Connecting material properties and redox flow cell cycling performance through analytical zero-dimensional models

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Abstract

Improvements in redox flow battery (RFB) performance and durability can be achieved through the development of new active materials, electrolytes, and membranes. While a rich design space exists for emerging materials, complex tradeoffs challenge the articulation of unambiguous target criteria, as the relationships between component selection and cycling performance are multifaceted. Here, we derive analytical solutions for zero-dimensional galvanostatic cell cycling models, enabling direct connections between material / electrolyte properties, cell operating conditions, and resulting performance metrics (e.g., energy efficiency, capacity fade). To demonstrate the utility of this modeling framework, we highlight several representative considerations for RFB design, including upper bound estimation, active species decay, and membrane / separator conductivity-selectivity tradeoffs. We also discuss modalities for extending this analytical framework to incorporate kinetic losses, distributed ohmic losses, and multiple spatial domains. Importantly, because the model is derived analytically, hundreds of cycles can be simulated in seconds, potentially facilitating detailed parametric sweeps, system optimization, and parameter estimation from cycling experiments. More broadly, this approach provides a means for assessing the impact of cell components that simultaneously influence multiple performance-defining processes, aiding in the elucidation of key descriptors and the identification of favorable materials combinations for specific applications.

Keywords: Redox flow batteries, zero-dimensional modeling, electrochemical engineering, energy storage, molecular engineering, crossover
1. Introduction

Redox flow batteries (RFBs) are electrochemical energy storage technologies that hold promise for improving the sustainability, efficiency, resiliency, and service life of the electric grid. In particular, the battery architecture features independently scalable energy and power, modular construction, and simplified maintenance, presenting opportunities for low-cost, long-duration storage.\(^1\) Despite these favorable characteristics, the projected capital costs, driven in large part by the constituent components of the system, prohibit widespread adoption, motivating research efforts to expand the materials repertoire, including novel redox couples, electrolytes, and membranes.\(^2,3\) Notably, the past decade has seen exciting advances, including the emergence of engineered molecules (e.g., redox-active organics, metal-centered coordination complexes) whose physical and electrochemical properties can be tuned through molecular functionalization.\(^4-6\) While such materials offer a new means of tuning RFB performance metrics, they also present new complexities for device operation, which include managing an array of parasitic processes (e.g., active species crossover, molecular decay, component degradation, side reactions) that result in heightened capacity fade and reduced cycling efficiencies.\(^3\) While incipient molecular engineering strategies may ultimately overcome these challenges, poorly-understood tradeoffs between molecular properties and cell performance frustrate the articulation of materials design criteria. There are a limited set of constitutive expressions that translate intrinsic material properties to measurable cycling behavior. Thus, it remains difficult to assess the extent to which improvements in specific properties or sets of properties impact cell performance and how such improvements should be weighed in the context of other, sometimes competing, design considerations.
Deconvoluting the relationships between material properties and cell performance can require days / weeks of cycling for a single cell, which challenges rigorous and systematic experimental investigations.\textsuperscript{7} Modeling can complement, augment, or even replace these studies by providing theoretical frameworks for interpreting cycling performance and for guiding the design of next-generation components and practical embodiments.\textsuperscript{8} Cell, stack, and system models can span a range of length and time scales depending on the level of granularity required to describe the processes under consideration. Multi-dimensional expressions (i.e., 2D, 3D) are often necessary for describing relevant electrochemical and fluid dynamic processes in the microscopic detail needed to mirror experimental data and to represent the spatial dependence of performance-limiting factors. Conversely, lower-dimensional models (i.e., 0D, 1D) employ more generalized assumptions about the underlying physical processes and device geometries, sacrificing precision to reduce computational complexity and simulation time. These mathematical analyses often lend themselves to useful analytical formulations which can be readily adapted by practitioners.

Zero-dimensional models have shown particular value for explaining flow battery cycling performance.\textsuperscript{9–17} These formulations describe time-dependent changes in redox species concentrations and ignore spatial variations, sacrificing microscopic precision for solvability. Further, zero-dimensional models can easily incorporate parasitic processes (e.g., molecular decay, crossover) which lead to evolving charge / discharge profiles, capacity fade, and diminished efficiencies. Despite these simplifications, the numerical methods used to solve the time-dependent differential equations remain computationally expensive and, because they scale with the cell lifetime, simulations of long-duration performance scenarios can become prohibitively slow. For example, several previously reported zero-dimensional models require ca. 30 – 120 s to generate a single charge-discharge cycle on laptop computers, meaning that longer simulations (tens to
hundreds of cycles) would take hours of computation time.\textsuperscript{10,12,18} This may be feasible for specific uses, but it discourages systematic modeling for extended cycling scenarios and parametric studies. While numerical implementations are necessary for certain instances,\textsuperscript{12,15} a range of cell architectures and operating conditions can be described by constitutive equations with analytical solutions. The development of analytical expressions that describe cycling behavior can drastically reduce the mathematical complexity of simulating durational performance in RFBs, potentially making such models more accessible to researchers with diverse technical backgrounds and varying computational resources.

Here, we develop an analytical framework for modeling galvanostatic cycling behavior in redox flow cells to illuminate the relationships between component material / electrolyte properties, cell operating conditions, and electrochemical performance. First, we derive explicit, analytical representations in the absence of capacity fade mechanisms to estimate upper bounds of accessible charge storage capacity and voltaic efficiency under idealized conditions where ohmic and mass transport losses dominate. Second, we introduce active species decay and self-discharge to simulate capacity fade in the absence of crossover. We then connect this expression to experimental observations in diagnostic flow cell architectures used to assess molecular decay rates. Third, we assess the impact of membrane selectivity and conductivity on capacity retention and energy efficiencies, illustrating the complex interplay of property combinations that govern species crossover over extended periods of cell cycling. Fourth and finally, we discuss modalities to further expand on this framework, including the incorporation of kinetic losses, non-uniform reaction distributions, and multiple spatial domains.

While prior reports have sought to develop and validate zero-dimensional models against cell cycling data,\textsuperscript{10,11,15} we pursue a more general approach, focusing on the derivation,
implementation, and overall utility of this modeling framework. Therefore, we contemplate questions that are of broad interest and importance to RFB cycling rather than address specific hypotheses surrounding a particular redox chemistry or device configuration. As such, we do not conduct an exhaustive parametric sweep of all adjustable variables but instead present representative analyses that emphasize the versatility of these models. Consequently, the results provided here validate several previously reported experimental observations and offer new considerations for individual component selection and cell design. We note that the simplified set of analytical expressions outlined here is relevant for a wide range of existing and emerging RFB chemistries, enabling the determination of more meaningful design guidelines for next-generation materials at an earlier stage of development and reducing the need for time- and materials-intensive experimental campaigns. Additionally, rapid computation times could facilitate the integration of cycling models into more complex mathematical frameworks, including techno-economic assessments,\textsuperscript{19--21} process control and optimization,\textsuperscript{22--24} parameter estimation from experimental systems,\textsuperscript{25} and synthetic data generation for machine learning,\textsuperscript{26,27} making this approach valuable for a broad swath of researchers.
2. Zero-dimensional cycling model

Here, we introduce a generalized, analytical zero-dimensional modeling framework to describe galvanostatic cycling in a redox flow cell. Initially, we introduce mass balance equations associated with the individual charged and discharged species (Section 2.1). Subsequently, we discuss modes of homogeneous active species decay (Section 2.2) and membrane crossover (Section 2.3) to define source and loss terms, and derive analytical solutions (Section 2.4) to the associated mass balance equations. Then we introduce electrochemical expressions to describe the cell voltage (Section 2.5) and relevant cell cycling metrics (Section 2.6). Finally, we discuss model implementation, including the software and hardware used to perform cell cycling simulations (Section 2.7). This model invokes the following overarching assumptions: (1) all processes occur at constant temperature (i.e., isothermal); (2) all domains are well-mixed such that species concentrations are uniform throughout; (3) operating conditions and electrolyte / flow cell properties remain constant throughout cycling; and (4) all redox reactions proceed through a one-electron transfer without chemical / electrochemical intermediates. All other assumptions will be described within the context of specific models and equations.

![Diagram](image)

Figure 1. Representative modeling domain explored in this work.
2.1. Reaction mass balances

In this modeling framework, we consider two species, $A$ and $B$, undergoing one-electron half-reactions shown in Equations (1) and (2).

$$A \rightleftharpoons A^+ + e^- \quad (1)$$

$$B \rightleftharpoons B^+ + e^- \quad (2)$$

$A$ and $A^+$ are treated as the positive electrolyte (posolyte) redox couple and undergo charge / discharge in the positive half-cell while $B$ and $B^+$ are treated as the negative electrolyte (negolyte) redox couple and undergo charge / discharge in the negative half-cell. Here, $A$ and $B^+$ reflect the discharged states while $A^+$ and $B$ reflect the charged states. Note that the nominal charges associated with $A^+$ and $B^+$ describe only their relative states of charge; however, the ionic charge of each species, $z_j$, may be any value (e.g., $-2$, $-1$, $0$, $+1$, $+2$) such that $z_{A^-} = z_A + 1$ and $z_{B^-} = z_B + 1$.

Broadly, zero-dimensional cycling models rely on solving mass balances for each species in the system; here, we assume that both half-cells are well-mixed and that the reaction takes place uniformly throughout the electrolyte volume. Hence, each reactor half-cell, electrolyte reservoir, and connecting tubing are treated as one continuous domain, resembling two stirred tank reactors as represented schematically in Figure 1. The mass balance for each species can be generally described by Equation (3) where the time, $t$ (s), is measured from the beginning of each half-cycle (i.e., charge or discharge) and the applied current, $I$ (A), is positive for the charging half-cycle and negative for the discharging half-cycle.

$$\frac{dC_{j}^{\infty,h}}{dt} = s_j \frac{I}{V^h F} + \sum R_j^h \quad (3)$$
\( V^h \) (m\(^3\)) is the total electrolyte volume in half-cell \( h \) (either the positive or negative electrolyte), \( C_{j}^{\nu,h} \) (mol m\(^{-3}\)) is the bulk concentration of species \( j \) in half-cell \( h \), \( s_j^h \) is the stoichiometric coefficient for the faradaic reaction (Table 1), \( F \) (96,485 C mol\(^{-1}\)) is the Faraday constant, and \( \sum R_j^h \) (mol m\(^{-3}\) s\(^{-1}\)) represents the sum of the source / sink terms for species \( j \), which comprise the chemical decomposition reactions and crossover taking place in each half-cell. Stoichiometric coefficients for the charged species, \( A^+ \) and \( B \), are excluded from the opposing half-cells, as the electrochemical potentials in those environments preclude their formation, meaning \( C_{A^+}^{\nu,-} = 0 \) and \( C_{B}^{\nu,+} = 0 \) at all times.

All of the mass balance equations are subject to an initial condition given by Equation (4).

\[
C_j^{\nu,h}(t = 0) = C_j^{\nu,h}
\]  

(4)

\( C_j^{\nu,h} \) (mol m\(^{-3}\)) is the initial concentration of species \( j \) at the beginning of the half-cycle. For example, the initial concentration at the beginning of the discharge step will equal the final concentration at the end of the charge step.

**Table 1.** Electrochemical reaction stoichiometric coefficients in each half-cell.

<table>
<thead>
<tr>
<th></th>
<th>Positive half-cell</th>
<th>Negative half-cell</th>
</tr>
</thead>
<tbody>
<tr>
<td>( s_A^h )</td>
<td>-1</td>
<td>0</td>
</tr>
<tr>
<td>( s_A^{\nu} )</td>
<td>1</td>
<td>---</td>
</tr>
<tr>
<td>( s_B^h )</td>
<td>---</td>
<td>1</td>
</tr>
<tr>
<td>( s_B^{\nu} )</td>
<td>0</td>
<td>-1</td>
</tr>
</tbody>
</table>
2.2. Homogeneous active species decay

Homogeneous decay processes associated with unstable redox active materials lead to capacity fade and reduced energy efficiencies. Following the approach of Silcox et al., we contemplate two mechanisms for decay—self-discharge and irreversible degradation. Homogeneous self-discharge (Equations (5) and (6)) is assumed to proceed by the charged active species (A$^+$ or B) reacting with the supporting electrolyte (supporting salt + solvent), contaminants, or wetted cell components and reverting to their discharged state.

\[
A^+ \xrightarrow{f_{A^+} k_{d,A^+}} A
\]

\[
B \xrightarrow{f_B k_{d,B}} B^+
\]

Here, $k_{d,A^+}$ and $k_{d,B}$ (s$^{-1}$) are the overall decay rate constants of A$^+$ and B, respectively. $f_{A^+}$ and $f_B$ (dimensionless) are the respective fractions of A$^+$ and B that decay via self-discharge. Note that while self-discharge is nominally a redox reaction, the electron is assumed to be irrecoverable.

Irreversible degradation (Equations (7) and (8)) occurs when the charged active species (A$^+$ or B) decomposes to form any number of non-redox-active products, generally denoted as D.

\[
A^+ \xrightarrow{(1-f_{A^+}) k_{d,A^+}} D
\]

\[
B \xrightarrow{(1-f_B) k_{d,B}} D
\]

Here, we assume that the decay products are benign and thus do not interfere with subsequent cell operation. Additionally, while there are certainly more complex decay mechanisms (e.g., dimerization, protonation / deprotonation reactions, formation of new electroactive products) that may be considered for specific chemistries, we assume first-order homogeneous kinetics as this simplifies subsequent mathematical treatments and has precedence in earlier studies.
2.3. Membrane crossover

The species transport model chosen for membrane crossover follows the work of Darling et al. who derived steady-state fluxes, accounting for diffusion, migration, and electro-osmotic convection terms. The active species flux through the membrane, $N_j$, subject to Dirichlet boundary conditions on either side of the membrane, is shown in Equations (9) and (10). Here, the flux is defined as positive for transport from the negative electrolyte to the positive electrolyte.

$$N_j = \frac{D_j^K_j}{l_m} \gamma_j \left( C_j^{\infty}- \frac{\exp(\gamma_j) - C_j^{\infty}}{\exp(\gamma_j) - 1} \right)$$

$$\gamma_j = -\left( \frac{z_j F}{\sigma_m RT} + \frac{\xi}{\nu C_{site} D_j^K F} \right) \frac{l_m}{A_m}$$

$D_j^n$ (m$^2$ s$^{-1}$) is the diffusion coefficient of species $j$ through the membrane, $K_j$ (dimensionless) is the membrane sorption coefficient of species $j$, $l_m$ (m) is the membrane thickness, $\gamma_j$ is a dimensionless flux parameter for species $j$, $\sigma_m$ (S m$^{-1}$) is the membrane conductivity, $R$ (8.314 J mol$^{-1}$ K$^{-1}$) is the universal gas constant, $T$ (K) is the absolute temperature, and $A_m$ (m$^2$) is the geometric membrane area which is equivalent to the geometric area of the electrochemical cell. For an ion-exchange membrane, $\xi$ (dimensionless) is the electro-osmotic coefficient, $\nu$ (dimensionless) is the molar ratio of solvent to fixed ion sites in the membrane, and $C_{site}$ (mol m$^{-3}$) is the concentration of fixed ion sites in the membrane.

Because the flux is linear with respect to the bulk species concentrations, Equation (9) can be conveniently expressed in terms of first-order “crossover rate constants”, $k_{c,j}^-$ and $k_{c,j}^+$ (s$^{-1}$), according to Equation (11).

$$\frac{N_j A_m}{V^+} = k_{c,j}^- C_j^{\infty} - k_{c,j}^+ C_j^{\infty}$$
To integrate membrane fluxes into the species mass balances, crossover-induced self-discharge reactions (Equation (12)) are assumed to occur instantaneously, consuming charged species at both membrane-electrolyte interfaces.\(^{35}\)

\[
A^+ + B \rightarrow A + B^+
\]  
\(\text{(12)}\)

As a result, the concentration of charged species (A\(^+\) and B) will always remain at zero in the opposite electrolyte. Finally, both crossover and species decay can be expressed as source terms, as shown in Table 2. Note that for symmetric chemistries, where the same parent compound is used on both sides of the battery but at different oxidation states (e.g., V\(^{2+}/V^{3+}\) and V\(^{4+}/V^{5+}\) on the negative and positive sides of the vanadium RFB, respectively), the comproportionation reactions differ from Equation (12), as species undergo additional changes in oxidation state upon crossover, altering the form of the source terms (see discussion in Section S1).\(^{10}\)

**Table 2.** Active species source terms, including both species decay and crossover.

<table>
<thead>
<tr>
<th>Positive half-cell</th>
<th>Negative half-cell</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\sum R^h_A) (f_A k_{d,A} C_{A,A}^{c,A} + k_{r,A} C_{A,A}^{c,A} - k_{e,A} C_{A,A}^{c,A} + k_{e,B} C_{B,B}^{c,B} )</td>
<td>((-k_{e,A} C_{A,A}^{c,A} + k_{r,A} C_{A,A}^{c,A} + k_{e,A} C_{A,A}^{c,A}) V^+ )</td>
</tr>
<tr>
<td>(\sum R^h_A) (\frac{-k_{d,A} C_{A,A}^{c,A} - k_{e,A} C_{A,A}^{c,A} - k_{e,B} C_{B,B}^{c,B}}{)</td>
<td>(---)</td>
</tr>
<tr>
<td>(\sum R^h_B) (k_{c,B} C_{B,B}^{c,B} - k_{c,B} C_{B,B}^{c,B} + k_{e,B} C_{B,B}^{c,B} )</td>
<td>(f_B k_{d,B} C_{B,B}^{c,B} + (k_{e,B} C_{B,B}^{c,B} + k_{e,A} C_{A,A}^{c,A} + k_{e,A} C_{A,A}^{c,A}) V^+ )</td>
</tr>
<tr>
<td>(\sum R^h_B) (---)</td>
<td>((-k_{d,B} C_{B,B}^{c,B} - k_{e,B} C_{B,B}^{c,B} + k_{e,A} C_{A,A}^{c,A}) V^+ )</td>
</tr>
</tbody>
</table>

**2.4.** Mass balance analytical solutions

The introduction of species decay and crossover results in a coupled system of time-dependent differential equations, which can be solved analytically for galvanostatic cycling.\(^{36}\) Because each
of the source terms are first order, the mass balances can be expressed as a vector differential
equation (Equations (13)) with initial conditions given by Equation (14).

\[ \frac{d}{dt} \mathbf{C} = \mathbf{b} - \mathbf{KC} \]  

(13)

\[ \mathbf{C}(t = 0) = \mathbf{C}^0 \]  

(14)

\( \mathbf{C} \) (mol m\(^{-3}\)) is a column vector containing the 6 bulk species concentrations of interest \( C_{A^\infty}^+, \)
\( C_{A^\infty}^-, \) \( C_{B^\infty}^+, \) \( C_{B^\infty}^-, \) \( C_{A\infty}^+, \) \( C_{A\infty}^- \), \( \mathbf{b} \) (mol m\(^{-3}\) s\(^{-1}\)) is a column vector containing constant reaction
terms, \( \mathbf{K} \) (mol m\(^{-3}\) s\(^{-1}\)) is a matrix containing the first-order rate constants, and \( \mathbf{C}^0 \) (mol m\(^{-3}\)) is a
column vector containing the initial concentrations. This equation can be transformed using the
eigendecomposition of \( \mathbf{K} \) according to Equation (15).

\[ \frac{d}{dt} (\mathbf{U}^{-1} \mathbf{C}) = \mathbf{U}^{-1} \mathbf{b} - \mathbf{U}^{-1} \Lambda \mathbf{U}^{-1} \mathbf{C} \]  

(15)

\( \mathbf{U} \) (dimensionless) and \( \Lambda \) (s\(^{-1}\)) are the eigenvector and diagonal eigenvalue matrices of \( \mathbf{K} \),
respectively. Performing a coordinate transform \( (\mathbf{\theta} = \mathbf{U}^{-1} \mathbf{C}, \ \mathbf{\theta}^0 = \mathbf{U}^{-1} \mathbf{C}^0, \text{ and } \mathbf{\beta} = \mathbf{U}^{-1} \mathbf{b}) \) results in
a system of linear, first-order differential equations, as shown by Equation (16), which can be
solved in terms of its individual elements to give Equation (17).

\[ \frac{d}{dt} \mathbf{\theta} = \mathbf{\beta} - \Lambda \mathbf{\theta} \]  

(16)

\[ \theta_i = \theta_i^0 \exp(-\lambda_i t) + \frac{\beta_i}{\lambda_i} (1 - \exp(-\lambda_i t)) \]  

(17)

\( \theta_i \) (mol m\(^{-3}\)), \( \theta_i^0 \) (mol m\(^{-3}\)), \( \beta_i \) (mol m\(^{-3}\) s\(^{-1}\)), and \( \lambda_i \) (s\(^{-1}\)) are the ith element of \( \mathbf{\theta}, \ \mathbf{\theta}^0, \ \mathbf{\beta}, \) and \( \Lambda \),
respectively. Finally, the concentration vector may be obtained by transforming the resulting
solution (Equation (18)).

\[ \mathbf{C} = \mathbf{U} \mathbf{\theta} \]  

(18)
2.5. Electrochemical thermodynamics and cell voltage

If the kinetics of the redox processes are sufficiently facile, then the electrode reactions can be assumed to occur instantaneously; thus, the electrode surfaces are always at equilibrium and the two electrode potentials can be described by the Nernst Equation (Equations (19) and (20)). Here, we assume ideal solution conditions such that concentrations may be used in place of activities.

\[
\Phi^+_i = E^{o,+} - \frac{RT}{F} \ln \left( \frac{C^{s}_A}{C^{s'}_A} \right) \quad (19)
\]

\[
\Phi^-_i = E^{o,-} - \frac{RT}{F} \ln \left( \frac{C^{s}_B}{C^{s'}_B} \right) \quad (20)
\]

\( \Phi^+_i \) and \( \Phi^-_i \) (V) are the electrode potentials for the positive and negative electrodes, respectively; \( E^{o,+} \) and \( E^{o,-} \) (V) are the formal redox potentials for the positive and negative redox reactions (Equations (1) and (2), respectively); and \( C^{s}_j \) (mol m\(^{-3}\)) is the surface concentration of species \( j \).

Assuming there is sufficient electrolyte flow, the species fluxes can be described by convective mass transport and related to the total current according to Equation (21).

\[
\frac{I}{FA_{ed}} = -s_j^{h} k_{m,j} \left( C^{o,h}_j - C^{s}_j \right) \quad (21)
\]

\( A_{ed} \) (m\(^2\)) is the accessible interfacial surface area of the electrode and \( k_{m,j} \) (m s\(^{-1}\)) is the convective mass transfer coefficient. In turn, this expression can be rearranged to describe the surface concentrations in terms of the bulk concentration using Equation (22).

\[
C^{s}_j = C^{o,h}_j + \frac{I}{FA_{ed}s_j^{h}k_{m,j}} \quad (22)
\]

The mass transfer coefficients are generally treated as empirical values, which can either be determined experimentally or predicted from the operating parameters, electrolyte and electrode
properties, and flow characteristics using dimensionless correlations. While there are a number of correlations that could be invoked,\textsuperscript{37,38} we adopt a model described by Barton \textit{et al.} and developed for an interdigitated flow field (\textbf{Equation (23)}) due to its consistency with our simulation conditions (\textit{vide infra}).\textsuperscript{39}

\[ k_{m,j} = 0.018 \left( \frac{Q}{n_{ch}l_{ch}l_{e}e} \right)^{0.68} \left( \frac{\rho}{\mu} \right)^{0.18} \left( D_j^\infty \right)^{0.5} \left( d_f \right)^{-0.32} \]  

(23)

$Q$ (m$^3$ s$^{-1}$) is the volumetric flow rate, $n_{ch}$ is the number of flow channels, $l_{ch}$ (m) is the length of each flow channel, $l_e$ (m) is the electrode thickness, $\varepsilon$ (dimensionless) is the electrode porosity, $\rho$ (kg m$^{-3}$) is the electrolyte density, $\mu$ (Pa s) is the electrolyte viscosity, $D_j^\infty$ (m$^2$ s$^{-1}$) is the bulk diffusion coefficient of species $j$, and $d_f$ (m) is the electrode fiber diameter.

Electrical resistances (e.g., contact resistance, wiring, electrodes) and ionic resistances (e.g., electrolyte conductivity, membrane conductivity) result in ohmic losses, as greater driving forces (voltages) are needed to pass charge through the electrochemical cell at a given rate (current). In many advanced flow cells, the membrane resistance, $R_m$ (\Omega), is the dominant contributor to ohmic losses, while additional contact resistances, $R_c$ (\Omega), tend to be minor.\textsuperscript{19} The membrane resistance is related to the membrane conductivity according to \textbf{Equation (24)}.

\[ R_m = \frac{l_m}{A_m \sigma_m} \]  

(24)

Assuming the various ionic and electronic resistances are constant and obey Ohm’s Law, the full cell voltage, $E_{cell}$ (V) can be described using \textbf{Equation (25)}.

\[ E_{cell} = E^{o+,} - E^{o-,} + I \left( R_m + R_c \right) - \frac{RT}{F} \ln \left( \frac{C_{A^+}^s}{C_{B^+}^s} \right) \]  

(25)
While not considered here, some aqueous systems exhibit pH differences across the membrane, giving rise to Donnan potentials that may also alter the cell voltage.\(^{40}\)

### 2.6. Cycling performance metrics

The metrics typically used to describe durational cell cycling performance are the charge and discharge capacities as well as the cycling efficiencies (i.e., coulombic efficiency, voltaic efficiency, energy efficiency).\(^{41}\) The capacity refers to the total amount of charge stored or released (\textbf{Equations (26) and (27)}).

\[
\begin{align*}
\text{Cap}_c &= \int_0^{t_c} Idt \\
\text{Cap}_d &= -\int_0^{t_d} Idt
\end{align*}
\]

\textbf{Equation (26)}

\textbf{Equation (27)}

Here, \(\text{Cap}_c\) and \(\text{Cap}_d\) (C) are the charge and discharge capacities, respectively, and \(t_c\) and \(t_d\) (s) are the total charge and discharge times, respectively. Note that the negative sign in \textbf{Equation (27)} accounts for the change in direction of the current. The charge and discharge times are usually determined by a voltage cutoff for galvanostatic operation, which is based on either the point when the limiting current is approached (i.e., the cell voltage grows exponentially) or the point when a pre-determined cell voltage is reached (e.g., to prevent unfavorable side reactions). For the limiting current case, which is used throughout this work, \(t_c\) and \(t_d\) can be calculated as the minimum time for one of the reacting species surface concentrations to approach zero. For a pre-determined cell voltage, \(t_c\) and \(t_d\) can be determined by solving \textbf{Equation (25)} as discussed in \textbf{Section S2}.

The cycling efficiencies, defined here in their fractional forms, can be derived from the capacities and the cell voltage. The coulombic efficiency, \(CE\), is the ratio between the discharge capacity and the charge capacity according to \textbf{Equation (28)}. 
The voltaic efficiency, $VE$, is defined as the ratio of the average discharge voltage to the average charge voltage according to Equation (29).

$$VE = \frac{E_d}{E_c} = \frac{1}{t_d} \int_{0}^{t_d} E_c(t) \, dt$$

$E_c$ and $E_d$ (V) are the average charge and discharge voltages, respectively. Lastly, the energy efficiency, $EE$, is the multiplicative product of the voltaic and coulombic efficiencies according to Equation (30).

$$EE = CE \times VE$$

2.7. Computational tools and model implementation

All simulations were performed using MATLAB® R2021b on a Dell Latitude 7290 laptop computer with an Intel® Core™ i7-8650U processor (quad-core, 1.90 GHz) and a random-access memory of 16 GB. Eigenvalues and eigenvectors were calculated using the *eig* function, nonlinear algebraic equations were solved implicitly using the *fsolve* function, and numerical integration was performed using the *cumtrapz* function.

To apply these models with relevant input parameters, all simulations are performed for a small-scale flow cell architecture with constant properties shown in Table 3. We use this configuration because it is common in our laboratory and has been adopted by several others in the research community. Thus, these conditions are representative of many studies in contemporary RFB literature, as experimental demonstrations exist for a wide range of materials, providing reliable engineering specifications and component properties. The device described here
is a 2.55 cm² flow cell featuring porous carbon electrodes and interdigitated flow fields. To maintain consistency across results shown here, we use 10 mL of electrolyte with an initial active species concentration of 500 mM in both half-cells. Finally, we assume intermediate values for the fluid dynamic properties of each electrolyte. Note that the parameters chosen here are based on our own published data and common properties observed in the literature and therefore do not represent the breadth of the design space; however, the model may be easily adapted for other cell geometries, material sets, and electrolytes by adjusting the inputs to Table 3.

The current densities explored in this work (0 – 300 mA cm⁻²) reflect a range of relatively low to moderately high charge / discharge rates used in experimental systems. Because we elect to start cycling with only the discharged species present (Table 3), the current is initially positive during the first half-cycle (charging). The open-circuit voltages (OCV = E°⁺⁺ – E°⁻⁻) used here span a range of possible RFB chemistries; voltages ca. 1 V are characteristic of aqueous cells whereas voltages ca. 2 – 3 V are characteristic of nonaqueous cells. For each cycle, the charge and discharge times are determined using the limiting current case; the concentrations and cell voltages are then calculated for 2000 evenly spaced time steps during each half-cycle. Considering that the cell voltage becomes infinite at t = t_c and t = t_d, we replace the infinite voltage with an arbitrary, finite value that is well above or below the OCV (≥ 500 mV). Simulating each full cycle (charge and discharge) took ca. 0.05 s on the aforementioned computational resources.
Table 3. Constant properties for simulations performed in this study.

<table>
<thead>
<tr>
<th>Property(^a)</th>
<th>Value</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>(A_m)</td>
<td>0.000255 m(^2)</td>
<td>45</td>
</tr>
<tr>
<td>(n_{eh})</td>
<td>7</td>
<td>39</td>
</tr>
<tr>
<td>(l_{eh})</td>
<td>0.016 m</td>
<td>39</td>
</tr>
<tr>
<td>(l_e)</td>
<td>0.00034 m</td>
<td>46</td>
</tr>
<tr>
<td>(A_{ed})</td>
<td>0.184 m(^2)</td>
<td>46</td>
</tr>
<tr>
<td>(\varepsilon)</td>
<td>0.75</td>
<td>39,47</td>
</tr>
<tr>
<td>(d_f)</td>
<td>(7 \times 10^{-6}) m</td>
<td>47</td>
</tr>
<tr>
<td>(V^+, V^-)</td>
<td>(1 \times 10^{-5}) m(^3)</td>
<td>45</td>
</tr>
<tr>
<td>(C_{A^{0+,+}}, C_{B^{0,-}})</td>
<td>500 mol m(^{-3})</td>
<td>---</td>
</tr>
<tr>
<td>(C_{A^{0+,+}}, C_{B^{0,-}})</td>
<td>0 mol m(^{-3})</td>
<td>---</td>
</tr>
<tr>
<td>(\rho)</td>
<td>1000 kg m(^{-3})</td>
<td>---</td>
</tr>
<tr>
<td>(\mu)</td>
<td>1 Pa s</td>
<td>---</td>
</tr>
<tr>
<td>(T)</td>
<td>298 K</td>
<td>---</td>
</tr>
</tbody>
</table>

\(^a\) Initial bulk concentrations are the concentrations at the beginning of the first half-cycle.
3. Results and discussion

The complete model presented above provides a computationally-efficient framework for combining multiple forms of performance decay (i.e., decomposition, self-discharge, crossover) and voltage losses (i.e., ohmic and mass transfer losses) to describe cell cycling performance. However, in many instances, further simplifications of these generalized equations are sufficient for predicting device performance and may be implemented using explicit mathematical representations. To this end, we explore varying levels of complexity for this zero-dimensional framework, extending from upper bound performance estimates (Section 3.1) to simulation of capacity fade where molecular decay dominates (Section 3.2) and where crossover dominates (Section 3.3). We also discuss methods to incorporate additional sources of voltage loss, including kinetic losses in porous electrodes (Section 3.4) and transport losses via reactant mixing in multiple spatial domains (Section 3.5).

3.1. Evaluating performance upper bounds

We begin by contemplating conditions where performance decay is negligible, which allows for the identification of upper bounds in accessible capacity and EE. Such bounding analyses enable simple correlations between electrochemical properties and performance metrics, which have practical utility for assessing design tradeoffs. For the idealized case where all species do not decay and do not crossover, $\sum R_j = 0$, and changes in concentration are driven entirely by the passage of current. As a result, following the first charging cycle, the capacity and VE do not vary from cycle to cycle and $CE = 1$. Here, we derive explicit analytical expressions for cycling performance metrics and demonstrate their value by connecting these outputs to more fundamental
cell properties (e.g., cell resistance, mass transport rates, species redox potentials) and operating conditions.

For galvanostatic cycling, the current is constant, allowing the mass balances to be solved by integrating Equation (3) to yield Equation (31).

\[
C_j^\infty = C_j^0 + \frac{s_i I}{V^2 F} t
\]

Using the time-dependent concentration profiles, cell performance metrics can be expressed as shown in Table 4. These explicit analytical equations provide a simplified means to explore how specific design factors contribute to performance. For example, they can be used to assess how a particular electrolyte composition and cell format will perform in the ideal case, establishing a baseline expectation for performance under a specified set of cycling conditions. As an illustrative example, the representative cycling behavior of a redox flow cell subjected to different current densities is shown in Figure 2a. Here, increasing current density has the benefit of yielding greater power density and more rapid cycles, but at the expense of higher overpotentials and thus lower \(VE\). Further quantifying these losses, Figure 2b presents the resultant \(VE\) as a function of the applied current density and area-specific ohmic resistance (\(\text{ASR}_\Omega = A_m (R_c + R_m)\)) for varying values of the OCV. Consistent with Figure 2a, increasing current density imposes larger ohmic and mass transport losses, lowering the \(VE\); here, ohmic losses are proportional to both the \(\text{ASR}_\Omega\) and current density, resulting in a strong dependence on both parameters. Importantly, the \(VE\) increases significantly with higher OCV, suggesting that higher voltage redox chemistries, such as those enabled by nonaqueous electrolytes, can tolerate greater \(\text{ASR}_\Omega\) while maintaining reasonable cycling efficiencies.
Table 4. Performance metrics for galvanostatic cell cycling in the absence of molecular decay or species crossover.

<table>
<thead>
<tr>
<th>Performance metric</th>
<th>Analytical expression</th>
</tr>
</thead>
<tbody>
<tr>
<td>Charge capacity</td>
<td>$Cap_c = It_c$</td>
</tr>
<tr>
<td>Discharge capacity</td>
<td>$Cap_d = -It_d$</td>
</tr>
<tr>
<td>Coulombic efficiency(^a)</td>
<td>$CE = 1$</td>
</tr>
<tr>
<td>Voltaic efficiency(^b)</td>
<td>$VE = \frac{E_d}{E_c}$</td>
</tr>
<tr>
<td>Charge time(^c)</td>
<td>$t_c = \min \left{ \frac{V^+ F}{I} \left( C_A^0 - \frac{I}{FA_{ed} k_{m,A}} \right), \frac{V^- F}{I} \left( C_B^{a_0} - \frac{I}{FA_{ed} k_{m,B'}} \right) \right}$</td>
</tr>
<tr>
<td>Discharge time(^c)</td>
<td>$t_d = \min \left{ -\frac{V^+ F}{I} \left( C_A^{a_0} + \frac{I}{FA_{ed} k_{m,A'}} \right), -\frac{V^- F}{I} \left( C_B^{a_0} + \frac{I}{FA_{ed} k_{m,B}} \right) \right}$</td>
</tr>
</tbody>
</table>

\(^a\) After the initial cycle  
\(^b\) Analytical expressions for the average voltages are provided in Section S3  
\(^c\) Assumes the voltage cutoff is based on the limiting current condition
Figure 2. (a) Representative charge / discharge profiles for cycling in the absence of parasitic losses. (b) Voltaic efficiency ($VE$) as a function of the applied current density and cell area-specific ohmic resistance ($ASR_o$) for electrolytes with varying open-circuit voltage (OCV). Black lines represent constant $VE$ ranging between 0.1 – 0.9 in increments of 0.1. For all simulations, $Q = 10$ mL min$^{-1}$ for both electrolytes and $D_j = 1 \times 10^{-9}$ m$^2$ s$^{-1}$ for all species.
These governing equations also enable the evaluation of more subtle connections between molecular properties and cell performance that can be difficult to disentangle from experiments. Such knowledge is useful in experimental design when considering suitable operating envelopes and in data interpretation when elucidating possible performance limitations. As a representative example, Figure 3 shows the combined effects of redox species diffusion coefficients on the accessible capacity for common ranges of current densities and flow rates used in experimental cells. Higher diffusion coefficients ($D_{j}^{\infty} = 10^{-10} - 10^{-9} \text{ m}^2 \text{ s}^{-1}$) are typical of smaller redox species (e.g., inorganic ions, organic molecules, metal coordination complexes) whereas lower values ($D_{j}^{\infty} = 10^{-12} - 10^{-11} \text{ m}^2 \text{ s}^{-1}$) are representative of larger macromolecular redox species (e.g., polymers, colloids). As expected, lower species mass transport rates reduce accessible capacity, setting effective upper bounds on useable current densities. For exceedingly slow mass transport, the applied current can exceed the limiting current, yielding zero accessible capacity. While high transport rates are desirable, enhancements in species diffusivity may have diminishing returns under conditions where the theoretical capacity is attainable through either decreasing the current density or increasing the volumetric flow rate. However, improvements in capacity utilization and cycling efficiencies must also be balanced with pumping losses, which scale with the pressure drop and volumetric flow rate (see discussion in Section S4). Relationships such as those explored in Figure 3 and Section S4 are relevant for balancing molecular engineering tradeoffs; the addition of substituent groups to redox molecules can shift redox potential, improve solubility / stability, and suppress crossover, albeit at the risk of reducing accessible capacity due to increasing molecular weight (lower diffusivity).
Figure 3. Accessible capacity as a function of the redox species diffusion coefficient for varying volumetric flow rates and current densities. The diffusion coefficients \( D_j^\infty \) are identical for all species.
3.2. Homogeneous active species decay

Next, we consider the influence of species decomposition and self-discharge that hamper the development of high-voltage chemistries,$^3,11,51$ as increasingly positive / negative redox potentials are reflective of more reactive charged states. Consequently, improving species stability is of significant interest, and the identification and mitigation of decay processes is key to advancing new chemistries based on engineered organic molecules and metal-centered coordination complexes.$^{28}$ Modeling cell performance in the absence of additional parasitic processes (e.g., crossover) has practical value for experimental stability studies (e.g., bulk electrolysis, symmetric cell cycling) and for understanding the extent to which species decay may impact full cell performance. For example, time-dependent decay rates determined through ex situ methods can be combined with cycling models to predict performance prior to extensive cell testing. Conversely, cell cycling data may be paired with analytical models to derive quantitative measures of decay kinetics.$^{11}$

For galvanostatic cycling, the mass balances are decoupled such that simple, explicit expressions may be written for the bulk concentrations. Analytical solutions for the charged species are shown in Equations (38) and (39).

\[
C_{A^*}^\infty = \frac{I}{V^h F k_{d,A^*}} + \left( C_{A^*}^0 - \frac{I}{V^h F k_{d,A^*}} \right) \exp \left( -k_{d,A^*} t \right)
\]  

(38)

\[
C_B^\infty = \frac{I}{V^h F k_{d,B}} + \left( C_B^0 - \frac{I}{V^h F k_{d,B}} \right) \exp \left( -k_{d,B} t \right)
\]  

(39)

These can then be integrated into mass balances for the discharged species to give Equations (40) and (41).
Finally, the combined expressions for the bulk concentrations can be used with Equations (22) and (25) to compute the cell voltage and other cycling metrics. Because the surface concentrations are nonlinear with time, the charge and discharge times must be calculated by solving nonlinear algebraic equations for each half-cycle using either the limiting current condition or the voltage cutoff condition (Section S2). Similarly, the VE (Equation (29)) requires numerical integration of the cell voltage.

To demonstrate the utility of these analytical models, we explore their use for describing cycling in symmetric cell architectures (i.e., the same redox species is present in both half-cells). Because the cell contains a single redox couple, the crossover fluxes are equal and opposite during charge and discharge, making the capacity fade primarily dependent on homogeneous decay.\textsuperscript{52,53} While in some instances, one of the half-cells may be oversized to make the other half-cell capacity-limiting,\textsuperscript{54} here we assume equal electrolyte volumes. Figure 4 shows predicted capacity fade for a range of decay rate constants, where the higher rate constants ($k_{d,A^+} > 10^{-7}$ s$^{-1}$) reflect relatively unstable active species and the lower rate constants represent more advanced chemistries. For context, state-of-the-art aqueous organic RFB redox couples exhibit capacity fade rates ca. 0.01% per day,\textsuperscript{28} which correspond to $k_{d,A^+}$ values of ca. $5 \times 10^{-9}$ s$^{-1}$ under the cycling conditions and assumptions used in this model. Thus, decay kinetics can be quantitatively translated to expected cycling lifetime in relevant experimental systems. While these results may be somewhat intuitive, the ability to predict capacity fade is relevant for experimental design (e.g.,
determining detection limits, experimental timeframes, and cycling conditions) and cell engineering.

**Figure 4.** Discharge capacity as a function of cycle number for varying species decay rate constants in a symmetric cell. The gray dashed line indicates the theoretical capacity. For all simulations, $I = 25.5$ mA (10 mA cm$^{-2}$), $f_{A^*} = 0.5$, $Q = 10$ mL min$^{-1}$ for both electrolytes, and $D_j^0 = 1 \times 10^{-9}$ m$^2$ s$^{-1}$ for all species.

We also investigate the role of experimental cycling conditions on the apparent redox species stability; specifically, the applied current density alters the observed capacity fade when measured against cycle number as shown in **Figure 5**. Considering homogeneous decay is a time-dependent process, the change in accessed capacity is dependent on the total cycling time (**Figure 5b**) rather than the number of cycles (**Figure 5a**). These model observations are consistent with previous experimental studies demonstrating this effect in bulk electrolysis experiments$^{55}$ as well as symmetric redox flow cells,$^{54}$ thus providing additional validation of such phenomena and further motivating the need for consistent testing and reporting metrics. Potential holds are sometimes
included at the end of each galvanostatic step to access the full capacity of the electrolyte, providing a more consistent measure of the species stability such that it is not as strictly dependent on the charging rate.\textsuperscript{54} This cycling profile can conceivably be emulated by alternating between equations that describe the galvanostatic process (\textbf{Equations (38) \textendash\ (41)}) and equations that describe the potentiostatic process (see \textbf{Section S5}).

\textbf{Figure 5.} Discharge capacity as a function of (a) cycle number and (b) cycling time for varying current densities. For all simulations, $k_{d,A} = 1 \times 10^{-5}$ s\textsuperscript{-1}, $f_A = 0.5$, $Q = 10$ mL min\textsuperscript{-1} for both electrolytes, and $D_j^\infty = 1 \times 10^{-9}$ m\textsuperscript{2} s\textsuperscript{-1} for all species.
3.3. Species crossover

We now introduce active species crossover into the modeling framework to assess property tradeoffs for membranes / separators. For this analysis, we assume the charged species are chemically stable \( (k_{d,A'} = k_{d,B} = 0) \), leading to a simplified derivation of the mass balances as detailed in Section S7. While the added crossover terms obscure a concise, explicit representation, the resulting analytical expressions still enable rapid computation of the mass balances, allowing for facile performance comparisons across a range of input parameters. Solving for the time-dependent species concentrations requires evaluating the eigendecomposition of the rate constant matrix \( \mathbf{K} \) during both charge and discharge, as the sign of the current changes. However, assuming transport properties in the membrane / separator do not change during cycling, these computations only need to be performed once at the outset. Using the eigenvalues and eigenvectors of \( \mathbf{K} \), the vector \( \theta \) can be determined from Equation (17) and then transformed into the concentration vector using Equation (18). Similar to the case of homogeneous species decay, the charge and discharge times must be determined by solving nonlinear algebraic equations at each half-cycle, either for the limiting current case or for the cutoff voltage case. The \( VE \), in turn, can be determined by numerically integrating the resultant cell voltage.

Of particular interest is the comparison of different membrane / separator property combinations that govern crossover fluxes; specifically, tradeoffs between ionic conductivity of and redox species diffusivity through the membrane / separator give rise to variable capacity fade rates, voltage losses, and \( EE \).\(^{19}\) Using this framework, we can establish clear connections between these fundamental transport parameters and cell performance metrics. However, we again note that the purpose of this report is to highlight representative comparisons as opposed to providing a comprehensive sweep of parameter combinations. For simplicity, we neglect the electro-osmotic
component of the flux \( (\xi = 0) \), set individual species diffusion coefficients equal to each other, assume the redox species share ionic charges (i.e., \( z_A = z_B = 1 \), \( z_{A'} = z_{B'} = 2 \)), assume unity absorption \((K_j = 1)\), and fix the membrane thickness \((l_m = 100 \mu m)\).

**Figure 6** shows capacity fade and cycling efficiencies for variable diffusion coefficients and membrane conductivities which reflect typical property ranges observed across both aqueous and nonaqueous redox flow cells. As expected, higher diffusion coefficients yield faster crossover rates, resulting in increased capacity fade rates (**Figure 6a**). The capacity initially decays rapidly before asymptotically approaching a steady value below 50% of the theoretical capacity, as mixing between the electrolytes slows diffusion (*vide infra*). Despite the marked capacity loss, the differing diffusion coefficients weakly impact the \( EE \), as the \( VE \) remains largely unaffected and the \( CE \) only varies between ca. 95% – 99%.

Interestingly, membrane conductivity has a significant influence on both capacity fade and \( EE \) (**Figure 6b**). Increasing conductivity reduces the driving force (i.e., potential drop) for ion migration, thus lowering crossover rates for ionic redox species, diminishing fade rates, and improving \( CE \). Further, enhancing membrane conductivity lowers ohmic losses during cell charge and discharge, enhancing \( VE \). Overall, this representative comparison suggests that membrane conductivity more strongly drives \( EE \) under these conditions. However, cycling stability requires the system to be reasonably tolerant to crossover-driven capacity fade, which can typically be achieved by using sufficiently-selective membranes or by generating compositionally-identical electrolytes on either side of the membrane via pre-mixing (i.e., spectator strategy).
Figure 6. (a) Discharge capacity and energy efficiency ($EE$) as a function of cycle number for varying redox species diffusion coefficients with constant conductivity ($\sigma_m = 10 \text{ mS cm}^{-1}$). (b) Discharge capacity and $EE$ as a function of cycle number for varying membrane conductivities with constant diffusion coefficients for all redox species ($D^m_j = 10^{-12} \text{ m}^2 \text{s}^{-1}$). For all simulations, $I = 25.5 \text{ mA (10 mA cm}^{-2})$, OCV $= 2 \text{ V}$, $C_{A^-} = C_{B^+} = 0 \text{ mol m}^{-3}$ for the first half-cycle, $l_m = 100 \text{ μm}$, $R_c = 0 \text{ Ω}$, $z_A = z_B = 1$, $z_{A^+} = z_{B^+} = 2$, $\xi = 0$, and $Q = 10 \text{ mL min}^{-1}$ for both electrolytes. For all species, $D_j^\infty = 1 \times 10^{-9} \text{ m}^2 \text{s}^{-1}$ and $K_j = 1$. 
Pre-mixing the positive and negative electrolytes can reduce diffusional driving forces for species crossover (i.e., pseudo-symmetry), which helps to maintain stable performance across the battery lifetime, albeit at the expense of achievable energy density, as mixing typically limits the solubility of either redox species.\textsuperscript{56} Considering that relative differences in species-specific crossover rates can still lead to concentration imbalances, this strategy may not always yield perfect capacity retention over extended cycling. However, capacity can typically be recovered by re-mixing the electrolytes at some predetermined threshold, provided other irreversible decay mechanisms are negligible. Using this framework, we can examine factors that influence crossover-driven capacity fade for pre-mixed cells and predict scenarios where remediation may be required. To this end, \textbf{Figure 7} highlights the influence of membrane conductivity and varying diffusion coefficients on capacity retention. Here, we fix $D_A^m = D_A^w$ and $D_B^m = D_B^w$ as a representative example, although we anticipate that deviation from this assumption will impact fade rates, which will further vary depending on other membrane-electrolyte properties (e.g., ionic charge, sorption coefficients) and cell operating conditions (e.g., applied current).

Despite the lower diffusional driving force due to pre-mixing, migration plays a sizeable role in the crossover rates, as the species flux is dependent on the magnitude of the electric field, which is augmented for less conductive membranes.\textsuperscript{35} Differences in crossover rates lead to concentration imbalances that manifest as capacity fade; however, as the species concentrations evolve over time, the diffusive and migration fluxes eventually approach a steady state, leading to stable capacities well below the expected theoretical capacity. Similar effects have been reported in earlier experimental cell cycling studies, where more selective (i.e., lower conductivity, lower permeability) membranes displayed higher capacity fade rates.\textsuperscript{57,58} Indeed, our model begins to shed further light on the theoretical underpinnings that govern these phenomenological
observations, further underscoring the value of this framework for understanding performance characteristics.

**Figure 7.** Discharge capacity as a function of cycle number for pre-mixed electrolytes with varying redox species diffusion coefficients ($D_A^m = D_B^m$) and varying membrane conductivities. The diffusion coefficients of $B$ and $B^+$ are also identical and fixed at $D_B^m = D_B^m = 10^{-12}$ m$^2$ s$^{-1}$. The gray dashed line indicates the theoretical capacity. For all simulations, $I = 25.5$ mA (10 mA cm$^{-2}$), $C_A^{\alpha, -} = C_B^{\alpha, +} = 500$ mol m$^{-3}$ for the first half-cycle, $l_m = 100$ μm, $R_e = 0$ Ω, $\zeta_A = \zeta_B = 1$, $\zeta_A^- = \zeta_B^+ = 2$, $\xi = 0$, and $Q = 10$ mL min$^{-1}$ for both electrolytes. For all species, $D_j^\infty = 1 \times 10^{-9}$ m$^2$ s$^{-1}$ and $K_j = 1$. 
3.4. Treatment of electrochemical kinetics

Thus far, we have contemplated redox couples, electrolyte formulations, and electrode combinations which obviate kinetic losses; however, several contemporary RFB chemistries (e.g., all-vanadium, iron-chromium) exhibit sluggish redox kinetics that contribute measurably to VE.\(^1\) While the derivation of analytical solutions to the mass balances for galvanostatic cycling is the primary focus of this work, it is worth considering how predictions for the cell voltage and VE may be refined through extensions of this mathematical framework.

Describing increasingly complex kinetic and ohmic losses presents a tradeoff between accurate predictions of the cell voltage and tractable simulation times. However, the need for incorporating these features ultimately depends on the redox couple properties, electrolyte conductivities, as well as electrode microstructures and surface chemistry. For example, sluggish redox reactions may necessitate treatment of electrochemical kinetics whereas thicker electrodes (e.g., carbon felts) and low electrolyte conductivities may require consideration of distributed ohmic losses. To exemplify these differences, we explore models for Butler-Volmer kinetics and one-dimensional (1D) porous electrodes as described in Section S7.

Figure 8 shows discharge voltage profiles simulated in the absence of capacity fade using Nernstian behavior (Equation (25)), uniform Butler-Volmer kinetics (Equation (S17)), and 1D porous electrode kinetics (Equation (S21)). For both Butler-Volmer kinetics and the porous electrode, we explore different kinetic rate constants \((k_o^+ = k_o^- = 10^{-3}, 10^{-5} \text{ cm s}^{-1})\) with typical outer-sphere, one-electron transfer coefficients \((\alpha_o^+ = \alpha_c^+ = \alpha_o^- = \alpha_c^- = 0.5)\). For the porous electrode, we use relatively low effective electrolyte conductivities \((\kappa_{\text{eff}} = 10 \text{ mS cm}^{-1})\) to accentuate disparities between the models. The relative times to generate each curve reflect the tradeoffs between accuracy and solvability; specifically, the Nernstian, uniform Butler-Volmer,
and 1D porous electrode simulations required ca. 0.03 s, 5 s, and 13.5 min per cycle, respectively. While porous electrode theory refines the cell voltage calculation, the increase in computation time required to solve boundary value problems challenges simulations that span tens to hundreds of cycles. Moreover, in some instances, this refinement has diminishing returns; for example, redox couples with faster kinetics \( k^{o,+} = k^{o,-} > 10^{-3} \text{ cm s}^{-1} \) are well-described by Nernstian behavior under most conditions, so more detailed kinetic expressions only slightly improve the accuracy. Lastly, we note that although the 1D porous electrode refines ohmic losses resulting from the electrolyte and electrode, these could also be crudely approximated using the Nernstian or uniform Butler-Volmer expressions through the \( R_c \) parameter.

**Figure 8.** Discharge voltage profiles in the absence of capacity fade for varying methods of calculating the cell voltage: Nernstian behavior, uniform Butler-Volmer kinetics (BV), and one-dimensional porous electrode kinetics (1D). For all simulations, ASR\( \Omega \) = 1 \( \Omega \text{ cm}^2 \), \( I = 255 \text{ mA} \) (100 mA cm\(^{-2}\)), \( Q = 10 \text{ mL min}^{-1} \) for both electrolytes, and \( D_f^{\infty} = 1 \times 10^{-9} \text{ m}^2 \text{ s}^{-1} \) for all species. For BV and 1D simulations, \( \alpha_a^+ = \alpha_c^+ = \alpha_a^- = \alpha_c^- = 0.5 \) and \( k^{o,+} = k^{o,-} \). For 1D simulations, \( \kappa_{\text{eff}} = 10 \text{ mS cm}^{-1} \).
3.5. Multiple electrolyte domains

This modeling framework also enables treatment of multiple spatial domains, which may be incorporated to better approximate cell behavior.\textsuperscript{15} Thus far, we have treated each half-cell as a well-mixed, continuous domain with homogeneous reactions occurring throughout. While this assumption is analytically convenient and captures cycling behavior reasonably well, differences in residence times between the electrochemical cell, electrolyte reservoirs, and connecting tubing may introduce spatial variations in concentration.\textsuperscript{10,15} These effects become more pronounced under conditions with high reactant conversion per pass (i.e., low flow rates and high current densities).

Fortunately, reactant flows manifest as first-order terms in the reactor mass balances, as material entering and leaving each domain is a linear function of the concentration and volumetric flow rate. For example, distinguishing the electrolyte storage tanks and redox flow cell yields the generalized mass balances shown in Equations (42) and (43).

\[
\frac{dC_{j}^{\text{rk,h}}}{dt} = \frac{Q}{V_{\text{rk,h}}} \left( C_{j}^{\text{fc,h}} - C_{j}^{\text{rk,h}} \right) + \sum R_{j}^{\text{rk,h}} 
\]

(42)

\[
\frac{dC_{j}^{\text{fc,h}}}{dt} = \frac{Q}{V_{\text{fc,h}}} \left( C_{j}^{\text{rk,h}} - C_{j}^{\text{fc,h}} \right) + s \frac{I}{V_{\text{fc,h}} F} + \sum R_{j}^{\text{fc,h}} 
\]

(43)

Here, $C_{j}^{\text{rk,h}}$ and $C_{j}^{\text{fc,h}}$ (mol m$^{-3}$) are the bulk concentrations of species $j$ in the tank and the flow cell, respectively; $V_{\text{rk,h}}$ and $V_{\text{fc,h}}$ are the electrolyte volumes in the tank and flow cell, respectively; $\sum R_{j}^{\text{rk,h}}$ and $\sum R_{j}^{\text{fc,h}}$ are loss terms in the tank and flow cell, respectively. Note that the loss terms in the tank comprise only species decay and self-discharge reactions whereas the loss terms in the flow cell also include crossover.
Combining the mass balances here results in a system of 12 coupled differential equations in contrast to 6 in the original formulation. However, solving this system of equations utilizes the same general strategy described in Equations (13) – (18) with volumetric flow rates incorporated into the matrix $K$. Thus, despite the small increases in computational complexity that arise with increasing spatial resolution, the presence of analytical solutions in more complex domains may still facilitate reductions in simulation time compared to numerical methods.
4. Conclusions

In this work, we derived an analytical, zero-dimensional model for galvanostatic cell cycling in a redox flow cell. This framework enables clear elucidation of the connections between cell material properties, operating conditions, and performance metrics, informing molecular, electrolyte, and cell design rules. To this end, we described several representative scenarios, characteristic in RFB research and development, that can be treated with varying degrees of analytical complexity. We showed that upper bound estimates for VE, accessible capacity, and cycling behavior may be obtained from explicit analytical equations. By incorporating redox species decay, we simulated the effects of decomposition and self-discharge on capacity fade for diagnostic symmetric cells. Treatment of species crossover allowed us to explore the role of membrane / separator conductivity-selectivity tradeoffs in predicting capacity fade and EE for asymmetric and pre-mixed (pseudo-symmetric) electrolytes. Lastly, we introduced modalities for including kinetic losses, distributed ohmic losses, and multiple spatial domains, highlighting routes for expanding this framework. Considering the relative simplicity and computational efficiency of the analytical models presented here, this approach is anticipated to be broadly useful for materials discovery, cell engineering and operation, as well as system-level techno-economic modeling.
CRediT authorship contribution statement

**Bertrand J. Neyhouse**: Conceptualization, Data curation, Investigation, Methodology, Software, Validation, Visualization, Supervision, Writing – original draft, Writing – review and editing.

**Jonathan Lee**: Investigation, Methodology, Software, Validation, Visualization, Writing – original draft, Writing – review and editing.

**Fikile R. Brushett**: Conceptualization, Funding acquisition, Project administration, Resources, Supervision, Writing – original draft, Writing – review and editing.

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Nomenclature

Roman symbols

\( A_{ed} \)  Accessible surface area of the electrode (m\(^2\))
\( A_m \)  Geometric membrane area (m\(^2\))
\( \text{ASR}_{\Omega} \)  Area-specific ohmic resistance (\( \Omega \) m\(^2\))
\( b \)  Constant reaction rate vector (mol m\(^{-3}\) s\(^{-1}\))
\( C \)  Concentration vector (mol m\(^{-3}\))
\( C^0 \)  Initial concentration vector (mol m\(^{-3}\))
\( C_{j}^{\infty,h} \)  Bulk concentration of species \( j \) in half-cell \( h \) (mol m\(^{-3}\))
\( C_{j}^{fc,h} \)  Bulk flow cell concentration of species \( j \) in half-cell \( h \) (mol m\(^{-3}\))
\( C_{j}^{o,h} \)  Initial concentration of species \( j \) in half-cell \( h \) at the beginning of each half-cycle (mol m\(^{-3}\))
\( C_{j}^{t,h} \)  Electrode surface concentration of species \( j \) in half-cell \( h \) (mol m\(^{-3}\))
\( C_{j}^{sk,h} \)  Bulk tank concentration of species \( j \) in half-cell \( h \) (mol m\(^{-3}\))
\( C_{site} \)  Concentration of fixed ion sites in the membrane (mol m\(^{-3}\))
\( \text{Cap}_c \)  Charge capacity (C)
\( \text{Cap}_d \)  Discharge capacity (C)
\( \text{CE} \)  Fractional coulombic efficiency
\( d_f \)  Electrode fiber diameter (m)
\( D_{j}^{e} \)  Diffusion coefficient of species \( j \) in the bulk (m\(^2\) s\(^{-1}\))
\( D_{j}^{m} \)  Diffusion coefficient of species \( j \) in the membrane (m\(^2\) s\(^{-1}\))
\( E_{j}^{o,h} \)  Formal redox potential in half-cell \( h \) (V)
\( \bar{E}_c \)  Average charging voltage (V)
\( \bar{E}_d \)  Average discharging voltage (V)
\( \text{EE} \)  Fractional energy efficiency
\( f_j \)  Fraction of \( j \) that decays via self-discharge
\( F \)  Faraday’s constant (96485 C mol\(^{-1}\))
\( I \)  Applied current, denoted as positive for charging and negative for discharging (A)
\( k_{c,j}^{h} \)  Crossover rate constant for species \( j \) in half-cell \( h \) (s\(^{-1}\))
\( k_{d,j} \)  Decay rate constant for species \( j \) (s\(^{-1}\))
\( k_{m,j} \)  Mass transfer coefficient of species \( j \) (m s\(^{-1}\))
\( k_{o}^{h} \)  Standard rate constant in half-cell \( h \) (m s\(^{-1}\))
\( K \)  Rate constant matrix (s\(^{-1}\))
\( K_j \)  Membrane sorption coefficient of species \( j \)
\( l_{ch} \) Length of flow field channels (m)
\( l_e \) Electrode thickness (m)
\( l_m \) Membrane thickness (m)
\( n_{ch} \) Number of flow field channels
\( N_j \) Flux of species \( j \) through the membrane (mol m\(^{-2}\) s\(^{-1}\))
\( OCV \) Open-circuit voltage (V)
\( Q \) Volumetric flow rate (m\(^3\) s\(^{-1}\))
\( R \) Universal gas constant (8.314 J mol\(^{-1}\) K\(^{-1}\))
\( R_c \) Additional ohmic resistances (\(\Omega\))
\( R_{fc,h}^j \) Flow cell source term for species \( j \) in half-cell \( h \) (mol m\(^{-3}\) s\(^{-1}\))
\( R_{h}^j \) Source term for species \( j \) in half-cell \( h \) (mol m\(^{-3}\) s\(^{-1}\))
\( R_{tk,h}^j \) Storage tank source term for species \( j \) in half-cell \( h \) (mol m\(^{-3}\) s\(^{-1}\))
\( R_m \) Membrane ohmic resistance (\(\Omega\))
\( s_{j}^h \) Stoichiometric coefficient of species \( j \) in half-cell \( h \)
\( t \) Time (s)
\( t_c \) Charge time (s)
\( t_d \) Discharge time (s)
\( T \) Temperature (K)
\( U \) Eigenvector matrix of \( K \)
\( V_{fc,h} \) Flow cell volume in half-cell \( h \) (m\(^3\))
\( V^h \) Total electrolyte volume in half-cell \( h \) (m\(^3\))
\( V_{tk,h} \) Tank volume in half-cell \( h \) (m\(^3\))
\( VE \) Fractional voltaic efficiency
\( x \) Position in the porous electrode (m)
\( z_j \) Ionic charge of species \( j \)

**Greek symbols**

\( \alpha_{a}^h \) Anodic transfer coefficient in half-cell \( h \)
\( \alpha_{c}^h \) Cathodic transfer coefficient in half-cell \( h \)
\( \beta_i \) \( i^{th} \) element of vector \( \beta \) (mol m\(^{-3}\) s\(^{-1}\))
\( \beta \) Transformed constant reaction rate vector (mol m\(^{-3}\) s\(^{-1}\))
\( \gamma_j \) Dimensionless flux parameter
\( \varepsilon \) Electrode porosity
\( \theta_i \) \( i^{th} \) element of vector \( \Theta \) (mol m\(^{-3}\))
\( \theta_i \)  
\( i \)th element of vector \( \Theta^o \) (mol m\(^{-3}\))

\( \Theta \)  
Transformed concentration vector (mol m\(^{-3}\))

\( \Theta^o \)  
Transformed initial concentration vector (mol m\(^{-3}\))

\( \kappa_{\text{eff}} \)  
Effective electrolyte conductivity (S m\(^{-1}\))

\( \lambda_i \)  
\( i \)th element of matrix \( \Lambda \) (s\(^{-1}\))

\( \Lambda \)  
Diagonal eigenvalue matrix of \( K \) (s\(^{-1}\))

\( \mu \)  
Electrolyte viscosity (Pa s)

\( \nu \)  
Molar ratio of solvent to fixed ion sites in the membrane

\( \xi \)  
Dimensionless electro-osmotic coefficient

\( \rho \)  
Electrolyte density (kg m\(^{-3}\))

\( \sigma_m \)  
Membrane conductivity (S m\(^{-1}\))

\( \Phi^h \)  
Electrode potential in half-cell \( h \) (V)
5. References


