)_{r=0} = 0 \quad (27)$$

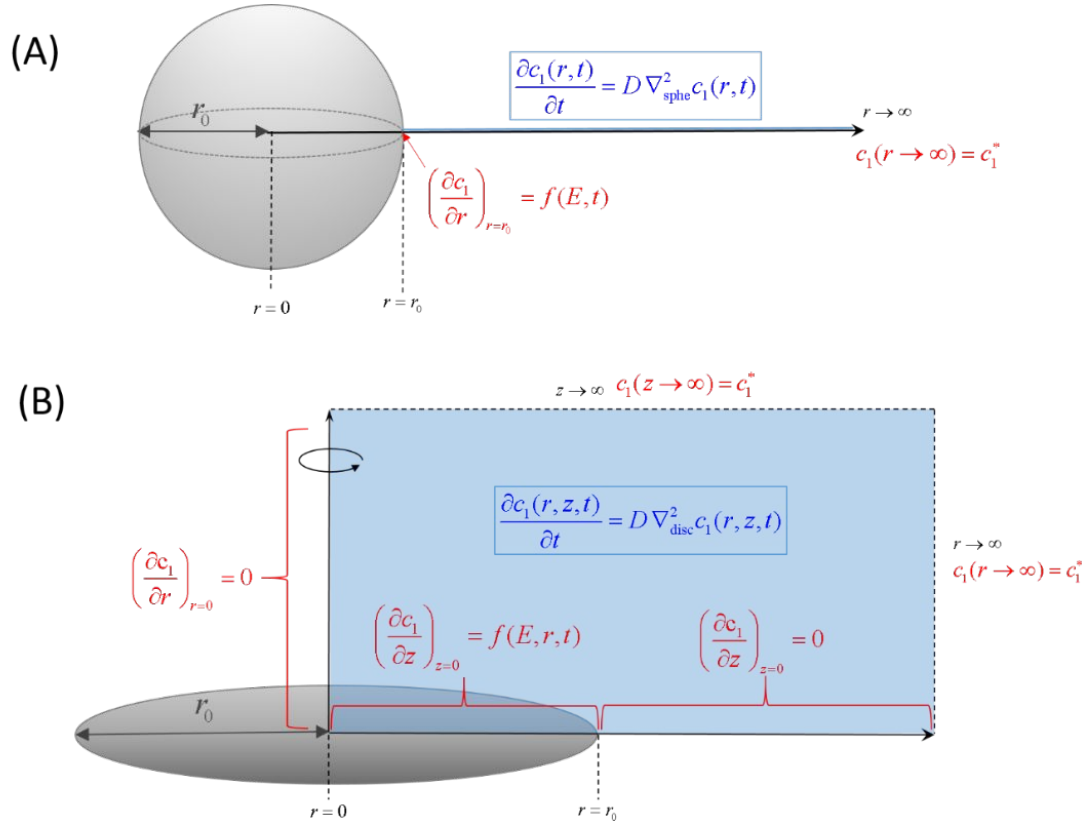
Insulating supporting surface

$$t > 0, r > r_0, z = 0: \left(\frac{\partial c_1(r, z, t)}{\partial z} \right)_{z=0} = 0 \quad (28)$$

Eqs. (24)-(26) for the CEC mechanism are formally identical whatever the shape and size of the electrode, the influence of which is included in the Laplacian operator, ∇_G^2 , and in the parameter Λ^G , which also accounts for the influence of the homogeneous chemical kinetics (see Table S1, where the particular cases of the CE and EC mechanisms are also included).^b

^b It is worth highlighting that the bvp (24)-(26) is fully equivalent to that of the E_{irrev} mechanism, with Λ being independent of the electrode geometry in this case (see Table S1)^{5,12}.

Figure S1. Schematics of the boundary value problems corresponding to **(A)** spherical and **(B)** disc electrodes (see Table S1 for definitions).



SI-2. Analytical solution of the CEC mechanism in single pulse techniques under spherical diffusion

To solve the problem given by general Eqs. (24)-(26) in the particular case of spherical diffusion we introduce the following variable change,

$$u_1(r, t) = \frac{c_1(r, t) - c_1^*}{c_1^*} \frac{r}{r_0} \quad (29)$$

Thus, Eqs. (24)-(26) become into,

$$\frac{\partial u_1(r, t)}{\partial t} - D \frac{\partial^2 u_1(r, t)}{\partial r^2} = 0 \quad (30)$$

$$\left. \begin{array}{l} t = 0, \quad r \geq r_0 \\ t \geq 0, \quad r \rightarrow \infty \end{array} \right\} u_1(r, t) = 0 \quad (31)$$

$$t > 0, r = r_0,$$

$$\left(\frac{\partial u_1(r, t)}{\partial r} \right)_{r=r_0} = \Lambda^{\text{sp}} (A + B) \gamma^{\text{sp}} \left[u_1(r_0, t) - \frac{u_{1, \text{eq}}^{\text{sur}}}{\gamma^{\text{sp}}} \right] \quad (32)$$

where,

$$\gamma^{\text{sp}} = 1 + \frac{1}{r_0 \Lambda^{\text{sp}} (A + B)} \quad (33)$$

$$u_{1, \text{eq}}^{\text{sur}} = \frac{c_{1, \text{eq}}^{\text{sur}} - c_1^*}{c_1^*} \quad (34)$$

and the expressions for Λ^{sp} , A , B and $c_{1, \text{eq}}^{\text{sur}}$ are given in Table S1.

By introducing the variables,

$$s = \frac{r - r_0}{2\sqrt{Dt}} \quad (35)$$

$$\chi^{\text{sp}} = 2\sqrt{Dt} \Lambda^{\text{sp}} (A + B) \gamma^{\text{sp}} \quad (36)$$

Eqs. (30)-(32) turn into:

$$\frac{\partial^2 u_1(s, \chi^{\text{sp}})}{\partial s^2} + 2s \frac{\partial u_1(s, \chi^{\text{sp}})}{\partial s} - 2\chi^{\text{sp}} \frac{\partial u_1(s, \chi^{\text{sp}})}{\partial \chi^{\text{sp}}} = 0 \quad (37)$$

$$s \rightarrow \infty, \quad u_1(s \rightarrow \infty) = 0 \quad (38)$$

$s = 0$:

$$\left(\frac{\partial u_1(s, \chi^{\text{sp}})}{\partial s} \right)_{s=0} = \chi^{\text{sp}} \left[u_1(0, \chi^{\text{sp}}) - \frac{u_{1, \text{eq}}^{\text{sur}}}{\gamma^{\text{sp}}} \right] \quad (39)$$

The solution of Eq. (37) with the boundary conditions given by Eqs. (38)-(39) can be written as follows^{9,10},

$$u_1(r, t) = u_1(s, \chi^{sp}) = \sum_{j=0}^{\infty} \sigma_j(s) (\chi^{sp})^j \quad (40)$$

By introducing Eq. (40) in Eq. (37) the following equation is obtained,

$$\sigma_j''(s) + 2s\sigma_j'(s) - 2j\sigma_j(s) = 0 \quad (41)$$

with the boundary conditions (Eqs. (38) and (39)),

$$s \rightarrow \infty, \quad \sigma_j(s \rightarrow \infty) = 0 \quad j \geq 0 \quad (42)$$

$$s = 0, \quad \sigma_0'(0) = 0 ; \quad \sigma_1'(0) = \sigma_0(0) - u_{1,eq}^{sur} / \gamma^{sp} ; \quad \sigma_j'(0) = \sigma_{j-1}(0) \quad (j \geq 2) \quad (43)$$

with¹⁰

$$\sigma_j(s) = h_j \Psi_j(s) \quad j \geq 0 \quad (44)$$

where $\Psi_j(s)$ are the Koutecký functions, which fulfill⁹⁻¹¹

$$\lim_{s \rightarrow 0} \Psi_j(s) = 1 ; \quad \lim_{s \rightarrow \infty} \Psi_j(s) = 0 ; \quad \Psi_j'(s) = -p_j \Psi_{j-1}(s) ; \quad \Psi_0(s) = 1 - erf(s) \quad (45)$$

with p_j being

$$p_j = \frac{2\Gamma\left(1 + \frac{j}{2}\right)}{\Gamma\left(\frac{1}{2} + \frac{j}{2}\right)} \quad (46)$$

and Γ is the gamma function. From the above,

$$\sigma_j(0) = h_j ; \quad \sigma_j'(0) = -p_j h_j \quad j \geq 0 \quad (47)$$

and introducing Eqs. (47) into Eq. (43), it is obtained that,

$$h_0 = 0 ; \quad h_j = \frac{(-1)^{j+1} u_{1,eq}^{sur}}{\prod_{l=1}^j p_l \gamma^{sp}} \quad (j \geq 1) \quad (48)$$

Thus, from (44)-(45) and (48),

$$\sigma_0(s) = 0 ; \quad \sigma_j(s) = \frac{u_{1,eq}^{sur}}{\gamma^{sp}} \frac{(-1)^{j+1}}{\prod_{l=1}^j p_l} \Psi_j(s) \quad (j \geq 1) \quad (49)$$

and from Eq. (40),

$$u_1(r,t) = \frac{1}{\gamma^{sp}} \left(u_1(r,t)_{eq} - \frac{2}{\sqrt{\pi}} \frac{u_{1,eq}^{sur}}{\chi^{sp}} \sum_{j=0}^{\infty} \frac{(-1)^j}{\prod_{l=0}^j p_l} \Psi_j(s) (\chi^{sp})^{j+1} \right) \quad (50)$$

where

$$u_1(r,t)_{eq} = u_{1,eq}^{sur} \operatorname{erfc}(s) \quad (51)$$

From Eq. (50), at the electrode surface ($r = r_0$) it is immediately obtained,

$$u_1(r_0,t) = \frac{u_{1,eq}^{sur}}{\gamma^{sp}} \left(1 - \frac{2}{\sqrt{\pi}} \frac{F(\chi^{sp})}{\chi^{sp}} \right) \quad (52)$$

taking into account that:

$$F(\chi^{sp}) = \sum_{j=0}^{\infty} \frac{(-1)^j (\chi^{sp})^{j+1}}{\prod_{l=0}^j p_l} = \sqrt{\pi} \frac{\chi^{sp}}{2} e^{(\chi^{sp}/2)^2} \operatorname{erfc}(\chi^{sp}/2) \quad (53)$$

The expressions for $c_1(r,t)$ and $c_1(r_0,t)$ can be obtained from Eqs. (50) and (52), respectively, taking into account Eq. (29). Thus,

$$c_1(r,t) = \frac{1}{\gamma^{sp}} \left(c_1(r,t)_{eq} + c_1^*(\gamma^{sp} - 1) + \frac{2}{\sqrt{\pi}} \frac{r_0}{r} \frac{c_1^* - c_{1,eq}^{sur}}{\chi^{sp}} \sum_{j=0}^{\infty} \frac{(-1)^j}{\prod_{l=0}^j p_l} \Psi_j(s) (\chi^{sp})^{j+1} \right) \quad (54)$$

$$c_1(r_0,t) = \frac{1}{\gamma^{sp}} \left(c_{1,eq}^{sur} + c_1^*(\gamma^{sp} - 1) + \frac{2}{\sqrt{\pi}} \frac{c_1^* - c_{1,eq}^{sur}}{\chi^{sp}} F(\chi^{sp}) \right) \quad (55)$$

where $c_1(r,t)_{eq}$ for a total electrochemical and chemical equilibrium process has the following expression¹⁰,

$$c_1(r,t)_{eq} = c_1^* + \frac{r_0}{r} (c_{1,eq}^{sur} - c_1^*) \operatorname{erfc}(s) \quad (56)$$

Eq. (54) together with Eq. (57),

$$I^{sp} = FSD \left(\frac{\partial c_1(r,t)}{\partial r} \right)_{r=r_0} \quad (57)$$

leads to the expression for the current-potential-time response of the CEC mechanism given by Eq. (3) of the main text.

SI-2.1. Particular cases of Eq. (3) of the main text

From equation (3) of the main text, a wide range of particular cases can be derived as a function of the electrode radius (r_0) and the chemical kinetics (κ_i , $i=1,2$) and thermodynamics (K_i , $i=1,2$), which define the chief parameter of the solution, χ^{sp} (Eq. (7) of the main text):

- **Macroelectrodes** ($r_0 \rightarrow \infty$), Eq. (3) of the main text becomes into¹²,

$$\frac{j_{\text{macro}}}{j_{\text{eq}}^{\text{macro}}} = F(\chi^{\text{macro}}) \quad (58)$$

where $j_{\text{eq}}^{\text{macro}}$ is obtained from Eq. (4) of the main text with $\delta_d^{sp}(r \rightarrow \infty) \rightarrow \delta_d^{\text{macro}} = \sqrt{\pi D t}$ (Eq. (6)

of the main text) and χ^{macro} is (Eq. (7) of the main text),

$$\chi^{\text{macro}} = 2\sqrt{Dt} \Lambda^{\text{macro}} \left(\frac{1 + K_2 + (1 + K_1)e^\eta}{K_2} \right) \quad (59)$$

with Λ^{macro} obtained from Eq. (8) of the main text with $\delta_{r,i}^{sp}(r \rightarrow \infty) \equiv \delta_{r,i}^{\text{macro}} = \sqrt{D / \kappa_i}$ ($i=1,2$) (Eq. (9) of the main text). Thus, a transient current response is always obtained for the mechanisms considered under linear diffusion.

- For $\chi^{sp} \geq 19.4$ (Eq. (7) of the main text), it is fulfilled that $\frac{F(\chi^{sp})}{\chi^{sp}} \approx \frac{\sqrt{\pi}}{2} \left(\frac{1}{1 + \sqrt{\pi} \frac{\chi^{sp}}{2}} \right)$

with a relative error of less than 5%³ such that equation (3) of the main text, after some mathematical manipulations, simplifies to:

$$\frac{j^{sp}}{j_{\text{eq}}^{sp}} = \delta_d^{sp} \frac{\Lambda^{sp} (1 + K_2 + (1 + K_1)e^\eta)}{K_2 + \delta_d^{sp} \Lambda^{sp} (1 + K_2 + (1 + K_1)e^\eta)} \quad (60)$$

This expression is also attained by applying the so-called diffusive-kinetic steady state (dkss) assumption³ to the original bvp (Eqs. (24)-(26))¹³, which considers that the mathematical form of $c_1(r,t)$ is the same as that corresponding to a pseudo-species undergoing a simple reversible CT (E_{rev} mechanism) (Eq. (56)).

Expression (60) provides accurate results for the current at microelectrodes (both under transient and steady state conditions, see below) and also at macroelectrodes when the chemical kinetics is fast enough (*i.e.*, $\chi^{\text{macro}} \geq 19.4$ with χ^{macro} being given by equation (59))³.

- **Microelectrodes** with $\frac{1}{10}\sqrt{\frac{D}{\kappa_i}} \leq r_0 \leq \frac{1}{20}\sqrt{\pi Dt}$. When the electrode size is small

enough, then it is possible to assume that $\frac{1}{r_0} + \frac{1}{\sqrt{\pi Dt}} \approx \frac{1}{r_0}$ (error less than 5% for $r_0 \leq \sqrt{\pi Dt} / 20$)

so that $\delta_d^{\text{sp}} \rightarrow \delta_d^{\text{microsp}} = r_0$ (Eq. (6) of the main text) and a time-independent, kinetic-sensitive current response is obtained from both Eqs. (3) of the main text and (60) for the mechanism considered³:

$$\frac{i^{\text{microsp}}}{i_{\text{eq}}^{\text{microsp}}} = r_0 \frac{\Lambda^{\text{sp}} (1 + K_2 + (1 + K_1)e^{\eta})}{K_2 + r_0 \Lambda^{\text{sp}} (1 + K_2 + (1 + K_1)e^{\eta})} \quad (61)$$

where $i_{\text{eq}}^{\text{microsp}}$ is given by Eq. (4) of the main text with the above-mentioned value of δ_d^{sp} .

- **Ultramicroelectrodes** ($r_0 \leq \frac{1}{10}\sqrt{\frac{D}{\kappa_i}}$ and $r_0 > 100 \text{ nm}^{14}$). Under these conditions,

it is fulfilled that $\delta_d^{\text{u-microsp}} = \delta_{r,i}^{\text{u-microsp}} \rightarrow r_0$ (Eqs. (6) and (9) of the main text) and the current response is independent of time and of the chemical kinetics given that its influence is masked by the enhanced mass transport by diffusion^{3,15}. Hence, Eqs. (3) of the main text and (60) become coincident with the response of an E_{rev} mechanism.

Section SI-3. Cyclic voltammetry of the CEC mechanism at (hemi)spherical and disc electrodes

In Figure S2 the dimensionless cyclic voltammograms (Ψ_{CV}^G vs $E - E^{0'}$) of the CEC_{irrev} mechanism ($K_2 \rightarrow \infty$) at spherical ($G \equiv sp$, solid lines) and disc ($G \equiv disc$, dashed lines) electrodes are plotted for a variety of electrode sizes and chemical kinetics. In all cases, the curves of the E_{rev} mechanism (in red) are also shown as a reference.

As can be observed, differences between spherical and disc electrodes are more apparent as the electrode shrinks, being negligible, as expected, at macroelectrodes (Fig. S2A) where diffusion is linear regardless of the electrode shape. Otherwise, in Figures S2B ($r_0 = 20 \mu m$) and S2C ($r_0 = 1 \mu m$), the current density is larger at disc electrodes than at spherical ones given the more efficient diffusive transport at microdiscs (see also Fig. 3 of the main manuscript). Accordingly, the chemical kinetics is undetectable in a higher degree at discs than at (hemi)spheres of the same radius. Hence, as can be seen in Figure S2C, the total equilibrium limit is attained at slightly faster kinetics at microdiscs than at microspheres.

Figure S2. Cyclic voltammetry of the $\text{CEC}_{\text{irrev}}$ mechanism ($K_2 \rightarrow \infty$) at spherical (solid lines) and disc (dashed lines) electrodes as function of the chemical kinetics ($\kappa_1 = \kappa_2$ for the sake of simplicity) for three electrode radii (r_0): **(A)** 1 cm, **(B)** 20 μm and **(C)** 1 μm . Other conditions as in Figure 2 of the main text.

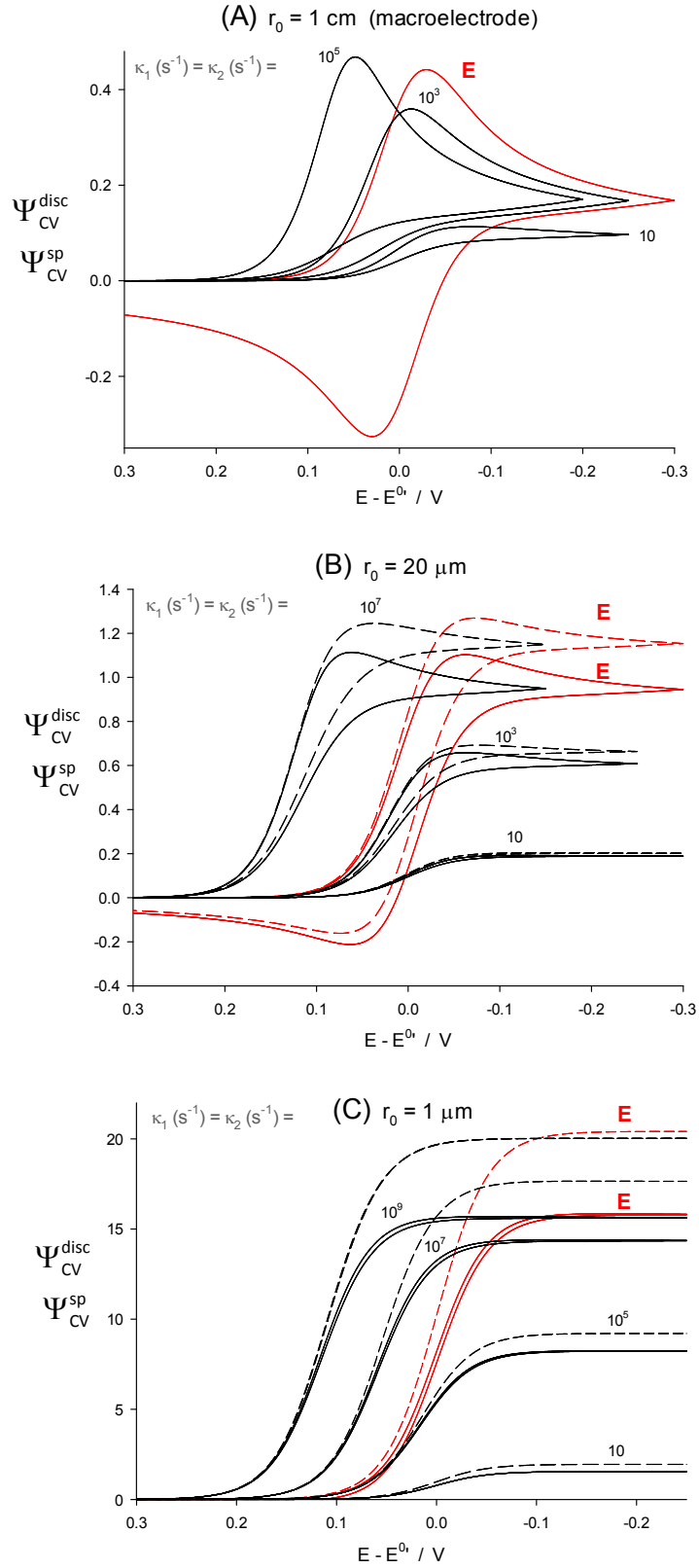
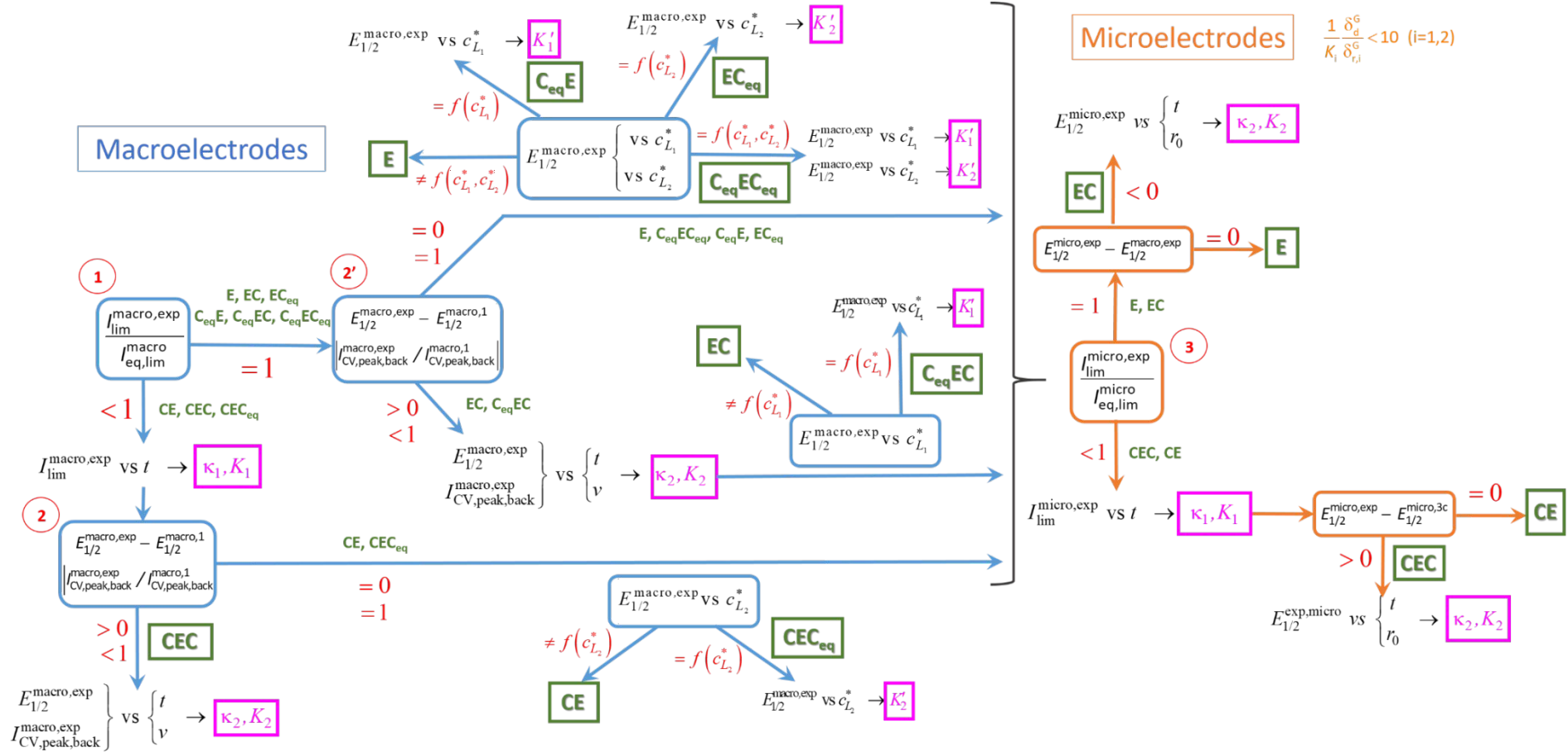


Table S1. Definitions of the variables and parameters of the general boundary value problem for different mechanisms.

CEC mechanism: $B \xrightleftharpoons[k_2]{k_1} C; \quad C + e^- \rightleftharpoons D; \quad D \xrightleftharpoons[k_4]{k_3} E$	
$c_1(q, t) = c_B(q, t) + c_C(q, t)$	Other Mechanisms as Particular Cases
$\Lambda^G = \frac{K_2}{\langle \delta_{r,1}^G \rangle K_1 (1 + K_2) + \langle \delta_{r,2}^G \rangle K_2 (1 + K_1) e^{\eta(t)}} \quad (G \equiv \text{electrode geometry}), \quad A = \frac{1 + K_2}{K_2}, \quad B = \frac{(1 + K_1) e^{\eta(t)}}{K_2}$ $\eta(t) = \frac{F}{RT} (E(t) - E^{0'}) \quad \text{where } E^{0'} \text{ is the formal potential of the redox couple C/D}$ $\delta_{r,i}^{sp} = \frac{1}{\left(\frac{1}{r_0} + \sqrt{\frac{K_i}{D}} \right)} \left\{ \begin{array}{l} \xrightarrow{r_0 \rightarrow \infty} \delta_{r,i}^{macro} = \sqrt{\frac{D}{K_i}} \\ \xrightarrow{r_0 \rightarrow 0} \delta_{r,i}^{ultramicro} = r_0 \end{array} \right.$ $\langle \delta_{r,i}^{disc} \rangle = r_0 \frac{\pi}{4} \left\{ \frac{1 + 1.3650 r_0 \sqrt{\frac{K_i}{D}} + 0.8826 r_0^2 \frac{K_i}{D} + 0.32853 \left(r_0^2 \frac{K_i}{D} \right)^{3/2} + 0.063566 \left(r_0^2 \frac{K_i}{D} \right)^2}{1 + 2.0016 r_0 \sqrt{\frac{K_i}{D}} + 1.8235 r_0^2 \frac{K_i}{D} + 0.96367 \left(r_0^2 \frac{K_i}{D} \right)^{3/2} + 0.307949 \left(r_0^2 \frac{K_i}{D} \right)^2 + 0.049925 \left(r_0^2 \frac{K_i}{D} \right)^{5/2}} \right\} \quad (i=1, 2)$	<p>$K_2 \rightarrow 0$: CE mechanism</p> $c_1(q, t) = c_B(q, t) + c_C(q, t)$ $\Lambda^G = \frac{1}{\langle \delta_{r,1}^G \rangle K_1}, \quad A = 1, \quad B = (1 + K_1) e^{\eta(t)}$
	<p>$K_1 \rightarrow 0$: EC mechanism</p> $c_1(q, t) = c_C(q, t)$ $\Lambda^G = \frac{1}{\langle \delta_{r,2}^G \rangle e^{\eta(t)}}, \quad A = \frac{1 + K_2}{K_2}, \quad B = \frac{e^{\eta(t)}}{K_2}$
E_{irrev} mechanism: $C + e^- \xrightleftharpoons[k_b]{k_f} D \quad c_1(q, t) = c_C(q, t), \quad \Lambda = \frac{k_f}{D}, \quad A = 1, \quad B = e^{\eta(t)}$ with k_f and k_b being the heterogeneous rate constant of reduction and oxidation, respectively.	
$c_{1,eq}^{sur} = (c_1^* + c_2^*) \frac{B}{A+B}; \quad \nabla_{sp}^2 = \frac{\partial^2}{\partial r^2} + \frac{2}{r} \frac{\partial}{\partial r}; \quad \nabla_{disc}^2 = \frac{\partial^2}{\partial r^2} + \frac{1}{r} \frac{\partial}{\partial r} + \frac{\partial^2}{\partial z^2}$	

Figure S3. Extended experimental protocol for the elucidation and characterization of the different particular cases included in the CEC mechanism. In those cases where the preceding and/or following chemical kinetics is too fast to be determined under linear diffusion conditions (C_{eq} step), the corresponding equilibrium constants are accessible if the interconversions B-to-C and D-to-E (see Scheme (I) of the main text) are mediated by chemical species (L_1 and L_2 , respectively), the concentration of which can be varied experimentally. Thus, the analysis of the variation of $E_{1/2}^{macro,exp}$ with their concentrations, $c_{L_1}^*$ and $c_{L_2}^*$, with Eq. (16) of the main text yields the values of the true equilibrium constants $K'_1 = K_1 / c_{L_1}^*$ and $K'_2 = K_2 / c_{L_2}^*$.



REFERENCES

- (1) Oldham, K. B.; Feldberg, S. W. Principle of Unchanging Total Concentration and Its Implications for Modeling Unsupported Transient Voltammetry. *J. Phys. Chem. B* **1999**, *103* (10), 1699–1704.
- (2) Molina, A.; Gonzalez, J.; Henstridge, M. C.; Compton, R. G. Voltammetry of Electrochemically Reversible Systems at Electrodes of Any Geometry: A General, Explicit Analytical Characterization. *J. Phys. Chem. C* **2011**, *115* (10), 4054–4062.
- (3) Molina, A.; Morales, I.; López-Tenés, M. Chronoamperometric Behaviour of a CE Process with Fast Chemical Reactions at Spherical Electrodes and Microelectrodes. Comparison with a Catalytic Reaction. *Electrochem. commun.* **2006**, *8* (6), 1062–1070.
- (4) Molina, A.; Martínez-Ortiz, F.; Laborda, E.; Morales, I. Rigorous Analytical Solution for a Preceding Chemical Reaction in Normal Pulse Voltammetry at Spherical Electrodes and Microelectrodes. *J. Electroanal. Chem.* **2009**, *633* (1), 7–14.
- (5) Heyrovský, J.; Kůta, J. *Principles of Polarography*; Pub. House of Czechoslovak Academy of Sciences: Prague, 1965.
- (6) Rajendran, L.; Sangaranarayanan, M. V. Diffusion at Ultramicro Disk Electrodes: Chronoamperometric Current for Steady-State EC' Reaction Using Scattering Analogue Techniques. *J. Phys. Chem. B* **1999**, *103*, 1518–1524.
- (7) Molina, A.; Laborda, E.; González, J. The Reaction Layer at Microdiscs: A Cornerstone for the Analytical Theoretical Treatment of Homogeneous Chemical Kinetics at Non-Uniformly Accessible Microelectrodes. *Electrochem. commun.* **2016**, *71*, 18–22.
- (8) Molina, A.; González, J.; Laborda, E.; Compton, R. G. Reprint of “Analytical Theoretical Approach to the Transient and Steady State Voltammetric Response of Reaction Mechanisms. Linear Diffusion and Reaction Layers at Micro- and Submicroelectrodes of Arbitrary Geometry.” *J. Electroanal. Chem.* **2017**, *793*, 104–112.
- (9) Koutecký, J.; Čížek, J. Anwendung Der Methode Der Dimensionslosen Parameter Für Die Lösung von Transportproblemen Bei Der Elektrolyse Mit Konstantem Strom an Flacher Und Kugelförmiger Elektrode. *Collect. Czechoslov. Chem. Commun.* **1957**, *22* (3), 914–928.
- (10) Molina, A.; González, J. *Pulse Voltammetry in Physical Electrochemistry and*

Electroanalysis; Scholz, F., Ed.; Monographs in Electrochemistry; Springer International Publishing: Berlin, 2016.

- (11) Koutecký, J.; Koryta, J. The General Theory of Polarographic Kinetic Currents. *Electrochim. Acta* **1961**, 3 (4), 318–339.
- (12) Molina, A.; López-Tenés, M.; Laborda, E. Unified Theoretical Treatment of the Eirrev, CE, EC and CEC Mechanisms under Voltammetric Conditions. *Electrochem. commun.* **2018**, 92, 48–55.
- (13) Molina, A.; Laborda, E.; Gómez-Gil, J. M.; Martínez-Ortiz, F.; Compton, R. G. Analytical Solutions for the Study of Homogeneous First-Order Chemical Kinetics via UV-Vis Spectroelectrochemistry. *J. Electroanal. Chem.* **2017**, 819 (June 2017), 202–213.
- (14) Smith, C. P.; White, H. S. Theory of the Voltammetric Response of Electrodes of Submicron Dimensions. Violation of Electroneutrality in the Presence of Excess Supporting Electrolyte. *Anal. Chem.* **1993**, 65 (23), 3343–3353.
- (15) Galceran, J.; Puy, J.; Salvador, J.; Cecília, J.; van Leeuwen, H. P. Voltammetric Lability of Metal Complexes at Spherical Microelectrodes with Various Radii. *J. Electroanal. Chem.* **2001**, 505 (1), 85–94.