

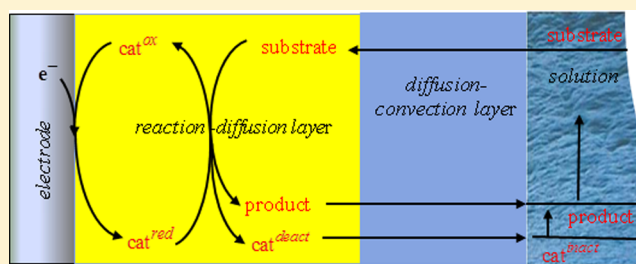
Benchmarking of Homogeneous Electrocatalysts: Overpotential, Turnover Frequency, Limiting Turnover Number

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S Supporting Information

ABSTRACT: In relation to contemporary energy challenges, a number of molecular catalysts for the activation of small molecules, mainly based on transition metal complexes, have been developed. The time has thus come to develop tools allowing the benchmarking of these numerous catalysts. Two main factors of merit are addressed. One involves their intrinsic catalytic performances through the comparison of “catalytic Tafel plots” relating the turnover frequency to the overpotential independently of the characteristics of the electrochemical cell. The other examines the effect of deactivation of the catalyst during the course of electrolysis. It introduces the notion of the limiting turnover number as a second key element of catalyst benchmarking. How these two factors combine with one another to control the course of electrolysis is analyzed in detail, leading to procedures that allow their separate estimation from measurements of the current, the charge passed, and the decay of the catalyst concentration. Illustrative examples from literature data are discussed.



INTRODUCTION

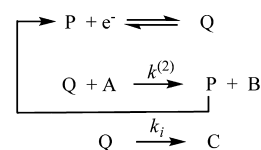
Catalysis of electrochemical reactions is currently attracting intense interest in response to issues raised by contemporary energy challenges.^{1–8} The ultimate goal is to use sunlight energy to carry out the reductive or oxidative transformations of small molecules involved in these issues. A route toward this objective is to first convert solar energy into electricity, which is then used to electrochemically reduce or oxidized the target molecules. Catalysis is required in most cases to carry out these reactions. It calls mainly upon transition-metal complexes (notably, for water,^{9–16} proton,^{17–22} dioxygen,^{23–28} and carbon dioxide^{27,29–36}).

The large number and diversity of available catalysts make it timely to develop reliable tools for comparing them to one another. Two factors of merit are essential in this respect. One is the expression of the intrinsic catalytic properties of the catalyst, independently from the characteristics of the electrochemical cell used in each particular case. The second has to do with the stability of the catalyst over time. These two aspects relate to the notions of overpotential (η), turnover frequency (TOF), and turnover number (TON). The first of these two facets of the problem has been addressed in the case where the catalysts are unconditionally stable in the framework of H₂ evolution³⁷ and CO₂ reduction into CO.^{35,38–42} In the present contribution, we treat the whole problem after having analyzed the benchmarking procedure to be followed within the period of time where the catalyst may be considered as stable.⁴³

The TOF and TON will be defined later on, but we may from now define the overpotential, η , as the difference between the standard potential and the actual potential for the trans-

formation of the substrate, A, into the product, B: $\eta = E_{A/B}^0 - E$. We start from the basic reaction scheme shown in Scheme 1, in

Scheme 1



which the catalytic reaction is a simple one-electron/one-step process based on a fast redox couple P/Q (standard potential $E_{P/Q}^0$). The active form of the catalyst, Q, then reacts with the substrate, A, yielding the target product, B, and regenerating the oxidized form of the catalyst, P, with a second-order rate constant $k^{(2)}$ (the reasoning is developed for reductions; transposition to oxidations is straightforward). Deactivation of the catalyst is a first-order reaction that gives rise to an unreactive degradation product, C, with a first-order or pseudo-first-order rate constant k_i . Another simplification is the assumption that the concentration of the substrate is maintained constant, as when it is the solvent (e.g., oxidation or reduction of water) or a constant-pressure gas (e.g., CO₂, H₂, O₂). In cases where the substrate tends to be significantly consumed during electrolysis, devices ensuring its continuous (or even automatic) replenishment are easy to devise. In most circumstances, this should not even be necessary for catalysis

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of H₂ evolution since the cathodic reaction is advantageously associated with an anodic reaction (e.g., oxidation of water) that stoichiometrically regenerates the protons consumed at the cathode. Under these conditions, Scheme 1 also covers the case where the inactivation of the catalyst may involve the substrate, as in the case of, for example, CO₂ or H⁺, which may destroy the ligand of a catalytically active metal complex. The catalytic reaction is thus pseudo-first-order with a rate constant $k = k^{(2)}C_A^0$.

For the sake of simplicity, we also restrict our analysis to reactions giving rise to a single product, designated as B in Scheme 1.

Although catalytic reaction schemes are usually more complex in current practice, often involving two-electron/two-step processes, the simple scheme in Scheme 1 captures the essential features of the problem and allows the pertinent notions and parameters to be put forward. Examples of adaptation to such two-electron/two-step schemes will be given afterward.

The case of homogeneous catalysis, where the catalyst molecules are dispersed in the solution together with the substrate and may diffuse to or from the electrode surface, will be treated here. However, systems in which the catalyst is immobilized on the electrode surface within a porous film also have their advantages and are sometimes considered as more promising than homogeneous systems. However, it should be borne in mind that, dealing precisely with progressive inactivation of the catalyst, homogeneous systems possess a definite advantage over electrocatalytic films. The volume of the solution indeed plays the role of a stock of catalyst molecules that can replace those that have been inactivated during each catalytic cycle.

The data treatments proposed below do not require any particular cell design and instrumentation, provided they entail compensation or minimization of ohmic drop.

RESULTS AND DISCUSSION

As a preliminary to the discussion of catalytic systems, we will first take a look at what happens in direct electrolyses, with no help of a catalyst, to see how the current flowing through the electrode is related to the transformation of the substrate into the product and how this relationship depends on the physical characteristics of the electrochemical cell.

Noncatalyzed Electrolysis. Figure 1 summarizes the steady-state situation for a direct, noncatalyzed, reductive electrolysis of the substrate A to yield the product B (symbols used in Figure 1 and elsewhere are defined in Chart 1). A steady state ensues from the balance between diffusion and forced convection (generated by agitation of the solution or by liquid circulation in flow cells). It is characterized by a diffusion–convection layer whose thickness, δ , is smaller with a more vigorous rate of agitation or liquid circulation. The boundary conditions at the electrode/diffusion–convection layer interface and at the diffusion–convection layer/solution interface entail the linear concentration profiles shown in red in Figure 1 in the case where the substrate concentration in solution is constant or maintained constant throughout electrolysis and, in addition, the electrode potential is set at a value negative enough for the concentration of A at the electrode surface to be nil. The way in which the time-dependent production of B is related to its flux in the steady-state diffusion–convection layer (and therefore to the current) lies in the boundary conditions at the diffusion–convection

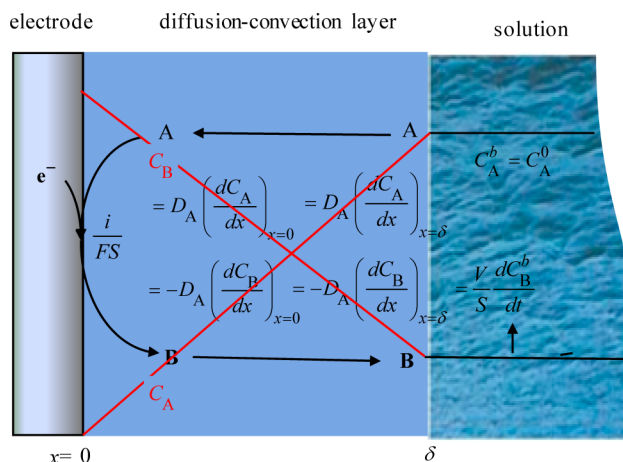


Figure 1. Noncatalyzed reduction of the substrate A into the product B at steady state.

Chart 1. Definitions of Symbols

A: substrate, P, Q: oxidized and reduced forms of the catalyst, C: inactivated form
C_A^0 : bulk substrate concentration, C_P^0 : total concentration of catalyst
D_A : diffusion coefficient of the substrate, A, and the product, B
D_P : diffusion coefficient of the catalyst oxidized (P), reduced (Q) and inactivated (C) form
E : electrode potential, $E_{P/Q}^0$: standard potential of the catalyst couple, $E_{A/B}^0$: standard potential of the substrate/product couple
S : electrode surface area
V : volume of the solution
i : current
$k^{(2)}$: second order rate constant of the catalytic reaction, k : pseudo first order rate constant of the catalytic reaction, k_i : first order or pseudo order rate constant of inactivation of the catalyst
t : time, t_{cell} : time constant of the electrochemical cell, t_{chem} : time constant characterizing the catalytic reaction and the inactivation of the catalyst
x : distance from the electrode surface
δ : thickness of the diffusion-convection layer
μ : thickness of the catalytic reaction-diffusion layer

layer/solution interface (see the equation in Figure 1). As shown in the Supporting Information (SI), it follows that the current is constant, given by

$$i = \frac{FSD_A C_A^0}{\delta}$$

and also that the bulk concentration of B (C_B^b) increases linearly with time according to the expression

$$C_B^b = C_A^0 \frac{t}{t_{cell}}$$

where t_{cell} is the time constant of the cell, given by

$$t_{cell} = \frac{V\delta}{SD_A}$$

Minimizing the time constant of the cell in order to speed up electrolysis may be achieved by decreasing the ratio of the volume to the surface area and/or decreasing the thickness of the diffusion–convection layer by raising the rate of agitation or the rate of liquid circulation.

Homogeneous Catalysis with a Stable Catalyst. Figure 2 summarizes the steady-state association between the catalytic reaction and transport of catalyst, substrate, and product with

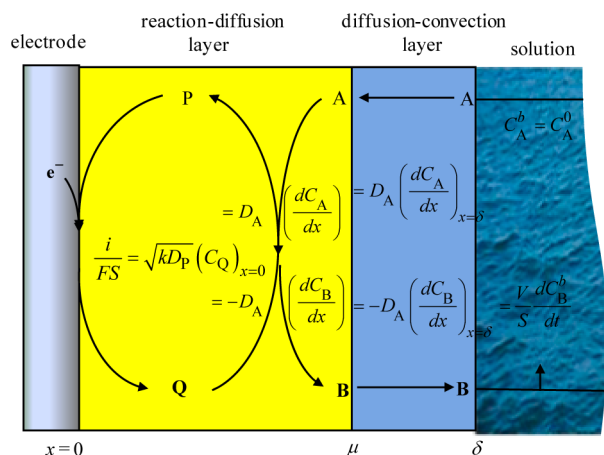


Figure 2. Homogeneous catalysis of the reduction of the substrate A into the product B at steady state.

all pertinent boundary conditions and the relationship according to which the product B builds up in the bulk of the solution. Compared with the preceding situation, an additional layer appears, namely, a reaction–diffusion layer adjacent to the electrode surface that arises from mutual compensation of the diffusion of the active form of the catalyst, Q, and the catalytic reaction. The achievement of these “pure kinetic conditions”⁴⁴ requires that the catalytic reaction is fast compared with diffusion, which is indeed the case for catalytic systems of practical interest. The thickness of the reaction–diffusion layer (μ) is on the order of $(D_A/k)^{1/2}$. Pure kinetic conditions entail that the reaction–diffusion layer is much thinner than the diffusion–convection layer (Figure 2 is somewhat misleading in this respect, since the relative thicknesses of these layers are reversed because of graphical constraints).

As shown in the SI, under these pure kinetic conditions and when the P/Q electron transfer is fast (and thus obeys the Nernst equation), the catalytic current is given by

$$\frac{i}{FS} = \sqrt{kD_P} \frac{C_P^0}{1 + \exp\left[\frac{F}{RT}(E - E_{P/Q}^0)\right]}$$

and the space profile of Q within the reaction–diffusion layer is given by

$$C_Q(x) = (C_Q)_{x=0} \exp\left(-\sqrt{\frac{k}{D_P}} x\right)$$

Within the time when the catalyst is stable, the turnover frequency may be defined as

$$TOF = \frac{d(\text{mol(B)})/dt}{\text{mol(Q)}}$$

where $d(\text{mol(B)})/dt$ is the rate at which the number of moles of product is generated and mol(Q) is the number of moles of catalyst involved in the production of B.

The rate $d(\text{mol(B)})/dt$ is directly related to the current by means of the boundary relationships at the three interfaces of the system (electrode/reaction–diffusion layer, reaction–diffusion layer/diffusion–convection layer, and diffusion–convection layer/solution):

$$\frac{d(\text{mol(B)})}{dt} = V \frac{dC_B^b}{dt} = \frac{i}{F}$$

A convenient definition of mol(Q) is the maximal number of moles of active catalyst Q that may be generated at sufficiently negative electrode potentials when all of the P is reduced at the electrode surface ($E \ll E^0$). Insofar as the catalyst is stable, the catalyst molecules that are actually involved in the reaction are only those contained in the reaction–diffusion layer, i.e.:

$$\text{mol(Q)} = S \sqrt{\frac{D_P}{k}} C_P^0$$

The ensuing expression for the TOF,

$$TOF = \frac{k}{1 + \exp\left[\frac{F}{RT}(E_{A/B}^0 - E_{P/Q}^0)\right] \exp\left(-\frac{F\eta}{RT}\right)}$$

allows the construction of a “catalytic Tafel plot” that relates the TOF to the overpotential, as represented in Figure 3. This is

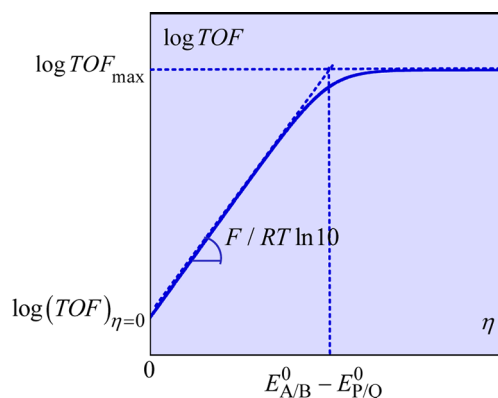


Figure 3. Homogeneous catalysis: catalytic Tafel plot.

a representation of the intrinsic properties of a given catalyst, which allows a comparison between catalysts independently of the particular electrochemical cell used in each case, bearing in mind that good catalysts have their representative plots in the top left part of the diagram and vice versa for bad catalysts. For a given catalyst, the catalytic Tafel plot allows a rational trade-off between rapidity and energy: in the rising portion of the diagram, faster reactions imply larger overpotentials and vice versa.

The independence of the catalytic Tafel plot vis-à-vis the characteristics of the electrochemical cell does not imply that these have no practical interest. Indeed, an important practical feature of the operation is the increase in the concentration of the product in the volume of the solution per unit of time:

$$\frac{dC_B^b}{dt} = \left(\frac{S}{V}\right) \left(TOF \sqrt{\frac{D_P}{k}} C_P^0\right)$$

indicating that for a given catalyst and a given value of its concentration, the rapidity of the electrolysis increases in proportion to the electrode surface area/volume ratio. As expected when pure kinetic conditions are achieved, the rapidity of electrolysis does not depend on the characteristics of the diffusion–convection layer, in particular the rate of agitation or of liquid circulation.

Homogeneous Catalysis with an Unstable Catalyst. After these preliminaries, we consider now the interference of a

reaction that concurrently destroys the catalyst, as pictured in Scheme 1. The analysis of this competition (see the SI) shows that in addition to the cell time constant t_{cell} , another time constant, t_{chem} , must be introduced (see Table 1). The time constant t_{chem} characterizes the chemical events taking place in the vicinity of the electrode and in the solution, namely, catalysis and degradation of the catalyst. The time dependence of the various quantities of interest are listed in Table 1. They are all exponential with a pace based on t_{chem} and, in some cases, on t_{chem}^{max} , which is the maximal value that t_{chem} can take and is

Table 1. Expressions for the Quantities of Interest

Time constant of the cell	$t_{cell} = \frac{V\delta}{SD_p}$
Time constant for catalysis and catalyst degradation	General case $\frac{t_{chem}}{t_{cell}} = 1 + \frac{\left\{ \frac{k}{k+k_i} + \exp\left[\frac{F}{RT}(E-E_{PQ}^0)\right] \right\} \sqrt{\frac{D_p}{k+k_i}}}{\frac{k_i}{k+k_i}}$
	$\frac{t_{chem}^{max}}{t_{cell}} = 1 + \frac{\sqrt{\frac{D_p}{k+k_i}}}{\frac{k_i}{k}}$
	$k_i \ll k$ $\frac{t_{chem}}{t_{cell}} = \frac{\left\{ 1 + \exp\left[\frac{F}{RT}(E-E_{PQ}^0)\right] \right\} \sqrt{\frac{D_p}{k}}}{\frac{k_i}{k}}$ $\frac{t_{chem}^{max}}{t_{cell}} = \frac{\sqrt{\frac{D_p}{k}}}{\frac{k_i}{k}}$
Current	$i = \left(\frac{FVC_p^0}{t_{chem}} \frac{k+k_i}{k_i} \right) \exp\left(-\frac{t}{t_{chem}}\right)$
Charge	$q = FVC_p^0 \frac{k+k_i}{k_i} \left[1 - \exp\left(-\frac{t}{t_{chem}}\right) \right]$
Product concentration	$C_B^b = \frac{k}{k_i} C_P^0 \left[1 - \exp\left(-\frac{t}{t_{chem}}\right) \right]$
Catalyst concentration	$C_P^b = C_P^0 \exp\left(-\frac{t}{t_{chem}}\right)$
Turnover frequency	$TOF = \frac{\frac{k}{k_i} \frac{1}{t_{chem}} \exp\left(-\frac{t}{t_{chem}}\right)}{1 + \frac{1 - k_i t_{chem}^{max}}{k_i t_{chem}^{max}} \exp\left(-\frac{t}{t_{chem}^{max}}\right)}$
Turnover number	$TON = \frac{\frac{k}{k_i} \left[1 - \exp\left(-\frac{t}{t_{chem}}\right) \right]}{1 + \frac{1 - k_i t_{chem}^{max}}{k_i t_{chem}^{max}} \exp\left(-\frac{t}{t_{chem}^{max}}\right)}$

asymptotically reached when the electrode potential is way past the catalyst standard potential. The competition between catalysis and catalyst consumption shows up in two ways in the expression of t_{chem} , namely, by the ratio of the two rate constants, k_i/k , and by the ratio of the thicknesses of the reaction–diffusion layer, $\mu = [D_p/(k+k_i)]^{1/2}$, and the diffusion–convection layer, δ . The variations of various quantities of interest as functions of the electrolysis time are shown in Figure 4.

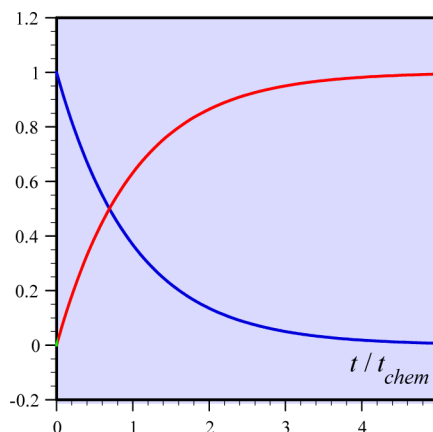


Figure 4. Homogeneous catalysis: variation of various quantities of interest as functions of electrolysis time. Blue: decay of the catalyst bulk concentration, C_P^b/C_P^0 , and the current, $i/[FVC_p^0(1+k/k_i)/t_{chem}]$. Red: buildup of the product, $C_B^b/(kC_P^0/k_i)$, and the charge passed, $q/[FVC_p^0(1+k/k_i)]$.

The results of electrolysis may therefore be analyzed as follows. The decay of the current gives access to the characteristic time t_{chem} . This can also be obtained from the decay of the catalyst concentration, which can be monitored by any electrochemical or spectrochemical analytical method. The buildup of charge allows access to both t_{chem} and k/k_i . These can also be derived from the buildup of the product in the solution. It is desirable to cross-check these various ways of obtaining the same quantities.

The definitions of the turnover number and turnover frequency, for which expressions are given in Table 1, required modification compared with the case of a stable catalyst (see the preceding section). In these definitions,

$$TOF = \frac{d(\text{mol(B)})/dt}{\text{mol(Q)}} = \frac{V dC_B/dt}{\text{mol(Q)}}$$

$$TON = \frac{\text{mol(B)}}{\text{mol(Q)}} = \frac{VC_B}{\text{mol(Q)}}$$

the definitions of the numerators remain the same as before and can be calculated using the appropriate expressions in Table 1. What changes is the definition of mol(Q) , which is now given by

$$\text{mol(Q)} = \left[S \int_0^\infty (C_Q)_{x=0, \max, t} \exp\left(-\sqrt{\frac{(k+k_i)C_A^0}{D_p}} x\right) dx \right] + \text{mol(C)}$$

The first term, which represents the maximum of the active catalyst molecules within the reaction–diffusion layer, as was the case for a stable catalyst, must now be complemented by a

term corresponding to the amount of catalyst that has been transformed into the inactive form, C, since the beginning of the electrolysis:

$$\text{mol}(C) = VC_{C,\text{max}}^b$$

The expressions for the *TOF* and *TON* given in Table 1 ensue (see the SI).

The *TON* reaches a limiting value as the electrolysis goes on, for which the very simple expression is

$$\text{TON}^{\text{lim}} = \frac{k}{k_i}$$

TON^{lim} is, together with the catalytic Tafel plot, an essential factor of merit for a given catalyst. It can be obtained from the limit of the buildup of charge or product when all of the catalyst has disappeared. However, it is not necessary to await the complete disappearance of the catalyst. It suffices to follow the procedures described above for the determination of k/k_i to obtain TON^{lim} .

What about the turnover frequency and the catalytic Tafel plot when the catalyst is not stable as discussed in this section? We may assume that k_i/k is relatively small, as otherwise the catalyst would not be worth considering. Under these conditions,

$$\frac{t_{\text{chem}}}{t_{\text{cell}}} = \frac{\left\{ 1 + \exp\left[\frac{F}{RT}(E - E_{\text{PQ}}^0)\right] \right\} \frac{\sqrt{D_P/k}}{\delta}}{k_i/k}$$

and

$$\frac{t_{\text{chem}}^{\text{max}}}{t_{\text{cell}}} = \frac{\frac{\sqrt{D_P/k}}{\delta}}{k_i/k}$$

As shown in the SI, it follows that at the start of the electrolysis the expression for the *TOF*,

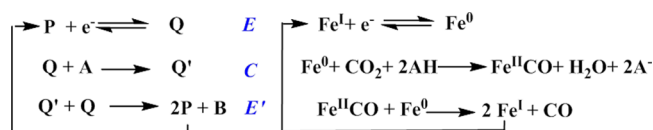
$$\text{TOF} = \frac{k}{1 + \exp\left[\frac{F}{RT}(E - E_{\text{PQ}}^0)\right]}$$

gives rise to the same catalytic Tafel plot as when the catalyst is unconditionally stable.

Adaptations for Two-Electron Processes. As already mentioned, catalytic reaction schemes are usually more complex in practice than the simple one-electron mechanism treated above (Scheme 1). Two-electron/two-step processes are often encountered, and numerous reaction schemes can be involved, as listed and analyzed elsewhere in the case where the catalyst is stable.⁴⁵ They are designed by combinations of the letters E (electron transfers), and C (chemical step). The sequencing of the standard potentials of the two-electron transfers is one of the key parameters of the overall process. Variants in which the second electron transfer may take place in solution (E') rather than at the electrode surface (E) should also be taken into account. It is clear that consideration of all of these possible reaction schemes, with the instability of the catalyst included as an additional parameter in each case, would convert the present contribution into a taxonomic nightmare. We have adopted a compromise, namely, providing two extreme examples of the adaptation of the analysis to two-electron schemes.

The first, an ECE' scheme as depicted in a general way at the left in Scheme 2, involves one of the simplest situations one can

Scheme 2. ECE' Process^a

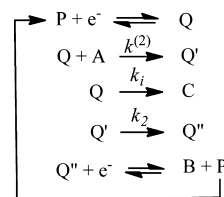


^a"Fe" represents iron tetraphenylporphyrin.

envison (an experimental example is provided by the catalysis of the electrochemical CO₂-to-CO conversion by iron(0) tetraphenylporphyrin (Scheme 2 right).⁴⁰ Provided that the second electron transfer is easier than the first, the catalytic time constant, current densities, charge, *TOF*, *TON*, and time-dependent bulk concentrations can be easily obtained from the expressions given in Table 1 derived for the one-electron scheme, taking into account a stoichiometric factor of 2 (see the SI, particularly Table S3).

Analysis of the second example, an ECCE scheme (Scheme 3), is somewhat more arduous. It is detailed in the SI, leading to

Scheme 3. ECCE Process



the relationships gathered in Table S5. Scheme 3 shows the mechanism of the reaction taken as an experimental example in the next section.

With these two tutorial examples, the reader should be able to treat any two-electron/two-step reaction scheme. However, it may also be necessary to adapt the preceding treatments to cases where the catalytic reaction leads to more than one product. This is indeed a quite common event in catalytic processes. Although this circumstance is a complicating factor, the analysis remains based on the same principles but in addition calls for the measurement of the time evolution of each product.

Experimental Examples. We illustrate the analysis of catalyst inactivation with data previously obtained in the electrochemical reduction of CO₂ to CO catalyzed by electrogenerated iron(0) 5,15-bis(2',6'-dihydroxyphenyl)-10,20-bis(pentafluorophenyl)porphyrin⁴⁶ (FCAT) (Figure 5) in *N,N'*-dimethylformamide (DMF) in the presence of added phenol (see the SI for experimental details). The Faradaic yield is close to 100%, and thus, the charge passed mirrors the production of CO. A previous cyclic voltammetry investigation of FCAT showed that the mechanism involved is as represented in Scheme 3 (see the SI for the corresponding relationships associated with this mechanism).⁴¹ As can be seen in Figure 5, the charge passed over a long period of time can be satisfactorily modeled by an exponential increase, leading to the expression $q = q_{\text{lim}}[1 - \exp(-t/t_{\text{chem}})]$ with $q_{\text{lim}} = 2FVC_P^0(1 + k/k_i) = 600$ C and $t_{\text{chem}} = 916$ min. It has to be mentioned that the small deviations of the rate of catalyst inactivation from the exponential law may be due to experimental constraints. Indeed, the characteristic time decay t_{chem} depends on δ , the applied potential E , and the second electron transfer heterogeneous rate constant (see Table S5 in the SI), which

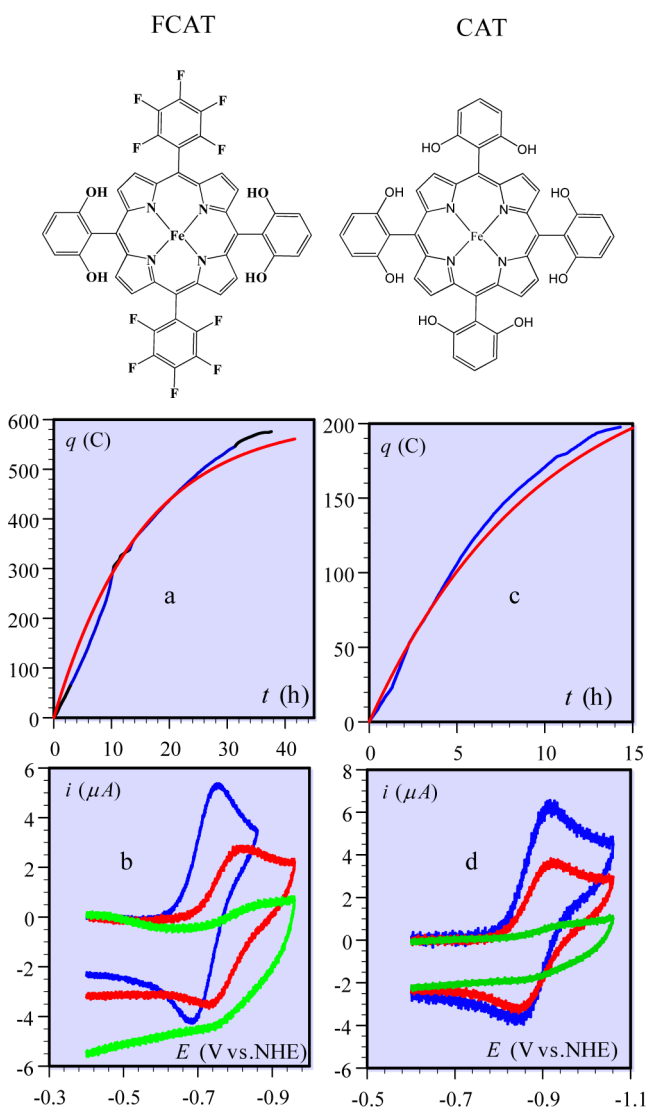


Figure 5. (a, c) Electrolysis in 10 mL of CO_2 -saturated DMF + 0.1 M $n\text{-Bu}_4\text{NPF}_6$ in the presence of 1 mM catalyst and 3 M PhOH: (a) FCAT at -1.08 V vs NHE; (c) CAT at -1.14 V vs NHE. Black: charge passed as a function of time. Red: fit to an exponential function. (b, d) Cyclic voltammograms of the solutions at a glassy carbon electrode, showing the $\text{Fe}^{\text{II}}/\text{Fe}^{\text{I}}$ waves after electrolysis with (b) FCAT for 0 h (blue), 13.2 h (red), and 37.7 h (green) and (d) CAT for 0 h (blue), 2.3 h (red), and 14.3 h (green).

can all vary during the electrolysis because the electrolysis is periodically stopped to check that CO is the only product formed and both the position of the reference electrode (and ohmic compensation) and the stirring conditions may change somewhat when the electrolysis is restarted.

The stability factor of merit for FCAT, $\text{TON}_{\text{FCAT}}^{\text{lim}} = k/k_i = 310$ is obtained from the limiting value of the charge passed, $q_{\text{lim}} = 600$ C. Inactivation of FCAT upon electrolysis can also be followed by cyclic voltammetry, which shows the disappearance of the $\text{Fe}^{\text{II}}/\text{Fe}^{\text{I}}$ wave (Figure 5b). The rate of $\text{Fe}^{\text{II}}/\text{Fe}^{\text{I}}$ wave disappearance is in agreement with the charge increase. It should be noted that because of the mechanism at work (Scheme 3), the initial catalyst P is rapidly transformed into Q'' . Hence, the $\text{Fe}^{\text{II}}/\text{Fe}^{\text{I}}$ wave observed in cyclic voltammetry involves an oxidized form of Q'' .

A similar series of experiments was performed with the electrogenerated iron(0) 5,10,15,20-tetrakis(2',6'-dihydroxyphenyl)porphyrin (CAT) as the catalyst (Figure 5), following the same mechanism as with FCAT,⁴² leading to $q_{\text{lim}} = 250$ C and $t_{\text{chem}} = 580$ min and hence $\text{TON}_{\text{FCAT}}^{\text{lim}} = 130$ (Figure 5). Again, inactivation of CAT upon electrolysis was confirmed by cyclic voltammetry.

Some relevant information can be found in the literature for other catalysts of the CO_2 -to-CO electrochemical conversion. In the absence of detailed mechanistic information, we assume that those catalysts follow a simple two-electron process as described in Scheme S2 in the SI. For example, ref 47 indicates that after 15 h of electrolysis, 8% of the m -(triphos)₂Pd₂ catalyst was consumed and 190 mol of CO was produced per mole of catalyst, leading to $\text{TON}_{\text{Pd}}^{\text{lim}} = 2375$. A limiting TON of 110 can be evaluated for the $\text{Re}(\text{bpy})(\text{CO})_3(\text{py})$ catalyst in the presence of 0.8 M $\text{CF}_3\text{CH}_2\text{OH}$ from the indication that there is a 0.9% decay of catalyst per catalytic cycle.⁴⁸ With $\text{Ru}(\text{tpy})(\text{bpy})$ as the catalyst, after 5 h of electrolysis, 25% degradation can be inferred from the current decrease while 5 mol of CO were formed per mole of catalyst; hence the corresponding limiting TON is 20.⁴⁹ It is clear, however, that these figures should be confirmed by more detailed observations of the time variations of the charge passed and product formed as well as the decay of the catalyst concentration.

CONCLUDING REMARKS

Table 1 summarizes the evolution during electrolysis of the current flowing through the electrode, the charge passed from the start of electrolysis, and the decay of the bulk concentration of the catalyst. It is remarkable that the pace of this time evolution could be characterized by a single parameter in the form of a time constant that associates the rate constants for catalysis and inactivation of the catalyst with the diffusion coefficient of the catalyst and the time constant of the cell. Another interesting result is that the turnover number, which expresses the number of cycles performed by a catalyst molecule, reaches a limit that is simply equal to the ratio of the rate constants for catalysis and catalyst deactivation. This essential factor of merit of the catalyst can be determined at the end of the electrolysis when the catalyst has entirely disappeared. However, it may be more conveniently obtained before complete inactivation of the catalyst by observation of the time variations of the charge passed, the product formed, and the decay of the catalyst concentration in solution. In practical terms, the most interesting situation is when the ratio of the catalyst deactivation rate to the catalysis rate is small, even though the catalyst is not unconditionally stable. In that case, the catalytic Tafel plot can be derived from the observation of the turnover frequency during the early stage of electrolysis. It should also be borne in mind that this turnover frequency versus overpotential relationship can be derived from less tedious cyclic voltammetry experiments, in which catalyst inactivation plays a marginal role.^{39–41} Literature data that could serve to illustrate these analyses are scarce to date, mostly because results for only a few or even a single electrolysis time are usually reported. We hope that this will change in the near future to the benefit of a more lucid benchmarking of catalysts.

■ ASSOCIATED CONTENT

S Supporting Information

Experimental details and derivations of equations. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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