Interpreting the Electrocatalytic Voltammetry of Homogeneous Catalysts by the Foot of the Wave Analysis and Its Wider Implications

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Mechanistic studies of electrocatalytic reactions play a crucial role in developing efficient electrocatalysts and solar-fuel devices. The foot of the wave analysis (FOWA) for cyclic voltammetry, recently developed by Savéant and Costentin, provides a powerful means to evaluate the performance of molecular electrocatalysts. However, there is a considerable amount of confusion in the community on how to interpret FOWA in multi-electron electrochemical reactions. Herein, we further expand their earlier models from the Nernstian region to all scenarios (i.e. including non-Nernstian behavior) and systematically examine individual parameters, such as formal potentials and reaction rate constants, to explore deeper insights and limitation. Detailed analysis from in-silico voltammograms based on different mechanistic models reveals characteristic features of FOWA traces for different kinetic phenomena, which is useful to diagnose kinetic profiles and elucidate the limits of FOWA. The lessons learned from these analyses are further used to reconcile the discrepancy of rate constants determined by FOWA versus other methods, such as time-resolved spectroscopy, for molecular electrocatalysts that catalyze proton reduction or the reduction of $\text{CO}_2$ to CO. Such reconciliation demonstrates that electrochemical methods along with FOWA can serve as an alternative tool to determine kinetic information and probe mechanistic insights, which otherwise may be challenging and complicated to be achieved by conventional methods. In addition, general guidelines and warnings are also presented to avoid potential errors or mishandling when using FOWA.

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- Wang and Johnson_manuscript.pdf (2.29 MiB)
- Wang and Johnson_FINAL supporting materials I.pdf (2.64 MiB)
- Wang and Johnson_support II_math.pdf (354.74 KiB)
Interpreting the Electrocatalytic Voltammetry of Homogeneous Catalysts by the Foot of the Wave Analysis and Its Wider Implications

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Abstract

Mechanistic studies of electrocatalytic reactions play a crucial role in developing efficient electrocatalysts and solar-fuel devices. The foot of the wave analysis (FOWA) for cyclic voltammetry, recently developed by Savéant and Costentin, provides a powerful means to evaluate the performance of molecular electrocatalysts. However, there is a considerable amount of confusion in the community on how to interpret FOWA in multi-electron electrochemical reactions. Herein, we further expand their earlier models from the Nernstian region to all scenarios (i.e. including non-Nernstian behavior) and systematically examine individual parameters, such as formal potentials and reaction rate constants, to explore deeper insights and limitation. Detailed analysis from in-silico voltammograms based on different mechanistic models reveals characteristic features of FOWA traces for different kinetic phenomena, which is useful to diagnose kinetic profiles and elucidate the limits of FOWA. The lessons learned from these analyses are further used to reconcile the discrepancy of rate constants determined by FOWA versus other methods, such as time-resolved spectroscopy, for molecular electrocatalysts that catalyze proton reduction or the reduction of CO₂ to CO. Such reconciliation demonstrates that electrochemical methods along with FOWA can serve as an alternative tool to determine kinetic information and probe mechanistic insights, which otherwise may be challenging and complicated to be achieved by conventional methods. In addition, general guidelines and warnings are also presented to avoid potential errors or mishandling when using FOWA.
Introduction

In the past decade, the development of electrocatalysts to facilitate electrochemical reactions, has been a major focus in the fields of solar fuels and organic synthesis. Most fuel-forming reactions, such as hydrogen evolution or CO₂ reduction, associated with multiple electron and proton transfer steps, lead to high energy barriers during the reaction. Introducing an electrocatalyst is expected to lower such energy barriers and facilitate the reaction. The most widely-used technique to probe the properties of electrocatalysts is voltammetry, which provides direct and rapid information regarding the relationship between driving force (i.e. overpotential) and catalytic turnover (i.e. current) compared to rather complicated alternative methods, such as chemical redox-titration methods monitored by spectroscopy or other means. However, understanding detailed mechanistic schemes behind voltammograms are challenging due to complicated and intertwining processes, such as mass transport, electron transfer, chemical reaction, and interfacial chemistry between an electrode and reactants.

Recently, the development of the foot of the wave analysis (FOWA) of cyclic voltammograms by Savéant and Costentin has provided a feasible method to benchmark molecular electrocatalysts by turnover frequency (TOF) and turnover number (TON). The main idea behind FOWA is that electrocatalysis follows pure kinetic conditions within Nernstian behavior (i.e. rapid electrode kinetics) in the region of low overpotential, before side phenomena, such as substrate depletion or catalyst deactivation, take place. Therefore, the FOWA equation can be expressed as the equation 1 for the EC scheme (E: electron transfer step between the electrode and catalyst, and C: chemical reaction step). Dividing the catalytic current by \( i_p \) (current in the absence of substrate) circumvents the requirement for independent determination of the electrode surface area and the diffusion coefficient to obtain a rate constant. According to equation 1, the kinetic rate constant \( k_1' \) can be determined from the slope in a FOWA plot where \( 1/(1+\exp[f(E-E_l)]) \) (the applied potential, \( E \)) is plotted against \( i/i_p \).

Subsequently, FOWA equations and procedures have been further developed for two-electron electrochemical mechanisms (such as ECEC or EECC) of a homogeneous catalyst operating with a similar expression as equation 1, which allows one to determine rate constants and construct catalytic Tafel plots to compare performance between electrocatalysts.

\[
\frac{i}{i_p} = \frac{2.24 \sqrt{\frac{R T}{F^2 n^2}} k_1' C_A^0}{1 + \exp[f(E-E_l)]} \quad (1)
\]

(More detailed discussions of equation 1 can be found later)
However, there is a considerable amount of confusion in the literature regarding how to interpret FOWA and determine a rate constant in a multi-electron electrochemical reaction. As suggested by eq 1, ideally, the FOWA plot is expected to be linear. Nevertheless, non-linear FOWA plots even in the absence of side-phenomena have been proposed in the ECEC scheme. As shown in Figure 1, the rate constant determined from a curved FOWA plot (vide infra) is that of the faster first chemical step instead of the rate-limiting rate constant. Also, deviation from linearity can also arise due to slow interfacial electron transfer, which has been treated for the EC mechanism\textsuperscript{3a}, and may become significant with certain homogeneous molecular catalysts.

![Figure 1](image.png)

**Figure 1.** Electrocatalytic voltammograms for two-electron reaction (ECEC) and their corresponding FOWA plots (Inset figure) in the absence of side phenomena. More details will be discussed later.

Here, we further explore two-electron electrocatalytic reactions from Nernstian behavior to all scenarios and systematically investigate the influence of formal potentials, rate constants of chemical steps and interfacial electron transfer on voltammograms and FOWA plots through in-silico modelling. The findings allow us to decipher intertwined parameters. For example, we are able to demonstrate how different characteristic features of FOWA plots (such as a linear or curved shape) depend on these individual parameters, which provides valuable identification of kinetic profiles in both a qualitative and quantitative manner. More importantly, FOWA has been widely applied to benchmarking electrocatalysts but the lack of correct analysis of the FOW, such as the range of a FOWA trace selected for determining kinetic parameters, can lead to greatly underestimate kinetic rate constants. The lessons learned
from these in-silico voltammograms guide us to establish procedures to determine kinetic values within different features of FOWA plots and a table to identify reaction mechanisms. Finally, a combination of case studies and experimental data were investigated in this context. The information gained from these analyses lead to reconcile the discrepancy of kinetic values between FOWA and spectroscopic methods reported in literature.

**Models**

Here, two-electron catalytic mechanisms under *steady-state* conditions in the *reduction direction* are studied, which can be fuel-forming reactions, such as \( \text{H}_2 \) evolution and the reduction of \( \text{CO}_2 \) to \( \text{CO} \)/formate. The same results can be applied for the oxidation direction. Two cases (ECEC and EECC) for two-electron electrocatalytic reactions as shown in Scheme 1 are mainly investigated herein since they are the most commonly invoked mechanistic schemes. The derivation of the equations describing other mechanisms (such as CECE, ECCE and CEEC) are also given in the supporting material, which lead to the same or very similar equations as in either ECEC or EECC. In all cases, interfacial electron transfer (i.e. E-step) is governed by Butler-Volmer behavior. The kinetic rate constants for chemical steps are independent of electrode potential. The equations derived from all cases are assumed to be in the pure kinetic region without substrate depletion (zone KS) according to the zone diagram developed by Savéant and co-workers,\(^5\) and therefore steady-state approximation can be applied. As a result, a steady-state S-shape voltammogram can be achieved and is independent of scan rate. Such behaviors have been observed for several electrocatalysts for \( \text{H}_2 \) evolution and \( \text{CO}_2 \) reduction.

![Scheme 1. EECC and ECEC reaction scheme.](image)

EECC mechanism, O: oxidized state, I: one-electron reduced state, R: two-electron reduced state. A and Z are the two co-substrates
involved with the chemical steps, and P is the product. RA refers to the two-electron reduced substrate-bound intermediate state. In the ECEC mechanism, IA and IB refer to the one-electron and two-electron reduced substrate-bound intermediate state.

The general expressions for ECEC and EECC are shown in eq 2 and 3. The detailed derivation processes and all definitions of symbols can be found in the supporting information II. All equations can be simply composed of three components as shown below. For a stationary electrode with an electrode area, S, the limiting current \( i_{\text{lim}} \) (i.e. plateau current) is governed by the pseudo first order rate constants for the chemical steps \( k_1 \) or \( k_2 \), total concentration of electrocatalysts, \( C^* \), diffusion coefficient, \( D \) and Faraday constant, \( F \). In principle, the rate constant for the rate-limiting step can be determined through \( i_{\text{lim}} \) when the plateau current is achieved. The denominator contains terms, G and H, where the former can be treated as a thermodynamic contribution and the latter is governed by the rate of interfacial electron transfer. The values of \( E_1 \) and \( E_2 \) represent the formal potential for the first and second electron transfer and the notation \( \varepsilon_n \) represents \( \exp[f(E-E_n)] \). When the rate for interfacial electron transfer is rapid via either high overpotential or large standard electron exchange rate constants for interfacial electron transfer, \( k_0 \), the term H vanishes, and therefore the equation can be simplified to the expression for Nernstian behavior. Here, the effects of substrate depletion, product inhibition and catalyst deactivation are not considered. In general, these effects can lead to a concave feature in the FOWA plots as shown in ref 3a. (vide infra)

| ECEC  | \( k_1 = k_1'C_A^o \); \( k_2 = k_2'C_Z^o \) |
|-------|---------------------------------------------|

|   | \( i = \frac{2SFC^*\sqrt{D_{\text{cat}}}}{\frac{1}{\sqrt{k_1}} + \frac{1}{\sqrt{k_2}}} G_{ECEC} + H_{ECEC} \) | \( i_{\text{lim}} = \frac{2SFC^*\sqrt{D_{\text{cat}}}}{\frac{1}{\sqrt{k_1}} + \frac{1}{\sqrt{k_2}}} \) |

\[
G_{ECEC} = \frac{\varepsilon_1}{\sqrt{k_1}} + \frac{\varepsilon_2}{\sqrt{k_2}} \\
H_{ECEC} = \frac{\sqrt{D_{\text{cat}}}}{k_0\exp[-\alpha f(E-E_1)]} + \frac{\sqrt{D_{\text{cat}}}}{k_0\exp[-\alpha f(E-E_2)]}
\]
The parameters as described below were used to model voltammograms and investigate the effects of terms G and H on FOWA plots. The potential difference between $E_1$ and $E_2$ (i.e. ±ΔE) of 0, 30, 60, 120, 200 and 400 mV respectively were chosen to prepare in-silico voltammograms and examine how these differences affect FOWA plots and the determination of kinetic parameters. A diffusion coefficient ($D_{cat}$) of 10$^{-5}$ cm$^2$ s$^{-1}$ was used in all simulations.

For the kinetic variables, the different ratios, $\gamma$, defined as log ($k_0/k_1$) or log($k_0/k_2$), were used to interrogate the roles of interfacial electron transfer. The symmetry factor ($\alpha$) was set as 0.5 for all simulations. In addition, $E_{cat/2}$ is defined as the potential at which the current is equal to the half of $i_{lim}$. The scan rate ν = 0.1 V s$^{-1}$ was used unless specifically mentioned. The peak current, $i_p$ in the absence of substrates under the Nernstian behavior can be obtained by the Randles-Sevcik equation.$^6$ Otherwise, finite difference method$^7$ was employed to numerically obtain a value for $i_p$ in the quasi-reversible and irreversible region. Matlab was used for modelling voltammograms unless specifically mentioned.

In practice, complications arising from the depletion of substrate can affect the shape of voltammograms as described earlier. When this occurs, the current-potential curves are peak-shaped, and the current no longer reflects the rate of the catalytic reaction, but rather the diffusion of substrate to the electrode. Extracting meaningful kinetic information from these situations is less straightforward; however, the influence of substrate depletion can be mitigated by increasing the ratio of substrate to catalyst or by raising the scan rate. It is also important to note that a Faradaic efficiency close to unity is required in order to apply FOWA appropriately.

| EECC | $k_1 = k_1'C_A^o$ | $k_2 = k_2'C_Z^o$ |
|------|-------------------|-------------------|

\[
i = \frac{2ȘFC^*\sqrt{D_{cat}}}{\left\{\frac{1}{\sqrt{k_1}} + \frac{1}{\sqrt{k_2}} \left(\frac{1}{\sqrt{k_2}}\right)\right\} + G_{EECC} + H_{EECC}}
\]

\[
i_{lim} = \frac{2ȘFC^*\sqrt{D_{cat}}}{\left\{\frac{1}{\sqrt{k_1}} + \frac{1}{\sqrt{k_2}} \left(\frac{1}{\sqrt{k_2}}\right)\right\} + G_{EECC} + H_{EECC}}
\]

\[
G_{EECC} = \frac{\varepsilon_1\varepsilon_2}{\sqrt{k_1}} + \frac{\varepsilon_2}{\sqrt{k_1}}
\]

\[
H_{EECC} = \frac{\sqrt{D_{cat}}}{k_0\exp[-\alpha f (E-E_1)]} + \frac{(1+\varepsilon_1)\sqrt{D_{cat}}}{k_0\exp[-\alpha f (E-E_2)]}
\]
Results

EC catalytic mechanism

Seminal works by Savéant and co-workers have elucidated the theoretical basis for the EC catalytic mechanism and demonstrated its application to experimental systems. Here, we first start with a brief overview of this relatively simple mechanism, because it can serve as a basis for comparison to more complicated systems as discussed later for multi-electron reactions. The relation between the catalytic current, \( i \) and applied potential, \( E \) can be expressed as below:

\[
\begin{align*}
    \frac{O + e^{-} \rightarrow R}{R + A \rightarrow O + P} & \quad E_1 \\
    k_1 & = k'_1 C^0_A \\
    i & = \frac{F S C^* \sqrt{D_{cat} k_1}}{1 + G_{EC} + H_{EC}} \quad (4) \\
    i_{lim} & = F S C^* \sqrt{k_1 D_{cat}} \\
    G_{EC} & = \varepsilon_1 \\
    H_{EC} & = \frac{\sqrt{D_{cat}}}{k_o \exp\left[-\alpha f(E-E_1)\right]} 
\end{align*}
\]

Scheme 2. EC reaction scheme and the equation depicted for the EC reaction. O: oxidized state. R: reduced state. A is the substrate, and P is the product.

Dividing equation 4 by the peak current \( i_p \) under Nernstian conditions leads to equation 1, and FOWA plots were constructed by plotting \( 1/(1+\varepsilon_1) \) vs. \( i/i_p \). Figure 2 shows EC-scheme voltammograms and FOWA plots varying the ratio of \( \gamma \). The straight lines from Nernstian behavior start to deviate when interfacial electron transfer becomes sluggish and convex curves are observed when \( \gamma \) is smaller than ca. \(-2.78\) (Figure 2c and Figure S1). Compared to the concave curve due to substrate depletion as shown in Figure 2b, the convex feature can be attributed to the requirement of high overpotentials to facilitate fast interfacial electron transfer for the overall reaction. This is why a rapidly rising trace is observed when \( i \) approaches \( i_{lim} \). On the other hand, substrate depletion, product inhibition or catalyst deactivation mainly affect the value of the numerator. \(^3a\) \((k_1 \) or \( C^* \) is affected by product inhibition, \( C^* \) is affected by catalyst deactivation, and \( C^0_A \) is affected by substrate depletion). Such a concave shape of the FOWA plot by these three factors are expected to be prominent in the Nernstian region. Therefore, the features of a FOWA plot can be used to diagnose different phenomena.
Now focusing on the extraction of kinetic parameters, a range of $i/i_p$ between $5 \times 10^{-3}$ to $5 \times 10^{-2}$ was chosen for a linear fitting to determine pseudo-first order rate constants as shown in Figure 2c (the reason why this range is taken for the determination of rate constants will be discussed later). The rate constant, $k_1$ determined by FOWA leads to ca 10% difference compared to the value used for simulations when $\gamma$ is $-3.4$. When $\gamma$ is $-4.9$, the value obtained from FOWA leads to an order-of-magnitude difference (Figure S2). In comparison, the exact value of $k_1$ was determined from the FOWA traces in the case of substrate depletion.
Figure 2 Voltammograms and FOWA plots for the EC mechanism. (a) Steady-state S-shape voltammograms in the pure kinetic region without substrate depletion. Different ratios of $\gamma$ used for simulations are labelled with voltammograms. $E_1$ is set as $-0.2$ V and $k_1 = 100$ s$^{-1}$ ($C_A = 1$ M, $k'_1 = 10^2$ M$^{-1}$ s$^{-1}$). The vertical dashed line indicates $E_{cat/2}$. (b) Substrate depletion
occurs. The gray, cyan and purple traces refer to $C_A = 2 \text{ mM}$, $k'_1 = 5 \times 10^4 \text{ M}^{-1} \text{s}^{-1}$; $C_A = 0.01 \text{ M}$, $k'_1 = 10^4 \text{ M}^{-1} \text{s}^{-1}$, and $C_A = 0.1 \text{ M}, k'_1 = 10^3 \text{ M}^{-1} \text{s}^{-1}$ respectively. (c) FOWA figure.

The other important feature is that $E_{\text{cat/2}}$ is equal to the formal potential of the catalyst (i.e. $E_l$) in the absence of substrate. The relative value between $E_{\text{cat/2}}$ and $E_l$ is useful to diagnose relative rate constants for multiple-electron electrochemical reactions as discussed later if the electrode kinetics are Nernstian. Noticeably, $E_{\text{cat/2}}$ also deviates from $E_l$ when non-Nernstian behavior occurs, but the shift is in the negative direction (green trace in Figure 2a).

**Homogeneous ECEC and EECC systems** Compared to the EC scheme, the general equations for ECEC (eq 2) and EECC (eq 3) are more complicated because an additional exponential function is required to depict a second electrochemical process. Such an extra exponential function is expected to complicate FOWA traces. Approximate EC-type equations (i.e. $i_{\text{lim}} = [1/(1+\varepsilon_1 \text{ or } 2)]$) in the Nernstian region have been reported assuming $\Delta E$ is large.\(^{3b}\) Here, the influence of each parameter of eq 2 and eq 3 on the FOWA plots are further interrogated for gaining wider insights and understanding important limitations. For example, compared to the EC scheme (eq 4), equation 2 for the ECEC scheme contains two additional terms in G and one additional term in H, both of which describe the second electrochemical process. Consequently, different ratios of $\varepsilon_1/\varepsilon_2$ or $k_1/k_2$ can have a great impact on whether or not eq 2 can be simplified to the EC-type equation for FOWA; therefore, the features of FOWA plots directly reflect different thermodynamic and kinetic parameters.

**ECEC scheme**

**Category I.** $E_l < E_2$

This scenario is the most commonly proposed mechanism among electrocatalysts in the literature,\(^8\) where the second electrochemical process is more thermodynamically feasible than the first one. Therefore, the formal potential $E_l$ is used as $[1/(1+\varepsilon_1)]$ in the x-axis of the FOWA plot.

$1_{\text{ECEC}}, k_1 > k_2$

Figure 3 shows voltammograms, FOWA plots and $k_l$ values determined by FOWA in different conditions within Nernstian conditions. The key findings from Figure 3 can be summarized as follows. First, in the voltammograms shown in Figure 3a and 3d, the more negative onset potential for electrocatalysis is observed when $E_l$ is more negative. Also, when the value of $k_1/k_2$ is larger, the value of $E_{\text{cat/2}}$ shifts to be more positive following the relation $E_{\text{cat/2}} = E_1 +$
\( \frac{RT}{F} \ln \left( \frac{k_1}{k_2} \right) \) as shown before\(^3\). The corresponding FOWA traces reveal a more rapidly rising and curved shape as the ratio of \( k_1/k_2 \) becomes larger or \( \Delta E \) increases (Figure 3b vs 3e). Secondly, the faster rate constant of the first chemical step, \( k_1 \), can be determined by FOWA. In such cases, a curved FOWA trace is obtained, as is generally observed in literature. However, as \( \Delta E \) becomes small, \( k_1 \) determined by FOWA, defined as \( k_{1,\text{FOWA}} \), shows large deviations from the actual value as seen in Figure 3c and 3f. For example, \( k_{1,\text{FOWA}} \) is more than one order-of-magnitude smaller than \( k_1 \) used for the simulations with \( k_1/k_2=1000 \) (\( \Delta E = -60 \) mV) and approximately 0.5 times that of \( k_1 \) with \( k_1/k_2 = 10 \) (when \( \Delta E = -60 \) mV). The greatly underestimated \( k_1 \) values are due to the fact that there is a large contribution from \( \varepsilon_2 \), thus equation 2 cannot be simplified to the Nernstian EC-type equation. Figure 4 further summarises the difference between the most precise \( k_{1,\text{FOWA}} \) value that can be determined by FOWA and \( k_1 \) when varying the ratio of \( k_1/k_2 \) and \( \Delta E \).

As shown in Figure 4, the difference between \( k_{1,\text{FOWA}} \) and \( k_1 \) is within an order of magnitude when the difference between \( E_2 \) and \( E_I \) is larger than 0.15 V. In such a situation, the denominator in eq 2 simplifies to \( \frac{1}{\sqrt{k_2}} + \frac{1}{\sqrt{k_1}} (1+\varepsilon_1) \) (i.e. \( i = \frac{2FSC^∗\sqrt{D_{cat}k_1}}{1+\varepsilon_1+\frac{\sqrt{k_1}}{\sqrt{k_2}}} \) eq 5). Accordingly, the FOWA trace is expected to be curved as shown in Figure 3b and 3e due to the additional term, \( \frac{\sqrt{k_1}}{\sqrt{k_2}} \) compared to eq 4 under Nernstian conditions. It follows that \( k_1 \) can be determined from FOWA plots (as demonstrated mathematically in SI II, section 3), and the rate-limiting constant, \( k_2 \), should be determined from the plateau current. To obtain as precise a \( k_{1,\text{FOWA}} \) value as possible, fitting the range between the earliest starting potential far from catalysis occurring and the first few points is required as shown in black points of Figure 3c and 3f (see mathematical proof in SI II, section 3). We termed this range as the ideal range. However, in practice, this range is not possible to obtain due to a large contribution from non-Faradaic current, which compromises analysis. The difference between \( k_{1,\text{FOWA}} \) and \( k_1 \) is sensitive to the range of data selected for fitting. For example, taking values of 1/(1+\( \varepsilon_1 \)) (with corresponding range of \( i/i_p \) in parentheses) from 7x10^{-5} to 7x10^{-4} (5x10^{-3} – 5x10^{-2}), 0.001 to 0.005 (0.069 – 0.307), and 0.01 to 0.02 (0.541 – 0.877). (see Figure S3, \( E_I = -0.2 \) V, \( k_1/k_2 = 1000 \) in Figure 3b olive line). The corresponding values of \( k_{1,\text{FOWA}} \) are 945, 795 and 443 \( \text{s}^{-1} \) respectively compared to 975 \( \text{s}^{-1} \) obtained from the ideal range.

Alternatively, we chose the experimentally accessible range of \( i/i_p \) between 5x10^{-3} and 5x10^{-2} (as shown in the red points of Figure 3c and 3d, defined as the empirical range) for
fitting to determine $k_1$ at a scan rate of 0.1 V s$^{-1}$. In general, the double layer capacitance of a typical electrode is approximate 1 – 40 µF cm$^{-2}$. Therefore, the observed onset of the catalytic current can be roughly estimated as $10^{-8}$ A (assuming a 1 mM concentration of catalyst and a 3 mm diameter glassy carbon electrode) above any background current. According to the Randles-Sevcik equation, the peak current under these conditions is approximately $10^{-5}$ A, and therefore, the reliable range to determine kinetic values should be approximate in the range of $10^{-3} < il/i_p < 10^{-1}$. We will later use experimental results to further justify the selection of this range. From now on, all $k_{1,\text{FOWA}}$ values are determined through this so-called empirical range unless stated otherwise.

The effect of substrate depletion (i.e. the peak shape instead of the S-shape in the voltammograms) on the FOWA trace was further examined. The characteristic shape, a rapidly rising curve compared to the deviation from a straight line as shown in Figure 2c for EC, can still be observed in the early range of FOWA trace as shown in Figure S6 and S7. Therefore, this distinct feature can serve as a diagnostic feature for $I_{ECEC}$ mechanism as opposed to other different features discussed later.

When considering non-Nernstian behavior, a convex curve in the FOWA plots can be observed as shown in the EC scheme previously (Figure S4). Figure 3c and 3f summarize the effect of varying the ratio, $\gamma$, to obtain within 10% and an order-of-magnitude difference in $k_{1,\text{FOWA}}$ vs. $k_1$, which clearly exhibits that the deviation of $k_{1,\text{FOWA}}$ is large with slow electrode kinetics as expected. However, the effect is lessened when the ratio $k_1/k_2$ is small.
Figure 3 Voltammograms, FOWA plots, and the kinetic rate constants determined by FOWA for the ECEC mechanism ($E_1 < E_2$ and $k_1 > k_2$). The following values are used for simulations.\( k_1 = 1000 \text{ or } 10 \text{ s}^{-1} \), \( k_2 = 1 \text{ s}^{-1} \) and \( E_2 = 0 \text{ V}, \nu = 0.1 \text{ V s}^{-1} \). The dashed voltammogram refers to the absence of substrate with $E_I = -0.4 \text{ V}$, and the vertical dashed line corresponds to $E_{cat/2}$ for the corresponding catalytic wave ($E_I = -0.4 \text{ V}$). For clarity, only the redox wave for $E_I$ is simulated and presented here. The horizontal dashed lines in (c) and (f) refers to 10% (upper line) or an order-of-magnitude (lower line) difference of $k_{I,FOWA}$.
respectively compared to \( k_i \). The lowest value for \( \log (k_d/k_i) \) is labelled in the corresponding margin.

**Figure 4. Evaluation of the difference between \( k_{1,FOWA} \) and the \( k_i \) value for the ECEC mechanism (\( E_1 < E_2 \)).** \( k_{1,FOWA} \) is determined by fitting data points from the ideal range. The dashed area refers to region where \( k_{FOWA} \) is much closer to \( k_2 \) (within one order-of-magnitude). The difference between \( k_{2,FOWA} \) and \( k_2 \) as a function of the same parameters is shown in Figure S5.

2. \( E_{CEC}. k_i < k_2 \)

First, the Nernstian scenario is discussed. Voltammograms, FOWA plots, and \( k_{1,FOWA} \) in different conditions are presented in Figure 5. Compared to \( 1_{ECEC} \), two striking differences are observed: \( E_{cat/2} \) is equal to \( E_1 \) in all the voltammograms, and FOWA traces are linear or close to be linear. Since \( k_2 \) is larger than \( k_i \), the denominator for eq 5 can be further simplified as \( \frac{1}{\sqrt{k_1}} (1+\varepsilon_1) \) (i.e. \( \frac{2FSC\sqrt{D_{cat}k_1}}{1+\varepsilon_1} \) eq 6), if \( \varepsilon_1 \) is at least 60 mV larger than \( \varepsilon_2 \). Therefore, the rate-limiting \( k_1 \) value can be determined from the slope. Alternatively, if S-shaped voltammograms are observed, the \( k_i \) value can be directly obtained through \( i_{lim} \). The difference between \( k_{1,FOWA} \) and \( k_i \) is less sensitive to \( \Delta E \) compared to \( 1_{ECEC} \), but \( k_{1,FOWA} \) starts to be less accurate when \( k_2 \) approaches \( k_i \) (Figure 5c vs Figure 5f). In non-Nernstian conditions, the deviation from
Linarity starts to become evident, as shown in Figure S8. Compared to $I_{ECEC}$ in non-Nernstian conditions, $2_{ECEC}$ proves to be less sensitive to $\Delta E$.

Figure 5. Voltammograms, FOWA plots, and the kinetic rate constants determined by FOWA for the ECEC mechanism ($E_1 < E_2$ and $k_1 < k_2$). The following values are used for simulations. $k_1 = 1$ s$^{-1}$, $k_2 = 1000$ or 10 s$^{-1}$ and $E_2 = 0$ V, $\nu = 0.1$ V s$^{-1}$. The dashed voltammogram refers to the absence of substrate with $E_1 = -0.4$ V, and the vertical dashed line corresponds to $E_{cat/2}$ for the corresponding catalytic wave ($E_i = -0.4$ V). For clarity, only the redox wave for $E_1$ was simulated and presented here. The horizontal dashed lines in (c) and (f)
refers to 10% difference in $k_{1,FOWA}$ compared to $k_1$. The lowest value for log ($k_0/k_2$) is labelled in the corresponding margin.

**Category II. $E_1 > E_2$**

Since $E_2$ is more negative than $E_1$, the expression $[1/(1+\varepsilon_2)]$ should be used for the x-axis in the FOWA plot. However, in practice, the determination of $E_2$ for the intermediate species, “IA”, is challenging because $E_2$ cannot be directly evaluated from CV in the absence of substrate. This value may be estimated through theoretical calculations. Alternatively, a pre-wave feature attributed to “IA” species before electrocatalysis can sometimes be observed in the voltammogram due to a higher driving force required for the second electrochemical processes. Therefore, $k_1$ can be estimated by varying scan rates and substrate concentration, “A” (detailed methods can be found in ref. 5-6). The value of $k_2$ can be further estimated by $i_{lim}$ (eq 2). Finally, $E_2$ can be determined by the relation of $E_{cat/2} = E_2 + \frac{RT}{F} \ln\left(\frac{k_2}{k_1}\right)$ discussed earlier if $k_2$ is larger than $k_1$. The extent of $\Delta E$ and sluggish interfacial electron transfer are expected to have a great impact on the accuracy of these analyses.

$3_{ECEC} k_1 > k_2$ and $4_{ECEC} k_1 < k_2$

Equation 2 described for ECEC can be regarded as two separate EC steps. Therefore, $3_{ECEC}$ and $4_{ECEC}$ have the same behavior as described above for $2_{ECEC}$ and $1_{ECEC}$ respectively.

**EECC scheme**

**Category I. $E_2 < E_1$**

In this scenario, both formal potentials of $E_1$ and $E_2$ can be evaluated by CV in the absence of substrate, and the expression $[1/(1+\varepsilon_2)]$ should be used for the x-axis of the FOWA plots.

$5_{EECC}. k_1 > k_2$

The rate constant, $k_1$, can be determined, in the same manner to $1_{ECEC}$ or $4_{ECEC}$ due to the similarity between eq2 and eq3. However, greater errors were found in this case as shown in the insets of Figure 6c and 6f respectively (and Figure S10) using $1/[1+\varepsilon_2]$ for the x-axis, considering only Nernstian conditions. This is due to the fact that eq 3 contains the product of two exponential functions, $\varepsilon_1\varepsilon_2$, compared to the single exponential function in eq2. Consequently, an even larger $\Delta E$ is required to simplify eq3 to $i = \frac{2FSC^*}{\sqrt{D_{cat}k_1}} \frac{1}{1+\varepsilon_2} + \frac{\sqrt{k_2}}{\sqrt{k_1}} \frac{1}{1+\frac{k_2}{k_1}}$ eq 7. In
this case, as suggested by eq 7, $k_1$ can be determined by FOWA and $k_2$ can be determined from $i_{\text{lim}}$. Another noticeable difference of FOWA plots between EECC and ECEC is the feature of a lag phase observed in the EECC mechanism (inset in Figure 6b/e vs. Figure 3b/e) when $\Delta E$ is smaller than ca. –60 mV, which can serve as an indicator for the different mechanisms.

Since both formal potentials can be obtained from CVs in the absence of substrate, an alternative expression of the x-axis, $1/[1+(1+\varepsilon_1)\varepsilon_2]$ for FOWA plots was used to determine $k_1$. With this new expression, all FOWA traces with varying $\Delta E$ values nearly overlap as shown in Figure 6b and 6e, thus leading to a much more precise $k_{1,FOWA}$ without any limitation by a small $\Delta E$. For slow electrode kinetics, the convex curve of FOWA plots was observed from the two different expressions of the x-axis (Figure S11); however, the x-axis value evaluated as $1/[1+(1+\varepsilon_1)\varepsilon_2]$ leads to the more precise determination of $k_{1,FOWA}$. 
Figure 6. Voltammograms, FOWA plots and the kinetic rate constants determined by FOWA for the EECC mechanism ($E_1 > E_2$ and $k_1 > k_2$). The following values are used for simulations. $k_1 = 1000$ or $10$ s$^{-1}$, $k_2 = 1$ s$^{-1}$ and $E_L = 0$ V, $\nu = 0.1$ V s$^{-1}$. The dashed voltammogram refers to the absence of substrate with $E_i = -0.4$ V, and the vertical dashed line corresponds to $E_{cat/2}$ for the corresponding catalytic wave ($E_i = -0.4$ V). For clarity, only the redox wave for $E_2$ was simulated and presented here. The horizontal dashed lines in (c) and (f) refers to 10% difference in $k_{1\_FOWA}$ compared to $k_1$. The lowest value for log ($k_0/k_1$) is labelled
in the corresponding margin. The insets in (b) and (e) show FOWA plots using $1/(1+\varepsilon_2)$ for the x-axis, and the insets in (c) and (f) show the resulting $k_{l,FOWA}$ values.

**6EECC. $k_1 < k_2$**

Within Nernstian behavior, equation 7 can be simply expressed as 
$$i = \frac{2FSC^*vD_{cat}k_1}{1+\varepsilon_2} \text{ eq 8.}$$

Therefore, a straight line is expected in which $k_1$ (i.e. rate-limiting step) is obtained. The greater difference of $k_{l,FOWA}$ determined by using $1/[1+\varepsilon_2]$ as the x-axis occurs when $\Delta E$ is small due to the presence of a “lag phase” as shown in the insets of Figure 7b and 7e. Alternatively, the $i_{lim}$ value can be used to determine the $k_1$ value without any limiting value for $\Delta E$, if S-shape voltammograms can be obtained. As discussed in the previous case, using $1/[1+(1+\varepsilon_1)\varepsilon_2]$ can lead to much higher accuracy. Accordingly, $k_{l,FOWA}$ obtained is the exactly same as $k_1$ as shown in Figure 7c and 7f. For non-Nernstian behavior, the deviation from a straight line starts to be observed. The estimation of the $k_{l,FOWA}$ values including deviation due to the slow electrode kinetics can be found in Figure S14.
Figure 7. Voltammograms, FOWA plots and the kinetic rate constants determined by FOWA for the EECC mechanism ($E_1 > E_2$ and $k_1 < k_2$). The following values are used for simulations: $k_1 = 1 \text{s}^{-1}$, $k_2 = 1000$ or $10 \text{s}^{-1}$ and $E_1 = 0 \text{V}$, $\nu = 0.1 \text{V s}^{-1}$. The dashed voltammogram refers to the absence of substrate with $E_1 = -0.4 \text{V}$, and the vertical dashed line corresponds to $E_{cat/2}$ for the corresponding catalytic wave ($E_1 = -0.4 \text{V}$). For clarity, only the redox wave for $E_2$ was simulated and presented here. The horizontal dashed lines in (c) and (f) refers to 10% error in $k_{1,FOWA}$ compared to $k_1$. The lowest value for log ($k_0/k_2$) is labelled in this error margin.
The insets in (b) and (e) show FOWA plots using $1/(1+\epsilon_2)$ for the x-axis, and the insets in (c) and (f) show the resulting $k_{1,FOWA}$ values.

**Category II. $E_2 > E_1$**

This condition is highly unlikely to occur when the second electron transfer is more feasible without involving a chemical step that stabilizes the one-electron reduced species. If such molecular catalysts indeed exist, it is expected to have a very rapid rate for the first chemical steps ($k_1 \geq k_2$) since two-electron reduced species should be very reactive and $\Delta E$ is expected to be very small. The FOWA trace rises very rapidly as shown in Figure S15, due to the more favorable second electrochemical process. This leads to overestimated kinetic values from FOWA.

**ECE\textsubscript{dim} scheme**

The voltammograms for a Nernstian homolytic reaction (ECE\textsubscript{dim})\textsuperscript{3b} as shown in Scheme 3 were also modelled to compare with EEC and EECC. The expression of $1/(1+\epsilon_1)^{1.5}$ for FOWA can only be achieved with the assumption of pre-equilibrium conditions (i.e. $k_{-1}^r \gg k_2^r [RA]$). Otherwise, the current-potential equations for other conditions are not possible to be arranged simply with $1/(1+\epsilon_1)^{\delta}$ ($\delta$: constant) as the x-axis.\textsuperscript{9} In pre-equilibrium conditions, the voltammograms and FOWA traces are greatly influenced by pre-equilibrium constants, $K_{ECE\textsubscript{dim}} = \frac{k_{+1}^r c_A}{k_{-1}^r}$ as suggested from Eq 9. The linear FOWA traces start to deviate and become curved when $K_{ECE\textsubscript{dim}}$ is larger than ca 0.3, which also affects values determined by FOWA (as shown in Figure S16). Therefore, unambiguous distinction between the ECE\textsubscript{dim} or ECEC/EECC schemes relies on the analysis of the dependence of $i_{lim}$ on $[C^*]^{1.5}$ or $[C^*]^{10}$. More detailed discussions can be found in SI. Table 1 summarizes all key characteristics for different mechanisms.
\[
\frac{i}{i_P} = 2.59 \sqrt{\frac{k_1^e C^e R T}{F \nu}} \times \frac{(k_1^e C^o)}{(1 + \frac{k_1^e C^o}{k_{-1}^e + \varepsilon_1})^{1.5}} \tag{9}
\]

\[
\dot{i}_{lim} = \sqrt{\frac{4k_2^e D_{cat}}{3}} \times \frac{(k_1^e C^o)}{(1 + \frac{k_1^e C^o}{k_{-1}^e})^{1.5}} (C^*)^{1.5}
\]

**Scheme 3.** The *pre-equilibrium homolytic reaction* (ECE\textsubscript{dim}). O: oxidized state, R: one-electron reduced state, A is the substrate involved with the chemical steps, and P is the product formed by homogeneous reaction between two substrate-bound intermediate state, RA.
Table 1. Summary of key feature of homogeneous EECC and ECEC in the foot wave of the analysis.

| Thermodynamic parameters | ECEC FOWA-axis: $1/[1 + \varepsilon_2]$ | EECC FOWA-axis: $1/[1 + (1 + \varepsilon_1)\varepsilon_2]$ |
|--------------------------|---------------------------------|---------------------------------|
| Mechanism                | $E_1 > E_2$                     | $E_1 > E_2$                     |
| Characteristic feature   |                                 |                                 |
| Kinetic information      | $k_1 < k_2$                     | $k_1 < k_2$                     |
|                         | $k_2$ from FOWA                 | $k_1$ from FOWA                 |
|                         | $k_1$ from $i_{lim}$            | or $i_{lim}$                    |
|                         | Sensitive to $\Delta E$, i.e.   | Less sensitive to $\Delta E$, i.e. |
|                         | great errors in $k_2$ calculated from FOWA for $\Delta E < 150$ mV. | small errors in $k_2$ calculated from FOWA for $\Delta E < 60$ mV. |
|                         | $E_{cat/2} = E_2 + \frac{1}{2} \ln \left(1 + \frac{k_1}{k_2}\right)$ | $E_{cat} = E_2$ |

$E_1 < E_2$

| ECEC FOWA-axis: $1/[1 + \varepsilon_1]$ | EECC FOWA-axis: $1/[1 + \varepsilon_1]$ |
|---------------------------------|---------------------------------|
| Mechanism                       | $E_1 < E_2$                     | $E_1 < E_2$                     |
| Characteristic feature          |                                 |                                 |
| Kinetic information             | $k_1 < k_2$                     | $k_1 > k_2$                     |
| $k_1$ from FOWA                 | $k_1$ from FOWA                 | $k_2$ from $i_{lim}$            |
| or $i_{lim}$                    | or $i_{lim}$                    | or $i_{lim}$                    |
| Less sensitive to $\Delta E$, i.e. small errors in $k_1$ calculated from FOWA for $\Delta E < 60$ mV. | Sensitive to $\Delta E$, i.e. great errors in $k_1$ calculated from FOWA for $\Delta E < 150$ mV. |
| $E_{cat/2} = E_1$               | $E_{cat/2} = E_1$               |

Unlikely scenario in practice

- $k_2$ or $k_1$ from $i_{lim}$
- *FOWA is not applicable*
Limitations and Implication

In principle, an ideal and efficient catalyst for two-electron electrochemical reactions is expected to have a small difference between $E_1$ and $E_2$ with both values close to the thermodynamic value for the overall reaction. However, the inaccuracy of rate constants determined by FOWA increases as $\Delta E$ becomes smaller. For EECC, the limit of accuracy by a small $\Delta E$ can be relieved using $1/[1+(1+\varepsilon_1)\varepsilon_2]$ as the x-axis. For ECEC, to avoid such errors, the direct simulations of voltammogram is required. On the other hand, if the difference within an order-of-magnitude range is acceptable, the rate constants determined by FOWA with $\Delta E >$ ca. 0.1 V can give a reasonable value. In the case of substrate depletion, the $k_{1,FOWA}$ values determined by FOWA become even less accurate, particularly when $\Delta E$ becomes small (Figure S6 vs S7). Nevertheless, the characteristic features for different mechanistic profiles still remains, which can help identify the rate-limiting chemical step.

As shown earlier, the determination of the slope from a FOWA trace is sensitive to the selection of $E_1$ or $E_2$ for calculating x-axis values and the selection of the fitting range. For example, it is challenging to determine $E_2$ in the $4_{ECEC}$ mechanism. Applying a more negative $E_2$ in calculating $1/(1+\varepsilon_2)$ can lead to an overestimated kinetic value. In addition, in most systems, high scan rates are required to reach $i_{lim}$, which could lead to more inaccurate estimation of rate constants due to the higher capacitive current. However, the corresponding features of FOWA traces contain useful information. For example, different curvatures of FOWA traces are expected to be observed from a series of modifications of a $1_{ECEC}$-mechanism molecular electrocatalyst by functional groups, which can provide direct information and comparison on how chemical properties or electronic structure influence the chemical step. Finally, it is worth noting that catalytic Tafel plots cannot be constructed in a meaningful way if the FOWA trace is curved and $i_{lim}$ cannot be achieved in the voltammogram.

Regarding the limit by interfacial electron transfer, a convex feature in the FOWA plots indicates that slow electrode kinetics affect the overall performance of electrocatalysts. Assuming a difference within an order-of-magnitude range for rate constants determined by FOWA is acceptable, the limit of $\gamma$ is between ca. $-4$ and $-5.5$ within the range of rate constants studied here for ECEC and EECC. This regime should be accessible in most systems without considering the effect of interfacial electron transfer. Alternatively, equation 1 describing the Nernstian EC mechanism can be replaced with eq 10 for all scenarios. As eq 10 itself (derived in SI II, section 4) suggests, the determination of the slope by plotting the left side of the
equation against $1/(1+\varepsilon_1)$ leads to a precise $k'_1$ value. The rate constant, $k_0$ between catalysts and an electrode can be estimated through a trumpet plot$^6$ and the diffusion coefficient can be determined by a variety of methods.$^6$ In the case of multi-electron reactions (ECEC and EECC), the situation is more complex resulting from additional terms as shown in eq 2 and 3. If $\Delta E$ is large enough, a similar non-Nernstian EC equation (eq 10) can be derived for ECEC. Otherwise, extraction of reliable rate constants for chemical steps may then require fitting the experimental voltammograms.

$$\frac{i}{i_p} = \frac{2.24 \sqrt{\frac{k'_1 c^0_A}{Fv}}} {1 - 0.446 \times \frac{1}{(i_p)} \times \frac{\sqrt{D_{cat} Fv}}{k_0} \varepsilon_0^{0.5}} (10)$$

Finally, we briefly discuss electrochemical reactions beyond two-electron processes, such as four-electron oxygen reduction and water oxidation. The determination of rate constants by FOWA is expected to be even more sensitive to $\Delta E$. For example, the equation describing a four electron, Nernstian ECECECEC mechanism can be expressed as

$$i = \frac{4SFC^* \sqrt{D_{cat}}}{\sqrt{k_1} + \sqrt{k_2} + \sqrt{k_3} + \sqrt{k_4} + G_{ECECECEC}} \quad (11)$$

$$G_{ECEC} = \frac{\varepsilon_1}{\sqrt{k_1}} + \frac{\varepsilon_2}{\sqrt{k_2}} + \frac{\varepsilon_3}{\sqrt{k_3}} + \frac{\varepsilon_4}{\sqrt{k_4}}$$

To simplify eq 11 to the EC-type expression for FOWA, one of the formal potentials is required to be dominantly more negative than the rest. Under such conditions, the performance of the catalyst is expected to be poor. In most decent electrocatalysts, the formal potential of each electron transfer is expected to be close to the thermodynamic potential of the overall reaction.$^{11a}$ Furthermore, other mechanisms, such as EECCECEC, must contain the product of multiple exponential functions, which creates even more difficulty to simplify the expression to the EC-type equation (for example, EECC vs ECEC as discussed earlier). A careful analysis of the mechanistic scheme is required, which recently has been demonstrated.$^{13}$
Figure 8. Molecular structure of electrocatalysts discussed in the case study. $1^{\text{Ni}}$ and $2^{\text{Co}}$ are H$_2$-evolving catalysts and $3^{\text{Re}}$ is a CO$_2$-reducing catalyst.

Case A. H$_2$-evolving catalyst

Inspired by hydrogenases, based on featuring a proton shuttle, Ni($\text{Ph}_2\text{PPh}_2$)$_2$ (1$^{\text{Ni}}$), cobaloxime (2$^{\text{Co}}$), and their analogues are among most widely studied molecular catalysts for H$_2$ evolution.\textsuperscript{8, 14} For 1$^{\text{Ni}}$ and 2$^{\text{Co}}$, re-examination of earlier voltammograms reported from the literature clearly indicated that an ECEC mechanism occurs with $k_1 > k_2$.\textsuperscript{8, 15} because $E_{\text{cat/2}}$ in the voltammogram of both complexes is clearly shifted to more positive potentials during electrocatalysis compared to $E_1$ in the absence of protons. These simple assessments are consistent with the recent detailed studies of both complexes and their analogues by CV in combination of FOWA (curved FOWA traces observed) and spectroscopic methods.\textsuperscript{4, 16} For example, the rate constant for the first protonation process measured by transient spectroscopy\textsuperscript{17}, is $4 \times 10^9 \text{M}^{-1}\text{s}^{-1}$, which is within a reasonable agreement to the value $3 \times 10^8 \text{M}^{-1}\text{s}^{-1}$ determined by FOWA\textsuperscript{16b}. The lower value obtained from FOWA may be ascribed to the range used for determining a rate constant, small $\Delta E$ value (~0.1 V)\textsuperscript{16b, 18} or different experimental conditions (such as a stronger acid used in transient spectroscopy).

To demonstrate the empirical fitting range ($i/i_p$ between $10^{-3}$ and $10^{-1}$) for FOWA plots suggested earlier when extracting kinetic information, a proton-reduction catalyst, 2$^{\text{Co}}$, was examined in the presence of chloroacetic acid (Figure S19) in the framework of an ECEC
reaction where $E_1 < E_2$. Indeed, the curvature of the FOWA plots (Figure 9) indicate that $k'_1$ is larger than $k'_2$, and resulted in $k'_1 = 755 \text{ M}^{-1} \text{ s}^{-1}$ (Fig. S21). Using this value obtained from FOWA and the standard rate constant ($k_0$) for the Co$^{II}$/I couple (trumpet plot, Fig. S18), plotting the experimental CVs with the simulated current-potential curves derived from of eq. 2 resulted in reasonable fits (Figure S23). This confirms that satisfactory accuracy can be achieved when determining rate constants by using the earliest possible range for fitting of the FOWA plots.

**Figure 9.** FOWA plots of 1 mM $2^{Co}$ in 0.1 M TBAPF$_6$/MeCN with addition of various concentrations of chloroacetic acid (from bottom to top 2 mM, 4 mM, 6 mM, 8 mM, 12 mM, and 16 mM). Inset shows region used for linear fitting.

**Case B. CO$_2$-reducing catalyst**

The Re(4,4’-‘Bu$_2$bpyp)(CO$_3$)(Cl) (4,4’-‘Bu$_2$bpyp = 4,4’-di-tert-butyl-2,2’-bipyridine) complex (4$^{Re}$), as shown in Figure 8, is known to catalyze CO$_2$ to CO photochemically$^{19}$ and electrochemically$^{20}$ with almost 100% Faradaic efficiency. Recently, Kubiak and co-workers studied 4$^{Re}$, modified with different substituents on bpy and various labile ligands$^{20b}$ and pointed out the rate constants determined by FOWA are larger (5-100 times, Table S4 from ref. 20b) than the values (ca. $\sim 10^3 \text{ s}^{-1}$) obtained from the plateau current.$^{20b}$ Re-examination of FOWA figures for Re(tBu-bpy)(CO$_3$)$^{-}$ revealed a curve feature which indicates the first chemical step is faster than the second chemical step.$^{21}$ The pseudo first order rate value determined by FOWA was reported as ca $8\times 10^4 \text{ s}^{-1}$, which corresponds to the first chemical step. The rate constant determined by a plateau current is 2601 $\text{ s}^{-1}$, which is in good agreement
with the value obtained from the stopped-flow spectroscopy, ca 4000 s$^{-1}$. These results indicate that the proposed mechanism based on electrochemical results are consistent with conclusion drawn by spectroscopic and DFT studies.

**Case C. The role of $E_{\text{cat}/2}$**

Plotting $1/(1+\exp(f(E-E_{\text{cat}/2}))$ as the x-axis for constructing a FOWA plot also has been suggested as an alternative method to identify the reaction sequence due to a deviation from a straight line in the low overpotential range in FOWA plots. However, taking the ECEC mechanism as an example, a straight line is expected in the FOWA plot according to the expression obtained by combining eq 5 and $E_{\text{cat}/2} = E_1 + \frac{RT}{F} \ln\left(\frac{k_1}{k_2}\right)$. Indeed, in our in-silico voltammograms, only a completely straight line was observed regardless of mechanism (Figure S24) and the rate constant of the rate-limiting step could be determined. Such results are expected because this expression in the x-axis is similar to the Heyrovsky-Ilkovic equation that is generally applied to evaluate the number of electrons involved with the electrochemical reaction of interest. In addition, in the early range of the x-axis of the FOWA plot (i.e. the low overpotential), electrocatalysis should be in the pure kinetic regime within steady-state conditions. The observed deviation in the early stage of the FOWA plot using $E_{\text{cat}/2}$ may be due to capacitive current or other side reactions.

**Conclusion**

The idea of the FOWA plot developed by Savéant and Costentin for interpreting steady-state electrocatalytic voltammetry is similar to the principle of the Lineweaver-Burk equation rearranged from the Michaelis-Menten kinetics for studying enzyme kinetics. It is more accessible for determining kinetic parameters compared to the complicated fitting of the steady-state S shape voltammograms. Key features of FOWA plots presented here offer further mechanistic insights and aid in evaluating kinetic profiles as summarized in Table 1. In general, the rate constants determined from FOWA would be expected to be underestimated due to its inherent limit compared to the conventional methods, such as time-resolved spectroscopy. Nevertheless, voltammetry is widely accessible to study electrocatalysts of interest due to its wide range of electrode potential values and timescales. All of these features highlight the convenience and importance of FOWA. Finally, the similar principle can also be applied to heterogeneous systems, such as protein film electrochemistry. We are under way to further analyze the correlation between mechanistic insights and FOWA expressions in heterogeneous systems.
Supporting information

The experimental conditions, further figures and simulations can be found in the supporting information I, and detailed derivations for equations can be found in supporting information II.

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**TOC figure**
Supporting Information I

Interpreting the Electrocatalytic Voltammetry of Homogeneous Catalysts by the Foot of the Wave Analysis and Its Wider Implications

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Experimental conditions
Cyclic voltammetry was performed using a three-electrode configuration cell connected to an Autolab PGSTAT100 potentiostat. The electrode setup included a working glassy carbon electrode (0.071 cm²), a Pt counter electrode and a non-aqueous reference electrode containing Ag/Ag(NO₃) 0.01 M dissolved in acetonitrile, referenced to the ferrocenium/ferrocene couple (Fc⁺/0). The reference and counter electrodes were separated from the working compartment by a salt bridge with a glass frit. Tetrabutylammonium hexafluorophosphate (TBAPF₆) 0.1 M was used as the supporting electrolyte. All electrochemical experiments were performed under argon.
Results of in-silico modelling

Figure S1. FOWA traces for the EC mechanism varying $\gamma$ values. The value of $\gamma$ used for simulations can be found at the top-left corner. As $\gamma$ decreases, the convex feature of FOWA trace becomes apparent. The dashed trace indicates $\gamma = -2.8$ where the FOWA traces start to deviate from a straight line in Nernstian behavior, though the precise $k_l$ value still can be determined by FOWA. (see Figure S2)
Figure S2. The $k_I$ values determined by FOWA ($k_{I_FOWA}$) in the range of $i/i_p$ between $5 \times 10^{-3}$ and $5 \times 10^{-2}$. When $\gamma$ is $-3.4$, a 10% difference between $k_{I_FOWA}$ and $k_I$ used for simulations is observed.
Figure S3. FOWA traces for the ECEC mechanism, $k_1/k_2 = 1000$ and $E_1-E_2 = -0.2$ V. The ranges used to determine the rate constants via FOWA are highlighted (thick lines) (see the main text).
Figure S4. FOWA traces for the ECEC mechanism ($I_{ECEC}$ case) varying $\gamma$ values. The value of $\gamma$ used for simulations can be found at the top-left corner. As $\gamma$ decreases, the convex feature of the FOWA trace becomes apparent. $\Delta E = -0.4$ and $k_1/k_2 = 1000$ was used for simulations.
Figure S5. Evaluation of the difference between $k_{FOWA}$ and $k_2$ value for the ECEC mechanism ($E_1 < E_2$). $k_{FOWA}$ is determined by fitting data points from the ideal range. The dashed area refers to region where $k_{FOWA}$ is much closer to the $k_2$ value (within one order-of-magnitude).
Figure S6. The effect of substrate depletion in ECEC mechanism ($E_1 < E_2$, $\Delta E = -0.4$ V).
For $k_1 > k_2$ (a, b, and c), $k_1 = 10^4$ s$^{-1}$ and $k_2 = 10$ s$^{-1}$ were used for simulations. For $k_1 < k_2$ (d, e, and f) $k_1 = 10$ s$^{-1}$ and $k_2 = 10^4$ s$^{-1}$. In both cases, $E_1 = -0.4$ V, $E_2 = 0$ V, $v = 0.1$ V s$^{-1}$ and the concentration of substrate ($C_A$) is shown in the figure. The dashed line shows the corresponding voltammogram in the absence of substrate. (a and d) The dotted lines in (c) and (f) refer to $k_1$ values used for simulations. CVs were simulated with DigiElch.
Figure S7. The effect of substrate depletion in ECEC mechanism \((E_1 < E_2, \Delta E = -0.12 \text{ V})\).

For \(k_1 > k_2\) (a, b, and c), \(k_1 = 10^4 \text{ s}^{-1}\) and \(k_2 = 10 \text{ s}^{-1}\) were used for simulations. For \(k_1 < k_2\) (d, e, and f) \(k_1 = 10 \text{ s}^{-1}\) and \(k_2 = 10^4 \text{ s}^{-1}\). In both cases, \(E_1 = -0.12 \text{ V}\), \(E_2 = 0 \text{ V}\), \(v = 0.1 \text{ V s}^{-1}\) and the concentration of substrate \((C_A)\) is shown in the figure. The dashed line shows the corresponding voltammogram in the absence of substrate (a and d). The dotted lines in Figure c and f refer to \(k_1\) values used for simulations. CVs were simulated with DigiElch.
Figure S8. FOWA traces for the ECEC mechanism ($2_{ECEC}$ case) varying $\gamma$ values. The value $\gamma$ of used for simulations can be found at the top-left corner. As $\gamma$ decreases, the convex feature of FOWA trace becomes prominent. $\Delta E = -0.4$ and $k_1/k_2 = 0.001$ were used for simulations.
Figure S9. Kinetic rate constants determined by FOWA in ECEC mechanism ($E_1 < E_2$ and $k_1 < k_2$) The dashed line refers to 10% (upper dashed line) or an order-of-magnitude (lower dashed line) difference of $k_{1,FOWA}$ respectively compared to $k_I$. The lowest value for log ($k_0/k_2$) is labelled in the corresponding margin.
Figure S10. Evaluation of the difference between \( k_{l,FOWA} \) and the \( k_l \) value for the EECC mechanism.
Figure S11. FOWA traces for the EECC mechanism ($5_{EECC}$ case) varying $\gamma$ values. The value of $\gamma$ used for simulations can be found in the top-left hand corner. As $\gamma$ decreases, the convex feature of FOWA trace becomes prominent. $\Delta E = 0.4$ and $k_1/k_2 = 1000$ were used for simulations.
Figure S12. Kinetic rate constants determined by FOWA in EECC mechanism ($E_1 > E_2$ and $k_1 > k_2$) The dashed line refers to 10% (upper dashed line) or an order-of-magnitude (lower dashed line) difference of $k_{I_{-FOWA}}$ compared to $k_I$. The lowest ratio for log ($k_0/k_1$) is labelled in the corresponding margin. The expression of $[1+(1+\varepsilon_1)\varepsilon_2]$ is used for the x-axis of the FOWA plots and for determining the rate constants.
Figure S13. Comparison between the FOWA expression using $1/[1+(1+\varepsilon_1)\varepsilon_2]$ (purple) and $1/(1+\varepsilon_2)$ (black). The arrow indicates the best range to determine $k_{I,FOWA}$ for applying $1/(1+\varepsilon_2)$ for FOWA plots.
Figure S14. Kinetic rate constants determined by FOWA in EECC mechanism ($E_1 > E_2$ and $k_1 < k_2$). The dashed line refers to 10% (upper dashed line) or an order-of-magnitude (lower dashed line) error of $k_{1_{\text{FOWA}}}$ compared to $k_1$. The lowest number for log ($k_d/k_2$) is labelled in the corresponding margin. The expression $[1+(1+\varepsilon_1)\varepsilon_2]$ is used as the x-axis value for the FOWA plots and for determining rate constants.
Figure S15. FOWA in EECC mechanism ($E_1 < E_2$ and $k_1 > k_2$). The following values are used for simulations. $k_1 = 1000 \text{ s}^{-1}$, $k_2 = 1 \text{ s}^{-1}$ and $E_1 = 0 \text{ V}$, scan rate: $0.1 \text{ V s}^{-1}$. 
In order to meet the pre-equilibrium condition (the detailed derivation can be found in SI II), the relation, $k_2'k_1'C_AoC_R(k_1')^2 \ll 1$ needs to be met. The following values were used for simulating in-silico voltammograms in Figure S16a: $E_1 = -0.2$ V, $k_1' = 10^7$ M$^{-1}$ s$^{-1}$, $k_2' = 10^{-7}$ M$^{-1}$ s$^{-1}$, $C_R = 1$ mM (i.e. total concentration of catalysts, C$^*$). Assuming $\frac{k_2'k_1'C_AoC_R}{(k_1')^2} = 10^{-3}$, the acid concentration (from $10^{-5}$ to $10^2$ M) is varied to obtain the corresponding $k_1'$. Then, the pre-equilibrium constant $K_{ECE} = \frac{k_1'C_Ao}{k_1'}$ was calculated and shown in the figure above. The vertical dot line in Figure S16a refers to $-0.2$ V. The FOWA plots are shown in Figure S16b where $i/i_p$ is plotted against $[1/(1+\varepsilon_1)]^{1.5}$, which is the correct expression for ECE$_{dim}$. To compare, $[1/(1+\varepsilon_1)]$ as the x-axis for the FOWA plots is also shown in Figure S16c.

The curved FOWA trace is due to the contribution from $K_{ECE}$ in the denominator of the equation 9, $(1 + \frac{k_1'C_Ao}{k_1'} + \varepsilon_1)^{1.5}$. The reasons for curved FOWA trace observed in the ECE$_{dim}$ scheme is...
the same as discussed in $I_{ECE}$. Therefore, in order to determine the precise kinetic rate constant in the curved FOWA trace for $ECE_{dim}$, fitting the range is required to be very close to the initial data points. Finally, $k'_2$ and $K_{ECE}$ can be determined through the analysis of both FOWA and $i_{lim}$.

The $i_{lim}$ can be expressed as

$$i_{lim} = \sqrt{\frac{4k'_2D_{cat}}{3}} \frac{(k'_1C^0_A)}{(k'_{-1})} \frac{(C^*)^{1.5}}{(1+\frac{k'_1C^0_A}{k'_{-1}})^{1.5}}$$

Clearly, the $i_{lim}$ is restricted by the fraction $\frac{k'_1C^0_A}{(1+\frac{k'_1C^0_A}{k'_{-1}})^{1.5}}$. The maximum value for $\frac{k'_1C^0_A}{(1+\frac{k'_1C^0_A}{k'_{-1}})^{1.5}}$ is ca. 0.385 when $K_{ECE} = \frac{k'_1C^0_A}{k'_{-1}}$ is equal to 2.
Electrochemical studies of $2^{\text{Co}}$

**Figure S17.** Plot of peak current vs. $\nu^{1/2}$ for 1 mM $2^{\text{Co}}$ in 0.1 M TBAPF$_6$/MeCN. The diffusion coefficient ($D_{\text{cat}} = 2.2 \times 10^{-5}$ cm$^2$ s$^{-1}$) is determined by the slope.

**Figure S18.** Trumpet plot for 1 mM $2^{\text{Co}}$ in 0.1 M TBAPF$_6$/MeCN. The solid line is a plot of the peak potential $E_p$ vs. log($\nu$), obtained from CVs simulated with finite difference method for a homogeneous single electron transfer reaction where $\alpha = 0.35$ and $D_{\text{cat}} = 2.2 \times 10^{-5}$ cm$^2$ s$^{-1}$. The obtained value of $k_o$ is 0.085 cm s$^{-1}$. 
Figure S19. CVs of the catalytic wave (c.a. −1.1 V) for 1 mM $2^{\text{Co}}$ in 0.1 M TBAPF$_6$/MeCN with addition of various concentrations of chloroacetic acid (mM).

Figure S20. Normalized CVs of the catalytic wave (c.a. −1.1 V) for 1 mM $2^{\text{Co}}$ in 0.1 M TBAPF$_6$/MeCN with addition of various concentrations of chloroacetic acid (mM). Baseline correction was performed by subtracting the residual current from the Co$^{III/II}$ wave. Reverse scan has been removed for clarity.
Figure S21. Plot of $k_{\text{FOWA}}$ obtained from fits of FOWA plots in Figure 9 (main manuscript) vs. chloroacetic acid concentration (M). The slope of a linear fit gave the second order rate constant $k_1' = 755 \text{ M}^{-1} \text{s}^{-1}$.

Figure S22. Plateau current normalized to the peak current in absence of substrate plotted versus acid concentration for 1 mM $2^{\text{Co}}$ in 0.1 M TBAPF$_6$/MeCN. The slope gave a value for $k_2'$ of $240 \text{ M}^{-1} \text{s}^{-1}$.
Figure S23. Catalytic voltammograms of 1 mM $2^\text{Co}$ in 0.1 M TBAPF$_6$/MeCN with acid concentrations (dashed lines: 2 mM, black; 4 mM red; 6 mM, blue; 8 mM magenta; 12 mM green). The solid lines are plots of eq 2 from main manuscript using $k'_1 \sim 800$ M$^{-1}$ s$^{-1}$ obtained from FOWA (other parameters for fitting: $k'_2 = 600$ M$^{-1}$ s$^{-1}$; $E_2 = -0.80$ V; $k_o = 0.085$ cm s$^{-1}$; $\alpha = 0.5$, $D_{cat} = 2.2 \times 10^{-5}$ cm$^2$ s$^{-1}$). Deviation of the experimental CVs from the fitted curves near the plateau results from substrate depletion. This is confirmed by the fact the experimentally determined $k'_2$ is underestimated (240 M$^{-1}$ s$^{-1}$) compared to the value obtained by eq 2 (600 M$^{-1}$ s$^{-1}$), which assumes no substrate depletion. Reverse scan has been removed for clarity.
**Figure S24.** FOWA plots using $1/(1+E_{\text{cat}/2})$ as the x-axis for the ECEC mechanism in Nernstian conditions. Simulation parameters: $E_2 = 0$ V, $k_2 = 1$ s$^{-1}$, $v = 0.1$ V s$^{-1}$.
Interpreting the Electrocatalytic Voltammetry of Homogeneous Catalysts by the Foot of the Wave Analysis and Its Wider Implications

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Supporting Information II

1 Overview

In this supporting material document, homogeneous two-electron reduction electrocatalytic reactions occurring at the electrode through different mechanistic models were derived. The derivation in the oxidation direction can be applied in the same manner.

As described in the main text, all electrochemical reactions tackled here are assumed to be in the pure kinetic zone according to the zone diagram developed by Savéant and co-workers. Therefore, the steady-state approximation can be applied to the system of interest. Also, the diffusion coefficient is assumed to be the same for all species since diffusion coefficients for most small molecules are similar, around $10^{-5} \text{ cm}^2/\text{s}$. The bulk concentration of substrate and co-substrates are assumed to maintain constant since only a very small amount of substrates are consumed in the diffusion layer where the electrochemical reaction take places.
Here are definition of symbols used in the report.

$C_0^x$: bulk concentration of the subscript species
$[C_x]_0$: concentration of subscript species at the electrode surface
$C^*$: total concentration of catalysts in the solution
$D_{cat}$: diffusion coefficient of the catalyst
$E$: electrode potential
$E_1$: formal potential for the first electron transfer
$E_2$: formal potential for the second electron transfer
$F$: Faraday constant
$R'$: ideal gas constant
$T$: absolute temperature

\[ f = \frac{F}{R'T} \]

$i$: current
$k_0$: standard electron exchange rate constant
$k_{fx}(x = 1 \text{ or } 2)$: heterogenerous rate constant for reduction
$k_{bx}(x = 1 \text{ or } 2)$: heterogenerous rate constant for oxidation
$k'_{x}(x = 1 \text{ or } 2)$: rate constant for a chemical step
$S$: electrode surface area
$t$: time
$x$: distance
$\alpha$: transfer coefficient
$\upsilon$: scan rate

In all models, the chemical reaction (C step) is irreversible and electrode kinetics (E step) follow the Butler-Volmer equation. Therefore, the rate constants for interfacial electron transfer between the electrode and redox species can be expressed as

\[ k_f = k_0 \exp[-\alpha f(E - E_{eq})] \quad \text{(Reduction)} \]  
\[ k_b = k_0 \exp[(1 - \alpha)f(E - E_{eq})] \quad \text{(Oxidation)} \]  

Here, $\alpha$ is assumed to be 0.5 and let

\[ \varepsilon_x = \frac{k_{bx}}{k_{fx}} = \exp[f(E - E_{eq})] \]
\[ x=1 \text{ or } 2 \]

Therefore, the current $i$ is equal to

\[ \frac{i_1}{FS} = k_f[CO]_0 - k_b[R]_0 \]  

where $CO$ is oxidised species and $CR$ is reduced species.
2 The Homogeneous System

2.1 EECC scheme

First, we consider the EECC mechanism as shown in scheme 1.

\[ \begin{align*}
O + e^- & \xrightleftharpoons[k_{hl}]{k_{bl}} I & & E_1 \\
I + e^- & \xrightleftharpoons[k_{h2}]{k_{p2}} R & & E_2 \\
R + A & \rightarrow RA \\
RA + Z & \xrightleftharpoons[k_{z2}]{k_{z1}'} O + P
\end{align*} \]

**Scheme S1** The scheme for the EECC mechanism. The oxidised species, O, one-electron reduced species, I and two-electron reduced species, R. A and Z are the two co-substrates involved with the chemical steps, and P is the product. RA refers to the two-electron reduced substrate-bound intermediate state.

Therefore, the rate equations can be described as follows:

\[
\begin{align*}
\frac{\partial C_O(x,t)}{\partial t} &= D_{cat} \frac{\partial^2 C_O(x,t)}{\partial x^2} + k_2' C_Z^0 C_{RA} \\
\frac{\partial C_I(x,t)}{\partial t} &= D_{cat} \frac{\partial^2 C_I(x,t)}{\partial x^2} \\
\frac{\partial C_R(x,t)}{\partial t} &= D_{cat} \frac{\partial^2 C_R(x,t)}{\partial x^2} - k_1' C_A^0 C_R \\
\frac{\partial C_{RA}(x,t)}{\partial t} &= D_{cat} \frac{\partial^2 C_{RA}(x,t)}{\partial x^2} + k_1' C_A^0 C_R - k_2' C_Z^0 C_{RA}
\end{align*}
\]

Boundary conditions are as follows:

At \( t=0 \), \( C_O(x,0) = C^*; C_I = C_R = C_{RA} = 0 \)
Also, the concentration of electrocatalysts, \( C_O \) are \( C^* \) when electrocatalysts are far from the electrode (i.e. outside the diffusional layer, the consumption of \( C_O \) is negligible. Therefore, \( C_O \) can be seen as \( C^*_O \))

\[
\lim_{x \to \infty} C_O(x, t) = C^* \tag{2.6}
\]

For the conservation of mass,

\[
C_O + C_I + C_R + C_{RA} = C^* \tag{2.7}
\]

\[
[C_O]_0 + [C_I]_0 + [C_R]_0 + [C_{RA}]_0 = C^* \tag{2.8}
\]

For the current, \( i \) determined by E steps, the following equations can be obtained.

\[
\frac{i_1}{FS} = D_{cat} \left[ \frac{\partial C_O(x, t)}{\partial x} \right]_{x=0} = -D_{cat} \left[ \frac{\partial C_I(x, t)}{\partial x} \right]_{x=0} = k_{f1}[C_O]_0 - k_{b1}[C_I]_0 \tag{2.9}
\]

\[
\frac{i_2}{FS} = D_{cat} \left[ \frac{\partial C_I(x, t)}{\partial x} \right]_{x=0} = -D_{cat} \left[ \frac{\partial C_R(x, t)}{\partial x} \right]_{x=0} = k_{f2}[C_I]_0 - k_{b2}[C_R]_0 \tag{2.10}
\]

Since the kinetic zone is assumed, the steady-state approximation can be applied. Therefore, eq 2.1-4 is equal to nil.

Solving eq 2.3 with the boundary condition(eq 2.5), the concentration of \( C_R \) is

\[
D_{cat} \frac{\partial^2 C_R(x, t)}{\partial x^2} - k'_1 C_A^0 C_R = 0 \tag{2.11}
\]

\[
C_R = [C_R]_0 e^{x \left( -\sqrt{\frac{k'_1 C_A^0}{D_{cat}}} x \right)} \tag{2.12}
\]

Taking eq 2.12 into eq 2.10

\[
\sqrt{k'_1 C_A^0 D_{cat}[C_R]_0} = k_{f2}[C_I]_0 - k_{b2}[C_R]_0 \tag{2.13}
\]

\[
[C_R]_0 = \frac{k_{f2}[C_I]_0}{\sqrt{k'_1 C_A^0 D_{cat} + k_{b2}}} \tag{2.14}
\]

Taking eq 2.12 into eq 2.4

\[
D_{cat} \frac{\partial^2 C_{RA}(x, t)}{\partial x^2} - k'_2 C_A^0 C_{RA} = -k'_1 C_A^0 [C_R]_0 e^{x \left( -\sqrt{\frac{k'_1 C_A^0}{D_{cat}}} x \right)} \tag{2.15}
\]

Solving the differential eq 2.15 with the boundary condition, \( \left[ \frac{\partial C_{RA}}{\partial x} \right]_{x=0} = 0 \) (no electron transfer between the species RA and electrode surface occurring. Therefore, the flux is
The current, taking eq 2.12 into eq 2.10 with the relation of eq 2.14 and 2.21, we can get

\[ C_{RA} = \frac{k'_1 C_A^0}{k'_1 C_A^0 - k'_2 C_Z^0} \sqrt{\frac{k'_1 C_A^0}{k'_2 C_Z^0}} [C_R]_0 e^{\exp(-\sqrt{\frac{k'_1 C_A^0}{D_{cat}}} x)} - \frac{k'_1 C_A^0}{k'_1 C_A^0 - k'_2 C_Z^0} [C_R]_0 e^{\exp(-\sqrt{\frac{k'_1 C_A^0}{D_{cat}}} x)} \]  
(2.16)

\[ [C_{RA}]_0 = \frac{k'_1 C_A^0}{k'_1 C_A^0 - k'_2 C_Z^0} [C_R]_0(\sqrt{\frac{k'_1 C_A^0}{k'_2 C_Z^0}} - 1) \]  
(2.17)

Taking eq 2.16 into eq 2.1 with the boundary condition (eq 2.6) and solving the differential equation, we can get

\[ C_O = -\frac{k'_1 C_A^0}{k'_1 C_A^0 - k'_2 C_Z^0} \sqrt{\frac{k'_1 C_A^0}{k'_2 C_Z^0}} [C_R]_0 e^{\exp(-\sqrt{\frac{k'_1 C_A^0}{D_{cat}}} x)} + \frac{k'_2 C_Z^0}{k'_1 C_A^0 - k'_2 C_Z^0} [C_R]_0 e^{\exp(-\sqrt{\frac{k'_1 C_A^0}{D_{cat}}} x)} + C^* \]  
(2.18)

Taking eq 2.18 to eq 2.9, the following equations are obtained

\[ \sqrt{\frac{k'_2 C_Z^0 D_{cat}}{k'_1 C_A^0 - k'_2 C_Z^0}} \sqrt{\frac{k'_1 C_A^0}{k'_2 C_Z^0}} [C_R]_0 - \sqrt{\frac{k'_1 C_A^0 D_{cat}}{k'_1 C_A^0 - k'_2 C_Z^0}} [C_R]_0 = k_f [C_O]_0 - k_{b1} [C_I]_0 \]

\[ \sqrt{\frac{k'_1 C_A^0 D_{cat}}{k'_1 C_A^0 - k'_2 C_Z^0}} [C_R]_0 = k_f [C_O]_0 - k_{b1} [C_I]_0 \]  
(2.19)

rearrange eq 2.7 with eq 2.14, 2.17 and 2.19, the following equation can be obtained:

\[ W \sqrt{\frac{k'_1 C_A^0 D_{cat}}{k_f 1}} [C_I]_0 + \frac{k_{b1}}{k_f 1} [C_I]_0 + [C_I]_0 + W [C_I]_0 + W \frac{k'_1 C_A^0}{k'_1 C_A^0 - k'_2 C_Z^0} (\sqrt{\frac{k'_1 C_A^0}{k'_2 C_Z^0}} - 1) [C_I]_0 = C^* \]  
(2.20)

\[ W = \frac{k_f 2}{\sqrt{\frac{k'_1 C_A^0 D_{cat}}{k_f 1} + k_{b2}}} \]

Therefore,

\[ [C_I]_0 = \frac{C^*}{1 + \frac{k_f 2 \sqrt{\frac{k'_1 C_A^0 D_{cat}}{k_f 1 (\sqrt{\frac{k'_1 C_A^0 D_{cat} + k_{b2}})} + \frac{k_{b2}}{k_f 1 (\sqrt{\frac{k'_1 C_A^0 D_{cat} + k_{b2}})} + \frac{k_{b2}}{k_f 1 (\sqrt{\frac{k'_1 C_A^0 D_{cat} + k_{b2}})} (\sqrt{\frac{k'_1 C_A^0}{k'_2 C_Z^0}} - 1)) + k_{b1}}{k_f 1}}}} \]  
(2.21)

Taking eq 2.12 into eq 2.10 with the relation of eq 2.14 and 2.21. The current, \( i_2 \) is

\[ i_2 = \frac{FS \sqrt{\frac{k'_1 C_A^0 D_{cat}}{k_f 2}} C^*}{1 + \frac{k_{b1}}{k_f 2} + \frac{k_{b2}}{k_f 1 k_f 2} + \sqrt{\frac{k'_1 C_A^0}{k'_2 C_Z^0}} (\frac{1}{\sqrt{\frac{k'_1 C_A^0 D_{cat}}{k_f 2}} + \frac{k'_2 C_Z^0}{k_f 2}} + \frac{k'_1 C_A^0 D_{cat}}{k_f 1} + \frac{k_{b2}}{k_f 1 (\sqrt{\frac{k'_1 C_A^0 D_{cat} + k_{b2}})} + \frac{k_{b2}}{k_f 1 (\sqrt{\frac{k'_1 C_A^0 D_{cat} + k_{b2}}}) (\sqrt{\frac{k'_1 C_A^0}{k'_2 C_Z^0}} - 1)) + k_{b1}}{k_f 1}}}} \]  
(2.22)
For $i_1$, the same derivation is applied after taking eq 2.18 into eq 2.9 with the relation of eq 2.14 and 2.21. The final result for $i_1$ is the same as $i_2$. Therefore,

$$i = i_1 + i_2$$

$$i = \frac{2FS\sqrt{k'C_A^0D_{cat}C^*}}{1 + \frac{k_b}{k_f} + \frac{k_b}{k_f} + \frac{k_b}{k_f} + \frac{1}{\sqrt{k'C_A^0}}} + \frac{\sqrt{k'C_A^0D_{cat}}}{k_f} + \frac{\sqrt{k'C_A^0D_{cat}}}{k_f} + \frac{k_b}{k_f} \sqrt{k'C_A^0D_{cat}}$$

or

$$i = \frac{2FS\sqrt{D_{cat}C^*}}{\sqrt{k'C_A^0} + \frac{1}{\sqrt{k'C_A^0} + \frac{1}{k_f} + \frac{1}{k_f} + \frac{1}{\sqrt{k'C_A^0}}} + \frac{\sqrt{k'C_A^0D_{cat}}}{k_f} + \frac{\sqrt{k'C_A^0D_{cat}}}{k_f} + \frac{k_b}{k_f} \sqrt{k'C_A^0D_{cat}}}$$

(2.23)

2.2 ECEC scheme

The reaction mechanism for ECEC can be expressed as below:

Scheme S2 The scheme for the ECEC mechanism. The oxidised species: O and one-electron reduced species: I. IA and IB refers to the one-electron and two-electron reduced substrate-bound intermediate state. A and Z are the two co-substrates involved with the chemical steps, and P is the product.

The rate equations can be expressed as below:

$$\frac{\partial C_O(x,t)}{\partial t} = D_{cat} \frac{\partial^2 C_O(x,t)}{\partial^2 x} + k_2'C_ZC_{IB}$$

(2.25)

$$\frac{\partial C_I(x,t)}{\partial t} = D_{cat} \frac{\partial^2 C_I(x,t)}{\partial^2 x} - k_1'C_A^0C_I$$

(2.26)

$$\frac{\partial C_{IA}(x,t)}{\partial t} = D_{cat} \frac{\partial^2 C_{IA}(x,t)}{\partial^2 x} + k_1'C_A^0C_I$$

(2.27)
\[
\frac{\partial C_{IB}(x, t)}{\partial t} = D_{\text{cat}} \frac{\partial^2 C_{IB}(x, t)}{\partial^2 x} - k'_2 C_2^0 C_{IB} \tag{2.28}
\]

Also,

At \( t=0 \), \( C_O(x, 0) = C^*; C_I = C_{IA} = C_{IB} = 0 \)
\[
\lim_{x \to \infty} C_O(x, t) = C^* \tag{2.29}
\]
\[
C_O + C_I + C_{IA} + C_{IB} = C^* \tag{2.30}
\]
\[
[C_O]_0 + [C_I]_0 + [C_{IA}]_0 + [C_{IB}]_0 = C^* \tag{2.31}
\]

\[
\frac{i_1}{FS} = D_{\text{cat}} \left[ \frac{\partial C_O(x, t)}{\partial x} \right]_{x=0} = -D_{\text{cat}} \left[ \frac{\partial C_I(x, t)}{\partial x} \right]_{x=0} = k_{f1}[C_O]_0 - k_{b1}[C_I]_0 \tag{2.32}
\]
\[
\frac{i_2}{FS} = D_{\text{cat}} \left[ \frac{\partial C_{IA}(x, t)}{\partial x} \right]_{x=0} = -D_{\text{cat}} \left[ \frac{\partial C_{IB}(x, t)}{\partial x} \right]_{x=0} = k_{f2}[C_{IA}]_0 - k_{b2}[C_{IB}]_0 \tag{2.33}
\]

With steady-state approximation, eq 2.25-28 is equal to nil.

Solving eq 2.26 an 2.28 with the boundary condition (eq 2.29)

\[
C_I = [C_I]_0 \exp(\sqrt{-\frac{k_1' C_2^0}{D_{\text{cat}}} x}) \tag{2.34}
\]
\[
C_{IB} = [C_{IB}]_0 \exp(\sqrt{-\frac{k_2' C_2^0}{D_{\text{cat}}} x}) \tag{2.35}
\]

Taking eq 2.34 into eq 2.32 and eq 2.35 into eq 2.33 respectively, we can obtain

\[
[C_I]_0 = \frac{k_{f1}[C_O]_0}{\sqrt{k_1' C_2^0 D_{\text{cat}}} + k_{b1}} \tag{2.36}
\]
\[
W_1 = \frac{k_{f1}}{\sqrt{k_1' C_2^0 D_{\text{cat}}} + k_{b1}}
\]
\[
[C_{IB}]_0 = \frac{k_{f2}[C_{IA}]_0}{\sqrt{k_2' C_2^0 D_{\text{cat}}} + k_{b2}} \tag{2.37}
\]
\[
W_2 = \frac{k_{f2}}{\sqrt{k_2' C_2^0 D_{\text{cat}}} + k_{b2}}
\]

Taking eq 2.35 into eq 2.25, we can obtain

\[
D_{\text{cat}} \frac{\partial^2 C_O(x, t)}{\partial^2 x} = -k_2' C_2^0 [C_{IB}]_0 \exp(\sqrt{-\frac{k_2' C_2^0}{D_{\text{cat}}} x}) \tag{2.38}
\]
Solving the differential eq 2.38 with eq 2.37 and the boundary condition (eq 2.29), we can obtain

\[ [C_O] = -W_2[C_{IA}]_0 \exp(-\sqrt{\frac{k_i C_0^0}{D_{cat}}} x) + C^* \]  

(2.39)

Taking eq 2.39 into eq 2.32

\[ W_2\sqrt{k_i C_0^0 D_{cat}} [C_{IA}]_0 = k_{f1}[C_O]_0 - k_{b1}[C_I]_0 \]  

(2.40)

Use \([C_I]_0\) and \([C_{IB}]_0\) as the base respectively via eq 2.36-37 and 2.40, the following relations can be obtained

For \([C_I]_0\)

\[ [C_O]_0 = \frac{1}{W_1} [C_I]_0 \]  

(2.41)

\[ [C_{IA}]_0 = \frac{k_{f1}}{W_1} - k_{b1} \frac{W_1}{W_2 \sqrt{k_i C_0^0 D_{cat}}} [C_I]_0 \]  

(2.42)

\[ [C_{IB}]_0 = \frac{k_{f1}}{W_1} - k_{b1} \frac{W_1}{W_2 \sqrt{k_i C_0^0 D_{cat}}} [C_I]_0 \]  

(2.43)

For \([C_{IB}]_0\)

\[ [C_O]_0 = \frac{\sqrt{k_i C_0^0 D_{cat}}}{k_{f1} - W_1 k_{b1}} [C_{IB}]_0 \]  

(2.44)

\[ [C_I]_0 = \frac{W_1 \sqrt{k_i C_0^0 D_{cat}}}{k_{f1} - W_1 k_{b1}} [C_{IB}]_0 \]  

(2.45)

\[ [C_{IA}]_0 = \frac{1}{W_2} [C_{IB}]_0 \]  

(2.46)

Taking eq 2.41-43 into eq 2.31,

\[ [C_I]_0 = \frac{C^*}{1 + \frac{k_{b1}}{k_{f1}} + \sqrt{\frac{k_i C_0^0}{k_i C_A^0}} + \frac{\sqrt{k_i C_0^0 D_{cat}}}{k_{f1}} + \frac{\sqrt{k_i C_0^0 D_{cat}}}{k_{f2}} + \frac{k_{b2}}{k_{f2}} \sqrt{\frac{k_i C_0^0}{k_i C_A^0}}} \]  

(2.47)

Similarly, taking eq 2.44-46 into eq 2.31,

\[ [C_{IB}]_0 = \frac{C^*}{1 + \frac{k_{b2}}{k_{f2}} + \sqrt{\frac{k_i C_0^0}{k_i C_A^0}} + \frac{\sqrt{k_i C_0^0 D_{cat}}}{k_{f1}} + \frac{\sqrt{k_i C_0^0 D_{cat}}}{k_{f2}} + \frac{k_{b1}}{k_{f1}} \sqrt{\frac{k_i C_0^0}{k_i C_A^0}}} \]  

(2.48)

Therefore, \(i_1\) and \(i_2\) can be obtained through eq 2.32-35.

\[ i_1 = \frac{1}{\sqrt{k_i C_A^0}} + \frac{1}{\sqrt{k_i C_A^0}} \frac{1}{k_{f1}} \sqrt{\frac{k_i C_0^0}{k_i C_A^0}} + \frac{k_{b1}}{k_{f1}} \frac{1}{\sqrt{k_i C_A^0}} + \frac{k_{b2}}{k_{f2}} \frac{1}{\sqrt{k_i C_A^0}} + \frac{\sqrt{D_{cat}}}{k_{f1}} + \frac{\sqrt{D_{cat}}}{k_{f2}} \]  

(2.49)

\[ i_2 = \frac{FSC^* \sqrt{D_{cat}}}{\sqrt{k_i C_A^0}} + \frac{k_{b1}}{k_{f1}} \frac{1}{\sqrt{k_i C_A^0}} + \frac{k_{b2}}{k_{f2}} \frac{1}{\sqrt{k_i C_A^0}} + \frac{\sqrt{D_{cat}}}{k_{f1}} + \frac{\sqrt{D_{cat}}}{k_{f2}} \]  

(2.50)
Or
\[ i = i_1 + i_2 = \frac{2FSC^*\sqrt{D_{\text{cat}}}}{\sqrt{k_1^0C_A^0} + \frac{1}{\sqrt{k_2^0C_Z^0}} + \frac{k_{b_1}}{k_{f_1}} \frac{1}{\sqrt{k_1^0C_A^0}} + \frac{k_{b_2}}{k_{f_2}} \frac{1}{\sqrt{k_2^0C_Z^0}} + \sqrt{D_{\text{cat}}}} \] (2.51)

### 2.3 ECCE (or CEEC) scheme

![Scheme S3](image)

**Scheme S3** The scheme for the ECCE mechanism. The oxidised species, O, and one-electron reduced species I. A and Z are the two co-substrates involved with the chemical steps, and P is the product. For chemical steps, IA and IAZ are intermediate species after the first and second chemical reaction respectively.

The rate equations can be described as follows:

\[
\frac{\partial C_O(x,t)}{\partial t} = D_{\text{cat}} \frac{\partial^2 C_O(x,t)}{\partial^2 x} \quad (2.52)
\]

\[
\frac{\partial C_I(x,t)}{\partial t} = D_{\text{cat}} \frac{\partial^2 C_I(x,t)}{\partial^2 x} - k_1^0C_A^0C_I \quad (2.53)
\]

\[
\frac{\partial C_{IA}(x,t)}{\partial t} = D_{\text{cat}} \frac{\partial^2 C_{IA}(x,t)}{\partial^2 x} + k_1^0C_A^0C_I - k_2^0C_Z^0C_{IA} \quad (2.54)
\]

\[
\frac{\partial C_{IAZ}(x,t)}{\partial t} = D_{\text{cat}} \frac{\partial^2 C_{IAZ}(x,t)}{\partial^2 x} + k_2^0C_Z^0C_{IA} \quad (2.55)
\]

For boundary condition,

At \( t=0 \), \( C_O(x,0) = C^*; C_I = C_{IA} = C_{IAZ} = 0 \)

\[
\lim_{x \to \infty} C_O(x,t) = C^* \quad (2.56)
\]

\[
\left[ \frac{\partial C_{IA}}{\partial x} \right]_{x=0} = 0
\]
And

\[ C_O + C_I + C_{IA} + C_{IAZ} = C^* \]  
\[ [C_O]_0 + [C_I]_0 + [C_{IA}]_0 + [C_{IAZ}]_0 = C^* \]  

For the current,

\[ \frac{i_1}{FS} = D_{cat}\frac{\partial C_O(x,t)}{\partial x}\bigg|_{x=0} = -D_{cat}\frac{\partial C_I(x,t)}{\partial x}\bigg|_{x=0} = k_f1[C_O]_0 - k_b1[C_I]_0 \]  
\[ \frac{i_2}{FS} = D_{cat}\frac{\partial C_{IA}(x,t)}{\partial x}\bigg|_{x=0} = -D_{cat}\frac{\partial C_O(x,t)}{\partial x}\bigg|_{x=0} = k_f2[C_{IA}]_0 - k_b2[C_O]_0 \]  

(assume no reaction between \([P]\) and the electrode)

With the steady-state approximation, eq 2.52-2.55 are equal to nil.

Solving eq 2.53 with the boundary conditions,

\[ C_I = [C_I]_0\exp\left(-\sqrt{\frac{k_1'C_A^0}{D_{cat}}}x\right) \]  
(2.61)

Taking eq (2.61) into eq (2.59)

\[ \sqrt{k_1'C_A^0D_{cat}[C_I]_0} = k_f1[C_O]_0 - k_b1[C_I]_0 \]  
(2.62)

\[ [C_I]_0 = \frac{k_f1[C_O]_0}{\sqrt{k_1'C_A^0D_{cat}} + k_b1} \]  
(2.63)

Taking eq (2.61) into eq (2.54)

\[ D_{cat}\frac{\partial^2 C_{IA}(x,t)}{\partial x^2} - k_2'C_A^0[C_{IA}]_0 = -k_1'C_A^0[C_I]_0\exp\left(-\sqrt{\frac{k_1'C_A^0}{D_{cat}}}x\right) \]  
(2.64)

Solving the differential eq (2.64), the following equations are obtained

\[ C_{IA} = \frac{k_1'C_A^0}{k_1'C_A^0 - k_2'C_A^0} \sqrt{\frac{k_1'C_A^0}{k_2'C_A^0}[C_I]_0\exp\left(-\sqrt{\frac{k_2'C_A^0}{D_{cat}}}x\right)} - \frac{k_1'C_A^0}{k_1'C_A^0 - k_2'C_A^0}[C_I]_0\exp\left(-\sqrt{\frac{k_1'C_A^0}{D_{cat}}}x\right) \]  
(2.65)

\[ [C_{IA}]_0 = \frac{k_1'C_A^0}{k_1'C_A^0 - k_2'C_A^0}[C_I]_0\left(\sqrt{\frac{k_1'C_A^0}{k_2'C_A^0}} - 1\right) \]  
(2.66)

Taking eq (2.65) into eq (2.55) and solving the differential equation with boundary conditions, we can get

\[ C_{IAZ} = -\frac{k_1'C_A^0}{k_1'C_A^0 - k_2'C_A^0} \sqrt{\frac{k_1'C_A^0}{k_2'C_A^0}[C_I]_0\exp\left(-\sqrt{\frac{k_2'C_A^0}{D_{cat}}}x\right)} + \frac{k_2'C_A^0}{k_1'C_A^0 - k_2'C_A^0}[C_I]_0\exp\left(-\sqrt{\frac{k_1'C_A^0}{D_{cat}}}x\right) \]  
(2.67)
Taking eq 2.67 to eq 2.60, the following equation is obtained

\[
\sqrt{k'_{1}C_{A}^{0}}D_{cat}[C_{I}]_{0} = k_{f2}[C_{IZA}]_{0} - k_{b2}[C_{O}]_{0}
\]  

(2.68)

Rearranging eq 2.58 with eq 2.63, 2.66 and 2.68, the following equation can be obtained

\[
W' \sqrt{\frac{k'_{1}C_{A}^{0}}{k_{f1}}} D_{cat}[C_{O}]_{0} + \frac{k_{b1}}{k_{f1}}[C_{O}]_{0} + W'[C_{O}]_{0} + W' \frac{k'_{1}C_{A}^{0}}{k'_{1}C_{A}^{0} - k_{2}^{*}C_{Z}^{0}} \left( \sqrt{k'_{1}C_{A}^{0}} - 1 \right)[C_{O}]_{0} = C^{*}
\]

(2.69)

Therefore,

\[
W' = \frac{k_{f1}}{\sqrt{k'_{1}C_{A}^{0}}D_{cat} + k_{b1}}
\]

(2.70)

Taking eq 2.61 into eq 2.59 with the relation of eq 2.63 and 2.70, the current, \(i_{1}\) is

\[
i_{1} = \frac{FS\sqrt{k'_{1}C_{A}^{0}}D_{cat}C^{*}}{1 + \frac{k_{b1}}{k_{f1}} + \frac{k_{b1}k_{b2}}{k_{f1}k_{f2}} + \sqrt{\frac{k'_{1}C_{A}^{0}}{k_{2}^{*}C_{Z}^{0}}} \left( \frac{1}{1 + \sqrt{\frac{k'_{1}C_{A}^{0}}{k_{2}^{*}C_{Z}^{0}}}} + \frac{k'_{1}C_{A}^{0}}{k_{f1}} \right) + \frac{k'_{1}C_{A}^{0}}{k_{f2}} + \frac{k'_{1}C_{A}^{0}}{k_{f1}}}
\]

(2.71)

For \(i_{2}\), the same derivation is applied after taking eq 2.67 into eq 2.60 with the relation of eq 2.63 and 2.69. The final result for \(i_{1}\) is the same as \(i_{2}\).

Therefore,

\[
i = i_{1} + i_{2}
\]

\[
i = \frac{2FS\sqrt{k'_{1}C_{A}^{0}}D_{cat}C^{*}}{1 + \frac{k_{b1}}{k_{f1}} + \frac{k_{b1}k_{b2}}{k_{f1}k_{f2}} + \sqrt{\frac{k'_{1}C_{A}^{0}}{k_{2}^{*}C_{Z}^{0}}} \left( \frac{1}{1 + \sqrt{\frac{k'_{1}C_{A}^{0}}{k_{2}^{*}C_{Z}^{0}}}} + \frac{k'_{1}C_{A}^{0}}{k_{f1}} \right) + \frac{k'_{1}C_{A}^{0}}{k_{f2}} + \frac{k'_{1}C_{A}^{0}}{k_{f1}}}
\]

or

\[
i = \frac{2FS\sqrt{k_{2}^{*}C_{Z}^{0}}C^{*}}{1 + \frac{k_{b1}}{k_{f1}} + \frac{k_{b1}k_{b2}}{k_{f1}k_{f2}} + \sqrt{\frac{k'_{1}C_{A}^{0}}{k_{2}^{*}C_{Z}^{0}}} \left( \frac{1}{1 + \sqrt{\frac{k'_{1}C_{A}^{0}}{k_{2}^{*}C_{Z}^{0}}}} + \frac{k'_{1}C_{A}^{0}}{k_{f1}} \right) + \frac{k'_{1}C_{A}^{0}}{k_{f2}} + \frac{k'_{1}C_{A}^{0}}{k_{f1}}}
\]

(2.72)

(2.73)

The current obtained from the ECCE mechanism is the same as the one from the EECC mechanism. For the CEEC scheme, the same derivation processes can be followed and the same result can be obtained.
2.4 CECE scheme

The reaction mechanism for CECE can be expressed as below:

\[
\begin{align*}
O + A & \xrightarrow{k_1^d} OA \\
OA + e^- & \xrightleftharpoons[k_{hl}]{k_{fl}} IA \quad E_1 \\
IA + Z & \xrightarrow{k_2^d} IAZ \\
IAZ + e^- & \xrightleftharpoons[k_{l2}]{k_{l2}} O + P \quad E_2
\end{align*}
\]

**Scheme S4** The scheme for the CECE mechanism. For the C steps, A and Z are the two co-substrates involved with the chemical steps, and P is the product. For the E steps, the oxidised species, O; one-electron reduced intermediate species IA, and IAZ after the second chemical step.

The rate equations can be expressed as

\[
\begin{align*}
\frac{\partial C_O(x, t)}{\partial t} &= D_{cat} \frac{\partial^2 C_O(x, t)}{\partial x^2} - k_1^d C_A^0 C_O \\
\frac{\partial C_{OA}(x, t)}{\partial t} &= D_{cat} \frac{\partial^2 C_{OA}(x, t)}{\partial x^2} + k_1^d C_A^0 C_O \\
\frac{\partial C_{IA}(x, t)}{\partial t} &= D_{cat} \frac{\partial^2 C_{IA}(x, t)}{\partial x^2} - k_2^d C_Z^0 C_{IA} \\
\frac{\partial C_{IAZ}(x, t)}{\partial t} &= D_{cat} \frac{\partial^2 C_{IAZ}(x, t)}{\partial x^2} + k_2^d C_Z^0 C_{IA}
\end{align*}
\]  

(2.74) \hspace{1cm} (2.75) \hspace{1cm} (2.76) \hspace{1cm} (2.77)

For boundary condition,

\[
\text{At } t=0, \quad C_O(x, 0) = C^*; C_{OA} = C_{IA} = C_{IAZ} = 0
\]  

(2.78)

For the conservation of mass,

\[
\begin{align*}
C_O + C_{OA} + C_{IA} + C_{IAZ} &= C^* \\
[C_O]_0 + [C_{OA}]_0 + [C_{IA}]_0 + [C_{IAZ}]_0 &= C^*
\end{align*}
\]  

(2.79) \hspace{1cm} (2.80)
For the current,

\[
\frac{i_1}{FS} = D_{cat}\left[\frac{\partial C_{OA}(x,t)}{\partial x}\right]_{x=0} = -D_{cat}\left[\frac{\partial C_{IA}(x,t)}{\partial x}\right]_{x=0} = k_f1[C_{OA}]_0 - k_{b1}[C_{IA}]_0 \quad (2.81)
\]

\[
\frac{i_2}{FS} = D_{cat}\left[\frac{\partial C_{IAZ}(x,t)}{\partial x}\right]_{x=0} = -D_{cat}\left[\frac{\partial C_{O}(x,t)}{\partial x}\right]_{x=0} = k_f2[C_{IAZ}]_0 - k_{b2}[C_O]_0 \quad (2.82)
\]

With steady-state approximation, eq 2.74-77 is equal to nil.

Solving eq 2.74 an 2.76 with the boundary condition,

\[
C_{O} = [C_{O}]_0 \exp\left(-\sqrt{\frac{k_f1C_{O0}}{D_{cat}}}x\right) \quad (2.84)
\]

\[
C_{IA} = [C_{IA}]_0 \exp\left(-\sqrt{\frac{k_f2C_{Z0}}{D_{cat}}}x\right) \quad (2.85)
\]

Taking eq 2.84 into eq 2.83 and eq 2.85 into eq 2.82 respectively, we can obtain

\[
[C_{O}]_0 = \frac{k_f2[C_{IA}]_0}{\sqrt{k_f1C_{IA0}D_{cat}} + k_{b2}} \quad (2.86)
\]

\[
W_1 = \frac{k_f2}{\sqrt{k_f1C_{IA0}D_{cat}} + k_{b2}}
\]

\[
[C_{IA}]_0 = \frac{k_f1[C_{O}]_0}{\sqrt{k_f2C_{Z0}D_{cat}} + k_{b1}} \quad (2.87)
\]

\[
W_2 = \frac{k_f1}{\sqrt{k_f2C_{Z0}D_{cat}} + k_{b1}}
\]

Taking eq 2.85 into eq 2.77, we can obtain

\[
D_{cat}\frac{\partial^2 C_{IAZ}(x,t)}{\partial^2 x} = -k_f2C_{Z0}[C_{IA}]_0 \exp\left(-\sqrt{\frac{k_f2C_{Z0}}{D_{cat}}}x\right) \quad (2.88)
\]

Solving the differential eq 2.88 with the boundary condition , we can obtain

\[
[C_{IAZ}] = -W_2[C_{OA}]_0 \exp\left(-\sqrt{\frac{k_f2C_{Z0}}{D_{cat}}}x\right) \quad (2.89)
\]

Taking eq 2.89 into eq 2.83

\[
W_2\sqrt{k_f2C_{Z0}D_{cat}}[C_{OA}]_0 = k_f2[C_{IAZ}]_0 - k_{b2}[C_O]_0 \quad (2.90)
\]

Use[C_{O}]_0 and [C_{IA}]_0 as the base respectively via 2.86, 2.87 and 2.90, the following equations can be obtained
For \([CO]_0\)

\[
[C_{IAZ}]_0 = \frac{1}{W_1} [CO]_0
\] (2.91)

\[
[C_{OA}]_0 = \frac{k_{f2}}{W_1} - k_{b2} \sqrt{k_{2}^{\prime} C_{1}^{2} D_{cat}} [CO]_0
\] (2.92)

\[
[C_{IA}]_0 = \frac{k_{f2}}{W_1} - k_{b2} \sqrt{k_{2}^{\prime} C_{2}^{2} D_{cat}} [CO]_0
\] (2.93)

For \([C_{IA}]_0\)

\[
[C_{IAZ}]_0 = \frac{\sqrt{k_{2}^{\prime} C_{1}^{2} D_{cat}}}{k_{f2} - W_1 k_{b2}} [C_{IA}]_0
\] (2.94)

\[
[C_{O}]_0 = \frac{W_1 \sqrt{k_{2}^{\prime} C_{1}^{2} D_{cat}}}{k_{f2} - W_1 k_{b2}} [C_{IA}]_0
\] (2.95)

\[
[C_{OA}]_0 = \frac{1}{W_2} [C_{IA}]_0
\] (2.96)

Taking eq 2.91-93 into eq 2.80,

\[
[C_{O}]_0 = \frac{C^{*}}{1 + \frac{k_{b2}}{k_{f2}} + \frac{\sqrt{k_{1}^{\prime} C_{A}^{2}}}{k_{f1}} + \frac{\sqrt{k_{1}^{\prime} C_{A}^{2} D_{cat}}}{k_{f2}} + \frac{k_{b1}}{k_{f1}} \sqrt{k_{2}^{\prime} C_{Z}^{2}}}
\] (2.97)

Similarly, Taking eq 2.94-96 into eq 2.80,

\[
[C_{IA}]_0 = \frac{C^{*}}{1 + \frac{k_{b1}}{k_{f1}} + \frac{\sqrt{k_{2}^{\prime} C_{Z}^{2}}}{k_{f1}} + \frac{\sqrt{k_{2}^{\prime} C_{Z}^{2} D_{cat}}}{k_{f2}} + \frac{k_{b2}}{k_{f2}} \sqrt{k_{1}^{\prime} C_{A}^{2}}}
\] (2.98)

Therefore \(i_1\) and \(i_2\) can be obtained via eq 2.82-2.85 for the CECE scheme, which is identical with the result from the ECEC scheme.

\[
i_2 = \frac{1}{\sqrt{k_{1}^{\prime} C_{A}^{2}}} + \frac{1}{\sqrt{k_{2}^{\prime} C_{Z}^{2}}} + \frac{k_{b1}}{k_{f1}} + \frac{k_{b2}}{k_{f2}} \frac{1}{\sqrt{k_{1}^{\prime} C_{A}^{2}}} + \frac{\sqrt{D_{cat}}}{k_{f1}} + \frac{\sqrt{D_{cat}}}{k_{f2}}
\] (2.99)

\[
i_1 = \frac{1}{\sqrt{k_{2}^{\prime} C_{Z}^{2}}} + \frac{1}{\sqrt{k_{1}^{\prime} C_{A}^{2}}} + \frac{k_{b1}}{k_{f1}} + \frac{k_{b2}}{k_{f2}} \frac{1}{\sqrt{k_{2}^{\prime} C_{Z}^{2}}} + \frac{\sqrt{D_{cat}}}{k_{f1}} + \frac{\sqrt{D_{cat}}}{k_{f2}}
\] (2.100)

Therefore,

\[
i = i_1 + i_2 = \frac{2FSC^{*} \sqrt{D_{cat}}}{\frac{1}{\sqrt{k_{1}^{\prime} C_{A}^{2}}} + \frac{1}{\sqrt{k_{2}^{\prime} C_{Z}^{2}}} + \frac{k_{b1}}{k_{f1}} + \frac{k_{b2}}{k_{f2}} \frac{1}{\sqrt{k_{1}^{\prime} C_{A}^{2}}} + \frac{\sqrt{D_{cat}}}{k_{f1}} + \frac{\sqrt{D_{cat}}}{k_{f2}}}
\] (2.101)
2.5 EEC$_{\text{dim}}$ scheme (Homolytic process)

The reaction mechanism for EEC$_{\text{dim}}$ can be expressed as below:

\[ \text{O} + e^- \xrightarrow{k_f} \text{R} \quad E_l \]

\[ \text{R} + \text{A} \xrightarrow{k_{i'}} \text{RA} \]

\[ \text{RA} + \text{RA} \xrightarrow{k_{2'}} \text{O} + \text{P} \]

**Scheme S5** The scheme for the EEC$_{\text{dim}}$ mechanism. The oxidised species, O; one-electron reduced, R. A is a substrate involved with a chemical step, and P is the product.

The rate equations can be expressed as below:

\[
\frac{\partial C_O(x,t)}{\partial t} = D_{\text{cat}} \frac{\partial^2 C_O(x,t)}{\partial x^2} + 2k_2'C_{RA}^2 \tag{2.102}
\]

\[
\frac{\partial C_R(x,t)}{\partial t} = D_{\text{cat}} \frac{\partial^2 C_R(x,t)}{\partial x^2} - k_1'C_A^0C_R + k_{-1}'C_{RA} \tag{2.103}
\]

\[
\frac{\partial C_{RA}(x,t)}{\partial t} = D_{\text{cat}} \frac{\partial^2 C_{RA}(x,t)}{\partial x^2} + k_1'C_A^0C_R - k_{-1}'C_{RA} - 2k_2'C_{RA}^2 \tag{2.104}
\]

The current is

\[
\frac{i_1}{FS} = D_{\text{cat}} [\frac{\partial C_O(x,t)}{\partial x}]_{x=0} = -D_{\text{cat}} [\frac{\partial C_R(x,t)}{\partial x}]_{x=0} = k_f[C_O]_0 - k_b[C_R]_0 \tag{2.105}
\]

With the steady approximation in the time domain (the kinetic region) and space domain (the system is homogeneous, therefore, \(\frac{\partial C_{RA}}{\partial x} = 0\).)

The equation 2.104 is obtained as below,

\[
k_1'C_A^0C_R - k_{-1}'C_{RA} - 2k_2'C_{RA}^2 = 0 \tag{2.106}
\]

Therefore,

\[
C_{RA} = \frac{-k_{-1}' + k_{-1}' \sqrt{1 + 8k_1'C_A^0k_{-1}'C_R}}{4k_2'} \tag{2.107}
\]

Assuming \(\frac{k_1'C_A^0k_{-1}'}{k_2'}C_R << 0\). Therefore, the Taylor expansion \((\sqrt{1+8x} = 1+4x-8x^2+\ldots)\) for eq 2.107 leads to

\[
C_{RA} = \frac{k_1'C_A^0}{k_{-1}'}C_R \tag{2.108}
\]
(i.e. pre-equilibrium condition)

or

\[ [C_{RA}]_0 = \frac{k'_1 C_A^0}{k'_{-1}} [C_R]_0 \]

According to the conservation of mass,

\[
\left( \frac{\partial C_R(x, t)}{\partial t} + \frac{\partial C_{RA}(x, t)}{\partial t} + \frac{\partial C_O(x, t)}{\partial t} \right) = D_{cat} \left( \frac{\partial^2 C_R(x, t)}{\partial^2 x} + \frac{\partial^2 C_{RA}(x, t)}{\partial^2 x} + \frac{\partial^2 C_O(x, t)}{\partial^2 x} \right) = 0
\]

\[
\frac{\partial^2 C_{RA}(x, t)}{\partial^2 x} = 0
\]

\[
\frac{\partial^2 C_R(x, t)}{\partial^2 x} = -\frac{\partial^2 C_O(x, t)}{\partial^2 x}
\]

Therefore,

\[
D_{cat} \frac{\partial^2 C_R}{\partial^2 x} = 2k'_2 \left( \frac{k'_1 C_A^0}{k'_{-1}} \right)^2 \frac{C_R^2}{2} \tag{2.109}
\]

Let \( B = \frac{2k'_2}{D_{cat}} \left( \frac{k'_1 C_A^0}{k'_{-1}} \right)^2 \)

According to the chain rule,

\[
(F^2)' = 2FF'
\]

\[
((F^2))' = 2F'F''
\]

The eq2.109 can be arranged to

\[
[(\frac{\partial C_R}{\partial x})^2]' = 2 \frac{\partial^2 C_R}{\partial x} \frac{\partial C_R}{\partial x} \tag{2.110}
\]

Integral of both side of eq 2.110 with respect to x between 0 to ∞,

\[
\int_0^\infty \left( \frac{\partial C_R}{\partial x} \right)^2 \ dx = \int_0^\infty 2BC_R^2 \frac{\partial C_R}{\partial x} \ dx \tag{2.111}
\]

Also,

\[
x = 0, C_R = [C_R]_0 \\
x = \infty, C_R = 0
\]

Therefore,

\[
\left( \frac{\partial C_R}{\partial x} \right)^2 \bigg|_{[C_R]_0}^{\infty} = \frac{2B}{3} \left( \frac{C_R^3}{C_R^0} \right) \bigg|_{[C_R]_0}^{\infty} \tag{2.112}
\]

Therefore, the current \( i \) is

\[
i = FSD_{cat} \sqrt{\frac{2B}{3} \left( \frac{C_R^3}{C_R^0} \right)^{\frac{3}{2}}} \tag{2.113}
\]
Following the Nerstian equation and mass balance
\[ \epsilon_1 = \frac{[CO]_0}{[CR]_0} \]  
\[ [CO]_0 + [CR]_0 + [CRA]_0 = C^* \]  

According to eq 2.108, 2.114-2.115 and 2.113,

The current \( i \) can be rearranged as below,

\[ i = FS \sqrt[3]{\frac{4D_{cat}k'_2 k'_1 C_A^0}{2k'_{-1}} (C^*)^3} \left( 1 + \frac{k'_1 C_A}{k'_{-1}} + \epsilon_1 \right)^{\frac{3}{2}} \]  

(2.116)

3 The Slope Determined by the FOWA Plot In the Nerstian Behaviour

For Nernstian EC mechanism, the current can be expressed as below

\[ i = \frac{FSC^* \sqrt{D_{cat}k'_1 C_A^0}}{1 + \exp[f(E - E_1)]]} \]  

(3.1)

For a FOWA plot, plot \( \frac{i}{i_p} \) against \( \frac{1}{1 + \exp[f(E - E_1)]} \). Therefore, the pseudo fast rate constant (i.e. \( k'_1 C_A^0 \)) can be determined from the slope. Therefore, The equations for the straight and curve FOWA traces can be simply expressed as below respectively:

\[ i = \frac{a}{1 + \exp[f(\Delta E)]]} \]  

(3.2)

\[ i = \frac{b}{1 + \exp[f(\Delta E)]} + \frac{b}{a} \]  

(3.3)

Let \( M \) equal to \( \frac{1}{1 + \exp[f(\Delta E)]} \) (i.e. x value in the x-axis in the FOWA plot)

Therefore

\[ \Delta E = \frac{1}{f}(ln \frac{1}{M} - 1) \]  

(3.4)

Therefore, eq. 3.2 and 3.3 can be rearranged as

\[ i = \frac{a}{1 + \exp[ln \frac{1}{M} - 1)]} \]  

(3.5)

\[ i = \frac{b}{1 + \exp[ln \frac{1}{M} - 1]} + \frac{b}{a} \]  

(3.6)

Take the derivative of eq 3.5 and 3.6 against \( M \) (i.e. slope),
eq 3.5 is equal to \( a \)
eq 3.6 is equal to \( \frac{b a^2}{(a + b M)^2} \). When \( M \) approaches 0 (i.e. \( \Delta E \) is large), eq 3.6 is close to \( b \)
4 The General EC FOWA Equation

The Randles-Sevcik equation is used to calculate the peak of current, \( i_p \), which is equal to

\[
    i_p = 0.446FSC^* \sqrt{\frac{D_{cat}Fυ}{RT}} \tag{4.1}
\]

However, one needs to bear in mind that when the electrode kinetics is sluggish (i.e. under non-Nernstian conditions), the Butler-volmer equation is applied instead. The peak current gradually reduces as the \( k_0 \) value decreases. Determining the precise \( i_p \) is required with more complicated numerical or analytical methods. The peak current for catalysts in the absence of substrates between the reversible and irreversible condition is ca 1.26 times different (0.44 vs 0.35).

For the electrocatalytic current for EC mechanism as shown in the main text, it can be expressed as

\[
    i = \frac{FSC^*\sqrt{D_{cat}k'_1C_A^0}}{1 + \varepsilon_1 + \sqrt{\frac{D_{cat}k'_1C_A^0}{k_f1}}} \tag{4.2}
\]

The result of eq 4.1 divided by eq 4.2 is

\[
    \frac{i_p}{i} = \frac{1 + \varepsilon_1 + \sqrt{\frac{D_{cat}k'_1C_A^0}{k_f1}}}{2.24\sqrt{\frac{R'T}{Fυ}}\sqrt{k'_1C_A^0}} \tag{4.3}
\]

Therefore,

\[
    2.24\left(\frac{i_p}{i}\right)\sqrt{\frac{R'T}{Fυ}}\sqrt{k'_1C_A^0} = 1 + \varepsilon_1 + \frac{\sqrt{D_{cat}k'_1C_A^0}}{k_f1}
\]

\[
    \frac{i_p}{i} - (0.446)\frac{\sqrt{D_{cat}Fυ}}{k_f1} = \frac{1 + \varepsilon_1}{2.24\sqrt{\frac{k'_1C_A^0}{fυ}}}
\]

The final equation is

\[
    \frac{i_p}{i} = 2.24\left(\frac{i_p}{i}\right)\frac{\sqrt{D_{cat}Fυ}}{1 + \varepsilon_1} \tag{4.4}
\]

\[
    k_f1 = k_0exp[-αf(E - E_{eq})]; α = 0.5
\]
