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Insights into Aqueous Organic Redox Flow Batteries: Key Physicochemical Determinants of Electrochemical Behavior

Department of Mechanical and Materials Engineering

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Abstract

The development of high-performance organic redox flow batteries (ORFBs) is vital to enable cost-effective and sustainable energy storage solutions for renewable energy systems. This thesis focuses on the role of physicochemical properties—solubility, redox potential, and kinetic parameters (electron transfer rate constant k_0 and diffusion coefficient D_0)—in determining the performance of ORFBs operating in alkaline media. Particular attention is given to anolytes, or negative redox-active species, capable of two-electron storage, such as quinones, phenazines, and other organic molecules with tunable redox properties. The use of two-electron storage compounds offers the potential to enhance the charge storage capacity per molecule, yet their design and optimization remain a significant challenge due to limited chemical stability and solubility.

This thesis investigates how structural modifications influence the solubility and redox potentials of these compounds and how these changes translate into improved energy density and power density of the battery. Additionally, while k_0 and D_0 are often reported in literature, their individual impact on battery performance is rarely analyzed. Voltametric simulations are conducted to assess the effect of these kinetic parameters on battery reversibility and efficiency. The preliminary findings indicate that variations in D_0 have minimal effect on performance, whereas changes in k_0 significantly influence the reversibility of the redox process.

By combining a comprehensive literature review with computational simulations, this thesis aims to identify the most influential physicochemical factors for designing next-generation ORFB anolytes. The results are expected to guide the development of organic molecules with improved electrochemical performance for large-scale, long-duration energy storage.

Key words: Redox Flow Batteries, Organic Redox Flow Battery (ORFB), Aqueous Organic Redox Flow Battery (AORFB), Electrochemical Kinetics, Electron Transfer Rate Constant (k_0), Diffusion Coefficient (D_0), Multi-Electron Transfer, Cyclic Voltammetry (CV), Convective Mass Transport, Molecular Engineering

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List of Abbreviations

Term	Definition
RFB	Redox Flow Battery, a type of rechargeable battery where energy is stored in liquid electrolytes flowing through electrochemical cells
ORFB	Organic Redox Flow Battery, a flow battery that uses organic molecules as redox-active species
DFT	Density functional theory
VRFB	Vanadium Redox Flow Battery, a flow battery using vanadium ions in different oxidation states as the redox couples
AORFB	Aqueous Organic Redox Flow Battery, a flow battery using water-based electrolytes with organic redox-active molecules
RALs	Redox-active liquids
ROM	Redox-Active Organic Molecule, an organic compound capable of reversible electron transfer in a battery
AEMs	Anion exchange membranes
MCCs	Metal coordination complexes
AIRFB	Aqueous Iron-Based Redox Flow Battery, a flow battery system that utilizes iron redox couples dissolved in an aqueous electrolyte to enable reversible electron transfer for energy storage.
SHE	Standard hydrogen electrode
TEMPO	2,2,6,6-Tetramethylpiperidine-1-oxyl, a stable free radical commonly used as a redox-active organic species in batteries
Power density	The amount of power delivered per unit electrode area (mW cm^{-2})
Energy density	The amount of energy stored per unit volume or mass of electrolyte (Wh L^{-1} or Wh kg^{-1})
Rate constant of electron transfer (k_0)	A kinetic parameter representing the intrinsic speed of electron transfer at an electrode (cm/s) k_f = Rate for forward reaction , k_b = Rate for backward reaction
k_c	chemical reaction rate constant
Diffusion coefficient (D_0)	A parameter describing how fast a species moves through the electrolyte due to concentration gradients (cm^2/s)
Solubility	Maximum concentration of a redox-active species that can dissolve in the electrolyte under given conditions (M)
Peak-to-peak separation (ΔE_p)	The difference between the anodic peak potential (Epa) and the cathodic peak potential (Epc), used to assess reversibility of a redox system
Peak current ratio (I_{pa}/I_{pc})	Ratio of anodic to cathodic peak currents, used as a qualitative and quantitative measure of redox reversibility

Randles–Sevcik equation	Relates peak current (ip) to the square root of scan rate (v) for diffusion-controlled electrochemical processes, used to quantify mass transport and electron transfer
Nicholson's Ψ parameter	A dimensionless kinetic parameter used in cyclic voltammetry to quantify the degree of reversibility of an electron transfer reaction. It relates the peak-to-peak separation (ΔEp) to the standard heterogeneous electron transfer rate constant (k_0), the diffusion coefficient (D_o), and the scan rate (v). Ψ increases with faster kinetics and more reversible systems.
CV	Cyclic Voltammetry

1 Introduction

Electrochemical energy storage plays a critical role in modern energy systems, enabling efficient utilization of renewable energy sources and improving grid stability. Among the various electrochemical energy storage technologies, redox reactions have long been recognized as a fundamental mechanism for electron transfer between chemical species, making them an effective approach for storing electrical energy. The concept of redox-based energy storage dates back to the late 18th century; however, its relevance has grown significantly in recent decades due to the increasing demand for large-scale energy storage solutions.

Lithium-ion batteries (LIBs) have emerged as the dominant energy storage technology due to their high energy density and well-established commercial availability. Despite these advantages, LIBs face significant challenges when applied to large-scale energy storage, including concerns over resource availability, cost, safety, and limited cycle life. These limitations hinder their scalability and economic feasibility for grid-level applications.

In contrast, Redox flow batteries (RFBs) have gained attention as a viable alternative for stationary energy storage systems. Their unique architecture allows for independent scaling of power and energy capacity, providing greater flexibility for grid applications. Furthermore, RFBs offer enhanced safety, extended cycle life, and the potential for lower operational costs compared to conventional lithium-based systems. This thesis highlights the advantages of organic compounds in this type of battery system and examines the key findings from continuing research on the physicochemical characteristics that define the usability and application of redox flow batteries.

1.1 Overview of Redox Flow Batteries (RFBs)

Redox flow batteries (RFBs) are a class of electrochemical energy storage devices that utilize redox-active species to store and release electrical energy. Unlike compact lithium-ion batteries, RFBs operate by continuously circulating electrolyte solution through an electrochemical cell. [1] RFBs are appropriate for a variety of power needs because of their wide power range of 0.02 to 50MW. RFBs provide special benefits with variable discharge times ranging from 0.01 to 10 hours and impressive lifespans of 5000 to 13,000 cycles. [2]

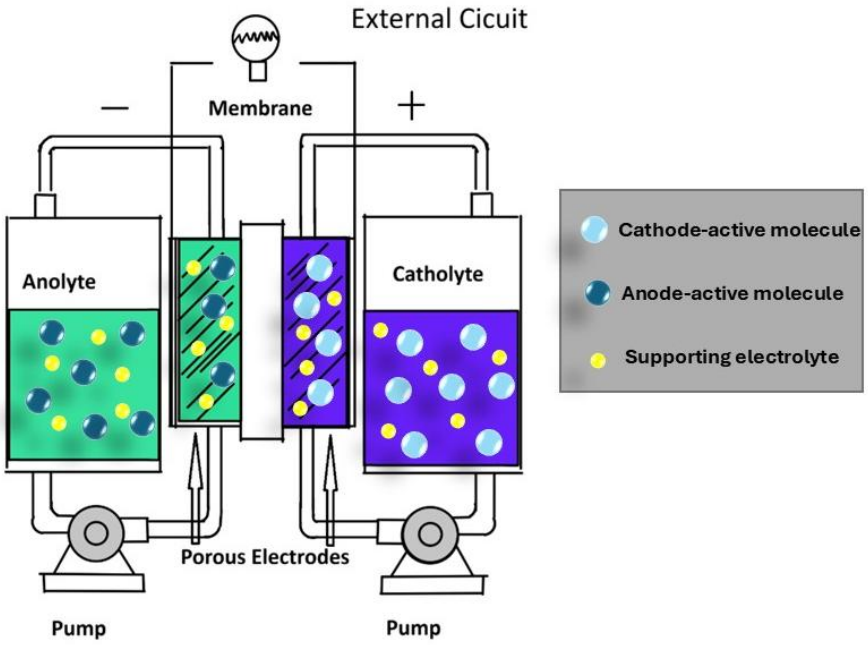

Figure 1: Diagram For Redox flow battery

An American Government agency, National Aeronautics and Space Administration (NASA) first proposed the idea of RFBs in the 1970s, using $Fe^{3+/2+}$ and $Cr^{3+/2+}$ as redox-active couples in the cathode and anode sides, respectively. [3] These solutions contain active species that undergo reversible oxidation and reduction reactions, allowing for repeated charge and discharge cycles with minimal capacity degradation. For the active species to efficiently transform chemical energy into electrical energy, they must possess high redox reactivity and electron transfer rate. To maximize the desired qualities in this scenario, choosing the right active species is crucial. [4,5]

In Figure 1. we can see a RFB system consists of two electrolyte reservoirs, pumps, an electrochemical cell, and an ion-exchange membrane that separates the two compartments while permitting ion transfer to maintain charge neutrality. The electrode surfaces inside the reaction chamber are where the electrochemical reactions take place, there electrons are either accepted or donated by the redox-active species. The ability to store active materials in external tanks rather than within the electrodes enables independent scaling of power (determined by the cell stack size) and energy capacity (determined by electrolyte volume). This design feature

makes RFBs particularly suitable for grid-scale applications requiring flexible and long-duration energy storage. [6,7]

Currently, the most widely studied and commercialized RFB system is the vanadium redox flow battery (VRFB), which employs vanadium ions in different oxidation states as the electroactive species. [8] While VRFBs offer excellent stability and high reversibility, their widespread adoption is limited by the high cost, toxicity, and corrosive nature of vanadium-based electrolytes. These challenges have driven research efforts toward alternative redox chemistries, particularly organic redox flow batteries (ORFBs), which utilize organic molecules as electroactive materials. ORFBs have the potential to offer tunable redox properties, higher solubility, and lower environmental impact compared to their inorganic counterparts. [9]

Despite the numerous advantages of RFBs, several technical challenges remain, including improving the solubility of redox-active species, enhancing redox potential to increase energy density, and optimizing kinetic properties such as the rate constant of electron transfer ($\mathbf{k_0}$) and diffusion coefficient ($\boldsymbol{D_0}$). This thesis will focus on analyzing these key physicochemical properties and their impact on RFB performance, with a particular emphasis on the role of organic electroactive materials in alkaline aqueous electrolytes.

1.2 Importance of Physicochemical Properties for Battery Performance

The performance of redox flow batteries (RFBs) is directly influenced by the physicochemical properties of the redox-active materials used in their electrolytes. Key parameters such as solubility, redox potential, and electron-transfer kinetics play a crucial role in determining the energy density, power output, and overall efficiency of these systems. [10,11]

Early RFB designs relied on vanadium-based electrolytes due to their relatively high solubility and favourable redox potential [12]. Organic materials offer tunable electrochemical properties, but their adoption has been hindered by their typically lower solubilities in aqueous electrolytes, which limits energy density. [13]

Redox flow batteries (RFBs) suffer from reduced power output and capacity, precipitation and stability issues, and increased system size and cost because of the low solubility of redox-active materials in their electrolytes. To enhance solubility and redox performance, researchers have explored molecular modifications such as functional group substitutions and hydrotropic additives. Adjusting the functional groups of quinones and viologens has been shown to shift redox potentials and increase solubility, thereby improving battery capacity. Furthermore,

hydrotropes have shown promise for raising the concentration of organic redox-active chemicals in aqueous electrolytes, such as amphiphilic molecules that improve solubility without creating micelles. These strategies enable the design of high-energy-density RFBs while maintaining electrochemical stability. [14-16]

Beyond solubility and redox potential, the kinetics of electron transfer, characterized by the standard rate constant (k_0) and the diffusion coefficient (D_0), significantly impact charge transfer efficiency and reversibility. [17,18] In flow-assisted RFB systems where diffusion is largely mitigated by convective transport, performance becomes increasingly dependent on electron-transfer kinetics. Variations in the standard rate constant can dramatically affect reaction rates and energy losses due to overpotential, particularly if k_0 falls below $\sim 10^{-5}$ cm/s, a threshold identified as critical for maintaining high efficiency in practical applications. [19] This thesis will further investigate these physicochemical factors through voltametric simulations to determine their relative contributions to RFB efficiency and scalability.

1.3 Objective of the thesis work

The study aims to:

a) Examine how solubility of redox active material and redox potential affect the energy density and efficiency of RFBs, with a particular focus on organic redox-active materials.

b) Analyze the advantages of two-electron storage capacity over one-electron systems in the design of high-performance negative electrolytes (anolytes).

c) Investigate the role of alkaline solvents in enhancing solubility and redox potential, using molecular structure comparisons of quinones, phenoxazines, and phenazines.

d) Assess the relative impact of (k_0) and (D_0) on battery performance through voltametric simulations, clarifying why changes in (k_0) significantly influence reversibility while (D_0) has a lesser effect.

By bridging the gap in understanding the relationship between these physicochemical parameters and RFB efficiency, this research will provide insights into optimizing organic electrolyte formulations for next-generation flow battery technologies.

2 Fundamentals of Redox Flow Batteries

Understanding the principles of redox flow batteries (RFBs) is essential for comprehending how these systems function, how their performance is assessed, and how they might be enhanced for real-world uses. Designing effective, long-lasting, and high-energy-density RFB systems requires a thorough understanding of the fundamental concepts, including electrochemical reactions, cell architecture, electrolyte composition, and ion transport.

The essential components, working principles, and electrochemical mechanisms that control the functioning of redox flow batteries will all be covered in this chapter. The background information required to examine performance constraints, material choices, and upcoming advancements in RFB technology will be provided by this foundation.

2.1 Definition and Working Principle of RFBs

The redox active species in RFBs undergo reversible interconversion between reduced and oxidized states, all of which were dissolved in liquid form. Prior to being pumped into and out of the cell's reaction chamber, the solutions are stored in tanks as shown in figure 1. [20] The two electrolyte streams flow independently through the electrochemical cell, where charge and discharge reactions occur at the electrode surfaces. Both species are separated by an ion-selective membrane or separator. This membrane permits the transport of charge-balancing ions between half-cells while preventing the physical crossover and direct mixing of redox species. [21] The working principle of an RFB is based on the redox reactions of these active materials. During charging, electrons are supplied to the negative electrolyte (reduction) and extracted from the positive electrolyte (oxidation), storing energy chemically. Upon discharge, the reverse reactions occur, and the stored energy is released as electrical power [22]. This architecture allows for decoupling of power and energy: The volume and concentration of electrolyte kept in the tanks govern the energy capacity, whilst the size and quantity of electrochemical cells influence the power. [23, 24]

Electrolytes in RFBs typically consist of a solvent such as water or an organic medium to dissolve the electroactive species, a supporting salt to ensure ionic conductivity, and the redox-active component itself. [25] These components must be carefully selected to ensure favorable electrochemical properties, long-term stability, and compatibility with system materials. The

modularity, design flexibility, and safety of RFBs make them particularly well-suited for grid-scale and long-duration energy storage applications.

2.2 Active Species in RFBs (Anolyte and Catholyte)

The two key electrolyte compartments: the anolyte (negative electrolyte) and the catholyte (positive electrolyte) contain redox-active species that participate in electron exchange reactions at the anode and cathode during charging and discharging cycles.

RFB systems can be classified based on the nature of their active materials:

2.2.1 All-Inorganic Systems

All-Inorganic systems rely entirely on inorganic redox-active species, such as transition metals or halides. A well-known example includes the vanadium redox flow battery (VRFB), which uses different oxidation states of vanadium ions (V^{2+}/V^{3+} in the anolyte and VO^{2+}/VO_2^{+} in the catholyte). Another example is the Zinc/iodide system, where two electrons are transferred at both the positive ($3I^- \rightarrow I_3^- + 2e^-$) and negative ($Zn \rightarrow Zn^{2+} + 2e^-$) electrodes, enabling the exchange of four electrons per cycle, thereby enhancing energy density. [26]

2.2.2 All-Organic Systems

All-Organic systems use organic molecules in both the anolyte and catholyte, offering tunability, sustainability, and potential cost benefits. Quinones and anthraquinone derivatives are prominent examples due to their high solubility and adjustable redox potentials. For instance, Methyl viologen (MV) anolyte / 4-HO-TEMPO catholyte with a cell voltage of 1.2–1.4 V. [27]

2.2.3 Hybrid Organic/Inorganic Systems

Hybrid RFBs utilize one organic and one inorganic redox-active species. This hybrid category aims to combine the advantages of high redox tunability from organics and stable redox kinetics from inorganic metals while attempting to overcome their respective limitations.

For example:

Chloranil (QCl_4) as the organic catholyte and Cd^{2+}/Cd^0 as the inorganic anolyte in a membrane-free design. [28] Tiron (4,5-dihydroxy-1,3-benzenedisulfonic acid) paired with a Pb/Pb^{2+} anode showed reasonable energy efficiency but had stability issues due to irreversible hydroxylation.

[29] 15D3GAQ (an anthraquinone derivative) with Li^+ as the counter ion in non-aqueous media is another example of hybrid redox flow batteries. [30]

2.3 Effect of PH of the electrolyte solutions on solubility and stability

There are notable variations in the performance, efficiency, and operating features of alkaline and acidic organic redox flow batteries (RFBs). While acidic systems can profit from special electrochemical characteristics, alkaline systems often have greater cell voltages and better energy densities. By using a mixed HCl and H_2SO_4 supporting electrolyte, Li et al. [31] enhanced the energy density of VRFBs to 40 Wh L^{-1} and vanadium's solubility to 2.5 M. Differential pH strategies have been employed to increase cell potential. Another example where the PTA/TironA ARFB operates in an acidic environment (1.0 M H_2SO_4) and achieves a cell potential of 0.92 V, which is not in par with most alkaline solvents. [32] For instance, a battery utilizing bromine catholyte at pH 2 and anthraquinone-2,7-disulfonate anolyte at pH 8 achieved a cell potential of 1.3 V, surpassing typical aqueous limits. [33] In terms of performance and voltage, alkaline RFBs, those that use zinc-polyiodide, can reach cell voltages of up to 1.89 V, which is noticeably greater than the 1.6 V seen in acidic arrangements. [34,35] Despite having a lower voltage, acidic systems can take advantage of particular redox couples that, in some circumstances, may improve stability and efficiency. [2] In terms of electrochemical kinetics, the dihydroxyphenazine sulfonate (DHPS) and ferro-/ferricyanide systems are two examples of alkaline batteries that frequently exhibit superior kinetics because of their reduced resistance and improved ion transport. [36] However, for acidic systems to function at their best, especially in bipolar membrane designs, catalyzed reactions may be necessary. [37] Reports on material properties and stability has shown that, organic molecules in alkaline RFBs, such as anthraquinones, are engineered for high solubility and capacity, contributing to their overall efficiency. [38] On the other hand, acidic systems can utilize a broader range of organic electrolytes, which may offer unique advantages in specific applications but may encounter limitations in long-term stability and scalability compared to their alkaline counterparts. [36]

2.4 Emphasis on High PH (Alkaline) solvents

The importance of alkaline media in maximizing solubility in redox flow batteries is underscored by its role in enhancing ion transport, stability, and overall battery performance.

Alkaline environments facilitate the solubility of active materials, which is crucial for efficient energy storage and conversion. This section will explore the key aspects of how alkaline media contributes to the solubility and performance of redox flow batteries. One of the key advantages of alkaline media is the ion transport by facilitating the movement of hydroxide ions (OH−), which are crucial for the performance of Anion exchange membranes (AEMs). The choice of alkaline solvent, such as sodium hydroxide or potassium hydroxide, can enhance the solubility of specific ROMs (Redox-Active Organic Molecule), thereby improving energy density and battery efficiency. [39] AEMs tailored for alkaline conditions demonstrate high ionic conductivity up to 58.2 mS cm^{-1} resulting in improved energy efficiency and operational stability. [40,41] Iron-based complexes like Fe(TEA-2S) exhibit high solubility in alkaline media, reaching up to 1.85 M, which is essential for achieving high charge capacity and reducing long-term capacity decay. [42] Similarly, organic redox-active molecules such as anthraquinones benefit from the alkaline environment, which facilitates greater structural tunability and stability. This increased stability in both inorganic and organic species helps maintain consistent performance over extended cycling, making alkaline media an attractive choice for high-efficiency, durable energy storage systems. [43] Performance metrics for alkaline RFBs reflect these material advantages, with reported coulombic efficiencies reaching up to 99.93% and energy efficiencies around 83.5%, due to the optimal stability and solubility of active species. [42][44] However, despite these promising attributes, challenges such as electrode and membrane corrosion, as well as long-term material degradation, remain significant hurdles. Addressing these issues is critical for realizing the full potential and commercial viability of alkaline redox flow battery systems.

2.5 Aqueous and Non-Aqueous Systems

Aqueous redox flow batteries (RFBs) utilize water-based electrolytes, offering a cost-effective, safe, and environmentally friendly solution for grid-scale energy storage. Among the most extensively studied aqueous systems is the all-vanadium redox flow battery (VRFB), which employs vanadium ions in varying oxidation states (V^{2+}/V^{3+} at the negative electrode and VO^{2+}/VO_2^{+} at the positive electrode) as the active species. Other notable aqueous RFB systems include iron-chromium and zinc-bromine batteries, which rely on well-established inorganic redox couples for their electrochemical functionality. [45]

Despite their advantages, aqueous RFBs are inherently constrained by the narrow electrochemical stability window of water, typically below 1.5 V. This limitation directly

impacts the achievable cell voltage and overall energy density, making aqueous systems less competitive than their non-aqueous counterparts in high-energy applications [46]. Nonetheless, the simplicity, low material cost, and operational safety of aqueous RFBs have sustained significant research interest and development.

The performance of aqueous RFBs is influenced by several factors, including the redox potential and solubility of the active species, membrane conductivity, and overall cell architecture. For instance, the VRFB can attain energy efficiencies in the range of 80–90% under optimized operating conditions [45]. To overcome the energy density limitations imposed by aqueous media, recent research efforts have focused on enhancing the solubility and chemical stability of redox-active species.

Aqueous electrolytes containing alkaline solute and certain organic redox-active molecules is a potential approach. Compounds such as anthraquinones and phenazines have demonstrated favorable characteristics, including tunable redox potentials, high solubility, and enhanced electrochemical stability. Through molecular engineering, these organic compounds can be structurally optimized to further improve their capacity, stability, and compatibility with alkaline environments, thereby enabling aqueous RFBs with higher energy densities and extended cycle life. [47]

Non-aqueous redox flow batteries (RFBs) represent a promising class of energy storage systems that leverage organic solvents to overcome the electrochemical limitations of aqueous counterparts. By utilizing solvents such as acetonitrile, carbonates, or ethers, non-aqueous RFBs benefit from a significantly wider electrochemical stability window up to 5 V, thereby enabling higher cell voltages and energy densities. [46] The core chemistry of these systems typically involves redox-active organic molecules (ROMs) or metal-organic complexes dissolved in these non-aqueous media, offering a diverse platform for molecular tuning and performance optimization.

Among the various ROMs explored, tetrathiafulvalene (TTF) derivatives have attracted considerable attention due to their high solubility, customizable redox potentials, and ability to support multi-electron transfer reactions[47,48]. In particular, TTF compounds functionalized with perfluorophenyl groups exhibit elevated oxidation potentials and excellent chemical stability in non-aqueous environments, making them ideal candidates for high-voltage applications. This has been demonstrated in systems where TTF-based catholytes, paired with lithium metal anodes, achieved operational energy densities of up to 96 Wh/L and sustained

capacity retention of 83.1% over 16.8 days of continuous cycling [48]. Non-aqueous organic solvents, such as N,N-dimethylformamide (DMF), allow for higher operating potentials beyond 1.23 V, as demonstrated using tris(4-bromophenyl)amine and oxygen in a new redox system. [49]

Hybrid lithium-organic RFBs have further exemplified the potential of non-aqueous systems. These batteries have reported cell voltages of approximately 3.5 V and volumetric energy densities of 50 Wh/L for ferrocene and 126 Wh/L for TEMPO-based electrolytes.[50] significantly outperforming typical aqueous systems. Additionally, the creation of redox-active materials with multi-electron transfer capabilities, like imide-based anolytes, has been the focus of recent research, which increases energy density and extends cycling life. [46]

In addition to advancements in redox chemistry, engineering efforts have targeted improvements in membrane and separator technologies. The introduction of mechanically robust crosslinked membranes and nanoporous separators has led to enhanced ionic selectivity, reduced crossover of active species, and improved operational durability [51,52]. Together, these innovations underscore the growing maturity and potential of non-aqueous RFBs as high-performance energy storage solutions suitable for a broad range of applications. Table 1. Summarizes the differences between aqueous and non-aqueous RFBs.

Table 1. Comparison of Aqueous and Non-Aqueous RFBs

Parameter	Aqueous RFBs	Non-Aqueous RFBs
Solvent	Water-based solvent	Organic solvents
Redox Active Species	Vanadium ions (V^{2+}/V^{3+} and VO^{2+}/VO_2^{+}) – used in traditional VRFBs. Ferricyanide/ferrocyanide ($[Fe(CN)_6]^{3-}/[Fe(CN)_6]^{4-}$) etc.	Ferrocene and derivatives (e.g., dimethylferrocene, vinylferrocene) etc.
Energy Density	Limited by the narrow electrochemical window of water (typically < 1.5 V)	Higher energy density due to wider electrochemical window (up to 5 V)
Solubility	Limited by the solubility of inorganic ions in water	Higher solubility of organic molecules in organic solvents
Stability	Susceptible to degradation due to water electrolysis and side reactions	Improved stability due to the wider electrochemical window and organic solvents

Parameter	Aqueous RFBs	Non-Aqueous RFBs
Cost	Lower cost due to the use of water and inorganic materials	Higher cost due to the use of organic solvents and advanced materials
Applications	Grid-scale energy storage, renewable energy integration	Grid-scale energy storage, high-energy-density applications

3 Key Physicochemical Properties of Organic Redox Active Materials

The performance of redox flow batteries (RFBs), particularly organic redox flow batteries (ORFBs), is intricately linked to the physicochemical properties of the redox-active materials used. Parameters such as solubility, redox potential, the number of electrons transferred, and reaction kinetics all contribute to the overall energy density, power output, and operational stability of the system. [53] High energy density allows for greater energy storage, while power output reflects the system's ability to deliver energy quickly. Operational stability ensures that these systems can maintain performance over time without significant degradation. While these properties are often reported independently in the literature, their interdependent effects on battery performance are less frequently discussed in a systematic way. This chapter aims to dissect these properties, elucidating how each parameter influences different aspects of RFB operation, and highlighting the challenges and trade-offs involved in optimizing electroactive compounds for aqueous alkaline systems.

3.1 Solubility of AORBFs: Impact on Energy and Power Density

Solubility refers to the maximum concentration of the redox-active species (electrolyte materials) that can be dissolved in the solvent, which is often water or an organic solvent. Solubility plays a central role in defining the energy density of a redox flow battery. In flow battery systems, the redox-active species are dissolved in the electrolyte solution; thus, the concentration of the electroactive molecule directly correlates with how much charge the electrolyte can store. Higher solubility enables a greater volumetric capacity and greater concentrations of active species, which in turn enhances the energy density of the battery. For example, many organic molecules exhibit promising redox behavior but suffer from limited aqueous solubility, which restricts their practical use. Strategies such as introducing hydrophilic functional groups or using hydrotropes have been employed to overcome solubility limits.

The 6-quinoxalinecarboxylic acid (QCA) anolyte AORFB demonstrated a cell voltage of 1.28 V and a power density of 199 mW cm^{-2}, showcasing the benefits of high solubility (5.5M). [54] Enhanced solubility often also leads to improved cycle stability, as seen with the viologen that retained 92.4% capacity after 200 cycles [55].

However, improving solubility often affects other parameters such as redox potential or chemical stability, necessitating a balanced molecular design. In this context, solubility is not just a material constraint but a critical design consideration in tailoring high-capacity, long-lasting ORFB systems. Several strategies have been explored to improve solubility, leading to advancements in battery performance.

3.1.1 Discussion on solubilizing groups in organic compounds

Different solubilizing groups can be used to enhance the solubility of flow battery systems. Incorporating hydrophilic functional groups, such as sulfonate and carboxylate, into viologen derivatives has been shown to increase solubility. For instance, a modified viologen achieved a solubility of 3.0 M, enhancing its energy density and stability. [55] In another study an innovative approach uses surfactants to encapsulate redox-active materials, significantly improving their solubility. For example, the solubility of TEMPO was enhanced by an order of magnitude, leading to a tenfold increase in energy density. [56] The design of molecules with high polarity and asymmetry can also enhance solubility. The energy density of the carboxylate functionalized viologen $(CBu)_2V$/$(NH)_4Fe(CN)_6$ AORFB is 9.5 Wh/L, with power densities reaching up to 85 mW/cm². The high solubility of $(CBu)_2V$, over 2.1 M, contributes significantly to these performance metrics and demonstrates the importance of molecular structure in solubility. [57]

Energy density in nonaqueous redox flow batteries is limited by the solubility of redox-active organic molecules. A study demonstrates that high solubility of cationic oligomers enables asymmetric RFBs with improved energy density, achieving 22.2 Wh/L without a supporting electrolyte [58]. The 4-carboxylic-2,2,6,6-tetramethylpiperidin-N-oxyl (4-CO_2Na-TEMPO) exhibits a solubility of 1.5 M, three times higher than 4-OH-TEMPO, enabling an energy density of 14.7 W h L^{-1} in aqueous organic redox flow batteries using cation-exchange membranes [59,60]

3.2 Redox Potential: Role in determining battery voltage

The redox potential of electroactive species directly governs the cell voltage of a redox flow battery. Higher redox potentials correlate with increased voltage output, which is crucial for

enhancing the energy density and efficiency of these systems. In an RFB, the overall cell voltage is defined by the potential difference between the catholyte and the anolyte. For aqueous systems, this potential window is constrained by the electrolysis of water, typically between 0 V and 1.23 V versus the standard hydrogen electrode (SHE). [61] As such, identifying redox-active compounds that undergo reversible redox reactions near these limits is essential for maximizing battery voltage while maintaining aqueous stability. In organic RFBs, molecular engineering techniques allow for the fine-tuning of redox potentials through structural modifications, such as the addition or repositioning of electron-donating or electron-withdrawing functional groups. [62] For anolytes, more negative redox potentials are particularly desirable, as they shift the cell voltage upward when paired with suitable catholytes. [63] However, highly negative potentials can introduce issues such as reduced chemical stability or increased reactivity with water or supporting salts, highlighting the delicate balance between voltage optimization and long-term durability. [64]

The redox potential significantly influences battery voltage; lower redox potentials, like the phenazine derivative 2,3-O-DBAP at -0.699 V vs. SHE, contribute to higher average discharge voltages, enhancing overall performance and stability in aqueous organic redox flow batteries. [65] An example where higher redox potentials lead to increased voltage output can be shown in the study, incorporating di-aminocyclopropenium substituents raised the redox potential by ∼300 mV, enabling the batteries to achieve voltages up to 2.0 V .[66] Organic compounds with elevated redox potentials, such as benzoquinone derivatives, can achieve voltages exceeding 3.99 V when optimized with electron-withdrawing substituents. [67]

3.3 Molecular engineering to improve stability and reversibility.

Molecular engineering plays a pivotal role in enhancing the electrochemical performance, stability, and reversibility of redox-active liquids (RALs) employed in redox flow batteries (RFBs). Strategic modification of molecular structures can significantly influence key physicochemical parameters, including redox potential, solubility, stability, and electron-transfer kinetics, all of which directly impact the overall energy efficiency and cycle life of RFB systems. [68]

A central goal in RAL design is the maximization of volumetric energy density, which is directly linked to the solubility of redox-active species. Through the incorporation of hydrophilic or ionizable substituents, solubility in aqueous and nonaqueous solvents can be substantially increased, allowing for higher concentrations of active species and thus greater

stored energy per unit volume. Beyond solubility, redox kinetics are profoundly affected by the electronic and steric nature of substituent groups. Electron-donating or -withdrawing groups can tune the redox potential and modulate the rate of electron transfer by altering the electronic environment around the redox center, thereby influencing the standard heterogeneous rate constant.[69] Stability and reversibility are equally critical for long-term performance, particularly in aqueous systems where hydrolysis, radical decomposition, or dimerization can degrade redox species over extended cycling. For example, targeted functionalization of molecules such as 4-hydroxy-TEMPO (4-OH-TEMPO) has demonstrated significant improvements in both chemical stability and electrochemical reversibility. [70] The introduction of hydrophilic groups not only enhances aqueous solubility but also stabilizes the oxidized and reduced forms of the molecule against degradation pathways. [71] Another example of molecular engineering where, An azo-compound tailored with hydrophilic groups: the solubility was improved from nearly zero to ~2 M in alkaline environment. [72]

Moreover, molecular rigidity and resonance stabilization have been identified as important structural features that contribute to redox species longevity. Molecules with delocalized charge distributions or aromatic scaffolds tend to exhibit better reversibility by minimizing structural reorganization energy during redox cycling. [73]

Density Functional Theory (DFT**)** is a quantum-mechanical method that computes the electronic structure of matter by expressing the energy as a functional of the electron density, as formalized by the Hohenberg–Kohn theorems. [74] In this context, rational molecular design, guided by Density functional theory (DFT) and other computational methods, can accelerate the discovery of novel redox-active materials with optimized redox potentials, minimal overpotentials, and long-term cycling durability. [75] Molecular engineering offers a versatile and effective approach to improving the key parameters that govern redox flow battery performance. By tailoring redox-active molecules at the atomic and functional-group level, it is possible to significantly enhance solubility, stability, and reversibility, thereby enabling the development of high-efficiency, long-life RFB systems suitable for grid-scale energy storage applications.

3.4 Number of Electrons transfered: Impact on storage capacity and reversibility

The number of electron transfers in RFBs can vary depending on the specific chemistry and materials used. This section explores the electron transfer mechanisms in different types of

RFBs, highlighting examples from recent research. The number of electrons transferred in organic redox flow batteries (ORFBs) significantly impacts their storage capacity and reversibility. [76] This relationship is crucial for optimizing battery performance, particularly in large-scale energy storage applications.

VRFBs typically involve a single electron transfer per vanadium ion in each half-cell reaction. The vanadium ions undergo redox reactions between V(II)/V(III) at the negative electrode and V(IV)/V(V) at the positive electrode, each involving one electron transfer per ion. [77]

One-electron transfer systems, characterized by a single redox couple undergoing a single electron exchange, offer notable advantages in terms of reaction simplicity, kinetic performance, and voltaic efficiency. These systems typically involve straightforward redox mechanisms with minimal intermediates, leading to faster kinetics and reduced complexity. For instance, in lithium-oxygen batteries, the one-electron transfer results in the formation of superoxide ions (LiO_2), while in organic radical batteries, nitroxide radicals ($NO^{\cdot}$) undergo a one-electron oxidation to form NO^+, enabling rapid and reversible redox behavior. [78,79] The simplicity of these reactions often translates to higher heterogeneous electron transfer rate constants, as evidenced by the ten-fold increase observed in the $NO^+/NO^{\cdot}$ couple compared to the two-electron $NO^{\cdot}/NO^-$ system [80]. Moreover, the reduced number of reaction steps in one-electron systems minimizes side reactions and overpotentials, thereby enhancing voltaic efficiency. This efficiency is particularly apparent in lithium-oxygen batteries, where the one-electron process achieves superior energy efficiency relative to the two-electron peroxide pathway (Li_2O_2), largely due to reduced energy losses and faster kinetics. [78] Materials employed in these systems, such as nitroxide radicals and gel-polymer electrolytes, are specifically chosen for their high redox potentials and ability to stabilize reactive intermediates, further supporting rapid and efficient charge transfer. [78,81] Overall, one-electron transfer systems, despite their lower theoretical energy density, are highly suitable for high-power applications requiring fast and efficient cycling.

3.5 Analysis of two-electron storage capacity and its significance

Recent studies have demonstrated that RFB systems utilizing such multi-electron redox species can achieve high current densities, with some reports reaching nearly 300 mA/cm^2 at operational voltages around 0.5 V. [82] These values are promising for practical applications, indicating not only effective charge transport but also robust redox kinetics and reversibility under high-demand conditions.

A study in RFBs have explored two-electron transfer systems to enhance energy density. For instance, ammonium-functionalized naphthalene diimide (NDI) in aqueous organic RFBs (AORFBs) can achieve stable two-electron transfers, significantly improving the capacity and efficiency of the battery. [83] Similarly, nonaqueous organic RFBs using anthraquinone anolyte and phenothiazine catholyte materials have demonstrated two-electron transfer reactions, which effectively double the charge storage capacity compared to single-electron systems. [84] Six reversible redox couples across roughly 2 V are demonstrated in the research, which discusses metal coordination complexes (MCCs) that facilitate multiple electron transfers. In order to maximize energy density, two electron transfers must be made at each electrode. Active species solubilities must be close to 0.7 M for symmetric cells to function well. [85] In the studied nonaqueous organic redox flow battery, two-electron transfer reactions (2e−) were achieved using anthraquinone (AQ4) as the anolyte and phenothiazine (PT3) as the catholyte. The battery demonstrated doubled charge storage capacities indicative of these 2e− processes. However, the stability of the second redox event was limited, affecting cyclability. The first electron transfer reactions exhibited significantly better durability, highlighting the challenges in achieving long-term performance for 2e− products under flow cell conditions. [86]

Similar to energy density , energy storage is directly proportional to the number of electrons exchanged per molecule during the redox process. Compounds capable of two-electron transfer, such as gallocyanine, enhance charge storage capacity, allowing for more energy to be stored per molecule compared to single-electron systems, assuming similar concentrations and cell voltages. This two-electron transfer mechanism contributes to high reversibility, achieving nearly 100% Coulombic efficiency over multiple cycles. [87] Increased charge storage capacity is critical for improving the volumetric and gravimetric energy density of RFBs, especially when space and weight constraints are significant considerations.

Beyond storage capacity, the number of electrons transferred also influences the electrochemical reversibility of the redox couple. Two-electron transfers can sometimes introduce complications such as intermediate species formation or disproportionation reactions, which may compromise cycling stability. However, when properly designed, organic compounds with reversible two-electron redox behavior such as certain quinones and phenazines, can deliver excellent performance metrics. [84, 88]

Two electrons are transferred at the positive electrode ($3I^- \rightarrow I_3^- + 2e^-$) and two electrons are transferred at the negative electrode ($Zn \rightarrow Zn^{2+} + 2e^-$) in the iodine/iodide system covered in

the study. [89] As a result, in this system, four electrons are exchanged for every full cycle of the redox reactions.

Two-electron transfer systems, in contrast to their one-electron counterparts, involve the transfer of two electrons per redox-active species, either through a concerted two-electron step or via two successive one-electron transfers. These systems are inherently more complex, often involving reactive intermediates and requiring precise control over reaction conditions to maintain reversibility and efficiency. In organic-based redox flow batteries, the use of structurally engineered di-carbonyl compounds has proven effective in stabilizing the dianion state, thereby supporting reversible two-electron cycling. [90] Despite their higher theoretical energy density derived from the increased charge per molecule, two-electron systems often suffer from slower kinetics. This is due to the additional reaction steps and the energy barriers associated with the formation and stabilization of intermediate species. For example, during the two-electron oxygen reduction process, the second electron transfer is typically hindered by high reorganization energy and slower diffusion kinetics of ions such as Li^+ [91]. Likewise, organic compounds designed for two-electron storage must overcome challenges related to the solubility and stability of their dianionic forms, which can lead to kinetic inefficiencies. [90]

However, recent advances in material and molecular engineering have shown promise in addressing these limitations. The deployment of AQDS as a redox mediator in zinc-air systems, for example, has yielded rate constants (k_0) as high as 7.2×10^{-3} cm/s demonstrating that under optimized conditions, even two-electron reactions can achieve rapid kinetics [92]. Despite these improvements, two-electron systems often exhibit lower voltaic efficiency compared to simpler one-electron mechanisms. The disparity in redox potentials between the two electron transfer steps and the likelihood of side reactions contribute to energy losses and higher overpotentials. In some organic-based redox flow batteries, this leads to noticeable declines in overall efficiency.[93] Nonetheless, by carefully tuning the molecular structure and redox potentials of the active species, researchers have begun to overcome these challenges. For instance, the use of readily available dicarbonyl compounds with well-defined redox characteristics has shown encouraging results in stabilizing multiple redox states, thereby enhancing both reversibility and energy efficiency. [90]

In conclusion, Materials suitable for two-electron transfer must be capable of accommodating multiple oxidation states while maintaining solubility and structural integrity throughout

charge-discharge cycles. This requirement has driven the design of sophisticated molecules and nanostructures.

Table 2. Summary of Key Differences

Aspect	One-Electron Systems	Two-Electron Systems
Reaction Mechanism	Single redox couple with a single electron transfer step.	Multiple redox couples with two successive or concerted electron transfer steps.
Reaction Kinetics	Generally faster due to the simplicity of the mechanism.	Often slower due to multiple steps or intermediates, but can be optimized with mediators.
Energy Efficiency	Higher voltaic efficiency due to minimized side reactions.	Lower voltaic efficiency due to increased complexity, but higher theoretical energy density.
Material Requirements	Materials with well-defined redox couples and fast electron transfer kinetics.	Materials that support multiple redox states with stability and solubility.

3.6 Kinetics: Rate constant (k_0) and Diffusion Coefficient (D_0)

The diffusion coefficient (D_0) and standard heterogeneous electron transfer rate constant (k_0) are critical kinetic parameters governing the performance of redox flow batteries. The diffusion coefficient quantifies how rapidly electroactive species migrate through the electrolyte. A higher D_0 enhances mass transport, allowing active species to more readily reach the electrode surface, thus reducing concentration polarization under high current densities. This leads to improved electrolyte utilization and contributes to better battery efficiency, particularly in systems operating at fast charge/discharge rates.[94]

Complementing this, the standard rate constant (k_0) reflects the intrinsic speed of electron transfer at the electrode interface. [95] A high ko value implies rapid redox kinetics, which supports reversibility and minimizes activation overpotentials during battery cycling. Together, D_0 and k_0 influence the shape of voltammograms and the operational limits of current density and power output. These parameters are often evaluated experimentally through techniques

such as linear sweep voltammetry (LSV) at varying rotation speeds, enabling the application of Koutecký-Levich (K–L) analysis as in eqn (1). [96, 97]

The Combined Current Density Equation:

$$\frac{1}{J} = \frac{1}{J_k} + \frac{1}{0.620 \times n \times F \times D^{\frac{2}{3}} \times \nu^{-\frac{1}{6}} \times C \times \omega^{\frac{1}{2}}} \quad \ldots (1)$$

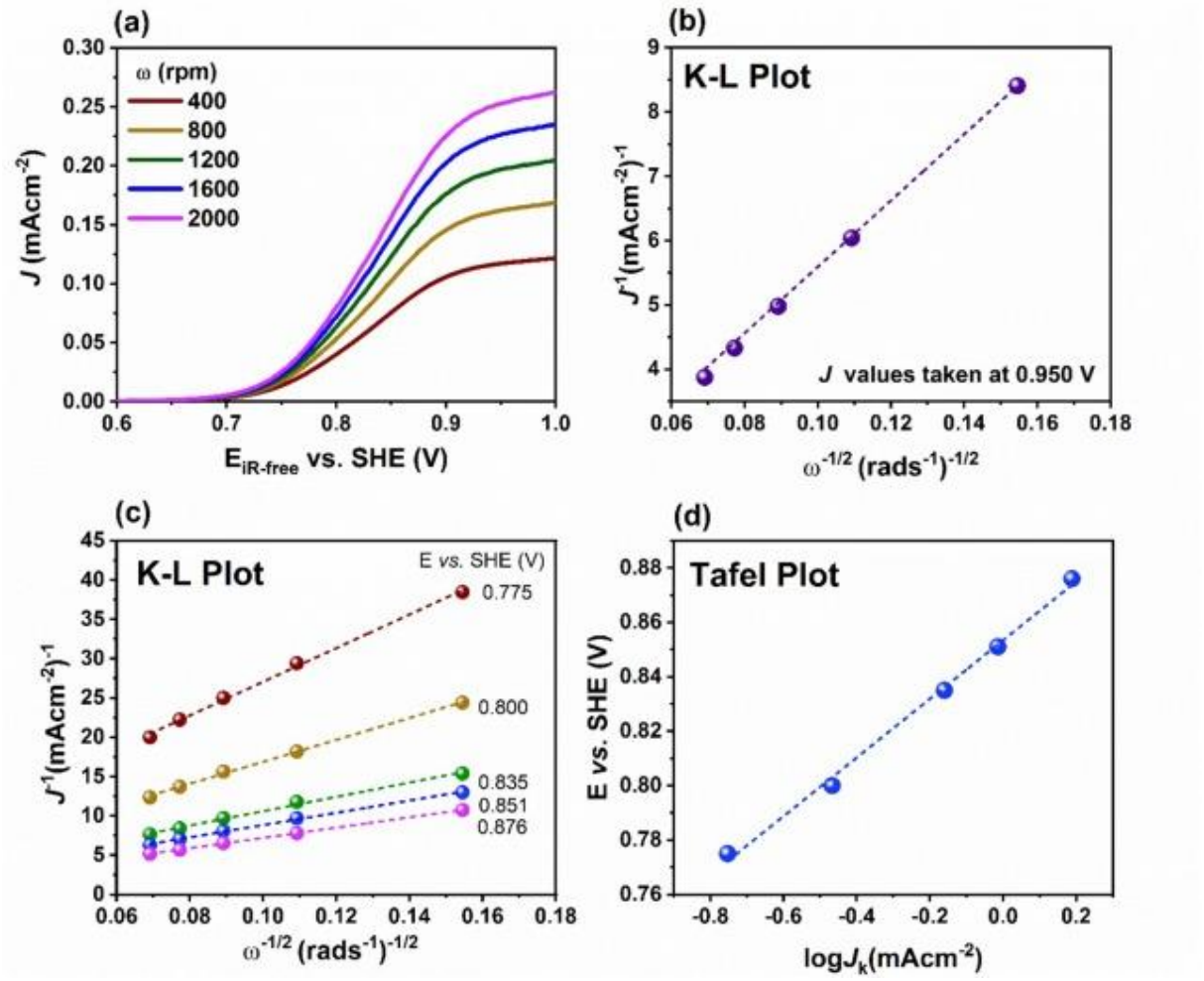

Figure 2 : Fig. 5. (a) LSV curves at different rotation speeds and a 10 mVs^{-1} potential scan rate for the ZnTPPS (1 mM) in an acetate buffer aqueous electrolyte (0.1 M, pH = 4.6), (b-c) Koutecký-Levich (J^{-1} vs. $\omega^{-1/2}$) plots to extrapolation of the diffusion coefficient and the kinetic current density respectively, (d) Tafel plot adopted to the standard kinetic rate constant calculation.

Source : Picture taken from [94]

In figure 2. Jorge et al. [94] shows Well-defined diffusion-limited current plateaus in such experiments, as observed with compounds like ZnTPPs, validate the estimation of D_0, while fitting of Tafel or Butler-Volmer models aids in determining k_0. Although both parameters are important, emerging evidence from simulation and experimental studies suggests that variations

in ko exert a more significant impact on battery reversibility and performance than comparable changes in D_0. [94]

3.6.1 Mass Transport and Kinetics in Redox Flow Batteries

The transport of mass within a solution is primarily governed by factors such as the molecular size and shape, the nature of the supporting electrolyte (particularly its viscosity), and temperature. The diffusion coefficient (D_0) is commonly assessed using the Levich (Eq. 2) and Cottrell (Eq. 3) equations:

(Levich Equation):

$$i = 0.620 \times n \times F \times A \times C^0 \times D^{\frac{2}{3}} \times \omega^{\frac{1}{2}} \times \nu^{-1/6} \quad \dots (2)$$

In Eq. 2, i denotes the limiting current, which corresponds to the maximum diffusion-controlled current measured. $\boldsymbol{A}$ is the electrode surface area, while $\boldsymbol{n}$ represents the number of electrons transferred during the redox reaction. $\boldsymbol{F}$ is the Faraday constant (96,485 C/mol), relating the amount of electric charge per mole of electrons. $\boldsymbol{C_0}$ refers to the bulk concentration of the electroactive species, and $\boldsymbol{D}$ is the diffusion coefficient, which quantifies how rapidly the redox species move through the solution. The angular rotation rate $\boldsymbol{(\omega)}$ of the electrode determines the rate at which fresh solution is brought to the surface, influencing mass transport, while $\boldsymbol{\nu}$ represents the kinematic viscosity of the electrolyte, affecting the hydrodynamic boundary layer thickness and consequently the diffusion process.

(Cottrell Equation):

$$i = \frac{n \times F \times A \times C_0 \times D_0^{\frac{2}{3}}}{(\pi \times t)^{\frac{1}{2}}} \quad \dots (3)$$

Here, t represents time, and the rest of the parameters are consistent with those in Eq. 2.

Overpotentials (also called polarization losses) add to the ideal cell voltage drop, meaning the actual operating voltage during charge/discharge is lower than the thermodynamic (open-circuit) voltage. [98] To improve mass transport, the electrolyte flow rate in a redox flow battery (RFB) system can be increased, which helps reduce mass transport overpotentials. The electron transfer rate constant (k_0) plays a vital role and depends on the structure of redox-active compounds, electrode type, supporting electrolyte, and temperature.

(Standard Rate Constant for Slow Kinetics):

$$i_0 = n \times F \times A \times C_0 \times k_0 \quad \ldots(4)$$

This equation is applicable when $k_0 < 0.02$ cm/s, using linear scan voltammetry (LSV) with a rotating disk electrode.

For fast kinetics ($k_0 > 0.02$ cm/s), a more nuanced analysis is necessary. Nicholson's method, using the peak potential difference (ΔE_p) from cyclic voltammetry (CV), provides a more reliable lower-bound estimate of k_0.

(Nicholson's Ψ Parameter):

$$\Psi = \frac{0.6288 + 0.0021 \times \Delta Ep}{1 - 0.017 \times \Delta Ep} \quad \ldots(5)$$

(Nicholson's Rate Constant Estimation):

$$k_0 = \Psi \times \left[\frac{\pi \times D_0 \times n \times F}{R \times T \times v}\right]^{\frac{1}{2}} \quad \ldots(6)$$

Using Koutecký-Levich and Tafel analyses for fast kinetics might lead to substantial underestimation of k_0. For example, methyl viologen's first redox reaction was estimated at 0.022 cm/s via Koutecký-Levich, but Nicholson's method yielded a value of 0.35 cm/s. [99]

4 Electroactive Materials for Flow Batteries

4.1 History of inorganic compounds in Redox Flow Systems

Electroactive materials are the core components of flow batteries, as they determine the system's voltage, energy density, and overall performance. This section provides an overview of the development of both inorganic and organic redox-active compounds that have been used in flow battery technologies, from early metal-based systems to more recent organic molecular designs.

In 1949, Kangro patented the first battery version that resembled modern flow batteries. [100] This setup achieved a cell voltage of 1.75 V by using $Cr_2(SO_4)_3$ as the cathode and anode active material and 2 m sulfuric acid as the supporting electrolyte [101]. As possible redox-active materials, $TiCl_4$, Ti/Fe, Ti/Cr, Ti/Cl_2, and Cr/Fe were also found. An Fe/Cr system that was recorded by the National Aeronautics and Space Administration (NASA) in the 1970s attracted a lot of interest. $Fe^{3+}/Fe^{2+}//Cr^{3+}/Cr^{2+}$ dissolved in an acidified electrolyte with an array of solar cells was used in conjunction with a 1 kW/13 kWh demonstration. [102] Exxon and Gould Inc. developed the first hybrid-flow batteries in the 1970s and 1980s, respectively. [103]

Rapid capacity deterioration in this redox flow battery (RFB) device was caused by redox-active species crossing across through the used anion-exchange membrane. [104] In later studies, mixed electrolytes were used. No commercially feasible membrane was available at that time, and membranes that were custom-fabricated did not meet the necessary requirements for resistivity and selectivity. Bradley's 1885 patent application is where the aqueous Zn/Br2 battery first appeared [105]. Several companies are either developing or currently selling the Fe/Cr, Zn/Br2, all-vanadium, Fe/Zn, and all-iron flow batteries. A patent was obtained by Skyllas-Kazacos and Robins in 1986 for the vanadium redox flow battery (VRFB). [106] This device achieves an open circuit voltage (OCV) of 1.3 V by using the redox coupling $VO^{2+}/VO^{2+}//\ V^{3+}/V^{2+}$ [107].

In recent developments within metal-based redox flow batteries, the iodine/iodide system has shown promising performance due to its efficient electron exchange mechanism. In this system, two electrons are transferred at the positive electrode via the redox reaction of iodine, while at the negative electrode, zinc undergoes oxidation. [89] This results in enhancing the theoretical capacity and energy density of the battery. Such multi-electron transfer mechanisms are particularly advantageous for developing high-capacity, cost-effective flow battery systems.

4.2 Transition towards Organic Redox Flow Batteries

In this part we will discuss why research has been notably increasing towards organic redox flow technology and the facts that inorganic options are lacking. Lithium-based battery systems remain the most cost-effective and energy-dense option for small-scale applications; however, their limitations in scalability, cost, and safety pose challenges for grid-level energy storage. In contrast, redox flow batteries (RFBs) offer a promising alternative, providing advantages in cost efficiency, safety, and long-term storage capacity. [108]

Vanadium redox flow batteries (VRFBs), first patented in 1986, remain the most widely used and stable redox flow battery technology due to the unique electrochemical properties of vanadium. Vanadium-based flow batteries and other IRFBs often use strong acids (e.g., sulfuric acid). Sulfuric acid, though effective in dissolving active materials like vanadium ions, is highly corrosive, leading to the degradation of cell components such as membranes, electrodes, and current collectors over extended operation. It poses risks of leakage, and environmental hazards as well. Vanadium extraction and disposal pose significant environmental challenges due to mining and toxic waste generation. Additionally, vanadium itself is a scarce resource with a highly volatile market price, making VRFBs an expensive option compared to emerging organic alternatives. The fundamental limitation of VRFBs stems from their reliance on single-electron transfer per vanadium species, which restricts their energy density. Furthermore, temperature sensitivity between 10–40°C imposes additional operational constraints, necessitating complex thermal management systems. Given these limitations, alternative flow battery chemistries, such as organic redox flow batteries (ORFBs), are being actively explored to address issues related to cost, sustainability, and electrochemical performance. [109,110]

Organic active materials, can be synthesized from abundant and inexpensive sources, significantly reducing the overall cost of the battery system. Some organic-based electrolytes have already demonstrated costs as low as USD$35 $(kWh)^{-1}$ (based on half-cell estimations), compared to the USD$150 $(kWh)^{-1}$ target for commercial viability. [111] Unlike inorganic materials, which have fixed electrochemical properties, organic molecules can be tailored at a molecular level through synthetic chemistry to improve solubility, redox potential, and reaction kinetics. This flexibility allows for optimization in terms of energy density, stability, and voltage window, making them highly adaptable for different applications. ORFBs using non-aqueous electrolytes have proven to achieve cell voltages beyond 4.5V, significantly higher than traditional vanadium-based systems (typically around 1.3V). This higher voltage leads to

improved energy density, bringing ORFBs closer to competing with lithium-ion batteries (LIBs) in terms of 150 Wh/kg and 210 Wh/L, compared to LIBs at 120 Wh/kg and 270 Wh/L [112]. Many organic molecules, such as methyl-para-benzoquinone, exhibit high solubility in organic solvents (e.g., up to 6 mol dm^{-3} in acetonitrile), leading to higher electrolyte energy density [112]. As explained in section **3.6**, organic redox couples can also undergo multi-electron transfers, which increases the capacity per molecule, further improving battery performance. ORFBs, particularly those using non-aqueous electrolytes, can operate in less corrosive environments and eliminate issues related to hydrogen and oxygen evolution, leading to longer cycle life and safer operation. ORFBs can be designed with biodegradable organic materials, reducing long-term environmental impact. The development of organic redox species, such as chlorinated spirobifluorene ammonium salts, has shown potential for high redox potentials (up to 1.05 V) and excellent cycling stability. [112]

4.3 Challenges of organic compounds in (ORFBs)

There are certain challenges that surface in the development of organic redox flow technology, research focused on these aspects is highlighted in this section. For example , several intrinsic limitations of the aqueous electrolyte and organic compounds hinder their practical implementation. Water's electrochemical stability limits the potential range constrains the voltage output and energy density of AORFBs. [113] This restricts their practical applications, alongside issues like chemical lability and membrane fouling. [114] Aqueous organic redox flow batteries (AORFBs) face several challenges that hinder their widespread implementation despite the advantages of tunable redox-active materials. One major limitation is the poor solubility of many organic compounds in aqueous electrolytes, which restricts the achievable concentration of electroactive species and consequently reduces the battery’s overall energy capacity. In addition, species crossover—the undesired diffusion of redox-active molecules across the membrane from one half-cell to the other, leading to efficiency losses and performance degradation. Another critical issue arises from viscosity variations during different states of charge (SOC), which can result in non-uniform distribution within the porous electrode and negatively impact charge transport and reaction kinetics. Furthermore, organic redox species are prone to side reactions, such as parasitic bromination in acidic environments, which compromises chemical stability and reduces cycle life. This contributes to the generally short

lifespan of many organic compounds, posing a barrier for long-term cycling performance. Economic constraints also play a key role; the viability of AORFBs is closely tied to the electrolyte's molecular weight (because the cost of stored energy directly depends on how much active material purchase to store 1 kWh.), achievable concentration, and the intrinsic stability of the active materials. Lastly, many organic molecules display incompatibility with commonly used membranes like Nafion, resulting in poor ion permeability and sluggish charge transfer across the cell. These combined challenges underline the need for advanced molecular design and system-level engineering to enhance the practicality of AORFBs. [115]

One other main challenge for the development of all-organic RFBs is to identify a redox pair for the positive side with sufficiently high stability and redox potential that enables battery cell potentials above 1 V. [116] Analyzing the current-voltage (I-V) characteristics is an important approach for overcoming these challenges.

5 Voltammetric Simulations of RFBs: A Deeper Analysis

5.1 Introduction to voltammetric simulations

Techniques such as cyclic voltammetry are fundamental electroanalytical tools used to investigate the redox behavior of electroactive species for example to assess the reversibility of redox reactions, ensuring that the systems can undergo multiple charge-discharge cycles without significant degradation. [87] these techniques are essential for evaluating the kinetics, and electrochemical stability of redox-active materials. Simulations based on cyclic voltammetry allow researchers to predict and analyze how different physicochemical parameters such as number of electrons, the rate constant of electron transfer (k_0) and the diffusion coefficient (D_0) influence the overall performance of an electrochemical system.

A cyclic voltammogram is generated by linearly sweeping the potential of a working electrode between two voltage limits while recording the resulting current. This creates a characteristic current–voltage (I–V) curve that provides detailed insight into the redox processes occurring at the electrode interface. [117] For a reversible redox system, the CV exhibits well-defined oxidation (anodic) and reduction (cathodic) peaks. One of the key indicators of reversibility is the peak-to-peak separation (ΔE_p), defined as the difference between the anodic peak potential (E_{pa}) and the cathodic peak potential (E_{pc}):

$$\Delta E_p = E_{pa} - E_{pc} \quad \dots (7)$$

For a reversible one-electron transfer at 25 °C, the theoretical ΔE_p is approximately 59 mV. This value increases as the system deviates from ideal behavior, typically due to slower electron transfer kinetics, coupled chemical reactions, or diffusional limitations, indicating quasi-reversible or irreversible behavior. The magnitude of ΔE_p, the symmetry of the peaks, and the peak current ratios (I_{pa}/I_{pc}) all serve as qualitative and quantitative measures of the redox system's reversibility and electrochemical performance.

In reversible systems, the peak currents are also directly proportional to the square root of the scan rate (ν), consistent with diffusion-controlled processes, as described by the Randles-Sevcik equation:

$$i_p = 0.4463\, nFAC_0 \left(D_0 \frac{nF}{RT} v\right)^{1/2} \quad \dots (8)$$

where n is the number of electrons transferred, A is the electrode area, D_0 is the diffusion coefficient, C_0 is the concentration of the redox species, and v is the scan rate. This relation is often used to estimate D_0 experimentally [118,119].

These simulations are particularly useful because they can identify the feature that most strongly influences battery performance by allowing the independent change of kinetic and diffusional parameters, which is not always possible through experimentation. It will be demonstrated that the peak positions, shapes, and separations offer a sophisticated insight into the conversion of physicochemical characteristics into electrochemical behavior, which in turn directs the design and selection of superior electrolyte materials for high-performance flow batteries.

5.2 Simulation methodology

To investigate the electron transfer dynamics at the electrode–electrolyte interface of a three-electrode electrochemical system, a previously developed time-dependent cyclic voltammetry (CV) model is used built by Jenna et al. [120] in the COMSOL Multiphysics 6.0 environment. The model consisted of two "Transport of Diluted Species" physics interfaces: one representing the diffusion and transformation of the oxidized species and the second describing the electrode reaction of the reduced species. One interface was used to model the oxidized species on the electrode surface, incorporating both the electron transfer and a subsequent homogeneous chemical decomposition reaction in the bulk solution. The other interface simulated the behavior of the reduced species undergoing redox conversion. A triangular waveform was employed to simulate a linear potential sweep across time, mimicking typical CV measurements.

The governing equation for species transport was the transient diffusion-reaction equation:

$$\partial c_i/\partial t + \nabla \cdot (-D_i \nabla c_i) = R_i \quad \ldots (9)$$

where c_i is the concentration of species i, D_i is the diffusion coefficient, and R_i is the reaction term corresponding to the redox and chemical processes.

To simulate the applied potential, a triangle function was implemented, enabling a linear sweep in both forward and reverse directions. The redox reaction at the electrode surface involved the reversible exchange between a species, while the oxidized species could undergo a subsequent irreversible chemical decomposition in the bulk solution. This degradation pathway introduced

a third species representing the decomposition products. Importantly, the presence of these products could influence the electrode kinetics by passivating the electrode surface or reducing the availability of redox-active species.

The simulation aimed to extract key kinetic and transport parameters, including the standard heterogeneous electron transfer rate constant k_0, diffusion coefficient D_0, and the chemical reaction rate constant k_c, by calibrating the simulated voltammograms against experimental CV data. The simulation process included adjusting D_0 to fit the oxidation peak current, modifying k_c to align with the reduction peak current, and tuning k_0 to match the peak potential separation.

The charge transfer coefficient α was assumed to be 0.5 for all simulations. The quality of the fit was assessed based on the agreement between the experimental and simulated values of peak positions and currents for both forward and reverse scans.

Studies and details of the numerical model are provided in the corresponding Electronic Supplementary Information of the source study by Jenna Hannonen. [120]

5.3 Impact of key properties on Cyclic voltammogram

The k_0 rate constant for redox reactions in flow batteries is typically in the range of 10^{-2}–10cm/s, while the diffusion coefficient (D_0) is approximately (2.0–4.0) × 10–5 cm²/s, as determined through cyclic voltammetry analysis. [121]

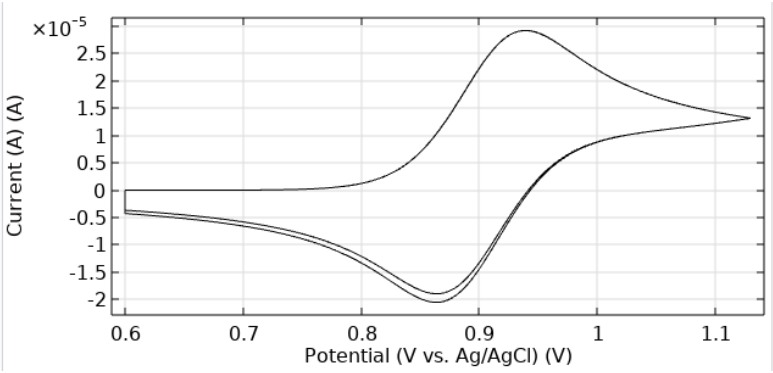

Figure 3: Simulated cyclic voltammogram (CV) generated in COMSOL with k_0 = 0.01 cm/s and D_0 = 1 × 10^{-6} cm²/s, showing the electrochemical response of a reversible redox couple under standard conditions.

Figure 3. presents a representative cyclic voltammogram (CV) generated using a COMSOL-based simulation under controlled conditions, illustrating the fundamental characteristics of a reversible redox system. The simulation assumes a standard rate constant k_0 of 0.01 cm/s and a

diffusion coefficient (D_0) of 1×10^{-6} cm^2/s , which are typical values used to model moderately fast electron transfer reactions. The graph displays the characteristic duck -shaped curve of a single-electron redox couple, showing symmetric anodic and cathodic peaks centered around the formal potential.

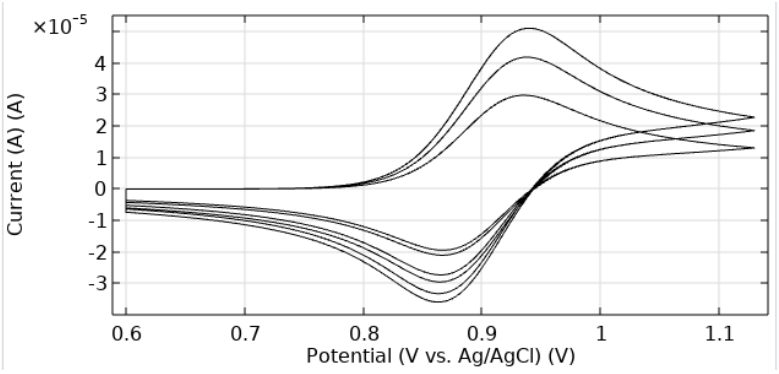

Figure 4: COMSOL-simulated cyclic voltammograms (CVs) obtained with a fixed standard rate constant (k_0 = 0.05 cm/s) and varying diffusion coefficients (D_0 = 1 × 10^{-6} – 3 × 10^{-6} cm^2/s), illustrating the dependence of the CV response on diffusion properties.

In Figure 4. simulated CV plot, the electron transfer kinetics were kept constant with a standard rate constant k_0 =0.05 cm/s , while the diffusion coefficient D_0 was varied sequentially from 1×10^{-6} to 3×10^{-6} cm^2/s. The resulting voltammograms exhibit subtle but noticeable differences. As the diffusion coefficient increases, the peak currents become slightly higher and the overall shape of the CV becomes sharper, indicating faster mass transport of the redox species toward the electrode surface. This is consistent with the Randles-Sevcik equation, where the peak current is proportional to D_0. However, the effect remains relatively modest under these conditions because the system is under kinetic control due to the low k_0, thus limiting the influence of diffusion alone. This figure demonstrates that while higher diffusion coefficients improve current response, their impact can be muted if the electron transfer is not sufficiently fast.

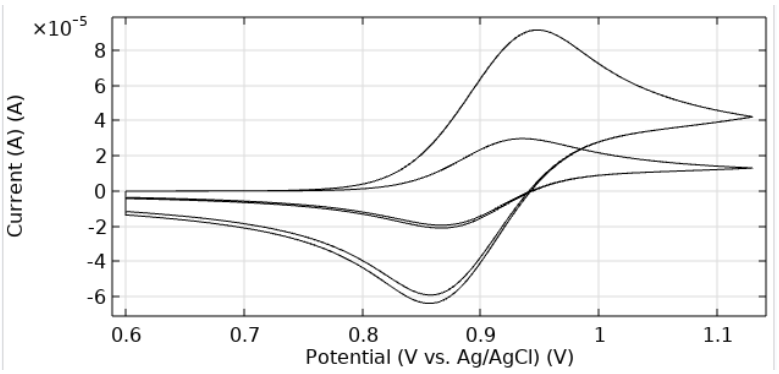

Figure 5: COMSOL-simulated cyclic voltammograms (CVs) obtained with a fixed standard rate constant (k_0 = 0.01 cm/s) and diffusion coefficients varied from 1 × 10^{-6} to 1 × 10^{-5} cm²/s, illustrating the influence of diffusion rate on CV response.

Figure 5. illustrates the impact of increasing the diffusion coefficient (D_0) by an order of magnitude from 1×10^{-6} to 1×10^{-5} cm^2/s while keeping the electron transfer rate constant fixed at k_0=0.01 cm/s. The resulting voltammograms exhibit a pronounced transformation in shape and peak current. The curve corresponding to the higher diffusion coefficient shows significantly increased peak heights and a more symmetric, steeper profile, characteristic of enhanced mass transport and more efficient redox cycling. In contrast, the curve with the lower diffusion coefficient is more broadened and flattened, indicating limited transport of redox species to the electrode surface. This highlights how a higher diffusion coefficient can strongly boost current response, reduce peak-to-peak separation, and mimic more reversible electrochemical behavior, even when the kinetics are not extremely fast. This contrast visually emphasizes the importance of molecular mobility in electrochemical systems, especially in systems governed by diffusion-limited processes.

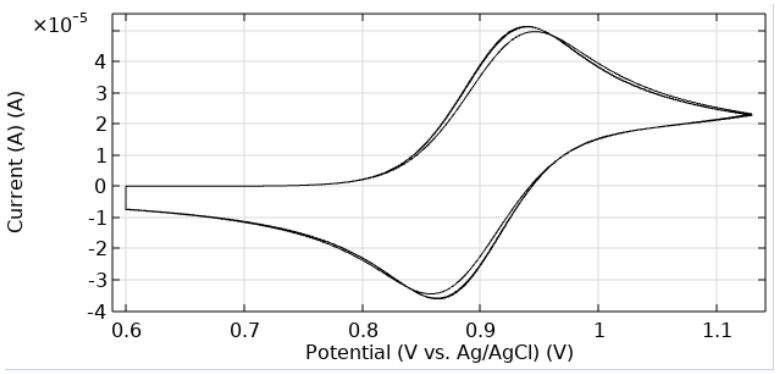

Figure 6: COMSOL-simulated cyclic voltammograms (CVs) at a constant diffusion coefficient (D_0 = 3 × 10^{-6} cm²/s) and varying standard rate constants (k_0 = 0.01, 0.05, and 0.1 cm/s), demonstrating the influence of electron transfer kinetics on the CV profile.

In figure 6. simulated voltammograms at a fixed diffusion coefficient D_0 =3×10^{-6} cm^2/s for three different electron transfer rate constants: k_0=0.01, 0.05, and 0.1 cm/s. The resulting curves reveal only marginal differences in current response and peak shape, suggesting that, within this range, the system behaves close to quasi-reversible or reversible conditions. The peak currents and peak separations remain nearly identical across the three cases, indicating that variations in k0 beyond a certain threshold produce diminishing returns in terms of improving electrochemical reversibility. This illustrates that under conditions where mass transport (diffusion) dominates, modest increases in reaction kinetics do not substantially alter the voltammetric response. Hence, in diffusion-governed systems, optimizing kinetic parameters

alone might not yield significant performance gains unless accompanied by improved mass transport properties.

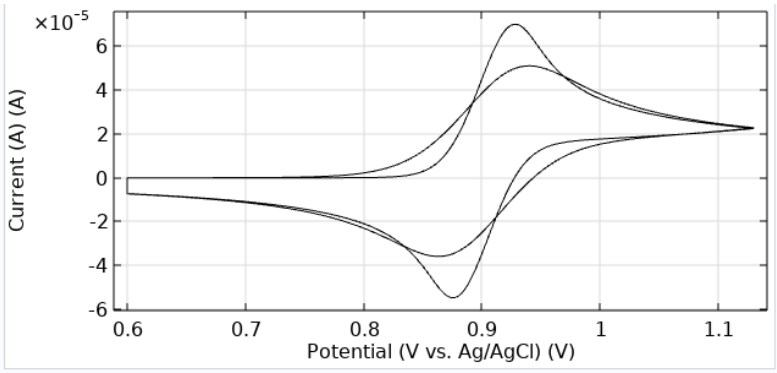

Figure 7: COMSOL-simulated cyclic voltammograms comparing single-electron (n = 1) and two-electron (n = 2) transfer processes, with D_0 = 1 × 10^{-6} cm²/s and k_0 = 0.01 cm/s.

The figure 7. compares cyclic voltammograms simulated for a system undergoing a single-electron transfer (n=1) and a two-electron transfer (n=2), using the same diffusion coefficient D_0=1×10^{-6} cm^2/s and standard rate constant (k_0=0.01 cm/s). The resulting curves exhibit clear and significant differences. The peak current for the two-electron process is noticeably higher and the overall shape of the voltammogram becomes sharper and more defined. This reflects the direct proportionality of peak current to *n*, as described by the Randles–Ševčík equation (8). The increased charge transfer per molecule enhances the current response, an important electrochemical characteristic of two-electron storage systems is the reduced peak-to-peak separation observed in their cyclic voltammograms compared to single-electron processes. In a reversible one-electron transfer, the theoretical peak-to-peak separation (ΔE_p) is approximately 59 mV at room temperature, assuming Nernstian behavior. In contrast, for a concerted two-electron transfer, the peak-to-peak separation is theoretically smaller, approximately 29 mV, due to the transfer of two electrons per redox event occurring at the same redox potential. This results in closer anodic and cathodic peaks and a sharper, more symmetric voltammetric profile, indicating more efficient electron utilization per unit potential change. However, in practice, two-electron processes often proceed via stepwise mechanisms, involving intermediate species. [122]

While idealized models suggest that concerted two-electron transfers exhibit smaller peak-to-peak separations (ΔE_p) due to simultaneous electron transfer at a single potential, real systems often deviate significantly from this behavior. In practice, two-electron transfers usually proceed via two sequential steps, each with its own activation barrier and redox potential. This

stepwise mechanism introduces additional complexity, often resulting in quasi-reversible or even irreversible behavior, especially when the electron transfer kinetics are not fast. Simulated voltammograms demonstrate that the peak separation increases when the second electron transfer is significantly more favorable thermodynamically, leading to two distinct redox waves. Moreover, homogeneous disproportionation reactions involving the intermediate species (e.g., $2B \rightarrow A + C$) can further distort the voltammetric profile, broadening the peaks and complicating analysis. In contrast to the simplistic expectation of reduced peak separation, the simulations also demonstrate a considerable dependence of ΔEp on scan rate and kinetic parameters (k_f, k_b), showing the sensitivity of two-electron systems to both thermodynamic and kinetic factors. [122]

5.4 Results and discussion: Which parameter influences performance of Redox Flow Batteries the most?

The voltammetric simulation figures in COMSOL Multiphysics reveal that among the physicochemical parameters analyzed (the diffusion coefficient D_0 and the electron transfer rate constant k_0), the diffusion coefficient exerts a more visually prominent influence on the shape of the simulated current–potential curves. Specifically, variations in D_0 significantly alter the peak current and the overall morphology of the voltammograms. In contrast, the influence of k_0 within the simulated diffusion-dominated system appears comparatively minimal, with only subtle modifications observed in the voltammetric profiles. However, it is important to contextualize these findings within the operational characteristics of flow batteries. In a typical redox flow battery (RFB), the electrolyte is circulated through the electrochemical cell by means of a pump-driven flow system. This convective transport mechanism substantially mitigates the role of molecular diffusion by enabling controlled and continuous delivery of redox-active species to the electrode surfaces. As a result, the relevance of diffusion-controlled mass transport, which dominates in quiescent (non-flowing) electrochemical systems, becomes significantly diminished. [123]

Consequently, under realistic flow conditions, the electron transfer kinetics characterized by the standard rate constant k_0 emerge as a more critical determinant of cell performance. A higher k_0 facilitates faster electron transfer at the electrode–electrolyte interface, thereby reducing overpotential losses and improving overall energy efficiency. Although it is intuitively correct that redox-active species with high diffusion coefficients would also contribute

positively to performance in a pumped system, their effect is somewhat overshadowed by the convective transport provided by the flow mechanism

In such pump diffusion systems, the standard electron transfer rate constant k_0 becomes a primary performance-limiting factor, particularly at higher current densities. A higher k_0 accelerates interfacial electron transfer, reduces kinetic overpotentials, and improves charge/discharge efficiency. This observation aligns with prior studies which emphasize the central role of kinetics in flow-based systems where convective flow dominates mass transport. [124] Though high diffusion coefficients still contribute positively by smoothing concentration gradients and minimizing reactant depletion zones, their influence is secondary to that of electron transfer kinetics in pump-circulated systems. [125] This distinction also has direct implications for scalability and operational flexibility. Pump diffusion systems offer a modular and scalable architecture, ideal for grid-scale energy storage applications. The ability to dynamically adjust flow rates allows for responsive management of energy demands and fine-tuning of reaction environments, thereby optimizing performance across a range of operating conditions. Conversely, diffusion-dependent systems, which rely on passive transport mechanisms, often suffer from reduced efficiency and limited scalability due to the slower and less controllable movement of electroactive species. While they may benefit from mechanical simplicity and potentially lower maintenance requirements, these advantages are often outweighed by performance constraints in high-demand scenarios. [126]

We can conclude from section **3.6** that number of electrons transferred per redox event shows pronounced impact on performance. The simulations show that transitioning from a one-electron to a two-electron redox process introduces substantial changes in the voltammetric response. In particular, the formation of an intermediate redox species (denoted B), which is prone to homogeneous disproportionation ($2B \rightarrow A + C$), leads to broader, more complex voltammograms. This reaction pathway introduces additional peaks or shoulder features and alters peak current ratios and positions, reflecting a non-trivial redistribution of redox species during the potential sweep. This is due to the presence of intermediate species (e.g., B in $A \rightleftharpoons B \rightleftharpoons C$). The presence of such disproportionation reactions complicates the interpretation of the voltammogram and introduces kinetic and thermodynamic limitations. [122] However, if the two-electron transfer process can be engineered to proceed reversibly, either by stabilizing intermediate species or optimizing reaction conditions, it holds the potential to significantly enhance power density and energy efficiency. In particular, if the second electron transfer is much more thermodynamically favorable, it can shift the redox waves further apart, producing

distinct dual-peak patterns. Multi-electron redox couples inherently offer higher charge storage per mole of active material, making them highly attractive for grid-scale storage applications.

6 Conclusion and Future Directions

6.1 Summary of findings

This thesis investigated the fundamental physicochemical parameters that govern the electrochemical performance of aqueous organic redox flow batteries (AORFBs), with a particular focus on diffusion coefficient (D_0), electron transfer rate constant k_0, and multi-electron redox mechanisms. Through the use of voltammetric simulations performed in COMSOL Multiphysics, it was possible to systematically isolate and analyze the impact of each parameter on the cyclic voltammetric behavior of electroactive species.

In static, diffusion-limited simulations, the diffusion coefficient emerged as the most influential factor shaping the voltammetric response. Increases in D_0 led to notable changes in peak current and overall curve morphology, consistent with the expectations of Fickian diffusion-limited transport. Conversely, alterations in the electron transfer kinetics k_0 within this model induced relatively minor effects, suggesting that under diffusion-dominated conditions, mass transport is the primary bottleneck to electrochemical performance.

However, this trend undergoes a significant reversal under conditions representative of practical flow battery operation, where convective mass transport via pump-driven circulation dominates. In such systems, electrolyte flow is no longer constrained by molecular diffusion, and species are delivered rapidly to the electrode surface. As a result, the influence of the diffusion coefficient diminishes, and electron transfer kinetics become the principal determinant of performance. High k_0 values lead to faster interfacial electron exchange, reduced kinetic overpotentials, and improved charge/discharge efficiency—particularly critical at high current densities typical of grid-scale energy storage applications.

Another major contribution of this work is the exploration of multi-electron redox systems. Simulations showed that the inclusion of a second electron transfer step introduces substantial changes in the voltammetric profile, including broader peaks, multiple redox features, and greater sensitivity to scan rate and kinetic parameters. Unlike single-electron systems, where peak-to-peak separation (ΔEp) is relatively narrow and well-defined, two-electron systems often display complex, quasi-reversible behavior further altering the voltammogram.

Figures included in this thesis provide visual comparisons between single- and multi-electron voltammograms under varying kinetic and thermodynamic conditions. These graphical

analyses help to clearly illustrate the performance-enhancing potential of multi-electron storage systems when designed with optimized k_0, D_0, and redox potential alignment.

The simulation results demonstrated that the magnitude of peak separation and shape complexity in multi-electron systems is influenced by both the standard potentials (E_0) of the two redox steps and the kinetic asymmetry between the forward and reverse rate constants. These insights highlight the importance of balancing redox potential spacing and kinetic rates to achieve both high energy density and favorable reversibility.

Homogeneous side reactions and intermediate species dynamics play a pivotal role in shaping the voltammetric behavior of complex redox systems.

These findings collectively underscore the need for an integrated approach to RFB design that considers molecular properties, reaction kinetics, and system-level engineering to advance the development of high-performance, scalable energy storage solutions.

Table 3. Key Physicochemical Parameters in Redox Flow Batteries (RFBs) and Their Impact on Performance

Parameter	Key Insights from This Study
Solubility	- **Higher solubility → higher energy density** due to increased concentration of active materials. - **Improved cycle stability**, as better-dissolved species minimize precipitation and side reactions. - **Possible trade-offs** with redox potential or chemical stability when modifying molecular structure.
Redox Potential (E^o)	Determines cell voltage and energy density; influences efficiency.
Number of Electrons (n)	Increases theoretical charge storage per molecule; introduces complex voltammetric features due to intermediate species, affects Coulombic efficiency. Two-electron systems show broader peaks, multiple redox waves, and sensitivity to kinetic asymmetry; require careful molecular design to stabilize intermediates
Kinetics: Rate Constant (k_0)	Faster k_0 improves charge/discharge rates and power density. Critical under flow conditions; faster k_0 enhances charge/discharge efficiency, especially at high current densities
Diffusion Coefficient (D_0)	Dominates CV response under diffusion-limited conditions; less influential under convective flow typical of practical RFBs, dominates mostly in static simulations. Higher D_0 reduces concentration polarization, improves electrode utilization, and enhances performance at high current densities.
pH (electrolyte environment)	Alkaline systems exhibit higher cell voltages (up to 1.89 V), greater solubility, and improved ion transport, leading to higher energy densities and efficiencies. Acidic systems enable broader redox couple selection and enhanced stability in certain cases but often operate at lower voltages (~1.6 V). Optimal pH balance or differential pH strategies can enhance overall cell potential and performance.

Table 3. summarizes the key aspects of this literature review. In conclusion, this thesis establishes these aspects that are necessary for the transition from theoretical modeling to practical flow battery operation:

6.2 Practical implications for RFB development

The findings of this study have several significant practical implications for the continued advancement and commercial deployment of Redox Flow Batteries (RFBs) in grid-scale energy storage applications. Although RFBs have several intrinsic benefits, including long cycle life, operational flexibility, and decoupled energy and power scaling, ongoing issues with energy density, cost, system complexity, and material performance have prevented them from being widely used. This thesis provides key insights into how addressing these challenges at the electrochemical and system levels can directly inform design strategies for next-generation RFBs.

One of the central practical challenges in RFB development is the low energy density of current systems, which directly impacts the footprint, capital cost, and feasibility of large-scale installations. The results presented herein demonstrate the substantial benefits of incorporating multi-electron redox-active species, which can significantly enhance the volumetric energy density of electrolytes by increasing the number of charges stored per molecule. However, realizing this advantage in practice requires overcoming kinetic and mechanistic limitations, including the stabilization of intermediate species and the suppression of undesirable homogeneous reactions such as disproportionation. Thus, the rational molecular design of redox-active compounds with optimized redox potential spacing, high solubility, fast electron transfer kinetics k_0 and electrochemical reversibility—represents a critical research direction for improving energy density without sacrificing performance or longevity.

In addition to material innovations, system-level engineering improvements are essential. Optimization of flow fields, stack design, and electrode architecture can greatly enhance mass transport, current distribution, and electrolyte utilization, ultimately improving power density and round-trip efficiency. As highlighted in the simulations, diffusion plays a minor role under flow-assisted conditions, underscoring the importance of fluid dynamics and flow cell optimization in practical applications. Tailoring flow rates and minimizing pressure losses can contribute to reduced parasitic energy consumption, lower operational costs, and improved system scalability.

Another key implication concerns cost reduction, particularly in the context of materials sourcing and system integration. Employing earth-abundant elements and designing ligands or supporting electrolytes from inexpensive, readily available feedstocks can help reduce the capital expenditure associated with electrolyte formulation. Additionally, solid-liquid hybrid

storage approaches, where redox-active materials are immobilized or suspended—have emerged as a promising strategy for increasing energy density and reducing costs related to large tank volumes and fluid handling infrastructure. From a manufacturing perspective, improving the reproducibility and scalability of redox-active molecule synthesis remains a major challenge. Robust synthetic routes that can be translated from lab to pilot scale with minimal purification steps and high yields are essential. Similarly, advances in testing protocols and diagnostic tools will be critical for accurate characterization of kinetic parameters, long-term cycling behavior, and degradation mechanisms. These tools can support more informed material selection and system diagnostics, ultimately improving battery reliability and safety.

Furthermore, the integration of RFBs with renewable energy sources such as wind and solar power presents a compelling use case due to their ability to provide long-duration energy storage and smooth fluctuations in power generation. However, this requires improving not only energy and power density but also the cycle life and efficiency of storage systems under variable operating conditions. Enhancements in electrolyte stability, membrane durability, and corrosion resistance of hardware components are essential to reduce maintenance requirements and extend service life.

Addressing the life-cycle costs and environmental footprint of RFB systems is necessary for their sustainable deployment. This includes not only reducing upfront capital costs but also minimizing operational and end-of-life impacts through recyclable components, low-toxicity formulations, and energy-efficient production methods.

In conclusion, the practical implications of this thesis extend across molecular design, system architecture, manufacturing, and deployment strategies. By advancing the understanding of how electrochemical parameters such as k0, D_0, and redox mechanism influence performance, this work contributes to the foundation upon which next-generation RFBs can be engineered to meet the demands of cost-effective, efficient, and durable energy storage for renewable integration and grid stability.

6.3 Recommendations for future research in organic negolytes and RFB technology

To further advance the development of organic redox flow batteries (ORFBs) and facilitate their transition from laboratory-scale systems to commercially viable energy storage technologies, several strategic research directions are recommended. These recommendations span molecular

design, electrolyte formulation, system architecture, and fundamental electrochemical understanding—each of which is critical for improving the energy density, power density, efficiency, and operational longevity of ORFB systems.

First and foremost, the development of robust redox-active molecules and electrolytes remains a foundational requirement for achieving high-performance ORFBs. Ideal redox-active organic compounds should exhibit a combination of properties that directly enhance all major performance metrics: high solubility (to improve volumetric capacity and energy density), highly positive or negative redox potentials (to expand cell voltage and thereby energy and power densities), fast electron-transfer kinetics $k0$ (to enable efficient operation under high current densities), excellent electrochemical and chemical stability (to prolong cycling lifetime), and low production cost (to enhance commercial viability). Achieving this multifaceted optimization demands an integrative approach that combines density functional theory (DFT) screening as introduced in section **3.3**, physical organic chemistry, and targeted molecular engineering to design and validate novel candidates with desirable electrochemical characteristics.

In addition to redox-active species, future research must focus on the development of highly conductive, low-viscosity, noncorrosive, nonflammable, and environmentally benign electrolytes. These properties are critical for ensuring operational safety, lowering system resistance, and minimizing maintenance requirements in large-scale systems. The synergistic optimization of redox molecules and supporting electrolytes; taking into account solubility, compatibility, ion conductivity, and viscosity will be necessary to meet the stringent requirements of high-performance ORFBs, particularly in nonaqueous and alkaline environments where stability windows and compatibility can pose significant challenges.

Second, a deeper understanding of the solution chemistry and electrochemical behavior of redox-active organic molecules is essential. This includes their redox mechanisms, degradation pathways, and interactions with electrolyte components. Rigorous half-cell testing remains a powerful method for rapidly assessing the intrinsic stability of redox-active materials, with post-cycling analyses providing mechanistic insights into capacity fading and degradation. Complementary to these experimental approaches, DFT calculations and computational electrochemistry offer predictive tools for elucidating electronic structure, redox potential trends, solvation effects, and reaction energetics—guiding the rational design of new redox-active candidates with improved performance.

A significant limitation for ORFBs, discussed in section **4.1** is that particularly in nonaqueous setups, is the migration of active materials through the membrane or separator, resulting in charge imbalance and capacity degradation. Therefore, the development of highly selective, ion-conductive membranes is an urgent priority. [104] Such membranes must demonstrate excellent selectivity to ionic species while minimizing the permeation of active redox molecules, particularly under long-term operation and repeated cycling. Advances in membrane technology will play a decisive role in enhancing coulombic efficiency, preserving electrolyte integrity, and enabling the use of more diverse redox chemistries.

Moreover, the design of flow cell architecture and electrode configuration warrants further investigation. While various cell designs have been proposed, there remains a lack of systematic, parallel evaluations to determine how electrode geometry, porosity, and catalytic activity affect key performance metrics such as energy efficiency, power density, and rate capability. Future research should aim to establish standardized testing protocols and comparative studies to enable more reliable benchmarking of different flow battery configurations.

Organic redox materials also offer substantial technological advantages over their inorganic counterparts. These include an unparalleled molecular design space, tunable physicochemical properties, and the potential for lower environmental and economic costs due to synthetic accessibility and sustainability. [127] However, it is important to note that inorganic redox couples, such as $FeCl_2$ or $ZnBr_2$, continue to offer cost-effective, scalable solutions and should not be overlooked in the broader context of RFB development.

Recent progress in weakly alkaline aqueous ORFBs (AORFBs) suggests promising avenues for further exploration. These systems benefit from enhanced stability windows and reduced material degradation but currently lack suitable catholytes to fully exploit their potential. The development of compatible and reversible catholytes for alkaline media could enable high-performance AORFBs with improved efficiency and cycling life.

Finally, the integration of RFBs with renewable energy systems, particularly photovoltaic (PV) technologies, presents a promising opportunity for sustainable energy harvesting and storage. Notably, certain AORFB and aqueous iron-based RFB (AIRFB) chemistries have already been

integrated with solar cells, offering a pathway toward direct solar energy storage in a modular and scalable form.

In conclusion, the future of ORFB technology hinges on interdisciplinary innovation across organic synthesis, electrochemistry, materials science, and system engineering. Through targeted research and coordinated development efforts, ORFBs hold the potential to become a cornerstone of next-generation grid-scale energy storage systems, capable of meeting the demands of a low-carbon, renewable-powered energy infrastructure.

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8 Appendices

Author Declaration on the Use of AI Tools

The use of AI tools in the preparation of this thesis was limited strictly to language refinement, including sentence restructuring, formatting, and reduction of redundancy. All conceptual development, analysis, and literature synthesis are solely the work of the author.