Extending and Automating Quantitative Microelectrode Voltammetry through an Oblate Spheroidal Coordinate Framework

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Abstract

Voltammetry is a ubiquitous electroanalytical method that can be used to help probe sustainable electrochemical technologies. When conducted with a microelectrode (radius ca. μm), voltammetry enables special interrogation of electrolyte solutions by minimizing distortions and enabling near-steady-state measurements, potentially unlocking in situ or operando analyses. Methodologies aimed to evaluate the behavior of redox-active species often leverage well-established, physically-grounded expressions that can be extended to examine electrolyte solutions under non-ideal conditions (e.g., signal convolution from multiple redox events) by simulating the entire voltammogram. Such models are typically framed in cylindrical coordinates, but leveraging oblate spheroidal coordinates can result in less cumbersome mathematical treatment. Here, we utilize this orthogonal coordinate system to develop and validate frameworks that can be used to derive closed-form steady-state—along with finite difference transient—microelectrode voltammogram models for single and sequential electron transfer mechanisms. We subsequently apply these steady-state models to estimate multiple features from simulated transient voltammograms and from nonaqueous electrolyte solutions containing N-[2-(methoxyethoxy)ethyl]phenothiazine, finding the framework is particularly adept at estimating the degree to which an electrolyte solution is charged (its “state-of-charge”) and remains intact (its “state-of-health”). Finally, we highlight potential extensions of this method towards advancing in situ or operando diagnostic methods.

Keywords: ultramicroelectrode voltammetry, modeling, simulation, diagnostics, feature estimation, state-of-charge, state-of-health
1. Introduction

Voltammetry is a foundational analytical method widely used to qualitatively and quantitatively characterize electrode processes in electrochemistry and electrochemical engineering.\textsuperscript{1–10} In most common applications, known physical relationships based on reaction-transport processes are used to discern key physical (thermodynamic, kinetic, and transport) properties of dissolved analytes at dilute concentrations.\textsuperscript{1,2,11} Knowledge of these descriptors can, in turn, offer insight into (electro)chemical phenomena under more complex conditions, such as the individual species concentrations in multi-component electrolytes and/or degradation rates of unstable intermediates.\textsuperscript{9,12} Accordingly, significant effort has been devoted to modeling voltammetric systems, and voltammograms in dilute electrolytes may be numerically, semi-analytically, and analytically simulated in an array of programming languages (e.g., C++, MATLAB\textsuperscript{®}) as well as in commercial or open-source software packages (e.g., COMSOL\textsuperscript{®}, EC-Lab\textsuperscript{®}).\textsuperscript{11,13–19}

Broadly, voltammetric methods polarize the working electrode to observe reactant fluxes that manifest as current, providing mechanistic insight into redox processes of interest.\textsuperscript{20–24} A key differentiating factor in this electrochemical response is the radius of the working electrode—macroelectrodes describe radii that are ca. 1–5 mm whereas microelectrodes describe radii that are ca. 5–50 μm. The smaller working microelectrode radius is shorter than the linear boundary layer thickness, meaning material can readily approach the electrode from the sides—or non-axial direction—to enable radial, diffusion-dominant steady-state concentration gradients and currents that are distinct from the linear and transient gradients engendered by larger electrodes.\textsuperscript{1,11} These different modes of mass transport can also be formulated using a process time scale argument; for macroelectrodes, the experiment duration (ca. 200 s) is shorter than the steady-state time scale (ca.
2000 s)—defined as the approximate time for the boundary layer to expand the length of one electrode radius—whereas the opposite is true for microelectrodes (steady-state time scale ca. 0.01 s). The smaller working electrode radius also presents unique opportunities for microelectrode voltammetry; for example, currents are on the order of nA, resulting in negligible ohmic (iR) potential distortions and small capacitive charging currents. Importantly, when a microelectrode is sufficiently polarized, the steady-state material fluxes to the electrode surface lead to separate oxidative and reductive steady-state current plateaus. These features make microelectrode voltammetry an especially powerful electroanalytical method provided environmental disturbances are minimized and undesired electrode processes (e.g., fouling) are controlled.

Prior studies have leveraged the limiting current behavior of microelectrode voltammetry, which can be analytically expressed for several electrode geometries (e.g., hemispherical and disk electrodes), to estimate concentrations of reacting species within an electrolyte solution. Although such approaches have considerable utility, there are circumstances where steady-state currents do not provide enough information to sufficiently evaluate voltammograms. For example, signal convolution from multiple redox-active species may frustrate such analyses, along with voltammograms that do not have fully developed plateau currents—specifically, voltammograms whose cutoff or turnaround potentials are close enough to the formal redox potential that no clear plateau is observed (e.g., to avoid electrode or electrolyte solution degradation at extreme potentials). More generally, by only considering plateau currents, the remainder of the voltammogram, which offers insights into reaction kinetics and thermodynamics, is ignored. Accordingly, analytical and numerical models have been developed to more completely describe microelectrode voltammograms, enabling the estimation of thermodynamic, kinetic, and transport descriptors.
While previously-developed reaction-transport models can accurately capture the electrochemical response of microelectrodes across the full range of potentials, they are often complex and cumbersome as compared to macroelectrode voltammetry models,\textsuperscript{1,11} which, in turn, limits their portability and utility within the broader experimental community. Thorough and rigorous mathematical analyses have been conducted for spherical microelectrodes, which can be readily modeled in a single spatial dimension;\textsuperscript{1,2} however, mathematical treatments of disk microelectrodes are not as widely described—perhaps because they require consideration of two spatial dimensions—even though such electrodes are more commonly used in experiments because of their relative ease of manufacturing and numerous commercial offerings.\textsuperscript{1,2} Disk microelectrode models often contemplate a single electron transfer half-reaction posed in cylindrical coordinates.\textsuperscript{11,27,28}

\[
R \rightleftharpoons O + e^-. \tag{1}
\]

In Equation (1), $R$ is the reduced species, $O$ is the oxidized species, and $e^-$ represents a single electron. Depending on the redox couple identity, the electron transfer can either be diffusively limited (“electrochemically reversible”), kinetically limited (“electrochemically irreversible”), or limited by both—“electrochemically quasireversible”. For an electrochemically reversible redox couple, the mass conservation relation (Equation (2)), along with the corresponding boundary conditions (Equations (3)–(7)), can be expressed as:

\[
\frac{\partial C_j}{\partial t} = D_j \nabla^2 C_j = D_j \left( \frac{\partial^2 C_j}{\partial r^2} + \frac{1}{r} \frac{\partial C_j}{\partial r} + \frac{\partial^2 C_j}{\partial z^2} \right) \tag{2}
\]

\[
C_j(r \to \infty, z) = C_j(r, z \to \infty) = C_{j,\infty} \tag{3}
\]

\[
\left. \left( \frac{\partial C_j}{\partial r} \right) \right|_{r=0} = 0 \tag{4}
\]
\[
\left( \frac{\partial C_R(r \leq r_e, z)}{\partial z} \right)_{z=0} + d_o \left( \frac{\partial C_o(r \leq r_e, z)}{\partial z} \right)_{z=0} = 0
\]  
(5)

\[
C_r(r \leq r_e, z) = C_o(r \leq r_e, z) \exp \left( -\frac{F\phi}{R_o T} \right)
\]  
(6)

\[
\left( \frac{\partial C_j(r > r_e, z)}{\partial z} \right)_{z=0} = 0
\]  
(7)

Equations (2)–(7) are expressed in cylindrical coordinates, where \( j (-) \) represents either species \( R, O \), or \( S \) (vide infra); \( C_j \) (mol m\(^{-3}\)) is the concentration of species \( j \); \( t \) (s) is the time; \( r \) (m) is the radial spatial coordinate and \( z \) (m) is the axial spatial coordinate; \( D_j \) (m\(^2\) s\(^{-1}\)) is the diffusion coefficient of species \( j \); \( C_j,\infty \) (mol m\(^{-3}\)) is the bulk / initial concentration of species \( j \); \( r_e \) (m) is the radius of the working electrode; \( d_j \) (–) is the ratio of diffusion coefficients \( D_j D_R^{-1} \); \( \phi = E - E_0 \) (V) is the overpotential, where \( E \) (V vs. a reference redox event) is the applied potential and \( E_0 \) (V vs. a reference redox event) is the formal redox potential of Equation (1); \( R_o \) (8.314 J mol\(^{-1}\) K\(^{-1}\)) is the universal gas constant; \( T \) (K) is the absolute temperature; and \( F \) (96485 C mol\(^{-1}\)) is the Faraday constant. Note that Equation (6) is an idealized representation of the Nernst equation; concentrations are used in the place of activities, and the formal redox potential is used in the place of the standard redox potential.

Mathematical treatment of Equations (2)–(7) can be challenging due to the piecewise boundary conditions in Equations (6) and (7) (illustrated in Figure 1a); the separate nature of the electrochemically active and electrochemically inactive surfaces leads to singularities at the perimeter of the electrode \( (r,z) = (r_e,0) \) which is inconvenient for analytical\(^{14}\) or numerical\(^{11}\) treatments. This issue may be avoided by shifting to a different orthogonal coordinate system. The
oblate spheroidal coordinate system parameterizes the $\xi (-)$ and $\eta (-)$ coordinates, which are converted to $r$ and $z$ coordinates via the following relationships.$^{29}$

$$z = r_c \xi \eta$$  \hspace{1cm} (8)

$$r = r_c \sqrt{(1+\xi^2)(1-\eta^2)}$$  \hspace{1cm} (9)

Oblate spheroidal coordinates are especially useful for disk-type microelectrodes, as the boundary conditions are no longer piecewise—simplifying mathematical treatment—as illustrated in Figure 1b.

**Figure 1.** Modeling domain of a microelectrode in (a) cylindrical coordinates, parameterized in $(r, z)$, and (b) oblate spheroidal coordinates, parameterized in $(\xi, \eta)$.

This coordinate transform was pioneered in the field of electrochemical engineering by Professor John Newman, whose early work provided an analytical solution for the potential field extending from a rotating disk electrode.$^{29}$ This approach has since been expanded to microelectrodes, unlocking analytical expressions for steady-state voltammograms of electrochemically reversible redox couples,$^{30}$ transient voltammograms can also be simulated using numerical methods$^{18,31}$ and analytical Laplace transforms.$^7$ Indeed, implementing the oblate
spheroidal coordinate system, in place of a cylindrical coordinate system, can often simplify electron transfer model derivations\textsuperscript{30,32} to improve the utility and portability of microelectrode voltammogram models. While steady-state and transient voltammetry models can solve the forward problem—that is, simulating a voltammogram given a set of parameters—they may also be used to solve the inverse problem (e.g., estimating a parameter set given a voltammogram), which, in turn, can be used to estimate the identities and concentrations of analytes in an electrolyte solution via automated algorithms.\textsuperscript{19} Closed-form expressions are readily adoptable for this purpose, as they can be computed nearly instantaneously and can be derived with relative ease using the oblate spheroidal coordinate framework. Though models that simulate transience are more difficult to employ for solving the inverse problem (i.e., longer simulation times), oblate spheroidal coordinates still overcome the singularity at the electrode perimeter and thus remain an attractive option for numerical methods.\textsuperscript{18,31,33}

Here, building on prior work, we present frameworks to derive closed-form expressions and numerical simulators using oblate spheroidal coordinates for multiple mechanisms of electron transfer when diffusion is the dominant mode of transport. We subsequently use the resulting steady-state expressions to estimate underlying parameters (e.g., formal redox potential, diffusion coefficients) and operational characteristics (e.g., the concentration of solution constituents) using least squares fitting. This methodology enables quantitative modeling and evaluation of electrolyte solution behavior under conditions with unknown and/or evolving analyte compositions, as might be expected within electrochemical technologies (e.g., rechargeable batteries). We first outline the general procedure used to derive analytical steady-state solutions for the current at a disk microelectrode using oblate spheroidal coordinates, which we validate against a previously-reported expression for a single electron transfer derived in cylindrical coordinates.\textsuperscript{28} We then use
this framework to derive a general steady-state expression for two sequential electron transfers to demonstrate its ability to model more complex electrode processes.\textsuperscript{5,21,24,34} Subsequently, we use oblate spheroidal coordinates to develop, code, and validate a numerical simulator capable of generating disk microelectrode voltammograms across conditions that cannot be accurately modeled using the steady-state approach. Finally, we regress the steady-state models to both numerically simulated and experimental voltammograms to assess the efficacy of estimating relevant parameters for an electrolyte solution containing redox-active compounds. By developing these modeling and regression frameworks, the diagnostic capabilities of microelectrode voltammetry may be expanded to characterize complex (e.g., multicomponent) electrolyte solutions accurately, in an automated fashion, and in near-real time.

2. Methods

2.1. Theoretical framework

2.1.1. Single electron transfer

We first present our derivation framework by evaluating an electrochemically reversible single electron transfer according to \textbf{Equation (1)} (i.e., \(R \rightleftharpoons O + e^-\)). The full transient system—including the conservation equation, boundary conditions, and initial conditions—encompassing \textbf{Equation (1)} can be expressed in \textbf{Equations (10)–(14)} using transformations previously discussed in literature.\textsuperscript{11,31}

\[
\begin{align*}
\frac{\partial c_j}{\partial \tau} &= r_i^2 d_j \left( \nabla^2 c_j \right) = \frac{d_j}{\left(\xi^2 + \eta^2\right)} \left[ \frac{\partial}{\partial \xi} \left[ \left(1 + \xi^2\right) \frac{\partial c_j}{\partial \xi} \right] + \frac{\partial}{\partial \eta} \left[ \left(1 - \eta^2\right) \frac{\partial c_j}{\partial \eta} \right] \right] \quad (10) \\
c_j(\xi, \eta, \tau = 0) &= c_j(\xi \rightarrow \infty, \eta, \tau) = c_{j,o} \quad (11)
\end{align*}
\]
\[
\frac{\partial c_R}{\partial \xi} \bigg|_{\xi=0} + d_o \frac{\partial c_O}{\partial \xi} \bigg|_{\xi=0} = 0
\]  
(12)

\[
\frac{\partial c_j}{\partial \eta} \bigg|_{\eta=0} = \frac{\partial c_j}{\partial \eta} |_{\eta=1} = 0
\]  
(13)

\[
c_R(\xi = 0, \eta, \tau) = c_O(\xi = 0, \eta, \tau) \exp \left(-\frac{F \varphi}{R \alpha T}\right)
\]  
(14)

In Equations (10)–(14), \( \tau = tD_p r_c^{-2} \) (–) is the dimensionless time; \( c_j \) (–) is the dimensionless concentration of species \( j \) normalized by \( C_{\text{total,0}} \) (mol m\(^{-3}\)), the total bulk concentration of all species—namely, \( C_{\text{total,0}} = C_{R,0} + C_{O,0} \) or \( C_{\text{total,0}} = C_{R,0} + C_{S,0} + C_{O,0} \) (vide infra)—and \( c_{j,0} \) (–) is the dimensionless bulk / initial concentration of species \( j \). The steady-state system of equations, with the same boundary conditions and no initial conditions, reduces to Equation (15).

\[
0 = \left\{ \frac{\partial}{\partial \xi} \left[ (1 + \xi^2) \frac{\partial c_j}{\partial \xi} \right] + \frac{\partial}{\partial \eta} \left[ (1 - \eta^2) \frac{\partial c_j}{\partial \eta} \right] \right\}
\]  
(15)

This equation may be analytically solved using a separation of variables approach, where \( c_j(\xi, \eta) = Q(\xi)P(\eta) \); \( Q(\xi) \) is only a function of \( \xi \), while \( P(\eta) \) is only a function of \( \eta \).

\[
\frac{d}{d\eta} \left[ (1 - \eta^2) \frac{d(P(\eta))}{d\eta} \right] + l(l+1)P(\eta) = 0
\]  
(16)

\[
\frac{d}{d\xi} \left[ (1 + \xi^2) \frac{d(Q(\xi))}{d\xi} \right] - l(l+1)Q(\xi) = 0
\]  
(17)

In Equations (16) and (17), \( l \) is a variable that is typically a whole number (i.e., \( l = 0, 1, 2, \ldots \)) whose value is dictated by the boundary conditions. Equation (16) is Legendre’s equation. For the no-flux boundary conditions to hold at \( \eta = 0 \) and \( \eta = 1 \), \( l \) must be zero; consequently, the
solution for \textbf{Equation (16)} is $P(\eta) = 1$. It must also hold true that $l = 0$ for \textbf{Equation (17)}; this leads to the general solution of $Q(\xi) = a_1 \tan^{-1}(\xi) + a_2$, where $a_1$ and $a_2$ are generic constants of integration. As such, the general solution to \textbf{Equation (15)} is expressed in \textbf{Equation (18)}.

$$
c_r(\xi, \eta) = b_1 \tan^{-1}(\xi) + b_2 \\
c_o(\xi, \eta) = b_3 \tan^{-1}(\xi) + b_4
$$

\textbf{(18)}

The relevant boundary conditions can be applied to solve for the constants of integration $b_i$, $i \in \{1, 2, 3, 4\}$. The resulting expression, in turn, can be differentiated and incorporated into the general expression for the steady-state current (\textbf{Equation (19)}) to solve for the current of an electrochemically reversible single electron transfer (\textbf{Equation (20)}).

$$
I(\varphi) = -2\pi F D_o C_{\text{total,} \infty} r e \frac{d c_o}{d \xi}(\varphi) \bigg|_{\xi = 0}
$$

\textbf{(19)}

$$
I(\varphi) = 4F D_o C_{\text{total,} \infty} r e \left( \frac{f_R \exp \left( \frac{F \varphi}{R_o T} \right) - f_o}{1 + d_o \exp \left( \frac{F \varphi}{R_o T} \right)} \right)
$$

\textbf{(20)}

In \textbf{Equation (20)}, $I$ (A) is the current and $f_j$ (–) is the fraction of species $j$ in the bulk. Note that in this work, oxidative and reductive processes are defined to have positive and negative currents, respectively. Also note that $f_R$ and $f_o$ are constrained according to \textbf{Equations (21)} and (22):

$$
f_R + f_o = 1
$$

\textbf{(21)}

$$
f_o = \frac{C_{O, \infty}}{C_{\text{total,} \infty}}
$$

\textbf{(22)}
**Equation (20)** is the analytical steady-state solution used to evaluate the correctness of the overall modeling approach for a single electron transfer. We note that an analogous expression can be derived for electrochemically quasireversible electron transfers, but this equation is inexact\(^\text{27}\) and as such will not be discussed in greater detail herein.

2.1.2. Sequential electron transfers

The same general approach can be invoked to solve for a sequential electron transfer mechanism, expressed in **Equation (23).**

\[
R \rightleftharpoons S + e^- \rightleftharpoons O + e^-
\]  

(23)

Where \( S \) refers to the semi-oxidized (or semi-reduced) species. Note that only two sequential, electrochemically reversible electron transfers are considered. The bulk composition is assumed to be at equilibrium—that is, comproportionation / disproportionation occurs much more quickly (ca. 5-50 μs)\(^\text{35}\) than the heterogeneous electrode reaction (ca. 0.01-100 s).\(^\text{1}\) The boundary conditions, in turn, are analogous to those posed for the single electron transfer; specifically, **Equations (10), (11), and (13)** remain the same. **Equation (12)** is modified as follows to enforce net zero species flux:

\[
\frac{\partial c_R}{\partial \xi} \bigg|_{\xi=0} + d_s \frac{\partial c_S}{\partial \xi} \bigg|_{\xi=0} + d_o \frac{\partial c_O}{\partial \xi} \bigg|_{\xi=0} = 0
\]  

(24)

Further, **Equation (14)** is expanded to account for the two Nernstian conditions present in the three-component system.

\[
c_R(\xi = 0, \eta, \tau) = c_S(\xi = 0, \eta, \tau) \exp \left( \frac{-F\varphi_1}{R\alpha T} \right)
\]  

(25)
\[ c_s(\xi = 0, \eta, \tau) = c_0(\xi = 0, \eta, \tau) \exp \left( -\frac{F\varphi_2}{R_T} \right) \]  

(26)

Where \( \varphi_1 \) (V) is the overpotential for the electron transfer \( R \rightleftharpoons S + e^- \); \( \varphi_1 = E - E_{0,1} \), where \( E_{0,1} \) (V vs. a reference redox event) is the corresponding formal redox potential. \( \varphi_2 = E - E_{0,2} \) (V) is the analog for the electron transfer \( S \rightleftharpoons O + e^- \), where \( E_{0,2} \) (V vs. a reference redox event) is the formal redox potential for the second electron transfer. The general steady-state concentration profiles are analogous to Equation (18).

\[
\begin{align*}
    c_1(\xi, \eta) &= b_1 \tan^{-1}(\xi) + b_2 \\
    c_2(\xi, \eta) &= b_3 \tan^{-1}(\xi) + b_4 \\
    c_3(\xi, \eta) &= b_5 \tan^{-1}(\xi) + b_6
\end{align*}
\]  

(27)

The unknown constants can be found by formulating and solving a linear system of equations using the boundary conditions and substituted into the expression for the total current (Equation (28)), resulting in an expression for the current for two sequential electrochemically reversible electron transfers (Equation (29)).

\[
I(\varphi_1, \varphi_2) = I_1(\varphi_1) + I_2(\varphi_2) = 2\pi F D_R C_{\text{total,=}e} \left( \frac{\partial c_1}{\partial \xi}(\varphi_1) \right)_{\xi=0} - d_o \left( \frac{\partial c_2}{\partial \xi}(\varphi_2) \right)_{\xi=0}
\]  

(28)

\[
I(\varphi_1, \varphi_2) = \frac{4F D_R C_{\text{total,=}e}}{1 + d_s \exp \left( \frac{F \varphi_1}{R_T} \right) + d_o \exp \left( \frac{F (\varphi_1 + \varphi_2)}{R_T} \right)} \]

\[
\left\{ f_s \left[ d_s \exp \left( \frac{F \varphi_1}{R_T} \right) + 2d_o \exp \left( \frac{F (\varphi_1 + \varphi_2)}{R_T} \right) \right] + f_s \left[ d_s \exp \left( \frac{F (\varphi_1 + \varphi_2)}{R_T} \right) - 1 \right] + f_o \left[ -d_o \left( 2 + d_s \exp \left( \frac{F \varphi_1}{R_T} \right) \right) \right] \right\}
\]  

(29)

In Equation (28), \( I_1 \) (A) is the current generated by the reaction \( R \rightleftharpoons S + e^- \), while \( I_2 \) (A) is the current generated by the reaction \( S \rightleftharpoons O + e^- \). We note that for the sequential electron
transfer mechanism, $f_R$, $f_S$, and $f_O$ are related not only by the constraints that all fractions must sum to unity and by the amount of positive charge stored in this redox couple (respectively shown via Equations (21) and (22) for a single electron transfer) but also by the equilibrium arising from rapid comproportionation / disproportionation. As a result, the constraints on the three fractions are described in Equations (30)–(32), resulting in a unique set of species fractions given a particular degree of system oxidation, along with both formal redox potentials.

$$f_R + f_S + f_O = 1 \quad (30)$$

$$\frac{f_S + 2f_O}{2} = \frac{C_{S,\infty} + 2C_{O,\infty}}{2C_{\text{total},\infty}} \quad (31)$$

$$\frac{f_S^2}{f_R f_O} = \exp \left( \frac{F (E_{0,2} - E_{0,1})}{R_G T} \right) \quad (32)$$

2.2. Computational methods

Most simulations were run on MATLAB® R2020a using an Intel® Core™ i7-7500U CPU @ 2.70 GHz 2.90 GHz (16 GB RAM) laptop computer. The generation of synthetic data for evaluating the accuracy of parameters (vide infra) was performed on MATLAB® R2019b using an Intel® Xeon® CPU E5-2687W 0 @ 3.10 GHz 3.10 GHz (128 GB RAM) workstation computer. The closed-form expressions were evaluated almost instantaneously—on average ca. 1 ms for a single electron transfer and on average < 40 ms for sequential electron transfers. Further, our model validations are summarized using a checklist recently developed for theoretical battery studies (Table S3).³⁶

Our in-house numerical scheme integrates the approaches of Compton, Laborda, and Ward¹¹, Myland and Oldham¹⁸, and Qian et al.³¹ by using an alternating direction implicit finite-difference
simulator in oblate spheroidal coordinates to track all species concentrations. The algorithm simulates an electrochemically reversible single electron transfer using Equations (10)–(14) and models an electrochemically quasireversible single electron transfer using the Butler-Volmer formulation, in which Equation (14) is replaced with Equation (33).

\[
\left. \frac{\partial c_{\xi}}{\partial \xi} \right|_{\xi=0} = K_0 \eta \left( c_o (\xi = 0, \eta) \exp \left( \frac{-\alpha_c F \varphi}{R_g T} \right) - c_r (\xi = 0, \eta) \exp \left( \frac{(1-\alpha_c) F \varphi}{R_g T} \right) \right) \tag{33}
\]

In Equation (33), \( K_0 = k_0 r_e D_0^{-1} \) (–) is the dimensionless heterogeneous rate constant—\( k_0 \) (m s\(^{-1}\)) is the dimensional analog—and \( \alpha_c \) (–), set to 0.5, is the cathodic transfer coefficient. Electrochemically reversible sequential electron transfers are simulated using Equations (10), (11), (13), (24), (25), and (26). When two sequential electrochemically quasireversible electron transfers are simulated, Equations (25) and (26) are replaced with Equations (34) and (35).

\[
\left. \frac{\partial c_{\xi}}{\partial \xi} \right|_{\xi=0} = K_{0,1} \eta \left( c_s (\xi = 0, \eta) \exp \left( \frac{-\alpha_{c,1} F \varphi_1}{R_g T} \right) - c_r (\xi = 0, \eta) \exp \left( \frac{(1-\alpha_{c,1}) F \varphi_1}{R_g T} \right) \right) \tag{34}
\]

\[
\left. \frac{\partial c_{\xi}}{\partial \xi} \right|_{\xi=0} = K_{0,2} \eta \left( c_o (\xi = 0, \eta) \exp \left( \frac{-\alpha_{c,2} F \varphi_2}{R_g T} \right) - c_s (\xi = 0, \eta) \exp \left( \frac{(1-\alpha_{c,2}) F \varphi_2}{R_g T} \right) \right) \tag{35}
\]

In Equations (34) and (35), \( K_{0,q} \) and \( \alpha_{c,q} \) (\( q = 1, 2 \)) represent the dimensionless heterogeneous rate constant and cathodic transfer coefficient for the \( q \)th electron transfer, respectively. The reported current for both electrode processes is evaluated in a similar manner to Equations (19) and (28), except the concentration gradient must be numerically integrated (using a trapezoidal approximation) across the \( \eta \in [0,1] \) domain, since the surface species concentration may not necessarily be uniform. We implement parallelization using MATLAB’s “parfor” command, and minimization was performed using “fmincon”, MATLAB’s minimization routine that accounts
for constraints (e.g., by enforcing lower and upper values to bound an estimated descriptor). The numerical simulations with 2000 time steps were evaluated in ca. 400 s on the laptop computer; further details on—and explicit mathematic formulations of—the finite difference framework can be found in the Supplementary Information (SI).

COMSOL® Multiphysics (version 5.6) was used to assess the fidelity of the in-house finite difference simulator. All COMSOL® programs were executed on the previously-mentioned laptop computer, and mesh information used to discretize and solve the electrochemical model is included in the SI. The electrochemical model utilized by COMSOL® evaluates a single electron transfer (Equation (1)) using Equations (36)–(38). For transparency, we list the equations used by COMSOL®—as reported in the program itself and within supporting documentation; we also note similarities between the COMSOL® and in-house formulations.37,38

$$\frac{\partial C_i}{\partial t} + \nabla \cdot J_i = R_i$$  \hspace{1cm} (36)

$$J_i = -D_i \nabla C_i$$ \hspace{1cm} (37)

$$\phi_i = 0$$ \hspace{1cm} (38)

In Equations (36)–(38), the vector $J_i$ (mol m$^{-2}$ s$^{-1}$) is the flux of species $i$, $R_i$ (mol m$^{-3}$ s$^{-1}$)—here, set to 0—is the volumetric reaction rate, and $\phi_i$ (V) is the electrolyte potential or ohmic drop.38 This set of equations is represented by Equation (2) in the in-house model.

The boundary conditions are as follows: a no-flux boundary condition (Equation (39)) is applied as a semi-infinite boundary condition far from the electrode; axial symmetry (i.e., no flux) is applied to the $r = 0$ axis and on the insulating surface surrounding the electrode; charged species flux is equated to the current passed (Equation (40)); and an electroanalytical Butler-Volmer expression (Equation (41)) with a cathodic transfer coefficient, also set to 0.5, is
leveraged, which in turn was integrated across the microelectrode surface in Equation (42). Only reduced species is initially present.

\[-\mathbf{n} \cdot (\mathbf{J}_i + \mathbf{u}C_i) = 0\]  

(39)

\[-\mathbf{n} \cdot \mathbf{J}_i = \frac{\nu_i i_{\text{curr}}}{n_e F}\]  

(40)

\[i_{\text{curr}} = n_e F k_0 \left(C_{R,S'} \exp \left(\frac{(n_e - \alpha_c) F \varphi}{R_G T}\right) - C_{O,S} \exp \left(-\alpha_e F \varphi\right)\right)\]  

(41)

\[I = \int_{S'} i_{\text{curr}} dA\]  

(42)

In Equations (39)–(42), \(\mathbf{n}\) indicates the normal vector in the radial or axial direction, \(\mathbf{u}\) (m s\(^{-1}\)) is the velocity vector (here, 0), \(\nu_i\) (-) is the stoichiometric coefficient implicitly present in the redox reaction within Equation (1) (respectively 1 and \(-1\) for \(R\) and \(O\) within the COMSOL® module), \(n_e\) (-) is the number of electrons transferred (here, 1), \(i_{\text{curr}}\) (A m\(^{-2}\)) is the current density equal to the flux of charge to the electrode surface (represented by \(S'\)), \(C_{j,S'}\) (mol m\(^{-3}\)) is the concentration of species \(j\) on \(S'\), \(dA\) is a generic areal element (m\(^2\)), and \(T\) is the absolute temperature (here, 298.15 K); Equations (39)–(42) are analogous to Equations (7), (19), (33). Two boundary probes were applied to calculate the total current (A) and electric potential (V) across the microelectrode radius, and the simulated technique was cyclic voltammetry. As shown in Table S1, a parametric sweep was conducted across nine values of \(k_0\) for both the COMSOL® and in-house algorithms. Each simulation, in turn, involved \(ca. 200–250\) time steps and took \(\leq 35\) s, meaning the entire parametric sweep took \(\leq 10\) min; nine simulations were conducted per sweep. Further details are described in the SI.
2.3. Experimental methods and procedure

All chemicals were used as received, and all experiments were conducted in a glovebox (MBraun Labmaster, H₂O < 5 ppm, O₂ < 1 ppm) filled with argon (Airgas, purity of ca. 100 %, catalog number AR UHP300). The glovebox temperature was ca. 27 °C. All the materials were opened and stored in the glovebox and were directly transferred from their container to a 5 mL volumetric flask with a plastic spatula to ensure the mass of material in the solution matched the balance reading (Mettler Toledo, Balance XS64, 61 g capacity with ± 0.1 mg readability). Every solution studied contained between 5–25 mM of either ferrocene (Sigma Aldrich, 98 %, F408), N-[2-(2-methoxyethoxy)ethyl]phenothiazine (MEEPT, Tokyo Chemical Industry Co., M3068, > 98.0 %), and / or MEEPT–tetrafluoroborate (MEEPT–BF₄) — synthesized and purified as previously described³⁹,⁴⁰—along with 0.5 M tetraethylammonium tetrafluoroborate (TEABF₄, Gotion, > 99.9 %) in acetonitrile (Sigma-Aldrich®, 34851, ≥ 99.9 %). Ferrocene was also used as an internal standard for the reference electrode⁴¹ in a separate solution (also containing 0.5 M TEABF₄ in acetonitrile) at a concentration of ca. 8 mM. The working electrode was a gold disk microelectrode (Bioanalytical Systems, Inc. (BASi), 10 µm nominal dia., MF-2006)—referred to as the “microelectrode”—or a glassy carbon disk electrode (CH Instruments, 3 mm dia., CHI104)—referred to as the “macroelectrode”. Both were polished with 0.05 µm alumina powder (Buehler MicroPolish Powder, 4010075) in deionized water (Millipore, 18.2 MΩ cm) and dried with compressed air. Neither lens paper nor sonication was utilized in the polishing process. After polishing, care was taken to ensure the prepared electrode surfaces did not contact any materials aside from air (and in the glovebox, Ar) prior to immersion in the solution of interest. A Ag/Ag⁺ electrode was prepared using a non-aqueous reference electrode kit (BASi, MF-2062) filled with 10 mM silver tetrafluoroborate (AgBF₄, Aldrich®, ≥ 99.99 %, 483052) in a solution of 0.5 M
TEABF₄ and acetonitrile. The counter electrode was a platinum (Pt) coil electrode (BASi, 99.95 %, MW-1033). When not in use, the Ag/Ag⁺ reference electrode was stored in the glovebox in a fill solution of the same composition.

Two voltammetry techniques were employed: cyclic voltammetry (CV) and cyclic square wave (CSW) voltammetry. CV was performed using both the microelectrode and macroelectrode, whereas CSW voltammetry was only performed with the macroelectrode. Generally, macroelectrode voltammograms were evaluated to estimate the true values of the parameters during experimental validation of the models (vide infra) and to verify the microelectrode radius—further details are found in the SI. All microelectrode studies were conducted using a CHI630E potentiostat (CH Instruments, Inc.) and processed using software provided by the same company (“CHI630E Electrochemical Analyzer”). All macroelectrode experiments were conducted using a VSP potentiostat (BioLogic) with EC-Lab® software; all data was processed with Microsoft Excel and MATLAB® R2020a. The potential range for all MEEPT experiments was from −0.3 V to 0.75 V vs. the Ag/Ag⁺ reference redox event, while the range for ferrocene studies was from −0.3 V to 0.4 V vs. the Ag/Ag⁺ reference redox event. Specifically, the most negative and initial potential was set to be ca. 300 mV lower than the formal redox potential of ferrocene, while the most positive (and the turnaround) potential of the voltammetric experiment was set to be ca. 200–300 mV higher than the formal redox potential of MEEPT or ferrocene to minimally influence the voltammogram shape¹ while avoiding solution or electrode decomposition that may occur at extreme potentials.²⁵

Microelectrode voltammograms were acquired at a scan rate of 10 mV s⁻¹, with a rest time of 2 s before acquisition, a potential resolution of 1 mV, a sensitivity of 1 × 10⁻⁸ A V⁻¹, and the same potential bounds as those collected for the macroelectrode studies. Nine microelectrode
voltammograms were acquired for electrolyte solutions containing MEEPT for statistical rigor, while only six were obtained for electrolyte solutions containing ferrocene to enable statistical rigor while minimizing possible electrode fouling.\textsuperscript{42,43}

Macroelectrode cyclic voltammograms were obtained at 10, 25, 50, 100, 200, and 500 mV s\textsuperscript{–1}, with all voltammograms corrected for resistance-driven potential distortions using “iR determination with electrochemical impedance spectroscopy” (the “ZIR” protocol);\textsuperscript{44} the working electrode potential was set to its open-circuit value, a delay of 10 % of the period duration was added before the measurement, a sinusoidal potential with a 20 mV amplitude and a 100 kHz frequency was applied, and the reported resistance was averaged over four measurements. The resistance was compensated 85 % by the software during the experiment; the remaining 15 % was not corrected post experiment, as macroelectrode cyclic voltammograms were solely used to estimate the diffusion coefficients of reduced and oxidized MEEPT, a process that only utilizes the peak current (via Randles-Ševčík analysis). We note the baseline currents should not be appreciably distorted, as the potential of the uncompensated peak was at least ca. 300 mV from the turnaround potential in all cases. We also note that the solution resistance was not fully compensated during acquisition to avoid possible oscillations in the potentiostat.\textsuperscript{44} After each cyclic voltammogram was obtained, the electrolyte solution was manually swirled or agitated to allow the boundary layer to reset.

CSW voltammograms were obtained using the same potential bounds as those in the cyclic voltammograms. The pulse duration (per half-period) was 100 ms, the step height was 10 mV, and the pulse height was 50 mV, resulting in an effective scan rate of 50 mV s\textsuperscript{–1}. The potential was held at the initial, most negative (reductive) potential for 2 s before the initial positive (oxidizing) sweep, and the reported current for each potential step was determined by averaging the raw
current over the last 30% of the step. At least six CSW voltammograms were obtained at these same conditions for all solutions tested. The “ZIR” protocol was performed the same way as with CV; further, the electrolyte solution was manually swirled or agitated to allow the boundary layer to reset.

To calibrate the applied potential to that of the ferrocene redox event and to estimate the radius of the microelectrode, a separate electrolyte solution of ferrocene was used to avoid signal convolution from either MEEPT or MEEPT–BF₄. To enable rapid transfer of the three-electrode configuration between electrolyte solutions, a separate vial containing only acetonitrile (no analyte or supporting salt) was used to rinse the electrodes. More specifically, after removing the electrodes from MEEPT- or MEEPT–BF₄-containing electrolyte solutions, they were gently dried with Kimwipes—avoiding direct contact with the working electrode surface—and then transferred to the solvent-containing vial. After residing and being intermittently swirled in the solution for 10–20 s, the electrodes were again removed, gently dried with Kimwipes, and inserted into the ferrocene-containing electrolyte solution. Though somewhat labor-intensive, this approach reduces the potential for cross-contamination, as illustrated in the SI.

3. Results and discussion

3.1. Analysis of the steady-state electrochemically reversible case

Exact closed-form expressions are powerful tools for steady-state modeling and can also serve as a sufficient proxy for transient behavior closely resembling the steady-state (vide infra). The rapidity with which closed-form expressions can be computed make these models especially useful for parameter estimation routines. In particular, the analytical equations, **Equations (20)** and (29), if validated, can be used to interpret the behavior of microelectrode voltammograms. We find the
expression obtained for a steady-state electrochemically reversible electron transfer (i.e., Nernstian, Equation (20)) aligns with the expression previously derived from cylindrical coordinates. Though we have not been able to find a derivation of Equation (29) in the peer-reviewed literature, the mathematic treatment is identical to that of Equation (20) until the evaluation of the integration constants, suggesting that the validation of the single electron transfer model strongly supports the sequential model expression. To illustrate the versatility of these general models, the expressions from Equations (20) and (29) are plotted in Figure 2 at various degrees of system oxidation—referred to as the state-of-charge (SOC)—and, for the sequential electron transfer mechanism, various gaps in the formal redox potential of each electron-transfer event (denoted as \( \Delta E_0 = E_{0,2} - E_{0,1} \) (V)). Overall, Figure 2 illustrates that closed-form expressions that describe the electrochemical response of a microelectrode can enable near instantaneous simulation of different electrode processes across a wide range of conditions, in turn demonstrating its potential ability to model diverse electrode processes that may occur within electrolyte solutions.
Figure 2. Plots of steady-state microelectrode voltammograms simulated using closed-form expressions for (a) an electrochemically reversible single electron transfer at various SOCs and (b) electrochemically reversible sequential electron transfers at various formal electrode potential gaps ($\Delta E = E_{0.2} - E_{0.1}$) and SOCs. The average formal electrode potential $E_{\text{avg}} = 0.5(E_{0.1} + E_{0.2})$ was 0 V vs. an arbitrary reference, the total concentration was 1 mM, and the diffusion coefficients for all species were set to $1 \times 10^{-9}$ m$^2$ s$^{-1}$, the working electrode radius is 5 μm, and the temperature is 298.15 K. SOCs and formal redox potential gaps (the latter only applicable for (b)) are shown on the color bars on the right. The exact SOCs are (descending the color bar) 0, 0.25, 0.5, 0.75, and 1, while the exact formal electrode potential gaps are (again, descending) 0, 150, 300, 450, and 600 mV. Note that, by convention, a SOC of zero means that only the reduced species is present in the bulk. As shown in (a), all positive currents are oxidative (anodic), and negative currents are reductive (cathodic).

3.2. Numerical simulation of transient voltammograms via oblate spheroidal coordinates

While closed-form expressions for steady-state voltammograms are generally useful for electroanalysis, certain scientifically relevant scenarios (e.g., transience, kinetically-limited electron transfers) cannot be accurately captured, necessitating alternative simulation approaches. By introducing transience, the mass conservation equation becomes dependent on three variables (two spatial and one temporal)—as shown in **Equation (10)**—resulting in a more mathematically complex equation that, to our knowledge, has yet to be reduced to a closed-form solution (though accurate empirical approximations have been formulated).\(^1\) As such, **Equation (10)** must be solved numerically, though the transformation from cylindrical coordinates to oblate spheroidal
coordinates still simplifies model construction, since the boundary conditions remain homogeneous with no singularities. Accordingly, we opt to generate an alternating direction implicit finite-difference numerical simulator to model transient voltammograms under a range of conditions, exemplified in Figure 3a, and to validate the analytical steady-state findings by simulating transient voltammograms at slow scan rates (vide infra).

To validate the numerical simulator constructed using oblate spheroidal coordinates, microelectrode voltammograms were generated in COMSOL® using the procedure outlined in Section 2.2. Specifically, the COMSOL® simulations were run at nine different heterogeneous rate constants—ranging from \(1 \times 10^{-6}\) to \(1 \times 10^{-2}\) m s\(^{-1}\)—to explore various degrees of electrochemical reversibility, from nearly irreversible to nearly reversible.\(^{26}\) These results were directly compared to the results from the in-house simulator modeled using the same set of parameters, visualized in Figure 3b.
Figure 3. Transient voltammograms simulated with a finite difference numerical simulator. (a) Electrochemically reversible sequential electron transfers simulated at various scan rates, demonstrating the ability of the numerical simulator to model relevant yet complex redox mechanisms under transient conditions. (b) Validation of the numerical simulator. Butler-Volmer single electron transfers were simulated at a scan rate of 10 mV s\(^{-1}\) with increasing heterogeneous rate constant (\(k_0\)) values from \(1 \times 10^{-6}\) – \(1 \times 10^{-2}\) m s\(^{-1}\). Exact values of \(k_0\), descending the color bar, are \(1 \times 10^{-0.5g}\) m s\(^{-1}\), \(g \in \{4, 5, \ldots, 11, 12\}\). In all cases, the formal redox potential is 0 V vs. an arbitrary reference, only the reduced species is in the bulk at a concentration of 1 mM, the working electrode radius is 5 μm, the diffusion coefficients of the oxidized and reduced species are both \(1 \times 10^{-9}\) m\(^2\) s\(^{-1}\), and the temperature is 298.15 K. Note the color bar only applies to panel (b). As shown in (a), all positive currents are oxidative (anodic), negative currents are reductive (cathodic), and the horizontal arrow indicates the initial sweep direction is oxidative.

The COMSOL\textsuperscript{®} and in-house numerical simulation results are well-aligned, validating the in-house numerical simulator as an analytical tool—indeed, the maximum difference between the in-house and COMSOL\textsuperscript{®}-simulated plateau currents at the (oxidative) turnaround potential is less than 1 %. We note that it is challenging to further evaluate the numerical values of the errors, as the number of time steps the in-house simulator uses (2000) exceeds that of the COMSOL\textsuperscript{®} simulations (ca. 200-250), stymying direct comparison without interpolation. The in-house MATLAB\textsuperscript{®} numerical model is used for the remainder of this work; since the closed form expressions are also modeled in MATLAB\textsuperscript{®}, direct comparisons can be made between the two. Separately, simulators coded from scratch have some advantages; routines built upon physical
relationships can be written in open-source languages (e.g., Python) to increase accessibility and can offer greater versatility for probing uncommon or novel mechanisms not easily integrated into commercial software packages. In other instances, COMSOL® may be the preferred option, such as when simulation speed is important (i.e., ca. 35 s for a COMSOL® simulation compared to ca. 400 s for an in-house finite-difference simulation).

3.3. Detailed analysis of steady-state expressions via numerical simulations

The fast computation times for solving analytical expressions can enable rapid parameter estimation procedures for purposes such as predicting the identities and concentrations of analytes in electrolyte solutions. Our approach to evaluate the efficacy of our single and sequential electron transfer models is inspired by a previous automated approach that evaluates electrochemical kinetics (an exercise beyond the scope of this work) using the Marquardt algorithm, in turn motivated by the works of Oldham and Zoski and of Mirkin and Bard.\textsuperscript{45-47} Specifically, we evaluated the accuracy of two parameter sets. One set is denoted as the “fundamental” set, which consists of the electrochemical and transport descriptors; for the single electron transfer model, $E_0$, $D_R$, and $D_O$ were estimated, whereas for the sequential electron transfer model, $E_{0,1}$, $E_{0,2}$, $D_R$, $D_S$, and $D_O$ were estimated. This scenario is intended to represent a typical evaluation of a novel analyte, where the input concentration is known from electrolyte solution preparation but other parameters, such as the formal redox potential and diffusion coefficients, are unknown.

The second parameter set is denoted as the “operational” set, where $E_0$, the SOC, and the state-of-health (SOH)—the latter two often used to characterize electrochemical energy storage systems—were estimated. As mentioned in Section 3.1, the SOC represents the degree of system oxidation—\textbf{Equation (43)} for a single electron transfer and \textbf{Equation (44)} for two sequential
electron transfers, respectively—while the SOH here represents the ratio of the total concentration to the maximum concentration $C_{total,\infty}^{\text{max}}$ (mol m$^{-3}$) within this particular study (Equation (45)). $E_0$ was estimated because the thermodynamic formal electrode potential is a function of SOC via the Nernst equation (Equations (14) and (25)).

$$\text{SOC} = f_o$$

$$\text{SOC} = \frac{f_s + 2f_o}{2}$$

$$\text{SOH} = \frac{C_{total,\infty}}{C_{total,\infty}^{\text{max}}}$$

This scenario, in turn, reflects situations where fundamental descriptors are already known, perhaps from prior experiments, but the current state of the electrolyte solution (e.g., SOC and SOH) is not, as may be the case within an operating device.

Our procedure uses least squares regression according to Equation (46).

$$\theta_{\text{best}} = \arg\min_{\theta} \left( \left\| I_{\text{obs}} - I(\theta) \right\|_2^2 \right)$$

In Equation (46), $\Theta$ (multiple units) is a vector of unknown descriptors to be estimated. For example, $\Theta$ could be a vector of electrochemical and transport descriptors (specifically, $E_0$, $D_R$, and $D_O$) or operational characteristics such as the SOC or SOH. $I_{\text{obs}}$ (A) is the vector of measured currents (either experimentally or numerically generated) of the entire voltammogram, $I(\theta)$ (A) is the vector of modeled currents of the entire voltammogram, and $\theta_{\text{best}}$ (multiple units) is the set of descriptors that minimizes the 2-norm of the errors ($\left\| I_{\text{obs}} - I(\theta) \right\|_2$). By treating the input parameters for the numerical simulator as ground truth, the predicted parameters ($\theta_{\text{best}}$) can be
compared with the known values to provide a representative estimate of how well the analytical expressions may predict relevant descriptors.

The in-house numerical simulator can be used to assess the accuracy of steady-state models, as transient voltammograms can be readily simulated at various known parameter sets while capturing the partially-transient nature of experimental data.\textsuperscript{47} As such, the predictive ability of both the reversible single electron and sequential electron transfer models was evaluated by numerically simulating multiple voltammograms at a scan rate of 10 mV s\textsuperscript{-1}, a typical scan rate used in experimental microelectrode studies. Parameter sweeps were performed where one parameter was varied at a time (others were held constant), and the error in the resulting estimates were evaluated; the chosen values reflect commonly-observed conditions encountered in electrochemical studies.\textsuperscript{9,21,48,49} For the single electron model, $d_O$, SOC, and SOH were varied across 11 equally-spaced values; $d_O$ ranged between 0.5 and 2, the SOC ranged between 0 and 1, and the SOH varied between 1/11 to 1. For the sequential electron model, these same three parameters, along with $\Delta E_0$ and $d_s$, were varied across 11 equally-spaced values; the ranges for $d_O$, SOC, and SOH were unchanged, $\Delta E_0$ ranged between 0 and 0.4 V, and $d_s$ ranged between 0.5 and 2. Parameter sweeps for each model took < 3 h on the aforementioned workstation computational resource.

The objective function in \textbf{Equation (46)} was minimized to estimate $\theta_{\text{best}}$. In this scenario, $I_{\text{obs}}$ is generated by the numerical simulations \textit{a priori}, and $I(\theta)$ is the steady-state model parameterized by $\theta$. In addition, the initial guess for the formal electrode potential was varied across seven values—from −30 to +30 mV of the known true formal electrode potential at 10 mV intervals. As a result, for each parameter varied, 77 optimizations were performed for the study
involving numerical simulations; 63 were performed when evaluating the experimental data. The combined simulation time for all seven initial guesses was $< 50 \text{ s}$ for every instance on the previously described laptop computational resource, potentially enabling near-real time analyses. Subsequently, $\theta_{\text{best}}$ was compared to the known parameter set used to generate the numerical simulation via the root mean squared error (RMSE), defined in Equation (47).

$$\text{RMSE}_i = \sqrt{\frac{1}{N_1} \sum_{k=1}^{N_1} \left( (\theta_{i,k,\text{true}} - \theta_{i,k,\text{guess}})^2 \right)}$$  \hspace{1cm} (47)

In Equation (47), $\text{RMSE}_i$ (varied units) is the root mean squared error of parameter $i$ (e.g., $E_0$, $D_O$), $N_1$ (–) is the total number of trials evaluated in the calculated value of $\text{RMSE}_i$ (11 for synthetically-generated data, nine for experimental data), $k$ (–) is a counter for each trial, $\theta_{i,k,\text{true}}$ (varied units) is the value of the known parameter $i$ of the $k^{th}$ trial, and $\theta_{i,k,\text{guess}}$ (varied units) is the analogue for the estimated parameter—we note the vectorized form of $\theta_{k,\text{true}}$ (multiple units) and $\theta_{k,\text{guess}}$ (multiple units) have the same parameter ordering as $\theta$ and $\theta_{\text{best}}$. Generally, the RMSE can be considered an average error; for example, if the estimated value of $D_R$ is $1 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$ with a RMSE of $1 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$, the true and unknown value of $D_R$ can loosely (i.e., not according to a specific probability distribution) be considered to lie between $0.9–1.1 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$. Further, statistical analyses can also be performed on the RMSE values themselves—that is, an array of RMSEs can have a mean and a variance. Here, seven values of $\text{RMSE}_i$ (one per initial guess) were calculated for every study. The average of these seven errors for synthetic data of a single electron transfer is plotted in Figure 4; the standard deviation of these errors is also reported as error bars, and the total time to evaluate all 77 optimizations for each bar
(\(t_{\text{sim}} \text{ (s)}\)) is less than 20 s (Figure 4b). Representative synthetic voltammograms and their data-model fits used within this regression process can be found in the SI.

Figure 4. Error of feature estimation (\(n = 77\) for each bar), evaluated in its entirety in less than 20 s, using the electrochemically reversible single electron transfer steady-state model. Two instances are explored. The first is (a) the “fundamental” scenario, and the second graph estimates (b) the “operational” scenario. Note that the error bars in (b) are present but small (< \(1 \times 10^{-10}\) for all parameters). For both panels, the abscissa indicates the feature whose accuracy is being evaluated, and the ordinate depicts the average percent error across multiple voltammogram pairs. The bar shading pattern denotes the specific parameter being varied to generate the set of voltammograms evaluated; all other parameters are held at a constant value. All transient voltammograms used for this analysis were simulated at a scan rate of 10 mV s\(^{-1}\), and the error bars represent one standard deviation from end-to-end.

Figure 4 illustrates that the parameters are estimated with lower accuracy for the “fundamental” set (maximum RMSE ca. \(1 \times 10^{-10}\) m\(^2\) s\(^{-1}\) for \(D_o\)) and with greater accuracy for the “operational” case (maximum RMSE ca. \(0.014\) for the SOH). Overall, Figure 4 demonstrates that the closed-form steady-state expression for the current from a microelectrode may be used to accurately estimate the SOC and SOH of an electrolyte solution containing redox-active compounds, a finding consistent with previous operando studies.\(^{9,12}\) However, the framework may not be as well suited to extract fundamental electrochemical parameters, as greater parameter estimation errors are exhibited. We suspect that the poorer estimation of the “fundamental” parameter set occurs
because $E_0$ and $d_o$ can be challenging to simultaneously and uniquely determine, since the mid-point potential is a function of both.\textsuperscript{2} That said, other electrochemical and spectroscopic techniques (e.g., macroelectrode cyclic voltammograms,\textsuperscript{1,2} diffusion ordered spectroscopy\textsuperscript{50}) may also be employed to estimate this parameter set.

The analogous procedure was also performed for the sequential electron transfer mechanism, with the results detailed in Figure 5; example data-model fits are also found in the SI. This analysis follows the same trend as Figure 4; specifically, the errors for the “fundamental” parameter estimation are significantly larger, with the maximum RMSE now approximately $5 \times 10^{-10}$ m$^2$ s$^{-1}$ (again for $D_o$). This larger error, as compared to the results in Figure 4, is tentatively attributed to the greater number of adjustable parameters—five in the sequential model compared to three in the single electron model—some of which are coupled. The total simulation time for all 77 optimizations also increased, with the maximum value now less than 50 s (Figure 5b). Analogously, the RMSE for the “operational” parameters is also small in Figure 5, never rising above 0.012 (again for the SOH). Overall, Figures 4 and 5 exhibit the same trends; the model appears well-suited to simultaneously estimate the SOC and SOH of an electrochemical system, which is of utility for evaluating the dynamic behavior of electrochemical system in near-real time. In contrast, the current framework may not be as capable of accurately estimating fundamental parameters.
Figure 5. Error of feature estimation ($n = 77$ for each bar), evaluated in its entirety in less than 50 s, using the electrochemically reversible sequential electron transfer steady-state model. The two bar plots are ordered in a fashion analogous to Figure 4: (a) estimation of the “fundamental” parameter set and (b) estimation of the “operational” parameter set. Note that the error bars in (b) are present but small ($< 1 \times 10^{-10}$ for all parameters). All transient voltammograms used for this analysis were simulated at a scan rate of 10 mV s$^{-1}$, and the error bars represent one standard deviation from end-to-end.

3.4. Experimental validation

Experimental data was also evaluated alongside the numerical simulations to assess how well the framework can estimate characteristics of an actual electrochemical solution. To this end, a model single electron transfer compound, MEEPT, was studied. This compound has precedence as a positive charge-storage species for use in nonaqueous redox flow batteries and is chemically stable in both relevant oxidation states ($R$ and $O$, per Equation (1)).$^{25,39}$

The measured values of the operational parameters—assumed to be ground truth for this study—were independently evaluated based on the masses of MEEPT and MEEPT–BF$_4$ added; Randles-Ševčík analyses and peak potential averaging were used to estimate the underlying “fundamental” parameters ($E_0$, $D_R$, and $D_O$) from macroelectrode voltammetry experiments conducted in solutions with SOCs of 0 and 1. Two additional solutions at intermediate SOC values
(ca. ⅓ and ⅔) were evaluated to determine whether the protocol can estimate operational parameters. The estimated formal electrode potentials and the diffusion coefficient of MEEPT are similar to those reported in literature, while the oxidized diffusion coefficient for MEEPT–BF₄ was not found; further details on the analysis are found in the SI, and the results of the automated SOC and SOH estimation are illustrated in Figure 6, where all 63 optimizations were performed in a total time of less than 25 s (Figure 6b).

**Figure 6.** Evaluation of model accuracy using experimental microelectrode voltammograms of MEEPT and MEEPT–BF₄. Two solutions of SOCs of ca. ⅓ (top curve in panel (a)) and ⅔ (bottom curve) were studied. The ⅓ SOC solution contained ca. 9.39 mM MEEPT, 4.46 mM MEEPT–BF₄, and 0.53 M TEABF₄, while the ⅔ SOC solution contained ca. 7.33 mM MEEPT, 14.54 mM MEEPT–BF₄, and 0.55 M TEABF₄, both in acetonitrile. (a) Experimental data (dots) and the fitted model (solid line). Positive currents are oxidative (anodic), and negative currents are reductive (cathodic). (b) Error of the fundamental parameter set for sequential electron transfers (n = 63 for each bar), evaluated in its entirety in less than 25 s. All experimental voltammograms used for this analysis were acquired at a scan rate of 10 mV s⁻¹. The magnitude of every error bar—not visualized—is < 1 × 10⁻¹¹ in all instances.

**Figure 6a** shows good agreement between the experimental and modeled responses at two different SOCs and two different total concentrations. Further, the errors of the estimated parameters (Figure 6b) are on the order of those found in Figure 4b, initially validating the results from the studies involving numerically simulated voltammograms. However, the largest error is
now < 0.04, rather than the previously observed lower values of < 0.015. This increase in error may have multiple causes, including inaccurate estimations in the fundamental parameters—themselves estimated from experimental data, rather than directly set by the user—and other experimental errors (e.g., measurement precision). These factors may result in minor differences in accuracy between experimental and synthetic data, but the errors remain within the same order of magnitude. Overall, the experiments performed in this work evince that the microelectrode models employed can estimate operational parameters almost as accurately as was predicted using synthetic data. This encouraging finding suggests that component concentrations in electrolyte solutions may be rapidly and accurately estimated in an automated fashion using microelectrode voltammetry. As such, these models are being further explored, both to capture a wider range of redox reaction conditions (e.g., combined migration-diffusion transport) and to complement other characterization techniques (e.g., macroelectrode voltammetry, UV-Vis spectroscopy) to augment (perhaps in situ or operando) electrochemical analyses of electrolyte solutions.

4. Conclusions

Microelectrode voltammetry is a powerful approach to studying the behavior of electrolyte solutions, but models must consider two spatial dimensions (radial and axial) which increases computational complexity, potentially limiting the utility of microelectrode simulation frameworks. In this study, we used oblate spheroidal coordinates to model the voltammetric responses of disk microelectrodes and developed a framework that enables users to derive closed-form steady-state expressions for multiple electron transfer mechanisms (single and sequential electron transfers) with greater ease. The coordinate system was also leveraged to simplify the construction of an alternating direction implicit finite-difference simulator, useful for scenarios
under which the analytical solutions only approximate microelectrode behavior. The in-house numerical simulator was successfully validated against COMSOL®, a commercial multiphysics simulator. The closed-form expressions, in turn, were shown to be capable of accurately estimating parameters from transient voltammograms—both numerically simulated and experimentally obtained—validating the predictive power of this approach.

Oblate spheroidal coordinates are an amenable coordinate system for electrochemical systems containing a disk—or more generally an oblate hemispheroid—electrode surrounded by an insulating surface; herein, we have demonstrated that this coordinate system is particularly useful in simulating microelectrode voltammograms of electrolyte solutions containing redox-active compounds at low concentrations. This framework may be extended to construct simulators that capture more complex physical phenomena (e.g., simultaneous analyte migration and diffusion) encountered in electrochemical systems. The results from this framework may also be paired with other experiments to infer more information about the solution being studied than would be possible from any single technique alone.

Our in-house automated parameter estimation routine can also be extended to accelerate additional voltammetry data analyses previously conducted manually. For example, exact or approximate closed-form solutions may be leveraged to estimate the SOC and SOH of electrolyte solutions in electrochemical devices (e.g., redox flow batteries) in an automated fashion and in near-real time. In sum, future work will aim to expand the capabilities and utility of this modeling framework to more comprehensively analyze the behavior of electrolyte solutions within practical electrochemical embodiments.
5. Acknowledgments

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6. Glossary

*Latin variables*

- $a_1$: Constant of integration ($\cdot$)
- $a_2$: Constant of integration ($\cdot$)
- $b_1$: Constant of integration ($\cdot$)
- $b_2$: Constant of integration ($\cdot$)
- $b_3$: Constant of integration ($\cdot$)
- $b_4$: Constant of integration ($\cdot$)
- $b_5$: Constant of integration ($\cdot$)
- $b_6$: Constant of integration ($\cdot$)
- $C_j$: Concentration of species $j$ (mol m$^{-3}$)
- $C_{j,\infty}$: Bulk or initial concentration of $j$ (mol m$^{-3}$)
- $C_{j,\text{surf}}$: Concentration of species $j$ on the surface of the electrode (mol m$^{-3}$)
- $C_{\text{total,}\infty}$: Total bulk concentration of all species (mol m$^{-3}$)
- $c_j$: Dimensionless concentration of species $j$ ($\cdot$)
- $c_{j,\infty}$: Dimensionless bulk or initial concentration of $j$ ($\cdot$)
- $D_j$: Diffusion coefficient of species $j$ (m$^2$ s$^{-1}$)
- $dA$: Generic areal element (m$^2$)
- $d_j$: Ratio of diffusion coefficients $D_j/D_{R}^{-1}$ ($\cdot$)
- $E$: Applied electrode potential (V vs. reference redox event)
- $E_0$: Formal redox potential for a species of interest (V vs. reference redox event)
- $E_{0,1}$: Formal redox potential for the more reductive electron transfer in a sequential mechanism (V vs. reference redox event)
- $E_{0,2}$: Formal redox potential for the more oxidative electron transfer in a sequential mechanism (V vs. reference redox event)
- $E_{0,\text{avg}}$: Average of the reductive and oxidative redox potentials of a sequential electron transfer mechanism (V vs. reference redox event)
- $F$: Faraday constant (96485 C mol$^{-1}$)
- $f_j$: Fraction of species $j$ in the bulk ($\cdot$)
- $g$: Indexing counter ($\cdot$)
- $I$: Current (A)
- $I(\theta)$: Vector of modeled currents (A)
- $I_1$: Current generated by the more reductive electron transfer in a sequential mechanism (A)
\( I_2 \)  Current generated by the more oxidative 
electron transfer in a sequential 
mechanism (A)
\( I_a \)  Anodic current symbol (A)
\( I_c \)  Cathodic current symbol (A)
\( I_{\text{obs}} \)  Vector of measured currents (A)
\( i \)  Indexing counter (–)
\( i_{\text{curr}} \)  Current density (A m\(^{-2}\))
\( iR \)  Ohmic potential distortion (V)
\( J_i \)  Flux vector of species \( i \) (mol m\(^{-2}\) s\(^{-1}\))
\( j \)  Indexing counter (–)
\( K_0 \)  Dimensionless heterogeneous rate constant (–)
\( K_{0,1} \)  Dimensionless heterogeneous rate constant for the more reductive 
electron transfer in a sequential mechanism (–)
\( K_{0,2} \)  Dimensionless heterogeneous rate constant for the more oxidative 
electron transfer in a sequential mechanism (–)
\( k \)  Indexing counter (–)
\( K_O \)  Heterogeneous rate constant (m s\(^{-1}\))
\( l \)  Indexing counter (–)
\( N_t \)  Number of total trials evaluated to calculate errors (–)
\( n \)  Number of optimizations performed (–)
\( n \)  Normal vector in the radial or axial direction (m)
\( n_e \)  Number of electrons transferred (–)
\( P \)  A function used in the separation of variables approach only 
dependent on \( \eta \) (–)
\( Q \)  A function used in the separation of variables approach only 
dependent on \( \xi \) (–)
\( q \)  Indexing counter (–)
\( R_G \)  Universal gas constant (8.314 J mol\(^{-1}\) K\(^{-1}\))
\( R_i \)  Volumetric reaction rate of species \( i \) (mol m\(^{-3}\) s\(^{-1}\))
\( \text{RMSE}_i \) Root mean squared error of parameter \( i \) (varied units)
\( r \)  Radial spatial coordinate (m)
\( r_e \)  Working electrode radius (m)
\( \text{SOC} \)  State-of-charge (–)
\( \text{SOH} \)  State-of-health (–)
\( T \)  Absolute temperature (K)
\( t \)  Time (s)
\( t_{\text{sim}} \) Total time to conduct \( n \) regressions on synthetic or 
experimental data (s)
\( u \)  Velocity vector (m s\(^{-1}\))
\( z \)  Axial spatial coordinate (m)
Greek variables

\( \alpha_c \) \text{ Cathodic transfer coefficient (–) } \\
\( \alpha_{c,1} \) \text{ Cathodic transfer coefficient for the more reductive electron transfer in a sequential mechanism (–) } \\
\( \alpha_{c,2} \) \text{ Cathodic transfer coefficient for the more oxidative electron transfer in a sequential mechanism (–) } \\
\( \Delta E_0 \) \text{ Difference in redox potentials in a sequential electron transfer mechanism (V) } \\
\( \eta \) \text{ Oblate spheroidal coordinate perpendicular to the microelectrode surface (–) } \\
\( \theta \) \text{ Generic vector of electrochemical and transport parameters (multiple units) } \\
\( \theta_{\text{best}} \) \text{ Vector of best-fit electrochemical and transport parameters (multiple units) } \\
\( \theta_{i,k,\text{guess}} \) \text{ Value of the estimated parameter } i \text{ of the } k \text{ th trial (varied units) } \\
\( \theta_{i,k,\text{guess}} \) \text{ Vector of estimated parameters for the } k \text{ th trial (multiple units) } \\
\( \theta_{i,k,\text{true}} \) \text{ Value of the true parameter } i \text{ of the } k \text{ th trial (varied units) } \\
\( \theta_{i,k,\text{true}} \) \text{ Vector of true parameters for the } k \text{ th trial (multiple units) } \\
\( \xi \) \text{ Oblate spheroidal coordinate parallel to the microelectrode surface (–) } \\
\( \tau \) \text{ Dimensionless time (–) } \\
\( \nu_i \) \text{ Stoichiometric coefficient of species } i \text{ (–) } \\
\( \phi_l \) \text{ Electrolyte potential or ohmic drop (V) } \\
\( \phi \) \text{ Dimensional overpotential (V) } \\
\( \phi_1 \) \text{ Dimensional overpotential for the more reductive electron transfer in a sequential mechanism (V) } \\
\( \phi_2 \) \text{ Dimensional overpotential for the more oxidative electron transfer in a sequential mechanism (V) } \\

Latin symbols

\( O \) \text{ Oxidized form of a redox couple } \\
\( R \) \text{ Reduced form of a redox couple } \\
\( S \) \text{ Semi-oxidized, or semi-reduced, form of a redox couple } \\
\( S' \) \text{ A generic surface }
7. CRediT Authorship Statement

A.M.F., Jr. performed the conceptualization, methodology, software, validation, formal analysis, investigation, data curation, writing–original draft, writing–review and editing, and visualization. B.J.N. performed the conceptualization, methodology, validation, investigation, writing–original draft, writing–review and editing, and visualization. K.M.T. performed the methodology, software, validation, investigation, writing–original draft, writing–review and editing, and visualization. Y.-M.C. performed the funding acquisition and resources. F.R.B. performed the conceptualization, funding acquisition, project administration, resources, supervision, visualization, writing–original draft, writing–review and editing.

8. Competing Interests and Funding

The authors declare no competing financial interest.
9. References


