A compact analytical formalism for current transients in electrochemical systems

Pradeep R. Nair† and Muhammad A. Alam

Micro- and nanostructured electrodes form an integral part of a wide variety of electrochemical systems for biomolecular detection, batteries, solar cells, scanning electrochemical microscopy, etc. Given the complexity of the electrode structures, the Butler–Volmer formalism of redox reactions, and the diffusion transport of redox species, it is hardly surprising that only a few problems are amenable to closed-form, compact analytical solutions. While numerical solutions are widely used, it is often difficult to integrate the insights gained into the design and optimization of electrochemical systems. In this article, we develop a comprehensive analytical formalism for current transients that not only anticipate the responses of complex electrode structures to complicated voltammetry measurements, but also intuitively interpret diverse experiments such as redox detection of molecules at nanogap electrodes, scanning electrochemical microscopy, etc. The results from the analytical model, well supported through detailed numerical simulations and experimental data from the literature, have broad implications in the design and optimization of nanostructured electrodes for healthcare and energy storage applications.

1 Introduction

Various types of voltammetry (or chronoamperometry) constitute the basic characterization techniques for electrochemical systems and provide valuable information regarding the geometry and reaction constants of complex nanostructured electrodes. Since the landmark article by Nicholson and Shain in 1964 for numerical solution of the voltammetry problems, the field has witnessed tremendous research activity to unravel the dynamics of electrochemical processes at electrodes. As most problems are not amenable to closed-form analytical solutions, various numerical simulation schemes had to be developed, to analyze the response of electrochemical systems. Nevertheless, analytical solutions often provide crucial and nontrivial insights into various sub-processes that help significantly in design and further optimization. In this article, we develop a closed-form, compact analytical formulation for current transients at microelectrodes based on the well known reaction–diffusion formalism and use these solutions to study the dynamics of redox kinetics at microelectrodes. Apart from predicting the trends for classical electrode geometries like planar, cylindrical, and spherical surfaces, our analytical results also anticipate the important trends for fractal electrodes.

This article is arranged as follows: in Section II, we develop the detailed analytical formalism to study the current transients at generic electrodes. In Section III, we apply the analytical model to study (a) potential step voltammetry, (b) linear sweep voltammetry, (c) redox detection of molecules at nanogap electrodes, and (d) scanning electrochemical microscopy (SECM). Although these topics are discussed/researched individually by using specialized numerical techniques and approaches, in general, the field lacks a common analytical framework that will help cross-connect the inferences and conclusions of various subtopics in a systematic way. For example, while closed-form analytical solutions are available for potential step voltammetry, linear sweep voltammetry depends primarily on numerical simulations even for the simplest configurations. Here the results are typically given in a tabular format or require complex numerical integration. Similarly, analytical description of redox detection of molecules is available only for simple geometries while numerical simulations are required for other structures. The scenario is not different for SECM, where the analytical expressions are limited to curve-fitting of numerical data. In this manuscript, we show that the above mentioned wide ranging electrochemical measurements can be uniquely and succinctly described through a comprehensive analytical formalism in terms of a single mathematical concept of “Transient Diffusion Equivalent Capacitance (TDEC).” This mathematical concept of TDEC is a way of solving diffusion equation and must not be confused with other physical capacitance such as double-layer capacitance, because after all, they do not even have the same dimension. We validate our analytical model by comparing with numerical simulation and/or experimental data, as appropriate. Indeed, so long the basic assumptions of isotropic Fickian diffusion and heterogeneous redox
reactions are valid, we are yet to find a system whose numerical solution is not well approximated by the analytical formula proposed in this manuscript. After discussing the implications and impacts of the new model, we summarize the results in Section IV. Detailed derivations and numerical simulation methodology are reserved for appendices.

II.A Model system

The model system consists of a working electrode (WE) immersed in a solution of target molecules (see Fig. 1a; for simplicity, a planar electrode is shown in the illustration, although the formalism we develop in subsequent sections will be applicable to a wide variety of nonplanar electrode structures). Oxidation/reduction of the redox species occurs at the electrode surface, depending on the applied potential (against a reference electrode, usually Ag/AgCl). The electrochemical reaction at the electrode surface is characterized as

\[ R \leftrightarrow O + e \]  

where R and O denote the reduced and oxidized species, respectively. The concentration of R near the electrode surface reduces as the reaction proceeds. Thus, the dynamics of electrochemical reaction can be described through a reaction–diffusion process which involves a redox reaction with net rate, \( N \), given by

\[ N = -k_F \rho_{x,R} + k_R \rho_{x,O} \]  

where \( k_F \) and \( k_R \) are the forward and reverse reaction constants and \( \rho \) denotes the concentration (not the mass density, see Table 1 for a list of variables used in this manuscript) of the corresponding species. Note the convention for subscripts associated with \( \rho \); the first subscript denotes the spatial location ('s' means the WE surface), while the second denotes the reactant species. The rate constants, \( k_F \) and \( k_R \), depend on the potential of the working electrode and will be considered explicitly later (see eqn (13), Section II.B.). The concentration profiles for R and O are dictated by the diffusion equation

\[ \frac{\partial \rho_{R,O}}{\partial t} = D_{R,O} \nabla^2 \rho_{R,O} \]  

where \( D \) is the diffusion coefficient of the corresponding species and \( \nabla^2 \) denotes the Laplacian operator in an appropriate coordinate system. Eqn (2) and (3) determine the dynamics of the system. As eqn (2) also represents the current density at the electrode surface, the net electrode current is given as

\[ I = -q \int (N) dS, \]  

where the integration is over the electrode surface area and \( q \) is the electronic charge. Assuming uniform distribution of reactants around the electrode and spatial homogeneity of reaction constants, eqn (4) can be re-written as

\[ I = \mathcal{A} q (k_F \rho_{x,R} - k_R \rho_{x,O}), \]  

where \( \mathcal{A} \) is the electrode surface area. Flux or mass conservation at the electrode surface leads to

\[ D_R \nabla \rho_{x,R} = -D_O \nabla \rho_{x,O} = \text{eqn } (2). \]  

Eqn (2)–(6) along with the initial conditions for \( \rho_{R,O} \) determine the behavior of the model system described in this section.

Fig. 1  (a) Schematic of a WE introduced to an electrolyte. (b) The reaction \( R \leftrightarrow O + e \) occurs at the electrode surface, with diffusion-limited transport of R and O in the electrolyte, and the reaction rate at the WE-electrolyte interface is dictated by the Butler–Volmer formalism. (c) Schematic of a typical concentration profile of R at times \( t_1 \) and \( t_2 \). The blue dashed lines indicate the concentration gradient and hence diffusion flux at the surface. (d) Linear concentration profile approximation to aid analytical derivations. Note that the concentration gradient at the surface remains the same for both (c) and (d). Although the schematic and concentration profiles are shown for a planar electrode, the analytical formalism developed in this article is applicable for a wide variety of electrode structures.
Before we proceed with the solution methodology, let us now discuss the various assumptions involved in eqn (2)–(6). Note that (a) our model system ignores the transient effects due to the electrolyte double layer charging process and/or any uncompensated resistance. The influence of such effects on current transients is elaborately discussed in the literature.\(^3\) (b) For redox systems, we assume isotropic diffusion limited transport and neglect any migration component \(i.e.,\) migration of ions in the electric field. Usually, this assumption is valid as an excess electrolyte is almost always present at much higher concentrations in most systems. Any associated electric field effects are strongly screened by the electrolyte (the Debye screening length is of the order of a few nm for mM electrolyte concentrations\(^2\)). Moreover, our numerical simulations (results not discussed in this article) with an additional migration component (proportional to the electric field) in the presence of excess electrolyte show negligible deviations from the analytical solutions. Indeed, a recent study also indicates that results based on diffusion analysis can be applied to nanoscale electrodes in the presence of excess electrolyte\(^19\) (although there have been some reports on non-linear transport phenomena near nanoscale electrodes\(^20\)). Further, we assume that (c) the diffusion flux is symmetrical over the electrodes (eqn (5)), and (d) the Butler–Volmer formalism is used to describe the reaction coefficients (eqn (13)). Finally, (e) we develop compact analytical solutions (eqn (16), Section II.B.) based on a first order perturbation solution of the reaction–diffusion equations described by eqn (2)–(6). For illustrative purposes, (f) we assume that \(D_R = D_O = D\), although this assumption is not necessary and the complete expression (eqn (A4)) is available for cases where \(D_R \neq D_O\). Therefore, we believe that while the closed-form analytical solutions discussed in this article might have to be refined to reflect the complexities associated with electrolyte screening, finite size of molecules, anisotropy of diffusion/reaction, etc., the correlations are likely to be relatively minor and the solutions provided here can be interpreted as good approximations.

### II.B General solution

Here, we first develop an analytical solution for the transient current at a planar WE (eqn (7)–(10)) and then extend it to various other electrode geometries (eqn (11)). Consider a 1-D planar system with a WE introduced at \(t = 0\) (Fig. 1b, with cross-sectional area \(A_{\text{planar}}\)) in the presence of an analyte solution with only R species at a concentration \(p_R\) (O molecules are absent at \(t = 0\)). As the reaction proceeds, R is converted to O at the electrode surface and diffusion dictates the transport of molecules in the system. As described in the previous section, the net current at the electrode is determined by the reaction and diffusion of reactants to the electrode surface (eqn (4)–(6)). Schematics of spatial concentration profiles at two different times, \(t_1\) and \(t_2\), are shown in Fig. 1c. The dashed lines represent the concentration gradient and hence the diffusion flux at the electrode surface. The finite reaction rate at the WE and the diffusion process determine the non-zero concentration of R at \(x = 0\). From the theory of planar electrodes with fast reaction rates (\(k_R \rightarrow \infty\), \(p_{R,i} \rightarrow 0\)), we know that the concentration profiles, \(p_{R,i}\), vary as \(\text{erf}(x/\sqrt{4Dt})\), ref. 3. For such a system, the
concentration gradient, $\Phi(x)$, is given as $\Phi(x) \propto (4Dt)^{-0.5}e^{x^2/4Dt}$. Hence, the diffusion flux at $x = 0$ is given as $\Phi(x = 0) \propto W^{-1}$, where $W$ is known as the diffusion layer thickness and is given by $W \sim (kD_Dt)^{-0.5}$ by classical diffusion theory, where $k$ is a constant. This key insight allows us to approximate the concentration profiles in Fig. 1c with the linearized profile shown in Fig. 1d, such that the net diffusion flux towards the electrode surface is not affected (compare the gradients at $x = 0$ for both Fig. 1c and Fig. 1d, we assume that the bulk concentration is maintained for $x > W$). Note that we make this approximation only to derive a closed-form analytical solution for current transients. The analytical solutions are then compared with detailed numerical simulations and the literature in Section III, which are, of course, not limited by any such assumptions for concentration profiles.

The integrated current until time $t'$ is given by the net amount of species R that was oxidized (i.e., the depleted triangle at time $t = t_1$ in Fig. 1d; also see similar discussion associated with eqn (1.4.30), Section 1.4.3 of ref. 3, the textbook by Bard and Faulkner), so that

$$I(t) = \int_0^t qA_{\text{planar}} \frac{W}{2} \left( \rho_{W, R} - \rho_{s, R} \right).$$

which on differentiation with time $t'$ implies,

$$\frac{I(t)}{qA_{\text{planar}}} = \left( \rho_{W, R} - \rho_{s, R} \right) \frac{dW}{2Dt} + \frac{W}{2} \left( \frac{d\rho_{W, R}}{dt} - \frac{d\rho_{s, R}}{dt} \right).$$

The second term on the right hand side of eqn (8) can be evaluated by assuming linear diffusion [see Fig. 1d], i.e.

$$\frac{d\rho_{W, R}}{dt} = \frac{d\rho_{W, R}}{dW} \frac{dW}{dt} = 0.$$  

This is because, by definition, $\rho_{W, R}$ does not vary with $W$. As the redox reaction at the electrode proceeds, the species R will be depleted further away from the electrode surface. As mentioned before, the diffusion layer thickness is given by $W \sim (kD_Dt)^{-0.5}$. Although different definitions of $k$ = 1, 2, $\pi$, or 4 are used in the literature (see Section 5.2.1 of ref. 3), we assume $k = 4$ (for additional discussion on the implication of $k$ for practical applications, see Section III.A). Using this relationship and eqn (9), we can rewrite eqn (8) as

$$I(t) = qA_{\text{planar}} \frac{W}{2} \left( \rho_{W, R} - \rho_{s, R} \right) - qA_e \frac{W}{2} \frac{d\rho_{s, R}}{dt}.$$  

Eqn (10) represents the current at a planar WE at time $t'$ for the density profile shown in Fig. 1d. Eqn (10) reduces to the expected steady state current for a linearly varying concentration profile (second term on the RHS becomes zero under such conditions). The seeds of the above analysis are already present in the classic textbook of Bard and Faulkner (Section 1.4.3, ref. 3) as a pedagogical tool for planar systems, however, here we generalize the idea to a much broader context of the complex system with arbitrary configuration of electrode geometries, as shown below.

Using the terminology provided in Table 2 with $\rho_{W, R} = \rho_R$, eqn (10) can be re-written for electrodes of arbitrary geometry as

$$I(t) = qC_{D_{SS}}(\rho_R - \rho_{s, R}) - qA_e \frac{W}{2} \frac{d\rho_{s, R}}{dt}.$$  

where $A_e$ denotes the electrode area. For example, $A_e = A_{\text{planar}}$ and $C_{D_{SS}} = A_{\text{planar}}D_p/W$ for planar systems, but the values will be different for other electrode geometries. The parameter $C_{D_{SS}}$ is known as diffusion equivalent capacitance. Note that $C_{D_{SS}}$ has the same functional form as the electrical capacitance between two electrodes separated by a distance $W$, except that the dielectric permittivity is replaced by the diffusion coefficient, $D$ (see Table 1). This concept of diffusion equivalent capacitance follows from the elegant analogy of diffusion problems in the bio-chemical literature to Laplace’s equation of electrostatics and it provides rich insights and powerful analysis techniques that has been used by the biophysics community with significant success (see Appendix A for detailed discussion on $C_{D_{SS}}$). The introduction of $C_{D_{SS}}$ is an important step as it allows us to generalize eqn (10) beyond 1D planar systems (note that we assumed linear concentration profiles for deriving eqn (10)) to eqn (11) which holds good for electrodes with arbitrary geometry (e.g., cylindrical, spherical electrodes, see the corresponding $C_{D_{SS}}$ in Table 1 and Appendix A).

<table>
<thead>
<tr>
<th>Electrode</th>
<th>$A_e$</th>
<th>$C_{D_{SS}}$</th>
<th>$C_{D_{SS}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Planar</td>
<td>$A_{\text{planar}}$</td>
<td>$A_eD/W$</td>
<td>$A_eD/\sqrt{4Dt}$</td>
</tr>
<tr>
<td>Cylindrical</td>
<td>$2\pi a_0$</td>
<td>$\log \left( \frac{W + a_0}{a_0} \right)$</td>
<td>$\log \left( \frac{\sqrt{4Dt} + a_0}{a_0} \right)$</td>
</tr>
<tr>
<td>Spherical</td>
<td>$4\pi a_0^2$</td>
<td>$\frac{4\pi D}{a_0^{-1} - \left( W + a_0 \right)^{-2}}$</td>
<td>$\frac{4\pi D}{a_0^{-1} - \left( \sqrt{4Dt} + a_0 \right)^{-1}}$</td>
</tr>
<tr>
<td>Microdisk</td>
<td>$\pi a_0^2$</td>
<td>$\frac{2\pi D}{W} \left( \frac{\sinh \left( 2\pi \gamma \left( W + a_0 \right) \right)}{a_0 \gamma} \right)$</td>
<td>$\frac{2\pi D}{\left( \sinh \left( 2\pi \gamma \left( \sqrt{4Dt} + a_0 \right) \right) \right)}$</td>
</tr>
<tr>
<td>Array</td>
<td>$2\pi a_0$</td>
<td>$\pi a_0 \gamma$</td>
<td>$\pi a_0 \gamma$</td>
</tr>
</tbody>
</table>
Eqn (11) represents the transient current at a microelectrode with a surface concentration $\rho_{s,R}$ and a bulk concentration $\rho_B$ at a distance $W$ from the electrode. However, both $\rho_{s,R}$ and $W$ are time dependent and are unknown. $\rho_{s,R}$ is dictated by the rate of redox reaction (eqn (2)) and the diffusion process (eqn (3)), while $W$ varies as $\sqrt{t}$, as discussed earlier. The time dependent variation of $\rho_{s,R}$ can be accounted through a generalized perturbation approach (using eqn (6) and (11), assuming $D_B = D_0 = D$ without loss of generality, see Appendix B for detailed derivation), and we find that the transient current at electrodes of arbitrary shape is given by

$$I(t) = q A_e \rho_R \left( \frac{k_F}{1 + A_e C_{D(i)}^{-1}} \left( k_F + k_R \right) \right) - q A_e \frac{W}{2} \frac{d \rho_R}{dt}. \quad \text{(12)}$$

Note that eqn (12) explicitly incorporates the effects of finite reaction rates $k_F$ and $k_R$ (see eqn (2)). The major conceptual addition to eqn (11) is the introduction of $C_{D(i)}$, the time dependent version of diffusion equivalent capacitance $C_{D,SS}$ (TDEC, see Appendix B for detailed discussion). As discussed before, $C_{D,SS}$ (and hence $C_{D(i)}$) is obtained by exploiting the analogy between diffusion problem and electrostatic systems. We note that the functional form of $C_{D(i)}$ is exactly the same as the electrostatic capacitance of the electrode system. The two major modifications are - (i) dielectric permittivity is replaced with diffusion coefficient $D$ and (ii) the spatial separation parameter $W$ is replaced by $\sqrt{D \Delta t}$, the diffusion distance.\(^a\) For example, consider planar systems (see Table 2). It is well known that the electrostatic capacitance\(^a\) of a system of planar electrodes is given as $A_e D/W$, where $\varepsilon$ is the dielectric permittivity. Now as suggested before, by replacing $\varepsilon$ with $D$ and $W$ with $\sqrt{D \Delta t}$, $C_{D(i)}$ of planar systems is given as $A_e D / \sqrt{4D \Delta t}$. $C_{D(i)}$ for other systems described in Table 2 directly follows this methodology. We emphasize that as TDEC is a mathematical technique to solve transient diffusion equation by exploiting its analogy to electrostatic problem, $C_{D(i)}$ has appropriate dimension for the problem being solved (not that of a typical electrical capacitance). The constants $k_F$ and $k_R$ are bias dependent and in the Butler–Volmer formalism\(^3\) are given as

$$k_F = k_0 e^{(1-\alpha)/\left(E_A - E_0\right)},$$

$$k_R = k_0 e^{-\alpha/\left(E_A - E_0\right)}, \quad \text{(13)}$$

where $k_0$ is the heterogeneous rate constant, $\alpha$ is the transfer coefficient (usually, $\alpha = 0.5$), $f = F/RT$, $F$ is the Faraday’s constant, $R$ is the universal gas constant, $T$ is the temperature, $E_A$ is the applied bias at the WE and $E_0$ is the formal potential of the reaction. We assume that any effects of the electric field on the reaction rates are factored in through appropriate parameterization.\(^a\) Using eqn (13), the general solution for transient current at a WE is given as

$$I(t) = q A_e \rho_R \left( \frac{F e^{(1-\alpha)/\left(E_A - E_0\right)}}{k_0 A_e C_{D(i)}^{-1} \left( e^{(1-\alpha)/\left(E_A - E_0\right)} + e^{-\alpha/\left(E_A - E_0\right)} \right)} \right) - q A_e \frac{W}{2} \frac{d \rho_R}{dt}. \quad \text{(14)}$$

We assume that the bias applied to the WE is of the form $E_A = E_i + vt$, where $E_i$ is the initial potential and $v$ is the sweep rate. The rate of change of surface concentration, $d\rho_{s,w}/dt$, is influenced by the applied bias $E_A$ and the sweep rate $v$. In general, we find that

$$\frac{d \rho_{s,R}}{dt} = -\rho_B \frac{v \beta f e^{\alpha/\left(E_A - E_0\right)}}{(1 + e^{\beta/\left(E_A - E_0\right)})^2} \quad \text{(15)}$$

is a good approximation (see Appendix C for derivation, $\beta$ is a factor to capture the deviation from Nernst behavior due to the diffusion limited transport of molecules, $0 < \beta < 1$). Similarly, to evaluate $W$ in the second term on the RHS of eqn (14), we realize that for $E_A < E_0$, redox reaction at the WE is negligible and $W \rightarrow 0$, on the other hand, for $E_A \gg E_0$, $W$ approaches $\sqrt{2Dt}$. This asymptotic behavior can be captured by using an interpolation function of the form $W \sim \sqrt{2Dt e^{\beta/\left(E_A - E_0\right)}}/\left(1 + e^{\beta/\left(E_A - E_0\right)}\right)^{1/2}$.

Using eqn (14) and (15), we find that the transient current for a time varying potential at the electrode is given as

$$I(t) = q A_e \rho_R \left( \frac{F e^{(1-\alpha)/\left(E_A - E_0\right)}}{k_0 A_e C_{D(i)}^{-1} \left( e^{(1-\alpha)/\left(E_A - E_0\right)} + e^{-\alpha/\left(E_A - E_0\right)} \right)} \right) + q A_e \rho_R \sqrt{2Dt} \frac{v \beta f e^{\alpha/\left(E_A - E_0\right)}}{(1 + e^{\beta/\left(E_A - E_0\right)})^{1/2}}. \quad \text{(16)}$$

Eqn (16) is the key result of this article and provides closed-form analytical solutions for the transient response of electrodes with arbitrary geometry. Note that the geometry of the electrode and the transient diffusion of reactants are incorporated through the parameter $C_{D(i)}$. Appropriate $C_{D(i)}$ (see Table 2) and eqn (16) allow us to study the dynamics of various electrochemical processes at nanostructured electrodes. In general, eqn (16) implies that the transient current at a WE consists of two components: (i) a component due to the bulk diffusion effects (first term on the RHS, called the diffusion component) and (ii) the second component due to the rate of consumption of reduced species $R$ at the WE (second term on the RHS, called the reaction component). The relative magnitude of these two components has interesting implications in the transient behavior of micro- and nanostructured electrodes, as discussed in Section III.B.

The above analysis completes the derivation for transient currents at microelectrodes. Note that we have, so far, not placed any restriction on the shape of the electrode. Moreover, the analysis has relied only on simple, physical arguments that obviate the need for a complex Laplace-transform approach, series solution, or complicated numerical simulations, typically found in electrochemical textbooks.\(^a\) As mentioned before, an approach similar to our analysis is given as a semi-empirical proof for Cottrell equation in ref. 3 (i.e., restricted only for potentiostatic measurements of planar systems). However, our approach, based on transient diffusion equivalent capacitance, has been generalized to other complex systems with a wide variety of electrode shapes and operating conditions. The conceptual power of our approach lies in the fact that (i) it can integrate multiple topics that may otherwise appear only weakly
related into a single conceptual framework, and that (ii) it transforms a complex, transient, unsteady state mass transport problem into a benign (and often already solved) problem of steady-state transport.

III Results

We now illustrate the validity and generality of our approach by comparing it against a set of well known electrochemical experiments. We first consider (a) potential step voltammetry and (b) linear sweep voltammetry. In the later sections we illustrate the generality of eqn (16) by considering complex scenarios like (c) redox detection of biomolecules using multiple electrodes and (d) scanning electrochemical microscopy. This heuristic validation does not exclude the possibility that there may be other problems that the analytical solutions cannot fully encapsulate, but the solution will nonetheless offer significant insights into the problem. We start with the potential step voltammetry:

III.A Potential step voltammetry (PSV)

In PSV, a step-bias $E_A$ is applied to the WE at time $t = 0$ (see Fig. 2a). Any potential step bias, in general, can be visualized to consist of two segments: (a) the ramp process in which the electrode potential is increased to $E_A$ such that $0 < t < 0^*$, $v \rightarrow \infty$ ($0^*$ denotes the time required by the system to raise the electrode potential to $E_A$) and (b) the potential is held fixed at $E_A$ for the rest of the measurement such that $t > 0^*$, $v = 0$. The reaction component (second term on the RHS of eqn (16)) is negligible during part (a) as $t \sim 0$. The same component is negligible during part (b) as $v = 0$. Hence the transient current for PSV (using eqn (16)) is given by

$$I(t) = qA_e \rho_R \left( \frac{1}{k_0} + \frac{A_e}{C_{D(f)}} \left( \frac{e^{(1-a)/(E_A-E_0)}}{e^{(1-a)/(E_A-E_0)} + e^{-(1-a)/(E_A-E_0)}} \right) \right). \quad (17)$$

Analytical results are available in the literature for the response of planar, cylindrical, and spherical electrodes for infinite reaction rates at the WE (i.e., $k_0 \rightarrow \infty$, $E_A \gg E_0$). Fig. 2b-d show that eqn (17) compares well with the literature (solid symbols, ref. 3 and 9–11) and numerical simulation results (open symbols, refer Appendix D for details) for $E_A > E_0$. At the same time, eqn (17) accurately predicts the response for $E_A < E_0$ as well, thus providing a general formalism to study the transient response of nanostructured electrodes.

Eqn (17), with appropriate $C_{D(f)}$, anticipates well-established results from the traditional literature on current transients at microelectrodes. The diffusion limited current at an electrode (with $E_A \gg E_0$ in eqn (17)) is given by

$$R(t) \approx q\rho_RC_{D(f)}. \quad (18)$$

For planar systems (refer Table 2) with $C_{D(f)} = A_{\text{planar}}D/4Dt$, eqn (18) indicates that $R(t) \propto t^{-1/2}$, the famous Cottrel current.$^{1,2}$

---

**Fig. 2** Comparison of eqn (17) with results from literature for potentiostatic measurements. (a) Schematic of a potentiostatic measurement. At $t = 0$, a voltage step is applied at the electrode. Transient response of (b) planar, (c) cylindrical ($a_0 = 1 \mu$m), and (d) spherical electrodes ($a_0 = 2 \mu$m) (current (A) per unit surface area for $\rho_R = 1$ mol cm$^{-3}$ is plotted in each case). The solid symbols represent results from the literature (planar,$^2$ cylindrical,$^3$ and spherical,$^4$), the open symbols represent numerical simulation results of this work ($E_{A1} = E_0 + 0.2$ V; $E_{A2} = E_0 - 0.1$ V; $E_{A3} = E_0 - 0.2$ V, see Appendix D for details), and the solid lines represent analytical results (eqn (17)). Note that apart from reproducing the results in the literature for ideal electrodes with large bias ($E_A > E_0$), the analytical results match well with numerical simulation results for small bias ($E_A < E_0$) also.
(Fig. 2b). Note that since we use \( \sqrt{4Dt} \) as the definition for diffusion layer thickness, eqn (18) for planar systems differs from the Cottrell expression by a factor of \( 4/\sqrt{\pi} \). However, as discussed earlier, although this definition is not unique (ref. 3), we can still anticipate key features of diffusion limited current at various electrodes. For example, the same formalism with appropriate \( C_{D(k)} \) predicts the \( \sim 1/\log(t) \) response of cylindrical electrodes\(^\text{a}\) (Fig. 2c). For spherical systems at large \( t \),

\[
C_{D(k)} = \frac{4\pi D}{a_0^{-1} - (\sqrt{6Dt} + a_0)} \sim 4\pi Da_0,
\]

Eqn (18) now reduces to \( I(t \to \infty) = q\rho_w 4\pi Da_0 \), the well-established diffusion limited current towards a spherical electrode\(^\text{a}\) (Fig. 2d). Similarly, eqn (18) with appropriate \( C_{D(k)} \) compares well with the empirical formula in the literature for disk microelectrodes.\(^2\) For such electrodes, eqn (18) predicts the diffusion limited current \( i.e., as t \to \infty \), using \( C_{D(k)} \) from Table 1 is \( I(t \to \infty) = q\rho_w 4\pi Da_0 \), in accordance with the literature.\(^3\) It is well known that the current density at a planar electrode is much lower compared to spherical and cylindrical electrodes due to the diffusion limited transport of reactants.\(^4\) In addition to predicting the results for the diffusion dominated regime, eqn (17) accurately anticipates the results for the reaction dominated regime. For very small \( k_0 \), eqn (17) reduces to \( I(k_0 \to 0) = q\rho_w A_k \), \( \epsilon (1 - \epsilon) \), i.e., the reaction current is proportional to the electrode area and varies exponentially with the applied bias. Further, the results in Fig. 2 indicate that analytical solutions compare well with numerical simulations for the range of bias, \( E_{A1} \) to \( E_{A3} \), a variation of over 6 orders in magnitude of reaction constants.

Eqn (17) provides a unique, compact, and generic formalism to understand and predict the current transients on a wide variety of microelectrodes. Note that the effects of finite reaction rates are incorporated into this formalism and can be extended to electrodes of arbitrary shape with appropriate parameterization of diffusion equivalent capacitance, \( C_{D(k)} \). Although electrodes with size in the \( \mu m \) regime were used for validation purposes in Fig. 2, the model is equally valid for nanoscale electrodes (so long the presumption of Fickian diffusion is valid, also see the discussion on an array of nanoscale electrodes, Section III.B. and Fig. 4). Further, the model accurately anticipates the electrochemical response at Nernst equilibrium, as and when it occurs as a function of various parameters like \( k_0, E_0 \), and \( D \). (e.g., biases \( E_{A2} \) and \( E_{A3} \) in Fig. 2). We will now discuss the applicability of the new model to a more complex experiment, i.e., linear sweep voltammetry.

III.B Linear sweep voltammetry (LSV)

In LSV, the bias applied to the WE is a function of time, \( i.e., E_A = E_i + vt \), where \( E_i \) is the initial potential and \( v \) is the sweep rate (we assume \( E_i = 0 \) for convenience, see Fig. 3a). The transient current in this case is given by eqn (16). Fig. 3b–d show that, once again, the closed-form analytical result, eqn (16), reproduces the results from the literature as well as numerical simulation (see Appendix D for details on numerical simulations) results very well for planar, cylindrical and spherical electrodes. Literature data for planar and spherical electrodes are from ref. 3 (numerical results provided in a tabulated

![Fig. 3](https://pubs.rsc.org/en/content/articlelanding/2012/an/b200314f/download)  

**Fig. 3** Comparison of the analytical model with the literature for LSV measurement. (a) Schematic of a LSV measurement. At \( t = 0 \), a linearly increasing voltage \( (v = 60 \text{ mV s}^{-1}) \) is applied at the electrode \( \rho = 60 \text{ mV s}^{-1} \). Comparison of results for (b) planar, (c) cylindrical \( (a_0 = 1 \text{ um}) \), and (d) spherical electrodes \( (a_0 = 2 \text{ um}) \). The solid symbols represent results from the literature (ref. 3 and 14), the open symbols represent numerical simulation results of this work and the lines represent analytical results. The solid (blue) curves indicate the total current, eqn (16), while the grey (green) lines represent the diffusion component (first term on the RHS of eqn (16)). Note that the reaction component is of comparable magnitude to the diffusion component only for the planar system. For cylindrical and spherical systems, the diffusion current density is so high that it dominates the total response. For comparison purposes, the parameters are so chosen that \( k_0 \rho \Delta V^{-0.3} > 10 \) (ref. 3, see Appendix D).
format) while those for cylindrical electrodes are from ref. 14 based on numerical integration. Note that the planar electrodes show a peak in the transient current while such peaks are not so prominent in cylindrical and spherical systems. Although analytical solutions in the form of series summation, semi-integrals, etc. are well known specific cases, eqn (16) provides a general solution protocol with compact analytical solutions for PSV/LSV of arbitrary electrode configurations and the model developed in this article allows experimentalists to anticipate their experimental trends without resorting to numerical simulations. Our results also predict all qualitative features of transient current as discussed below.

**Dimensional effects on LSV.** It is well known that spherical electrodes display quasi-steady state behavior during LSV (Fig. 3d), while planar electrodes exhibit well defined peaks with significant transient overshoot (Fig. 3b). Although, these effects are usually attributed to the dimensional effects of diffusion towards microelectrodes, eqn (16) provides interesting insights into this curious phenomenon. For planar systems, the reaction current density is of comparable magnitude to the diffusion current component (see Fig. 3b, the grey (green) curve indicates the diffusion component and the solid (blue) curve denotes the total current). Therefore, as the reaction component is significant only at $E_A \sim E_m$, there is a well-defined peak at the corresponding bias condition for the planar systems. However, since the diffusion flux in the spherical electrode is orders of magnitude larger than the reaction component, spherical electrodes exhibit quasi-steady state behavior during LSV. Only for extremely fast voltage sweeps, can the reaction component for spherical electrodes become comparable to its diffusion component and lead to peaks in transient currents comparable to those in planar electrodes.

**Dependence of LSV on sweep rate, v.** Eqn (16) can be expressed in terms of $E_A (E_A(t) = vt)$, as

$$I(t) = \frac{q \rho_R C_{Df}}{1 + e^{-t/(E_A - E_m)}} + \frac{q A_e \rho_R (D_f)^{1/2} \sqrt{2E_A(t)}}{2} \frac{\beta f e^{2n} (E_A - E_m)}{(1 + \beta f (E_A - E_m))^2}. \quad (19)$$

As mentioned before, the first term on the RHS represents the diffusion component while the second term represents the reaction component. Note that the second term (reaction component) is always proportional to $v^{0.5}$ while the sweep rate dependence of the diffusion component (second term) depends on electrode geometry. For planar systems, using Table 2, as $C_{DK} = D(2D)^{-0.5} = (D_f)^{0.5} E_A(t)^{0.5}$, the diffusion component (first term) is proportional to $v^{0.5}$. Hence, eqn (19) indicates that for planar systems, $I(t) \propto \sqrt{Dv}$, in accordance with well established results of LSV. For spherical systems, we find that $C_{DK} \sim \theta^0 \sim (E/v)^0$. As described in the previous section, the diffusion component is much larger than the reaction component and hence LSV is independent of $v$ for spherical systems. Again, at extremely fast sweeps, spherical systems would also exhibit $v^{0.5}$ behavior as they resemble planar systems at short time $t'$. The same analysis also predicts that while $I(t) \propto \sqrt{D}$ for planar systems, $I(t) \propto \sqrt{D}$ for spherical systems, again reproducing well known trends in the literature. Our results also indicate that the analytical solutions compare well with numerical simulation results for a broad range of sweep rates ($6 \text{ mV s}^{-1}$ to $10 \text{ V s}^{-1}$) as well.

**Fig. 4** Application of the analytical model to an array of nanoscale electrodes. (a) 2D cross-section of an array where $L$ denotes the spacing between individual cylindrical electrodes (schematic and not drawn to scale), (b) Concentration profile of $R$ during LSV for $L = 0.5 \mu m$ and $a_b = 20 \text{ nm}$. (c) and (d) indicate the response of two arrays with different electrode spacing. Note that the same analytical formula predicts widely different behavior of two systems (see Appendix D for simulation details).
**Microelectrode arrays.** Periodic arrays of micro- or nanoscale electrodes (Fig. 4a) are often used for sensitive calibration of LSV, yet the problem has only been addressed by numerical solution. Instead, the analytical formalism can be used to describe the qualitative features of LSV with microelectrode arrays. The important parameters that characterize an array are the size of the individual electrodes and the spacing between them. For such an array of cylindrical electrodes the appropriate expression for \( C_{D(t)} \) is given as:

\[
C_{D(t)} = \frac{2\pi D}{\log(\sinh(2\pi\sqrt{2Df + a_D \gamma}))} \quad (20)
\]

where \( \gamma \) denotes the density of nanowire (NW) array. For a given sweep rate, the spacing of the electrodes or rather the density dictates the LSV characteristics. Accordingly, the array shows a pronounced peak similar to planar systems at high densities (Fig. 4c), while the array response is analogous to cylindrical systems at low densities (Fig. 4d). Note that the widely varying behavior of microelectrode arrays is accurately predicted by our approach and this formalism could provide an alternate methodology to the numerical simulation based diffusion domain analysis for nanostructured electrodes.

**Fractal electrodes.** Finally, we explore the problem of fractal electrodes through the analytical formulation developed in the previous sections (see Fig. 5a). The response of fractal electrodes to voltammetry has been a topic of active research for several decades. In fractal electrodes, the electrode spacing is according to a power-law distribution dictated by the fractal dimension \( D_F \). This unique spatial distribution of fractal electrodes is also reflected in their current transients (as a power law in time). Accordingly, two remarkable and well known results from current transients at fractal electrodes are:

- In a PSV, \( I(t) \propto t^{(1-D_F)/2} \), and
- In LSV, the current scales with sweep rate as \( I \propto \nu^{(D_F-1)/2} \).

Both these well known trends are reproduced in our analytical framework. For fractal systems (\( 1 < D_F < 3 \)), we have \( C_{D(t)} \propto t^{(1-D_F)/2} \) (or equivalently, \( C_{R(t)} \propto (E/V)^{(1-D_F)/2} \) [ref. 36 and 37]). Using eqn (18) and (19), we find that \( I(t) \propto t^{(1-D_F)/2} \) for PSV and \( I(t) \propto \nu^{(D_F-1)/2} \) for LSV, respectively, thus reproducing well known results on current transients towards fractal electrodes. Fig. 5b shows the concentration profile near a fractal electrode, while the inset shows a comparison of sweep rate scaling exponents from numerical simulations with experimental results from the literature.

Both the simulations and experiments follow the trends predicted by analytical results. Note that our model, through a general analytical framework, predicts both the transient and steady state LSV of a wide variety of electrodes, a significant improvement on the previous literature.

**III.C Redox detection of molecules at nanogap electrodes**

In the previous section, we described analytically the dynamics of reversible reaction at a WE embedded in a semi-infinite medium. Such systems have many potentially important applications such as molecular detection. The sensitivity of molecular detection can be considerably improved and the signal can be amplified if additional electrodes are introduced (see Fig. 6). These new electrodes fundamentally change the diffusion geometry of the system. For example, consider a two electrode system (Fig. 6): electrode A (area \( A_A \)) and electrode B (area \( A_B \)) where the reactions described by eqn (1) and (2) occur. The transport of the species R and O between the electrodes is still given by eqn (3). Let the potentials \( E_A \) and \( E_B \) are applied at corresponding electrodes, respectively (corresponding over-potentials: \( \eta_A = E_A - E_0 \) and \( \eta_B = E_B - E_0 \)). We assume that the potentials are such that oxidation occurs at electrode A while reduction occurs at electrode B. Now the signal at electrode A, due to the oxidation of R, will be amplified by a significant factor as all oxidized molecules will undergo reduction at electrode B and are again available for oxidation at electrode A. This scheme is now successfully used to ultra-sensitive detection of redox species. For example, concentration fluctuations of redox molecules (ferrocenedimethanol\(^{10}\) and dopamine\(^{11}\)) in nanogap cavities have been reported recently. In addition, similar concepts are used for ultra-sensitive detection of biomolecules.\(^{12,13}\) Once again, however, the analysis of the problem has been limited only for simple electrode configurations,\(^5\) while others require complicated numerical solutions.\(^{15}\)

We now extend the analytical formalism developed in Section II to address the current amplification in redox detection using nanogap electrodes. We assume that potential sweeps applied, if any, are relatively slow to attain steady state characteristics (i.e., \( \nu \to 0 \), or the electrodes are closely spaced).

---

**Fig. 5** Model predictions for fractal electrodes. (a) Schematic of a fractal array (with rectangular individual electrodes). Note that the spacing between individual electrodes varies exponentially with \( D_F \). The inset shows the comparison of sweep rate scaling exponents: experimental data from the literature (ref. 30, solid symbols), numerical simulation results of this work (open symbols, see Appendix D for details), and analytical results ((\( D_F - 1)/2 \), solid lines).
Using eqn (11), the current at both electrodes should be equal at steady state (implies \( d\rho_{O,R}/dt = 0 \)) and is given as

\[
I_{RD} = qC_{D,SS}(\rho_{A,R} - \rho_{B,R}) = qC_{D,SS}(\rho_{B,O} - \rho_{A,O}).
\]

(21)

where the subscript RD denotes diffusion limited current in a redox detection scheme. The subscripts for the molecular density (\( \rho \)) denote the electrode location (A or B) and the molecular species (R or O), respectively. This current (eqn (21)) should be equal to the reaction currents given by eqn (5) at the corresponding electrodes, i.e.

\[
I_{RD} = qA_k(\rho^{(1-a)}_{A,R} - \rho^{(1-a)}_{A,O}) - A_k(\rho^{(1-a)}_{B,R} - \rho^{(1-a)}_{B,O}).
\]

(22)

Assuming same diffusion coefficients for R and O, mass conservation indicates that \( \rho_R = \rho_{A,R} + \rho_{A,O} \), while \( \rho_R \) is the initial concentration of reduced species. Using eqn (21) and (22), we obtain

\[
I_{RD} = q\rho_R C_{D,SS} \left( \frac{\rho^{(1-a)}_{A,R} - \rho^{(1-a)}_{A,O}}{A_{A}^{-1}} + \frac{\rho^{(1-a)}_{B,R} - \rho^{(1-a)}_{B,O}}{A_{B}^{-1}} \right).
\]

(23)

To compare the model (eqn (23)) with results from the literature and numerical simulations, we assume that while \( E_B \) is held fixed at a potential much lower than \( E_0 \) (so that O molecules are reduced to R at B), \( E_A \) is swept from a low to high bias (much greater than \( E_0 \)). Fig. 6 shows that our approach predicts the response for a wide variety of electrode configurations. Specifically, Fig. 6b indicates that eqn (23) accurately predicts the results for planar nanogap electrodes, as reported in ref. 5. The same formalism, with appropriate \( C_{D,SS} \) given in Table 1, anticipates the results for concentric cylindrical and concentric spherical electrodes (Fig. 6b). Note that as steady state conditions are implied, the positive and negative branches of current in Fig. 6b (i.e., the currents at electrodes A and B, respectively) are of the same magnitude. The application of eqn (23) is not limited to regular electrode configurations shown in Fig. 6b. For instance, it readily predicts the behavior of even complex systems like isolated nanowire (NW) electrodes (with \( C_{D,SS} = \pi D \left( \log \left( W/a_0 + \sqrt{(W/a_0)^2 - 1} \right) \right)^{-1} \), where \( W \) is the separation between NW electrodes and \( a_0 \) is the radius of the NW). The method can be extended to even random nanostructured electrodes, whose \( C_{D,SS} \) is not known analytically. With \( C_{D,SS} \) a priori numerically estimated, Fig. 6d illustrates that eqn (23) accurately anticipates the numerical simulation results (see Appendix D for details).

The amplification achieved by such multi-electrode schemes for sensitive detection of molecules can be understood in simple terms using eqn (23). For \( E_A \gg E_0 \) and \( E_B \ll E_0 \), the maximum achievable redox current is
Note that this current is time independent (for closely spaced electrodes) in contrast to the diffusion limited transient current, given by eqn (18), \( I(t) = qD \rho \frac{C_D}{C_{D,SS}} \). For planar structures, using \( C_{D,SS} \) from Table 1, eqn (24) reduces to

\[
I_{RD,\text{max}} = qD \rho C_{D,SS}A_{\text{planar}}/W \quad (A_{\text{planar}} \text{ is the area of the electrodes and } W \text{ the spacing}).
\]

The second electrode limits the diffusion distance to \( W \) and hence converts the transient \( t^{-1/2} \) response to a steady state current. Another interesting aspect of the solution is that Section III.A. indicates that the current density at a planar electrode is much lower compared to a spherical electrode due to the diffusion limited transport of reactants. Eqn (24) predicts that in a redox scheme, the current density for planar electrodes \( (I_{RD,\text{max}}/A_{\text{planar}} = qD \rho C_{D,SS}/W) \) is exactly the same as the steady state diffusion limited current density at a spherical electrode of similar dimensions (with \( a_0 = W \), refer Section III.A.). Hence by using nanogap planar electrodes, one can achieve higher current densities similar to nanoscale spherical electrodes. Eqn (24) indicates that any electrode geometry that maximizes \( C_{D,SS} \) will also maximize the signal in a redox detection scheme. The ideal candidate in such a scenario, given the advantages of massively parallel VLSI fabrication techniques, is interdigitated nanoscale gap electrodes. An interdigitated electrode array can increase \( C_{D,SS} \) through two factors: by placing the electrodes closer, \( W \) is reduced thus increasing \( C_{D,SS} \). Close spacing also allows higher density electrodes to be placed in a given region which also increases \( C_{D,SS} \).

**III.D Scanning electrochemical microscopy (SECM)**

The formalism described above for signal amplification due to redox kinetics in nanoelectrodes can be extended to other systems such as the SECM. In this scheme, a micro/nano-electrode is used to probe an electrochemically active substrate (Fig. 7a) and the signal characteristics depend on the geometry of the electrode, the substrate and the spacing between them. The SECM experiments are generally interpreted by numerical simulation with the use of analytical expressions confined to curve-fitting of numerical data. Instead, our model (eqn (23) and (24)) provides a general analytical solution for SECM, as follows.

For any electrode–substrate combination, the calculation of \( C_{D,SS} \) (available in the literature for a wide variety of electrode–substrate configurations) is sufficient to predict SECM characteristics (see eqn (24)). This is illustrated in Fig. 7b which compares the prediction of eqn (24) to 3D numerical simulation results from the literature for a microdisk SECM. In the vicinity of a conducting substrate, the effective \( C_{D,SS} \) of a microdisk electrode is given as

\[
C_{D,SS}(W) = 4Da_0 + \frac{\pi Da_0^2}{W},
\]

where \( W \) is the spacing from the conducting substrate. Hence, using eqn (24), the relative increase in the SECM current for a disc electrode is given as

\[
\frac{I_{\text{SECM}}(W)}{I_{\text{SECM}}(W \to \infty)} = \frac{C_{D,SS}(W)}{C_{D,SS}(W \to \infty)} = \frac{\pi a_0}{W} + 1,
\]

where \( I_{\text{SECM}} \) denotes the current in the presence of a conducting substrate. Fig. 7b shows that the analytical results match well

![Fig. 7](image-url)

**Fig. 7** Application of the model to SECM. (a) Schematic of SECM. Redox reactions at the SECM tip (bias – \( E_a \)) and substrate (bias – \( E_b \)) generate a feedback current to probe the substrate properties. (b) Comparison of the model (solid line) with results from the literature (for \( E_a \gg E_b \) and \( E_b \ll E_a \) symbols are from ref. 16). (c) Variation of spatial resolution of SECM as a function of probe spacing from the substrate. The inset shows the spatial profile of the redox current density in the substrate. (d) Minimum probe spacing from the substrate to distinguish an array of feature size \( L_4 \) (left inset). As predicted by the model, for \( L_4/W = 2 \), the peaks and the valleys can be clearly resolved.
with numerical simulation results in the literature, confirming the generic validity of the formalism developed in this article for current transients at various microelectrodes.

To further illustrate the relevance of the analytical formalism, consider the problem of maximum achievable spatial resolution by SECM. It is intuitively obvious that to maximize the spatial resolution, the SECM probe has to infinitesimally small. For such an ideal probe at a spacing \( W \) from the substrate (see Fig. 7a), the relative current density from a point at a distance \( r \) along the substrate is given by \( j(r) = (W^{2}/2\pi r^{2})(W^{2} + r^{2})^{-3/2} \) (obtained through a method of image analysis for \( C_{D,SS} \) of an ideal SECM probe above a planar substrate\(^{23} \)). Defining the spatial resolution, \( r_{s,\text{ideal}} \), as the region which provides a certain factor \( \alpha (0 < \alpha < 1) \) of the total current, we have \( r_{s,\text{ideal}} = W(1 - \alpha)^{-1}(2\alpha - \alpha^{2})^{-0.5} \).

For probes with finite size \( a_{0} \), the spatial resolution is \( r_{s,\text{finite}} = r_{s,\text{ideal}} + a_{0} \). Fig. 7c shows the variation of spatial resolution with SECM spacing for various \( a_{0} \). It is clear that even for ideal probes (\( a_{0} = 0 \)), the maximum achievable spatial resolution is directly proportional to \( W \). This analysis is particularly useful to determine the spacing required to “image” surface topology using SECM. To probe a surface with feature size \( L_{0} \) (see the inset of Fig. 7d for an illustration involving an interdigitated array electrode scheme) with \( \alpha = 0.5 \), we find that \( L_{0}/W = 2 \). As \( W \) is changed in different conditions from left to right, the current peaks reflect the surface topology and as predicted, at \( L_{0}/W = 2 \), the peaks and valleys in current can be distinguished.

### IV Conclusions

To summarize, we have developed a comprehensive analytical formalism to understand and predict the behavior of micro- and nanostructured electrodes under a wide variety of experimental conditions. The geometry of diffusion and electrodes along with the Butler–Volmer formalism for redox reactions occurring at electrode surfaces is uniquely captured in a closed-form, compact analytical expression. Our model indicates that the characteristics of any electrode geometry can be predicted using a single parameter, \( C_{D,SS} \), the diffusion equivalent capacitance. Through this approach, our analytical formalism anticipates diverse experiments like potentiostatic measurements, linear sweep voltammetry, redox detection of molecules, and SECM. Our methodology and results have interesting implications in the design and optimization of electrochemical systems using nanostructured electrodes like fuel cells, electrochemical batteries, dye sensitized solar cells, etc. While more accurate results can always be obtained for specific systems through detailed numerical simulation, this closed-form solution methodology has the potential to provide a simple yet powerful analysis that could anticipate key experimental trends and hence could assist in the design and optimization of new electrochemical systems.

### V Appendices

A **Electrostatic analogy for diffusion problems – concept of ‘diffusion equivalent capacitance’**

Eqn (3) represents the transient diffusion limited transport of redox species in the system. However, the time independent diffusion flux towards an electrode (dictated by \( D\nabla^{2}c = 0 \)) can easily be formulated from an analogy with Laplace’s equation of electrostatics (dictated by \( \varepsilon \nabla^{2}\Phi = 0 \), where \( \Phi \) is the potential, see ref. 21 for detailed discussions). Note that the diffusion current density \( -D\nabla c \) is analogous to the electric displacement vector \( -\varepsilon \nabla \Phi \) in electrostatic systems. Accordingly, the net diffusion flux towards an electrode is the analogue of the total electric charge (\( Q \)) in electrostatic systems. However, the total charge in electrostatic systems is expressed in terms of electrical capacitances as \( Q = C_{\text{elec}}(\Phi_{1} - \Phi_{2}) \), where \( (\Phi_{1} - \Phi_{2}) \) is the net potential difference between two conductors. The analogous net diffusion flux is given as \( I_{\text{tot}} = C_{D,SS}(\rho_{1} - \rho_{2}) \), where \( C_{D,SS} \) is known as the diffusion equivalent capacitance, and \( (\rho_{1} - \rho_{2}) \) is the net concentration difference. By analogy with electrostatic systems, note that \( C_{D,SS} \) has the same functional form of electrical capacitance except that the dielectric permittivity is replaced with diffusion coefficient. Note that, however, \( C_{D,SS} \) is not a capacitance and its units are different.

As the concept of ‘diffusion equivalent capacitance’ is not widely used in the electrochemistry literature, let us illustrate its general appeal of this formalism with a few simple examples. First, consider the steady state diffusion towards an infinitely long cylindrical electrode of radius \( a_{0} \). Let the concentration of R molecules be \( \rho_{R} \) at the electrode surface and \( \rho_{B} \) at a distance \( W \) from the electrode surface. Analytical solution of eqn (2) in cylindrical co-ordinates indicates that the total steady state diffusion flux (per unit length) is given by:

\[
I = q \frac{2\pi D_{0}}{\log \left( \frac{W + a_{0}}{a_{0}} \right)} (\rho_{B} - \rho_{R}).
\]

Eqn (11) under steady state conditions (i.e., with \( d/dt \to 0 \), the second term on the RHS of eqn (11) becomes zero) precisely predicts the same results when appropriate \( C_{D,SS} \) is used from Table 1. Similar analysis for spherical electrodes indicates that eqn (11) accurately predicts the current, although the concentration profile for R species varies as \( r^{-1} \), where \( r \) is the distance from the spherical electrode. More complex systems are explicitly considered in Section III. Note that, in this approach uses the wealth of information available in the electrostatics literature based on many decades of research and there is no need to solve the original mass transport equation. For those configurations whose electrostatic capacitance (and hence the functional form of diffusion equivalent capacitance, \( C_{D,SS} \)) is unknown, it can be computed for steady state conditions, with ideal Dirichlet boundary conditions. Again, this is a far simpler problem compared to the solution of the transient mass transport equation with Butler–Volmer kinetics as boundary conditions.

### B Derivation of eqn (12)

Eqn (11) represents the transient current at a microelectrode with a surface concentration \( \rho_{R} \) and bulk concentration at a distance \( W \) from the electrode. However, it is still not refined enough to use for electrochemical applications as both \( \rho_{R} \) and its time derivative are unknown.

We will now use a perturbation approach as follows: we first assume quasi-steady state conditions (which implies that the
time derivative \((d/dt)\) can be neglected) to derive a closed-form expression for \(\rho_{s,R}\). Under such quasi-steady state conditions, equating the total diffusion flux (first term on the RHS of eqn (11)) to reaction flux (eqn (6)), we obtain

\[
q_{C_{DSS}}(\rho_{W,R} - \rho_{s,R}) = A_g(k_f\rho_{s,R} - k_R\rho_{s,O}).
\]

(A1)

Application of eqn (6) for flux conservation leads to

\[
D_Rp_{s,R} + D_{OP}s_{s,O} = D_Rp_R.
\]

(A2)

Using eqn (A1) and (A2) and the boundary conditions \(\rho_{W,R} = \rho_{s,R}, \rho_{W,O} = 0\) (see Fig. 1d), we obtain the surface concentration of \(R\) as

\[
\rho_{s,R} = \rho_R \left( \frac{C_{DSS} + k_R D_R}{k_f + C_{DSS} + k_R D_R} \right).
\]

(A3)

Eqn (A3) represents the quasi-steady state surface concentration of the reduced species ‘R’ for a concentration profile shown in Fig. 1d. As the reaction proceeds, the use of such a boundary condition is not sufficient and the transient response is assumed to be significant. Based on the perturbation approach in ref. 23, the transient solution can be obtained by using the approximation \(W \sim (kD_H)^{\beta - 2}\), the diffusion distance. So we need to replace \(C_{DSS}\) in eqn (A3) by the appropriate \(C_{D(O)}\) as shown in Table 2 to obtain the time dependent surface concentration, as follows:

\[
\rho_{s,R(t)} = \rho_R \left( \frac{C_{D(O)} + k_R D_R}{k_f + C_{D(O)} + k_R D_R} \right).
\]

(A4)

Eqn (A4) is the time dependent surface concentration \(\rho_{s,R}\) obtained through a first order perturbation method. To estimate the transient current at an electrode, we require explicit solutions for both the time dependent \(\rho_{s,R}\) and its derivative (see eqn (11)). We could proceed further and use eqn (A4) to find the time derivative. However, the expressions for the time derivative so obtained are complex and not amenable to compact analytical formulations. So, as of now, we only replace \(\rho_{s,R}\) in the first term on the RHS of eqn (11) by the term given in eqn (A4) (also replace \(C_{DSS}\) on the RHS with \(C_{D(O)}\) with the assumption \(D_R = D_O = D\)). This completes the derivation of eqn (12).

C Derivation of eqn (15)

For a complete description of current transients at microelectrodes, we need to find an analytical expression for the second term on the RHS of eqn (14). Although the time evolution of \(\rho_{s,R}\) is predicted by eqn (A4) (with appropriate \(C_{D(O)}\) from Table 2), its time derivative is too complex for compact analytical evaluation. We realize that for those systems in which the time derivative is important (particularly LSV experiments with \(D_R = D_O\), see Section III.B., also supported by numerical simulation results), eqn (A3) indicates that

\[
\rho_{s,R} = \rho_R (1 + k_f/k_R)^{-1} = \rho_R (1 + e^{\beta(E_a - E_S)})^{-1},
\]

(A5)

where \(0 < \beta \leq 1\). For \(\beta = 1\), the above assumption is equivalent to the Nernst limit for the reaction \(R \leftrightarrow O + e\). Note that this approximation is made only to make the analytical expressions more tractable, and if necessary, better solutions can be obtained by using the time dependent form, eqn (A4). The time derivative of eqn (A5), with \(E_a = E_i + \nu t\), leads to eqn (16). Note that such transient effects are significant only for planar systems, as discussed in Section III.B.

D Numerical simulations

Eqn (3) for the reactants \(R\) and \(O\) is numerically solved implicitly using a finite difference scheme for the spatial domain and second order backward differentiation for time integration. At the electrode surfaces, eqn (6) is implemented as the boundary condition. The various simulation parameters used are (unless otherwise stated): \(D = 4.7 \times 10^{-6} \text{ cm}^{-2} \text{ s}^{-1}\), \(k_o = 0.2 \text{ cm s}^{-1}\), \(E_0 = 0.2 \text{ V}\), and \(\alpha = 0.5\). The accuracy of numerical simulations is evident from the comparison with similar results from the literature, as illustrated in Fig. 2–7.

Acknowledgements

The authors acknowledge computational and financial support from Network of Computational Nanotechnology (NCN), National Institute of Health (NIH; 2008-04984-03), and Materials Structures and Devices Center of the Semiconductor Research Center-Focus Center Research Program (MSD; 5710002706).

References