Enabling Low-Cost Electrolytes and Membranes for Redox Flow Batteries

by

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To all fellow electrochemists.
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ABSTRACT

The transition to renewable energy sources like solar and wind (which are intermittent) depends on the availability of low cost energy storage. Redox Flow batteries (RFBs) show promise as an alternative to lithium-ion batteries for long duration storage. Low-cost Organic redox-active molecules can potentially replace costly vanadium in RFBs, but their high rates of degradation prevent their use in practical RFBs. We use a combination of experiments, numerical simulations and data-driven methods to understand the degradation of organic molecules, and membrane crossover of active materials.

We develop and validate a zero-dimensional model as a tool to analyze the electrochemical performance of an organic flow cell. The model simulates voltage losses using parameters obtained from independent electrochemical impedance spectroscopy and voltammetry measurements to accurately simulate a symmetric ferro-/ferricyanide cell’s performance across a wide range of current densities and electrolyte flow rates. The model also simulates capacity fade caused by molecular degradation and a considerable variation in the capacity fade rates during cell cycling because of changes in the cycling protocol.

We then use ultraviolet-visible spectrophotometry and statistical inference techniques to understand molecular degradation in organic redox-active molecules and
elucidate the Michael attack decay mechanism for 4,5-dihydroxy-1,3-benzenedisulfonic acid (BQDS), a once-promising molecule for RFBs. Bayesian inference and multivariate curve resolution is used on the spectroscopic data to derive reaction orders and rates for Michael attack, estimate the spectra of intermediate species and establish a quantitative connection between molecular decay and capacity fade.

Several quinoxaline derivatives (despite promising electrochemical properties) demonstrate poor chemical stability (with capacity fade rates > 20%/day). We find the reduced form of 2,3-dimethylquinoxaline-6-carboxylic acid (DMeQUIC) losing redox-activity due to tautomerization in alkaline conditions. Using spectroscopic, electrochemical and data-driven techniques, we estimate the kinetic rate constants for the tautomerization reaction. Density functional theory (DFT) modeling qualitatively explains stability trends for several derivatives, among which quinoxaline-2-carboxylic acid showed a stable performance during mixed symmetric cell cycling.

Membrane crossover of redox-active molecules is another significant cause of capacity fade and we explore the use of sodium superionic conductor (NaSICON) membranes as a means to prevent it. NaSICON is stable in neutral and strongly alkaline sodium-containing electrolytes, but degrades rapidly when potassium-ions are present. NaSICON’s resistance decreases sharply on increasing temperature and decreasing thickness, and successfully blocks permanganate and polysulfide crossover. We then demonstrate a stable cycling ferrocyanide | permanganate flow cell for three weeks using a NaSICON membrane.

This work therefore presents a framework to enable researchers to understand and mitigate degradation of novel organic redox-active molecules in RFBs.

xxx
CHAPTER I

Introduction

1.1 Motivation

Renewable energy generation has witnessed rapid developments in recent years owing to a push to decarbonize the grid. However the intermittent nature of renewables such as solar and wind energy mandates the presence of economical and scalable energy storage. [1, 2, 3, 4] Redox-flow batteries (RFBs) show great promise of providing a viable solution. [5] RFBs consist of pair of redox-active reactants dissolved in electrolytes which store electrochemical energy. Interconversion between chemical energy and electricity is facilitated by pumping the electrolytes into an electrochemical cell, where the reactants undergo redox reactions at conductive electrodes that are charge-balanced by ion transfer through the membranes, which selectively permit ion-transfer of desired ions, and prevent the transfer of the redox-active reactants. The energy stored in the reactants can be reversibly converted into electricity. This design of RFBs provides it with a unique capability of scaling the power and energy capacity of the battery independently of one another. The energy stored is depen-
dent on the reservoir electrolyte volume and reactant concentrations. The power of RFBs scales with the conductance (which scales with size) of the reactor flow cell. As a result, when the ratio of energy to power (or discharge duration at rated power) increases, the levelized energy storage cost (in $/kWh) asymptotes to the cost of the electrolytes. [1, 2, 3, 4, 5, 6] This cost may be lower than that of standard enclosed (e.g. Li-ion) batteries if electrolyte chemicals are adequately inexpensive. [4] At present, state of the art RFBs use vanadium based redox reactants which are costly (account for over one-third of the total cost) and prevent the capital cost of the RFB system from falling to 150 $/kWh DOE target. [7] Therefore the development of low-cost electrolytes for the commercial viability of RFBs. Vanadium-based RFB development has received considerable research and commercial attention, [8, 9] however the price of vanadium undergoes large fluctuations and is high on average; the cost of electricity delivered by installed vanadium RFBs at scale might therefore not be significantly lower than next-generation Li-ion batteries. [6] The prospect of RFBs based on organic and/or organometallic active reactants is attractive because of much lower projected electrolyte costs relative to vanadium RFBs. [10] However, almost all lab-scale organic flow cells suffer from either lower energy/maximum power densities than vanadium systems, [11, 12, 13] rapid temporal capacity fade (>0.1%/day), [14] or both, which render corresponding RFBs unsuitable for deployment. In response, several studies have focused on synthesizing organic and organometallic molecules as potential RFB reactants that are chemically stable, highly soluble, and possess redox potentials that enable cell voltages above 1 V. [15, 16, 17, 18, 19, 20, 21] These efforts have yielded RFB chemistries with fairly high maximum power densities (e.g.
∼1 W cm$^2$ for a quinone-bromine chemistry), [22] and others with extremely low fade rates (< 0.01%/day). [23, 24].

While the aforementioned studies have shown several promising materials for practical RFBs, further research is needed to develop safe, low-cost and stable materials as low-cost alternatives to vanadium RFBs. Deploying experimental, computational and data-driven measures to further these goals forms the key motivation for this work.

1.2 Outline

The focus of this thesis is to combine computational, experimental and data-driven techniques to develop a better understanding of the factors that lead to capacity fade in organic RFBs. This includes determining degradation mechanisms for organic molecules, and identifying novel molecules that exhibit stable cycling behavior, and studying NaSICON membranes as an alternative to polymer membranes for preventing reactant crossover. Additionally, this chapter provides a techno-economic analysis in Sec. 1.3 which shows potential cost savings from developing low-cost redox-active materials and separator/membranes for RFBs as compared to RFBs using vanadium-based electrolytes and polymer membranes.

In Chapter II, a zero-dimensional model is developed to simulate the performance of RFBs. The model accurately predicts cell cycling behavior under a wide range of operating conditions, and demonstrates the effect of cycling protocol, i.e., the applied current and voltage limits, on the temporal capacity fade rate during cell cycling caused by reactant decay. The modular nature of this model allows the incorporation
of a wide range of degradation mechanisms, which may be determined by the user. Additionally, the model also simulates pH swing during cycling CO$_2$ capture and predicts the energy inputs and productivity rates for a variety of operating conditions and reactor design parameters.

Chapter III demonstrates a method that combines experimentally obtained UV-vis spectroscopic data with data-driven methods like Bayesian learning to confirm the reaction mechanism and predict rate constants for the Michael Addition of water to a high-potential redox-active molecule. The method developed is promising for determining unknown degradation mechanism and discerning between competing hypotheses for novel molecules being researched.

In Chapter IV, the method developed in Chapter III is applied to study the degradation of quinoxalines, which are a less studied but promising class of redox-active molecules. Competing hypotheses found in literature are tested to find tautomerization to be the primary cause of degradation. Quinoxaline derivatives are also found to be susceptible to membrane crossover, causing rapid capacity loss. However, a degradation resistant derivative is identified and tested, showing stable cycling in a compositionally symmetric cell.

Apart from molecular degradation, crossover of redox-active materials causes considerable capacity fade in RFBs, and prevents the use of several low-cost organic and inorganic molecules. Chapter V explores the stability of NaSICON in sodium containing electrolytes, and its degradation when potassium ions are present. The chapter then observes the effect of temperature on the conductivity of NaSICON, tests the ability of NaSICON to block crossover and enable stable cycling behavior.
for RFBs containing iron, manganese and phenazine based redox-active materials.

Chapter VI summarizes the findings of the chapters and discusses the opportunities for utilizing this work in future studies and directions for expanding upon it for researchers working in the field of organic flow batteries.

1.3 A techno-economic analysis of RFBs

An analysis by [25] shows that a 1000 kW RFB system designed for a 12 hour discharge duration has a capital cost of $380/kWh. Of this, 31% accrues to the cell stack components (assuming membrane and carbon felt costs of 500 and 20 $/m² respectively), 37% to vanadium-based electrolytes (costing $21/kg) and the remaining 32% (122$/kWh) to tanks, pumps, heat exchangers and balance of plant. The material costs of RFBs (/kWh) are calculated as

\[ C_m = \frac{3600 \times \left( \frac{c_p \times W_p}{N_p} + \frac{c_n \times W_n}{N_n} \right)}{V_{cell} \times F \times \eta_e \times \Delta_{SOC}}. \] (1.1)

The storage costs of the cell stack which includes separator membrane and graphite electrodes are calculated as

\[ C_{stack} = \frac{c_{sep} + 2c_g}{\iota_{ap} \times V_{cell} \times \eta_e \times \tau}. \] (1.2)

where the variables in Eqn. (1.1) and Eqn. (1.2) are shown in Table 1.1, with
subscripts $p$ and $n$ denoting the cathode and anode respectively.

Table 1.1: Description of variables used in computing RFB costs from materials and cell stack components

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</tbody>
</table>

We calculate the costs of a vanadium RFB and compare them to potential RFBs using economical materials like manganese (manganate/permanganate redox couple, explored further in Chapter V), zinc and a hypothetical low cost organic molecule in Fig. 1.1. The calculations for the vanadium RFB (with a polymer membrane costing $500/m^2$) are performed similar to [25], while those for the Mn—Zn and Mn—Organic RFBs assume a sodium superionic conductor (NaSICON) membrane (costing a hypothetical $10/m^2$). The precursors of NaSICON, namely Zirconium (IV) carbonate hydroxide (Zr(OH)$_2$CO$_3$.9.6H$_2$O, Ammonium phosphate monobasic and Sodium metasilicate penta hydrate cost and 1.2, 0.7 and 0.5 $$/kg respectively according to https://www.indiamart.com (accessed on September 9 2023). A NaSICON membrane of 0.5 mm thickness will require about 1.7 kg of precursor materials
assuming a density of 3.3 g/cm$^3$. [26] Based on these estimates an assumption of 10 $/m^2$ is made for NaSICON membrane costs.

The variables for these cells are stated in Table 1.2. We assume the RFBs to have a fixed cost pertaining to balance of plant ($C_{BOP}$) of $122/kWh, [25] with the total cost ($C_{RFB}$) calculated as

$$C_{RFB} = C_m + C_{stack} + C_{BOP}.$$  

(1.3)

Figure 1.1: Material, cell stack and total RFB cost calculations for a vanadium RFB using a polymer membrane and potential RFBs that may be built using zinc (anode) and permanganate (cathode) and another using a hypothetical organic molecule (anode) and permanganate (cathode) at various durations.

This analysis excludes the cost of supporting electrolytes and solvents leading to the material costs for the vanadium RFB to be $116/kWh instead of the $140/kWh
Table 1.2: Variables used in cost calculations for RFBs built using vanadium, zinc, manganese and a hypothetical organic molecule

| Variable | vanadium | Zn|Mn (Zn(OH)$_2$|MnO$_2$) | Organic|Mn |
|----------|----------|----------------|----------------|----------------|
| $c_n$ | $c_p$ ($/kg$) | 21|21 | 0.46|0.54 | 1|0.46 |
| W (g/mol) | 51|51 | 99.4|84 | 200|84 |
| N | 1|1 | 2|1 | 2|1 |
| $i_{ap}$ (kA/m$^2$) | 0.4 | 0.1 | 0.1 |
| $V_{cell}$ (V) | 1.26 | 1.9 | 1.5 |
| $\eta_e$ | 0.91 | 0.9 | 0.875 |
| $\Delta_{SOC}$ | 0.6 | 1 | 1 |
| $c_{sep}$ ($/m^2$) | 500 | 10 | 10 |
| $c_g$ ($/m^2$) | 20 | 20 | 20 |
| $C_{BOP}$ ($/kWh$) | 122 | 122 | 122 |

stated by [25]. Figure 1.1 that the material cost would fall to $1.5 and 4.0/kWh for a Zn—Mn and the hypothetical Organic—Mn RFB respectively (the costs for Zn(OH)$_2$ and MnO$_2$ in Table 1.2 were obtained from https://dir.indiamart.com/ accessed on September 1, 2023.), reducing total RFB cost (computed using Eqn. (1.3)) by over $110/kWh. A further reduction of $170/kWh can be achieved by replacing the polymer membrane with NaSICON for a rated discharge duration of 12 hours. Thus, the use of low-cost redox-active molecules and separator membranes can reduce the total cost by about 280 $/kWh. Further savings in reactor and BOP costs can be achieved by optimizing the cell design and using redox-active molecule pairs which provide a higher cell voltage, allow higher current densities and reactant concentrations than vanadium-based RFBs. [25]
1.4 Individual and group research statement

The work presented in this thesis was involved collaborations with coworkers in the David Kwabi lab along with others labs at the University of Michigan. These collaborations with co-workers and co-authors are summarily acknowledged in this section.

In Chapter II Sanat Vibhas Modak developed the zero-dimensional model and performed all associated simulations and experiments associated with it. David Kwabi supervised the research. A part of this work has been published [27] and adapted with permission. The part pertaining to CO$_2$ capture is a part of a manuscript titled “Assessing Performance Limits of Electrochemical CO$_2$ Separation using Exergy Loss Analysis and Zero-Dimensional Modeling” under review in ACS Sustainable Chemistry & Engineering.

Chapter III was adapted with permission from [28] Sanat Vibhas Modak., Xun Huan and David Kwabi designed the study; Sanat Vibhas Modak and Fairooz Oudeif conducted the experiments; Wanggang Shen performed Bayesian inference analysis; Siddhant Singh. performed MCR-ALS analysis; Dylan Herrera conducted DFT calculations under the supervision of Bryan Goldsmith; David Kwabi, Xun Huan and Bryan Goldsmith supervised and guided the research. All authors contributed towards the writing of this manuscript.

All experiments in Chapter IV were performed by Sanat Vibhas Modak except those pertaining to 2,3-dimethyl-1,2,3,4-tetrahydro-quinoxaline-6-carboxylic acid which were performed by Jessica Tami. Jessica Tami also contributed to the analysis and post-processing of NMR spectra. Daniel Pert contributed to the DFT calculations
while Wanggang Shen performed Bayesian inference calculations. Xun Huan, Anne McNeil, Bryan Goldsmith and David Kwabi supervised the research.

Chapter V was adapted with permission from [29]. Sanat Vibhas Modak performed the experiments pertaining to flow cell and H-cell testing of NaSICON membrane pellets. The NaSICON pellets were synthesized by Joseph Valle and Kang-Ting Tseng. Jeff Sakamoto and David Kwabi supervised the research. All authors contributed towards the writing of this manuscript.
CHAPTER II

A Zero-Dimensional Model for Electrochemical Behavior and Capacity Retention in Organic Flow Cells

2.1 Introduction

The development of practically viable novel RFB chemistries is hampered in part because it is challenging to understand capacity retention in lab-scale flow cells in terms of the interaction among the cell’s electrochemical properties, mode of operation, and the loss mechanisms to which its active reactants are susceptible. This challenge exists because multiple factors compose a flow cell’s electrochemical response, including: (1) charge transfer impedance and mass transport resistance; (2) the chemical and electrochemical stability of its active reactants; (3) its membrane’s permeability to active reactants; and (4) whether the flow cell is cycled at constant current, constant voltage or a combination of these protocols. [30] Quantifying the dynamic impact of these factors on voltage-current data and capacity retention of-
fers a pathway to understanding and efficiently developing new RFB chemistries and effective operating strategies of the same, but requires a framework that captures the above interactions while yielding predictions that are straightforward to compare to measurements from typical charge-discharge cycling experiments. Considerable effort has been expended on understanding the influence of electrode microstructure and chemistry on electrochemical properties of various flow cells using zero- [31, 32] one, [33, 34, 35] two, [36, 37, 38] and three-dimensional, [39, 40, 41, 42] analytical and data-driven numerical models. [43, 44, 45] High-dimensional models can represent complex electrochemical phenomena in minute detail, but tend to require long computational times and several fitting parameters, whereas low-dimensional models are simpler, but typically do not fully correspond to underlying electrochemical processes. In the organic flow battery literature, a number of studies have sought to determine reactant degradation mechanisms that are principally responsible for capacity fade in flow cells [46, 47, 48, 49] using in operando and ex situ chemical analysis of electrolyte composition. Nevertheless, the combined influence of electrochemical properties of a flow cell, cycling protocol and reactant loss mechanism on the observed capacity fade has not received significant attention.

We have developed a zero-dimensional multi-domain model of an organic flow cell that can account for how its electrochemical properties, mode of operation, and reactant loss mechanisms yield its voltage-current and capacity retention behavior. Electrochemical behavior is described in terms of voltage losses that originate from Faradaic and Ohmic charge transfer, mass transport resistance, as well as spatial variations in state-of-charge between the cell and electrolyte reservoir. Where re-
actants concentrations are low enough to obtain a mass transport-limited current, all variables in the model can be determined prior to the cycling experiment using electrochemical impedance spectroscopy (EIS) and voltammetry measurements. We assessed the model by comparing simulated voltage-current data to analogous experimental measurements for a compositionally symmetric cell containing the ferri-/ferrocyanide (Fe(CN)$_6^{3-}$/Fe(CN)$_6^{4-}$) redox couple, and found close agreement for constant-current and constant-voltage cycling, across a wide range of applied current densities (40–120 mA/cm$^2$) and electrolyte circulation rates (≈10–140 ml/min). We also demonstrate that our model is relevant to understanding capacity retention in organic flow cells by using it to simulate capacity fade under various hypothetical combinations of cycling protocol and reactant decay mechanism. This work shows that zero-dimensional modeling of organic flow cells is a practical way of understanding and optimizing their behavior.

2.2 Model Theory

We modeled a flow cell that consists of two electrolytes circulating through porous conductive electrodes on both sides of a separator or ion-permeable membrane. Each electrolyte comprised a redox couple that undergoes an electrochemical reaction, Ox + e$^-$ → Red, where Ox and Red are the oxidized and reduced states of the redox couple, respectively. Ox and Red need not be organic or organometallic species. The following is a description of how the model is implemented, and how it handles kinetic, Ohmic and mass transport-related voltage losses.
2.2.1 Multi-domain model implementation

We executed our model within a MATLAB Simulink multi-domain numerical framework that consists of “variable blocks,” which represent key parameters relevant to flow cell performance, and “operation blocks” which carry out mathematical operations on the outputs from the variable blocks (Fig. 2.1). These mathematical operations correspond to the equations that govern chemical and electrochemical processes in the flow cell, and their outputs are inputs to variable blocks. The variable blocks keep track of the flow cell’s voltage and current, the concentrations of all redox-active species within each electrolyte, etc Concentrations of the various active reactants evolve in time based on the applied current, and reactant loss mechanisms (e.g. decomposition and crossover). A conceptual representation of the workflow within the model is shown in Fig. 2.1. The cycling protocol sets a fixed applied current at which the cell is charged or discharged within user-defined terminal voltage limits. When the cell reaches either voltage limit, the protocol either reverses the cell’s polarity or first holds it at the voltage limit until the current decays to a preset cut-off value. Concentrations of reduced and oxidized forms of the active redox couple update according to Coulomb counting at each time step iteration, and determine the open-circuit voltage of the cell. These concentrations and the current collectively determine voltage losses which, given the open-circuit voltage, yields the cell voltage. The cell voltage continuously feeds into the cycling protocol, which decides the current magnitude and polarity for the next time step.
2.2.2 Electrochemical cycling and reactant concentration tracking

The model keeps track of reactant concentrations in each electrolyte using Coulomb counting, \([32, 50]\) i.e. integrating the current of the flow cell as a function of time since an initial composition. For instance, the concentration of molecules in the oxidized redox state of an electrolyte at any time \(t\) is:

\[
C_0 = C^T(1 - SOC_i) + \int_0^t \frac{I}{nF_{el}}. \tag{2.1}
\]

Here \(SOC_i\) is the initial state-of-charge (i.e. at time = 0), with the state-of-charge defined as the fraction of the electrolyte comprising reduced species, \([\text{red}] / ([\text{red}] + [\text{ox}])\). \(L_{el}\) is the volume of the electrolyte, and \(C^T\) is the total concentration of the
redox couple, ([red] + [ox]). \( I \) is the current, and is positive during oxidation and negative during reduction. We used an analogous relationship for the concentration of molecules in the reduced state.

### 2.2.3 Accounting for Voltage Losses

The voltage of the flow cell \( V \) is the sum of the open-circuit voltage (OCV) \( V_{OCV} \) and overpotentials arising from the series resistance of the cell, interfacial electron transfer between the electrode and active reactant, and mass transport, which we denote \( \Delta V_R, \Delta V_K, \) and \( \Delta V_{MT} \) respectively:

\[
V = V_{OCV} + \Delta V_R + \Delta V_K, CLS + \Delta V_K, NCLS + \Delta V_M T, CLS + \Delta V_M T, NCLS.
\] (2.2)

The subscripts “CLS” and “NCLS” denote variables related to capacity-limiting and non-capacity-limiting electrolytes, respectively. Note that these overpotentials are positive during charging of a flow cell and negative during discharge. We calculate the \( V_{OCV} \) using the Nernst equation in the dilute-solution limit, assuming that the standard potential of the redox couple in the CLS is equal to or higher than that in the NCLS:

\[
V_{OCV} = E_{cell}^0 - \frac{RT}{n_{NCLS}} \ln(\frac{1 - SOC_{NCLS}}{SOC_{NCLS}}) - \frac{RT}{n_{CLS}} \ln(\frac{1 - SOC_{CLS}}{SOC_{CLS}}).
\] (2.3)
The cell voltage $E_{cell}^0$ is the absolute value of the difference in standard potentials between the redox couples in the CLS and NCLS ($E_{CLS}^0 - E_{NCLS}^0$), and is zero in a compositionally symmetric cell. \[46\] R is the universal gas constant (8.314 J mol$^{-1}$ K$^{-1}$), T is ambient temperature (298 K), n is the number of electrons transferred per molecule, and F is Faraday’s Constant (96,485 C mol$^{-1}$). For simplicity, we assume for the remaining analysis that $n_{NCLS} = n_{CLS} = n$. The dilute-solution assumption is common in the RFB modeling literature \[32, 43\] and we justify in Sec. 2.4 its validity for ferri-/ferrocyanide at a total concentration of 100 mM, the highest concentration tested in this work. We calculated $\Delta V_K$ at each electrode assuming that the Butler-Volmer equation satisfactorily approximates its relationship to current. Note that at low activation overpotentials, the result from the Butler-Volmer equation is virtually indistinguishable from that obtained from the more accurate rate-driving force theory developed by Marcus and others. \[51\] Under this assumption, $|\Delta V_K|$ is:

$$
|\Delta V_K| = \Delta V_{K,CLS} + \Delta V_{K,NCLS}
$$

$$
= \frac{RT}{nF} \left\{ \ln \left[ \frac{|I|}{2I_{0,NCLS}} \right] + \sqrt{\ln \left[ \frac{|I|^2}{2I_{0,NCLS}^2} + 1 \right]} \right\} + \ln \left[ \frac{|I|}{2I_{0,CLS}} + \sqrt{\ln \left[ \frac{|I|^2}{2I_{0,CLS}^2} + 1 \right]} \right]. \tag{2.4}
$$

$I_0$ is the exchange current at the electrode in contact with the CLS or NCLS which, for an electron transfer coefficient $\alpha$ is $FAR_FCTk_0SOC^\alpha(1 - SOC)\alpha$. Here $k_0$ is the exchange rate constant (in cm/s), $R_F$ is the roughness factor, i.e. the ratio of active to geometric surface area ($cm^2_{active}/cm^2_{geo}$) and $A$ is the geometric area of the electrode.

$\Delta V_R$, is given by the relationship $\Delta V_R = IR$, where $R_s$ is the Ohmic series
resistance of the cell. A mass transport overpotential $\Delta V_{MT}$ arises when there is a difference between reactant concentrations at the electrode surface versus within the bulk solution. The concentration at the surface differs from the bulk concentration according to the following expression:

$$C_{R,s} - C_R = C_0 - C_{0,s} = \frac{C_{lim} I}{I_L}, \quad (2.5)$$

where $C_O$ and $C_R$ represent the bulk concentrations of oxidized and reduced species respectively, the subscript "s" denotes reactant concentrations at the electrode surface and $C_{lim}$ is the concentration of the current-limiting reactant ($C_R$ when $I > 0$ and $C_O$ when $I < 0$). The limiting current density, $I_L$ is defined as follows:

$$I_L = n F k_m C_{lim} A, \quad (2.6)$$

where $k_m$ is the mass transport coefficient, which is a function of the volumetric electrolyte flow rate $\dot{L}$, and is sensitive to how the flow field distributes electrolyte within the porous electrode. [31, 32, 50, 52]

The mass transport overpotential $\Delta V_{MT}$ is the difference between the Nernstian potential at the surface and the bulk; its absolute value is:

$$|\Delta V_{MT}| = \frac{RT}{nF} \left[\ln \frac{C_{R,s}}{C_{O,s}} - \ln \frac{C_R}{C_O}\right]. \quad (2.7)$$
By substituting expressions for surface concentrations from Eqn. (2.5) into Eqn. (2.7), we express $|\Delta V_{MT}|$ (the absolute value of the mass transport voltage loss) as a function of $I_L$, $I$, and bulk concentrations only:

$$|\Delta V_{MT}| = |\Delta V_{MT CLS}| + |\Delta V_{MT NCLS}|$$

$$= \frac{RT}{nF} \ln\left(1 - \frac{C^{T}I}{C_{O,CLS}I_{L,CLS} + C_{R,CLS}I}\right) \times \left(1 - \frac{C^{T}I}{C_{O,NCLS}I_{L,NCLS} + C_{R,NCLS}I}\right).$$

(2.8)

assuming, again, that the CLS is the high-potential reservoir and that the cell is being charged. $C_O$ and $C_R$ in Eqn. (2.8) exchange places when the cell is being discharged.

Within the multi-domain framework, we may also study the influence of a finite time for electrolyte flow between the cell and electrolyte reservoir on a flow cell’s performance, a factor that, to our knowledge, prior organic RFB modeling studies have not considered. We call this time the “cell-to-reservoir transport delay,” $t_{delay}$, where $t_{delay} = \frac{L_{manifold}}{\dot{L}}$, where $L_{manifold}$ is the total volume of the fluid line between the cell and reservoir. During cycling, $t_{delay}$ causes a deviation between the SOC (and thus the corresponding $V_{OCV}$) attained by electrolyte within the cell and that in the reservoir, in addition to a non-uniform SOC across the length of the manifold connecting the two. This deviation, if large, may impact the electrochemical performance of a flow cell significantly. We hereafter denote the difference in SOC between the reservoir and cell $\Delta SOC_{delay}$. We included the dynamic effects of $t_{delay}$ on flow cell behavior by using a Padé approximation to generate a transfer function that simulates a time lag between electrolyte leaving the reservoir and arriving at
the cell inlet, and another lag for leaving the cell outlet and reentering the reservoir. If $L_{\text{manifold}}$ is on the same order as the reservoir volume, as is possible in many laboratory-scale flow cell setups, the absolute value of $\Delta SOC_{\text{delay}}$ may be significant, and will increase with increasing applied current, decreasing electrolyte flow rate, or both. We experimentally demonstrate and account for this trend in the In operando SOC monitoring section.

### 2.2.4 Accounting for reactant decomposition and crossover

Our multi-domain framework can capture the influence of reactant decomposition (Fig. 2.1) and crossover through the membrane on the cell’s electrochemical performance. One may represent reactant loss through chemical decomposition via the appropriate decay rate law. For example, for a first order irreversible decay of the oxidized member of a redox couple according to rate constant $k'$ and reaction order $b$, the rate of decay will simply be:

$$R_{\text{decay}} = \frac{d[O_x]}{dt} = k'[O_x]^b.$$  \hfill (2.9)

$R_{\text{decay}}$ is the instantaneous rate of reactant decay, and will vary as the concentration of the oxidized species varies during cell cycling, as given in Eqn. (2.1); the decrease in the total concentration of all active species is the sum of the time integrals of the instantaneous decay rate for each active species in a given electrolyte. Capacity fade measured in a flow cell is a function of reactant decay in the CLS and the trajectory of its SOC during cycling. This trajectory is sensitive to the cy-
clinging protocol, which specifies an applied voltage/current and voltage/current limits that determine the duration of each discharge and charge half-cycle. Consequently, voltage losses determined by Eqn. (2.2) and their dependence on electrochemical properties of the flow cell can play a crucial role in controlling capacity retention in flow cells.

If the reactant in question decays into a redox-inactive species, its effect on the performance of a flow cell is equivalent to a decrease in concentration of one member of the redox pair. This scenario applies to several types of decomposition reactions to which organic RFB reactants are susceptible, such as tautomerization and nucleophilic attack (e.g. Michael reactions). [14] For other reactants, more complicated decomposition pathways are possible, such as decay into another redox-active molecule with distinct electrochemical properties, or chemical decay whose rate is dependent on the applied potential (see Sec. 2.5). Our model is capable of representing the effects of this class of reactant loss pathways on flow cell performance as well, given that it tracks the cell potential and concentrations of relevant species over time. In flow cells with a compositionally distinct pair of electrolytes, diffusion-driven reactant crossover would be identical in effect to reactant loss as in Eqn. (2.9), with $b$ equal to 1 and $k$ the product of membrane-electrode contact area and membrane permeability. In compositionally symmetric flow cells, reactant crossover may not result in net reactant loss, [53] and capacity fade is more likely to reflect reactant decay. [46] Note also that electromigration rather than diffusion might drive crossover; [54] provided a detailed mechanism is known, our model may include this effect as well.
2.2.5 Cycling protocols

Our model simulates constant-current and constant-voltage cycling protocols by accepting either the current or voltage as a fixed input, respectively. In the former case, the model keeps $I$ fixed and allows the cell voltage to evolve until it hits a preset limit; in the latter, it holds $V$ constant and adjusts the current such that the sum of voltage losses in Eqn. (2.2) is equal to $V - V_{OCV}$. The ability to simulate constant-voltage (CV) cycling is particularly important because, unlike constant-current (CC) cycling, the CV technique can access the full Coulombic capacity of redox-active species present in the capacity-limiting electrolyte; capacity values obtained with this method are fairly insensitive to temporal changes in the resistance of the cell, in contrast to analogous values from CC cycling. [14, 18, 46] It has recently been shown that capacity fade from combined constant-current constant-voltage (CCCV) cycling correlates with reactant loss in symmetric quinone-based flow cells, [46, 47] and a number of publications have adopted this protocol to evaluate chemical stability of various RFB reactants. [55, 56]

2.2.6 Modelling of pH swing and carbon dioxide capture

We are able to model pH swing and carbon dioxide (CO$_2$) capture by solving a set of equations that map the total alkalinity (TA) which changes in accordance with the SOC for a proton coupled electron transfer (PCET)active redox species, dissolved organic carbon (DIC) in accordance with Henry’s law and the equilibria between the three inorganic carbon species, namely CO$_2$, HCO$_3^-$ and CO$_3^{2-}$. The total alkalinity for a PCET active electrolyte is defined as
\[-2QH_2 = -2C^T(SOC) = [H^+] - [OH^-] - [HCO_3^-] - 2[CO_3^{2-}], \hspace{1cm} (2.10)\]

where \(QH_2\) is the reduced form of the PCET active species which binds to 2 protons. The PCET behavior induces a pH swing which in turn adds a term to Eqn. (2.3). The modified OCV equation is written as

\[
V_{OCV} = E_{OCV}^0 - \frac{RT}{n_{NCLS}} \ln \left( \frac{1 - SOC_{NCLS}}{SOC_{NCLS}} \right) - \frac{RT}{n_{CLS}} \ln \left( \frac{1 - SOC_{CLS}}{SOC_{CLS}} \right) + V_{pH}. \hspace{1cm} (2.11)
\]

We calculate \(V_{pH}\) for a PCET active molecule as

\[
V_{pH} = -\frac{RT}{nF} \ln [H^+] = 2.303 \frac{RT}{nF} pH. \hspace{1cm} (2.12)
\]

The equilibrium between dissolved CO\(_2\) and gas phase CO\(_2\) (governing invasion and outgassing) is given as

\[
[CO_2] = k_h \times P_{CO_2}. \hspace{1cm} (2.13)
\]

Where \(k_h\) is Henry’s constant which is equal to 0.035 M/bar. We then solve the equilibria between CO\(_2\) and HCO\(_3^-\) represented as
The equilibrium between $\text{HCO}_3^-$ and $\text{CO}_2^-$ as

$$\frac{[\text{CO}_3^{2-}][H^+]}{[\text{HCO}_3^-]} = k_{a,2}. \quad (2.15)$$

The equilibrium between $H^+$ and $OH^-$ is given as

$$[H^+][OH^-] = k_w. \quad (2.16)$$

Where $k_{a,1}$ and $k_{a,2}$ are $10^{-6}$ and $10^{-9.6}$ M respectively, and $k_w$ is $10^{-14}$ M$^2$. The DIC concentration in the solution is the sum of the concentration of the three carbon species and is

$$DIC = [\text{CO}_2] + [\text{HCO}_3^-] + [\text{CO}_3^{2-}]. \quad (2.17)$$

Solving equations Eqn. (2.13) to (2.17) we can rewrite equation Eqn. (2.10) as

$$-2C^T(SOC) = [H^+] - \frac{k_w}{[H]} - DIC \left( \frac{k_{a,1}[H^+] + 2k_{a,1}k_{a,2}}{+k_{a,1}[H^+] + k_{a,1}k_{a,2}} \right). \quad (2.18)$$
We then solve the equation for the rate of CO\textsubscript{2} invasion as

\[
\frac{d[CO_2]}{dt} = \frac{A_{c,i}}{L} \left( k_h P_{CO_2} - [CO_2] \right) \sqrt{D_{OH} k_{OH} [OH^-]} \tag{2.19}
\]

and

\[
\frac{d[CO_2]}{dt} = \frac{A_{c,o}}{L} \left( k_h P_{CO_2} - [CO_2] \right) k_{out}, \tag{2.20}
\]

where \( A_{c,i} \) and \( A_{c,o} \) are the invasion and outgassing liquid-gas contactor areas respectively, \( D_{OH} \) and \( k_{OH} \) are the diffusivity and invasion rate constant respectively, and \( k_{out} \) is the outgassing rate constant. We then estimate the energetic losses occurring due to the reversibility in the invasion and outgassing process as

\[
E_{exergy} = \frac{RT \int \ln \left( \frac{k_h P_{CO_2}}{[CO_2]} \right) dDIC}{\Delta DIC}, \tag{2.21}
\]

where \( \Delta DIC \) is the difference between DIC at the end of outgassing and invasion.

Since the model simulates a cell which invades CO\textsubscript{2} from a low pressure and outgasses to a stream at a higher pressure denoted by \( P_{CO_2,l} \) and \( P_{CO_2,h} \) respectively, \( P_{CO_2} \) equals \( P_{CO_2,l} \) during invasion and \( P_{CO_2,h} \) during outgassing. We apply \( P_{CO_2,l} \) at the start of the charging half-cycle, and switch to \( P_{CO_2,h} \) after the discharge half-cycle has begun and pH has reduced to 9 until the end of the discharge half cycle. Transfer of CO\textsubscript{2} from a lower pressure to a higher pressure involves overcoming a
thermodynamic energy barrier. This is the minimum thermodynamic work required for the transfer and is estimated as

\[ E_{\text{min}} = RT \ln \left( \frac{P_{\text{CO}_2, b}}{P_{\text{CO}_2, l}} \right). \]  (2.22)

The energetic input required for overcoming the exergy losses and minimum thermodynamic work is calculated from the integral of \( V_{pH} \) with respect to charge over a full cell cycle as

\[ E_{\text{CO}_2} = E_{\text{exergy}} + E_{\text{min}} = \frac{nFC^T \int V_{pH} dSOC}{\Delta DIC}. \]  (2.23)

The total energetic input over a full cycle incorporating the electrochemical losses and \( E_{\text{CO}_2} \) is calculated from the integral of the cell voltage multiplied by the current with respect to charge as

\[ E_{\text{CO}_2,\text{total}} = \frac{nFC^T \int V dSOC}{\Delta DIC}. \]  (2.24)

The cell losses comprise of the Ohmic, kinetic and mass transport losses. The Ohmic losses can be separated from the others as

\[ E_{\text{CO}_2,\text{Ohmic}} = \frac{nFC^T \int IR dSOC}{\Delta DIC}. \]  (2.25)
The specific energy input for overcoming the kinetic and mass transport losses is given as

\[
E_{CO_2,\text{kinetic+masstransport}} = E_{CO_2,\text{total}} - E_{CO_2,\text{Ohmic}} - E_{\text{exergy}}.
\] \hspace{1cm} (2.26)

The productivity of CO\(_2\) capture can be estimated as

\[
\Phi_{CO_2} = \frac{\Delta DIC \times L_{res,\text{CLE}}}{A \times t_{cyc}},
\] \hspace{1cm} (2.27)

where \(L_{res,\text{CLS}}\) is the volume of the CLS reservoir and \(t_{cyc}\) is the cycle time.

### 2.3 Materials and Methods

#### 2.3.1 Three-electrode measurements

A glassy carbon electrode (Pine Instruments, 5 mm diameter), graphite counter electrode and Ag/AgCl reference electrode (BASi, MF-2052 containing 3 M KCl) were used for three-electrode voltammetry measurements. The surface of the glassy carbon electrode was polished with 0.05 \(\mu\)m alumina solution on Texmet cloth before use. Cyclic voltammetry scans were conducted using a CH Instruments 7013E potentiostat with 85\% positive feedback iR compensation.
2.3.2 Raman spectroscopy

Raman spectroscopy experiments were conducted on a SYN-1024x256-OE IHR550 spectrometer and a Synapse CCD (Horiba) equipped with a 100X objective. A 532 nm diode laser was the incident excitation source. Each spectrum was the average of 20 scans collected for 1 s each.

2.3.3 Electrolyte, electrode and flow cell preparation

Potassium ferrocyanide ($\text{K}_4\text{Fe(CN)}_6$), potassium ferricyanide ($\text{K}_3\text{Fe(CN)}_6$), potassium hydroxide (KOH) and potassium chloride (KCl) were purchased from Sigma Aldrich and used as received. Flow cells were constructed with cell hardware from Fuel Cell Technologies (Albuquerque, New Mexico), and assembled into a zero-gap configuration, similar to a number of previous reports. [31, 57] Pyrosealed POCO graphite flow plates with serpentine flow patterns were used for both electrodes. Each electrode comprised a 5 cm$^2$ stack of one sheet of CE Tech GF020 graphite felt (Fuel Cell Store, 2.1 mm thick) or AvCarb G300A graphite felt (Fuel Cell Store, 3.4 mm thick). All electrodes were baked in air for 1 h at 400 °C prior to use. The outer portion of the space between the electrodes was gasketed by Viton sheets with the area over the electrodes cut out. A 30 μm-thick Fumasep E-630(K) ion-exchange membrane was used as the separator unless specified otherwise, and torque applied during cell assembly was 10 lb-ft on each of the eight bolts. Either a Longer DG-15 or Cole Parmer SK-77202–60 peristaltic pump circulated the electrolyte through the flow cell through fluorinated ethylene propylene (FEP) tubing of 1/16’ inner diameter. We obtained calibration curves for each pump that enabled translation from
revolutions per minute to a volumetric flow rate in ml/min.

We ran two symmetric flow cells with total ferri-/ferrocyanide concentrations of 20 and 100 mM to test the fidelity of our model to experiment. In both cells, 1 M KCl was the supporting electrolyte; the capacity-limiting electrolyte was 10 ml whereas the non-capacity-limiting electrolyte was 20 ml. We performed the cycling experiments using a CCCV cycling protocol to access the entire capacity of the CLS. Voltage loss characterization experiments i.e. potentiostatic EIS and polarization were ran after assembling the battery and prior to cycling. A Biologic VSP-300 potentiostat was used for all cell cycling, voltammetry and impedance spectroscopy measurements, the latter of which were obtained between 7 MHz and 25 mHz with an amplitude of 10 mV.

2.3.4 In operando potentiometric monitoring of SOC

We measured the solution potential of the CLS by immersing into it a graphite rod and Ag/AgCl reference electrode, and estimated its SOC using the Nernst equation in the dilute solution limit, based on the difference between the measured potential and standard redox potential of the Fe(CN)$_3^{3-}$/Fe(CN)$_4^{4-}$ (0.28 V vs Ag/AgCl):

\[
SOC = \frac{1}{1 + exp(\frac{F}{RT})(E - E_0)}.
\]  

(2.28)

where \(E\) is the electrolyte potential and \(E_0\) is the standard potential of the redox couple in the electrolyte, both defined with respect to the reference potential.
2.4 Results and Discussion

2.4.1 Experimental validation of model

We chose the Fe(CN)$_{6}^{3−}$/Fe(CN)$_{6}^{4−}$ redox couple to test our model because, given its fast redox kinetics (kinetic characterization in the SI), low cost and relatively high solubility in water, at 0.76 M for K$_4$Fe(CN)$_6$ and 1.31 M for K$_3$Fe(CN)$_6$, [14, 56] it is commonly deployed in the positive electrolytes of alkaline organic flow cells. [14] It is susceptible to a variety of chemical and electrochemical decay and self-discharge reactions, whose rates depend on the intensity of ultraviolet light present, [58] the oxidation state of the electrode (if carbon is used), [46] pH of the electrolyte [59] and choice of cation. [56] There is considerable debate regarding how some of these factors influence capacity fade. One study has shown that a symmetric K$_3$Fe(CN)$_6$/K$_4$Fe(CN)$_6$ flow cell at pH 14 experiences capacity fade at a rate equivalent to $\sim$ 21%/day, [59] and the authors concluded based on chemical analysis that irreversible loss of the cyanide ligand in Fe(CN)$_{6}^{4−}$ was responsible. More recent studies have however suggested that water oxidation by Fe(CN)$_{6}^{3−}$, leading to the latter’s self-discharge and a capacity imbalance in the cell, is responsible for the apparent fade, [46, 60] and that the fade rate can be slowed by using an electrode that is a poor catalyst for water oxidation. [60]

In support of the hypothesis that electrode chemistry has a significant influence on capacity fade, we found that using carbon paper electrodes resulted in a fade rate of 9%/day, whereas using graphite felt resulted in $\sim$ 0.01%/day(Fig. A.1), the latter being the lowest temporal fade rate we are aware of for this couple at pH 14. It
is unclear why carbon paper and graphite felt should differ so considerably in their
effect on capacity fade, given that carbon is a poor catalyst for water oxidation. One
potential explanation is that the graphite felt and carbon paper electrodes contain
differing amounts of iron, which is often present as an impurity in these materials
and can catalyze water splitting. In principle, our model is capable of shedding
light on this conundrum by predicting flow cell performance according to well-defined
hypotheses about the relationship between electrode surface chemistry/iron impurity
concentration and \( \text{Fe} (\text{CN})^{3-}_6/\text{Fe} (\text{CN})^{4-}_6 \) decay or self-discharge; this is an interesting
avenue for future research on the use of this couple in RFBs. To show that our model
predicts flow cell behavior in the absence of reactant instability, we compared its
results to experimental data from \( \text{Fe} (\text{CN})^{3-}_6/\text{Fe} (\text{CN})^{4-}_6 \) flow cells at pH 7, where water
oxidation by \( \text{Fe} (\text{CN})^{3-}_6 \) is thermodynamically infeasible and a symmetric cell showed
no discernible capacity fade over 12 days of continuous CCCV cycling (Fig. A.2).

2.4.2 Demonstration of the validity of the dilute-solution Nernst equation

We first demonstrate that the dilute-solution assumption relating SOC to \( V_{OCV} \)
in Eqn. (2.3) is valid for the \( \text{K}_3\text{Fe} (\text{CN})_6/\text{K}_4\text{Fe} (\text{CN})_6 \) couple. We measured the \( OCV \)
of a solution containing \( \text{K}_3\text{Fe} (\text{CN})_6 \) and \( \text{K}_4\text{Fe} (\text{CN})_6 \) at a total concentration of 100
mM as a function \( SOC \) by immersing into it a graphite rod and recording its po-
tential against an Ag/AgCl reference electrode. The \( SOC \) of the CLS was varied by
coulometric titration, and \( OCV \) measurements were made either after a 2 min rest at
a given \( SOC \), or continuously. Fig. 2.2 reports \( OCV \) measured with both methods
as a function of \( SOC \), together with \( V_{OCV} \) versus \( SOC \) assuming the dilute-solution Nernstian formula in Eqn. (2.28) and an \( E_0 \) for \( K_3\text{Fe(CN)}_6/K_4\text{Fe(CN)}_6 \) of 0.28 V vs Ag/AgCl. We obtained close agreement between the two measured values and the Nernst-estimated value for \( V_{OCV} \) versus \( SOC \), thus demonstrating the validity of the Nernst equation with the dilute-solution approximation for \( K_3\text{Fe(CN)}_6/K_4\text{Fe(CN)}_6 \) up to a \( C_T \) of 100 mM.

Figure 2.2: Verification of Nernstian voltage estimate as a function of \( SOC \) using potentiometric measurements of the CLS of a compositionally symmetric flow cell. The ideal Nernstian curve (orange line) closely agrees with potentiometric measurements of the CLS at rest (green circles) or during continuous coulometric titration (blue line). The CLS comprised 15 ml of 50 mM each of \( K_4\text{Fe(CN)}_6 \) and \( K_3\text{Fe(CN)}_6 \) in 1 M KOH. The NCLS was 40 ml. The membrane was Fumasep E-620(K) and electrodes were AvCarb G300A 3.4 mm thick graphite felt.
2.4.3 Measurement of series resistance, interfacial electron transfer resistance, and mass transport coefficient

We now describe experimental determination of the free parameters in our model. We used a combination of electrochemical impedance spectroscopy (EIS) and cyclic voltammetry measurements to determine $R_S$ and the charge transfer resistance. At small overpotentials, $R_{ct} = RT/Fi_o$ [61] and the exchange current $i_o$ is a function of the exchange rate constant $k^0$, transfer coefficient $\alpha$, and $R_F$:

$$i_0 = nFAR_FC^T_k_0SOC^\alpha(1 - SOC^{-1-\alpha}). \quad (2.29)$$

We obtained $R_S$ of a flow cell in contact with a single electrolyte reservoir containing 20 mM of K$_3$Fe(CN)$_6$/K$_4$Fe(CN)$_6$ at 50% SOC using EIS measurements at electrolyte flow rates between 10 and 160 mlmin$^{-1}$. EIS measurements at 12.7, 77.8 and 152.4 ml/min are shown in Fig. 2.3, while those at other flow rates are depicted in Fig. A.3. In the absence of asymmetric parasitic reactions, the electrolyte SOC remains fixed at 50% because any oxidation on one side of the flow cell is compensated by an equal amount of reduction on the other.
We determined $R_S$ from the high frequency x-axis intercept of the Nyquist impedance plot and report it at different flow rates in Table A.1. Its average value is 0.42 $\Omega$, or 2.1 $\Omega \text{cm}^2$ in area-specific terms. Although it is possible to obtain $R_{ct}$ and the mass transport resistance by fitting EIS spectra to a simple (e.g. Randles) equivalent circuit, we did not do so here, because our spectra would require a rather more complex equivalent circuit, with a non-trivial interpretation. Nevertheless, we observed an inverse relationship between the flow rate and size of the rightmost arc, which has been attributed in previous studies to decreasing mass transport (i.e. Warburg) resistance with increasing flow rate. [62]

We instead obtained $2R_{ct}$ by performing voltammetry measurements on the flow cell (Fig. 2.4a and b) and subtracting $R_S$ from the total polarization resistance at zero overpotential, $R_T$. $R_T$ is the inverse of the slope of the current versus voltage
plot at zero voltage. $R_T$ and $R_{ct}$ are also reported at different flow rates in Table A.1. Whereas $R_S$ varies only slightly with flow rate, $R_T$ and $R_{ct}$ are between 32 and 57% lower at intermediate flow rates than at the highest or lowest flow rates. The reason for the U-shaped trend in this instance is unclear, but it is worth noting that the error bars on $R_{ct}$ at the two highest flow rates overlap with that of the lowest flow rate of 10 ml min$^{-1}$. Thus, we used the average $R_{ct}$ (0.2 Ω) as the charge transfer resistance. This decision is supported by results from polarization measurements for a flow cell containing a higher total $[\text{Fe(CN)}_6]$ of 100 mM (Fig. A.4), where, above 10 ml min$^{-1}$, $R_T$ stays within 5% of 2.34 Ωcm$^2$.

![Figure 2.4](image)

**Figure 2.4:** (a) Cyclic voltammetry measurements at 10 mV s$^{-1}$ of a flow cell in contact with a single 65 ml reservoir containing 10 mM each of $\text{K}_4\text{Fe(CN)}_6$ and $\text{K}_3\text{Fe(CN)}_6$ in 1 M KCl. We fit each curve to the Butler-Volmer equation with a mass transport-limited current. (b) Values of $R_S$, $R_T$ and $R_{ct}$ versus flow rate. $R_S$ is the high-frequency x-axis intercept in EIS and $R_T$ is calculated from polarization curves; $R_{ct}$ is the result of subtracting $R_S$ from $R_T$.

Having determined from polarization measurements $R_{ct}$ and therefore $i_o$, we es-
timated $R_F$ by measuring $k_0$ using cyclic voltammetry of $K_3Fe(CN)_6/K_4Fe(CN)_6$ on a planar glassy carbon electrode, and substituting it into the expression for $i_o$ in Eqn. (2.29). Normalized cyclic voltammetry measurements of a solution containing 2 mM each of $K_4Fe(CN)_6$ and $K_3Fe(CN)_6$ between 20 mV s$^{-1}$ and 250 V s$^{-1}$ are shown in Fig. A.5. At scan rates higher than 20 mV s$^{-1}$, slow charge transfer kinetics relative to diffusion increases separation between anodic and cathodic potentials at peak current ($E_a$ and $E_c$, respectively), causing them to deviate progressively from the Nernstian value of 59 mV. We found the diffusivity of each member of the redox pair based on the slope of the peak current versus square root of scan rate within the reversible region (Fig. A.6a). Then, following Savéant, [63] we used the slope of normalized $E_c - E_0$ and $E_a - E_0$ versus the log of the scan rate (Fig. A.6b) to obtain $k_0$, [63] which was $2.2 \times 10^{-3} \pm 3.2 \times 10^{-4}$ cm s$^{-1}$ assuming $\alpha = 0.5$. Applying a different method for obtaining $k_0$ of flow battery reactants based on the relationship between the peak current and $E_c/E_a$, as explicated recently by Wang et al., [64] yielded a $k_0$ of $8.6 \times 10^{-4} \pm 1.2 \times 10^{-4}$ cm s$^{-1}$. Both $k_0$ values lie within the rather wide range of values reported in the literature for the $K_3Fe(CN)_6/K_4Fe(CN)_6$ rate constant on glassy carbon ($1.4 \times 10^{-5}$–0.14 cm s$^{-1}$ from Refs. [65, 66, 67]). Plugging into Eqn. (2.29) both our values of $k_0$, an $\alpha$ of 0.5 and $i_o$ yields $R_F$ values of $12.3 \pm 1.7$ (Savéant) [63] and $31.5 \pm 4.4$ (Wang) [64] cm$^2$ active/cm$^2$ geo.

These estimates of the active surface area of graphite felt may be inaccurate if $k_0$ differs significantly between the surface of the graphite felt in the flow cell and that of planar glassy carbon, [67] especially if Fe(CN)$_6$ redox kinetics are sensitive to electrode surface structure or chemistry, as has been reported. [68, 69] We there-
fore conducted capacitance measurements (Fig. A.7) of the graphite felt electrode to independently estimate \( k_0 \); assuming an areal capacitance of 20 \( \mu \text{F cm}^{-2} \) active, we derive an \( R_F \) value of 26 \( \pm 0.2 \) cm\(^2\) active cm\(^{-2}\)\ geo, which lies between our two glassy carbon-derived \( R_F \) values and, within uncertainty, agrees with that derived from Wang’s analysis of our kinetic measurements. Raman spectra of glassy carbon and graphite felt (Fig. A.8) show almost identical ratios of D to G band peak heights (\( \pm 1.3 \)), suggesting that both materials have similar levels of structural disorder and, presumably, interaction with \( \text{Fe(CN)}_6 \). X-ray photoelectron spectroscopy measurements would probe the surface electronic structure of graphite felt and glassy carbon in detail, but such measurements are beyond the scope of this study.

Our analysis assumes the series resistance of the porous electrode is negligible and that Faradaic electron transfer dominates power dissipation within it. This assumption is reasonable because we expect the electrode resistance to be small relative to the sum of Ohmic membrane and contact resistances. Assuming the series area-specific resistance of the electrode comprises electronic and ionic area-specific resistances (\( r_e \) and \( r_i \) ) in parallel, the area-specific electrode resistance is simply \( r_e r_i / (r_e + r_i) \). We estimate the half-cell electronic resistance as 0.07 \( \Omega \text{cm}^2 \) based on data from the manufacturer, and the ionic resistance as 3.4 \( \Omega \text{cm}^2 \), for an electrode porosity of 70\% in 1 M KCl. Because \( r_e \) is much smaller than \( r_i \), the electrode resistance (\( \pm 0.07 \Omega \text{cm}^2 \)) is virtually identical to its electronic component, and much smaller than the high-frequency resistance from EIS, \( \pm 2 \Omega \text{cm}^2 \). We therefore attribute the high-frequency resistance primarily to the sum of Ohmic membrane and contact resistances, as is common in the RFB literature. [34, 35, 70] In further

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support of the significance of Faradaic power dissipation, we note that geometric area-normalized applied current densities in this work (10-120 mA/cm$^2$) are either comparable to or much higher than the exchange current density, which is 27.5 mA/cm$^2$.

Fig. 2.5 describes how the mass transfer coefficient changes with flow rate ($\dot{L}$). We plot against flow rate $Ak_m/m$, denoted as $ak_m$ hereafter, where $a$ is the electrode area seen by the diffusion layer per unit volume and $m$ is the electrode volume. $ak_m$ is calculated using Eqn. (2.6), and $I_L$ obtained from Fig. 2.4a. Pulsation from the peristaltic pump resulted in an oscillating current, especially at high overpotentials. We fit the mean current to a version of the Butler-Volmer equation modified to include the mass transport overpotential, [61] and extracted $I_L$ together with a standard deviation that reflects the current oscillations. $ak_m$ has an almost linear relationship with flow rate between 10 and 107 ml/min which, assuming flow rate is proportional to flow velocity, is consistent with turbulent flow through a porous electrode. [61] We found that a power law relationship between $ak_m$ and flow rate with an exponent of 0.91 matched the data satisfactorily. This result is consistent with a previous study that found that $ak_m$ in symmetric Fe$^{2+}$/Fe$^{3+}$ flow cells containing porous carbon electrodes had a similar power law relationship to flow rate, with an exponent of 1.17 for a cell with serpentine flow fields. [35] As $a$ is unknown, we cannot extract $k_m$; however, it is reasonable to assume that $a$ does not vary with flow rate, and that the power law relationship describes how $k_m$ varies with flow rate. Despite our ignorance of $a$, what is necessary for an accurate flow cell simulation is how $I_L$ varies with flow rate, as that relationship determines $\Delta V_{MT}$ in Eqn. (2.8).
Figure 2.5: (a) Cyclic voltammetry measurements at 10 mV/s of a flow cell in contact with a single 65 ml reservoir containing 10 mM each of K$_4$Fe(CN)$_6$ and K$_3$Fe(CN)$_6$ in 1 M KCl. We fit each curve to the Butler-Volmer equation with a mass transport-limited current. (b) Values of $R_S$, $R_T$, and $R_{ct}$ versus flow rate. $R_S$ is the high-frequency x-axis intercept in EIS and $R_T$ is calculated from polarization curves; $R_{ct}$ is the result of subtracting $R_S$ from $R_T$.

2.4.4 Comparison of predicted to actual flow cell cycling results

Using the voltage loss parameters obtained above, and $t_{delay}$ values calculated from the relevant manifold volumes and flow rates, we examined our multi-domain model’s ability to model electrochemical behavior of an actual flow cell accurately. Fig. 2.6a and b show voltage versus time plots for simulated and actual CCCV cycling of a symmetric flow cell containing a total [Fe(CN)$_6$] of 20 mM, with a CLS volume of 20 ml and NCLS of 40 ml. We varied the applied current density during the CC period between 40 and 120 mA/cm$^2$ for a flow rate of 152 ml/min, and the electrolyte’s flow rate between 33 and 152 ml/min at an applied current of 100 mA/cm$^2$. Each half-
cycle terminated when the absolute value of the current density dropped below 1 mA/cm². At each flow rate between 10 and 107 ml/min, we constrained $ak_m$ to lie within one standard deviation of its independently obtained value in Fig. 2.5. At flow rates higher than 107 ml/min, where we could not measure a limiting current using voltammetry, $ak_m$ was unconstrained, and was lower than values extrapolated using the power law in Fig. 2.5 (Fig. A.9). The reason for this behavior is unclear. We nevertheless found very good broad agreement between experimental and simulated voltage and current curves for both charge and discharge over the full range of flow rates and current densities. Note that an erroneous estimate of voltage losses in Eqn. (2.2) would have led to a mismatch between the simulated and actual cell voltages where the switch from CC to CV cycling occurs. This error would then have carried over into the CV regime and manifested as a mismatch between the simulated and actual currents over time.
Figure 2.6: Comparison of simulated and experimental cycling behavior of a cell containing 20 mM Fe(CN)6 in 1 M KCl. (a and c) SOC and voltage versus time for an applied current of 500 mA (current density of 100 mA/cm²) and flow rates ranging from 33 to 152 ml/min. (b and d) SOC and voltage versus time for applied current densities ranging from 200 to 600 mA (40 to 120 mA/cm²) for a fixed flow rate of 152 ml/min.

The simulated data in Fig. 2.6a and b underscores the absence of such a mismatch, seen in Fig. 2.6c and d between simulated and actual SOC values of the CLS, obtained via Coulomb counting (see Eqn. (2.1)). In the CC region, SOC rises or falls
linearly with time as the current is fixed, but within the CV region, this relationship is non-linear, as the current varies in response to a fixed applied potential. Thus, looking at the time evolution of the SOC in the CV region is a convenient way of examining the agreement between experimental and simulated current values, and from Fig. 2.6c and d, the agreement is good; the difference between actual and simulated SOC values in the CV region is nowhere more than 2%. In sum, our model accurately simulates voltage losses in the CC region, the point of transition from CC to CV cycling, and the current transient in the CV region.

We also found good agreement between simulated and actual cycling results for a symmetric cell with a higher total [Fe(CN)_6] of 100 mM (Fig. 2.7). The applied current density ranged between 40 and 200 mA/cm² at 143 ml/min, and the flow rate between 32 and 143 ml/min at 160 mA/cm². We used in the simulation \( R_S \) and \( R_{ct} \) values from EIS and cyclic voltammetry measurements performed prior to CCCV cycling, but could not obtain \( a k_m \) versus flow rate because the active reactant concentration was too high to realize a mass transport-limited current at an overpotential where no water splitting occurs. We therefore left \( a k_m \) unconstrained, but nonetheless found that its relationship with flow rate came close to our results at 20 mM (Fig. A.9), i.e. a power law with an exponent of 0.92, as opposed to 0.91 for the 20 mM case. Ideally, one expects \( k_m \) at each flow rate to be concentration-independent, and therefore the same \( a k_m \) versus flow rate at 20 mM as 100 mM, but this conclusion obtains only if \( a \) does not vary. As the 100 mM cell build was different from that at 20 mM, we suspect that subtle differences in electrode compression and intrinsic area account for the dissimilarity in the absolute values of \( a k_m \) as a function
Figure 2.7: Comparison of simulated and experimental cycling behavior of a cell containing 100 mM Fe(CN)$_6$ in 1 M KCl. (a and c) SOC and voltage versus time for an applied current of 500 mA (current density of 160 mA/cm$^2$) and flow rates ranging from 33 to 143 ml/min. (b and d) SOC and voltage versus time for applied current densities ranging from 0.2 to 1 A (40 to 200 mA/cm$^2$) for a fixed flow rate of 143 ml/min.
2.4.5 In operando SOC monitoring and the effect of transport delay on $\Delta SOC_{\text{delay}}$

We sought to verify that the good fit between simulated and actual cycling results came about in part from a proper accounting of how $t_{\text{delay}}$ affects $\Delta SOC_{\text{delay}}$ using the transfer function described earlier. We first set $t_{\text{delay}}$ to zero (i.e. switched off transport delay in the simulations) and found that a profound mismatch between simulated and experimental charge-discharge behavior developed in some cases; Fig. A.10a and b illustrate this mismatch at 33.3 ml/min and 100 mA/cm$^2$ for the $SOC$ and voltage predictions, respectively.

Next, we confirmed that the transport delay resulted in an in operando difference between the "local" $SOC$ of the CLS reservoir and the "global" $SOC$ of the electrolyte, using a potentiometric sensor consisting of a graphite rod connected to an Ag/AgCl reference electrode. The measured voltage was used to estimate the CLS reservoir's "local" $SOC$ according to Eqn. (2.28). Fig. 2.8a reports the $SOC$ measured by the probe, as well as "global" $SOC$ values estimated from Coulomb counting in simulated and actual voltage-current data in a cell with total $[\text{Fe(CN)}_6] = 100$ mM. At a current density of 100 mA/cm$^2$ (current of 500 mA) and flow rates of 39 ml/min or higher, corresponding to a total $t_{\text{delay}}$ of 9 s or less, all three estimates converge. We attribute this convergence to the low value of $t_{\text{delay}}$, which corresponds to a flow cell that essentially behaves like a continuously stirred tank reactor. At 19 ml/min, however, there is a noticeable divergence between the local and global $SOC$ values, which we attribute primarily to the influence of a larger $t_{\text{delay}}$ (19 s, or 4% of half-cycle time). Nevertheless, our model accurately predicts the cycling behavior.
as seen from the voltage and SOC curves in Fig. 2.8a and b.

Figure 2.8: (a) Comparison of experimental and simulated global SOC and measured local SOC of the CLS versus time. A long transport delay results in an 8% gap in SOC at 19 ml/min. (b) Experimental and simulated voltage versus time. The cell was compositionally symmetric with a 15 ml CLS, 40 ml NCLS. Each side contained 50 mM each of K$_4$Fe(CN)$_6$ and K$_3$Fe(CN)$_6$ in 1 M KOH with a 20 µm Fumasep E-620(K) membrane and AvCarb G300A graphite felt electrodes.

We examined the influence of $t_{delay}$ on $\Delta SOC_{delay}$ within a more general framework by plotting $\Delta SOC_{delay}$ against the ratio between the applied current and the stoichiometric current, i.e. $I/nFC^T \dot{L}$ for all data in Fig. A.11a. Because this ratio
compares an electrochemical reaction rate to a convective mass transport-limited rate, we name it the electrochemical Damköhler number \((Da)\). [71, 52] We report in Fig. A.11b the time-averaged \(\Delta SOC_{\text{delay}}\) (i.e., difference between local and global \(SOC\) values) during the CC portion of each half-cycle versus \(Da\) for data in Fig. 2.8. As expected, \(\Delta SOC_{\text{delay}}\) increases with \(Da\) for each current density, but there is considerable variation in \(\Delta SOC_{\text{delay}}\) for similar \(Da\) values. To account for this scatter, we considered that the local SOC probe may either measure the \(SOC\) of a perfectly well mixed electrolyte reservoir, or an unmixed reservoir. We then computed \(\Delta SOC_{\text{delay}}\) under these two limits based on \(t_{\text{delay}}\), manifold and electrolyte reservoir volumes, as well as \(Da\) (detailed calculations in the SI) and found that all our data lie inside the envelope between the perfectly mixed and unmixed cases (blue and orange lines in Fig. A.11b).

2.4.6 The Effect of Cycling Protocol and Reactant Decay Mechanism on the Capacity Fade Rate: a Hypothetical Case Study.

Having demonstrated that our multi-domain model can accurately simulate the electrochemical behavior of a flow cell in the absence of reactant decay, we used it to simulate capacity fade during long cycling runs where active reactants are chemically unstable (Fig. 2.9). The observed temporal rate of capacity fade will depend on the loss mechanism to which the active reactants are susceptible, as well as the cycling protocol, a point that is gaining appreciation in the organic RFB literature. [46, 72, 73] Our model addresses how the interplay of these two factors quantitatively accounts for capacity retention.
Figure 2.9: (a) Comparison of experimental and simulated global SOC and measured local SOC of the CLS versus time. A long transport delay results in an 8% gap in SOC at 19 ml/min. (b) Experimental and simulated voltage versus time. The cell was compositionally symmetric with a 15 ml CLS, 40 ml NCLS. Each side contained 50 mM each of K₄Fe(CN)₆ and K₃Fe(CN)₆ in 1 M KOH with a 20 µm Fumasep E-620(K) membrane and AvCarb G300A graphite felt electrodes.
We modeled capacity retention of the CLS of a hypothetical symmetric cell containing a redox-active electrolyte with an indefinitely stable oxidized form and a reduced form susceptible to either a first or second order irreversible chemical decay to redox-inactive species. The instantaneous decay rate is given by substituting [Red] for [Ox] in Eqn. (2.9). The cycling mode was either CC, CV or CCCV (Fig. 2.9a and b). The rate of reactant loss is SOC-dependent; consequently, these various protocols will result in different distributions of residence times the CLS spends at each SOC (Fig. 2.9c), and thus different measured fade rates. Fig. 2.9d shows the normalized capacity versus time for six scenarios: CC cycling at ±200 mA between ±0.4 V; CV cycling between ±0.4 V with each half-cycle terminated when the absolute value of the current reaches 5 mA; two CCCV cycling regimes between ±0.4 V with an applied current of ±200 or ±500 mA; and two CCCV cycling at ±500 mA, one with voltage limits of +0.4 V and -0.15 V and another with +0.15 and -0.4 V, with the same low-current limit as the CV case. The flow rate was 56.9 ml/min, and for convenience, we adopted voltage loss parameters from the symmetric Fe(CN)6 cell with $C_T = 20$ mM. The first and second order decay constants were $2 \times 10^{-6}$ s$^{-1}$ and $10^{-4}$ M$^{-1}$s$^{-1}$, respectively.

Fig. 2.9e shows that the temporal capacity fade rate for the cell with the first order fade mechanism remains invariant for CCCV and CV cycling protocols in which the voltage limits are equidistant from the standard potential of the cell (8.3%/day), which is zero for the symmetric cell under study here. For voltage limits that are asymmetric about the standard potential, charge and discharge half-cycles are of unequal duration, and the higher the average SOC of the CLS, the greater the fade
rate. For the second order decay scenario, there is considerable variation in the cell capacity fade rate even if voltage limits are symmetric about the standard potential. The fade rate is lowest in the CC case at 5.3%/day, increases to 6.8%/day for the CCCV case with an applied current of ±500 mA and voltage limits of 0.4 and -0.15 V, and then plateaus at 6.7%/day for the higher current CCCV and CV cases with symmetric voltage limits. These results show that: (1) even in a relatively simple (i.e. compositionally symmetric) cell setup, the choice of cycling protocol can have a profound effect on the observed capacity fade rate; and (2) in principle, our model makes possible quantitative estimation of said fade rates based on a known or proposed reactant loss model, evaluation of a hypothesized model based on capacity retention measurements, or both.

The model can accommodate a vast range of organic and inorganic reactants, provided their kinetic and transport properties are known, which allows its use for a large range of RFB chemistries. It can also be modified to simulate hybrid flow/non-flow RFBs after a few modifications. Nevertheless, in its present form, it cannot simulate capacity fade resulting from the degradation of one redox couple into several redox-active couples with different electrochemical properties (i.e. redox potential, exchange rate constant, transfer coefficient) within the same electrolyte, as the total current will get divided unequally among different pairs. Such is the case with the Michael addition of water to 4,5-dihydroxybenzene-1,3-disulfonic acid (BQDS), [74, 75] or electrolytes containing a mixture of inorganic reactants. [76]
2.4.7 Carbon dioxide capture simulations

Having established the fundamental importance of exergy loss to governing the minimum energetic cost of any electrochemical CO$_2$ separation cycle based on its [CO$_2$] trajectory, we now turn to the question of how the total energetic cost of CO$_2$ separation may vary in operating cells. In addition to the minimum thermodynamic work of CO$_2$ separation (Eqn. (2.22)) and exergy losses from invasion and outgassing (Eqn. (2.19) and Eqn. (2.20) respectively), extra work to drive a specific current contribute significantly to the total energy input. This additional work, which we denote hereafter as a cell loss, may be required to overcome an Ohmic series resistance (e.g. due to the resistance of the membrane), and to drive interfacial charge transfer and mass transport. [61] Understanding how cell and exergy losses compose the total work, and the relationship between this total work and the rate of CO$_2$ capture, is critical for the design of electrochemical CO$_2$ separation systems that optimize the trade-off between the energetic cost and rate of CO$_2$ separation. From a modeling perspective, this task is challenging, because the voltage-current relationship - from which total work is calculated - is the result of a complex interplay among several dynamic variables/processes, which are schematically illustrated in Fig. 2.10 for a separation cycle driven by pH-swing/PCET. Here, the applied current determines not only the cell’s voltage losses, but is also the rate of change of the SOC and total alkalinity (TA) of the electrolyte. [77] The TA in turn regulates the instantaneous DIC speciation and pH of the electrolyte. At the same time, the pH also determines the open-circuit potential of the cell - via the Nernst Equation – and the kinetics of reactive CO$_2$ capture or release, which influences the trajectory of DIC. Any model
that considers these dynamic, recursive interrelationships, must also accommodate
the numerical stiffness induced by widely varying timescales at which different pro-
cesses can occur (e.g., CO$_2$ capture occurring more slowly than rate of change of
SOC).

Figure 2.10: Conceptual illustration of the interactions among variables /processes relevant
to electrochemical cycling of a flow cell (in black), pH swing (in blue) and the kinetics of
CO$_2$ capture or release (in orange)

We addressed this challenge by modifying the zero-dimensional electrochemical
model. The model in this section examines the impact of changes in the electrolyte’s
composition (pH, DIC, and SOC) from electrochemical proton coupled electron
transfer (PCET) and CO$_2$ capture/release on the total energetic cost and rate of CO$_2$
separation. The model system was a flow cell with a 7 mL, 79 mM capacity-limiting
electrolyte (CLE) containing a molecule active for an 2e$^-$, 2H$^+$ PCET reaction (Q
+ 2e$^-$ + 2H$^+$ $\leftrightarrow$ QH$_2$), and a 40 mL, 200 mM non-capacity-limiting electrolyte
(NCLE) with excess capacity that has the same standard potential as the CLE but is
not PCET-active. Voltage losses due to an Ohmic series resistance and mass trans-
port were considered, and interfacial charge transfer was assumed to be governed
by Butler-Volmer kinetics, as outlined in Sec. 2.2.3. We also assumed a Nernstian
relationship between pH and the open-circuit voltage (Eqn. (2.11)).

CO\textsubscript{2} capture and release were assumed to occur at the interfacial contact area between the CLE and its headspace gas (\(A_{c,i}\) and \(A_{c,o}\) for invasion and outgassing, though they were considered equal in this study), with the capture step rate-limited by liquid phase diffusion of CO\textsubscript{2} and its hydroxylation. [78, 79] Assuming the pH within the electrolyte is spatially homogeneous, and that aqueous CO\textsubscript{2}, HCO\textsubscript{3}\textsuperscript{−} and CO\textsubscript{3}\textsuperscript{2−} are in equilibrium, the rates of CO\textsubscript{2} capture and release are given in Eqn. (2.19) and Eqn. (2.20) respectively. [80]

Figure 2.11 shows the simulated cell potential, pH, [CO\textsubscript{2}] and DIC for a baseline constant-current, constant-voltage (CCCV) cycle in the absence and presence of CO\textsubscript{2} at an applied current density of 10 mA/cm\textsuperscript{2} for a CLE with \([C_T] = 79\) mM. Each half-cycle terminated once the voltage hit ± 0.4 V and the current density during the CV step decayed to 1 mA/cm\textsuperscript{2}. Charge and discharge correspond to reduction and oxidation of the CLE, and de-acidification/CO\textsubscript{2} capture and acidification/CO\textsubscript{2} release via appropriate changes in TA, respectively. The diffusivity of CO\textsubscript{2} in water (\(D_{OH} = 1.2 \times 10^{-5} cm^2/s\)) and \(k_{OH}\) the bimolecular rate constant of CO\textsubscript{2} hydroxylation \(CO_2 + OH^- \rightleftharpoons HCO_3^-\)). Parameters describing the electrochemical properties of the flow cell and CO\textsubscript{2} capture/release kinetics are summarized in Table A.2. In the absence of CO\textsubscript{2}, the voltage hysteresis between charge and discharge Figure 2.11a) is due only to cell losses, whereas there is no hysteresis in the pH vs SOC profile, as expected ( Figure 2.11b). In the CO\textsubscript{2}-concentrating cycle, we assumed that the CLE was exposed to a feed gas containing 5% CO\textsubscript{2} (0.05 bar) during charge, and then to 100% (1 bar) CO\textsubscript{2} during discharge once the pH dropped below 9. Upon charge, DIC
increased steadily with increasing SOC, from 1.81 mM at SOC = 0.001 to 106 mM at SOC = 0.999. The switch from 5% to 100% CO$_2$ during discharge incurred a spike in DIC because $[\text{CO}_2] < k_h \times P_{\text{CO}_2,h}$, but the situation reverses at SOC = 0.75, after which point CO$_2$ release was so rapid that $[\text{CO}_2]$ and $k_h \times P_{\text{CO}_2,l}$ were nearly identical for the rest of the discharge half-cycle. Our data are consistent with the consensus that in practical situations, reactive CO$_2$ capture will be the main determinant of the rate and energetic cost of the overall process of CO$_2$ separation. [81]

In the presence of CO$_2$, there is significant hysteresis in the pH profile; this is because whereas the pH increase during the charging half-cycle is insensitive to the presence of CO$_2$, the pH decrease upon discharge is buffered by (bi)carbonate.
Figure 2.11: (a) Potential, (b) pH, (c) DIC, and (d) $[\text{CO}_2]$ vs SOC during CCCV cycling at 10 mA/cm$^2$. Dashed and solid lines correspond to measurements in the absence and presence of CO$_2$, respectively. $P_{\text{CO}_2}$ at 0.05 and 1 bar are indicated in (c).

Because the model keeps track of the cell’s potential and current, as well as DIC, [CO$_2$] in the CLE and $P_{\text{CO}_2}$ in the CLE’s headspace over time, one can calculate not only the total work per mole of separated CO$_2$ ($E_{\text{CO}_2,\text{total}}$), but also the component of this work attributable to $E_{\text{exergy}}$, cell losses and $E_{\text{min}}$. This breakdown is shown in Fig. 2.12 for the data in Fig. 2.11, where cell losses are decomposed into a lumped contribution from charge transfer and mass transport losses, and a second
contribution from the Ohmic loss calculated according to Eqn. (2.24). Where $\Delta DIC$ is indicated on Fig. 2.11c. Applying this equation to the data in Fig. 2.11a and c yielded 42 kJ/mol$_{CO_2}$. As calculated from Eqn. (2.21) using numerical integration, exergy losses, $E_{CO_2}$, amounted to 20.5 kJ/mol$_{CO_2}$.

Figure 2.12: The total energetic cost of CO$_2$ separation in the baseline simulation in Fig. 2.11 expressed as a sum of $E_{CO_2}$ and cell losses, with the Ohmic and mass transport energy losses being calculated in Eqn. (2.25) and Eqn. (2.26) respectively.

Using the model’s output, it is also possible to calculate the net rate of CO$_2$ removal from the inlet feed per geometric area of the cell (Eqn. (2.27)). The productivity for the data in Fig. 2.11 was 0.98 mol$_{CO_2}$/m$^2$hr. The model therefore affords an approach for thoroughly exploring the relationships between exergy losses, and the total energetic cost and rate of CO$_2$ separation and the next section focuses on assessing performance limits for pH-swing-driven CO$_2$ capture using application oriented case-studies.
2.4.8 Assessing Energetic Cost and Rate of CO₂ Capture in Application-Oriented Case Studies

Given the increasing uptake in stationary power generation systems of natural gas as a substitute fuel for coal, the baseline scenario in Fig. 2.11 considered a feed containing 5% CO₂ as representative of flue gas from a natural gas plant. [82] It did not consider a reduction in $P_{CO₂,l}$ as CO₂ capture progressed. Nevertheless, an important practical criterion for point source capture applications is that a majority of the CO₂ in a given feed is removed. [83] We therefore also simulated CO₂ removal from a series of finite-sized gas inlets - where inlet $P_{CO₂,l}$ decreases during the capture step in proportion to the amount of CO₂ removed.

Figure A.12a shows the energetic cost of CO₂ capture from a 5% input feed and release to 1 bar as the of the size of the gas inlet decreases and the fraction of CO₂ captured (denoted hereafter as $f$) increases. The total energetic cost increases significantly as the input size decreases, from 42 kJ/mol$CO₂$ for an inlet of infinite size (i.e., a fixed $P_{CO₂,l}$ and $f = 0$), to 107 kJ/mol$CO₂$ for a 50 mL inlet reservoir, where $f$ is 99.2%. The energy penalty mainly comprises the exergy loss from invasion, which would be expected to increase with a decrease in the gas inlet size and thus decrease in average $P_{CO₂,l,inlet}$. The increase in energetic cost for CO₂ capture corresponds to a decrease in $Φ_{CO₂}$ from 0.98 mol$CO₂/(m^2hr)$ for the infinitely large inlet to 0.2 mol$CO₂/(m^2hr)$ for the 50 mL inlet (Fig. A.12b). Again, this result is reasonable, because as $P_{CO₂,l}$ in the inlet feed decreases, so too does the rate of CO₂ capture according to Eqn. (2.19). A notable implication of this finding is that lab-scale electrochemical measurements of flue gas capture of CO₂ in which the inlet $P_{CO₂,l}$ is
fixed, or exhibits a negligible decrease, might severely underestimate energy penalties that would be incurred in practical situations where near-complete extraction of CO₂ from a given feed is desired.

Figure A.13a shows the effect of changing the applied current density during CCCV cycling on the energetic cost of CO₂ concentration for an inlet of 200 mL and initial inlet $P_{CO_2,l}$ of 5%. The total energetic cost increases from 41.2 kJ/mol$_{CO_2}$ at 5 mA/cm$^2$ to 105.0 kJ/mol$_{CO_2}$ at 50 mA/cm$^2$, and 136.5 kJ/mol$_{CO_2}$ at 100 mA/cm$^2$. Clearly, the increase is mainly attributable to an increase in cell (especially Ohmic) rather than exergy losses. Corresponding to this increase in energetic cost is an increase in Φ$_{CO_2}$ from 0.37 mol$_{CO_2}/(m^2/hr)$ at 5 mA/cm$^2$ to 2.6 mol$_{CO_2}/(m^2/hr)$ at 50 mA/cm$^2$, and 3.3 molCO$_2$ mol$_{CO_2}/(m^2/hr)$ at 100 mA/cm$^2$ (Fig. A.13b). This increase in Φ$_{CO_2}$ originates from shorter cycle periods associated with increasing current density. Despite the shorter cycle periods, CO$_2$ uptake approaches completion ($f = 0.97$) within the range of current densities tested because of rapid CO$_2$ invasion kinetics and the inclusion of a CV step. In the absence of this CV step (i.e., constant-current cycling) $f$ decreases to 0.3 at the highest current density of 50 mA/cm$^2$, where the cycle period is apparently too short for CO$_2$ removal to approach completion. Note that for constant-current (CC) cycling at 5 mA/cm$^2$, the cycle period is long enough for CO$_2$ invasion to go to completion ($f = 0.97$), and the energetic cost is 40.8 kJ/mol$_{CO_2}$, close to the CCCV analogue.

Figure 2.13 shows that the above relationships among $f$, Φ$_{CO_2}$, and $E_{CO_2,total}$ can be understood in terms of the difference between the timescale allotted for deacidification/CO$_2$ invasion (during CCCV and CV cycling), and that required
for reactive CO$_2$ capture. As shown in Fig. 2.13a, the longer the invasion time, the more complete equilibration between gas- and solution-phase CO$_2$ during invasion, leading to higher $f$ and lower $E_{exergy}$.

There is a prominent ‘knee’ in the $f$ vs invasion time profile around 45 – 50 minutes, after which $f$ and $E_{exergy,capture}$ approach 0.99 and 29.8 kJ/mol$_{CO_2}$, respectively. We hypothesize that this knee occurs where the duration of the deacidification/CO$_2$ invasion half-cycle ($t_{invasion}$) begins to exceed the time required for reactive capture of all the available CO$_2$ ($t_{capture}$). As $t_{capture}$ exceeds the invasion time, the average [CO$_2$] progressively subceeds $k_h \times P_{CO_2,l}$, causing $E_{exergy}$ to increase and $f$ to decrease. $t_{capture}$ can be estimated by dividing the initial amount of CO$_2$ in the 200 mL inlet gas reservoir (in moles) by the rate of capture ($R_{capture}$) from Eqn. (2.19). However, because $P_{CO_2,l,inlet}$ (and thus $k_h \times P_{CO_2,l}$) and [OH$^-$] can decrease during CO$_2$ capture, $R_{capture}$ will not necessarily be fixed. We therefore calculated a range for $t_{capture}$ based on two extreme cases: one, representing a scenario with a small change in the pH of the CLE, where average $P_{CO_2,l}$ and [OH$^-$] are 2.5% and 0.08 M, respectively, and another scenario where average $P_{CO_2,l}$ and [OH$^-$] are 0.75% and 2.4 mM. This calculation yields $t_{capture}$ between 1.77 and 34.1 mins, with the latter limit preceding the occurrence of the knee by about 10 mins.
Figure 2.13: (a) Electrochemical work and capture fraction vs invasion time (b) CO\textsubscript{2} productivity vs invasion time. Constant-current cycling results at 10 mA/cm\textsuperscript{2} account for 0 < \( t_{\text{invasion}} \) < 45.7 min and constant-current constant-voltage cycling for 45.7 min < \( t_{\text{invasion}} \) < 59 min where 0.1 mA/cm\textsuperscript{2} < \( i_{\text{cutoff}} \) < 5 mA/cm\textsuperscript{2} with \( L_{\text{invasion}} = 200 \text{ mL} \) and \( k_{\text{OH}} = 8500 \text{ M}^{-1}\text{s}^{-1} \). The estimated timescale for reactive capture of all the CO\textsubscript{2} in the inlet is expected to lie within the grey zone in both plots. The blue data points correspond to \( k_{\text{OH}} = 85000 \text{ M}^{-1}\text{s}^{-1} \).

The competition between cycling and reactive capture timescales also governs the \( \Phi_{\text{CO}_2} \) vs invasion time profile (Fig. 2.13b), which exhibits a maximum around 45 mins. Below this point, there is progressively less time for complete removal of CO\textsubscript{2}; above it, the increasing cycle period induces no additional CO\textsubscript{2} capture as \( \approx 1 \).

These results provide some guidance on where homogeneous catalysis is likely to be effective. Because catalysis reduces the time-averaged difference between [CO\textsubscript{2}] and \( k_h \times P_{\text{CO}_2,l} \), it will be more effective in increasing \( \Phi_{\text{CO}_2} \) and decreasing \( E_{\text{exergy}} \) as the absolute value of [CO\textsubscript{2}] – \( k_h \times P_{\text{CO}_2,l} \) increases, which occurs as invasion durations fall short of the \( t_{\text{capture}} \) range indicated in Fig. 2.13. To verify this, we quantified the change in \( \Phi_{\text{CO}_2}, E_{\text{CO}_2,total}, \text{ and } E_{\text{exergy,capture}} \) brought about by a 10-fold increase
in $k_{OH}$ (from 8,500 to 85,000 M$^{-1}$s$^{-1}$) for CCCV cycling at 10 and 20 mA/cm$^2$ (blue data points in Fig. 2.13a and b). These conditions resulted in invasion half-cycle periods of 49.4 and 14.5 mins, respectively, i.e., at high and low $t_{invasion}$. In the former case, where $t_{invasion} \gg t_{capture}$, $E_{CO_2, total}$ decreased modestly, from 52.7 to 43.1 kJ/mol$_{CO_2}$, whereas $\Phi_{CO_2}$ was virtually identical to its uncatalyzed analogue (blue arrows in Fig. 2.13a and b). In the latter case, there was a slightly larger decrease in $E_{CO_2, total}$ from 103 to 91.4 kJ/mol$_{CO_2}$, and a dramatic increase in $\Phi_{CO_2}$ from 0.34 to 1.1 mol$_{CO_2}/(m^2 hr)$, in line with our expectations.

We also investigated the energetic cost of electrochemical direct air capture (DAC) of CO$_2$ from atmosphere, as DAC is increasingly being seen as an important option in our portfolio of climate stabilization strategies. [81] Fig. 2.14 reports potential, pH, DIC and [CO$_2$] over a CO$_2$-concentrating cycle where $P_{CO_2,l}$ was fixed at 410 ppm. All other parameters from the baseline scenario in Fig. 2.11 were retained except for the current density of 10 mA/cm$^2$. Cycling at 10 mA/cm$^2$ in 410 ppm afforded such a low cycle period (compared to the timescale required for CO$_2$ capture) that DIC at the end of invasion (1.28 mM) was lower than $k_h \times P_{CO_2,l}$ at 1 bar (35 mM), making outgassing thermodynamically impossible (data not shown). We therefore reduced the current density to 2 mA/cm$^2$. Under these conditions, DIC at the end of the charging half-cycle (Fig. 2.14c) was 47.9 mM, and $E_{CO_2, total}$ and $\Phi_{CO_2}$ were 142 kJ/mol$_{CO_2}$ and 0.07 mol$_{CO_2}/(m^2 hr)$, respectively. Some combination of a higher $A_c, i$ and an increase in CO$_2$ hydroxylation/hydration kinetics (e.g., via homogeneous catalysis, or a much higher $[CT]$) may further improve these metrics.
2.5 Discussion

Organic molecules under consideration as RFB reactants belong to many classes, and are susceptible to a wide range of decay mechanisms, including several forms of nucleophilic attack, [84] hydrolysis, tautomerization, [24, 85, 86] dimerization [87, 88, 89, 90] and disproportionation. [23, 47, 91, 92, 93, 94] These mechanisms exhibit varying levels of reversibility and diminution in redox activity of the active reac-
tant. [14] Consequently, there is a wide scope for using our model to rationalize how these decay pathways cause capacity fade at the cell level, and we illustrate this point with a few concrete examples from the organic RFB literature.

For a number of RFB chemistries, there is active debate regarding the dominant decay mechanisms controlling cell-level capacity fade. As noted previously, the ferri-/ferrocyanide couple is one such chemistry, and is known to be susceptible to light or hydroxide-induced decay or self-discharge, although the details as they pertain to capacity fade in RFBs are not universally agreed upon. Luo et al. [59] attribute rapid capacity fade in high-pH symmetric Fe(CN)$_6$ cells to homogeneous cleavage of the CN ligand in ferricyanide, [59] but Paéz et al. have recently presented evidence that any hydroxide-induced decay is effectively suppressed, even at pH 14, if the electrode has low catalytic activity for oxygen evolution. [60] Whether and how these two mechanisms are compatible, and the influence of electrode chemistry on capacity fade in other chemistries that appear to be vulnerable to this pathway [55] is a question that a self-consistent model linking the mechanism of reactant decay to capacity retention can address. 2,6-dihydroxyanthraquinone presents another case where the link between reactant decay and capacity fade is not fully understood. Evidence from a recent study [47] and prior literature [91, 93, 94] suggest that bimolecular disproportionation of the reduced quinone to a redox-inactive anthrone is responsible for capacity fade observed in corresponding cells; however, measurements of flow cell electrolyte composition during cycling indicate that dimerization and electrochemical decay mechanisms may also play a major role. [49, 48] Lastly, biomimetic alloxazine- and phenazine-based molecules are under investigation as RFB reactants, [24, 95, 96]
and both hydrolysis to redox-inactive species, [97] and dimerization to molecules with potentially reduced redox activity appear to be at cause in capacity fade. [95] The relative contributions of these two pathways to capacity retention is an open question.

There is an added layer of complexity to the influence of reactant decay on capacity fade in cases where chemical decay is either directly or indirectly induced by electrode polarization. Viologens present a case study of this situation, where a singly reduced viologen at one potential may be much more chemically stable than a doubly reduced viologen at a lower potential; [18, 98, 99] in such a case, the exact location of the voltage limit during either CC, CCCV or CV cycling will play a crucial role in capacity retention. Even if the voltage limit lies above the standard potential for the second reduction event, there may be significant reactant loss over time if a finite amount of the doubly reduced form is present at equilibrium. [100] In such a case, the capacity fade rate will be a complex function of the equilibrium amount of the doubly reduced form and the distribution of residence times the CLS spends at each $SOC$, both of which are controlled by the cycling regime.

It is worth noting that, in principle, the relative contributions of chemical versus electrochemical decay mechanisms to capacity fade can be explored by measuring reactant decay at various $SOC$ values and CV experiments, respectively. Nevertheless, measuring reactant degradation over time at different $SOC$ values ideally requires tracking the chemical composition and Coulombic capacity of an electrolyte over the course of days or weeks, which is time consuming. CV is likewise a useful technique for discerning the electrochemical properties of various redox couples. However, CV measurements are typically performed on planar electrodes with low reactant concen-
trations (±1 mM), whereas flow cell measurements involve bulk electrolysis of higher reactant concentrations (±0.1–1 M) within porous electrodes; these different conditions may limit application of CV-derived parameters to flow cell modeling. [67, 101] These issues, in addition to the fact that the cycling protocol also influences the capacity fade rate, motivate the development of a model that can capture the myriad chemical and electrochemical factors responsible for reactant degradation and capacity retention.

Several other factors can confound straightforward interpretation of capacity fade in organic flow cells. These factors include reactant crossover through the cell membrane driven by diffusion or pressure imbalances across the membrane; [51, 102, 103, 104] temporal changes to series and interfacial charge transfer resistance owing to variations in ambient temperature; self-discharge; parasitic reactions between active reactants and electrolyte impurities; and changes to reactant decay kinetics caused by drifts in electrolyte pH. Our work has shown that in principle, measurements of electrochemical behavior and capacity retention can be quantitatively compared to predictions of one or more hypothesized capacity fade mechanisms, and thus better understood. Because the capacity fade rate is highly sensitive to the combination of cycling protocol and intrinsic decay mechanism (Fig. 2.9e), one could use a judiciously chosen series of cycling protocols as a “design variable” that will generate a capacity fade rate profile or fingerprint, which would be unique to the underlying decay mechanism. Based on the degree of similarity or divergence between the experimental fingerprint and various simulated analogues, one could then eliminate, propose or refine the capacity fade mechanism(s) plausibly at play for a chemistry
under consideration for an organic RFB, with a quantified level of uncertainty. Using such an experimental design paradigm to understand capacity retention has the potential to enable accelerated testing and development of new RFB chemistries, especially those possessing low fade rates, and will be especially powerful when coupled with emerging methods for operando monitoring of electrolyte composition. [49, 48]

Results from the zero-dimensional model and exergy loss analysis have several implications for electrochemical CO$_2$ capture research and its further development for industrial application. First, they provide a framework for understanding how thermodynamic and kinetic factors (exergy and cell losses) compose the measured energy inputs in electrochemical CO$_2$ separation processes. Second, given its relevance to point source capture, it would be important for future experimental studies to mimic near-complete removal of CO$_2$ from simulated flue gas feeds, as the decrease in $P_{CO_2,l}$ accompanying such removal can dramatically increase $E_{CO_2,total}$. To our knowledge, no experimental studies have examined the impact of a decreasing $P_{CO_2,l}$ on $E_{CO_2,total}$, and only one has systematically examined $E_{CO_2,total}$ for $P_{CO_2,h}/P_{CO_2,l}$ ratios greater than 1. [105]

Finally, the model and exergy loss analysis presented here can inform techno-economic assessment of the lowest possible cost of CO$_2$ captured/avoided (in $/\text{ton}_{CO_2}$) in industrial contexts. For instance, for a given rate of CO$_2$ emitted from a fossil plant and a desired degree of extraction ($f$), one could calculate the optimal number of electrochemical cells to deploy based on the capital and operating cost of each cell, and the cost of electricity/fuel. Tradeoffs/relationships between the levelized CO$_2$ cost and $f$, energy input, or throughput can also be quantified.

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Acknowledgments

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3.1 Introduction

High fade rates (>0.1%/day) [106] render the vast majority of organic RFB chemistries unsuitable for practical deployment in RFB installations that are expected to last for decades. Because redox-active organic reactants encompass a wide range of molecular classes and are susceptible to a variety of decomposition mechanisms (e.g., nucleophilic attack, tautomerization, and hydrolysis), [106] understanding how reactant conversion or decay leads to capacity fade is a critical but often difficult task. Such understanding often requires the deployment of new operando measurement tools [107, 108, 109] and cycling protocols that allow the deconvolution of reactant decomposition from other sources of capacity fade. [110, 111, 112] For several candidate RFB reactants such as quinones, [113, 107, 108] iron-based organometallic
complexes [114, 115, 116] and nitrogen-containing aromatic molecules, [117, 118, 119] multiple hypotheses about the relationship between reactant decay and capacity fade have been advanced, some of which are mutually incompatible. [106] In other chemistries, such as one recently developed based on fluorenone, [120] there are complex equilibria among species in different redox and protonation states whose effect on capacity retention is not yet fully understood. [121] These challenges call for new techniques to discern the probabilities or relative contributions of various hypothesized mechanisms to capacity fade observed in flow cells. In particular, understanding and rigorously quantifying the degree to which data gathered from experiments confirm or challenge particular hypotheses about chemical versus electrochemical sources of capacity fade is critical for developing organic RFB chemistries.

Statistical learning of physical models and their parameters from experimental observations, broadly approached as an estimation or inference task, can be brought to bear on this issue. Estimation centers around the ideas of regression where the goal is to find the optimal value of parameters so that the model prediction best fits (explains) the observations (e.g., see [122]). However, these best fits are usually single-valued and do not quantify the uncertainty that is affected by, for example, the quantity and quality of observations. In contrast, inference seeks probabilistic solutions to convey the degree of uncertainty about different possible explanations that could have induced the observed data. Inference is typically carried out following the axioms of probability and Bayes’ theorem, [123, 124, 125] where an initial prior uncertainty distribution is appropriately updated to a posterior uncertainty distribution given the newly acquired observations. The Bayesian update rule nat-
urally incorporates new data that may materialize sequentially over time and offers a coherent representation of evidence aggregation. Bayesian inference is also advantageous for accommodating sparse, noisy, and indirect measurements, consolidating data sets from different sources and of varying quality, and permitting the injection of domain knowledge and expert opinion to the learning process. [126] Beyond parameter inference, the Bayesian framework also extends to model selection, [127, 128] allowing one to compare various “packages” of hypotheses and assumptions manifesting as different model structures and parameterizations (e.g., different reaction mechanisms).

Bayesian inference and related probabilistic techniques have been applied to several problems in electrocatalysis and battery science, including failure prediction [129] and the development of lifetime-extending charging protocols in Li-ion batteries, [130] analyte labeling, [131] model/variable selection and parameter estimation for Li-ion battery electrodes, [132] electrochemical cell design, [133, 134] Tafel slope interpretation, [135], and materials discovery. [136, 137] However, no studies of which we are aware have applied these techniques to understand capacity fade or reactant decay in organic RFBs, nor has Bayesian model selection been deployed in these contexts.

In this work, we apply Bayesian inference and multivariate curve resolution-alternating least squares (MCR-ALS) methods to spectroscopic analysis of the decomposition of oxidized 4,5-dihydroxy-1,3-benzenedisulfonic acid (BQDS) or Tiron, an ortho-hydroquinone derivative previously investigated as a positive electrolyte reactant in aqueous RFBs. [138, 139, 140] Whereas Bayesian inference applies broadly, MCR-ALS is specifically suited to spectrophotometry, as it uses iterative optimiza-
tion under well-defined physical constraints for resolving mixed signals in a multi-component system into its pure components. [141] MCR-ALS is applicable to understanding speciation in multi-component chemical systems via optical absorbance, where absorbance at a given wavelength might be linearly proportional to the concentrations of each component. Previous work has shown that oxidized BQDS is susceptible to a self-discharge reaction with water known as Michael addition/attack, [138, 139, 140, 142] which results in the formation of a series of hydroxyl-substituted para-hydroquinone species with lower redox potentials than BQDS. However, the intrinsic rates of Michael addition, and whether these rates are modified under operando cycling conditions, are not known. This information is critical for establishing a quantitative link between reactant decay/conversion and capacity fade.

The main contributions of our article are schematized in Fig. 3.1 and are as follows: 1. We performed Bayesian model selection to identify the most plausible kinetic scheme for the decay of BQDS based on ultraviolet-visible (UV-vis) spectrophotometry of a sacrificial oxidant, which acted as a reporter of Michael attack; 2. By applying Bayesian parameter inference and MCR-ALS to the UV-vis data, we obtained uncertainty-quantified estimates of the rates of Michael attack of BQDS both ex situ and inside an operating flow cell; and 3. We individually isolated the UV-vis spectra of all oxidation and Michael attack products by applying MCR-ALS to spectroscopic data obtained from the operando BQDS-containing flow cell.
Figure 3.1: We applied Bayesian model selection and inference, as well as multivariate curve resolution techniques, to spectroscopic data obtained ex situ and in operando flow cells in order to elucidate and quantify the kinetics of Michael attack of BQDS.

Our paper is structured as follows. Section 3.3.1 reports experimental details and measurements of Michael attack of BQDS ex situ via UV-vis spectrophotometry of the concentration of the sacrificial oxidant. Section 3.3.2 describes our application to the UV-vis data of Bayesian model selection and inference of the relevant decay
rate constants. Section 3.3.3 reports experimental details regarding BQDS oxidation and Michael attack under electrochemical cycling. In Section 3.3.4, we apply MCR-ALS to the *operando* UV-vis data, extracting the relevant decay rate constants as well as spectra for each oxidation/intermediate product. Finally, in Section 3.3.5 we corroborate our results using nuclear magnetic resonance (NMR) analysis and density functional theory (DFT) calculations of the reaction energetics for Michael addition to BQDS. Section 3.2 reports all experimental and computational methods. Our work demonstrates the promise of using statistical inference techniques to elucidate and distinguish between chemical and electrochemical mechanisms of capacity fade in organic RFBs, and, more generally, for understanding variable-timescale molecular transformations in other flow cell-based electrochemical applications.

3.2 Methods

3.2.1 Chemicals

BQDS, H$_2$SO$_4$, potassium dichromate, D$_2$O, CH$_3$SO$_3$D and Methylene Blue (MB) were procured from Sigma Aldrich and used as received.

3.2.2 Spectroscopic Measurement of Chemical Oxidation of BQDS and Michael Attack

UV-vis measurements of Michael attack of BQDS were conducted by monitoring the optical absorbance of K$_2$Cr$_2$O$_7$ after the addition of a known quantity of BQDS. For each measurement, an aqueous solution of 2 mL of K$_2$Cr$_2$O$_7$ was first prepared
in a polystyrene cuvette with a 10 mm path length and 1 M H$_2$SO$_4$ as supporting electrolyte; then BQDS was added to the solution and UV-vis spectra were recorded every 5 minutes. All UV-vis spectra were recorded at room temperature using a DH-mini light source from Ocean Insight and an HDX detector.

3.2.3 Flow Cell Preparation

Flow cells were constructed with cell hardware from Fuel Cell Technologies (Albuquerque, New Mexico), and assembled into a zero-gap configuration, similar to a previous report. [143] Pyrosealed POCO graphite flow plates with interdigitated flow patterns were used for both electrodes. Each electrode comprised a 5 cm$^2$ stack of one sheet of CE Tech GF020 graphite felt (Fuel Cell Store, uncompressed thickness of 2.0 mm). All electrodes were baked in air for 12 h at 400 °C prior to use. The outer portion of the space between the electrodes was gasketed by Viton sheets with the area over the electrodes cut out. A 120 µm-thick Nafion 115 (Fuel Cell Store) ion-exchange membrane was used as the separator in the BQDS-MB flow cells with and without in-line UV-vis monitoring, and torque applied during cell assembly was 13.6 Nm on each of the eight bolts. A Cole-Parmer Masterflex peristaltic pump circulated the electrolyte through the flow cell through fluorinated ethylene propylene tubing of 1.61 mm inner diameter. We obtained calibration curves for each pump that enabled translation from revolutions per minute to a volumetric flow rate in mL/min. For the flow-cell experiments, we used a volumetric flow rate of 30 mL/min. A Biologic VSP-300 potentiostat was used for all cell cycling and voltammetry.
3.2.4 In-line *operando* UV-vis Measurements

We monitored the rate of Michael attack of BQDS during its oxidation in an *operando* flow cell. This analysis was done by setting up an aqueous flow cell with a capacity-limiting electrolyte (CLE) comprising 8 mL of between 5 and 15 mM of BQDS, and directing the flow of electrolyte through an absorbance micro cross flow cell (Supp. Fig. 14) from Firebird Optics. In all cases, 20 mL of 20 mM of Methylene Blue (MB) was used as the redox-active material in the non-capacity-limiting (NCLE) (or counter) electrolyte. We used MB in the counter electrolyte because it has been shown to have higher chemical stability as measured from symmetric flow cell cycling [144] than anthraquinone 2,7-disulfonic acid, [145] which has been previously deployed in the negolyte of BQDS full cells. The lower voltage of the BQDS-MB flow cell (0.15 V) compared to a BQDS-AQDS cell (∼0.65 V) did not hinder our objective of investigating the degradation of BQDS. Our goal was to have a counter electrolyte with adequate excess capacity and stable redox behavior, not a high potential full-cell. The supporting electrolyte comprised 0.9 M H$_2$SO$_4$ and 0.1 M CH$_3$COOH; the CH$_3$COOH was used to prevent MB from coagulating. [146]

Although practical flow batteries may require the use of reactants with concentrations in excess of 0.5 M, we are constrained to lower concentrations due to the saturation limit of the spectrometer. Given that BQDS has a molar absorptivity of $2.4 \times 10^{-3}$ M$^{-1}$ cm$^{-1}$ (considering the peak at 234 nm), we would need an impractically short path length of $1.2 \times 10^{-3}$ cm or lower due to the saturation limit of the spectrometer if a 0.5 M concentration is to be used. This limitation does not exist for the *in situ* technique, where aliquots can be periodically drawn from the CLE and
diluted before UV-vis analysis. *In situ* UV-vis measurements may therefore readily permit analysis of reactant concentrations > 0.5 M, but at the expense of a lower time resolution than more continuous, *operando* measurements.

For each measurement, unless specified otherwise, UV-vis spectra were recorded every 5 seconds for the first hour, and then every 30 seconds for the next 10 to 20 hours. The spectrometer and detector used for this experiment were the same as the ones used in Section 3.2.2. BQDS was oxidized potentiostatically at a cell potential of 0.8 V, which is 0.6 V higher than the nominal potential of a BQDS-MB flow cell.

### 3.2.5 NMR Measurements and Simulations

150 µL aliquots of a BQDS electrolyte under oxidation in a BQDS-MB flow cell were taken intermittently and examined using Nuclear Magnetic Resonance (NMR) spectroscopy. The CLE comprised 100 mM of BQDS, whereas the counter electrolyte comprised 50 mM of Methylene Blue (MB) with a six-fold excess capacity. The cell was charged at a constant current of 0.5 A until a voltage of 1 V was obtained, after which it was held at 1 V for 24 hours. Aliquots were retrieved from the electrolyte after 5, 10, 20, 30, 60, 300, and 1440 minutes from the start of oxidation. Prior to NMR analysis, each aliquot was diluted to 20 mM with deuterated water (D$_2$O) as the solvent and 50 mM CH$_3$SO$_3$D was added as an internal standard.

NMR measurements were conducted on a Varian MR400 400 MHz (9.4 Tesla) Premium Shielded Magnet NMR spectrometer. The H-NMR simulations for BQDS derivatives were obtained using CDCl$_3$ as the solvent under a frequency of 300 MHz with the ChemDraw software version 18.2.
3.2.6 Bayesian Inference and Model Selection

In this section we present a general Bayesian framework for parameter inference and model selection. We then use these methods for our models and experiments in Section 3.3.

3.2.6.1 Bayesian Parameter Inference

Bayesian parameter inference is exercised on a given model $M$, such as the BQDS decay model in Fig. 3.1. We denote the collection of all model parameters (e.g., reaction orders and rate constants) by $\theta$, and all measurements (e.g., absorbance data obtained using UV-vis spectroscopy) by $y$. Under a Bayesian framework, the uncertainty of $\theta$ is represented by a probability density function (PDF). When new measurements are acquired, the uncertainty of $\theta$ is updated through Bayes’ rule:

$$p(\theta|y, M) = \frac{p(y|\theta, M)p(\theta|M)}{p(y|M)}$$

where $p(\theta|M)$ is the prior PDF representing the initial uncertainty of $\theta$ in model $M$ before having the new measurements $y$, and $p(\theta|y, M)$ is the posterior PDF representing the updated uncertainty after incorporating $y$. Furthermore, $p(y|\theta, M)$ is the likelihood PDF that provides a probabilistic description of the discrepancy between the model’s predictions and experimental observations, and $p(y|M) = \int p(y|\theta, M)p(\theta|M) d\theta$ is the Bayesian model evidence (also called the marginal likelihood) that acts as a normalization constant to ensure $p(\theta|y, M)$ remains a proper PDF (integrates to unity). Solving the Bayesian inference problem then entails com-
puting or characterizing the posterior $p(\theta|y, \mathcal{M})$.

The prior $p(\theta|\mathcal{M})$ may be chosen in either a non-informative or informative manner. In the former, for example, if reasonable lower and upper bounds are known for the model parameter, then a uniform distribution can be imposed across this range. Such “flat” distribution means that initially all values are equally probable and one does not favor any particular region; this non-informative prior also appeals to the Principle of Maximum Entropy. [147] In the latter, if historical data or domain experts are available, the prior PDF can be formed to incorporate this knowledge through techniques of expert elicitation. [126] In our work, we take a non-informative approach and adopt a uniform prior distribution.

The likelihood $p(y|\theta, \mathcal{M})$ quantifies how likely one is to observe $y$ if the model’s parameter values were actually $\theta$. Effectively, it provides a probability measure on the discrepancy between a model’s predictions and experimental observations, which may be induced by measurement noise or modeling error. We employ a commonly used likelihood form that involves additive Gaussian error:

$$y = g_{\mathcal{M}}(\theta) + \epsilon,$$

where $g_{\mathcal{M}}(\theta)$ is model $\mathcal{M}$’s prediction on the observable quantities if parameter values were $\theta$, and $\epsilon$ is a zero-mean Gaussian distribution $\mathcal{N}(0, \Sigma_{\epsilon})$. Subsequently, the likelihood PDF may be evaluated as $p(y|\theta, \mathcal{M}) = p_{\epsilon}(y - g_{\mathcal{M}}(\theta)) = \mathcal{N}(y - g_{\mathcal{M}}(\theta); 0, \Sigma_{\epsilon})$. Whereas such a zero-mean error assumption is commonly justified for measurement error from instruments, it is often inadequate to incorporate modeling error (i.e., systematic error due to incorrect assumptions in a model, such as the wrong num-
ber of Michael addition events to oxidized BQDS); however, this issue is separately addressed through Bayesian model selection in the next section.

Lastly, the Bayesian inference problem requires solving for the posterior. The posterior PDF is generally intractable to compute. Instead, one can characterize the posterior by generating samples from it, most commonly via Markov chain Monte Carlo (MCMC) methods. [148, 149] We therefore performed posterior sampling using the Metropolis-Hastings algorithm [150, 151] from PyMC3, a mature probabilistic programming Python package that can handle high dimensional parameter settings. [152]

### 3.2.6.2 Bayesian Model Selection

Bayesian parameter inference from the previous section provides a means to quantify parameter uncertainty for a given model $\mathcal{M}$. However, what if we wish to compare different models that are built on different assumptions, such as BQDS decay models with one versus two versus three Michael additions? Such a task of model selection can also be accomplished in a Bayesian framework. [127, 128] Among $n_M$ candidate models, the probability that the $i$th model $\mathcal{M}_i$, $i = 1, \ldots, n_M$ is the true data-generating model of experimental observations $y$ can also be expressed through Bayes’ rule:

$$P(\mathcal{M}_i | y) = \frac{p(y|\mathcal{M}_i)P(\mathcal{M}_i)}{p(y)}, \quad (3.3)$$

where $P(\mathcal{M}_i)$ is the prior probability mass function (PMF) of model $\mathcal{M}_i$, and $P(\mathcal{M}_i | y)$ is posterior PMF given observations $y$. The new model-likelihood term $p(y|\mathcal{M}_i)$ is in
fact the model evidence (denominator term) from Eqn. (3.1). \( p(y) = \sum_{i=1}^{n_M} p(y|M_i)P(M_i) \) still serves as a normalization constant but can be computed easily because \( M_i \) is discrete. If a uniform model prior is used—i.e., all models are initially equally probable with \( P(M_i) = 1/n_M \)—it follows that \( P(M_i|y) = p(y|M_i) \). The key to Bayesian model selection is therefore estimating the model evidence term \( p(y|M_i) \).

We elect to use a direct Monte Carlo integration to estimate the model evidence:

\[
P(y|M_i) = \int p(y|\theta_i, M_i)p(\theta_i|M_i) d\theta_i \approx \frac{1}{N} \sum_{j=1}^{N} p(y|\theta_i^{(j)}, M_i)
\]

(3.4)

where \( \theta_i \) denotes parameters of model \( M_i \), and \( \theta_i^{(j)}, j = 1, \ldots, N \) represents the \( j \)th sample of \( \theta_i \) drawn from the parameter-prior distribution \( p(\theta_i|M_i) \). This Monte Carlo estimator for the model evidence may endure high variance if the posterior concentrates narrowly within the prior (i.e., many of the prior samples may have a near-zero contribution to the summand in Eqn. (3.4)). More advanced techniques can be employed to improve the estimate, such as using importance sampling (e.g., Ch. 3.3 of [153]) or variational inference; [154] we leave the exploration of these advanced numerical methods for future work. The Bayesian methodology also has limitations. For example, the MCMC sampling algorithm for performing Bayesian inference can take a long time to mix (converge) if the posterior is sharply multimodal; in our work we mitigate this effect using multiple chains with randomized starting points. Computing the probabilities of several hypotheses using Bayesian model selection can also require many samples to stabilize and can be computationally expensive. Furthermore, Bayesian model selection is a method that identifies the most probable
hypothesis from a given candidate set; it is not designed to generate new hypotheses.

3.2.7 Multivariate Curve Resolution Analysis

We determined the UV-vis spectra of all intermediate species that evolved during BQDS oxidation, and calculated the rate constants of Michael attack of oxidized BQDS using the MCR alternating least squares (MCR-ALS) suite of applications. [141] The MCR-ALS technique is based on the matrix form of the Beer-Lambert Law:

\[ X = CS^T \]  \hspace{1cm} (3.5)

where \( X \) is a matrix containing the spectra taken at each time step, \( C \) is the matrix whose columns contain the concentration of each independent component in the system with time, and \( S \) is the matrix that contains the pure spectra (the product of molar absorption coefficient and path length) of each component in the system along its rows. The dimensions of \( X \) are \( t \times \lambda \), where \( \lambda \) is the number of wavelengths recorded by the UV-vis spectrometer, and \( t \) is the number of spectra recorded; the dimensions of \( C \) are \( t \times n \), where \( n \) is the number of components in the system; and the dimensions of \( S^T \) are \( n \times \lambda \). The Beer’s Law decomposition of a spectral matrix is illustrated in Fig. B.15.

MCR-ALS uses the alternating least squares technique for matrix decomposition to determine the matrices \( C \) and \( S \), thus allowing determination of the pure spectra for each of the components in the system and the associated rate constants of decomposition. Initial guesses for the factored matrices can be obtained using
either evolving factor analysis (EFA) or purest variables detection (SIMPLISMA) techniques, followed by the iterative alternating least squares procedure to find the best fitting matrices. [155, 156, 157] In this study we used the SIMPLISMA method. We also imposed additional constraints of non-negativity in spectra and concentrations, and closure (i.e., a fixed total concentration for all species) in order to reduce ambiguities in the matrix factorization. A key limitation of MCR-ALS is that it is only valid (assumes) for first order reactions; however this assumption is verified in our work with Bayesian inference results.

3.2.8 Density Functional Theory Calculations

All DFT calculations were performed in the NWChem computational chemistry software version 7.0.0. [158] Gibbs free energies of the species in the BQDS decomposition pathway were predicted. Each species in the pathway was geometry optimized using the B3LYP functional. The 6-311G** basis set was used. [159, 160] The COSMO model with default parameters was used to implicitly treat molecule solvation by water. [161] The convergence criteria in NWChem used were GMAX = 0.00045, GRMS = 0.00030, XMAX = 0.00180, XRMS = 0.00120, and the electronic energy convergence was $10^{-5}$ hartree. Vibrational, rotational, and translational enthalpic and entropic contributions (assuming an ideal gas with rigid rotor-harmonic oscillator) were included to estimate the free energies at standard state.
Data Availability

The code and data for Bayesian inference analysis have been deposited on the GitHub repository via DOI: 10.5281/zenodo.7807364, and the DFT files and data are available in the NOMAD repository via DOI: 10.17172/NOMAD/2023.01.14-1.

3.3 Results and Discussion

3.3.1 Spectroscopic Measurement of Michael Attack of BQDS

We first examined Michael attack of BQDS in 1 M H$_2$SO$_4$ via spectrophotometric tracking of the concentration of a sacrificial chemical oxidant. BQDS is attractive as a positive electrolyte reactant in aqueous organic RFBs because of its high solubility (4 M) [138] and redox potential (0.65 V vs Ag/AgCl, see cyclic voltammetry measurement in Fig. B.1). However, previous cell cycling experiments [138, 140] have shown that oxidized BQDS is susceptible to self discharge—this results in a progressively lower energy efficiency and the development of a Coulombic imbalance between the negative and positive electrolytes. Based on ex situ voltammetry and chemical analysis, it has been proposed that the origin of self discharge is one [140] or two [138] spontaneous nucleophilic additions of water to oxidized BQDS and its successive oxidized derivatives (denoted O$_1$, O$_2$, and O$_3$, respectively), which results in the formation of reduced, hydroxyl-substituted hydroquinone species (R$_1$, R$_2$ and R$_3$), as illustrated in Fig. 3.1. Note that self discharge of BQDS does not entail oxygen or hydrogen evolution from water. Rather, the Michael addition reaction entails the formation of an adduct between water and a quinone derivative, followed
by electron transfer within the adduct, and proton transfer between the adduct and solution. Because the overall result is that ketone groups in the quinone are reduced and protonated, the process is akin to discharge (reduction) of the quinone. Because oxidized BQDS and its successive oxidized derivatives (Fig. 3.1) are also susceptible to dimerization and other cyclization reactions with each corresponding reduced form, [142] it is necessary to maintain each redox couple in the oxidized form in order to isolate the rates of conversion of O₁ to O₂, O₂ to O₃, etc., hereafter denoted as \( k₁ \) and \( k₂ \), etc. We therefore sought a sacrificial oxidant that would maintain the oxidized form of each redox couple, and then to spectrophotometrically track the decrease in its concentration over time, the rate of which would correspond to the rate of Michael addition. The ideal oxidant must have (1) a redox potential that is high enough to oxidize BQDS but not to oxidize water, and (2) optical absorbance features that do not coincide with, or are negligible compared with those of BQDS. Both of these criteria are met by potassium dichromate (\( \text{K}_2\text{Cr}_2\text{O}_7 \)), which has a redox potential of 1.3 V vs SHE (Fig. B.1), and whose UV-vis spectrum exhibits prominent peaks at 350 and 445 nm (Fig. B.2a and b, where absorbance of BQDS is near zero. Two-electron oxidation of BQDS or any other reduced hydroquinone derivatives by one mole of dichromate is expected to proceed according to the reaction:

\[
\text{Cr}_2\text{O}_7^{2-} + 3 \text{R}_x^{2-} + 14 \text{H}^+ \rightarrow 2 \text{Cr}^{3+} + 3 \text{O}_x + 7 \text{H}_2\text{O} \quad (3.6)
\]

where \( \text{O}_x \) and \( \text{R}_x \) represent oxidized and reduced derivatives, respectively.

The reduction in [\( \text{K}_2\text{Cr}_2\text{O}_7 \)] in the presence of oxidized BQDS was consistent with two successive Michael additions. Figure 3.2a shows selected UV-vis spec-
tra of 0.5 mM $\text{K}_2\text{Cr}_2\text{O}_7$ after the addition of 0.2 mM BQDS. The intensity of the spectra decreased uniformly over the course of 20 hours, consistent with a decrease in $[\text{K}_2\text{Cr}_2\text{O}_7]$. Because $\text{K}_2\text{Cr}_2\text{O}_7$ was added in stoichiometric excess to BQDS, we tracked the decrease in the absorbance peak at 350 nm as a reporter of $[\text{K}_2\text{Cr}_2\text{O}_7]$, based on a calibration curve (Fig. B.2c) and thus the reaction depicted in Eqn. (3.6) (Fig. 3.2b). Upon the addition of the BQDS, there was an instantaneous 0.07 mM decrease in $[\text{K}_2\text{Cr}_2\text{O}_7]$ that was commensurate with two-electron oxidation of BQDS to its oxidized form $\text{O}_1$ (i.e., $\text{R}_1$ to $\text{O}_1$). Over the next hour, the rate of consumption of $\text{K}_2\text{Cr}_2\text{O}_7$ proceeded at an average of about 0.08 mM/h, before slowing to 0.001 mM/h over the subsequent 21 hours. The total consumed $[\text{K}_2\text{Cr}_2\text{O}_7]$ appeared to asymptotically approach 0.2 mM. This total consumption is consistent with three discrete two-electron oxidation events: one for conversion of $\text{R}_1$ to $\text{O}_1$, and one each for $\text{R}_2$ to $\text{O}_2$ and $\text{R}_2$ to $\text{O}_3$.

Control experiments confirmed that both BQDS and $\text{K}_2\text{Cr}_2\text{O}_7$ were required for the observed spectral changes. No spectral changes were observed for BQDS in the absence of $\text{K}_2\text{Cr}_2\text{O}_7$ (Fig. B.3)—consistent with water oxidation being insignificant—and vice versa (Fig. B.1). The control experiments also confirm the absence of any lamp drift because there is no shift observed in the zero-absorbance baseline above 500 nm over time as can be seen in Fig. 3.2a. We have also shown the lamp spectrum in Fig. B.4, where no observable drift is seen in the spectrum of the lamp. Oxidation of BQDS in a thin-layer spectroelectrochemical cell for 19 hours also revealed, consistent with previous work, [138, 140] the disappearance of the original BQDS redox feature, and the emergence of a new redox pair $\sim 200 \text{ mV}$ lower,
Figure 3.2: Tracking the progress of the Michael addition reaction using K$_2$Cr$_2$O$_7$ as a sacrificial oxidizer species, with the absorbance peak at 350 nm used to estimate the amount of K$_2$Cr$_2$O$_7$ consumed. (a) UV-vis spectra over time of a mixture of 0.2 mM BQDS and 0.5 mM K$_2$Cr$_2$O$_7$ in 1 M H$_2$SO$_4$. The decrease in the absorbance of the peak at 350 nm with time is highlighted in the inset. (b) Estimate of the concentration of K$_2$Cr$_2$O$_7$ consumed based on the peak intensity at 350 nm. (c) Estimates for the concentration of K$_2$Cr$_2$O$_7$ consumed for all experiments run with other concentrations of BQDS and K$_2$Cr$_2$O$_7$ normalized to an initial BQDS concentration of 0.2 mM.

around 0.65 V vs SHE (B.1). This new redox pair has been attributed to O$_3$ [138] as, being a para-quinone, it is expected to have a lower reduction potential than the ortho-quinone O$_1$. [162]

We conducted three more BQDS oxidation measurements with different initial BQDS concentrations (Fig. 3.2c), and initial [K$_2$Cr$_2$O$_7$]:[BQDS] ratios varying between 1.6 and 2.5—but always in excess of 1, which is the stoichiometric ratio required for three two-electron oxidation reactions based on Eqn. (3.6). Fig. B.5 reports the [K$_2$Cr$_2$O$_7$] consumed over time for these measurements. Each trace asymptotes close to the expected steady state. When normalized to the same BQDS concentration (Fig. 3.2c), the traces overlap, strongly suggesting the chemical decay of BQDS is first order in [O$_x$], in agreement with the decomposition scheme in Fig. 3.1.
3.3.2 Model Selection and Uncertainty-Quantified Rates of Michael Attack using Bayesian Inference and Multivariate Curve Resolution Analysis

Taken together, the spectroscopic data above constitute prima facie evidence that oxidized BQDS and its subsequent derivatives are susceptible to two, first-order Michael additions. We therefore sought to rigorously quantify the probability that the above data are explained by the model in Fig. 3.1, and then to calculate uncertainty-quantified reaction orders and rates for each individual Michael addition.

We first evaluated the most likely number of Michael addition reactions indicated by the above spectroscopic data, among one (i.e., conversion of O₁ to O₂), two (O₁ to O₂ to O₃) and three (O₁ to O₂ to O₃ to O₄). The unknown model parameters include reaction rates and orders for each individual transition (e.g., k₁, k₂, m₁ and m₂ for the model with two Michael additions). We chose a prior probability density function (PDF) of the reaction rate to be uniformly distributed over four orders of magnitude in log space, i.e., \( \log_{10} k \sim U[-6, -2] \) for all \( k \) terms, and a reaction order \( m \) that could take a value from \( \{0, 1, 2\} \) with uniform probability, i.e., \( \mathbb{P}(m = 0) = \mathbb{P}(m = 1) = \mathbb{P}(m = 2) = \frac{1}{3} \). We used the peak in the optical absorbance spectrum at 350 nm as our observation of \([\text{K}_2\text{Cr}_2\text{O}_7]\) because the optical absorbance from \(\text{K}_2\text{Cr}_2\text{O}_7\) at that wavelength is significantly stronger than that of BQDS (Fig. B.2a), its derivatives, [140] and \(\text{Cr}^{3+}\). Moreover, we assumed that the noise on absorbance of different snapshots are independent and identically distributed, such that the covariance matrix \(\Sigma_\epsilon\) of the additive Gaussian error \(\epsilon\) in Eqn. (3.2) is a diagonal matrix with identical entries. The scale of the additive noise was determined by
the standard deviation of the 350 nm peak from calibration curve measurements (Fig. B.2b). As shown in Fig. B.6, the standard deviation is about 0.0096 at 350 nm, therefore, we set $\Sigma_\epsilon$’s diagonal entries to $0.0096^2$.

Figure 3.3a shows the results of Bayesian model selection. The model posterior probabilities were computed following Eqn. (3.4), which comprises random sampling of rate constants and reaction orders from their prior distribution and then comparing their predictions of $K_2Cr_2O_7$ consumption with corresponding experimental values from UV-vis spectra. The Michael addition reaction was solved numerically using a 4th order Runge-Kutta time-marching algorithm, to ensure good numerical accuracy. We found using $N = 10^6$ samples in Eqn. (3.4) that the model with two Michael additions (i.e., conversion of O1 to O2 and then O3) has the highest model evidence among three candidate models. This result is consistent with the stoichiometry of $K_2Cr_2O_7$ consumption in Section 3.3.1.
Figure 3.3: Bayesian inference predictions for probabilities of competing models. (a) Results of Bayesian model selection, showing the probabilities that UV-vis data in Fig. 3.2 are explained by a decay model with one versus two versus three Michael addition reactions. The results indicate that two Michael additions has a significantly higher probability compared with the other models. (b) Marginal posterior probability distribution of the reaction orders ($m$) for the BQDS decay model with two Michael addition reactions ($P(m_1, m_2 | y, M)$). The combination $m_1 = m_2 = 1$ has a probability very close to 1.

We then applied Bayesian inference to ascertain unknown parameters for the most plausible model. We first determined the most probable $m$ values by computing $P(m_1, m_2 | y, M)$, then sampled $k$ while the reaction orders were fixed to their most probable values. This strategy was chosen instead of sampling $k$ and $m$ jointly because sampling from a mixed continuous-discrete space is computationally expensive, and there are only nine possible combinations of reaction order terms for the two-Michael addition model. Figure 3.3b shows the marginal posterior of $m_1$ and $m_2$. 
given the UV-vis data, which was computed through:

\[
\mathbb{P}(m_1, m_2|y, \mathcal{M}) = \int p(k_1, k_2, m_1, m_2|y, \mathcal{M}) \, dk_1 \, dk_2 \\
\propto \mathbb{P}(m_1, m_2|\mathcal{M}) \int p(y|k_1, k_2, m_1, m_2, \mathcal{M}) \, p(k_1, k_2|\mathcal{M}) \, dk_1 \, dk_2,
\]

(3.7)

where the integral was estimated by taking the average of likelihood values with \(k_1\) and \(k_2\) sampled from the prior. Our results revealed that the combination \(m_1 = m_2 = 1\)—that is, conversion of \(O_1\) to \(O_2\) and \(O_2\) to \(O_3\) both first order in \([O_x]\)—is the most likely, with a posterior probability close to 1. Importantly, our analysis rules out the rather unlikely possibility that the apparently first-order reactivity inferred in Section 3.3.1 was due to one reaction being zeroth order and the other being second order in \([O_x]\).

We next estimated the rate constants for each Michael addition using Bayesian parameter inference. Figure 3.4a plots samples generated from the posterior for reaction rates \(p(\log_{10} k_1, \log_{10} k_2|y, m_1 = 1, m_2 = 1, \mathcal{M})\) and Fig. 3.4b reports the logarithm of the un-normalized posterior PDF (i.e., of the numerator in Bayes’ rule Eqn. (3.1)). Our results indicate that there are two local maxima in the contour plot, but the bottom right local maxima has a much higher probability density value, and consequently only one high probability cluster emerged from the MCMC samples. The bottom right cluster corresponds to \(k_1 = 3.768 \times 10^{-4}\) and \(k_2 = 1.986 \times 10^{-5}\) s\(^{-1}\). The standard deviations of samples are \(1.248 \times 10^{-5}\) and \(2.684 \times 10^{-7}\) s\(^{-1}\) for \(k_1\) and \(k_2\), respectively. These results indicate that Michael attack to \(O_1\) is considerably
more rapid than to O₂, with half lives of conversion of 0.51 and 9.69 h, respectively.

Figure 3.4: Bayesian inference predictions of the Michael addition reaction constants. (a) Bayesian inference of the posterior distribution for \( k_1 \) and \( k_2 \). (b) Contour plot of the logarithm of the un-normalized posterior PDF (i.e., of the numerator in Bayes’ rule Eqn. (3.1)) for \( \log_{10} k_1 \) and \( \log_{10} k_2 \) at the most probable reaction orders \( m_1 = m_2 = 1 \). Blue points (cluster) are the MCMC samples, and the red point marks the sample with the highest posterior PDF located at \( k_1 = 3.768 \times 10^{-4} \) and \( k_2 = 1.986 \times 10^{-5} \) s\(^{-1}\). The green point marks the location of \( k_1 \) and \( k_2 \) obtained by applying MCR-ALS to the spectroscopic data corresponding to BQDS decay from \( \text{K}_2\text{Cr}_2\text{O}_7 \) consumption, whereas the purple point marks the location of \( k_1 \) and \( k_2 \) obtained by applying MCR-ALS to BQDS decay in \textit{operando}.

Figure 3.5a shows the expected temporal evolution in the concentration of all oxidized species for initial concentrations of 0.4 and 0.2 mM for \( \text{K}_2\text{Cr}_2\text{O}_7 \) and BQDS, respectively, reported in Fig. 3.2c, assuming first-order kinetics for Michael attack and \( k_1 \) and \( k_2 \) values set at the highest posterior probability (red point) from Fig. 3.4a. The temporal evolution of the same species in the other experiments with other initial \( \text{K}_2\text{Cr}_2\text{O}_7 \) and BQDS concentrations are shown in Fig. B.7. Figure 3.5b reports the computational temporal consumption of dichromate, normalized to an initial concentration of 0.2 mM and overlaid with similarly normalized experimental data.
in Fig. 3.2c. There is excellent agreement between the computational and experimental transients in [K₂Cr₂O₇], which strongly supports the validity of our Bayesian inference results.

Figure 3.5: Bayesian inference predictions of BQDS derivative concentrations. (a) Computational evolution of oxidized species for the case with 0.4 mM initial [K₂Cr₂O₇] and 0.2 mM initial [BQDS] assuming Bayesian-inferred rate constants, and (b) Computational and experimental estimates of consumption of K₂Cr₂O₇ over time, where the consumed K₂Cr₂O₇ concentration is normalized by dividing it by the initial BQDS concentration and multiplying by 0.2 mM.

In addition to Bayesian inference, we also estimated the decay rate constants by applying the MCR-ALS suite of applications to the spectroscopic data. Given the first-order reactivity of O₁ and O₂ determined above, the decay of BQDS and its oxidized derivatives can be modelled as a first-order multi-component kinetics
problem, as follows:

\[
\frac{d[O_1]}{dt} = -k_1[O_1] \quad (3.8)
\]
\[
\frac{d[O_2]}{dt} = k_1[O_1] - k_2[O_2] \quad (3.9)
\]
\[
\frac{d[O_3]}{dt} = k_2[O_2] \quad (3.10)
\]

where we have neglected the rapid chemical oxidation reactions. This system of equations has an analytical solution, shown in Eqn. (B.1) to (B.3) for \([O_1]\), \([O_2]\) and \([O_3]\) respectively in Appendix B.

The concentration of consumed \(K_2Cr_2O_7\) is a function of the instantaneous concentrations of \(O_2\) and \(O_3\):

\[
[K_2Cr_2O_7]_{\text{consumed}} = \frac{1}{3}[O_2] + \frac{2}{3}[O_3]. \quad (3.11)
\]

By substituting the analytical expressions for \(O_2\) and \(O_3\) into Eqn. (3.11), the consumed \([K_2Cr_2O_7]\) can be written as a function of \(k_1\) and \(k_2\). Thus, knowing the concentration of \(K_2Cr_2O_7\) at each time step permits one to determine the values of \(k_1\) and \(k_2\). We approached this problem by first calculating \([K_2Cr_2O_7]\) from each UV-vis spectrum based on the peak at 350 nm. This was done using MCR-ALS techniques (Appendix B). The values for \(k_1\) and \(k_2\) were then determined following Eqn. (3.11) by using the concentrations determined for consumed \([K_2Cr_2O_7]\) using MCR-ALS coupled with a fitting procedure from MATLAB’s curve fitting toolbox. [163] The results obtained for \(k_1\) and \(k_2\) for the four data sets with different initial
concentrations are presented in Table 3.1. The values for $k_1$ and $k_2$ averaged over these four data sets are $5.40 \times 10^{-4}$ s$^{-1}$ and $3.34 \times 10^{-4}$ s$^{-1}$, which are reasonably consistent with the decay rate constants calculated from Bayesian inference (green points in Fig. 3.4).

Table 3.1: Michael attack rate constants determined by fitting first-order kinetics to consumed $K_2Cr_2O_7$ concentration from UV-vis data. Rate constants obtained using Bayesian inference are shown for comparison.

<table>
<thead>
<tr>
<th>$[K_2Cr_2O_7]_0$ (mM)</th>
<th>$[BQDS]_0$ (mM)</th>
<th>$k_1$ (10$^{-4}$ s$^{-1}$)</th>
<th>$\sigma_{k_1}$ (10$^{-5}$ s$^{-1}$)</th>
<th>$k_2$ (10$^{-5}$ s$^{-1}$)</th>
<th>$\sigma_{k_2}$ (10$^{-7}$ s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.40</td>
<td>0.20</td>
<td>6.52</td>
<td>2.53</td>
<td>3.11</td>
<td>3.14</td>
</tr>
<tr>
<td>0.40</td>
<td>0.25</td>
<td>5.27</td>
<td>0.66</td>
<td>2.95</td>
<td>1.09</td>
</tr>
<tr>
<td>0.50</td>
<td>0.20</td>
<td>6.04</td>
<td>1.09</td>
<td>5.39</td>
<td>5.89</td>
</tr>
<tr>
<td>0.50</td>
<td>0.30</td>
<td>3.79</td>
<td>0.24</td>
<td>1.90</td>
<td>0.46</td>
</tr>
</tbody>
</table>

Average, MCR-ALS 5.40 3.34
Bayesian inference 3.77 1.25 1.99 2.68

3.3.3 Spectrophotometric Analysis of BQDS Decomposition in an *Operando* Flow Cell

The preceding spectroscopic measurements and analysis were aimed at quantifying the rate(s) of purely chemical decomposition of BQDS, i.e., in the absence of an applied potential or interaction with typical flow cell hardware (porous electrodes and membrane). To evaluate electrochemical BQDS decomposition during cycling of a flow cell, we set up a compositionally asymmetric flow cell whose capacity-limiting electrolyte (CLE) comprised 5–15 mM of BQDS in a supporting electrolyte of 0.9 M $H_2SO_4$ and 0.1 M $CH_3COOH$. An excess of Methylene Blue was used as the counter electrolyte, and the two electrolytes were separated by a Nafion 115 membrane. The CLE was circulated among the electrolyte reservoir, cell, and an absorbance micro
cross flow cell with a path length of 0.15 mm, for continuous UV-vis measurements (Fig. B.14). No K₂Cr₂O₇ was present in the CLE, meaning that all UV-vis spectra represented a concentration-weighted average of BQDS and all its oxidation/decay products.

Figure 3.6 reports operando UV-vis spectra of a CLE containing 15 mM of BQDS after potentiostatic oxidation at a cell voltage of 0.8 V. Over the course of the experiment, the absorbance peak at 305 nm in the R₁ spectrum diminished, while a new peak at 260 nm evolved, increased in intensity for roughly 2 hours, and then slowly reduced in intensity. A similar trend has been observed previously. [140]

We carried out two other experiments at BQDS concentrations of 5 and 8 mM but under otherwise identical potentiostatic conditions (Fig. B.8a and b, respectively); Fig. B.8c reports the current response for all three cells and Fig. B.8d shows the peak intensities at 260 and 305 nm coinciding when the UV-vis spectra are scaled
to a concentration of 5 mM. This concentration-independent scaling is consistent with first-order kinetics for all species conversions, as has been demonstrated in the preceding sections.

We verified that these spectral trends did not result from some spurious chemical interaction between BQDS and the hardware within the absorbance cross flow cell. To do so, we set up an identical flow cell without the cross flow cell apparatus, and periodically took aliquots from the CLE for in situ UV-vis analysis. Fig. B.8e reports the absorbance at 260 nm over time for two such in situ measurements; they show clear qualitative agreement with the UV-vis trends for the operando setup in Fig. B.8d.

For the practical application of this method to other molecules and mechanisms, certain constraints and limitations have to be considered. First, the UV-vis spectra of the reactants and the degradation products need to be intense enough to be detected and significantly distinct from one another. Second, a detectable amount of the degradation products must form during the experiment. To give an example, assuming a change in absorbance of at least 0.05 is required to detect a decay product whose molar absorptivity is $10^{-3}$ M$^{-1}$cm$^{-1}$, over a cycling period of no more than 10 days, the reactant/capacity fade rate should be at least 0.5 %/day. For timescales larger than 10 days, the in situ method can still be used, where aliquots can be drawn every few days and their UV-vis spectra analyzed.
3.3.4 Estimation of Decay Rate Constants and UV-vis Spectra of Oxidation Products

We next sought to extract pure UV-vis spectra of intermediate species $O_1$, $O_2$, and $O_3$ using the MCR-ALS suite of applications. [141] Isolating these pure spectra from the spectra in Fig. 3.6 is a challenge because the latter originate from a system with continuously varying proportions of four possible components: $R_1$, $O_1$, $O_2$, and $O_3$. Chemometric techniques such as MCR-ALS can overcome this challenge, because they use matrix factorization methods combined with suitable physical and chemical constraints to deconvolute the component spectra and determine the concentrations and pure spectral profiles of each component. MCR-ALS analysis was ran on the spectral data set within a truncated wavelength range of 230 nm to 500 nm. Each spectrum was represented as a row of a matrix, and initial estimates for the concentration matrix were made using the purest variable detection method (SIMPLISMA). [141, 156, 157] The system was analyzed as a four-component system comprising $R_1$, $O_1$, $O_2$ and $O_3$, with the constraints used to reduce the ambiguity in matrix decomposition being non-negativity of spectra and concentrations using a non-linear least squares method, as well as a stoichiometric balance closure constraint. A hard constraint for following a first-order kinetic model was also used. As a control, we ran MCR-ALS analysis on operando UV-vis spectra taken on a ferrocyanide-based electrolyte during bulk electrolytic cycling (Fig. B.9), and demonstrated that the technique successfully infers the correct spectral profiles and concentrations for ferrocyanide and ferricyanide (Fig. B.10) (Appendix B.0.3 for more details).
Estimates for the rate constant for electrochemical conversion of R to O (k), k1, and k2 are shown in Table 3.2. Figure 3.7 shows the estimated spectra from the experiment with [BQDS]0 = 8 mM. The estimated spectral profiles indicate that O2 and O3 have similar spectra, with O3 having a weaker peak centered around 260 nm compared to O2. This finding makes sense of the observation from the experimental UV-vis spectra that the peak at 260 nm rose and then fell during oxidative electrolysis of the BQDS electrolyte (Fig. B.8e). The larger variance for k2 than k1 is likely due to this phenomenon as well; the overlap in peak position for O2 and O3 limits the ability of MCR-ALS to distinguish between the two species. On the other hand, the rate constants k0 and k1 are relatively well determined and correspond to time constants on the order of a minute and half an hour, respectively. The estimated concentration profiles for R1, O1, O2, and O3 for an [BQDS]0 = 8 mM and other concentrations are shown in Fig. B.11 and the estimated spectra are shown in Fig. B.12.

Table 3.2: Rate constants for the oxidation of BQDS and subsequent Michael attack determined using MCR-ALS performed on the in-line UV-vis data from operando flow cells.

<table>
<thead>
<tr>
<th>[BQDS]0</th>
<th>k0 (10^{-2}s^{-1})</th>
<th>σk0 (10^{-5}s^{-1})</th>
<th>k1 (10^{-4}s^{-1})</th>
<th>σk1 (10^{-7}s^{-1})</th>
<th>k2 (10^{-5}s^{-1})</th>
<th>σk2 (10^{-9}s^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>5 mM</td>
<td>3.76</td>
<td>9.19</td>
<td>3.92</td>
<td>9.06</td>
<td>2.57</td>
<td>37.6</td>
</tr>
<tr>
<td>8 mM</td>
<td>4.68</td>
<td>5.67</td>
<td>5.67</td>
<td>7.11</td>
<td>0.78</td>
<td>7.56</td>
</tr>
<tr>
<td>15 mM</td>
<td>1.24</td>
<td>6.76</td>
<td>4.78</td>
<td>6.76</td>
<td>2.25</td>
<td>19.7</td>
</tr>
</tbody>
</table>
The mean values for $k_1$ and $k_2$ are plotted in Fig. 3.4 and superimposed on the uncertainty-quantified estimates of $k_1$ and $k_2$ obtained via Bayesian inference and those from MCR-ALS analysis on the ex situ BQDS decay data. Within uncertainty, there is good agreement among both sets of estimates, leading to the conclusion that reactant decay and thus capacity fade within a flow cell containing BQDS in the CLE is largely driven by chemical decay of the BQDS electrolyte based on the mechanism in Fig. 3.1.

### 3.3.5 Discussion

The decomposition mechanism in Fig. 3.1, which was first proposed in a study by Yang et al.,[138] was originally formulated based on NMR measurements of aliquots from a BQDS electrolyte after 2, 120 and 400 charge-discharge cycles in a flow cell.
cell. NMR is a more chemically specific technique than UV-vis, but it is difficult to quantify decay kinetics from such NMR measurements because if capacity fade is driven by a chemical decay—as has now been determined—the amount of time oxidized BQDS (or successive oxidized derivatives) are present in solution is a more relevant metric rather than the number of cycles spent in a flow cell.[106] Therefore, to verify that the water addition steps in Fig. 3.1 proceeded under potentiostatic conditions, we set up a flow cell with a BQDS-containing CLE and Methylene Blue counter electrolyte, and, over the course of 24 hours, drew aliquots from the CLE while it was under a fixed oxidative potential of 0.8 V.

The results of this experiment are shown in Fig. B.13a. The spectrum for BQDS contains two singlets at 7.17 and 7.41 ppm, corresponding to protons at the two unsubstituted aryl positions.[138, 142] After 1 hour, a singlet at 7.06 ppm is dominant, corresponding to the proton at the only unsubstituted aryl position in O$_2$. After 24 hours, the peak corresponding to the aromatic proton in O$_2$ disappeared, and no aromatic proton peaks were visible in the NMR scan, which would be expected given that all aryl positions are substituted in O$_3$. The evolution in NMR spectra and relative shifts in peak position are in line with our expectations based on NMR spectra simulated for O$_1$, O$_2$ and O$_3$ using ChemDraw (Fig. B.13b).

We also predicted the decomposition reaction thermodynamics for O$_1$ to R$_2$ and O$_2$ to R$_3$ using DFT modeling with the B3LYP functional and COSMO implicit solvation (Fig. 3.8). The Brønsted-Evans-Polanyi (BEP) principle observes that the difference in activation energy between two reactions of the same family is proportional to the difference of their reaction energies. Assuming the principle holds, DFT
calculations of the reaction energies allow the kinetics of the two reactions responsible for capacity fade, O$_1$ to R$_2$ and O$_2$ to R$_3$, to be compared qualitatively. The O$_1$ to R$_2$ reaction (Fig. 3.8a) is more thermodynamically favored than O$_2$ to R$_3$ (Fig. 3.8b), with overall free energy changes of $-61.7$ kJ/mol versus $-23.0$ kJ/mol, respectively. The first elementary step of the O$_2$ to R$_3$ pathway is much more endothermic ($\Delta G_{O2\rightarrow I4} = 107.8$ kJ/mol) than the first elementary step of the O$_1$ to R$_2$ pathway (i.e., $\Delta G_{O1\rightarrow I2} = 71.4$ kJ/mol). Subsequent steps for both reactions are downhill in free energy or essentially thermoneutral (i.e., I$_5$ to R$_3$). Thus, the first elementary step of O$_2$ to I$_4$ likely has the highest activation energy for both pathways based on the BEP principle. It follows that the O$_1$ to R$_2$ decomposition should occur more rapidly than that of O$_2$ to R$_3$ ($k_2 < k_1$), which is consistent with the results of applying MCR-ALS and Bayesian inference to our spectroscopic data. The DFT-predicted energetics qualitatively follow what is expected for apparent activation barriers calculated from the experimental values for $k_1$ and $k_1$ obtained in Section 3.3.2 and Section 3.3.4. Assuming transition state theory, and a pre-exponential factor of $k_b T/h = 6 \times 10^{12}$ s$^{-1}$, we obtained activation barriers of 86 and 91 kJ/mol for the conversion of O$_1$ to R$_2$ and O$_2$ to R$_3$, respectively.
Figure 3.8: DFT-computed reaction free energy diagram for decomposition of (a) $O_1$ to $R_2$ and (b) $O_2$ to $R_3$ at standard conditions.
Taken together, our DFT computations and NMR results strongly corroborate conclusions from Section 3.3.2 and Section 3.3.4. Thus, combining UV-vis spectroscopy—whether ex situ or from *operando* flow cells—with matrix-based curve resolution, as well as Bayesian model selection and parameter inference, is a viable strategy for elucidating the role of Michael attack in the decomposition of flow battery reactants. Importantly, our techniques are able to resolve processes occurring across a range of timescales, from a minute to several hours. In the context of ongoing efforts toward designing Michael attack-resistant quinone-based posolytes, [138, 164, 165] the methods demonstrated in this paper might be extended in future work toward high-throughput screening of other high-potential quinone derivatives, [162] or evaluating the correlation between the rate of Michael attack and a quinone’s redox potential.[166] Moreover, UV-vis signatures of intermediate species inferred from *operando* spectroscopy may be compared against ex situ spectra of decay species that have been proposed to feature in one or more hypothesized decay mechanisms. These campaigns may be extended to other molecular classes that are subject to Michael attack, and which are currently under consideration for organic flow battery applications, such as quinoxalines [167] and biphenols. [168]

More generally, the combination of spectrophotometry with statistical inference techniques as depicted by the workflow in Fig. 3.1 can be deployed in connection with a wider variety of decomposition mechanisms to which flow battery reactants from other molecular classes are susceptible. Although it might be difficult to use these methods to determine a completely unknown degradation mechanism, they may be used to verify a proposed hypothesis about the link between reactant decay and
capacity fade, choose between competing hypotheses (which might be found based on techniques such as NMR spectroscopy and mass spectrometry), or guide the design of cycling experiments in such a way as to extract decay rate parameters with high certainty and low experimental effort (i.e., via optimal experimental design [169]). In addition to UV-vis spectroscopy, it is also possible to apply Bayesian techniques to other forms of spectroscopic data where the signal may be proportional to concentration such as Fourier Transform Infrared (FTIR) spectroscopy. The decay rate parameters thus obtained may in turn be supplied to analytical or numerical electrochemical models that can simulate capacity retention for a given load/duty cycle (Chapter II), [170] thus paving the way to flow battery lifetime predictions. Even though we conduct our analysis for concentrations below 20 mM, we determined reaction kinetic rates and orders, so it should be possible to apply these to predict decay rates when practical concentrations (> 0.5 M) are used. Beyond capacity fade in organic RFBs, these methods may also be deployed for other flow cell-based applications in which charge transfer is accompanied by homogeneous chemical conversion(s), such as electrosynthesis [171] or (electro)chemical separations (e.g., CO₂ capture). [172]
CHAPTER IV

Substituent Impact on Quinoxaline Performance
and Degradation in Redox Flow Batteries

4.1 Introduction

Quinoxalines are an underexplored but promising class of negative electrolyte molecules in this respect because many derivatives have lower redox potentials [173, 174, 175] and higher solubilities [173, 176, 177] than typical anthraquinones and phenazines. The equivalent weight of quinoxaline (65 g/mol) is also lower than that of anthraquinone (104 g/mol) and phenazine (90 g/mol), and many substituted quinoxalines are straightforward to synthesize in one-step reactions using widely available precursors. [178, 179, 180] A handful of studies reported the cycling behavior of alkaline flow cells containing quinoxalines, [174, 20, 181] but all show rapid capacity fade (equivalent to > 20%/day). Progress in developing more stable quinoxalines is hindered because the connection between capacity fade and molecular decomposition mechanisms and rates is not well understood. For example, although reduced
quinoxalines are known to undergo tautomerization, [182, 183, 184] its impact on capacity retention in flow cells is unclear. A recent study suggested quinoxaline dimerization as the primary degradation mechanism driving capacity fade in alkaline electrolytes. [174] Other reports have proposed Michael attack or irreversible hydrogenation as possible decomposition mechanisms. [185, 186]

In this study, we investigate the relationship between capacity fade in quinoxaline-based RFBs and molecular decay by combining flow cell cycling with a suite of chemical analysis techniques, including ultraviolet-visible (UV-vis) spectroscopy, nuclear magnetic resonance (NMR) spectroscopy, and mass spectrometry. Using 2,3-dimethylquinoxaline-6-carboxylic acid (DMeQUIC) as a model quinoxaline, our analysis reveals that tautomerization of the reduced form of quinoxalines is primarily responsible for capacity fade rather than Michael addition, dimerization, or hydrogenation. By subjecting spectroscopic data obtained from operando flow cells to a Bayesian statistical inference protocol, we calculate the rate constant of tautomerization and show that it quantitatively explains fade rates observed in cycled cells. Using DFT calculations, we rationalize trends in tautomerization energetics of quinoxaline derivatives and suggest molecular design rules. We identify a more tautomerization-resistant quinoxaline-2-carboxylic acid (2QUIC) that did not exhibit capacity fade for 220 hours of flow cell cycling in a mixed symmetric configuration.
4.2 Materials and Methods

4.2.1 Chemicals

Sodium ferrocyanide (>98%), sodium hydroxide (>99%) and sodium chloride (>99%) were purchased from Sigma Aldrich. 2,3-dimethyl-quinoxaline-6-carboxylic acid (>97%), quinoxaline-6-carboxylic acid (>95%), 2,3-dimethylquinoxaline (>97%), quinoxaline-2-carboxylic acid (>97%), 2,3-bis(bromomethyl)quinoxaline (>97%), 3-amino-quinoxaline-2-carboxylic acid (QUI2C3A), sodium sulfite (98%), 3,4-diaminobenzoic acid (>97%), glyoxal sodium bisulfite (98%), dimethyl sulfoxide, and ethanol (absolute) were purchased from Fisher Scientific and used as received. Methane sulfonic acid-duterium, and methane sulfonic acid- sodium salt were purchased from Sigma Aldrich and used as received. 2,3-dimethyl-1,2,3,4-tetrahydroquinoxaline-6-carboxylic acid was used as received from 1 ClickChemistry. All electrolyte solutions were made with deionized water (18 MΩ·cm).

4.2.2 Ultraviolet-visible Spectroscopy

UV–vis spectroscopy was conducted on an Ocean-HDX-UV–VIS spectrometer HDX00518 (Ocean Insight). Spectroscopic measurements were taken using a 50 and 25 ms integration times for the ex situ and operando experiments, respectively, and averaged over 50 scans in both cases. The operando UV-vis cross flow cell was purchased from Firebird Optics, and had a path length of 60 µm. Unless otherwise noted, all ex situ measurements were conducted at a nominal 0.1 mM concentration of the active material in a supporting electrolyte of 3 M NaOH.
4.2.3 Cyclic Voltammetry

Three-electrode cyclic voltammograms (CVs) of all charge carriers studied in this work were conducted in 3 M NaOH, unless specified otherwise, using a 5 mm diameter glassy carbon disk electrode (Basi Inc.) along with an Ag/AgCl reference electrode (BaSI Inc.) and Pt wire (BaSI Inc.) as the counter electrode at a scan rate of 50 mV/s. All CVs were conducted at a nominal active material concentration of 1 mM, using a CH Instruments CHI7013E potentiostat.

4.2.4 Flow Cell Preparation and Cycling

Flow cells were constructed with hardware from Fuel Cell Technologies (Albuquerque, New Mexico) and assembled in a zero-gap configuration, similar to previous reports. [57, 31] Pyrosealed POCO graphite flow plates with serpentine flow patterns were used for both electrodes, and 50 µm-thick Nafion 212 (Fuel Cell Store) was used as the membrane. Each electrode comprised a 5 cm² sheet of CE Tech GF020 graphite felt (Fuel Cell Store, 2.1 mm thick). The electrodes were oven-dried in air for 12 h at 400 °C prior to use, whereas membranes were pretreated by soaking in the supporting electrolyte for 24 h before use in the cell. The electrodes and membrane were held in place using Viton sheets with the 5 cm² electrode area cut out. The torque applied during cell assembly was 13 Newton-meters on each of the eight bolts. Either a Longer DG-15/Cole Parmer SK-77202-60 peristaltic pump or a KNF NFB30 diaphragm pump circulated the electrolytes through the flow cell through fluorinated ethylene propylene tubing (inner diameter = 1/16”) sourced from McMaster Carr. Calibration curves were obtained for each pump that permitted translation from rev-
olutions per minute to a volumetric flow rate in mL/min. A flow rate of 50 mL/min was used in the cell cycling and operando flow cell experiments. All flow cells were cycled in a nitrogen glovebox with $\leq 2$ ppm O$_2$. The operando flow cell experiments were conducted outside the glovebox but the negative electrolyte was protected from atmospheric oxygen by maintaining a blanket of nitrogen gas in the headspace.

Sodium ferrocyanide (Na$_4$Fe(CN)$_6$) was used in the non-capacity-limiting electrolyte in all of our compositionally asymmetric cells. Unless otherwise noted, cycling experiments were performed using a constant-current, constant-voltage cycling protocol to access the entire capacity of the capacity-limiting electrolyte. [46] In this protocol, a constant current is applied to the cell until a specified potential limit is reached; the cell is then held at that potential until the current density reaches an absolute value of 1 mA/cm$^2$. A Biologic VSP potentiostat was used for the cell cycling measurements.

### 4.2.5 Permeability Measurements

Membrane permeability was measured using homemade glass H-cells with a liquid volume of 6 mL on each side were used, along with Viton gaskets to hold the membrane with an opening of 0.9 cm$^2$. The donating side was filled with the charge carrier and supporting electrolyte whereas the receiving side contained the supporting electrolyte only. The concentration of crossed over material in receiving side was characterized using UV-vis spectrophotometry and the permeability was calculated from the slope of crossed over concentration vs time based on Fick’s law.
4.2.6 Synthesis of sodium 2,3-bismethylsulfonate (DMeSQUI)

DMeSQUI was synthesized following a previously reported procedure (Fig. C.1b). [174] 0.632 g 2,3-bis(bromomethyl)quinoxaline (2 mmol) was stirred in dimethylsulfoxide (DMSO, 6 mL) and aqueous 1.1 M Na$_2$SO$_3$ (4 mL) at 100 °C for 16 h in a sealed vial. The resulting solution was then cooled and filtered through filter paper. The filtrate volume was reduced to 5 mL by evaporation by heating the solution and then ethanol (50 mL) was added. The resulting suspension was filtered using filter paper and the white precipitate was collected and dried.

The NMR spectrum of DMeSQUI is shown in Fig. C.2, and CV in Fig. C.3.

4.2.7 Mass Spectrometry and NMR Spectroscopy

Mass spectrometry was performed using an Agilent 6230 TOF Mass spectrometer with a C18 column on samples diluted to 100 µM in water with an injection volume of 20 µl. All measurements were carried out in negative ion mode.

All $^1$H and $^{13}$C-NMR spectra were acquired at room temperature in deuterated solvents using a Bruker Avance Neo 500. Proton NMR spectra were taken using a 2 s relaxation delay and carbon NMR spectra had a 1 s relaxation delay. All chemical shifts are reported in units of δ(ppm) relative to tetramethylsilane (TMS) and referenced to residual solvent. Peak multiplicities were reported in the following manner: singlet (s), doublet (d), doublet of doublets (dd), triplet (t), quartet (q), multiplet (m), and broad signal (br). We used a solution of 0.1 M NaOD and 0.05 M of either CH$_3$SO$_3$Na or CH$_3$SO$_3$Na (as specified for each experiment) in D$_2$O as the internal standard. For all our NMR measurements, we mixed 150 µl of the sample
solution with 600 µl of the internal standard by volume, and 600 µl of the resulting solution were put into the NMR tube.

4.2.8 Bayesian Inference

Upon reduction, DMeQUIC converts to rDMQ, which is understood to decompose into a transient, redox-active intermediate, tDMQ, and a final, redox-inactive form, fDMQ:

$$\text{DMeQUIC} \xrightarrow{k_0} r\text{DMQ} \xrightarrow{k_1} t\text{DMQ} \xrightarrow{k_2} f\text{DMQ}$$ (4.1)

Assuming first-order kinetics, the reactions can be described by the following equations:

$$\frac{d[D\text{MeQUIC}]}{dt} = -k_0[D\text{MeQUIC}]$$ (4.2)

$$\frac{d[r\text{DMQ}]}{dt} = k_0[D\text{MeQUIC}] - k_1[r\text{DMQ}]$$ (4.3)

$$\frac{d[t\text{DMQ}]}{dt} = k_1[r\text{DMQ}] - k_2[t\text{DMQ}]$$ (4.4)

$$\frac{d[f\text{DMQ}]}{dt} = k_2[t\text{DMQ}],$$ (4.5)

where $k_0$, $k_1$, and $k_2$ are rate constants that are unknown and of interest. The pure spectra (i.e., molar absorption coefficient at each wavelength) of rDMQ, tDMQ, and fDMQ (denoted hereafter as $S_{r\text{DMQ}}$, $S_{t\text{DMQ}}$ and $S_{f\text{DMQ}}$, respectively) are also unknown. Note that the pure spectrum of DMeQUIC (i.e., $S_{D\text{MeQUIC}}$) is known because the initial concentrations of all the other species (i.e., prior to DMeQUIC
reduction) are equal to zero.

We use $\theta$ to denote the collection of unknown parameters (rate constants and pure spectra), and $y_t$ to denote the observations (absorbance at time $t$). Following the Beer-Lambert law, the observation model is

$$y_t = G(\theta; S_{DMeQUIC}, t) + \epsilon$$

$$= \left[DMeQUIC\right]_t S_{DMeQUIC} + \left[rDMQ\right]_t S_{DMQ} + \left[tDMQ\right]_t S_{DMQ} + \left[fDMQ\right]_t S_{DMQ} + \epsilon,$$  

(4.6)

where the path length term is factored out. Here $[\text{DMeQUIC}]_t$, $[\text{rDMQ}]_t$, $[\text{tDMQ}]_t$ and $[\text{fDMQ}]_t$ are the concentrations solved by the reaction kinetics at time $t$, and $\epsilon$ is a noise term that follows a zero-mean Gaussian distribution $\mathcal{N}(0, \Sigma_\epsilon)$, where $\Sigma_\epsilon$ is a diagonal matrix with the identical entry 0.01$^2$ on the diagonal. The noise term represents the discrepancy between model prediction and experimental observation that may arise due to, for example, measurement variability and other factors not represented by the model. The probability density function (PDF) of likelihood for observing $y_t$ given underlying parameters being $\theta$ can be evaluated as

$$p(y_t | \theta) = p(y_t - G(\theta; S_{DMeQUIC}, t)) = \mathcal{N}(y_t - G(\theta; S_{DMeQUIC}, t); 0, \Sigma_\epsilon).$$

After the spectroscopic data is obtained, the uncertainty on unknown parameters $\theta$ can be updated via Bayes’ rule:

$$p(\theta | y) = \frac{p(y | \theta)p(\theta)}{p(y)} \propto p(y | \theta)p(\theta),$$  

(4.7)

where $p(\theta)$ is the prior PDF (i.e., the uncertainty before incorporating the observed
data), \( p(\theta | y) \) is the posterior PDF (i.e., the updated uncertainty after incorporating the observed data), \( p(y) \) is the model evidence (also known as the marginal likelihood) which is a constant with respect to parameters \( \theta \), and \( p(y | \theta) \) is the likelihood PDF described earlier. Assuming the independence of noise terms, the overall likelihood PDF can be factored to be the product of each data point’s individual likelihood:

\[
p(y | \theta) = \prod_t p(y_t | \theta).
\]  

(4.8)

We also adopt a Bayesian prior PDF that starts with all unknown parameters being independent:

\[
p(\theta) = p(k_0)p(k_1)p(k_2)p(S_{\text{IDMQ}})p(S_{\text{DMQ}})p(S_{\text{IDMQ}}),
\]  

(4.9)

where the prior of the logarithmic reaction rates follows a non-informative uniform distribution i.e., \( \log_{10} k \sim \mathcal{U}[-6, 0] \) for all \( k \) terms. We note that the independence assumption is only in the prior, and any dependence structure emerges in the posterior once data is incorporated. The prior distribution for the unknown pure spectra is chosen to incorporate three essential characteristics: 1) non-negativity of absorbance values, 2) a decreasing overall trend of absorbance values from low to high wavelengths, and 3) smoothness of the spectrum. Therefore, the prior of the unknown pure spectra is selected as a half-normal distribution (or equivalently a zero-mean normal distribution truncated below zero) with a decreasing standard deviation. Moreover, additional penalties on the first-order and second-order derivatives of the spectrum are incorporated into the prior to ensure smoothness. The prior PDF of
spectrum $S$ for $S \in \{S_{\text{rDMQ}}, S_{\text{tDMQ}}, S_{\text{fDMQ}}\}$ can be represented as
\[
p(S) = \prod_i \mathcal{HN}(S_i; \sigma_i) \times \mathcal{N}(\delta S_i; 0, 0.002^2) \times \mathcal{N}(\delta^2 S_i; 0, 0.002^2),
\]
(4.10)

where $i$ is the index of spectrum grid, $\mathcal{HN}$ represents the half-normal distribution, and $\sigma_i$ linearly decreases from 0.2 at the lowest wavelength to 0.001 at the highest wavelength (i.e., decreases from 0.2 at minimal $i$ to 0.001 at maximal $i$). The first-order difference $\delta S_i$ and the second-order difference $\delta^2 S_i$ are calculated using the finite difference method.

Because $\theta$ (capturing all unknown model parameters) is high dimensional due to the inclusion of unknown spectra (i.e., absorbance values recorded at each wavelength), estimating posteriors with grid discretization is impractical. We use Markov chain Monte Carlo (MCMC) [148, 149] to sample from the posterior instead. In particular, we utilize the Metropolis-Hastings algorithm [150, 151] implemented in PyMC3 [152] for this purpose. It is important to highlight that the inclusion of penalty terms in Eqn. (4.10) significantly enhances the smoothness of the sampled spectra. Without these penalty terms, the sampled spectra would exhibit a highly oscillatory pattern. These penalty terms, however, are solely included for the purpose of regularizing the posterior sampling. Once the samples are obtained, their posterior probabilities are re-evaluated without the penalty terms.

Unlike the work in Chapter III, the work in this chapter does not involve Bayesian model selection because of the much higher dimensionality of unknown parameters.
caused by the involvement of unknown spectra (i.e., UV-vis absorbance at each wavelength recorded, amounting to 2068 unknown absorbance values at each time step). Therefore, a vast number of samples would be required to accurately estimate the evidence term, where most would contribute near-zero likelihood values.

4.2.9 Density Functional Theory (DFT) Modeling

Density functional theory (DFT) calculations were used to predict energies for tautomerization, Michael attack, and dimerization, as well as redox potentials and pK\textsubscript{a} values of various quinoxaline derivatives. All DFT calculations were performed using the NWChem software [187] with the B3LYP exchange-correlation functional [188, 189] and the Def2-TZVPPD basis set. [190] The COSMO implicit solvation model with default parameters was used during geometry optimization to implicitly treat molecule solvation by water. [191, 192] A self-consistent field convergence energy of $1 \times 10^{-6}$ a.u. was used. To maintain charge neutrality, we model carboxylic and sulfonic acid functional groups without deprotonation.

The following equations were used to calculate the Gibbs free energies of reduction ($\Delta G_{\text{red}}$) and tautomerization ($\Delta G_{\text{taut}}$):

\[
\Delta G_{\text{red}} = G_{\text{enamine}} - G_{\text{H2}} - G_{\text{oxidized}} \tag{4.11}
\]

\[
\Delta G_{\text{taut}} = G_{\text{imine}} - G_{\text{enamine}} \tag{4.12}
\]

where $G_{\text{enamine}}$, $G_{\text{imine}}$, and $G_{\text{oxidized}}$ are the DFT-calculated Gibbs free energies of the enamine form \textit{i}, imine form \textit{iv} (see Fig. C.4), and oxidized form of the given
quinoxaline. The pK$_a$ values of the imine and enamine forms of quinoxaline derivatives were calculated as follows:

\[ pK_a = \frac{1}{RT \ln(10)} (G_{X^+} + G_{H^+} - G_{HX}) \]  \hspace{1cm} (4.13)

where $G_{X^-}$, $G_{HX}$, and $G_{H^+}$ are the Gibbs free energies of the deprotonated species, protonated species, and the solvated proton, respectively. $R$ is the ideal gas constant and $T$ is the temperature (298.15 K). The Gibbs free energy of the solvated proton ($G_{H^+}$) was estimated as $-270.0$ kcal/mol using the average value obtained via the direct method based on the experimental pK$_a$ values of ammonium, acetic acid, chloroacetic acid, and trichloroacetic acid (4.76, 0.70, 9.25, and 2.86, respectively) and the DFT-calculated free energies of the conjugate acid and base ($G_{H^+} = -267.4$, $-275.2$, $-271.7$, and $-265.8$ kcal/mol, respectively). [193]

Gibbs free energies were estimated at 298.15 K and 1 M species by correcting the DFT-calculated electronic energies for enthalpic and entropic effects:

\[ G = E_{elec} + G_{solvation} + H_{thermal} - TS_{aq} \]  \hspace{1cm} (4.14)

where $E_{elec}$ and $H_{thermal}$ are the DFT-calculated electronic energy and the thermal correction to enthalpy, which includes contributions from the zero-point energy and heat capacity. The aqueous-phase entropy $S_{aq}$ was estimated from the gas-phase entropy $S_{gas}$ using the following equation, which accounts for solvent-induced structural
order that changes the translational entropy of species in solution: [194]

\[ S_{aq} = S_{gas} - 0.46 \left( S_{gas} - 14.3 \frac{\text{cal}}{\text{mol} \cdot \text{K}} \right) \]  
(4.15)

Vibrational frequencies within the harmonic approximation were calculated using finite differences and used to determine \( H_{\text{thermal}} \) and \( S_{gas} \).

The standard redox potential \( (E^0) \) at pH 13 was calculated using the Nernst equation:

\[ E^0 = -\frac{\Delta G_{\text{red}}}{nF} - \frac{2RT}{nF \log_{10}(e)} \cdot pH \]  
(4.16)

where \( n \) is the number of electrons transferred (\( n = 2 \) for our study), \( F \) is Faraday’s constant, and \( e \) is Euler’s number. Additional details on computing Michael attack and dimerization energetics are given in the Supplementary Information. Computational data for this paper, including NWChem input and output files, are available in the NOMAD Repository at http://doi.org/10.17172/NOMAD/2023.09.08-1.

### 4.3 Results and Discussion

#### 4.3.1 Flow cell cycling of DMeQUIC

DMeQUIC was chosen as a model quinoxaline for several reasons. First, it has a low reduction potential (−1.09 vs Ag/AgCl at pH 13), leading to high open-circuit potentials against certain positive electrolyte materials: 1.35 V against ferrocyanide (Fig. 4.1), and 1.55 V against permanganate (as shown in Chapter V). Second, from
cyclic voltammogram (CV) measurements, it has moderately fast redox kinetics, with a 260 mV separation between cathodic and two anodic redox peaks at a scan rate of 50 mV/s. Third, it is commercially available.

We cycled 0.4 M of DMeQUIC against excess sodium ferrocyanide in an alkaline (pH 13) flow cell at 20 mA cm$^{-2}$ using a constant current-constant voltage (CCCV) protocol and found that the current efficiency and rate of capacity fade were strongly dependent on the potential limit applied on discharge (Fig. 4.2). During the first cycle (Fig. 4.2a), two voltage plateaus were present upon discharge, centered at ca. 1.1 and 0.0 V. About 40% of the charging (DMeQUIC reduction) capacity was recovered at the higher plateau and the remaining capacity at or below the lower plateau. These data suggest that the reduced form of DMeQUIC decomposed into

Figure 4.1: Cyclic voltammograms of 1 mM DMeQUIC and sodium ferrocyanide performed at a scan rate of 50 mV/s in a supporting electrolyte of 0.1 M NaOH and 1 M NaCl (pH 13).
at least one product that can be converted back to DMeQUIC at a high oxidative overpotential. These voltage-dependent variations in current efficiency manifested as differences in capacity retention during long-term CCCV cycling (Fig. 4.2b)—cycling at a discharge potential limit of 1.0 V (shallow discharge), there was a 90% loss of capacity within 5 h, whereas a similar capacity loss took about 60 h for cycling at a limit of $-0.1 \text{ V}$ (deep discharge). Voltammetric (Fig. C.5a and b) and UV-vis (Fig. C.5c and d) analysis of the cycled DMeQUIC electrolytes revealed diminution in redox activity and a clear change in chemical composition, respectively, indicating that capacity fade observed in Fig. 4.2b originated from decomposition of and loss of redox activity in the DMeQUIC electrolyte.

Figure 4.2: Flow cell cycling of DMeQUIC. (a) Potential vs capacity for shallow discharge (1.0 V discharge limit) and deep discharge ($-0.1 \text{ V}$ discharge limit) cycling. (b) Charge and discharge capacities vs time during shallow- and deep-discharge CCCV cycling at 20 mA cm$^{-2}$. The cells were charged to 1.6 V, and potential holds were applied until the current density fell to an absolute value of 1 mA/cm$^2$.

The decomposition of the reduced form of DMeQUIC and its recovery upon deep
discharge was supported by *operando* UV-vis (Fig. 4.3a–c) and *ex situ* $^1$H-NMR (Fig. 4.3d–f) spectroscopic data. Reduction (charging) of DMeQUIC resulted in distinct shifts in its UV-vis absorbance (Fig. 4.3b) and NMR (Fig. 4.3e) spectra. The NMR spectrum of the charged electrolyte suggests at least two components, consistent with reduced DMeQUIC and at least one decomposition product. DMeQUIC displays two singlet peaks at *ca.* 2.1 ppm, originating from the pair of methyl groups at the 2 and 3 positions of the pyrazine core, which each integrate to 3H. In the aromatic region of the spectrum, there are three peaks at 7.4 ppm (doublet), 7.0 ppm (singlet) and 7.6 ppm (doublet), together integrating to three protons, as expected for this substitution pattern. These peaks should be retained, but shifted, in the reduced (charged) form, with the addition of two N–H protons, which may not show due to exchange with the deuterated NMR solvent. Instead, the methyl groups become more differentiated, with one appearing at 2.0 ppm (similar to DMeQUIC) and another more upfield at 1.0 ppm, indicating that the latter is in a new chemical environment. In addition, there are new peaks at 3.8 ppm, which we believe correspond to new protons at the 2 and 3 positions on the pyrazine core (which should not be present in reduced DMeQUIC). The aromatic region shows five peaks, providing further evidence for two or more degradation products. The original UV-vis and NMR spectra for DMeQUIC are recovered after discharge at $-0.2$ V (Fig. 4.3c and Fig. 4.3f), but not at 1.0 V (Fig. 4.3c).
Figure 4.3: *Operando* UV-vis spectra of a 5 mM DMeQUIC solution in a DMeQUIC-Fe(CN)$_6$ flow cell (a) before cycling, (b) after charging the cell (reducing DMeQUIC) at 1.6 V and subsequently, (c) discharging the cell at −0.2 or 1.0 V. *Ex situ* $^1$H-NMR spectra of (d) an uncycled DMeQUIC solution, (d) DMeQUIC solution after reduction at 1.6 V, and (f) DMeQUIC solution after reduction followed by oxidation at a cell potential of −0.2 V. For each NMR measurement, 0.15 mL aliquots from the 400 mM DMeQUIC electrolyte were diluted by a factor of five with D$_2$O, and CH$_3$SO$_3$Na was added as a calibration standard.

4.3.2 Mechanistic analysis of DMeQUIC decomposition

We sought to understand the kinetics of DMeQUIC decomposition by combining *operando* UV-vis spectroscopy with Bayesian inference. The work in Chapter III demonstrated that Bayesian statistical analysis of UV-vis data from operating or-
ganic flow cells can identify the individual spectra of decomposition products and their respective rate(s) of evolution, thus quantitatively connecting charge carrier decomposition to capacity fade.

The data in Fig. 4.4a shows selected UV-vis spectra of a 5 mM DMeQUIC electrolyte during a 16 h potentiostatic reduction in a DMeQUIC-Fe(CN)$_6$ flow cell. DMeQUIC peaks at 245, 325, and 335 nm fell within the first 2 min of reduction, at the expense of a broad peak centered at 365 nm, which rose and grew until 10 min, before falling gradually afterward. Diminution of the 365 nm peak coincided with the emergence of two new peaks at 235 and 293 nm.

Bayesian inference determined that the time-varying absorbance profiles in Fig. 4.4a are well explained by the successive evolution of three unique species, whose pure spectra and temporal concentrations are shown in Fig. 4.4b and Fig. C.6, respectively. Given the cell cycling data in Sec. 4.3.1, we interpret the pure spectra to represent DMeQUIC, its reduced form (rDMQ), a transient but redox-active decay product of the reduced form (tDMQ), and a final, redox-inactive species (fDMQ). From the concentration profiles, first-order rate constants for conversion of DMeQUIC to rDMQ, rDMQ to tDMQ, and tDMQ to fDMQ were calculated to be $2.0 \times 10^{-2}$, $9.5 \times 10^{-5}$ and $1.4 \times 10^{-5}$ s$^{-1}$, respectively. First-order kinetics was supported by similar rates of molecular conversion upon reduction of DMeQUIC at concentrations of 4, 3, and 1 mM (Fig. C.7a–d). The concentration independence of these rates is inconsistent with DMeQUIC decay being rate-limited by a bimolecular mechanism such as dimerization.

The spectroscopy-derived rate constants are quantitatively consistent with the ca-
capacity fade rates in Fig. 4.2b. Assuming that capacity loss during shallow-discharge cycling is controlled by conversion of rDMQ to tDMQ yields a rate constant for that process of $1.8 \times 10^{-4} \text{ s}^{-1}$ (see Fig. C.8, Eqn. (C.1), Eqn. (C.2), and accompanying discussion), which agrees well with the corresponding value from spectroscopic/Bayesian analysis on the 5 mM DMeQUIC data. A similar estimation of the rate constant for conversion of tDMQ to fDMQ from cycling results at the lower discharge potential of $-0.1 \text{ V}$ yields $2.2 \times 10^{-5} \text{ s}^{-1}$, which is again in good agreement with the analogous value from Bayesian analysis of the spectra.

![Figure 4.4](image1)

Figure 4.4: (a) UV-vis spectra of 5 mM DMeQUIC after 0 min, 5 min, 2 h, and 16 h of potentiostatic reduction in a DMeQUIC-Fe(CN)$_6$ flow cell at 1.6 V. (b) Spectra of rDMQ, tDMQ and fDMQ estimated using Bayesian inference, displayed alongside the spectrum of DMeQUIC. The solid lines depict the Bayesian posterior mode, while the posterior uncertainty (standard deviation) has been substantially reduced and is not visible in the plot.

Analysis of electrochemically reduced DMeQUIC solutions using NMR spectroscopy and liquid chromatography-mass spectrometry (LC-MS) revealed that tautomerization accounted for the observed decomposition. Figure C.9 displays a two-
dimensional correlation spectroscopy (2D COSY) $^1$H-NMR spectrum of a DMeQUIC solution after full reduction in a flow cell and storage under inert (nitrogen) atmosphere for 1 week (in order to permit complete conversion of rDMQ to fDMQ). The signal previously observed at 3.8 ppm in Fig. 4.3e was found to be coupled to the three-proton signal at 1 ppm. We interpret this coupling to indicate that the proton represented by the 3.8 ppm signal is bonded to a carbon adjacent to the methyl carbon, which is consistent with enamine-imine tautomerization of reduced DMeQUIC (Fig. 4.5). Tautomer formation is further supported by $^{13}$C-NMR spectra of the same solutions (Fig. C.10). Uncycled DMeQUIC has no peaks between 30 and 120 ppm (Fig. C.10a), whereas reduced DMeQUIC has a peak at 48 ppm (Fig. C.10b) which is consistent with the presence of an sp$^3$-hybridized carbon bonded to N, as would occur in the tautomers in Fig. 4.5. LC-MS (Fig. C.11a and b) provided additional evidence for tautomerization, and against other potential decomposition mechanisms, such as Michael addition (Fig. C.12a) and full hydrogenation of the pyrazine core (Fig. C.12b). The DMeQUIC spectrum displayed the strongest peak at $m/z = 201.0652$, which is justified by its molar mass of 202.2130 g/mol and the deprotonation of the carboxylic acid group under alkaline conditions. The spectrum for reduced DMeQUIC displayed the strongest peak at $m/z = 203.0803$ (Fig. C.11b), which is explained by the net addition of two hydrogen atoms to DMeQUIC via two-electron reduction and concerted/stepwise protonation. This $m/z$ value is consistent with tautomerization because intramolecular transfer of a hydrogen atom will not change $m/z$. An $m/z$ of 201.0652 is however inconsistent with a Michael addition product (molar mass = 222.2440 g/mol) or full hydrogenation of the pyrazine core.
in DMeQUIC (molar mass = 206.2450 g/mol). To further rule out the fully hydrogenated species, we purchased the fully reduced quinoxaline as an authentic standard and observed a distinct NMR spectrum compared to the observed decomposition product (Fig. C.13a and b). These findings are in line with previous reports of enamine-imine tautomerization of quinoxalines [195, 196] and pyridopyrazines [197] after electrochemical reduction in alkaline media.

Figure 4.5: Schematic showing redox reaction that converts DMeQUIC to rDMQ, and subsequent tautomerization of rDMQ into redox-inactive tautomers fDMQ. DFT-calculated tautomerization free energies are indicated.

Although the above data support that fDMQ is a tautomer of rDMQ (Fig. 4.5), the exact structure of the intermediate tDMQ is not known. Nevertheless, it is plausible that tDMQ and fDMQ have similar chemical structures given that their Bayesian-inferred UV-vis spectra (Fig. 4.4b) are almost identical, and that the tautomer proton is present in the NMR spectra of the reduced form of DMeQUIC.
shortly after reduction (Fig. 4.3e) and after 1 week of storage in inert atmosphere (Fig. C.14). One possibility is that tDMQ is the deprotonated form of fDMQ, which is supported by previous work on phenacylquinolines showing that under alkaline conditions imine-enamine tautomerization can proceed via a deprotonated imine intermediate. [198]

4.3.3 Effect of functionalization on tautomerization energetics

We performed DFT modeling to elucidate the effect of functionalization on reduced quinoxaline tautomerization and quinoxaline stability. Previous work has shown that the equilibrium between enamine and imine forms of reduced quinoxalines in non-aqueous media can be strongly dependent on solvent and substituent chemistry.[199] For the five molecules that we study experimentally in Sec. 4.3.4, shown in Fig. 4.6a, tautomerization is predicted to be exothermic for the reduced forms of DMeQUI and DMeQUIC, whereas it is slightly endothermic for 6QUIC and DMeSQUI (∼2 kcal/mol) and highly endothermic (∼10 kcal/mol) for 2QUIC (Fig. C.15 and Fig. C.16). Generally, Michael addition (Fig. C.17) is predicted to be endothermic and is typically less thermodynamically favorable compared with tautomerization (Fig. C.15), consistent with our experimental observations. Likewise, dimerization of the quinoxaline derivatives was computed to be generally very endothermic (e.g., 55.9, 52.1, 53.6, and 48.4 kcal/mol for the reduced forms of 2QUIC, 6QUIC, DMeQUIC, and DMeQUI, respectively). We discuss three molecular properties that influence the tautomerization energetics and its link to molecular structure: (1) redox potential, (2) relative p$K_a$ values of the enamine and imine forms and
their connection to the electron-withdrawing group (EWG) strength of quinoxaline functional groups, and (3) hydrogen bonding between the pyrazine N-H and an H-acceptor functional group.

In addition to the experimentally tested derivatives, we also computationally modeled thirteen other derivatives including quinoxaline-2,3-disulfonic acid-6-carboxylic acid (DS6QUIC), quinoxaline (QUI), 2-acetylquinoxaline (2COCH3QUI), quinoxaline-2,3-dicarbonitrile (DCNQUI), quinoxaline-5-carboxylic acid (5QUIC), quinoxaline-5,8-dicarboxylic acid (5,8-QUIDC), quinoxaline-2,3-dicarbonitrile-6,7-disulfonic acid (DCNQUI-6,7-DS), quinoxaline-2-carbonitrile (2CNQUI), 2-nitroquinoxaline (2NO2QUI), quinoxaline-2-amine (2NQUI), 3-amino-quinoxaline-2-carboxylic acid (QUI2C3A), 2-methylquinoxaline (2MeQUI), and quinoxaline-2-carbaldehyde (2CHOQUI), as shown in Fig. 4.6b. The data in Fig. 4.6c shows the DFT-computed redox potentials at pH 13 against the free energy of tautomerization for all eighteen quinoxalines. We identify a weak but positive correlation between redox potential and tautomerization energy \( R^2 = 0.49 \), revealing a trade-off between a high open-circuit potential and resistance to tautomerization. The DFT-calculated redox potentials of the experimentally studied quinoxalines (indicated by red squares in Fig. 4.6c), which lie between \(-0.8\) and \(-1.2\) V vs Ag/AgCl at pH 13, agree moderately well with experimentally determined values from \(-1.0\) to \(-1.2\) V. Intuitively, the redox potential and tautomerization energy are related to the strength of the N-H bond of the pyrazine ring, which is modulated by the functional groups. A stronger N-H bond makes tautomerization from the enamine to the imine form more unfavorable because this process requires breaking the N-H bond and forming a C-H bond. In addition, it
makes reduction, which involves formation of the N-H bond, more favorable. Our analysis suggests that a strong N-H bond leads to favorable reduction, a more positive redox potential, and less favorable tautomerization.

Figure 4.6: (a) Molecules studied by DFT modeling that are cycled experimentally. (b) Molecules not experimentally cycled but also evaluated by DFT modeling. (c) Relationship between DFT-computed tautomerization free energy and DFT-computed redox potential at pH 13, 1 M species, and 298 K. Data points of molecules studied experimentally are indicated by red squares and other molecules evaluated only by DFT by blue circles. Tautomerization of DMeQUIC from the enamine to the imine form is shown schematically as an example, with other derivatives in (a) and (b) tautomerizing analogously. (d) Relationship between $\sigma^-$ Hammett constant of the substituent in position adjacent to pyrazine N and tautomerization energy for quinoxaline derivatives functionalized only in the position adjacent to the pyrazine N. (e) Comparison of DFT-calculated tautomerization energy and $pK_a$ values of imine (red squares) and enamine (black circles) forms of quinoxaline derivatives. Vertical grey lines are given to highlight the difference between the $pK_a$ values of the enamine and imine forms. Slopes of trendlines fitting $pK_a$ of the enamine (in black) or imine form (in red) as a function of tautomerization energy are indicated.
Hammett analysis reveals a relationship between the electron-withdrawing group (EWG) strength of the quinoxaline derivatives and tautomerization energetics. Quinoxaline derivatives with stronger EWGs have a more stable enamine form relative to the imine form, making tautomerization less favorable. The Hammett plot in Fig. 4.6d shows the effect of the $\sigma^-$ Hammett constant of the substituent adjacent to the pyrazine N (substituent $R$ in Fig. C.4) and the tautomerization free energy when there are no substituents in any other positions (that is, when only substituent $R$ is changed). Hammett substituent constants are taken from Hansch and coworkers. [200] Because we hypothesize tautomerization to occur via a deprotonated intermediate, we use the $\sigma^-$ Hammett constant as a measure of the ability of a substituent to strengthen the resonance stabilization of a negatively charged intermediate via its electron-withdrawing capacity. A positive correlation exists between $\sigma^-$ and tautomerization energy ($R^2 = 0.66$), meaning that a stronger EWG in the position adjacent to the pyrazine N would result in greater resistance to tautomerization. A similar relationship has been observed between the $\sigma_p$ or $\sigma_m$ Hammett constant and tautomerization equilibrium for 3-amylcarbamoylmethylene-2-oxo-1,2,3,4-tetrahydroquinoxalines.[199] This effect can be explained by the effect of EWGs on the $pK_a$ values of the enamine and imine forms of the reduced quinoxaline derivative in question.

By definition, the negative base-10 logarithm of the tautomerization equilibrium constant is equal to the $pK_a$ value of the N-H proton of the enamine minus the $pK_a$ of the unsaturated C-H proton of the imine (see Eqn. (C.7) and Fig. C.4 in SI for derivation).[201] Although DMeQUIC has an electron donating group, the inductive
effect of an EWG stabilizes the deprotonated intermediate tDMQ (Fig. C.16), thereby lowering the p$K_a$ of the enamine. Because tDMQ is a resonance structure of the deprotonated imine, its stabilization also lowers the p$K_a$ of the imine. However, stronger EWGs, which lead to a more positive tautomerization energy (Fig. 4.6d), lower the p$K_a$ of the imine approximately eight times as much as they lower the p$K_a$ of the enamine, as supported by our DFT calculations (Fig. 4.6e). For example, the enamine and imine forms of quinoxaline (QUI) have p$K_a$ values of 30.1 and 30.8, respectively. Upon substitution of an EWG in the position adjacent to the pyrazine N (−COCH$_3$, −COOH, or −CHO), the enamine p$K_a$ drops slightly (to 29.8, 28.5, and 27.5, respectively) while the imine p$K_a$ drops significantly (to 22.6, 21.1, and 17.4, respectively). Alternatively, the substitution of an electron-donating methyl group in the same position increases the enamine and imine p$K_a$ values to 30.5 and 32.4, respectively. This non-symmetric effect on the relative p$K_a$ values occurs because the pyrazine N is closer to the aromatic ring, and therefore its deprotonated form is more resonance-stabilized compared to the carbanion without the effect of an EWG. Consequently, the stabilizing effect of an EWG is more pronounced on the carbanion (or deprotonated imine), explaining the asymmetric effect on the p$K_a$ values of the imine and enamine manifested as the different slopes in Fig. 4.6e. Similar effects have been observed for the enol-keto tautomerism of β-diketones and β-ketoesters[201] and α-arylsulphaminopyridines.[202]

Another factor that results in unfavorable tautomerization is the stabilization of the enamine structure by the formation of a hydrogen bond between the H on the pyrazine N and a hydrogen bond acceptor group in an adjacent substituent, which
may contribute to the stability of 2QUIC to tautomerization. Also, because only one of the two pyrazine N-H groups of 5QUIC is hydrogen-bonded to the carboxylic acid group, only one of the two possible tautomerization pathways requires breaking the hydrogen bond. This pathway is associated with an unfavorable free energy change (+8.6 kcal/mol), in contrast to a slightly favorable free energy change associated with the alternative pathway that does not break the hydrogen bond (−1.0 kcal/mol). This observation suggests that the formation of a hydrogen bond with both pyrazine H atoms would enable strong resistance to tautomerization, and indeed, 5,8-QUIDC has a tautomerization free energy of +11.5 kcal/mol, more unfavorable than for 5QUIC. In theory, the two carboxylic acid groups of 5,8-QUIDC make this molecule not only resistant to tautomerization but also highly soluble; therefore, it is a potentially promising derivative for resisting capacity fade in aqueous organic redox flow batteries.

4.3.4 Flow cell cycling of other quinoxaline derivatives

We experimentally evaluated the influence of substituent position and chemistry on the cycling stability of a subset of quinoxaline derivatives (Fig. 4.6a) analyzed by DFT. DMeQUIC, DMeQUI, 6QUIC and 2QUIC were procured commercially, whereas DMeSQUI was synthesized for this study via a simple, one-step reaction (synthetic procedures are reported in Sec. 4.2.6, whereas CV and NMR characterization data for all experimentally tested derivatives are reported in the Supporting Information). The other derivatives analyzed by DFT that have endothermic tautomerization energies are not commercially available, with the exception of QUI2C3A. The
CV of QUI2C3A displayed a 1.1 V separation between cathodic and anodic redox peaks (Fig. C.18), which renders cycling of this molecule in a flow battery impractical.

Cycling results are shown in Fig. C.19a, which reports capacity (normalized to the theoretical capacity for a two-electron reduction) vs time for cycling at the current densities and voltage limits provided in Table C.1. First-order capacity fade rate constants were estimated from the slope of the line of best fit for normalized discharge capacity on a logarithmic scale against time (Fig. C.19b), and were found to vary over three orders of magnitude (Table 4.1), increasing in the following order: 2QUIC < DMeSQUI < DMeQUI < DMeQUIC < 6QUIC. We conducted CV measurements of all cycled electrolytes (Fig. C.20a–e) and discovered a strong correlation between the decrease in peak cathodic current and capacity lost during flow cell cycling (Fig. C.21).

Table 4.1: CV-derived standard redox potentials of experimentally tested quinoxaline derivatives and capacity fade rate constants from flow cell cycling.

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Fade rate constant (s$^{-1}$)</th>
<th>Redox potential (V vs. Ag/AgCl)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2QUIC</td>
<td>5.31 ± 0.04 × 10$^{-7}$</td>
<td>-0.95</td>
</tr>
<tr>
<td>DMeSQUI</td>
<td>4.33 ± 0.05 × 10$^{-6}$</td>
<td>-1.01</td>
</tr>
<tr>
<td>DMeQUI</td>
<td>2.71 ± 0.07 × 10$^{-5}$</td>
<td>-1.1</td>
</tr>
<tr>
<td>DMeQUIC</td>
<td>8.9 ± 0.2 × 10$^{-5}$</td>
<td>-1.12</td>
</tr>
<tr>
<td>6QUIC</td>
<td>3.5 ± 0.1 × 10$^{-4}$</td>
<td>-1.00</td>
</tr>
</tbody>
</table>

DFT-predicted tautomerization energetics rationalize experiments for quinoxaline stability; for example, the most stable derivative tested, 2QUIC, was predicted to have very endothermic tautomerization ($\Delta G_{taut} = +10.2$ kcal/mol) whereas the less stable molecules such as DMeQUIC and 6QUIC had values of $\Delta G_{taut}$ of $-2.5$
kcal/mol and 1.8 kcal/mol, respectively. We avoid quantitatively correlating tautomerization energetics to measured decay rates because the predicted thermodynamic driving force does not directly consider kinetic barriers, which can play a critical role in driving tautomerization. [184]

Because the permeability of Nafion to organic charge carriers under aqueous conditions translates to a capacity fade rate constant of up to $6 \times 10^{-7} \text{ s}^{-1}$, [15, 203] we evaluated the possibility that molecular crossover rather than decomposition accounted for most of the apparent capacity fade in the 2QUIC cell. The permeability of Nafion 212 to 2QUIC was measured using an H-cell configuration to be $2.5 \times 10^{-9} \text{ cm}^2/\text{s}$ (Fig. C.22a, b and c). Based on this permeability (calculated using Eqn. (C.8)), capacity fade from crossover would be about 6.9%/day, which is close to the 4.6%/day fade rate measured in the 2QUIC cell(Fig. 4.7). The 4.6%/day fade observed for 2QUIC is two orders of magnitude slower than that observed for DMeQUIC as can be inferred from their capacity fade rate constants shown in Fig. C.19 and Fig. C.8, respectively. The capacity fade experienced by 2QUIC and DMeQUIC is in line with the decline in cathodic peak current shown in Fig. C.21b and c respectively.
Therefore, to better assess the intrinsic chemical stability of 2QUIC, we cycled a mixed symmetric cell with 2QUIC and ferrocyanide on both sides (but still capacity-limited by 2QUIC) and it did not exhibit capacity fade (Fig. 4.8a) over 220 hours of cycling. CVs of 2QUIC in the cycled and uncycled electrolytes from the capacity-limiting side of the cell (Fig. C.23) were virtually identical, indicating no change in the redox capacity of the electrolyte. To our knowledge, these fade rates are the lowest ever measured for quinoxaline derivatives in aqueous redox flow cells. Taken as a whole, our cycling studies validate the design principles for tautomerization-resistant quinoxalines described in Sec. 4.3.3, and motivate the continued pursuit of quinoxaline derivatives that combine high chemical stability with fast kinetics, high solubility and low redox potential.
Figure 4.8: (a) Charge capacity, discharge capacity, and current efficiency vs time and (b) voltage profiles of selected cycles for the cycling of a mixed symmetric 2QUIC-ferrocyanide cell for 220 hours. The capacity-limiting side of the cell comprised 3 mL of 0.1 M 2QUIC, 0.2 M Na$_4$Fe(CN)$_6$ and 0.2 M NaOH; the non-capacity-limiting side comprised 7 mL of the same solution. The cell was cycled at a current density of 20 mA/cm$^2$ between 0.8 and 1.4 V, and potential holds were applied at the end of each half cycle until the current density decayed to an absolute value of 1 mA/cm$^2$. The dip in current efficiency between 140 and 170 hours, from an average of 99.9 % to 98%, was due to momentary contamination of the glovebox by oxygen. Parasitic oxygen reduction in the capacity-limiting side led to the accumulation of ferricyanide in the non-capacity-limiting side and thus led to an increase in cell potential between cycle 250 and 500 in Fig. 4.8b.

4.4 Conclusions

Quinoxalines are a class of redox-active molecules that have several attractive attributes as charge carriers in aqueous RFBs but have been hindered in these systems because of stability issues. Understanding the substituent impact on quinoxaline stability and thus capacity fade would aid the further development of these molecules for RFB systems that have long lifetimes and thus deliver electricity at low costs.

We study the cycling stability of a dimethyl- and carboxylate-substituted quinox-
aline (DMeQUIC) and discover that tautomerization of its reduced form is chiefly responsible for the observed capacity fade. Data from several complementary analytical techniques—including operando UV-vis spectroscopy, $^1$H-NMR spectroscopy, $^{13}$C-NMR spectroscopy, and mass spectrometry— rules out other mechanisms that have been proposed in the literature for quinoxaline degradation, such as dimerization, irreversible hydrogenation, and Michael addition of water. Bayesian inference is shown to be a useful data-driven technique to estimate the rate constants of quinoxaline tautomerization and deconvolution of the pure UV-vis spectra of the resulting products from operando spectroscopic measurements. Quantitative consistency between the kinetic parameters estimated from spectroscopy and rates of capacity fade measured at the cell level highlights the unique ability of combining Bayesian inference and operando UV-vis spectroscopy to elucidate the connection between molecular decomposition and capacity fade.

Using DFT modeling, we elucidate multiple design rules (i.e., tuning electron-withdrawing group strength and H-bonding strength) for tautomerization resistance in quinoxalines and identify more stable derivatives with those properties—the most stable among experimentally tested derivatives is quinoxaline-2-carboxylic acid (2QUIC), which showed no measurable capacity fade in a mixed symmetric cell configuration. In a compositionally asymmetric cell configuration with a Nafion 212 membrane, crossover-induced capacity fade was high (ca. 5%/day), likely due to the small molecular size of 2QUIC. Future work may address this issue via the development of membranes with higher permselectivity than Nafion 212, or the installation of multiple charged substituents to slow down crossover without overly compromising
the stability or synthesizability of the quinoxaline.

These findings will guide development of stable quinoxalines in aqueous RFBs. Additionally, the combination of experimental and statistical inference techniques demonstrated in this work is broadly adaptable to studying degradation mechanisms and capacity fade for other organic redox-active molecules.

Acknowledgments

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CHAPTER V

Correlating Stability and Performance of NaSICON Membranes for Aqueous Redox Flow Batteries

5.1 Introduction

Redox couples based on inorganic elements such as sulfur, iron, and manganese are attractive as RFB active species because they are earth-abundant, chemically stable, and compatible with aqueous supporting electrolytes, which are cheaper than nonaqueous variants. However, many of these inorganic species easily permeate conventional polymer-based RFB membranes, resulting in rapid capacity loss and thus added costs stemming from the need for frequent replacement of lost active materials. Several strategies for mitigating crossover or recovering crossed over species exist, but a particularly effective solution is the use of fully dense, single-ion-exchange membranes that permit conduction of charge-balancing ions but not crossover of active...
species.

A number of studies have deployed Na\(^+\)- and Li\(^+\)-superionic conducting ceramic membranes (i.e., NaSICON and LiSICON, respectively)\([216, 217]\) in aqueous flow cells containing a wide range of RFB chemistries, including redox couples based on transition metals like iron\([216, 218, 219]\) and zinc \([220, 221, 222]\) as well as organic molecules, \([221]\), sulfur \([220]\) and O\(_2\). \([217, 222, 223]\) However, several performance criteria for and challenges to commercially viable RFBs using these membranes remain unmet. First, because fairly thick membranes were used, area-specific cell resistances range between \(\sim\) 100 and 400 \(\Omega\text{cm}^2\), \([220, 221, 224]\) compared to \(< 5\Omega\text{cm}^2\) in typical, analogous flow cells with conventional polymer membranes. Consequently, the power densities achieved to date using ceramic membrane-containing aqueous flow cells are impractically low, ranging between 1 and 20 mW/cm\(^2\), as compared to about 100 mW/cm\(^2\) or greater for polymer membrane-containing analogues. The development of less resistive membranes is therefore an urgent requirement if aqueous RFBs with ceramic membranes are ever to be practical. Second, the membranes, which are typically brittle, must be mechanically stable, especially at the elevated operating temperatures (\(\sim \) 40–80 °C) expected for practical RFBs and for long enough durations in the presence of the electrolyte for their deployment to be feasible. Third, the morphology and chemical composition of the membrane, both in the bulk and at the membrane–electrolyte interface, should ideally be steady over time. However, multiple studies have indicated that NaSICON membranes, for instance, show some reactivity with certain aqueous solutions resulting from degradation along their grain boundaries. \([225, 226, 227]\) This degradation has been attributed to dissolution of
secondary phases, but the mechanism by which this dissolution occurs, its extent, and its implications for RFB performance are not well understood. It is therefore important to characterize the evolution of the resistance, microstructure, and chemical composition of these ceramic membranes while in contact with potential RFB electrolytes and understand how any observed changes ultimately affect RFB performance.

In this study, we examine the feasibility of von Alpen NaSICON with the chemical formula Na$_{3.1}$Zr$_{1.55}$Si$_{2.3}$P$_{0.7}$O$_{11}$ as an RFB membrane material, by performing concurrent measurements of resistance, permeability, and interfacial morphology as a function of electrolyte composition and cell temperature. We find that the resistance of NaSICON is stable for up to about a month while immersed in neutral to strongly alkaline ([OH$^{-}$] = 3 M) aqueous electrolytes. Its permeability to polysulfide-based and permanganate-based RFB reactants is negligible compared to that of a Nafion membrane; the latter used here as representative of conventional polymer-based RFB membranes. The glassy phase of the NaSICON microstructure at the membrane–electrolyte interface is susceptible to some etching while in contact with aqueous electrolytes. This etching worsens considerably when K$^{+}$ ions are present in the electrolyte, leading in certain instances to complete disintegration of the membrane. We demonstrate, nevertheless, that a $\approx$ 700 $\mu$m-thin NaSICON membrane can support cycling of a ferrocyanide—permanganate flow cell in strongly alkaline electrolyte ([OH$^{-}$] = 3 M), with negligible reactant crossover. NaSICON’s area-specific resistance (ASR) decreases with increasing temperature and decreasing membrane thickness; there is a 5.6× reduction in ASR from a 1.19 mm-thick membrane at 18
°C (101 Ωcm²) to a 0.61 mm-thick one at 70 °C (18 Ωcm²). There are processing strategies for lowering the thickness of the membrane to 100 µm or lower, which will result in power densities that are comparable to those of polymer membrane-containing flow cells. This work highlights the promise of ceramic membranes as effective separators in RFBs operating under neutral pH to strongly alkaline pH conditions. It also points to the need for further research on the long-term stability of the membrane and its interface with the electrolyte in solid-state membranes under investigation as separators in aqueous RFBs.

5.2 Materials and Methods

5.2.1 NaSICON Pellet Synthesis and Characterization

Von Alpen type NaSICON (Na₃₋₁ₓZrₓ₋₅₅Si₂₋₃P₀₋₇O₁₁) powders were synthesized from reagent grade Na₃PO₄·12H₂O, Na₂CO₃, ZrO₂, and SiO₂ precursors via calcination at 1100 °C for 10 h using the process outlined for S900C samples in [228]. NaSICON pellets were synthesized via a rapid induction hot pressing technique at 1200 °C for 40 min under flowing argon at a pressure of 47 MPa. The resulting billet with a 12.7 mm diameter and 6 mm height was then cut to desired thicknesses using a diamond saw, and pellets were polished down to a final 0.1 µm polish with diamond paste. Pellets were cut to thicknesses between 0.4 and 1.2 mm, and Au blocking electrodes were sputtered onto the pellets for electrochemical testing. Electrochemical impedance spectroscopy (EIS) on Au—NaSICON—Au symmetric cells with NaSICON pellets of varying thickness was performed on a Biologic VMP-
300 galvanostat/potentiostat. Frequencies from 50 mHz to 7 MHz were used with a perturbation voltage of 10 mV. Equivalent circuit modeling was used to determine grain resistance, grain boundary resistance, and total resistance for each pellet. Microstructural analysis of polished NaSICON sample surfaces before and after immersion in electrolytes was performed on a JEOL IT500 scanning electron microscope (SEM). Grayscale analysis of SEM images to determine area percentages of identified phases was performed using ImageJ software.

5.2.2 Electrolyte and H-Cell Preparation

Sodium ferrocyanide (Na$_4$Fe(CN)$_6$), potassium ferricyanide (K$_3$Fe(CN)$_6$), sodium permanganate monohydrate (NaMnO$_4$·H$_2$O), sodium sulfide nonahydrate (Na$_2$S·9H$_2$O), sulfur, sodium hydroxide (NaOH), potassium chloride (KCl), sodium sulfate (Na$_2$SO$_4$), and sodium chloride (NaCl) were purchased from Sigma Aldrich and used as received. 3,3’-(Phenazine-1,8-diyl)dipropionic acid (1,8-PFP) was procured from Prof. Yun-long Ji and used as received. Sodium disulfide (Na$_2$S$_2$) was prepared by dissolving Na$_2$S·9H$_2$O and sulfur in a 1:1 molar ratio. All electrolyte solutions were made with deionized water (18 MΩ cm).

Crossover measurements were executed with two types of H-cells. PermGear dialysis cells comprised two electrolyte reservoirs of 3.4 mL each on either side of a 16 mm diameter opening for the membrane, whereas custom-made two-compartment cells had reservoirs of either 6 or 1.5 mL on either side of 16 or 7 mm diameter openings, respectively. In both cases, the membrane area was defined by Viton gaskets. 183 µm-thick Nafion 117 was used as a representative polymer-based membrane and
was pretreated by soaking it in 1 M NaOH for 24 h. Permeability measurements were conducted by filling donating and receiving sides with equal volumes of supporting electrolyte and reactant and supporting electrolyte only, respectively. At different time intervals, the receiving side was characterized by ultraviolet–visible (UV–vis) spectrophotometry on an Ocean-HDX-UV–VIS spectrometer HDX00518 (Ocean Insight). Electrolyte volumes were checked periodically to ensure that there was negligible water flux across the membrane, which might affect the apparent reactant permeability. The concentration of crossed over species was calculated from a calibration curve, and the permeability $P$ (in cm²/s) was calculated from the slope of concentration vs time based on Fick’s law using the following equation:

$$P = -\frac{\Delta \ln (1 - \frac{2c_t}{c_0}) V_0 l}{\Delta t},$$

(5.1)

where $A$ is the effective membrane area (cm²), $t$ is the elapsed time (s), $c_t$ (mol/L) is the concentration of active species in the receiving side at time $t$, $V_0$ is the volume of the solution in either compartments, $l$ is the thickness of the membrane, $c_0$ is the initial concentration of the reactant in the donating side, and $\Delta$ represents a finite difference.

### 5.2.3 Time-Dependent NaSICON Impedance

EIS measurements were conducted on NaSICON-containing H-cells and flow cells to determine the impedance of each pellet over time in various electrolyte compositions. For impedance measurements in H-cells, a custom, two-chamber cell was
designed. Each chamber had a volume of 6 mL, and 6 mm diameter graphite rods were immersed in the electrolyte; the NaSICON pellet was sandwiched between three Viton rubber gaskets to prevent leakage around the pellet, and the diameter of the resulting electrolyte-exposed area was 10.7 mm. To measure the dependence of resistance on pellet thickness, pellets of different thicknesses were cut out of the same billet. Equivalent circuit modeling was again used to determine grain resistance, grain boundary resistance, and total resistance for each pellet.

5.2.4 Flow Cell Preparation and Temperature-Dependent NaSICON Impedance

Flow cells were constructed with cell hardware from Fuel Cell Technologies (Albuquerque, New Mexico) and assembled into a zero-gap configuration, similar to a number of previous reports. [57, 31] Pyrosealed POCO graphite flow plates with serpentine flow patterns were used for both electrodes. Each electrode comprised a 0.9 cm² (10.7 mm diameter disk) sheet of CE Tech GF020 graphite felt (Fuel Cell Store, 2.1 mm thick). The electrodes were baked in air for 1 h at 400 °C prior to use for the ferro-ferricyanide symmetric flow cell and for 12 h at 400 °C for the asymmetric cells. The outer portion of the space between the electrodes was gasketed by Viton sheets with the area over the electrodes cut out as shown in Fig. D.1. Torque applied during cell assembly was 10 lbf ft on each of the eight bolts. Either a Longer DG-15 or Cole Parmer SK-77202-60 peristaltic pump circulated the electrolyte through the flow cell through fluorinated ethylene propylene (FEP) tubing of 1/16” inner diameter. Calibration curves were obtained for each pump that permitted translation from revolutions per minute to a volumetric flow rate in mL/min. The Nafion membrane
was immersed in 1 M NaOH for 24 h before the cell was assembled.

EIS measurements were conducted on flow cells containing NaSICON pellets heated to a series of temperatures between 18 and 70 °C to determine the effect of temperature on their impedance. Both sides of the cell were fed by and emptied into one reservoir containing 1 M NaCl; the electrolyte was circulated at a flow rate of 55 mL/min. The cell was heated using two resistance heaters inserted into each end plate, and the input power was varied between 0 to 100 W to achieve cell temperatures ranging from 18 to 70 °C. Each EIS measurement was conducted 2 h after a given input power was chosen, to allow the cell temperature to reach steady state. The temperature of the cell was measured by proxy, by immersing a thermometer into the electrolyte reservoir.

A compositionally symmetric flow cell was constructed with a total ferri-/ferrocyanide concentration of 20 mM to test the stability of NaSICON under electrochemical cycling conditions. The supporting electrolyte comprised 1 M NaCl, and the capacity-limiting electrolyte (CLE) was 10 mL, whereas the noncapacity-limiting electrolyte (NCLE) was 25 mL. We performed the cycling experiments using a constant-current, constant-voltage (CCCV) cycling protocol to access the entire capacity of the CLE. [46] Compositionally asymmetric ferrocyanide—permanganate and 1,8-PFP—permanganate flow cells containing NaSICON or Nafion membranes were also tested. The former comprised 0.05 M Na₄Fe(CN)₆ and 0.2 M NaMnO₄ in the negolyte and posolyte, respectively, with 3 M NaOH as the supporting electrolyte, and the ferrocyanide electrolyte as the CLE in all cases. The latter comprised 0.05 M 1,8-PFP in the negolyte and between 0.075 and 0.4 M NaMnO₄ in the posolyte. EIS and polarization
were run after assembling the flow cell and prior to cycling. A Biologic VSP-300 potentiostat was used for voltammetry, EIS measurements, and cell cycling experiments with the Nafion 117 membrane. A Biologic VSP potentiostat was used for the cell cycling measurements with the NaSICON pellet. We used current densities of 2.8 and 10 mA/cm$^2$ for the NaSICON and Nafion membrane cells, respectively. EIS measurements were obtained between 7 MHz and 25 mHz with an amplitude of 10 mV. UV-vis and inductively coupled plasma mass spectrometry (ICP-MS) measurements were conducted on the uncycled and cycled electrolytes to assess reactant crossover. The ICP-MS experiments were conducted on a ThermoScientific iCAP Q ICP-MS spectrometer in KED Mode, which utilizes He gas to overcome polyatomic spectral interferences, and the instrumental drift from the plasma was accounted for by following a standard-sample bracketing procedure.

5.3 Results and Discussion

5.3.1 Microstructural Stability and Conductance

To assess the microstructural stability of NaSICON in the presence of typical RFB reactants, the pellets were imaged after 7–9 and 30 days of immersion in select electrolyte compositions under neutral to strongly alkaline conditions. Acidic solutions were not examined, as NaSICON is well known to rapidly decompose at pH < 7 via glass phase dissolution. [227, 229] The inorganic reactants tested included NaMnO$_4$ and Na$_2$S$_2$, whereas organic/organometallic reactants included ferrocyanide and a propionic acid-substituted phenazine (1,8-PFP) that has recently been shown
to exhibit extraordinarily high chemical and thermal stability among molecules under consideration for aqueous organic RFBs. [230] In all cases, it was found that the glass phase in the pellets was etched over time, whether or not an RFB reactant was also present in solution. The severity of etching was found to be highly sensitive to the concentration of K$^+$ ions in the electrolyte. Thus, the etching analysis was divided into two categories: (1) immersion of NaSICON in non-K$^+$-containing electrolytes and (2) immersion of NaSICON in K$^+$-containing electrolytes.

5.3.2 Immersion of NaSICON in Non-K$^+$-Containing Electrolytes

To assess the microstructural stability of NaSICON in the presence of typical RFB reactants, the pellets were imaged after 7-9 and 30 days of immersion in select electrolyte compositions under neutral to strongly alkaline conditions. [230] Fig. 5.1a shows the SEM image of a freshly synthesized NaSICON pellet, whereas the SEM image in Fig. 5.1b shows such etching after 30 days of immersion in an electrolyte containing 100 mM NaMnO$_4$ and 2 M NaOH, in the form of voids $\sim$ 100-300 nm in size; these voids were also evident after 7 days of immersion (Fig. D.2a). Similar degradation was observed in pellets immersed in electrolyte containing 100 mM Na$_4$Fe(CN)$_6$ in 1 M NaOH (Fig. D.2b), 100 mM 1,8-PFP in 2 M NaOH (Fig. D.2c,d), and 100 mM Na$_2$S$_2$ in 2 M NaCl (Fig. D.2e,f) and reactant-free supporting electrolytes containing NaOH and NaCl only. No degradation of NaSICON grains was observed across all samples. Table D.1 reports the apparent void area fraction of NaSICON as quantified by grayscale analysis after 7-9 and 30 days of immersion. In the reactant-containing electrolytes, the void area fraction increased from 0.7% in the pristine state to be-
between 3.1 and 4.85% after 30 days of immersion; this represents an increase in the absolute value of void area fraction of between 2.4 and 4.15%. The pellet immersed in reactant-free 2 M NaCl had the smallest void area fraction increase (1.9%) after 30 days; for pellets immersed in reactant-free NaOH solution, the 30-day void area increase scaled with alkalinity, from 3.8% in 1 M NaOH to 4.6% in 2 M NaOH to 5.8% in 3 M NaOH.

Figure 5.1: SEM images of (a) as-synthesized NaSICON pellet and (b) NaSICON sample immersed for 30 days in 100 mM NaMnO$_4$ and 2 M NaOH. Regions representative of grains (1), glass phase (2), and zirconia (3) are indicated in (a). Example regions of glass phase and grain boundary degradation (4) are indicated in (b).

It is worth noting that MnO$_4^-$, which is the most oxidizing reactant tested here based on redox potential, did not etch the glass phase to a significantly greater extent than the other reactants and that the corresponding pellet was mechanically intact. The 30 day increase in void area fraction for the pellet soaked in 0.1 M NaMnO$_4$ and 2 M NaOH was 3.44%, which is slightly lower than the 4.55% increase in reactant-free 2 M NaOH. Increasing the MnO$_4^-$ concentration did not accelerate etching; a pellet soaked in a solution comprising 1 M NaMnO$_4$ and 3 M NaOH experienced a 3.7% increase in void area fraction after 7 days (Fig. D.3), which is comparable to results at 0.1 M NaMnO$_4$. These results suggest that NaSICON might
be an appropriate membrane for enabling the MnO$_4^-$/MnO$_4^{2-}$ redox couple in positive electrolytes of strongly alkaline RFBs. [213, 231] MnO$_4$ is particularly promising because it has a redox potential that is 140 mV higher than that of the commonly used Fe(CN)$_6^{4-}$/Fe(CN)$_6^{3-}$ (Fig. D.4) and a higher solubility (over 4 M [213] vs less than 1 M [56] in water for NaMnO$_4$ and Na$_4$Fe(CN)$_6$, respectively).

Impedance measurements were periodically conducted on H-cells containing NaSICON pellets and showed that the resistance of NaSICON was very stable over time in reactant-free supporting electrolytes ranging from neutral pH (1 M NaCl) to strongly alkaline, i.e., 3 M NaOH (Fig. 5.2a,b). All Nyquist plots from the EIS measurements displayed a high-frequency intercept, $R_{HF}$, and a semicircular feature, $R_{GB}$, as exemplified in Fig. 5.2a for the measurement in 1 M NaCl. EIS fitting to the equivalent circuit in Fig. D.6 was used to obtain numerical values for $R_{HF}$ and $R_{GB}$. Control EIS measurements of each of the H-cells without the NaSICON pellet yielded no noticeable $R_{GB}$ (Fig. D.5a), and in each case, $R_{HF}$ was in good agreement with the solution resistance estimated from the H-cell’s dimensions and literature values for electrolyte conductivity (see Fig. D.5b and associated calculations).
Figure 5.2: EIS measurements of NaSICON pellets in various supporting electrolytes. (a) Nyquist plots for pellets immersed in 1 M NaCl and 3 M NaOH solutions, showing a similar impedance immediately after immersion vs after 13 and 15 days, respectively. (b) Area-specific $R_{GB}$ vs time for pellets immersed in various electrolyte compositions between pH 7 and 14.5.

$R_{HF}$ is the sum of Ohmic series resistances of the current collector, NaSICON pellet and liquid electrolyte, whereas $R_{GB}$ originates from Na$^+$ transport through grain boundaries, i.e., between the grains and glassy phase. The latter attribution is supported from fitting EIS measurements made on symmetric Au—NaSICON—Au cells (Fig. D.6a) to the modified equivalent circuit proposed by Huggins [232] (Fig. D.6b), which is a well-established model for NaSICON. [228] Capacitances for $R_{GB}$ in Fig. D.6a are within the $10^{-8} – 10^{-9}$ F/cm$^2$ range and are consistent with the range of literature values for the capacitance of the grain boundary ($10^{-11} – 10^{-8}$ F/cm$^2$), as opposed to that of the macroscopic interface between the pellet and electrolyte or current collector, which is expected to be in the $10^{-7} – 10^{-5}$ F/cm$^2$ range. [233] The capacitances corresponding to the semicircles in Fig. 5.2a and the Nyquist plots for all the other electrolytes were found to be in the 6-15 nF/cm$^2$ range and thus also
consistent with impedance at the grain boundaries within each pellet.

$R_{\text{GB}}$ was stable over the course of two weeks for NaSICON immersed in neutral pH to strongly alkaline electrolytes containing an NaOH concentration of up to 3 M (Fig. 5.2b), indicating that the etching of the glassy phase observed in Fig. 5.1 was limited to the surface of the pellet and that subsurface grain and grain boundary resistance were unaffected. Consistent with this claim, $R_{\text{HF}}$ also remained stable over the course of the experiment (Fig. D.7a). For data in Fig. D.7b, $R_{\text{HF}}$ from the control EIS measurements on pellet-free H-cells was subtracted from the corresponding value in Nyquist plots from pellet-containing H-cells. Fuentes et al. observed a trend for NaSICON pellets immersed in water partially consistent with ours, with grain boundary resistance increasing significantly and high frequency resistance remaining relatively constant. [227]

5.3.3 Immersion of NaSICON in $K^+$-Containing Electrolytes

Because supporting electrolytes containing potassium or a mixture of potassium and sodium ions have been shown to increase solubility of certain organic and inorganic RFB reactants, [234] a pellet was also immersed in 1 M KCl. That pellet broke apart into granules within 7 days of immersion (optical image in Fig. D.8a), and the SEM images of these granules (Fig. 5.3a,b) indicated a much more severe and extensive degradation of the glass phase than was observed in non-$K^+$-containing electrolytes. Close inspection of the images showed that the loss of structural integrity also involved the formation of extensive voids along grain boundaries, apparently due to glassy phase dissolution. The dissolution of the glassy phase is consistent with
the behavior observed by Fuentes et al., who analyzed the stability of NaSICON in water, [227] but the finding in this study that K$^+$ ions accelerate this dissolution is novel.

Figure 5.3: SEM images of remnants of a pellet immersed for 7 days in 100 mM KCl at (a) low and (b) high magnification. Example regions of glass phase and grain boundary degradation are indicated in (b) with black arrows.

Consistent with these SEM results, the grain boundary resistance of NaSICON increased when K$^+$ ions were present in the adjacent electrolyte. An attempt to systematically track the impedance of NaSICON in an H-cell containing 1 M KCl was unsuccessful because the pellet completely disintegrated (Fig. D.8a). Pellets immersed in electrolytes comprising 0.1 M K$_4$Fe(CN)$_6$ and 1 M NaCl, as well as 0.1 M K$_3$Fe(CN)$_6$ and 1 M NaCl where [K$^+$]/[Na$^+$] = 0.4 and 0.3, respectively, also disintegrated after a week. We then decreased [K$^+$]/[Na$^+$] to 0.2 by using electrolytes comprising 0.1 M K$_4$Fe(CN)$_6$ and 1 M Na$_2$SO$_4$ (Fig. D.8b) as well as 0.1 M K$_3$Fe(CN)$_6$ and 1 M Na$_2$SO$_4$ (Fig. D.8c). In this case, the pellet remained visually intact over the course of a month (Fig. D.8d) but showed a significant, though nonmonotonic, rise in non-R$_{HF}$ components of the total resistance, while R$_{HF}$ stayed approximately constant (Fig. D.8e). This rise in non-R$_{HF}$-related resistance, together with SEM
results in Fig. 5.3, suggests that K\(^+\) ions promote extensive etching and dissolution of the glassy phase into the liquid electrolyte. It is possible that the addition of K\(^+\) ions increases the solubility of the glassy phase at the pellet surface in the adjacent electrolyte.

Our observations are consistent with those of Allcorn et al., [103] who observed, upon immersion of a NaSICON pellet in a reactant-free 0.4 M Na\(_2\)SO\(_4\) electrolyte (pH 7), a transient decrease in the total conductivity, followed by 20 days of negligible change.

5.3.4 Permeability

Permeability of NaSICON to sodium permanganate and sodium disulfide was found to be immeasurably low, in contrast to the permeability of 183 µm-thick Nafion 117 to the same species (Fig. 5.4). Permeabilities were ascertained by occasionally taking aliquots from the receiving side of a dialysis H-cell, determining the concentration of crossed over species using UV-vis spectrophotometry and applying Eqn. (5.1) The donating side in all cases comprised 0.1 M of the reactant in 2 M NaOH, whereas the receiving side comprised 2 M NaOH. The resulting permeabilities of Nafion 117 to NaMnO\(_4\) and Na\(_2\)S\(_2\) were 2.47 \times 10^{-9} and 1.13 \times 10^{-9} \text{ cm}^2/\text{s}, respectively. More details of these measurements, including the raw UV-vis spectra, relevant calibration curves, and H-cell images, are shown in Fig. D.9 and Fig. D.10 for permanganate and disulfide measurements, respectively. Nafion permeabilities obtained here are comparable to the permeability of Nafion to ferricyanide, estimated by De Porcellinis et al. [235] to be 4.5 \times 10^{-9} \text{ cm}^2/\text{s}.
Figure 5.4: Measurements of the permeability of NaSICON and Nafion membranes to Na$_2$S$_2$ and NaMnO$_4$. The donating sides contained 0.1 M of NaMnO$_4$ and Na$_2$S$_2$ in a supporting electrolyte of 2 M NaOH, while the receiving sides contained 2 M NaOH only.

In contrast to Nafion, crossover of NaMnO$_4$ and Na$_2$S$_2$ through NaSICON was immeasurably low over the course of 5 and 12 weeks, respectively. An upper bound for the permeability of disulfide and permanganate through NaSICON was estimated based on the sensitivity of the spectrometer and is about $\sim 10^3$–$10^4$ times lower than that of Nafion. Moreover, both NaSICON pellets remained visually intact during the experiment, in agreement with the results in the section Sec. 5.3.1, showing that the microstructure of the NaSICON surface is stable in the presence of NaMnO$_4$ and Na$_2$S$_2$. The negligibly low permeabilities exhibited by NaSICON here strongly
indicate that it may be a suitable membrane for aqueous RFBs containing inorganic small-molecule reactants that may otherwise quickly permeate or degrade polymer-based membranes. Eliminating crossover is an attractive approach to enabling the use of permanganate and polysulfide in the posolyte and negolyte, respectively, in alkaline RFBs. Upon crossover, permanganate may precipitate as solid MnO$_2$ if the negolyte’s potential is sufficiently low, irreversibly decompose the negolyte reactant—especially if it is an organic molecule—or both. Polysulfide ions likewise will precipitate as solid sulfur if they cross over to a highly oxidizing positive electrolyte and may also cause precipitation of the posolyte reactant if it is a solid at its lowest oxidation state (e.g., permanganate will get reduced to solid MnO$_2$ in the presence of polysulfide). [231] Although a variety of strategies may be devised to recover and reuse crossed over species, [104, 236], precipitation can be detrimental to reactor performance if it leads to choking of the RFB’s flow fields, electrodes, and electrolyte manifolds, leading to irreversible capacity fade. It is worth noting that these problems are likely to be exacerbated in real-world RFBs for grid energy storage, where system temperatures are likely to be higher than ambient, and crossover rates thus proportionally faster. [205]

### 5.3.5 Thickness- and Temperature-Dependent Impedance of NaSICON

The total ASR of NaSICON decreased linearly with pellet thickness, from 101 Ω cm$^2$ at 1190 μm to 53 Ωcm$^2$ at 610 μm, as measured in a flow cell containing 1 M NaCl at 18 °C (Fig. 5.5a). The Nyquist plots displayed two semicircular features, the higher frequency (0.5–1.5 MHz) feature corresponding to $R_{GB}$, as previously introduced,
and a lower frequency (6–11 kHz) feature corresponding to charge transfer at the macroscopic interface between the pellet and porous carbon electrodes in the flow cell, which we denote as $R_{\text{INT}}$. The latter attribution is supported by the capacitance of that feature lying within the 6–15 $\mu$F/cm$^2$ range, which is consistent with charge transfer resistance for solid-state membranes. $R_{\text{HF}}$, $R_{\text{GB}}$, and $R_{\text{INT}}$ were found to vary linearly with pellet thickness (Fig. D.11a); however, the total conductivity of the pellets is expected to be independent of thickness and is 1.2 mS/cm for the data in Fig. 5.5a. This value is in good agreement with the conductivity of 1.1 mS/cm, measured on symmetric Au—NaSICON—Au cells bearing NaSICON pellets between 0.61 and 1.19 mm thick (Table D.3), and is also consistent with literature reports. [237, 238]

Figure 5.5: Characterizing the effect of NaSICON thickness and temperature on electrochemical impedance. Thickness-dependent Nyquist plots at (a) 18 and (b) 70 °C. (c) Total area-specific resistance ($\Omega \text{ cm}^2$) vs thickness (mm) of a series of NaSICON membranes at 18 and 70 °C.

Total NaSICON conductivity increased considerably with temperature, from 1.2 mS/cm at 18 °C (data in Figure 5a) to 3.3 mS/cm at 70 °C (Fig. 5.5b), as measured
in a heated flow cell with electrolytes containing 1 M NaCl. EIS measurements taken at various temperatures for a cell containing the 0.8 mm pellet (Fig. D.12a,b) showed that the increase in conductivity occurred largely due to the disappearance of $R_{\text{GB}}$ for temperatures above 25 °C, a 3× decrease in $R_{\text{INT}}$ (Fig. D.11a,b) and a 2.5× decrease in $R_{\text{HF}}$ (Figure S11c). Fig. 5.5c summarizes total ASR vs NaSICON thickness at 18 and 70 °C. The lowest ASR was $\sim$18 Ω cm$^2$ for the flow cell containing the thinnest, 610 µm-thick pellet at 70 °C. This ASR is about 5.6× lower than that measured for the thickest pellet (1190 µm) at 18 °C. Rodby et al. recently reported that a single ion-conducting ceramic membrane may be commercially attractive as an RFB separator if such a 6× reduction could be implemented at a moderate cost ($<100 \$ /m$^2$) and the membrane could be integrated into a high-voltage flow battery (>3 V). [236] The ASR trend lines in Fig. 5.5c indicate that an even lower ASR of $\sim$5 Ω cm$^2$ is achievable at 70 °C for a $\sim$100 µm-thick NaSICON pellet. Achieving this target or lower without any compromises to permeability and mechanical stability will dramatically relax the cost and voltage requirements for ceramic membrane-containing RFBs that are techno-economically attractive and thus potentially enable aqueous systems. Currently, there is substantial investment in the manufacturing of thin film (<50 µm) ceramic electrolyte membranes for solid-state Li batteries. In addition, the elements and precursors required to synthesize NaSICON are not necessarily expensive nor are they considered rare or unsustainable. Thus, at present, it is reasonable to consider it possible to establish a feasible commercialization pathway for the large-scale manufacturing of NaSICON thin films for aqueous RFBs in the near future.
5.3.6 Symmetric and Full Cell Cycling

Flow cell cycling demonstrated that NaSICON was effective in preventing reactant crossover and enabling high capacity retention. We assembled and subjected to long-term cycling compositionally symmetric (Fig. D.13a) and compositionally asymmetric (Fig. 5.6a) flow cells containing NaSICON pellets. The symmetric cell comprised electrolytes with a total $[\text{Fe(CN)}_6^{3-}]$ of 20 mM and a supporting electrolyte of 1 M NaCl and was cycled at 2.8 mA/cm$^2$. Each half-cycle ended with voltage holds at ±400 mV, to access the full capacity of the CLE. The cell had an average current efficiency of 99.5% and showed excellent capacity retention: the apparent 3% loss of capacity after a month of cycling was fully recovered after the CLE was shaken, indicating that the observed capacity fade was likely due to droplets of electrolyte clinging to the walls of the reservoir. Our results agree with those of Senthilkumar et al., [219] who observed a capacity fade rate equivalent to 0.04%/day for a hybrid Na metal/ferrocyanide flow cell. Because the electrolytes contained potassium ferricyanide ($[\text{K}^+] / [\text{Na}^+] = 0.029$), EIS measurements were periodically conducted to assess the influence of $\text{K}^+$ on the impedance of the NaSICON pellet (Fig. D.13b). We found that $R_{\text{HF}}$ was stable over the entire cycling period, while the total cell resistance increased steadily, from 120 Ω initially to ~250 Ω after ~40 days of cycling. These results are consistent with the finding in Sec. 5.3.1 that the presence of $\text{K}^+$ ions accelerates degradation of the grain boundary/glassy phase of NaSICON but not the grains.
Figure 5.6: Comparison of capacity retention in NaSICON and Nafion-containing ferrocyanide—permanganate flow cells. Cycling performance of ferrocyanide—permanganate cell with (a) NaSICON and (b) Nafion 117 membranes. The upward arrows indicate NCLE electrolyte replacements to correct imbalance, whereas the downward arrows indicate when 0.5 mL aliquots were drawn from the CLE and replaced with the uncycled electrolyte. UV–vis absorption spectra of 400×-diluted aliquots of cycled and uncycled negolytes from (c) NaSICON and (d) Nafion cells.

We cycled a compositionally asymmetric cell containing a CLE of 50 mM Na₄Fe(CN)₆ and an NCLE of 200 mM NaMnO₄, both in a supporting electrolyte of 3 M NaOH. The cell had a NaSICON membrane and was cycled within a voltage range of +0.4 to -0.05 V at a current density of 2.8 mA/cm² and with each half-cycle terminated with...
a voltage hold. As a control, a cell with identical electrolyte composition but containing Nafion 117 as the membrane was also cycled, with potential limits of +0.35 and 0 V and at a current density of 10 mA/cm². The average current efficiency for both cells was slightly greater than 100% (100.3 to 101%); this may be explained by water oxidation occurring concurrently with ferrocyanide oxidation in the CLE, as ferrocyanide’s redox potential is slightly above that for O₂ evolution at pH 14.5. [60, 239] It is possible that O₂ evolution occurs to a smaller extent at the NCLE because the O₂ evolution reaction is kinetically suppressed by the permanganate redox couple. [213] We observe an extremely low average capacity fade rate of 0.04%/day over the course of three weeks of cycling for the NaSICON pellet-containing cell and a much higher fade rate for the Nafion-containing cell, ranging between 0.5%/day for the first two weeks to 0.1%/day for the week thereafter. Periodic replacement of the NCLE was necessary to rebalance both cells because permanganate undergoes reduction over time in the presence of certain electrolyte-contacting materials, [231] leading to the permanganate electrolyte becoming the CLE and thereafter a steep decline in capacity. In the Nafion-containing cell, this rebalancing procedure revealed irreversible losses in capacity, ostensibly as a result of ferrocyanide crossover from the CLE to NCLE, permanganate crossover from the NCLE to CLE followed by irreversible degradation of Fe(CN)₆⁻, or some combination of both processes. The Nafion cell was cycled for a total of about 800 h and maintained a similar capacity retention rate to that prior to 500 h (Fig. D.14a). The NaSICON cell was stopped after 670 h of cycling due to a leakage that led to a rapid decline in capacity after 650 h. The cell showed no change in capacity after replacement of the NCLE
(Fig. D.14b), suggesting that the observed capacity fade might correspond to some ferrocyanide decay at high pH. The voltage–charge profiles for selected cycles and voltage–current profiles for 5 h of cycling are shown in Fig. D.15a,b, respectively. The voltage–charge profiles for the NaSICON are shown in Figure Fig. D.15c, and voltage–current profiles for 50 h of cycling are shown in Fig. D.15d.

UV–vis (Fig. 5.6c,d for NaSICON and Nafion cells, respectively) and ICP-MS measurements (Table D.3) of the CLE corroborated the conclusion that the irrecoverable capacity fade in the Nafion cell was due to loss of ferrocyanide from the CLE. The UV–vis spectra of aliquots taken from the NaSICON cell show nearly no change compared to the uncycled spectra (Fig. 5.6), whereas aliquots taken from the CLE of the Nafion cell after 14 days show a 6.2% decline in the absorbance of the ferrocyanide peak at 270 nm relative to an uncycled sample (Fig. 5.6d), in reasonably good agreement with the 5.8% loss of capacity (6.4% after normalizing for the 0.5 mL aliquot of electrolyte replacement). ICP measurements were also in agreement with the UV–vis results and indicated that both ferrocyanide and permanganate permeated Nafion during cycling. The ferrocyanide electrolyte from the Nafion cell had 1.49 and 1.84 mg/L of manganese after two and four weeks of cycling, respectively, whereas the uncycled solution contained no manganese (Table D.4). Also, 14.3 mg/L of iron was detected in the permanganate electrolyte cycled between 92 and 260 h, and 0.27 mg/L was detected in the electrolyte cycled between 260 and 670 h. In contrast, no manganese or iron was detected in the uncycled and cycled electrolytes of the NaSICON cell, further corroborating the ability of NaSICON to mitigate ferrocyanide and permanganate crossover.
The above results establish that NaSICON effectively prevents crossover of either member of the \( \text{MnO}_4^-/\text{MnO}_2^2^- \) - couple in a compositionally asymmetric configuration. Nevertheless, with a nominal voltage of only 140 mV (Fig. D.13), a ferrocyanide–permanganate cell cannot produce practically useful power. We therefore verified that NaSICON’s crossover prevention abilities extend to higher voltage systems by cycling 0.1 M of permanganate against 0.05 M of 1,8-PFP in the negolyte, both in 3 M NaOH. This cell has a nominal voltage of 1.2 V. A Nafion membrane-containing cell that was capacity-limited by 1,8-PFP exhibited a capacity fade rate of about 0.02%/day (Fig. D.16a,b), in reasonably good agreement with cycling results previously reported for a 1,8-PFP–\( \text{Fe(CN)}_6^{3-} \) cell operated at pH 14. [230] When the cell was capacity-limited by \( \text{MnO}_4^- \), however, the capacity fade rate increased to 3%/day (Figure S16c,d), consistent with \( \text{MnO}_4^- \) crossover-induced capacity fade. Replacing Nafion with NaSICON resulted in an immeasurably low-capacity fade rate for over 14 days of cycling (Fig. D.16e). The current efficiency averaged 94% after the first four days, which we attribute in part to self-reduction of permanganate; rebalancing, however, was not required given the 4-fold excess capacity from 1,8-PFP in the negolyte. Typical voltage profiles as well as energy and current efficiency vs cycle number for the NaSICON cell are shown in Fig. D.16e,f.

It is worth noting from Fig. D.16g that consistent access to about 99% of the theoretical capacity of the \( \text{MnO}_4^- \) electrolyte was obtained. To our knowledge, this work is the first to demonstrate full, temporally stable access to the \( \text{MnO}_4^-/\text{MnO}_2^2^- \) redox couple in a flow cell with a non-Nafion-based membrane. The \( \text{MnO}_4^-/\text{MnO}_2^2^- \) couple has several advantages over many of the reactants deployed against ceramic
Na$^+$-conducting membranes in previously reported aqueous cells, a representative sampling of which is reported in Table D.5. These advantages include a high solubility of 4 M in 7.5 M NaOH, (equivalent to a charge density of 107 Ah/L), as well as a high redox potential and a low cost in terms of $$/mol e^-$. These metrics are provided in Table D.5 and elaborated in the associated discussion.

In addition to eliminating crossover, NaSICON is more attractive than Nafion because it is expected to have a considerably lower cost at scale. Most nonfluorinated membranes with lower projected costs than Nafion are likely to be chemically unstable under the corrosive, alkaline conditions required for the $\text{MnO}_4^-$/MnO$_2$$^-$ to operate. [235] In fact, we attempted to cycle a ferrocyanide—permanganate cell at 3 M NaOH with a nonfluorinated Fumasep membrane, but the membrane completely disintegrated while in contact with the electrolyte.

Taken together, our results reveal that NaSICON membranes can enable a much wider pH and potential range for aqueous RFB chemistries than have been previously considered and can enable practical RFBs if ultrathin pellets can be fabricated and operated 20-50 °C above ambient temperature. In such future applications, careful attention must be paid to the membrane’s flexural strength, in addition to the evolution of its microstructure and resistance while in contact with the electrolyte. Although certain bulk mechanical properties of NaSICON have been previously measured, [240, 241, 242] the flexural strength of thin NaSICON membranes is unknown. Low flexural strength may result in fracture of the membrane while under stresses from compression against other cell components or pressure gradients caused by uneven electrolyte flow. Future work to analyze the trade-offs among membrane
thickness, temperature, and power density should be conducted. In addition, me-
chanical engineering design approaches (e.g., load-bearing supports, or stiff conformal
coatings) might be considered to ameliorate stresses that can cause fracture in thin
ceramic membranes for use in RFBs.

5.4 Conclusions

In this work, we demonstrated that von Alpen NaSICON is a potentially viable
material for aqueous RFBs operating under neutral to strongly alkaline conditions.
Measurements of resistance, permeability, and interfacial morphology as a function
of electrolyte composition and cell temperature were made. Cycling of composition-
ally symmetric and asymmetric flow cells revealed that NaSICON was effective in
preventing crossover of ferrocyanide and permanganate-based reactants and enabling
high capacity retention. The following conclusions can be made from our findings:

1. The glassy phase at the surface of NaSICON is susceptible to etching while
in contact with aqueous electrolytes. In non-$K^+$-containing electrolytes, the
etching increases slightly with pH, but the overall grain and grain boundary
resistance impedance of NaSICON is stable over time. In $K^+$-containing elec-
trolytes, the etching increases dramatically and leads to complete disintegration
of the pellet. On the basis of these results, NaSICON pellets with very little
to no glassy phase present are likely to be suitable as aqueous RFB mem-
branes. [243]

2. The total ASR of a NaSICON-containing flow cell decreases dramatically with
decreasing thickness and increasing temperature, falling 5.6-fold from 101 Ω cm² for a 1.1 mm pellet at 18 °C to ∼18 Ω cm² for a 610 µm-thick sample at 70 °C. We project that aqueous RFBs containing NaSICON membranes that are <100 µm thick will exhibit maximum power densities comparable to polymer membrane-containing analogues if operated above ambient temperature (40-80 °C). [243]

3. NaSICON is highly impermeable to permanganate and disulfide ions, in contrast to Nafion, which has a permeability to these species of ∼10⁻⁹ cm²/s. This difference in permeability translates to poorer capacity retention for Nafion-containing vs NaSICON-containing flow cells. A ferrocyanide—permanganate flow cell with a 3 M NaOH supporting electrolyte and a NaSICON membrane exhibited a much lower capacity fade rate (<0.04%/day over 3 weeks of cycling) than another cell with a Nafion membrane (0.1–0.5%/day). These results strongly suggest that with further optimization, NaSICON can enable practical aqueous RFBs featuring inorganic reactants such as those based on iron, manganese, and sulfur. [1, 208, 210, 231, 244] As was recently demonstrated by Yao et al., [245] many charge-storing reactants derived from these inorganic earth-abundant elements feature high solubilities (with volumetric charge densities up to and above 80 Ah/L) and extremely low degradation rates (less than 0.01%/day), potentially leading to competitively low levelized costs of electricity from RFBs using them.
CHAPTER VI

Conclusions and Future Work

The work presented in this thesis explores several aspects of capacity fade in organic RFBs that stem from chemical degradation of redox-active molecules and crossover through polymer membranes. A framework is developed to combine experimental techniques like UV-vis spectroscopy, cell cycling, mass spectrometry and NMR with data-driven techniques and computational models to determine the degradation mechanism, i.e., the chemical decay pathway of redox-active charge carriers and reaction rates, and test competing hypotheses for novel molecules where clear pathways are yet to be determined. This work also considers the effect of membrane crossover for commonly used polymer membranes and demonstrates the ability of sodium superionic conductor (NaSICON) membranes to prevent it, thus enabling the deployment of several organic and inorganic molecules.

In Chapter II we demonstrate the development of a zero-dimensional model that accurately simulates the performance of lab-scale flow cells under a wide range of operating parameters like the applied current, electrolyte flow rate and concentra-
tion. Our model determines voltage loss parameters from independent experiments and requires minimal tuning. The model is very modular in its construction and incorporates reactant degradation mechanisms like first and second order decay and crossover. The model simulates the effect of the cycling protocol on the observed capacity fade rate and finds a considerable amount of variation in the observed fade rate during cell cycling. This holds several practical implications because very often, experimental studies report capacity fade under one set of operating conditions, and are unable to predict molecular degradation rates and crossover. Computational models can help estimate fade rates for other cycling protocols and reactor builds saving experimental efforts, cost and time. Future studies developing models for RFBs can look at models that simulate cell cycling and degradation when more than one redox-active pairs of molecules are present in the electrolyte, organic molecules may remain redox-active after undergoing degradation albeit with altered redox properties as seen in Chapter III.

The model is further modified to simulate pH swing and CO$_2$ capture. It estimates the energetic costs and throughput rates for CO$_2$ capture under a wide range of operating conditions. The application-oriented case studies considered in this work explore the sensitivity of reactor design parameters like the liquid-gas contact area and the benefit derived from the use of catalysts facilitating CO$_2$ invasion and outgassing. The simulations demonstrate that increasing CO$_2$ invasion time increases productivity and reduces the specific energy input, and catalysing CO$_2$ invasion significantly improves productivity and reduces the specific energy input. However, beyond a point (invasion time $\geq$ 45 minutes), the specific energy input and
productivity do not show much change on further increments in invasion time. In this operating region, catalysing CO\textsubscript{2} invasion too does not affect the productivity, though it reduces the specific energy input. We also look at direct air CO\textsubscript{2} capture to find that it requires a significantly higher invasion time (achieved by using a lower current density) compared to flue-gas capture on account of the lower CO\textsubscript{2} partial pressure in air. The model therefore provides several cues to aid the development and optimization of future electrochemical cells that can capture CO\textsubscript{2} using pH swing. Future efforts in this regard can focus on simulating the performance of proton coupled electron transfer (PCET) active electrodes, which can swing the pH of the electrolyte and capture CO\textsubscript{2}.

Having observed the potential of computational models to predict capacity fade, it is important to identify the degradation mechanism of the redox-active molecule and associated reaction kinetics. In this regard, Chapter III demonstrates a technique that combines flow cell studies with UV-vis spectroscopy along with data-driven techniques like Bayesian inference and MCR-ALS to identify the reaction orders, steps, intermediates and kinetics. This technique was successfully applied to study Michael attack on BQDS, where the degradation mechanism was known, but little effort was directed towards comprehensively determining the reaction kinetics. We were able to put the aforementioned techniques together to corroborate two-step Michael attack on BQDS, (having a first-order reaction) and quantified the reaction kinetic constants for both steps. We found a good agreement between the findings of two experimental techniques i.e., \textit{ex situ} UV-vis that used K\textsubscript{2}Cr\textsubscript{2}O\textsubscript{7} as a sacrificial oxidizer species and \textit{operando} UV-vis which used a flow cell to continuously oxidize
BQDS and two data-driven techniques (Bayesian inference and MCR-ALS), thus demonstrating the robustness of our method. We also ensured that the chemical composition of the reactants, intermediates and products agreed with hypothesized mechanism with NMR, and found the thermodynamic favorability of Michael addition of water to BQDS using DFT. This study shows that combining various experimental techniques with data-driven ones proves to be a powerful technique for determining reaction pathways and rates, and holds the potential to be applied to several novel organic molecules (as is demonstrated in Chapter IV) that are being studied as potential candidates for deployment in low-cost RFBs.

Having gained confidence in the method we developed in Chapter III, we extended it to the study of degradation in quinoxaline derivatives, which remain a sparsely studied class of organic redox-active molecules. Despite several attractive attributes, quinoxaline derivatives have not seen much development due to impractically low stability. In Chapter IV we explore the degradation mechanism, and find it to be very different from the previously hypothesized mechanisms (like Michael addition of water, irreversible hydrogenation and dimerization). Our data from operando UV-vis analysis combined with Bayesian inference and extensive use of $^1$H-NMR, 2D COSY and $^{13}$C-NMR along with LC-MS find tautomerization to be primarily responsible for the degradation (or loss of redox activity) in a dimethyl- and carboxylate-substituted quinoxaline (which we use as our baseline molecule). We used DFT modelling to look at the effects of electron-withdrawing group strength, and H-bonding strength for tautomerization resistance and cycled many other quinoxaline derivatives (procured commercially and synthesized in house) to find quinoxaline-2-carboxylic
acid (2QUIC) to be the most stable with a redox potential that was 160 and 480 mV lower than 3,3’-(phenazine-1,8-diyl)dipropionic acid (1,8-PFP) [230] and (((9,10-dioxo-9,10-dihydroanthracene-2,6-diyl)bis(oxy))bis(propane-3,1-diyl))bis(phosphonic acid) (2,6 DPPEAQ) [246] respectively which are recently reported stable organic redox-active molecules. We found that a compositionally asymmetric flow cell with 2QUIC and ferrocyanide lost capacity at a rate of 5%/day, entirely due to membrane crossover through a Nafion 212 membrane. To corroborate the absence of any significant chemical degradation, a compositionally symmetric flow cell (where 2QUIC and ferrocyanide was mixed, and thus the posolyte and negolyte had an identical composition) was set up and showed an immeasurable low capacity fade rate for cell cycling over 200 hours. Thus we were successfully able to demonstrate our method to identify the degradation mechanism and a stable quinoxaline derivative.

This study opens up several possibilities for the exploration of other quinoxaline derivatives which can be resistant to tautomerization and may be identified using DFT and synthesized and tested experimentally. Future studies may focus on functionalizing quinoxalines which while chemically stable are more resistant to membrane crossover (which may be achieved with the addition of bulky charged groups), have high solubility and even lower redox potentials than 2QUIC. In addition to quinoxalines, this analysis may also be extended to pyrazines which have even lower redox potentials. [174] Future studies may also be aimed at exploring polymer membranes with higher permselectivity than Nafion 212 along with NaSICON membranes that better prevent crossover. These studies may also look to modify the zero-dimensional model to simulate the two-step degradation (and regeneration on
strong oxidation of transient reaction intermediates) process.

Chapter V explores the viability of NaSICON membranes in aqueous RFBs and their ability to mitigate reactant crossover. The work used resistance measurements to establish the stability of von Alpen NaSICON in various aqueous solvents and found NaSICON to be stable in sodium containing solutions. However, it found NaSICON to be unstable in potassium containing solutions, and using SEMs and resistance measurements. This was attributed this to glass phase etching, which lead to a loss of structural integrity and the eventual disintegration of membrane pellets. The study also found the area-specific resistance (ASR) to fall significantly on decreasing thickness and increasing temperature i.e. from 101 Ω cm$^2$ for a 1.1 mm thick pellet at 18 °C to 18 Ω cm$^2$ for a 0.6 mm thick pellet at 70 °C. The work observes the permeability of NaSICON to permanganate and disulfide ions to be immeasurably low. Mitigating crossover reduces the capacity fade rate in a ferrocyanide—permanganate from 0.1 - 0.5 %/day in a cell using Nafion to 0.04 %/day in a cell using NaSICON. NaSICON therefore has the potential to enable several chemistries that witness rapid capacity loss due to crossover through polymer membranes.

One drawback of NaSICON membranes at present is their higher ASR (\(\sim 10 \ \Omega \ cm^2\)) as compared to Nafion (\(\sim 1 \ \Omega \ cm^2\)). This difference in resistance may impede practical cell development due to increased voltage losses, lower current densities and larger reactor area requirements (which increase costs). However, NaSICON’s ASR may be brought to levels comparable to Nafion by taking measures like operating cells at higher temperatures as shown in this work, developing thin (\(\approx 0.1 \ mm\)) and
developing NaSICON with a higher conductivity (from the present $\approx 1 \text{ mS/cm}$ for von Alpen NaSICON), or a combination of these. Therefore, there exist a considerable number of possibilities for the improvement of NaSICON’s performance and to make it viable in practical RFBs and can inspire a significant number of studies in future.

Having looked at several aspects of enabling low-cost organic materials in organic RFBs, this work comprehensively presents computational and experimental studies to understand the causes for molecular degradation, degradation mechanism identification and mitigation along with the development of novel stable molecules. It also explores the significant challenge posed by membrane crossover and explores the use NaSICON as a measure to mitigate it. The author hopes that this work will be useful to future researchers seeking to develop novel redox-active organic and inorganic molecules and enable low-cost durable redox flow batteries that enable commercially viable grid-scale storage and aid the adoption of renewable energy.
APPENDICES
APPENDIX A

A Zero-Dimensional Model for Electrochemical Behavior and Capacity Retention in Organic Flow Cells
A.0.1 Capacity fade of Fe(CN)₆ in symmetric cell cycling

Figure A.1: Oxidation and reduction capacity versus time for symmetric Fe(CN)₆ cells during CCCV cycling with graphite felt and carbon paper electrodes. The cycling was conducted between voltage limits of +0.4 and -0.4 V; the applied current density in the CC region was ±50 mA/cm², and each half-cycle terminated when the absolute value of the current density fell below 3 mA/cm² in the CV region. For the graphite felt electrode cell, we changed this limit to 2 and 1 mA/cm², and there is no apparent change to the fade rate. We report capacity fade rates for the entire cycling period in %/day. For each cell, the capacity-limiting electrolyte was 15 mL, and had an initial composition of 50 mM each of K₄Fe(CN)₆ and K₃Fe(CN)₆, at pH 14. The non-capacity-limiting electrolyte was 40 mL and had the same starting composition. The membrane was Nafion 117.
Figure A.2: Oxidation and reduction capacity versus time for a symmetric Fe(CN)₆ cell during CCCV cycling with graphite felt electrodes at pH 7. The cycling was conducted between voltage limits of +0.4 and -0.4 V; the applied current in the CC region was ±50 mA/cm², and each half-cycle terminated when the absolute value of the current density fell below 1 mA/cm² in the CV region. The electrolyte volume in the CLS was 10 mL, and it had an initial composition of 50 mM each of K₄Fe(CN)₆ and K₃Fe(CN)₆, and 1 M KCl. The non-capacity-limiting electrolyte had a volume of 35 mL and had the same starting composition as the CLS; the membrane was Nafion 117.
A.0.2 Electrochemical Impedance spectroscopy (EIS) measurements at different flow rates

Figure A.3: Oxidation and reduction capacity versus time for a symmetric Fe(CN)6 cell during CCCV cycling with graphite felt electrodes at pH 7. The cycling was conducted between voltage limits of +0.4 and -0.4 V; the applied current in the CC region was \( \pm 50 \) mA/cm\(^2\), and each half-cycle terminated when the absolute value of the current density fell below 1 mA/cm\(^2\) in the CV region. The electrolyte volume in the CLS was 10 mL, and it had an initial composition of 50 mM each of K\(_4\)Fe(CN)\(_6\) and K\(_3\)Fe(CN)\(_6\), and 1 M KCl. The non-capacity-limiting electrolyte had a volume of 35 mL and had the same starting composition as the CLS; the membrane was Nafion 117.
Table A.1: Flow-rate dependent series, charge transfer and polarization resistance for a flow cell in contact with an electrolyte reservoir containing 20 mM Fe(CN)$_6$ at 50% SOC. The polarization curves were not obtained for the two highest flow rates as $I_L$ could not be determined.

<table>
<thead>
<tr>
<th>Flow Rate (mL/min)</th>
<th>$R_s$ (Ω)</th>
<th>$R_{ct}$ (Ω)</th>
<th>$R_T$ (Ω)</th>
</tr>
</thead>
<tbody>
<tr>
<td>12.7</td>
<td>0.37</td>
<td>0.24</td>
<td>0.85</td>
</tr>
<tr>
<td>33.3</td>
<td>0.38</td>
<td>0.12</td>
<td>0.62</td>
</tr>
<tr>
<td>56.9</td>
<td>0.39</td>
<td>0.12</td>
<td>0.63</td>
</tr>
<tr>
<td>77.8</td>
<td>0.40</td>
<td>0.19</td>
<td>0.78</td>
</tr>
<tr>
<td>106.5</td>
<td>0.41</td>
<td>0.27</td>
<td>0.95</td>
</tr>
<tr>
<td>130.5</td>
<td>0.39</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>152.4</td>
<td>0.41</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

A.0.3 Polarization resistance measurements of flow cell containing 100 mM of Fe(CN)$_6$

Figure A.4: Area-specific polarization and charge transfer resistance versus flow rate for a flow cell in contact with an electrolyte containing 100 mM of Fe(CN)$_6$ at 50% SOC.
A.0.4 Measurement of exchange rate constant of Fe(CN)$_6$

We measured cyclic voltammograms between 20 mV/s to 250 V/s for 2 mM K$_4$Fe(CN)$_6$ + 2 mM K$_3$Fe(CN)$_6$ in 1 M KCl on glassy carbon.

Figure A.5: Cyclic voltammetry measurements of a solution containing 2 mM each of K$_4$Fe(CN)$_6$ and K$_3$Fe(CN)$_6$ in 1 M KCl with a glassy carbon working electrode, an Ag/AgCl reference electrode and a platinum wire counter electrode. A normalized current is obtained by dividing it by the square root of the scan rate.

Within the reversible region (< 200 mV/s) we found a linear relationship between the peak current and square root of the scan rate (Fig. A.5), as is expected for freely diffusing redox-active species. (1) The diffusion coefficient D may be extracted based on the peak current $i_p$ and scan rate $S$: 

$$ E_0 = 0.28 \text{ (V)} $$
\[ D = \frac{i_p}{2.69 \times 10^6 S C T}. \]  

(A.1)

Applying this equation to results in Fig. A.5a yields a diffusion coefficient of \(4.9 \times 10^{-6} \text{ cm}^2 \text{s}^{-1}\) for K_3Fe(CN)_6. Within the irreversible region, the difference between the anodic and cathodic potentials at peak current deviates from its Nernstian value of 59 mV. Plotting the dimensionless difference between anodic and standard potential versus scan rate results in a Trumpet plot (2) (Fig. A.5b) from which we derive the exchange rate constant \(k_0\) for a known charge transfer coefficient \(\alpha\):

\[
F \frac{RT}{\alpha} (E_{p,a} - E_0) = 0.78 - \frac{1}{\alpha} \ln \left( k_0 \sqrt{\frac{RT}{\alpha F S D}} \right). 
\]  

(A.2)

This can be rearranged as

\[
F \frac{RT}{\alpha} (E_{p,a} - E_0) = 0.78 - \frac{1}{\alpha} \ln \left( k_0 \sqrt{\frac{RT}{\alpha F D}} \right) + \frac{1}{2\alpha} \ln S. 
\]  

(A.3)

with the left-hand side of the equation being the y-axis of the plot and \(\ln S\) the x-axis. The slope of the plot is \(1/2\alpha \approx 1\) for \(\alpha = 0.5\), and the intercept is:

\[
F \frac{RT}{\alpha} (E_{p,a} - E_0) = 0.78 - \frac{1}{\alpha} \ln \left( k_0 \sqrt{\frac{RT}{\alpha F D}} \right). 
\]  

(A.4)
Rearranging the terms allows us to calculate $k_0$ as

$$k_0 = \sqrt{\frac{\alpha n F D}{RT}} \exp 0.78 - \alpha \times \text{intercept}. \quad (A.5)$$

Another estimate of $k_0$ was obtained using the method presented in ref. (1), which relates the peak current to $\alpha F/RT(E(p, c - E_0))$:

$$i_p = 0.227 F A k_0 C^T - \frac{\alpha n F}{RT} - (E(p, c - E_0)). \quad (A.6)$$

The value of $k_0$ is

$$k_0 = \frac{\exp \text{intercept}}{0.227 F A C^T}. \quad (A.7)$$
Figure A.6: (a) Anodic and cathodic peak currents versus square root of the scan rate within the reversible region. (b) Non-dimensional difference between cathodic/anodic potentials at peak current and the standard potential versus the log of the scan rate. Irreversible behavior starts around 5 V/s, denoted with the rightmost vertical black line.
A.0.5 Capacitance measurements of graphite felt

Figure A.7: (a) Cyclic voltammetry measurements of a graphite felt electrode in 1 M KCl between 20 mV/s and 10 V/s. (b) Average current between -0.15 and 0.15 V vs Ag/AgCl versus scan rate.
A.0.6 Raman spectra of glassy carbon and graphite felt.

Figure A.8: Raman spectra of glassy carbon and graphite felt showing D and G bands from carbon in each material.
A.0.7 Experimental, simulated and fitted values of $ak_m$ versus flow rate for symmetric cells containing total $[\text{Fe(CN)}_6]$ of 20 and 100 mM.

Figure A.9: Product of mass transport coefficient and electrode area per volume versus electrolyte flow rate from experimental limiting currents (for data at a $CT$ of 20 mM only, in blue points) and simulation fits to CCCV data at 20 mM (yellow points) and 100 mM (orange points). Dotted blue and orange lines are fits of experimental data at 20 mM and simulation-derived data at 100 mM, respectively, to a power law.

A.0.8 Mismatch between simulated and experimental CCCV curves in the absence of $t_{delay}$. 
Figure A.10: \( \text{SOC} \) and cell voltage as a function of time for experimental and simulated CCCV measurements from a symmetric flow cell comprising a CLS of volume 20 mL with total \( \text{Fe(} \text{CN}_6 \text{)}_6 \) = 20 mM in 1 M KCl, and an NCLS of identical composition but a volume of 40 mL. The flow rate was 33.3 mL/min, and the applied current density was 100 mA/cm\(^2\). In the absence of a simulated \( \text{tdelay} \), a 21\% mismatch between experimental and simulated cycle times develops.
**A.0.9 The influence of $Da$ on $\Delta SOC_{delay}$**

$\Delta SOC_{delay}$ is given by:

$$\Delta SOC_{delay} = \Delta \dot{SOC} \times t_{delay} = \frac{I}{nFCT_{tot}} \times \frac{L_{manifold}}{L} = Da \frac{L_{manifold}}{L}. \quad (A.8)$$

$L_{tot}$ is the total electrolyte volume, i.e. the sum of the reservoir and manifold volumes. The transport delay leads to a difference between the global $SOC$ i.e. $SOC$ averaged over the total volume of the electrolyte and the $SOC$ within the reservoir alone, the latter of which we denote hereafter as $SOC_{res}$. Coulomb counting returns the global $SOC$, whereas a reference electrode immersed in the electrolyte measures $SOC_{res}$. Transport delays create differences among the global $SOC$, $SOC$ in the cell and $SOC_{res}$. If the electrolyte reservoir is not well mixed, particularly at high $Da$, the electrolyte in the immediate vicinity of the reference electrode may deviate significantly from the average $SOC_{res}$.

Fig. A.11a shows $SOC$ values at various points during the electrolyte’s roundtrip circuit between the flow cell and the electrolyte reservoir, and illustrates how transport delays cause spatial variations in $SOC$. We assume the electrolyte in the reservoir is well mixed, with $SOC$ spatially uniform at $SOC_{res}$, and no mixing within the manifolds. Consequently, under constant current operation, the electrolyte $SOC$ will vary linearly between the entrance to/exit of the cell and corresponding exit from/entrance to the electrolyte reservoir. The average $SOC$ in the manifold $\langle SOC \rangle_m$ is:
Figure A.11: (a) SOC values at various points during the electrolyte’s roundtrip circuit between the flow cell and the electrolyte reservoir, and illustrates the spatial variations in SOC caused by transport delays. Measured (b) —$(SOC)_{pot} - (SOC)_{global}$— versus $Da$ and limits for imperfect (orange line) and perfect (blue line) electrolyte mixing.

\[
\langle SOC \rangle_m = \frac{\langle SOC_{entrance} + SOC_{exit} \rangle}{2}.
\]  

(A.9)

The SOC of the electrolyte entering the cell from the reservoir will be

\[
SOC_{res} + \Delta SOC_{m,i} = SOC_{res} + Da \frac{L_{m,i}}{L_{tot}}.
\]  

(A.10)

where $L_{m,i}$ is the inlet manifold volume. The average SOC in the inlet manifold will be

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\[
\langle SOC \rangle_{m,i} = SOC_{res} + \frac{1}{2} Da \frac{L_{m,i}}{L_{tot}}.
\] (A.11)

The difference in SOC between the cell inlet and outlet will be \(-Da\), assuming oxidation. Hence the SOC leaving the cell (and entering the outlet manifold) will be

\[
SOC_{res} + Da \left( \frac{L_{m,i}}{L_{tot}} - 1 \right). 
\] (A.12)

The SOC leaving the outlet manifold and entering the reservoir will be

\[
SOC_{res} + Da \left( \frac{L_{m,i}}{L_{tot}} - 1 \right) + \Delta SOC_{m,o} = SOC_{res} + Da \left( \frac{L_{m,i}}{L_{tot}} + \frac{1}{2} \text{frac}L_{m,o}L_{tot} - 1 \right).
\] (A.13)

Hence the average SOC in the outlet manifold will be

\[
\langle SOC \rangle_{m,o} = SOC_{res} + Da \left( \frac{L_{m,i}}{L_{tot}} + \frac{1}{2} \text{frac}L_{m,o}L_{tot} - 1 \right). 
\] (A.14)

The global SOC is the volume-weighted average of the SOC in the manifolds and reservoir, and is given by
\[ SOC_{\text{global}} = \frac{L_{\text{res}}SOC_{\text{res}} + \langle SOC \rangle_{m,i}L_{m,i} + \langle SOC \rangle_{m,o}L_{m,o}}{L_{\text{tot}}}. \] (A.15)

where \( L_{\text{res}} \) is the volume of electrolyte in the reservoir. Substituting the values for the average manifold \( SOC \) values, we get

\[ SOC_{\text{global}} = SOC_{\text{res}} \frac{L_{\text{res}}}{L_{\text{tot}}} + \left( SOC_{\text{res}} + \frac{1}{2} Da \frac{L_{m,i}}{L_{\text{tot}}} \right) \frac{L_{m,i}}{L_{\text{tot}}} + \left[ SOC_{\text{res}} + Da \left( \frac{L_{m,i}}{L_{\text{tot}}} + \frac{1}{2} \frac{L_{m,o}}{L_{\text{tot}}} - 1 \right) \right] \frac{L_{m,o}}{L_{\text{tot}}}. \] (A.16)

Simplifying the terms, we get

\[ SOC_{\text{global}} = SOC_{\text{res}} + Da \left[ \frac{1}{2} \left( \frac{L_{m,i} + L_{m,o}}{L_{\text{tot}}} \right)^2 - \frac{L_{m,o}}{L_{\text{tot}}} \right]. \] (A.17)

Ideally, the reference electrode will measure \( SOC_{\text{res}} \) whereas the Coulomb counting estimate will yield \( SOC_{\text{global}} \). The difference between these two values is:

\[ SOC_{\text{error}} = SOC_{\text{global}} - SOC_{\text{res}} = Da \left[ \frac{1}{2} \left( \frac{L_{m,i} + L_{m,o}}{L_{\text{tot}}} \right)^2 - \frac{L_{m,o}}{L_{\text{tot}}} \right]. \] (A.18)

Insufficiently rapid mixing within the reservoir may cause the potentiometric measurement of the \( SOC \) in the reservoir, \( SOC_{\text{pot}} \), to differ from \( SOC_{\text{res}} \). The potentiometric estimate will however lie between \( SOC_{\text{res}} \) and the \( SOC \) entering the
reservoir from the outlet manifold, thus

\[ SOC_{res} \leq SOC_{pot} \leq SOC_{res} + Da \left( \frac{L_{m,i}}{L_{tot}} + \frac{L_{m,o}}{L_{tot}} - 1 \right) \]  \hspace{1cm} (A.19)

Hence, its divergence from the Coulomb counting estimate will be

\[ -Da \left[ \frac{1}{2} \left( \frac{L_{m,i}}{L_{tot}} + \frac{L_{m,o}}{L_{tot}} \right)^2 - \frac{L_{m,o}}{L_{tot}} \right] \leq SOC_{pot} - SOC_{global} \leq Da \left[ \frac{L_{m,i}}{L_{tot}} + 2 \frac{L_{m,o}}{L_{tot}} - \frac{1}{2} \left( \frac{L_{m,i} + L_{m,o}}{L_{tot}} \right)^2 \right] \]  \hspace{1cm} (A.20)

These limits are plotted in Fig. A.11b together with measured the measured

\[ -SOC_{pot} - SOC_{global} \]
A.1 CO₂ capture simulations

Table A.2: Electrochemical properties of the flow cell and CO₂ capture/release process parameters for the baseline simulation in Fig. 2.11.

<table>
<thead>
<tr>
<th>parameter</th>
<th>value</th>
<th>units</th>
</tr>
</thead>
<tbody>
<tr>
<td>$P_{CO₂,l}$</td>
<td>0.05</td>
<td>bar</td>
</tr>
<tr>
<td>$P_{CO₂,h}$</td>
<td>1</td>
<td>bar</td>
</tr>
<tr>
<td>Applied current density ($i = I/A$)</td>
<td>10</td>
<td>mA/cm²</td>
</tr>
<tr>
<td>Cutoff current density ($i_{cutoff}$)</td>
<td>1</td>
<td>mA/cm²</td>
</tr>
<tr>
<td>CO₂ hydroxylation rate constant ($k_{OH}$)</td>
<td>8500</td>
<td>M⁻¹s⁻¹</td>
</tr>
<tr>
<td>Geometric area (A)</td>
<td>5</td>
<td>cm²</td>
</tr>
<tr>
<td>gas-liquid contact area ($A_{c,i}$ and $A_{c,o}$)</td>
<td>48</td>
<td>cm²</td>
</tr>
<tr>
<td>outgassing rate constant ($k_{out}$)</td>
<td>0.05</td>
<td>cm/s</td>
</tr>
<tr>
<td>Ohmic resistance</td>
<td>2</td>
<td>$\Omega – cm²$</td>
</tr>
</tbody>
</table>
Figure A.12: (a) Electrochemical work (and breakdown into exergy- and cell-based losses) and capture fraction ($f$) vs volume of inlet CO$_2$ reservoir. (b) CO$_2$ productivity vs volume of inlet CO$_2$ reservoir for an initial $P_{CO_2,l} = 0.05$ bar, current density = 10 mA/cm$^2$, cutoff current density = 1 mA/cm$^2$ and $k_{OH} = 8500$ M$^{-1}$s$^{-1}$.

Figure A.13: (a) Electrochemical work (and breakdown into exergy- and cell-based losses) and capture fraction vs current density. (b) CO$_2$ productivity vs current density for inlet reservoir = 200 mL for an initial $P_{CO_2,l} = 0.05$ bar, cutoff current density = 1 mA/cm$^2$ and $k_{OH} = 8500$ M$^{-1}$s$^{-1}$.
APPENDIX B

Understanding Capacity Fade in Organic Redox-Flow Batteries by Combining Spectroscopy with Statistical Inference Techniques
Figure B.1: (a) Cyclic voltammograms of a freshly prepared solution of 0.3 mM BQDS and after oxidation for 19 hours at 0.95 V vs Ag/AgCl in a spectroelectrochemical cell. (b) A photograph of the spectroelectrochemical cell. The spectroelectrochemical cell has a printed platinum honeycomb mesh (allowing light to pass through it) as a working electrode with a counter electrode integrated into it with a path length of 1.7 mm.
Figure B.2: UV-vis spectra of (a) BQDS and (b) K$_2$Cr$_2$O$_7$ at 0.1, 0.2, 0.3 and 0.4 mM. (c) Calibration curves for BQDS and K$_2$Cr$_2$O$_7$ using absorbance at 234 and 290 nm for BQDS and 350 and 445 nm for K$_2$Cr$_2$O$_7$.

Figure B.3: UV-vis signatures of freshly prepared vs 1 day-old solutions of 0.4 mM K$_2$Cr$_2$O$_7$ and 0.3 mM BQDS in 1 M H$_2$SO$_4$. 

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Figure B.4: UV-vis spectrum of the lamp showing no observable change after 23 hours of operation, with the initial spectrum recorded after 1 hour after the lamp was switched on to allow the lamp to warm up.

Figure B.5: Estimates for the concentration of $\text{K}_2\text{Cr}_2\text{O}_7$ consumed due to Michael attack for the four combinations of initial BQDS and $\text{K}_2\text{Cr}_2\text{O}_7$ concentrations in Fig. 2. $[\text{K}_2\text{Cr}_2\text{O}_7]$ was estimated from the UV-vis peak intensity at 350 nm. The arrows depict the total amount of $\text{K}_2\text{Cr}_2\text{O}_7$ that would be expected to be consumed based on Eqn. (1).
B.0.1 First-order kinetics analytical solution

\[ [O_1] = [BQDS]_0 e^{-k_1 t} \]  \hspace{1cm} (B.1)

\[ [O_2] = [BQDS]_0 k_1 e^{-k_1 t} - [BQDS]_0 k_1 e^{-k_1 t} \frac{e^{k_1 t} - e^{k_2 t}}{k_1 - k_2} \]  \hspace{1cm} (B.2)

\[ [O_3] = [BQDS]_0 - [BQDS]_0 e^{-k_1 t} - [BQDS]_0 k_1 e^{-k_1 t} \frac{e^{k_1 t} - e^{k_2 t}}{k_1 - k_2} \]  \hspace{1cm} (B.3)

B.0.2 Determination of potassium dichromate concentration using MCR-ALS

A small wavelength range of 10 nm was chosen around the main potassium dichromate peak centered at 350 nm that does not have any interference from BQDS and its derivatives. The system was analyzed as a mono-component system with the initial concentration profile being determined by purest variables estimation (SIM-PLISMA). Non-negativity of concentrations and spectra was enforced along with a closure constraint, namely that the concentration of potassium dichromate is always less than the corrected initial concentration used. The initial concentration had to be corrected to account for the almost-instant consumption of R_1, which does not show up in the UV-vis spectrum.
Figure B.6: Standard deviation of absorbance measurements, where the dashed red line indicates the wavelength at which we take the measurements (350 nm) and its corresponding standard deviation of absorbance (0.0096).
Figure B.7: Simulated evolution of oxidized species for different initial $[K_2Cr_2O_7]$ and [BQDS] concentrations assuming Bayesian-inferred rate constants. (a) [BQDS] = 0.25 mM and $[K_2Cr_2O_7]$ = 0.4 mM, (b) [BQDS] = 0.2 mM and $[K_2Cr_2O_7]$ = 0.5 mM and (c) [BQDS] = 0.3 mM and $[K_2Cr_2O_7]$ = 0.5 mM.
Figure B.8: Evolution of the UV-vis spectra for the CLE of the BQDS flow cell at concentrations of (a) 8 mM and (b) 5 mM. (c) Absorbance over time at 260 and 305 nm for flow cells with 15, 8, and 5 mM BQDS. (d) Evolution of current over time for all the BQDS flow cells at an oxidizing potential of 0.8 V. (e) Absorbance over time at 260 nm for *in situ* UV-vis measurements of the CLE in BQDS flow cells with BQDS concentrations of 50 and 60 mM. Aliquots for UV-vis were diluted 200× to 0.25 and 0.3 mM, respectively. Trend lines have been added to guide the eye.
B.0.3 Estimation of ferrocyanide and ferricyanide spectra using MCR-ALS

To demonstrate the robustness of the MCR-ALS spectral inference technique as applied to UV-vis spectra in an operando flow cell, we set up a control experiment using a flow cell with a ferrocyanide-containing CLE. The UV-vis spectra of K$_3$Fe(CN)$_6$ and K$_4$Fe(CN)$_6$ are well known, and sufficiently differentiated that they can be used to monitor the state-of-charge (SOC) of a given ferri-/ferrocyanide electrolyte. Three different cycling protocols were deployed: one in which 10 mM of both K$_3$Fe(CN)$_6$ and K$_4$Fe(CN)$_6$ were cycled in a constant-current, constant-voltage (CCCV) mode; another in which 20 mM of K$_4$Fe(CN)$_6$ was oxidized to K$_3$Fe(CN)$_6$; and a third in which K$_3$Fe(CN)$_6$ was reduced to K$_4$Fe(CN)$_6$. MCR-ALS was used with initial guesses for the spectra done using a purest variables estimation and the constraints of non-negativity of concentrations and spectra as well as closure (mass balance) of the concentration profiles. The results for the inferred spectra and the concentration profiles are presented in B.10. The charge measured by the potentiostat is also shown in the CCCV data. There is an 8-second time lag between application of a current and change in the UV-vis spectrum, corresponding to the time taken by the electrolyte to flow through the manifolds of the operando flow cell setup. Accounting for this lag yields a very good overlap between spectroscopic (MCR-ALS derived) and coulometric (based on the amount of charge passed) SOC (inferred from K$_3$Fe(CN)$_6$ concentration) estimates.
Figure B.9: UV-vis spectra from the CLE of an *operando* symmetric flow cell upon application of 0.6 V while starting from (a) 20 mM K$_4$Fe(CN)$_6$, and (b) 20 mM K$_3$Fe(CN)$_6$. (c) Estimated SOC for the experiments in (a) and (b) using Coulomb counting and spectroscopy. (d) Accumulated charge and measured current vs time for the experiments shown in (a) and (b).
Figure B.10: (a) Predicted UV-vis spectra of ferrocyanide and ferricyanide compared to known experimental spectra. Comparison of Coulometric and MCR-ALS-derived concentration estimates for ferrocyanide and ferricyanide for applied potentials of (b) 0.6 V, resulting in $K_4\text{Fe(CN)}_6$ oxidation, (c) $-0.6 \text{ V}$, resulting in $K_3\text{Fe(CN)}_6$ reduction, and (d) Constant current-current voltage (CCCV) cycling.
Figure B.11: Concentration profiles of R$_1$, O$_1$, O$_2$, and O$_3$ derived from MCR-ALS analysis of operando spectra upon potentiostatic oxidation of BQDS in a flow cell at concentrations of (a) 5 mM, (b) 8 mM, and (c) 15 mM.
Figure B.12: Estimated spectra (using MCR-ALS) of BQDS derivatives for *operando* UV-vis experiments with BQDS concentrations of (a) 5 mM and (b) 15 mM.
Figure B.13: (a) NMR scans of BQDS aliquots taken at various time intervals. (b) Simulated NMR spectra of $O_1$, $O_2$, and $O_3$. The peak at 2.6 ppm comes from 40 mM methanesulfonic acid used as the internal standard.
Figure B.14: Photograph of flow cell setup with absorbance cross-flow cell for *operando* UV-vis measurements. Yellow arrows depict the flow of electrolyte from the reservoir to the cross-flow cell, electrochemical flow cell, and electrolyte pump.

Figure B.15: Beer-Lambert law represented as a spectral data matrix which is the product of concentration and pure spectra matrices.
APPENDIX C

Substituent Impact on Quinoxaline Performance and Degradation in Redox Flow Batteries

Figure C.1: Synthesis of DMeSQUI using 2,3-bis(bromomethyl)quinoxaline and sodium sulfite.
Figure C.2: $^1$H-NMR spectra of 50 mM DMeSQUI in a solution of 200 mM NaOD and 50 mM CH$_3$SO$_3$D as internal standard (I.S.) in D$_2$O.
Figure C.3: CV of 1 mM DMeSQUI in a 3 M NaOH solution at a 50 mV/s scan rate.

Figure C.4: Enamine-imine tautomerization mechanism of quinoxaline derivative 2RQUI, involving deprotonation of enamine $i$ to form $ii$, which is a resonance structure of $iii$, followed by protonation of $iii$ to form imine $iv$. $K_{a,imine}$, $K_{a,enamine}$, and $K_{tautomerization}$ are equilibrium constants for deprotonation of imine and enamine forms, and overall tautomerization, respectively.
C.0.1 Degradation of DMeQUIC

Figure C.5: UV-vis spectra of cycled and uncycled DMeQUIC electrolytes from the cells cycled with a discharge potential limit of (a) 1.0 V and (b) −0.1 V. The electrolytes were diluted by a factor of 4000 with a 3 M NaOH supporting electrolyte to reduce the nominal DMeQUIC concentration from 400 mM to 0.1 mM. Cyclic voltammograms of uncycled and cycled DMeQUIC and electrolytes from cells cycled with a discharge potential limit of (c) 1.0 V and (d) −0.1 V. The electrolytes were diluted by a factor of 400 in 3 M NaOH to arrive at a nominal DMeQUIC concentration of 1 mM and the scans were taken at 50 mV/s. The flow cells had a capacity-limiting electrolyte comprising 6 mL of 0.4 M DMeQUIC and 0.5 M NaOH and a non-capacity-limiting electrolyte comprising 20 mL of 0.4 M Na₄Fe(CN)₆ and 0.1 M NaOH. Nafion 212 was used as the separator. A current density of 20 mA/cm² was used and the constant voltage segments of the CCCV cycles ended when the current density decayed to an absolute value of 1 mA/cm².
Figure C.6: Temporal evolution of relative concentrations of DMeQUIC, reduced DMeQUIC (rDMQ), a transient, decay product of rDMQ (tDMQ) and a final decomposition product (fDMQ) based on Bayesian analysis of operando UV-vis spectroscopic data during DMeQUIC reduction. The plot lines depict the Bayesian posterior mode ± 1 standard deviation.
Figure C.7: *Operando* UV-vis spectra during DMeQUIC reduction in a flow cell for initial DMeQUIC concentrations of (a) 4 mM, (b) 3 mM, (c) 1 mM and (d) concentration normalized absorbance at 208 and 243 nm for 4, 3 and 1 mM concentrations. The reduction was performed by applying a 1.6 V potential against a counter electrolyte of excess Na₄Fe(CN)₆.
The capacity observed during shallow-discharge cycling, $Q_{sh}$, can be expressed as a function of the rate constant for rDMQ decay to tDMQ, $k_1$, according to

$$\frac{d \ln Q_{sh}}{dt} = -\overline{SOC}k_1$$  \hspace{1cm} (C.1) 

where $\overline{SOC}$ is the average state-of-charge during cycling. The analogous rate constant for tDMQ decay to fDMQ can be obtained from the capacity during deep discharge cycling according to

$$\frac{d \ln Q_{de}}{dt} = -\overline{SOC}k_2.$$  \hspace{1cm} (C.2)
Because the cells are cycled using a CCCV protocol that accesses the complete state-of-charge (SOC) range, we assume $\overline{SOC}$ is 50%. The slope of the natural log of the capacity fade curve will be half of the corresponding rate constant i.e., $k_1$ and $k_2$ during shallow and deep discharge, respectively. Hence the values of $k_1$ and $k_2$ are estimated from the slopes of $\ln Q_{sh}(-8.9 \times 10^{-5})$ and $\ln Q_{de}(-1.1 \times 10^{-5})$ with respect to time as $1.8 \times 10^{-4}$ and $2.2 \times 10^{-5}$ s$^{-1}$, respectively.

Figure C.9: 2-D $^1$H-NMR scans of DMeQUIC electrolyte (a) before and (b) after reduction and storage for seven days under a nitrogen atmosphere. The 400 mM DMeQUIC solutions were diluted to a concentration of 80 mM in the internal standard (I.S.) solution (with a resultant concentration of 40 mM CH$_3$SO$_3$D and 80 mM NaOD). The spectrum in (b) shows an off-diagonal peak for the peaks at 1.0 and 3.8 ppm (highlighted in purple). This indicates that the peak at 3.8 ppm is attributable to a proton present on a carbon adjacent to one of the methyl group (represented by the 1.0 ppm shift peak).
Figure C.10: $^{13}$C-NMR scans of 80 mM DMeQUIC (a) in its uncycled state, and (b) after reduction and storage in nitrogen atmosphere for seven days. A 400 mM DMeQUIC concentration was used for this experiment, and the uncycled and charged solutions were diluted to a concentration of 80 mM in D$_2$O.
Figure C.11: LC-MS scans of (a) uncycled DMeQUIC and (b) DMeQUIC after reduction in a flow cell and storage for seven days in nitrogen atmosphere.

Figure C.12: Reaction schemes showing the products of (a) Michael addition of water to rDMQ, and (b) irreversible hydrogenation of rDMQ.
Figure C.13: (a) $^1$H-NMR and (b) $^{13}$C-NMR spectra of 80 mM dihydrogenated DMeQUIC diastereomers with 40 mM CH$_3$SO$_3$Na as internal standard (I.S.). These spectra are different from that of cycled DMeQUIC indicating that dihydrogenation is not responsible for degradation of DMeQUIC.
Figure C.14: $^1$H-NMR spectrum of DMeQUIC after reduction in a flow cell against sodium ferrocyanide at pH 13 and storage in an inert nitrogen atmosphere for seven days. The reduction was performed on a 400 mM DMeQUIC solution in 500 mM NaOH. The DMeQUIC solution was diluted to a concentration of 80 mM using the internal standard (I.S.) solution as described in Sec. 4.2.7.

C.0.2 Supplemental Computational Details

The deprotonation energies shown in Fig. C.16 were calculated as follows:
\[
\Delta G_{\text{deprotonation}} = G_{X^-} + G_{H^+} - G_{HX} - \frac{RT \times pH}{\log_{10}(e)} \quad (C.3)
\]

where \(G_{X^-}, G_{HX}, \) and \(G_{H^+}\) are the Gibbs free energies of the deprotonated species, protonated species, and the solvated proton (\(-270.0 \text{ kcal/mol}\)), respectively. \(R\) is the ideal gas constant, \(T\) is the temperature (298.15 K), and \(e\) is Euler’s number. The free energy of protonation is calculated similarly:

\[
\Delta G_{\text{protonation}} = G_{HX} - G_{H^+} - G_{X^-} + \frac{RT \times pH}{\log_{10}(e)} \quad (C.4)
\]

Free energies of Michael addition (Fig. C.17) and dimerization (Fig. C.15) were calculated as follows:

\[
\Delta G_{\text{Michael addition}} = G_{\text{Michael adduct}} - G_{\text{imine}} - G_{\text{H}_2\text{O}} \quad (C.5)
\]

\[
\Delta G_{\text{dimerization}} = G_{\text{dimer}} + G_{\text{H}_2} - 2G_{\text{enamine}} \quad (C.6)
\]

The tautomerization of the enamine to the imine form can be broken into two steps: deprotonation of the enamine \(i\) to form \(ii\), which is a resonance structure of \(iii\), and protonation of \(iii\) to form imine \(iv\) (Fig. C.4). Since this process is reversible and occurs in equilibrium, the equilibrium constant for tautomerization \((K_{\text{taut}})\) can be related to the equilibrium constants for deprotonation of the enamine and imine.
forms \((K_{a,\text{enamine}} \text{ and } K_{a,\text{imine}})\):

\[
K_{\text{taut}} = \frac{K_{a,\text{enamine}}}{K_{a,\text{imine}}}
\]

\[
\log(K_{\text{taut}}) = \log(K_{a,\text{enamine}}) - \log(K_{a,\text{imine}})
\]

\[
-\log(K_{\text{taut}}) = -\log(K_{a,\text{enamine}}) - (-\log(K_{a,\text{imine}}))
\]

\[
pK_{\text{taut}} = pK_{a,\text{enamine}} - pK_{a,\text{imine}}
\]

A DFT-predicted free energy diagram of two possible tautomerization pathways of DMeQUIC is shown in Fig. C.16. The free energy of reduction (2.70 kcal/mol) to form rDMQ corresponds to a redox potential of \(-1.05\) V vs Ag/AgCl at pH 13, qualitatively consistent with the experimental value of \(-1.15\) V (Fig. 4.1). Although tautomerization of rDMQ to the imine form (fDMQ) is thermodynamically favorable \((\Delta G_{\text{taut}} = -2.51\) and \(-0.75\) kcal/mol for \(r\text{DMQ} \rightarrow f\text{DMQA}\) and \(r\text{DMQ} \rightarrow f\text{DMQB}\), respectively), the two forms of the deprotonated enamine intermediate \((d\text{DMQA/b})\) are thermodynamically unfavorable, involving a deprotonation free energy of 21.1 and 16.2 kcal/mol for tautomerization steps \(r\text{DMQ} \rightarrow d\text{DMQA}\) and \(r\text{DMQ} \rightarrow d\text{DMQB}\), respectively. However, tautomerization of the deprotonated imine dDMQ to the deprotonated enamine tDMQ is thermodynamically favorable \((-2.88\) and \(-1.49\) kcal/mol for pathways a and b, respectively). Michael addition of water to the imine form fDMQ involves an uphill free energy change of 10.2 and 8.2 kcal/mol for pathways \(f\text{DMQA} \rightarrow m\text{DMQA}\) and \(f\text{DMQB} \rightarrow m\text{DMQB}\), respectively (Fig. C.17). The hydroxylated intermediate hDMQ formed by attack of the \(sp^2\)-hybridized carbon atom adjacent to the pyrazine N by a hydroxyl group, which is then protonated
to form mDMQ, is very unfavorable, with a free energy of 33.1 and 26.5 kcal/mol for pathways fDMQa → hDMQa and fDMQb → hDMQb, respectively. This free energy analysis suggests that Michael addition is a thermodynamically unfavorable decay mechanism compared to tautomerization.

Figure C.15: DFT-calculated free energies of tautomerization and Michael addition sorted by increasing tautomerization energy for (a) five quinoxaline derivatives experimentally tested and (b) eight additional quinoxaline derivatives not experimentally tested. When there are two possible tautomers, the more exothermic tautomerization energy is used.
Figure C.16: Free energy diagram showing DFT-calculated energies of intermediates in tautomerization mechanism of DMeQUIC at pH 13 and 298.15 K. Structures of the oxidized form (DMeQUIC), reduced enamine form (rDMQ), deprotonated enamine (dDMQa/b), deprotonated imine (tDMQa/b), and reduced imine form (fDMQa/b) are shown.
Figure C.17: Mechanism for Michael attack of reduced imine form of DMeQUIC (fDMQa/b) to form hydroxylated intermediate (hDMQa/b) followed by Michael adduct (mDMQa/b).

Figure C.18: CV of QUI2C3A conducted at a scan rate of 50 mV/s using 3 M NaOH as the supporting electrolyte showing a separation of about 1.1 V between the anodic and cathodic redox peaks.
Figure C.19: (a) Discharge capacity vs time during cycling of 6QUIC, DMeQUI, DMeSQUI and 2QUIC in compositionally asymmetric flow cells with a ferrocyanide-based non-capacity-limiting electrolyte. The capacity is normalized to the theoretical two-electron capacity for each electrolyte and all cells were cycled using a CCCV protocol. (b) Discharge capacity on a log scale vs time. The dashed lines are fitted slopes, which yield the first-order capacity fade rate constant for each cell.

The cells for the aforementioned molecules were cycled using current densities and voltage limits given in Table C.1, using a CCCV protocol with the cell polarity reversing when the applied current density reached 1 mA/cm$^2$.

Table C.1: Applied current density, voltage range for flow cell cycling, and concentration of quinoxaline derivatives.

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Applied current density (mA/cm$^2$)</th>
<th>Cell voltage limits (V)</th>
<th>Concentration (mM)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2QUIC</td>
<td>20</td>
<td>0.8–1.4</td>
<td>400</td>
</tr>
<tr>
<td>DMeSQUI</td>
<td>10</td>
<td>0.8–1.5</td>
<td>100</td>
</tr>
<tr>
<td>DMeQUI</td>
<td>5</td>
<td>1.0–1.5</td>
<td>50</td>
</tr>
<tr>
<td>6QUIC</td>
<td>10</td>
<td>1.0–1.4</td>
<td>200</td>
</tr>
</tbody>
</table>
Figure C.20: CVs of cycled and uncycled quinoxaline electrolytes conducted at a nominal redox-active molecule concentration of 1 mM and a scan rate of 50 mV/s in a 3 M NaOH supporting electrolyte for (a) 6QUIC, (b) 2QUIC, (c) DMeQUIC, (d) DMeSQUI, and (e) DMeQUI.
Membrane permeability was calculated using the following equation:

\[
\text{Membrane permeability} = \frac{\text{Absorbance}}{\text{Concentration}}
\]
\[ P = -\frac{\Delta \ln(1 - \frac{2c_t}{c_0})}{\Delta t} \cdot \frac{Vl}{2A} \]  

where \( P \) is the permeability, \( c_t \) and \( c_0 \) are the concentrations of 2QUIC in the acceptor and donor side of the H-cell respectively, and \( V, l, \) and \( A \) are the acceptor side volume, membrane thickness, and membrane area, respectively.

Figure C.23: CVs of uncycled and cycled electrolytes from the capacity-limiting side of the 2QUIC mixed symmetric cell conducted at a 50 mV/s scan rate in a 3 M NaOH supporting electrolyte.
APPENDIX D

Correlating Stability and Performance of NaSICON Membranes for Aqueous Redox Flow Batteries
Figure D.1: Schematic of the cross section of the cell setup showing the gaskets used to hold the NaSICON pellet together with the graphite felt electrodes, and thus achieve a leak-proof seal.
Table D.1: Void area percentages from SEM images of NaSICON immersed in various electrolytes for different immersion times at 18 °C.

<table>
<thead>
<tr>
<th>Electrolyte</th>
<th>Immersion time</th>
<th>Void fraction (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pristine NaSICON</td>
<td>N/A</td>
<td>0.7 ± 0.31</td>
</tr>
<tr>
<td>1 M NaOH</td>
<td>7 days</td>
<td>3.13 ± 0.24</td>
</tr>
<tr>
<td></td>
<td>30 days</td>
<td>4.51 ± 0.28</td>
</tr>
<tr>
<td>2 M NaOH</td>
<td>7 days</td>
<td>3.44 ± 0.93</td>
</tr>
<tr>
<td></td>
<td>30 days</td>
<td>5.25 ± 0.32</td>
</tr>
<tr>
<td>3 M NaOH</td>
<td>7 days</td>
<td>4.85 ± 0.88</td>
</tr>
<tr>
<td></td>
<td>30 days</td>
<td>6.49 ± 0.50</td>
</tr>
<tr>
<td>2 M NaCl</td>
<td>7 days</td>
<td>2.02 ± 0.50</td>
</tr>
<tr>
<td></td>
<td>30 days</td>
<td>2.61 ± 0.27</td>
</tr>
<tr>
<td>100 mM PFP in 2 M NaOH</td>
<td>8 days</td>
<td>2.19 ± 0.21</td>
</tr>
<tr>
<td></td>
<td>30 days</td>
<td>3.41 ± 0.61</td>
</tr>
<tr>
<td>100 mM Na₄Fe(CN)₆ in 1 M NaOH</td>
<td>7 days</td>
<td>3.24 ± 0.48</td>
</tr>
<tr>
<td>100 mM NaMnO₄ in 2 M NaOH</td>
<td>9 days</td>
<td>2.13 ± 0.57</td>
</tr>
<tr>
<td></td>
<td>30 days</td>
<td>4.14 ± 0.56</td>
</tr>
<tr>
<td>100 mM Na₂S₂ in 2 M NaCl</td>
<td>8 days</td>
<td>3.14 ± 0.53</td>
</tr>
<tr>
<td></td>
<td>30 days</td>
<td>4.85 ± 0.87</td>
</tr>
</tbody>
</table>
Figure D.2: SEM images of NaSICON pellets after (a) 9 days immersion in 100 mM NaMnO$_4$ in 2 M NaOH, (b) 7 days of immersion in 100 mM Na$_4$Fe(CN)$_6$ in 1 M NaOH, (c) 8 days immersion in 100 mM 1,8 PFP in 2 M NaOH, (d) 30 days immersion in 100 mM 1,8 PFP in 2 M NaOH, (e) 8 days immersion in 100 mM Na$_2$S$_2$ in 2 M NaCl, and (f) 30 days immersion in 100 mM Na$_2$S$_2$ in 2 M NaCl.
Table D.2: Void area percentages from SEM images of a NaSICON pellet before and after soaking in solutions of 3 M NaOH, and 1 M NaMnO$_4$ + 3 M NaOH. Note that the void area fraction increase for the pellet in 3 M NaOH (4.0 %) is reasonably similar to the corresponding measurement in Table D.1 (4.15 %), highlighting the reproducibility of our results.

<table>
<thead>
<tr>
<th>Immersion time (days)</th>
<th>Void (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Before soaking</td>
<td>-</td>
</tr>
<tr>
<td>3 M NaOH + 1 M NaMnO$_4$</td>
<td>7</td>
</tr>
<tr>
<td>3 M NaOH</td>
<td>7</td>
</tr>
</tbody>
</table>

Figure D.3: SEM images of fragments of a NaSICON pellet (a) freshly prepared; (b) soaked in 3 M NaOH for a week; and (c) soaked in 3 M NaOH + 1 M NaMnO$_4$ for a week.
Figure D.4: Cyclic voltammograms of 5 mM potassium permanganate in 1 M KOH and 2 mM potassium ferrocyanide in 1 M KCl to illustrate the 140 mV higher redox potential of the MnO$_4^−$/MnO$_2^−$ couple. These measurements were performed with a 5 mm diameter glassy carbon working electrode and platinum counter electrode.
Figure D.5: (a) Nyquist plots of NaSICON pellets of varying thicknesses. (b) A schematic of the equivalent circuit used to model NaSICON pellets. CPE stands for “constant phase element”.
Figure D.6: (a) Estimated solution resistance (blue bars) of cells as a function of electrolyte composition, incorporating the cell geometry and ionic conductivity (orange bars) of the different electrolytes. (b) Nyquist plots from EIS measurements of blank H-cells (i.e. devoid of pellets) in different electrolytes, with $R_{HF}$ indicated.

The cell resistance is calculated using the cell geometry (calculated in $\Omega$) as:

$$R_{cell} = \frac{1}{k_{electrolyte}} \left( \frac{4}{\pi/4 \times 1.5^2} + \frac{0.5}{\pi/4 \times 1.07^2} + \frac{14}{\pi/4 \times 1.5^2} \right). \quad (D.1)$$

This estimate assumes the two chambers have a diameter of 1.5 cm and combined length of 4 cm; the junction between them comprises gaskets with an electrolyte-exposed diameter of 1.07 cm and total thickness of 0.5 cm. The total cell resistance is therefore the sum of the resistance of the two chambers and the opening in the gaskets. The electrolyte conductivity ($k_{electrolyte}$) is obtained from [247] and shown in Fig. D.3a.
Table D.3: Grain conductivity, percent of total resistance constituted by grain boundary resistance, and total conductivity of NaSICON pellets of varying thickness.

<table>
<thead>
<tr>
<th>Grain Conductivity (mS/cm)</th>
<th>Grain Boundary Resistance (% of total)</th>
<th>Total Conductivity (mS/cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.44 ± 0.93</td>
<td>51.6 ± 10.0</td>
<td>1.10 ± 0.16</td>
</tr>
</tbody>
</table>
Figure D.7: (a) Nyquist plots from EIS measurements on an H-cell without and with a 0.61 mm thick NaSICON pellet over time. The electrolyte was 2 M NaOH. (b) Area-specific $R_{HF}$ vs time for NaSICON pellet-containing H-cells with different supporting electrolytes.
Figure D.8: (a) Image of NaSICON pellet fragments after 1 week of immersion in a 1 M KCl solution. (b) Nyquist plots from EIS measurements for NaSICON pellets in a solution containing 0.1 M K₄Fe(CN)₆ in 1 M Na₂SO₄ supporting electrolyte, where [K⁺]/[Na⁺] = 0.2. (c) 0.1 M K₄Fe(CN)₆ in 1 M Na₂SO₄ supporting electrolyte, where [K⁺]/[Na⁺] = 0.15. (d) A visually intact NaSICON pellet. (e) R_HF and the sum of R_HF, R_GB and R_INT (R_T) vs time for NaSICON pellets in solutions from (b) and (c).
Figure D.9: NaSICON and Nafion permeability to sodium permanganate. (a) PermGear H-cell for measuring crossover of permanganate through a NaSICON pellet. (b) Custom-built H-cell for measuring permanganate crossover through Nafion. (c) Concentration of permanganate in the receiving side, as derived from UV-vis absorbance vs time for crossover measurements through Nafion 117. (d) Calibration curve showing absorbance of the UV-vis spectrum of permanganate at 572.4 nm vs concentration. (e) UV-vis spectra of permanganate at various known concentrations. (f) UV-vis measurements of receiving side as a function of time.
Figure D.10: NaSICON and Nafion permeability to sodium disulfide. (a) Absorbance of the UV-vis spectrum of sodium disulfide at 299.1 and 360.6 nm vs concentration. (b) Concentration of sodium disulfide in the receiving side vs time for crossover measurements through Nafion 117; the donating side had a concentration of 0.1 M in 2 M NaOH. (c) UV-vis measurements of disulfide at different concentrations. (d) UV-vis measurements of receiving side as a function of time.
Figure D.11: Area-specific resistance vs NaSICON thickness and temperature. (a) $R_{HF}$, $R_{GB}$ and $R_{INT}$ vs NaSICON thickness at 18 °C. (b) $R_{HF}$ and $R_{INT}$ vs NaSICON thickness at 70 °C. (c) $R_{HF}$ and $R_{INT}$ vs temperature for a 0.8 mm-thick NaSICON pellet.

Figure D.12: (a) Total ASR of NaSICON-containing flow cell as a function of temperature. (b) Nyquist plots from EIS measurements of flow cell containing a 0.8 mm-thick NaSICON pellet at various temperatures.
Figure D.13: (a) Capacity and current efficiency vs time for compositionally symmetric ferro/ferricyanide cell with NaSICON pellet. The CLE contained 10 mL of 10 mM Na₄Fe(CN)₆ and 10 mM K₃Fe(CN)₆ in 1 M NaCl supporting electrolyte, whereas the NCLE contained 25 mL of the same composition. The [K⁺]/[Na⁺] ratio was 0.029. A 0.9 cm², 0.65 mm-thick NaSICON pellet served as the membrane, and two 5 cm², 3.4 mm-thick AvCarb G300 graphite felt pieces were used as electrodes (one per side). The electrolytes were circulated at 80 mL/min, and the cell was cycled with a CCCV protocol, at 2.8 mA/cm² between ±400 mV; potentiostatic holds were terminated after the current density reached 0.055 mA/cm². (b) R_HF and sum of R_HF, R_GB and R_INT vs time, as calculated from fittings made to intermittent EIS measurements.
Figure D.14: Comparison of capacity retention in NaSICON- and Nafion-containing ferrocyanide—permanganate flow cells. Cycling performance of ferrocyanide—permanganate cell with (a) NaSICON and (b) Nafion 117 membranes. The upward arrows indicate NCLE electrolyte replacements to correct imbalance, whereas the downward arrows indicate when 0.5 mL aliquots were drawn from the CLE and replaced with uncycled electrolyte.
Table D.4: ICP results of the cycled and uncycled electrolytes in NaSICON and Nafion cells.

<table>
<thead>
<tr>
<th>Cell</th>
<th>Electrolyte</th>
<th>Manganese concentration (mg/l)</th>
<th>Iron concentration (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>CLE uncycled</td>
<td>Below detection limit</td>
<td></td>
</tr>
<tr>
<td></td>
<td>CLE 340 hours</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>CLE 800 hours</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>NCLE 92-260 hours</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>NCLE 260-670 hours</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>NCLE 670-800 hours</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Nafion</td>
<td></td>
<td>1.49</td>
<td>1.84</td>
</tr>
<tr>
<td></td>
<td>CLE uncycled</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>CLE 340 hours</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>NCLE 92-260 hours</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>NCLE 260-670 hours</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>NCLE 670-800 hours</td>
<td></td>
<td></td>
</tr>
<tr>
<td>NaSICON</td>
<td></td>
<td>Below detection limit</td>
<td></td>
</tr>
<tr>
<td></td>
<td>CLE uncycled</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>CLE 340 hours</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>CLE 670 hours cycled</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>NCLE uncycled hours</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>NCLE 340 hours</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Below detection limit</td>
<td></td>
</tr>
<tr>
<td></td>
<td>CLE uncycled</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>CLE 340 hours</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>CLE 670 hours cycled</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>NCLE uncycled hours</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>NCLE 340 hours</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

After 624 h of cycling, the Nafion cell was allowed to rest for 24 hours with the electrolyte pump switched off, to rule out the possibility that ferrocyanide degradation might account for capacity fade. No significant capacity loss was observed during this interval, thus implying that the fade observed is primarily due to crossover, and cell imbalance.

We show 50 hours of cycling for the cells with a NaSICON membrane as a single cycle takes more than five hours to complete.
Figure D.15: (a) Voltage versus capacity curves for selected cycles for the ferrocyanide—permanganate cell containing a Nafion membrane. (b) Voltage and current density vs time for the first 5 hours of cycling of the cell in (a). (c) Voltage versus capacity curves for selected cycles for the ferrocyanide—permanganate cell containing a NaSICON membrane. (d) Voltage and current density vs time for the first 50 hours of cycling of the cell in (c).
Table D.5: Aqueous redox-flow chemistries enabled by sodium-ion-conducting ceramic membranes.

<table>
<thead>
<tr>
<th>Redox reactant</th>
<th>Charge density (Ah/l)(^a)</th>
<th>Standard potential (V vs SHE)</th>
<th>[pH]</th>
<th>cell type</th>
<th>[precursor]</th>
<th>precursor cost $/kg ($/mol e(^-))(^b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Br(_2) [206, 224]</td>
<td>246 [248]</td>
<td>1.05 [206]</td>
<td>7</td>
<td>flow</td>
<td>ZnBr(_2)</td>
<td>12.3(1.38) [249]</td>
</tr>
<tr>
<td>I(_2) [206]</td>
<td>108</td>
<td>0.54 [206]</td>
<td>7</td>
<td>flow</td>
<td>KI</td>
<td>2.2(0.365) [250]</td>
</tr>
<tr>
<td>O(_2)</td>
<td>-</td>
<td>1.23</td>
<td>2</td>
<td>static</td>
<td></td>
<td></td>
</tr>
<tr>
<td>S(_2^-) [206, 220]</td>
<td>456 [251]</td>
<td>-0.5 [206]</td>
<td>13</td>
<td>flow static</td>
<td>ZnS [206], [sulfur]</td>
<td>0.3(0.009) [250]</td>
</tr>
<tr>
<td>Fe(Bpy)(_3) [^{[252]}]</td>
<td>4 [253]</td>
<td>1.03 [252]</td>
<td>7</td>
<td>flow</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe(OH)(_2) [218]</td>
<td>-</td>
<td>-0.88</td>
<td>13.5</td>
<td>static</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Zn(OH)(_2^-) [^{[224, 220, 254]}]</td>
<td>-</td>
<td>-1.2</td>
<td>13.5 [220]</td>
<td>static</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe(EDTA) [^{[252]}]</td>
<td></td>
<td>0.15</td>
<td>7</td>
<td>flow</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe(CN)(_6) [^{[255]}]</td>
<td>13.4</td>
<td>0.45</td>
<td>14</td>
<td>flow</td>
<td></td>
<td></td>
</tr>
<tr>
<td>MnO(_4^-) [^{[213]}] (this work)</td>
<td>96.5</td>
<td>0.59</td>
<td>14.5</td>
<td>flow</td>
<td>MnO(_2)</td>
<td>0.4(0.035)</td>
</tr>
</tbody>
</table>

We show 50 hours of cycling for the cells with a NaSICON membrane as a single cycle takes more than five hours to complete.

\(^a\) Calculated from solubility and moles of transferrable electrons per mole of reactant.

\(^b\) Precursor costs were obtained from indicated references. In the case of permanganate, costs were obtained from [https://dir.indiamart.com/impcat/manganese-dioxide.html](https://dir.indiamart.com/impcat/manganese-dioxide.html) (accessed on March 8, 2022).

The cost per mole of transferrable electrons ($/mol e^-$) was calculated from the precursor cost according to:

\[
\frac{\text{precursor cost ($/kg$)}}{\text{number of electrons}} 
\]

(D.2)
We opted to calculate precursor costs and $/\text{mol e-}$ for inorganic redox couples in which both oxidized and reduced species could exist as non-neutral species. Among potential posolyte reactants, $\text{MnO}_4$ has a charge density comparable to the halide electrolytes, but its cost is one to two orders of magnitude lower.
Figure D.16: Capacity, current efficiency (CE) and energy efficiency (EE) vs time for a flow cell containing (a) 7 mL of 0.05 M 1,8-PFP in the CLE, 20 mL 0.4 M NaMnO$_4$ in the NCLE and a Nafion membrane; (c) 20 mL 1,8-PFP in the NCLE, 6 mL 0.075 M NaMnO$_4$ in the CLE and a Nafion membrane; and (e) 20 mL 0.05 M 1,8-PFP in the NCLE, 4 mL 0.1 M NaMnO$_4$ in the CLE and a NaSICON membrane. Voltage and current profiles for the first 5 hours of cycling for cells in (a) and (c) are shown in (b) and (d) respectively, while those for 50 hours of cycling in (e) are shown in (f).
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