Electronic Supplementary Material (ESI) for Chemical Science.

Supporting Information II: Mathematical Background and Simulation Procedures

To model the EC' reaction mechanism shown below, we were guided by reports describing the model of a diffusive redox catalyst embedded in a polymer-gel like film and a homogenous substrate in solution.[1,2] Our model describes the reverse system of a diffusive homogenous catalyst, and a uniform, non-diffusive film substrate.

$$\mathbf{Q} \rightleftharpoons \mathbf{P} + \mathbf{e}^{-}$$
$$\mathbf{P} + \mathbf{A} \rightarrow \mathbf{Q} + \mathbf{B}$$

We begin by stating the system of reaction-diffusion equations required to solve within and outside of the film. Inside the film ($0 \leq x < d_f, d_f :=$ length of the film) and for $t > 0$ we have the following set of equations, where the terms P, Q, and A are concentrations of these respective species. (n.b. in the main text we use C_Q, C_P, and C_A, consistent with traditional electrochemical abbreviations, but for consistency with the MATLAB scripts, we use the shorter abbreviations here). These concentrations are also defined as a function of distance from the electrode and time, by P(x,t), Q (x,t), and A(x,t).

$$\frac{\partial P}{\partial t} = D_f\left(\frac{\partial^2 P}{\partial x^2}\right) - kPA$$

$$\frac{\partial Q}{\partial t} = D_f\left(\frac{\partial^2 Q}{\partial x^2}\right) + kPA$$

$$\frac{\partial A}{\partial t} = -kPA$$

The constant k represents the reaction rate constant for the reaction between oxidized catalyst P and the film substrate A. The constant D_f represents the diffusion coefficient of both the oxidized and reduced form of the catalyst within the film. Note that the equation for A contains no diffusive term, indicating that our theoretical film is completely incapable of transport in space. This implies that film depleted directly at the electrode's surface ($x = 0$) will not be replenished over time from another source from any given distance away. Consequently, once the film substrate has been entirely depleted at the electrode's surface, the catalytic anodic current will be driven by the diffusion of Q to the electrode's surface due to the reaction between P and A within the film, away from the electrode's surface. Outside of the film ($x > d_f$), for $t > 0$, we solve the set of linear diffusion equations

$$\frac{\partial P}{\partial t} = D_s\left(\frac{\partial^2 P}{\partial x^2}\right)$$

$$\frac{\partial Q}{\partial t} = D_s\left(\frac{\partial^2 Q}{\partial x^2}\right)$$

where, D_s is the diffusion coefficient of both P and Q in electrolyte solution. Furthermore, we will also define $\Gamma_A = A(0,t)$ to be the surface concentration of the film substrate and $\theta = \frac{\Gamma_A}{[\Gamma_A]_{max}}$ to be the ratio of the surface substrate concentration over the max potential film substrate concentration at the electrode's surface. Here, one can think of $[\Gamma_A]_{max}$ as representing the surface concentration of the film achieved when the surface of the electrode is completely inhibited and no current is capable of being passed.

The problem we wish to solve belongs to the half-line ($x \geq 0$) and we will work with a mixed set of semi-infinite boundary conditions. At the electrode surface, we stipulate the coupled set of robin boundary conditions given by the standard Butler-Volmer kinetics treatment.

$$D_f\left(\frac{\partial P}{\partial x}\right)(0,t) = k_s^{app}(\theta(t))exp\left(-\frac{F\alpha}{RT}(E - E^0)\right)P(0,t)$$
$$- k_s^{app}(\theta(t))exp\left(\frac{F(1-\alpha)}{RT}(E - E^0)\right)Q(0,t);$$

$$\left(\frac{\partial Q}{\partial x}\right)(0,t) = -\left(\frac{\partial P}{\partial x}\right)(0,t).$$

Where α is the transfer coefficient and k_s^{app} is the apparent electron transfer rate constant which is, at this point, just a generic function of the surface coverage θ. As $x \to \infty$, we employ the semi-infinite boundary condition

$$P(x \to \infty, t) = 0;$$

$$Q(x \to \infty, t) = Q^*.$$

Where, Q^* is the initial concentration of Q. In addition, we stipulate flux conservation across $x = d_f$ to ensure that both $Q(x,t)$ and $P(x,t)$ remain differentiable there.

$$\lim_{\varepsilon \to 0}(D_s(\frac{\partial P}{\partial x})_{x=d_f+\varepsilon} - D_f(\frac{\partial P}{\partial x})_{x=d_f-\varepsilon}) \to 0;$$

$$\lim_{\varepsilon \to 0}(D_s(\frac{\partial Q}{\partial x})_{x=d_f+\varepsilon} - D_f(\frac{\partial Q}{\partial x})_{x=d_f-\varepsilon}) \to 0.$$

Where ε is some real number greater than zero. The initial conditions $(t = 0)$ are given by

$$P(x,0) = 0;$$

$$Q(x,0) = Q^*;$$

$$A(x,0) = A^*.$$

Where $A^*$is the initial concentration of the film substrate within $0 \leq x \leq d_f$. Note that based on the definition of θ(t), we have that

$$\theta(0) = \frac{\Gamma_A^*}{[\Gamma_A]_{max}} = \frac{A(0,0)}{[\Gamma_A]_{max}} = \frac{A^*}{[\Gamma_A]_{max}}.$$

Therefore, we will stipulate that A^* is some constant less than the $[\Gamma_A]_{max}$ to ensure that θ resides between 0 and 1. Now that the problem has been posed, in order to perform feasible economic computation and to avoid potential round-off errors stemming from small concentration terms, we begin a dimensionless reformulation of the problem. To do so, we introduce the dimensionless concentrations

$$p = \frac{P}{Q^*}; \qquad q = \frac{Q}{Q^*}; \qquad a = \frac{A}{Q^*}.$$

and the dimensionless space and time coordinates y and τ

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

$$\tau = \frac{Fv}{RT}t.$$

Via application of the chain rule, we cast our system of reaction diffusion equations into dimensionless form to obtain that for $0 \leq y < 1$

$$\frac{\partial p}{\partial \tau} = \frac{D_f RT}{Fvd_f^2}\left(\frac{\partial^2 p}{\partial y^2}\right) - \frac{kQ^*RT}{Fv}pa;$$

$$\frac{\partial q}{\partial \tau} = \frac{D_f RT}{Fvd_f^2}\left(\frac{\partial^2 q}{\partial y^2}\right) + \frac{kQ^*RT}{Fv}pa;$$

$$\frac{\partial a}{\partial \tau} = -\frac{kQ^*RT}{Fv}pa.$$

One can check that the coefficients $\frac{D_f RT}{Fvd_f^2}$ and $\frac{kQ^*RT}{Fv}$ are completely dimensionless, we'll now define them as ω_f and λ, respectively. λ can be described as the as the dimensionless rate constant of the catalytic reaction and ω_f as the dimensionless diffusion coefficient within the film. Rewriting the previous set of equations within the film in terms of these new dimensionless coefficients, we obtain that for $0 \le y < 1$

$$\frac{\partial p}{\partial \tau} = \omega_f\left(\frac{\partial^2 p}{\partial y^2}\right) - \lambda pa;$$

$$\frac{\partial q}{\partial \tau} = \omega_f\left(\frac{\partial^2 q}{\partial y^2}\right) + \lambda pa;$$

$$\frac{\partial a}{\partial \tau} = -\lambda pa.$$

Similarly, outside of the film ($y > 1$) we obtain the dimensionless linear diffusion equations

$$\frac{\partial q}{\partial \tau} = \omega_s\left(\frac{\partial^2 p}{\partial y^2}\right);$$

$$\frac{\partial q}{\partial \tau} = \omega_s\left(\frac{\partial^2 p}{\partial y^2}\right).$$

Where $\omega_s = \frac{D_s RT}{Fvd_f^2}$ represents the dimensionless diffusion coefficient outside the film. In terms of our dimensionless reformulation, the boundary conditions at $x = 0$ and $x \to \infty$ become:

For $y = 0$

$$\left(\frac{\partial p}{\partial y}\right)_{y=0} = \frac{d_f k_s^{app}\big(\theta(\tau)\big)}{D_f} exp\left(-\frac{F\alpha}{RT}(E-E^0)\right)p(0,\tau)$$

$$-\frac{d_f k_s^{app}(\theta(\tau))}{D_f} exp\left(\frac{F(1-\alpha)}{RT}(E-E^0)\right)q(0,\tau);$$

$$\left(\frac{\partial q}{\partial y}\right)_{y=0} = -\left(\frac{\partial p}{\partial y}\right)_{y=0}.$$

And as $y \to \infty$, we have that

$$p(y \to \infty, \tau) \to 0$$

$$q(y \to \infty, \tau) \to 1$$

The flux conservation condition at $y = 1$ remains the same except now utilizing the dimensionless concentrations, p and q, rather than P and Q. The initial conditions at $\tau = 0$ are given by

$$p(y,0) = 0;$$

$$q(y,0) = 1;$$

$$a(y,0) = \gamma;$$

Where γ is defined as the excess factor $(\frac{A^*}{Q^*} = \gamma)$. In addition, the differential equation for the fractional surface coverage $\theta(\tau)$ is

$$\frac{\partial \theta}{\partial \tau} = \frac{-\lambda p(0,\tau)a(0,\tau)Q^*}{[\Gamma_A]_{max}} = \frac{-\lambda p(0,\tau)a(0,\tau)}{\gamma_{max}} = -\lambda p(0,\tau)\theta(0,\tau).$$

Where $\gamma_{max} = \frac{Q^*}{[\Gamma_A]_{max}} \geq \gamma$. The initial conditions for θ at $\tau = 0$ are thus given as

$$\theta(0) = \frac{\gamma}{\gamma_{max}}.$$

The dimensionless current Ψ is computed via the dimensionless flux equation

$$\Psi = \left(\frac{\partial p}{\partial y}\right)_{y=0} = \frac{I d_f}{FS^{app}(\theta(\tau))Q^* D_f}.$$

Where S^{app} is the apparent surface area of the electrode which could be a function of the fractional surface coverage θ.

Numerical Modeling and Simulation of a Modified EC′ Reaction with a Surface-bound Substrate

This supporting information will provide documentation for the attached MATLAB scripts and functions used to generate the simulated voltammograms in this report. The mathematical basis, including the governing system of differential equations and the derived dimensionless parameters, are given in the previous section.

Using provided MATLAB scripts to simulate CV – a quick start guide

Two MATLAB files are attached to this submission: Modified_EC_Mechanism_All_Dimensionless.m and Running_Modified_EC_Mechanism_All_Dimensionless.m. The former file contains the MATLAB function used to generate the voltammetric response of a homogeneous catalyst acting on a heterogeneous substrate and plot the resulting dimensionless current vs. potential curve, and will be described in more detail below. The latter file is a script for the user to run that passes experimental parameters to the function, and contains the option to save the resulting voltammogram to an Excel file.

Running the provided script will generate a plot within MATLAB of the voltammogram and will return arrays containing data for potential (*E*), current (*Iv*) and fractional surface coverage θ (*theta*). A sample plot is provided below, demonstrating that in the absence of catalysis, a diffusional voltammogram of ferrocene is obtained (**Figure S2)**.

The parameters to be set by the user are described below. See the above mathematical derivation for details of dimensionless governing parameters.

Variable name	Parameter	Default value
N	Spatial grid size	2000
Ts	Number of time steps	5000
w	Dimensionless diffusion coefficient	0.1
l	Dimensionless rate parameter	0.1
g	Excess factor	10
k0_val	Heterogeneous electron transfer rate constant	2000

init_coverage	Initial value of θ (fractional surface coverage)	0.9
ks_inhibition	Enable/disable inhibition of electron transfer rate based on fractional surface coverage*	0 (set to 1 to enable)
filename	Name of Excel file to write current vs. potential curve**	“sample_file.xlsx”
save_to_excel	Enable/disable writing generated voltammogram to Excel file	0 (set to 1 to enable) By default, potential is written to the cell range A2:A10002 and current is written to the cell range B2:B1002

Figure S1 User-defined parameters within provided MATLAB script Running_Modified_EC_Mechanism_All_Dimensionless.m. Default values for these inputs which produce an example catalytic wave are provided.

* See main text for details of limiting film geometries and respective mathematical treatments of inhibition effects

**Excel file must either be located in the same folder as the MATLAB scripts, or the full path to the file must be specified with this variable

Note: by default, 10000 data points are written to the specified Excel file, corresponding to 2*(Ts) values. If the value of Ts is varied, the cell ranges specified for writing must be changed as well to ensure that the full voltammogram is written to the spreadsheet.

Details of Numerical Simulation

The simulation space is a one-dimensional grid extending from the electrode surface ($x=0$) through the thickness of the film ($x = d_f$). Before simulation, these length values are non-dimensionalized by dividing through by df, providing the nondimensional spatial coordinates $y_0 = 0$ and $y_1 = 1$, for $y = x/d_f$. This grid is then divided into a linearly-spaced grid with N spatial steps of length h. Next, the dimensionless time τ is discretized according to the potential window of study and the number of time steps desired. The dimensionless parameters λ, ω, and γ are calculated using standard constants and the provided experimental parameters: scan rate, initial concentrations, film thickness, and diffusion coefficient. Finally, matrices are initialized to store the standard heterogeneous electron transfer rate constant, Butler-Volmer kinetic functions, concentration profiles, and the fractional surface coverage θ.

To solve the system of reaction-diffusion equations numerically, we employed the following finite-differencing scheme. First, the system of equations within the film are discretized in space alone using the standard second order central differencing formula. In addition, to maintain second order accuracy in space, the coupled robin boundary conditions at the electrode surface are approximated by a central difference, and thus a ghost node is introduced interior to the domain. The resulting large system of ODEs is then solved by a mixed implicit-explicit (IMEX) scheme; linear diffusion terms are treated implicitly using the backward Euler method, and nonlinear kinetic terms are treated explicitly using the forward Euler method. This IMEX scheme was chosen in order to avoid the use of a fully implicit solver, in which a nonlinear system of equations would need to be solved iteratively at each time step.[3] As a result, numerical calculations are much faster; however, stability issues arise owing to the stiffness of the nonlinear kinetic terms when larger values of the dimensionless rate parameter λ and the excess factor γ are used. To ensure numerical stability, we recommend using values of $\lambda \leq 1$ and $\omega \leq\ 1000$. If larger values of these parameters are desired, a larger number of time steps must be employed leading to longer run times.

Since the robin boundary conditions at the electrode surface are coupled, the matrices that result from the IMEX implementation that multiply the concentration profiles p and q are appended to include the kinetic Butler-Volmer coupling terms along the off the diagonal. As a consequence, concentration profile matrices for p and q are computed at each time step from a concatenated matrix denoted p_q in the MATLAB script.

Researchers hoping to improve on our current numerical implementation are recommended to employ a non-uniform grid with spatial grid points clustered close to the electrode surface to capture the pertinent dynamics of the reaction without using a large number of grid points. Additionally, the numerical implementation could benefit from the use of either a higher order IMEX method or a fully implicit solver when coefficients multiplying the nonlinear kinetic terms are large.

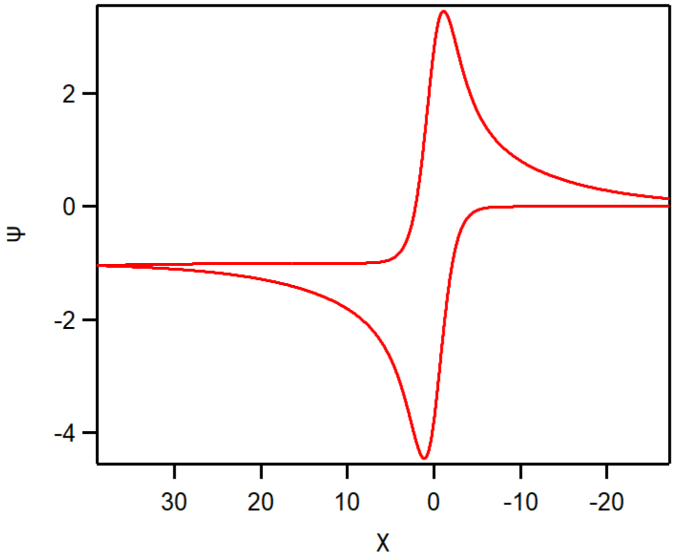

Figure S2 Simulation of cyclic voltammetry of species P in the absence of catalysis, to validate the modeling approach and numerical solution method implemented. Parameters used: ω = 0.01, λ = 0.1, g = 0.

References

(1) Costentin, C.; Saveant, J.-M. Cyclic Voltammetry Analysis of Electrocatalytic Films. *J. Phys. Chem. C* **2015**, *119* (22), 12174–12182. https://doi.org/10.1021/acs.jpcc.5b02376.

(2) Costentin, C.; Savéant, J. M. Cyclic Voltammetry of Fast Conducting Electrocatalytic Films. *Phys. Chem. Chem. Phys.* **2015**, *17* (29), 19350–19359. https://doi.org/10.1039/c5cp02825f.

(3) Ascher, U.M.; Ruuth, S. J.; Wetton, B.T.R. Implicit-Explict Methods for Time-Dependent PDE's. *SIAM J. Numer. Anal.* **1995**, *32*(3), 797–823. https://doi.org/10.1137/0732037