1.1 Introduction

The steady shift away from traditional fossil-fuel electricity generation in order to reduce greenhouse gas emissions has led to the growth of electricity generation from renewable energy sources as sustainable and clean alternatives.\textsuperscript{1} Especially, energy harvested from the wind and sun by matured technologies such as wind turbines and solar cells, respectively, have achieved considerable success in both implementation and commercialization.\textsuperscript{2} However, due to the intermittent and variable nature of these energy sources, the integration of renewables into the electrical grid remains limited.

The incorporation of large-scale energy storage has been identified to be of critical value to the implementation of renewables.\textsuperscript{3, 4} Energy storage is a potentially worthwhile method in providing a solution to the existing issues, improving the overall efficiency and reliability of the grid, as well as balancing the mismatch between supply and demand. A major storage classification is the Electrical Energy Storage (EES).\textsuperscript{5} EES consists of storage types that convert electricity into another form of energy, such as mechanical, electrical or electrochemical energy, and restores the energy into electricity on demand. Commercially mature technologies such as the flywheel, compressed air energy storage and hydroelectricity pumped-storage are examples of mechanical storage in which electricity is stored as kinetic or potential energy with high power ratings (> 1 MW). The second type, electrical energy storage, is predominantly based on supercapacitor technologies suitable for low energy density storage within short time periods. Last but not least, electricity can be stored using electrochemical technologies such as the secondary (rechargeable) battery, regenerative fuel cells and redox flow batteries (RFBs). In particular, RFBs are a leading candidate for large-scale energy storage and have gained increased levels of research interest because of numerous interesting features such as high efficiency, simple design, and capability to endure fluctuating power supply.\textsuperscript{6-9}

1.2 Redox flow battery technology

In an RFB, electrical energy is stored as chemical energy in the negolyte and posolyte fluids containing solvated redox-active molecules (shown schematically in Figure 1). Conventionally, RFBs are divided in two classes based on the type of electrolyte used, being either aqueous or non-aqueous solutions. During the charging of a RFB, the negolyte and posolyte fluids are passed over electrodes during which the redox-active molecules undergo an electrochemical reaction, namely a reduction and an oxidation, respectively. During discharging the flow of electrons is reversed and now the reduction is takes place in the posolyte and the oxidation in the negolyte. Inside the battery, the electrolytes are physically separated by a membrane which allows the penetration of charge-balancing ions.\textsuperscript{10-12} The perfluorosulfonated cation-exchange membrane, Nafion, has found tremendous application in early RFBs based on aqueous electrolytes, due to its
chemical stability and high proton conductivity. More recently, anion-exchange membranes, such as Fumasep and Neosepta, originating from water treatment technologies, have been successfully adopted in both aqueous and non-aqueous RFB systems. Another class of electrolyte separators are the commercial porous membranes, Daramic and Celgard, showing effective separation of the charge-storage material based on pore size exclusion.

Figure 1: Schematic depiction of the structure of a redox flow battery.

A prominent advantage of redox flow battery technology over other battery technologies is the decoupling of energy and power. After charging/discharging, the electrolytes are stored separately in two external tanks. The total energy output (battery capacity) depends on the volume of these reservoirs and can easily be increased by increasing the volume. Separately, the total power output can be altered by changing the area of the active surface of the electrodes. Together with the modular and flexible design of the RFB, it can be used for a wide range of applications, ranging from household storage to large-scale utility storage.

The performance of RFBs can be evaluated by several key parameters, namely the energy density, the capacity decay rate, the coulombic efficiency and energy efficiency. The energy density is determined by the energy output per unit volume of the total electrolyte of the system and depends predominantly on the (maximum) concentration of the active species in solution. The capacity decay rate is a measure of the (discharge) capacity fade in percentage per day and is an indication of battery degradation over time. Furthermore, the coulombic efficiency is determined by dividing the discharge output of the battery by the charge that was put in the battery. In principle, a coulombic efficiency of less than 100% indicates the presence of decay mechanisms occurring during battery operation. Lastly, the energy efficiency is expressed as the ratio of the time-integrated power output over
the power input during discharging and charging, respectively, at a specific current density.

The predominant degradation pathways known to cause battery capacity fade are cross-contamination of electrolytes, self-decomposition of charge-storage material, side reactions of the electrolyte, and electrode passivation.\textsuperscript{19} Degradation can occur both in ‘active’ state during battery operation and in the ‘resting’ state when no current or potential is applied to the system. Cross-contamination of electrolytes occurs when posolyte-active species migrate through the membrane and mix with the negolyte-active species, and vice-versa, leading to self-discharge of the battery, reduced coulombic efficiency and permanent capacity loss.\textsuperscript{20} Self-decomposition of the active species is a result of their intrinsic instability and is the predominant cause for capacity fade observed in RFBs consisting of organic redox-active material.\textsuperscript{19} This intrinsic instability, usually in the charged states, make the organic species prone to nucleophilic attack, disproportionation, tautomerization and/or polymerization which generally leads to irreversible losses. However, in some cases the redox-active species can be rejuvenated by either electrochemical regeneration\textsuperscript{21} or by aeration of the electrolyte.\textsuperscript{22} Side reactions of the electrolyte solvent are a major challenge for RFB based on aqueous electrolytes.\textsuperscript{23} Hydrogen evolution and oxygen evolution reactions are the main cause for solvent decomposition leading to capacity imbalances and pH fluctuations, especially for active species that have redox processes beyond the water-splitting potentials. Finally, for solid-hybrid RFBs, electrode passivation and dendrite formation are dominant causes for capacity decay and in some cases complete battery failure.\textsuperscript{24}

1.3 Metal-based RFBs

1.3.1 Early RFBs

One of the earliest redox flow batteries was developed at the National Aeronautics and Space Administration by Thaller in the ‘70s.\textsuperscript{25} The system utilized two metal redox couples Cr\textsuperscript{3+}/Cr\textsuperscript{2+} and Fe\textsuperscript{2+/3+} as the posolyte and negolyte, respectively, leading to a working voltage of 1.18 V. However, commercialization was frustrated due to major drawbacks such as high working temperature, poor electrochemical activity of the chromic/chromous couple and dramatic capacity decay caused by cross-contamination. During the next decades several other RFBs were developed with as prime example the all-vanadium RFB (VRFB) developed by Skyllas-Kazacos and coworkers.\textsuperscript{26-29} Interestingly, in these VRFBs the redox-active material in both electrolytes consists exclusively of vanadium sulfate salts. One half-cell electrolyte consists of a V\textsuperscript{2+/3+} redox couple and the other electrolyte of a VO\textsuperscript{2+/3+} redox couple, both in highly acidic solutions, leading to a cell voltage of 1.26 V. The implementation of a single-metal system for both sides of the battery diminishes the problem of irreversible degradation associated with physical crossover of the redox active material. However, due to the cationic redox-active species in these VRFBs, crossover through the proton exchange membrane separators is still a prominent dilemma leading to self-discharge of the battery.\textsuperscript{30} Although, currently
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the most wide-spread commercial RFB technology, further development of VRFBs has been hindered by limitations such as low energy density, high-cost of the ion-exchange membrane and the scarcity of vanadium. Another prominent class of flow batteries are the zinc-based hybrid RFBs. These batteries rely on the electrodeposition of a zinc-based negolyte, usually coupled with the redox processes of an organic or inorganic posolyte-active species, such as benzoquinone or bromine. Due to the low cost of zinc metal and the high energy densities of zinc-based systems, several of these hybrid flow batteries have been scaled up and commercialized. Although, large-scale implementation of this battery technology has been frustrated by poor battery lifetime due to zinc dendrite formation and other parasitic reaction.

1.3.2 Metal coordination complexes

Commercial RFBs, such as the VRFB, store electrical energy in aqueous electrolytes containing inorganic metal salts. The energy densities of these aqueous RFBs (ARFBs) are inherently limited by the narrow (1.23 V) electrochemical window of water. Instead, electrolytes based on non-aqueous solvents, which have significantly wider (>3 V) stability windows, could significantly increase the energy density of RFBs. The application of non-aqueous solvents, such as acetonitrile and dimethylformamide, containing metal complexes bearing organic ligands for battery purposes was first suggested by Singh in 1984. Over the last couple of decades, several research groups have reported the use of metal coordination complexes (MCCs) as charge-storage material with large cell voltages (>2 V) for non-aqueous RFBs (NARFB). The solubility of metal salts increases dramatically upon binding with simple organic ligands, such as bipyridine (bpy) and acetylacetonate (acac). Furthermore, it opens up the possibility for fine-tuning of the electrochemical properties of the charge-storage material by careful design of the ligand. The first example of an MCC as active species for NARFBs was reported in 1988 by Matsuda et al., who studied the stability of [Ru(bpy)_3]^{2+} in acetonitrile under flow cell cycling (Scheme 1). By using a symmetric setup both the oxidation and reduction processes of the [Ru(bpy)_3]^{2+} were exploited leading to a cell voltage of 2.6 V, which is significantly higher than the usual 1.26 V for VRFBs. However, poor coulombic efficiencies were observed due to chemical instability of the reduced species [Ru(bpy)_3]^{1+} and other side reactions occurring during charging. More recently, bipyridine complexes bearing more earth-abundant metals, like Fe, Ni and Co, were reported as active species for NARFBs showing decent coulombic efficiencies although significant capacity fade during cycling.
Another type of MCC which has been studied for its use as charge-storage material for ARFBs, are the \([\text{M(acac)}_3]\) complexes with a wide variety of metals such as \(\text{V}^{40}\), \(\text{Cr}^{41}\), \(\text{Mn}^{42}\), \(\text{Ru}^{43}\), \(\text{Fe}^{44}\) (Scheme 1). Unlike the bipyridine-based MCCs, the acetylacetonate-based complexes species are neutral in discharged state and thus show superior solubility in non-aqueous solvents. Despite the high solubility, most \([\text{M(acac)}_3]\) suffer from poor stability and low energy efficiencies during cycling. Cappillino et al. reported a battery study on the anionic vanadium complex \([\text{V(mnt)}_3]^{2-}\) bearing redox non-innocent dithiolene ligands (Scheme 1).\(^4\) The active material showed decent coulombic efficiencies however suffered from significant overpotentials as a result of high resistance in the static H-cell battery. Recently, Hogue et al. revisited the \([\text{V(mnt)}_3]^{2-}\) system and reported improved efficiencies by performing cycling studies in flow. In addition to that, several other metals were tested, such as \(\text{Fe}\), \(\text{Co}\), \(\text{Ni}\) and \(\text{Cu}\), showing comparable flow battery performances.\(^5\)

### 1.3.3 Ferrocene

Iron is one of the most abundant elements in the earth’s crust and relatively inexpensive in comparison to vanadium and zinc. The metal is highly suitable for cheap large-scale storage applications, both when implemented in the solid state and as solubilized material.\(^6\) Ferrocene, an organometallic compound, is well-known for its use as a quasi-reference material in electrochemical measurements due to highly reversible redox chemistry.\(^7\) Reversible oxidation of ferrocene occurs...
at potentials around ~0.7 V vs standard hydrogen electrode (SHE) depending on the solvent and supporting electrolyte. Hence, researchers have shown increased interest in applying ferrocene (and derivatives) as charge-storage material in both aqueous and non-aqueous battery systems. However, because of the limited solubility in aqueous media, initial focus was aimed toward the use of ferrocene in nonaqueous electrolytes.\textsuperscript{49-53} The first battery cycling study of ferrocene (and other metallocenes) was reported by Hwang \textit{et al.}, who observed decent stability over three cycles with cell potentials around 1.2 V.\textsuperscript{49} Furthermore, simple modification of the cyclopentadienyl rings resulted in significantly increased cell voltages up to 2.2 V. Extended cycling studies were reported by Ding \textit{et al.} with capacity retention over 99\% per cycle in dimethylformamide, highlighting the long-term storage capabilities of ferrocene.\textsuperscript{50} Recently, the group of Toghill revisited the ferrocene/ferrocenium redox couple as model chemistry for NARFB research (Figure 2).\textsuperscript{51}

Battery cycling studies were performed in a single redox couple configuration, in which the negolyte and posolyte contain ferrocene and ferrocenium tetrafluoroborate, respectively. With this battery configuration the cycling of only the ferrocene/ferrocenium redox couple can be studied, without the need for additional redox materials, severely decreasing the complexity of the system. Strictly speaking, a flow cell with a single redox couple configuration is not a battery as it is not capable of storing energy and should only be used as a model system for evaluating electrochemical performance.
After battery cycling of the single redox couple flow cell for over 7 days in acetonitrile, about 80% of the initial capacity was retained. A systematic study was performed to investigate the mechanism of capacity fade. After careful examination the authors concluded that chemical decomposition of the oxidized species, most likely caused by reaction with trace oxygen, solvent or supporting electrolyte salt, was the predominant cause of the capacity fade.

The reversible oxidation of ferrocene occurs within the electrochemical window of water, making it suitable for implementation in aqueous storage systems. However, the application of ferrocene active species in ARFBs has been rather limited due to its poor water solubility. Hydrophilic groups, like sulfonates and quaternary ammonium ions, can be attached to the cyclopentadienyl rings to improve the solubility in water. Several of these water-soluble ferrocene derivatives have been tested in a flow regime. Because of the high stability of the ferrocene/ferrocenium redox couple in both aqueous and nonaqueous electrolytes, the redox couple is often paired with organic redox-active material for use in semi-organic RFBs. Another iron-containing active species which is widely used in (semi-organic) RFB systems is ferrocyanide, owing to its high chemical stability and excellent solubility in aqueous electrolytes.

1.4 (All) organic RFBs

The overall cost of RFBs depend not only on the cell components, such as the membrane and electrodes, but predominantly on the price of the active species. Various promising metal-based redox chemistries have been developed for both aqueous and non-aqueous RFBs. Some systems, like the VRFB and zinc-based hybrid RFB, have reached the stage of commercialization, however, the capital costs of these systems remain too high for deep market penetration. This is mainly due to low solubility and high molar mass of the electroactive material. In order to address the challenges facing RFB development, several research groups have highlighted the use of electrolytes based on inexpensive and sustainable redox-active organic material. Most redox-active organic material (ROM) consist of carbon, nitrogen, oxygen and hydrogen, which are all earth-abundant elements, making them relatively sustainable and cost-efficient material. Furthermore, the synthetic tunability of ROMs for altering chemical stability, electrochemical properties and solubility make them highly attractive alternative energy materials for high energy density organic RFBs (ORFBs).

1.4.1 Non-aqueous ORFBs

Non-aqueous solvents, such as acetonitrile, dimethylformamide and cyclic carbonates, offer a wider window of electrochemical stability than water. Hence, these non-aqueous ORFBs (NAORFBs) have the ability to operate at higher cell voltages. Some drawbacks associated with the use of non-aqueous solvents are higher costs, lower ionic conductivities, toxicity and flammability. Most commonly, two different redox-active materials are used as charge-storage materials, one
dissolved in the negolyte and the other in the posolyte. In 2011, Li et al. were the first to demonstrate a non-aqueous ORFB (NAORFB) consisting of two ROMs as charge-storage materials. The posolyte-active 2,2,6,6-tetramethylpiperidinyloxy (TEMPO) radical was used in combination with the negolyte-active N-methylphthalamide which resulted in a theoretical cell voltage of 1.6 V in acetonitrile. During charging, oxidation of the nitroxide radical to the oxoammonium cation occurs concurrently with the reduction of N-methylphthalamide to the corresponding radical anion, and with their reverse reactions taking place during the discharge (Scheme 2). Stable cycling was observed for 20 charge/discharge cycles with coulombic efficiencies exceeding 90%, demonstrating ROMs to be promising active materials for the application in ORFBs.

Inspired by the pioneering work of Li et al., many other ROMs were developed and tested for application as charge-storage materials in NAORFBs. Aside from TEMPO, other common posolyte-active materials that have been implemented in NAORFBs are phenothiazines, dialkoxybenzenes, and cyclopropenium derivatives. To facilitate the negative half-reaction of NAORFBs, a number of negolyte-active materials have been developed, including phthalimides, pyridinium derivatives, fluorenones, and quinoxalines. The general chemical structures of these ROMs are depicted in Scheme 3.

**Scheme 2**: Redox processes of TEMPO (posolyte) and N-methylphthalamide (negolyte).
Scheme 3: Common posolyte-active and negolyte-active materials for non-aqueous ORFBs.

Recently, azobenzenes were reported as a promising class of organic negolytes for non-aqueous storage applications, achieving low-potential reduction processes, high solubilities (>4 M in common organic solvents), and excellent chemical stability.89, 90 Zhang and coworkers identified the optimal electrolyte composition of azobenzene, lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) dissolved in dimethylformamide for a high energy density NAORFB (Figure 3).89 A RFB was constructed with 1.0 M azobenzene and cycled for over 100 days (~100 cycles) with only 0.16% capacity loss per day, showing the great potential of azobenzenes as ROMs for next-generation NAORFBs.

Figure 3: (top) Structure of azobenzene and its reversible reduction process. (left) Cyclic voltammogram of azobenzene in LiTFSI/DMF. (right) Discharge capacities and cycling efficiencies for each cycle of a RFB with 1.0 M azobenzene in 1.0 M LiTFSI/DMF. Adapted from Zhang et al.,89 with permission from the Springer Nature.
1.4.2 Aqueous ORFBs

In comparison to most organic solvents, water is very cheap, earth-abundant and non-toxic. These characteristics make aqueous RFBs a potentially safe and cost-effective technology for grid scale storage applications. During the last decade, the development of organic charge-storage material for aqueous ORFBs (AORFBs) has grown tremendously.\textsuperscript{91, 92} However, the solubility of these organic redox-active material is usually a major obstacle, leading to low energy densities. A common strategy to obtain water soluble electroactive organic compounds is to introduce hydrophilic groups such as -OH, -NMe\textsubscript{3}+ and -SO\textsubscript{3}.\textsuperscript{93, 94} Also in AORFBs, the TEMPO radical finds great utilization as posolyte-active material, as it displays an electrochemically reversible oxidation close to the potential limit of water in neutral aqueous media paired with fast reaction kinetics.\textsuperscript{95-104} Another common class of ROMs used to facilitate the positive electrode reaction are the hydroquinones, due to their reversible two-electron oxidation processes.\textsuperscript{105-108} On the negative side of the battery, predominantly viologen\textsuperscript{109-113}, (anthra)quinone\textsuperscript{114-122}, and alloxazine\textsuperscript{123, 124} redox-active species are implemented as these molecules show highly reversible reduction chemistry with excellent cycling stability. The general chemical structures of these ROMs are depicted in Scheme 4.

Scheme 4: Common posolyte-active and negolyte-active materials for aqueous ORFBs.

In 2015, the Aziz group reported the use of 2,6-dihydroxyanthraquinone (2,6-DHAQ) as negolyte-active material.\textsuperscript{125} The organic molecule exhibited a reasonable solubility of 0.6 M in KOH solution at pH 14. Battery cycling was performed with negolyte consisting of 0.5 M 2,6-DHAQ dipotassium salt and posolyte with 0.4 M ferrocyanide, both dissolved in 1 M KOH. With an open-circuit voltage (OCV) of 1.2 V, the RFB showed excellent battery performance, with coulombic efficiencies exceeding 99% and energy efficiencies at 84%. Due to electrolyte leakage from the system, a continuous capacity loss of 0.1% per cycle was observed during cycling. A couple of years later, the Aziz group revisited their system and developed a 2,6-DHAQ derivative that included highly solubilizing...
carboxylate functional groups.\textsuperscript{126} The functionalized anthraquinone 2,6-DBEAQ exhibited improved solubility of up to six times in KOH solution at pH 14. Moreover, cycling studies in a single redox couple configuration, in which the negolyte and posolyte both contain 0.65 M 2,6-DBEAQ (at 50% SOC), demonstrated a capacity fade rate of less than 0.01% per day (Figure 4), highlighting the potential of quinone-based RFBs for commercial implementation.

\begin{figure}
\centering
\includegraphics[width=0.5\textwidth]{figure4.png}
\caption{Charge and discharge capacities for each cycle of an volumetrically unbalanced RFB in a single redox couple configuration with 0.65 M 2,6-DBEAQ (at 50\% SOC) in KOH (aq.) at pH 14. Reproduced from Kwabi et al.,\textsuperscript{126} with permission from Elsevier.}
\end{figure}
1.5 Symmetric ORFBs

Despite many great developments in the field of organic redox flow batteries, most batteries still suffer from two major issues: degradation and/or cross-contamination of the redox active material. These phenomena can occur both during charging and discharging cycles, but also in the “resting state” of the battery. To address the complications due to cross-contamination of electrolytes, research groups have focussed their interest on the development of symmetric ORFBs (SORFBs). The term “symmetric” implies that the RFB consist of one single parent molecule that can be both reversibly reduced and oxidized to facilitate the negative and positive electrode half-reactions, respectively. In a recent article by Potash et al., the authors elegantly explain with the help of simulations the key advantages of a symmetric RFB over a conventional RFB. Two of these simulations concerning the capacity retention are shown in Figure 5. Both simulations include some mechanism of capacity loss: (a) irreversible degradation of 0.1% of electrolyte per cycle and (b) physical crossover losses where one fifth of one of the electrolytes migrates to the other compartment.

![Figure 5](image-url)

Figure 5: Simulated cycling data for a conventional RFB and a symmetric RFB with the cell polarity reversed every 20 cycles. Two mechanisms of capacity loss are simulated: (a) irreversible degradation of the electrolyte; (b) physical crossover losses. Reproduced from Potash et al., with permission from ECS.

From both figures it can be derived that by the implementation of a symmetric system, with inversion of cell polarity every number of cycles, the lifetime of a
battery can be significantly increased. Especially in the case of physical crossover there are virtually no losses in capacity as crossover of the redox-active species merely leads to self-discharge by (clean) comproportionation and not to degradation. Hence, the implementation of a single bipolar organic material as a charge-storage material in a RFB has critical advantages over the use of two compounds, for instance the simplified flow cell design (as the same material is used in both cell compartments), the significantly reduced synthesis effort and the prevention of long-term capacity decay by providing a solution to the problematic cross-contamination of electrolyte.

There are two main strategies known in literature for the design of bipolar charge-storage material: (1) Combining known negolyte-active and posolyte-active species by a covalent bridge, electrostatic interactions or by the formation of eutectic mixtures. (2) Designing and synthesizing organic compounds which have multiple stable oxidation states.

1.5.1 Covalently bridged acceptor-donor molecules

Early examples of covalently bridged bipolar organic molecules are the so-called “combi-molecules” studied in aqueous electrolytes by Schubert and coworkers.\textsuperscript{128,129} These combi-molecules contain both a posolyte-active TEMPO and a negolyte-active phenazine or viologen functional group, tethered by an insulating linker, shown in Scheme 5 as I and II, respectively. Both systems operated with a cell voltage of approximately 1.2 V and showed decent capacity retention during cycling, but both suffered greatly from very low energy density due to limited solubility in water. However, these combi-molecules can be seen as pioneers on the pathway toward bipolar organic alternatives to the all-vanadium RFBs.

![Scheme 5: Combi-molecules for symmetric aqueous RFBs.\textsuperscript{128-130}]

More recently, Nambafu \textit{et al.} introduced a new combi-molecule based on the commercially available riboflavin, better known as vitamin B, and a TEMPO radical (III).\textsuperscript{130} With a theoretical cell voltage of 1.23 V and decent solubility (> 1M) in aqueous electrolyte, the combi-molecule was tested in a flow setup. Unfortunately, all long-term cycling experiments showed severe capacity fade which the authors
attributed to the decomposition of the posolyte-active TEMPO moiety of the combi-
molecule.

Inspired by the early work of the Schubert group, quite a number of combi-
molecules have been reported for use in symmetric non-aqueous RFBs. Very
recently, Shao and coworkers synthesized a combi-molecule PDI-TEMPO based
on two TEMPO radicals attached to pyromellitic dianhydride (Figure 6). The
combi-molecule displayed two quasi-reversible one-electron reduction processes
and a single two-electron oxidation process resulting in a theoretical cell voltage of
2.17 V in acetonitrile. A symmetric RFB consisting of 0.5 M PDI-TEMPO in
[Bu₄N][PF₆]/acetonitrile was evaluated over 100 cycles, demonstrating high
coulombic efficiencies above 90%. Although, capacity decay during cycling due to
degradation of the charged species in the negolyte appeared to be a major issue.

Figure 6: (top) Structure of PDI-TEMPO and its reversible bipolar electrochemistry. (left) Cyclic
voltammogram of PDI-TEMPO in [Bu₄N][PF₆]/acetonitrile. (right) Charge and discharge capacities and
cycling efficiencies for each cycle of a symmetric RFB with 0.5 M PDI-TEMPO in 1.0 M
[Bu₄N][PF₆]/acetonitrile. Adapted from Nambafu et al., with permission from the Elsevier.

1.5.2 Ionic compounds & eutectic mixtures

Another approach is the use of bipolar ionic compounds as active species, in which
two redox-active ionic species are bound by electrostatic interactions. To the best
of my knowledge, two bipolar ionic species are known in literature and are both
based on viologen diiodide salts (Scheme 6). Liu et al. reported the
application of N,N'-dimethyl-4,4-bipyridinium diiodide (IV) as bipolar active material
for symmetric aqueous ORFBs. In this system, the reversible reduction of
viologen and reversible oxidation of iodide facilitate the negative and positive
electrode half-reactions, respectively, leading to a theoretical cell voltage of 1.02 V.
Long-term cycling of a flow battery containing 0.1 M IV in aqueous sodium chloride
electrolyte showed very high capacity retention of nearly 99% after 100 cycles.
Similarly, Zhao and coworkers studied the battery performance of a mono-N-
alkylated bipyridinium iodide salt (V). The bipolar ionic compound, aside from its
use as both negolyte and posolyte material, also served as the supporting
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electrolyte. The authors were able to construct a symmetric flow battery consisting solely of $\text{V}$ dissolved in water, which operated at an OCV of 1.2 V. Unfortunately, the flow battery showed quite severe capacity fade due to electrode passivation caused by iodine deposition on the electrode surface. Cunningly, the authors were able to fully recover the battery capacity by regularly installing new carbon electrodes.

Scheme 6: Bipolar electrolytes based on ionic salts of viologen diiodide derivatives and on eutectic mixtures of 1,1-dimethylferrocene and $N$-butylphthalamide.$^{139-141}$

A newly emerging strategy is the use of bipolar eutectic electrolytes as charge-storage material for symmetric RFB systems. Zhang et al. reported the formation of eutectic electrolytes by physically mixing $N$-butylphthalamide and 1,1-dimethylferrocene in a 1:1 ratio (VI in Scheme x).$^{141}$ The eutectic mixture enabled a high concentration (up to 3.5 M) of both redox-active material with a theoretical cell voltage of 1.8 V based on cyclic voltammetry. The battery performance of VI was evaluated at 0.1 M concentration in acetonitrile in a flow regime. With a capacity retention of approximately 72% of the initial value after 500 cycles, the authors demonstrated that eutectic mixtures offer both high energy densities as well as stable cycling.

1.5.3 Stable organic radicals

Several strategies for the design of bipolar charge-storage material have been discussed so far. A major disadvantage of these designs, which utilize combimolecules, bipolar ionic compounds or eutectic mixtures, is that theoretically only 50% of the active material at either side of the battery can be used during cycling. On the other hand, the use of intrinsically bipolar material allows for the use of all electroactive material in solution. Organic radicals have been identified as intrinsically bipolar material, as the singly occupied molecular orbital (SOMO) of the organic radical allows for both reduction and oxidation processes to occur within the same organic framework. However, many organic radicals have very short lifetimes as the unpaired electron make them highly reactive, with dimerization being the most common pathway of degradation.$^{142, 143}$ There are several factors that influence the stability of organic radicals: the presence of electron-donating and -withdrawing groups (captodative effect), delocalization of the unpaired electron, and steric hindrance around the radical center.$^{144}$ An organic radical that combines all three factors is the 2-phenyl-4,4,5,5-tetramethylimidazoline-1-oxyl-3-oxide (PTIO). In 2016, Duan et al. reported the use of this highly stable nitronyl nitroxide radical as bipolar redox material for symmetric non-aqueous flow batteries.
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Cyclic voltammetry demonstrated the excellent electrochemical reversibility of PTIO featuring a theoretical cell voltage of 1.73 V. However, galvanostatic cycling of a symmetric RFB with 0.5 M PTIO exhibited severe capacity decay, most likely caused by decomposition of the charged species.

![Figure 7](image1.png)

Figure 7: (top) Structure of PTIO and its reversible bipolar electrochemistry. (left) Cyclic voltammogram of PTIO at 100 mV/s. (right) Charge and discharge capacities and cycling efficiencies for each cycle of a symmetric RFB with 0.5 M PTIO in 1.0 M [Bu4N][PF6]/acetonitrile. Adapted from Duan et al.,145 with permission from the Royal Society of Chemistry.

Another prime example of a bipolar organic radical as charge-storage material is the benzoyl pyridine radical studied by the group of Sanford (Figure 8).146 Initial test showed quite severe degradation of the redox-active species. However, by systematic evaluation of the supporting electrolyte the lifetime of the redox-active species was substantially increased. As a result, the authors were able to cycle through both the oxidation and reduction of the radical in a symmetric flow cell for more than a hundred cycles without any detectable decay.
Figure 8: (top) Normalized charge and discharges capacity for each cycle with various supporting electrolytes in acetonitrile. (bottom) Charge and discharge capacities for each cycle of a symmetric RFB with 100 mM active material concentration. Adapted from Hendriks et al.,146 with permission from American Chemical Society.

A promising class of bipolar redox-active charge-storage materials for symmetric RFBs are the verdazyl radicals. Verdazyls are a family of neutral radicals that are air- and water-stable, sterically unprotected, and resistant toward dimerization.147-149 Electrochemical studies have shown that these radicals can be reversibly reduced and oxidized (Scheme 7)150-153 Furthermore, the electrochemical properties of this class of radicals can be easily be tuned by introduction of electron-donating and withdrawing groups.

Scheme 7: Reversible reduction and oxidation of verdazyl radicals.

Recently, the Charlton et al. reported a study on the 3-phenyl-1,5-di-p-tolyverdazyl radical as a possible bipolar redox-active material for symmetric RFBs.154 Cyclic
voltammetry studies in acetonitrile showed two quasi-reversible redox couples (-0.17 V and -1.15 V vs. Ag+/Ag). With a theoretical cell voltage of about 1 V, the radical was investigated in a non-flowing symmetric coin cell. The coin cell was charged and discharged for 50 cycles during which the performance of the verdazyl was investigated (Figure 9). While the static cell showed reasonable coulombic efficiency of 94%, the charging and discharging capacities dropped substantially during cycling to about a third of its theoretical value by the 50th cycle. By studying the electrolyte composition after cycling by cyclic voltammetry, the authors suggested that the fade in capacity is mainly caused by degradation of the anionic species which is formed during charging, and not by cross contamination of charged species.

Figure 9: (a) Voltage curves for the first 3 cycles of a symmetric static battery cell with 3-phenyl-1,5-di-p-tolylverdazyl. (b) Charge and discharge capacities (as percentage of theoretical capacity) and coulombic efficiency for each cycle. Reproduced from Charlton et al.,154 with permission from Elsevier.

1,2,4-Benzotriazin-4-yl radicals, more commonly known as Blatter radicals, were first reported by Blatter in the late ‘60s.155 The structure of the Blatter radical is closely related to the verdazyl radical as in both species the unpaired electron is formally centred on a nitrogen atom within a nitrogen-rich heterocycle (Scheme 8). In actuality, for Blatter radicals this unpaired electron is heavily delocalized over both the triazine core and the fused aromatic ring. This causes the radicals to have excellent chemical stability, also toward air and water, and some even retain their properties after storage for more than three decades, as was reported by Gubaidullin et al. for the 1,3-diphenyl-1,4-dihydro-1,2,4-benzotriaziny-4-yl radical.156 Similar to other bench-stable organic radicals, Blatter radicals have many

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interesting physical properties making them highly suitable for applications in functional materials such as molecular electronics, liquid crystal photoconductors and molecular sensors.\textsuperscript{157, 158}

\begin{center}
\includegraphics[width=0.6\textwidth]{scheme8.png}
\end{center}

\textbf{Scheme 8:} Schematic representation of the basic structure of a Blatter radical and its reversible bipolar electrochemistry.

One particular property that is of interest for the battery community is the bipolar electrochemistry of the Blatter radicals. The radicals, with 11\textpi electrons, can reversibly undergo a one-electron oxidation and reduction event generating the closed-shell cation and anion, respectively (Scheme 8). Most commonly, the two redox processes are separated by approximately 1.1 V when probed by voltammetric measurements, making the radicals suitable for application in both aqueous and non-aqueous (symmetric) battery systems.\textsuperscript{159-161}

Very recently, the group of Schubert demonstrated the use of a Blatter radical as polymeric charge-storage material for solid-state organic batteries (Figure 10).\textsuperscript{162} First, a norbornene group was attached to a Blatter radical by click-chemistry, followed by cross-metathesis with the diester of 1,4-butanediol and 5-norbornene carboxylic acid (\textbf{CL}). Electrode films were prepared by mixing a slurry with 20 wt\% cross-linked polymeric Blatter radical \textbf{PBR}, 10 wt\% cellulose binder and 70 wt\% Super P conductive carbon black, which was subsequently cast and dried on aluminum foil. The bipolar electrochemistry of the \textbf{PBR} electrodes were probed by cyclic voltammetry in a beaker cell in solvent mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC). When utilizing the ionic liquid 1-butyl-1-methyl pyrrolidonium bis(trifluoromethane)sulfonimide (Pyr\textsubscript{1,4}TFSI) as supporting electrolyte, both redox processes showed quasi-reversible behavior (Figure 10). Whereas, with LiTFSI as electrolyte salt, the reduction process was not observed, attributed to the slow migration of lithium cations through the polymer particles. The \textbf{PBR} electrodes were tested in all-organic coin cell setups as either cathode or anode material in 1 M Pyr\textsubscript{1,4}TFSI in EC/DMC 3:7 (v/v).
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Figure 10: (top) Synthesis of Blatter radical polymer PBR by cross-metathesis with CL. (left) Beaker cell cyclic voltammogram of PBR electrodes in EC/DMC 3:7 (v/v) with 0.1 M Pyr1,4TFSI at various scan rates. (right) All-organic coin cell setup with electrodes containing 20 wt% PBR in EC/DMC 3:7 (v/v) with 0.1 M Pyr1,4TFSI as cathode-active material vs. activated carbon as anode-active material. Adapted from Saal et al.,162 with permission from Elsevier.

All cells were constructed with activated carbon as the counter electrode material. When PBR was used as a cathode-active material, a capacity retention of 95% was observed after a 1000 charge/discharge cycles, indicating high stability of the Blatter-containing polymer in both radical and cationic state. In contrast, when used as anode-active material, the battery could only be charged (reduction of PBR) and not discharged (reoxidation of reduced PBR). The authors hypothesize that the anionic species undergoes side reactions which hamper the reoxidation. Due to the instability of PBR as anode-active material, a fully symmetric all-organic battery could not be constructed.
1.6 Conclusion and outline of the thesis

Redox flow batteries are prime candidates for stationary large-scale storage due to their decoupling of power and energy, simplicity of design, and ability to endure fluctuating power supply from renewable resources. Several technologies have already been commercialized, including the all-vanadium RFB and zinc-based hybrid RFB. However, deep market penetration of these systems has been hindered by various techno-economic challenges. Battery chemistries based on redox-active organic molecules (ROMs) hold considerable promise as cheap and sustainable alternatives to traditional metal-based RFBs. In this chapter some important classes of organic electroactive material have been discussed. In particular, (anthra)quinones, TEMPO radicals and viologens stand out for their excellent battery performance in both aqueous and non-aqueous RFBs. The majority of current organic RFBs are based on two different active materials as positive and negative electrolyte and often suffer from cross-contamination of electrolytes leading to irreversible capacity loss. To alleviate issues caused by crossover of electrolyte, there has been a surge in development of symmetric RFBs, which have identical electrolyte composition on both sides of the battery.

While undeniable progress in the field of redox flow batteries has been made, major room for further improvements and novel applications still remains. In this thesis we present new developments in the field of organic RFBs. In particular, our goal was to study new bipolar redox-active organic molecules for the utilization as active species in symmetric RFBs in both aqueous and non-aqueous media. Two classes of stable organic radicals are applied as intrinsic bipolar active material and their battery performance is discussed in detail focusing on stability, tuneability and possible degradation pathways of these compounds.

First, in chapter 1, we introduced the field of redox flow battery technology and highlighted recent advances and future challenges.

Chapter 2 focusses on the Kuhn-type verdazyl radicals as bipolar electroactive material for symmetric RFBs. We probe the stability and reactivity of the radicals across all three relevant states of charge. Furthermore, their battery performance is examined and key insights into factors that contribute to molecular decomposition during battery cycling are provided.

In chapter 3 and 4, we demonstrate that 1,2,4-benzotriazin-4-yl radicals, commonly known as Blatter radicals, are a highly promising class of bipolar active materials for symmetric RFBs. Chapter 3 explores the known bipolar electrochemistry of Blatter radicals in organic solvents from the cyclic voltammetry timescale (seconds to minutes) to the timescale required for battery applications (weeks and more). These compounds display exceptional capacity retention during battery cycling, demonstrating the high stability of Blatter radicals in all states of charge. Moreover, battery performance is unaffected by the addition of water. In chapter 4, several water-soluble Blatter radicals are designed, synthesized and studied as bipolar redox active material for symmetric aqueous RFBs. The features
of Blatter radicals uncovered in our study open new avenues for the development of bipolar organic charge-storage materials targeting both aqueous and non-aqueous electrolytes.

Finally, in chapter 5 we develop techniques to study Blatter radicals as electroactive material in a flow setup using online NMR spectroscopic monitoring. Using both $^1$H and $^{19}$F NMR spectroscopy, we investigate changes in electrolyte properties and battery performance.

1.7 References


Chapter 1

[27] Sum, E.; Rychcik, M.; Skyllas-kazacos, M., Investigation of the V(III)/V(II) system for use in the positive half-cell of a redox battery. J. Power Sources 1985, 16 (2), 85-95.
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Chapter 1


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