Developing Novel Charge-Carriers for High-Energy Density Aqueous and Non-Aqueous Redox Flow Batteries

by

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May 1st, 2019

A dissertation submitted to the Faculty of the Graduate School of the University at Buffalo, The State University of New York in partial fulfillment of the requirements for the degree of Doctor of Philosophy

Department of Chemistry
To my beloved mother and father
Acknowledgements

First and foremost, I would like to express my deepest appreciation to my advisor. Let me start by saying that there are absolutely no proper words to convey my sincere gratitude and respect to Prof. Timothy R. Cook. Dear Dr. Cook, I am indebted to you for taking me in to the Cook group as a pioneering member. Thank you for believing in someone with no background in electrochemistry (I literally had not even heard about cyclic voltammetry before) to work on the redox flow battery project. Your profound belief in my work and faith has encouraged me to improve my skillset every day and become a better scientist. I am forever grateful for your continuous support, patience, kindness, and motivation throughout the last five years. I am truly amazed by your wide range of knowledge and the way you successfully manage many orthogonal projects in our group. The fact that you can instantly switch from one project to another to discuss and advice your students is truly remarkable and is a quality I am striving to develop…maybe with time…at least I hope! I always enjoyed the nonspecific scientific discussions we had, which were not only stimulating but was nurtured innovation. I would also like to extend my gratitude to you for making me realize the importance of small things, be it the font size in a presentation or tick marks in a figure, which can make a big difference in scientific communication. Your style of teaching, mentoring and training has been a blessing to us and I am forever thankful to you for all the guidance throughout my PhD and for all other invaluable advice on life. I would like to finish by saying that I have not met anyone like you who is an exceptional chemist, an amazing teacher, a gifted artist, a talented guitarist, ukulelist and a really good singer, and someone who has a great sense of humor, but most importantly a very kind human being with a good heart and I am so proud to say you are my mentor and a friend for life. Thank you!

I would like to extend my sincere thanks to my thesis committee, Prof. David Lacy, Prof. David Watson, and Prof. Javid Rzayev for generously giving me their time to offer me valuable comments toward improving my work. Dr. Lacy, I am very grateful to you for all the discussions
on various topics in electrochemistry that we have had throughout the last few years, which have always enabled me to expand my knowledge and better understand the concepts and thank you for writing me letters of recommendation whenever I needed without any hesitation. Dr. Watson and Dr. Rzayev, thank you so much for all your relentless support and guidance over the last five years.

I thank my fellow lab mates for making the Cook lab a supportive working environment and all of you have made graduate school a wonderful experience for me. Many thanks to Cressa, Amanda, Cory, and Matt for being the best lab mates I could have asked for as a first year graduate student. I will always remember the fun times we have had together including the late night hangouts in the lab, food outings, and birthday surprises. Special thanks to Cressa for being a great companion who inspired me to be a strong, independent, better researcher and to Amanda for being my first American friend who has uplifted me since day one. I will always cherish the sweet moments we have shared, especially the tea parties during CHE 322. I would also like to acknowledge the unwavering guidance I received from Dr. Yuzhen Zhang, the first postdoctoral researcher in the Cook lab. Yuzhen, you have been a role model to me in the lab and I will always admire your strong work ethic, which has reinforced my belief that hard work is the key to success.

I am most grateful to all the collaborators for lending me their expertise and intuition to scientific and technical problems, especially Prof. Ellen Matson (Assistant Professor, Department of Chemistry, University of Rochester) and Dr. Alan Friedman (Research Associate Professor, Department of Materials Design and Innovation, University at Buffalo).

There are two other people that I would like to convey my heartfelt gratitude, both of whom I have never met in person, but who were extremely kind to offer guidance in the initial days of graduate school. Dr. Matthew Sartin, you were instrumental in clarifying a number of scientific issues I had as a naive first year graduate student and thank you for being very kind and taking your valuable time to send me lengthy emails addressing my queries. I really do hope we will
meet some day in future so that I can personally thank you for all your help. Mr. Rob Roberts (Bio-Logic, USA) is someone whose help cannot be overestimated. Thank you Rob for sharing your unparalleled knowledge and practical suggestions to set up the electrochemical station in the Cook lab. I really do appreciate your assistance throughout the duration of my PhD.

To all my friends I met in Buffalo; this city has become a home away from home only because of you all. Thank you for all the good memories. Special thanks to my friends from back home Sri Lanka, who are now scattered all around the world, for their unswerving support and the encouraging words whenever I needed them the most.

To best parents and husband, that anyone could ever ask for: dear amma, thatthha, and Rashika, you are my three pillars of strength and I simply don’t know what I would do without the three of you. I cannot thank you enough for supporting and encouraging me in every possible way in all of my pursuits. Your unconditional love and knowing that you are always there for me is the reason I am inspired to follow my dreams and goals. You are the best in the world and I love you!

Finally, I thank everyone else who has supported me in one way or the other during this amazing journey for without any of you, this research work would not have been possible.

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v
### Contents

Acknowledgements ......................................................................................................................... iii
List of Figures ................................................................................................................................. viii
Abstract ........................................................................................................................................... xii

Chapter 01-Introduction ..................................................................................................................... 1
  1.1. Electrochemical Energy Storage for a Renewable Energy Future ........................................... 1
  1.2. Redox Flow Batteries as Electrochemical EES Devices .......................................................... 3
  1.3. A Brief Overview of Active Species in Redox Flow Batteries .............................................. 6
  1.4. Motivation to Further Explore Redox Active Molecules as Charge-Carriers for RFBs..10
  1.5. Scope and Outline of Thesis ................................................................................................. 11

Chapter 02-Characterization of a BODIPY Dye as an Active Species for Redox Flow Batteries 15
  2.1. Introduction ........................................................................................................................... 15
  2.2. Results and Discussion .......................................................................................................... 16
    2.2.1 Voltammetric behavior of PM 567 in CH$_3$CN with a Pt working electrode ................. 16
    2.2.2 Bulk electrolysis followed by cyclic voltammetry ......................................................... 17
    2.2.3 Analyzing the products of bulk electrolysis ................................................................. 22
    2.2.4 PM 567 as a precursor for active species in an all-organic RFB .................................. 24
    2.2.5 Diffusion coefficients and heterogeneous electron transfer rate constants ............... 24
    2.2.6 Solubility ....................................................................................................................... 24
    2.2.7 Charge-discharge experiments ...................................................................................... 25
  2.3. Conclusions ........................................................................................................................... 27
  2.4. Supporting Information ......................................................................................................... 28

Chapter 03-Repurposing an Industrial Dye, Methylene Blue, as an Active Component for Redox Flow Batteries 42
  3.1. Introduction ........................................................................................................................... 42
  3.2. Results and Discussion .......................................................................................................... 43
    3.2.1 Cyclic voltammetry of methylene blue ........................................................................ 43
    3.2.2 Rotating Disk Voltammetry of methylene blue ............................................................. 44
    3.2.3 Bulk cycling of methylene blue using chronoamperometry ....................................... 45
    3.2.4 Investigations on the observed capacity decay ............................................................. 46
    3.2.5 Symmetric charge-discharge cycling ............................................................................ 47
    3.2.6 Spectroelectrochemistry experiments .......................................................................... 49
    3.2.7 Expected energy densities from a methylene blue RFB system .................................. 50
  3.3. Conclusions ........................................................................................................................... 50
List of Figures

Chapter 01

Figure 1.1. Electricity generation by source in 2018 (Data Source: EIA) ........................................... 1

Figure 1.2. Power fluctuations caused by intermittent renewable energy sources (a) and the power stabilization using electrochemical energy storage (b) ...................................................... 2

Figure 1.3. Diagram of an all-liquid redox flow battery ................................................................. 3

Figure 1.4. Schematic of charge transport in some first-generation aqRFB systems ..................... 8

Figure 1.5. Schematic of charge transport in some coordination complexes used as naRFB active species ....................................................................................................................... 9

Chapter 02

Figure 2.1. Cyclic voltammograms recorded with a scan rate of 0.5Vs⁻¹ at a platinum working electrode in 6mm PM567 and 100mm TBAPF₆ in acetonitrile at room temperature .......... 16

Figure 2.2. Cyclic voltammograms recorded with a scan rate of 0.5Vs⁻¹ at a platinum working electrode before and after the bulk oxidation of a solution of ferrocene and TBAPF₆ in acetonitrile at room temperature ............................................................................................................. 18

Figure 2.3. UV/Vis absorbance spectra of the bulk oxidized solution of ferrocene and TBAPF₆ in acetonitrile at room temperature .............................................................................................. 19

Figure 2.4. Cyclic voltammograms recorded at a platinum working electrode (0.5Vs⁻¹ scan rate) and UV/Vis spectra of in the bulk oxidized solution PM567 and TBAPF₆ in acetonitrile at room temperature ............................................................................................................. 20

Figure 2.5. Cyclic voltammograms recorded at a platinum working electrode (0.5Vs⁻¹ scan rate) and UV/Vis spectra of in the bulk reduced solution PM567 and TBAPF₆ in acetonitrile at room temperature ............................................................................................................. 21

Figure 2.6. Experimental FT-ICR-MS of PM567, oxidized PM567, and reduced PM567 .......... 22
Figure 2.7. Calculated (red) and experimental (black) FT-ICR-MS peaks of oxidized and reduced PM567 ..............................................................23

Figure 2.8. Representative constant current cycling curves for 1 mm PM567 and 100 mm TBAPF₆ in acetonitrile; charging current 0.12 mA and discharging current 0.04 mA; at room temperature ..........................................................26

Figure 2.9. Charge capacity, discharge capacity, and coulombic efficiency of the PM567 cell ..............................................................26

Chapter 03

Figure 3.1. Repeated 50 cycles of CVs using a 0.1 mM MB in 0.5 M H₂SO₄ solution obtained at Pt working electrode at a scan rate of 300 mV/s; room temperature .........................43

Figure 3.1. Repeated 50 cycles of CVs using a 0.1 mM MB in 0.5 M H₂SO₄ solution obtained at Pt working electrode at a scan rate of 300 mV/s; room temperature .........................43

Figure 3.2. Rotating disk data (a), Levich plot (b), Koutecky-Levich plot (c), and Tafel plot (d) 45

Figure 3.2. Rotating disk data (a), Levich plot (b), Koutecky-Levich plot (c), and Tafel plot (d) 45

Figure 3.3. Digital photograph of the MB solutions after immersing different membranes for 24 hours and the images of membranes before and after dipping in MB solutions ..........47

Figure 3.3. Digital photograph of the MB solutions after immersing different membranes for 24 hours and the images of membranes before and after dipping in MB solutions ..........47

Figure 3.4. Galvanostatic cycling profiles of methylene blue with Nafion NE1305 proton-exchange membrane: 1st cycle to 3rd cycle (a) and 10th cycle to 12th cycle (b) .................48

Figure 3.4. Galvanostatic cycling profiles of methylene blue with Nafion NE1305 proton-exchange membrane: 1st cycle to 3rd cycle (a) and 10th cycle to 12th cycle (b) .................48

Figure 3.5. Percent state-of-charge and coulombic efficiencies for 12 cycles with Nafion NE1035 proton-exchange membrane over 30 hrs (top) and 50 cycles with AMI 7001 anion-exchange membrane over 7 days (bottom) ........................................................................49
Chapter 04

Figure 4.1. Cyclic voltammograms recorded with a glassy carbon electrode under saturated and dilute conditions in 0.05 M TBAPF$_6$/CH$_3$CN. Scan rate 300 mV/s; measurements recorded at room temperature in a nitrogen-filled glove box. Potential windows for each CV experiment were as follows; −1 to 1 V for Fc and TEMPO, −2 to 0.5 V for [Co(Cp)$_2$]PF$_6$, and −2.5 to 0.2 V for N-meth. ..................................................................................................................................................65

Figure 4.2. Conductivities of electrolyte solutions at different concentrations .........................66

Figure 4.3. Combinations of organic electrolytes employed in this study for charge-discharge experiments..................................................................................................................................................67

Figure 4.4. Representative charge-discharge curves using 0.01 M active species in 0.05 M TBAPF$_6$/CH$_3$CN, and respective coulombic, voltage, and energy efficiencies for the first 15 cycles of each system..................................................................................................................................................69

Figure 4.5. Charge-discharge curves for Fc/[Co(Cp)$_2$]PF$_6$ in 0.05 M TBAPF$_6$/CH$_3$CN at different concentrations (A); coulombic, voltage, and energy efficiencies for the first 5 cycles (B); Nyquist plots for impedance before, and after cycling at different concentration ............70

Figure 4.6. Charge-discharge curves for Fc/N-meth in 0.05 M TBAPF$_6$/CH$_3$CN at different concentrations (A); coulombic, voltage, and energy efficiencies for the first 5 cycles (B); Nyquist plots for impedance before, and after cycling at different concentrations. ............72

Figure 4.7. Charge-discharge curves for TEMPO/N-meth in 0.05 M TBAPF$_6$/CH$_3$CN at different concentrations (A); coulombic, voltage, and energy efficiencies for the first 5/7 cycles (B). 74

Figure 4.8. Charge-discharge curves for TEMPO/ [Co(Cp)$_2$]PF$_6$ in 0.05 M TBAPF$_6$/CH$_3$CN at different concentrations (A); coulombic, voltage, and energy efficiencies for the first 3/5 cycles (B); Nyquist plots for impedance before, and after cycling at different concentrations ..................................................................................................................................................75

Figure 4.9. UV-Vis absorbance spectra of the supporting electrolyte compartment before and after 24 hours at dilute and saturated concentrations. ..................................................................................................................................................76
Chapter 05

Figure 5.1. Cyclic voltammograms of individual species (...) and mixtures (-) obtained at a scan rate of 500 mV/s using a glassy carbon working electrode; (+) = posolyte side, (-) = negolyte side .................................................................85

Figure 5.2. Peak current vs. square root of scan rate plots as individual and mixtures of species .................................................................................................................................86

Figure 5.3. Charge retention (a, b) and coulombic efficiency (c, d) plots for individual and mixture bulk cycling ...............................................................................................................................88

Figure 5.4. Cyclic voltammograms obtained before and after charge-discharge experiments using cation and anion exchange membranes; (+) = posolyte side, (-) = negolyte side......89

Figure 5.5. UV-vis absorbance of oxidized and reduced active species mixtures .........................90

Figure 5.6. Charge-discharge experiment results using an anion exchange membrane at a diluted concentration and cyclic voltammograms obtained before after cycling; (+) = posolyte side, (-) = negolyte side .................................................................91

Figure 5.7. Charge-discharge experiment results using a cation exchange membrane at a diluted concentration and cyclic voltammograms obtained before after cycling; (+) = posolyte side, (-) = negolyte side ..............................................................................................92

Figure 5.8. CVs obtained at 0.05 M concentration at a scan rate of 50 mV/s using a glassy carbon working electrode.............................................................................................................................93

Figure 5.9. A long term charge-discharge cycle performed at 50 mM active species concentration and cyclic voltammograms obtained before and after cycling; (+) = posolyte side, (-) = negolyte side ..................................................................................................................94

Figure 5.10. Representative charge-discharge cycles at 0.1 M (a) and 0.2 M (b) active species concentrations ...............................................................................................................................95
Abstract

The main objective of this thesis has been to investigate new charge carriers for redox flow batteries (RFBs) to address stability, solubility, and energy density limitations in existing systems. Using cyclic voltammetry (CV), chronoamperometry, and charge-discharge cycling as primary electroanalytical techniques, a range of redox active molecules were evaluated. In addition, UV-vis spectroscopy, spectroelectrochemistry and mass-spectrometry were also employed to further analyze the redox active materials.

A fluorescent boron-dipyrromethene (BODIPY) dye (PM567) was explored as suitable active material for an all organic symmetric non-aqueous RFB. A theoretical cell potential of 2.32 V was predicted from CV experiments. It was found that the oxidized and reduced, PM567 does not remain intact; however, the products of bulk electrolysis evolved over time to show stable redox behavior, making the dye a precursor for the active species of an RFB. In a separate study, we hypothesized that the redox properties of an environmentally damaging organic dye, methylene blue, make it suitable for use in the electrolyte solutions of aqueous redox flow batteries. Electrochemical analyses of aqueous methylene blue solutions established the dye as a pH tunable, two-electron redox transfer agent with fast transfer kinetics, motivating the recycling of dye-containing wastewater as the basis for flow battery electrolyte solutions. The active material concentration is critically linked to the energy capacity of a RFB. We identified a research gap in electrochemical behaviors at the solubility limit of charge carriers compared to dilute conditions. This thesis features a systematic study which revealed that the cycling behaviors are concentration dependent and membrane crossover together with fouling are major contributors to performance losses. We also demonstrated the suitability of the mixed-component catholyte and anolyte solutions for high-energy density non-aqueous RFBs, which has the effect of increasing the overall concentration and the number of electrons transferred.
Chapter 01-Introduction

1.1. Electrochemical Energy Storage for a Renewable Energy Future

The past few decades have witnessed a growth of worldwide consumption of electrical energy. The U.S. Energy Information Administration (EIA) projects a 28% growth in global energy consumption over the next two decades.\(^1\) In the existing electrical grid, a large percentage of electricity (63%) is supplied from the combustion of fossil fuels such as coal, natural gas, and oil (Figure 1.1).

![Figure 1.1. Electricity generation by source in 2018 (Data Source: EIA)](image)

However, the long-term unavailability and environmental repercussions of fossil fuel sources such as greenhouse gas emissions have led to worldwide efforts to develop technologies that convert renewables (e.g. solar, wind) into electrical energy. Although recent advances in solar and wind-based energy conversion have been promising and increasingly economical, the intrinsic limitations of these systems (e.g. susceptibility to intermittent weather patterns) present a challenge to integrating renewable power into commercial use.\(^2,3\) As such, the development of efficient, low-cost electrical energy storage (EES) technologies is imperative for the incorporation of renewable energy sources into the electrical grid (Figure 1.2). Currently, the lack of storage capability means that energy must be generated to meet demand in real time. The development
of grid-scale energy storage provides a means to separate production from use, both enabling the use of intermittent renewables but also allowing for electricity generation to occur during off-peak times when costs are lower. Electrical energy storage (EES) refers to the capture of electrical energy produced at one time for use at a later time. Historically EES has played three main roles. First, it reduces electricity costs by storing electricity obtained at off-peak times when its price is lower for later use during high-price peak hours. Secondly, in order to improve the reliability of the power supply, EES systems support users when power network failures occur due to natural disasters, for example. Their third role is to maintain and improve power quality. In a nutshell, EES is expected to solve excessive power fluctuations and undependable power supply issues, which are associated with the use of large amounts of renewable energy.

Currently, there are around 10 different technologies available for EES, which can be broadly classified as mechanical, electrochemical, or electrical. Pumped hydro installations currently account for the largest capacity (~95%) form of active grid electrical energy storage available worldwide. Thermal storage, compressed air, flywheels, and batteries comprise the remaining less

Figure 1.2. Power fluctuations caused by intermittent renewable energy sources (a) and the power stabilization using electrochemical energy storage (b)
than ~5% of storage capacity. Pumped hydro storage is a mechanical EES system that use the stored potential and kinetic energy of water is a green, safe, reliable, and an efficient technology. However, there can be large impacts on the environment and the population surrounding a project owing to the infrastructure of a pumped hydro power plant. Hydro power plants have high capital costs and the reservoirs are limited due to special geographical and geological requirements. Compared to the mechanical devices, electrochemical energy storage systems such as rechargeable batteries, have advantages including lower total cost and less environmental impact.

1.2. Redox Flow Batteries as Electrochemical EES Devices

Redox flow batteries (RFBs) have gained momentum in recent years as large capacity EES systems, which can be used in tandem with wind and solar power generation to provide a stable supply of renewable energy. Although different structural variants are emerging, the all-liquid design is the most established RFB type up to date. The basic anatomy of an all-liquid RFB is shown in Figure 1.3.

![Figure 1.3. Diagram of an all-liquid redox flow battery](image-url)
An RFB architecture has three main components; the main cell, external reservoirs and a flow system. The main cell has separate compartments for positive (redox couple with a higher reduction potential) and negative (redox couple with a lower reduction potential) electrolyte solutions comprising two separate current collectors defined as cathode and anode, respectively. An ion exchange membrane is employed to isolate positive/catholyte and negative/anolyte electroactive species while allowing ions to pass through in order to complete the electrical circuit. The electrolyte solution in a RFB is typically composed of dissolved charge-carrier/active species, supporting electrolyte, and solvent. An electrical power source, such as a solar panel, is used to charge the RFB. During charging, the electroactive species stored in the external tanks are pumped over the electrode surfaces in the main cell where electron transfer/redox reactions take place serving as the impetus for energy storage. The reverse reactions take place at the electrode surfaces when the device is connected to a load.

The main parameters of a RFB that defines its performance are: 1) volumetric energy density, which is the amount of energy stored in a given volume; 2) power density, which indicates how fast a battery can discharge; and 3) coulombic efficiency, which keeps track of how many electrons are stored in a battery versus how many you get out when using it. These parameters are determined by various components of the cell. For instance, power density of a RFB is determined by the size of the electrodes and energy density is governed by the volume of electrolyte solution in the storage tanks. Hence, tuning of these various components allows control over this EES technology.

The fundamental expression for the volumetric energy density (U in J/L) of a RFB is shown in Equation (1).\(^\text{11}\)

\[
U = \int_0^C \frac{V_{cell}(q) dq}{Vol_{total}}
\]  

(1)
In Equation (1), $V_{\text{cell}}$ is the cell voltage, $q$ is the charge and $\text{Vol}_{\text{total}}$ is the total volume of the electrolyte solution. Following the Nernst Equation, $V_{\text{cell}}$ is determined by the equilibrium potential ($E$) difference between catholyte and anolyte species in a RFB. Generally, the equilibrium potential difference at the 50% state of charge is used as the theoretical cell voltage of a RFB. This theoretical cell voltage is a constant for any given catholyte and anolyte combination and is easily determined by the difference of the standard potentials ($E_{\text{cathode}}^0 - E_{\text{anode}}^0$) of the two redox couples. Equation (2) is obtained when $V_{\text{cell}}$ at the 50% state of charge is used in Equation (1).

$$U = \frac{V_{\text{cell}}}{\text{Vol}_{\text{total}}} \int_0^C dq$$ \hspace{1cm} (2)

$q$ is the total charge of a RFB, which is obtained by Equation (3).

$$q = nFC_{\text{active}} \frac{1}{2} \text{Vol}_{\text{total}}$$ \hspace{1cm} (3)

Where, $n$ is the number of electrons involved in the redox process, $C_{\text{active}}$ the redox active species concentration, and $F$ is Faraday’s constant. In calculating the total charge of a RFB, only one half-cell is considered, hence the $\frac{1}{2}$ in Equation (3). By substituting $q$ in Equation (2) with Equation (3), the following Equation (4) for energy density of a RFB is obtained.

$$U = \frac{1}{2} nFV_{\text{cell}}C_{\text{active}}$$ \hspace{1cm} (4)

The energy output of a RFB can be determined by multiplying the energy density obtained from Equation (4), by the total volume of electrolyte solution stored in the two external reservoirs.

Depending on the solvent, RFBs are categorized as aqueous or non-aqueous. The generation of hydrogen and oxygen via water splitting ($E^0 = 1.23$ V) limits the working voltages of aqueous systems. In practice, the over potentials associated with $O_2$ and $H_2$ evolution widen the solvent window depending on the electrode material used, a subject of great interest in the design of electrolysis systems where hydrogen and oxygen are desired products.\textsuperscript{12} The voltage limitation associated with water-based systems has motivated the development of non-aqueous electrolyte
materials using organic solvents with wider potential windows. Non-aqueous RFBs (naRFBs) using organic solvents to dissolve electrolyte species are attractive as high-energy density EES devices due to the broader voltage windows compared to aqueous RFBs (aqRFBs).\textsuperscript{13–15} However, naRFBs suffer from high internal resistance and lower solubility relative to aqueous designs. These limitations motivate research to maximize conductivity and solubility in organic solvents, identify new redox active agents, and develop new membrane materials optimized for use in non-aqueous environments.\textsuperscript{16}

RFBs provide resilient and reversible high capacity energy storage and guarantee load levelling that is required to embed renewable energy sources in the electrical grid. Although traditional battery cells rely on internal solid electrodes for energy storage, RFBs use the circulation of two soluble redox couples.\textsuperscript{9,8} For instance, in a lithium ion battery, Li\textsuperscript{+} are intercalated into the electrodes; the Li\textsuperscript{+} content in the electrolyte solution in combination with the size of electrodes, determine the energy of the battery. Power of a lithium ion battery is controlled by the size of the electrodes. Accordingly, power and energy factors are coupled in a lithium ion battery. In a RFB, power is determined by the size of the electrodes or the stack, and volume of electrolyte solution in the storage tanks dictate the energy.\textsuperscript{17} As a result, energy (stored capacity) and power (energy provided per unit time) of a RFB are independent from each other. This decoupling enables RFBs to achieve flexible energy scaling in a more cost-effective manner compared to other battery technologies. RFBs also possess advantages in long term applications. This can be attributed to the fact that electrodes in the device are not fatigued over time since the electrochemical reactions at the liquid/solid interface are fast.\textsuperscript{17} In contrast, electrodes in a lithium ion battery gets drained with time owing to the insertion of Li\textsuperscript{+} ions.

\textbf{1.3. A Brief Overview of Active Species in Redox Flow Batteries}

Active species, also known as charge-carriers in a RFB device are responsible for the conversion of chemical energy to electrical energy. These charge-carrier molecules determine
the overall cell voltage, reversibility (rechargeability of the device), kinetics (how fast it can be charged/discharged), and stability (how long can energy be stored) expected from a RFB. Since the introduction of the all-liquid RFB technology in 1974, by Thaller et al at NASA, a variety of electrolyte materials have been evaluated as active species. The existing all-liquid RFB charge carriers include metal ions, metal coordination complexes, organic molecules, and polymers. A moderate library of redox active molecules of each category have been studied as suitable charge-carriers for RFBs.

The first-generation all-liquid RFB systems include chromium/iron, vanadium chloride/polyhalide, bromine/polysulphide, and zinc/mercury. These electroactive species are referred to as ‘dual active species’ and use water as the solvent. The most noticeable challenge associated with these systems are the crossover of active species through the membrane. For instance, in the bromine/polysulphide RFB, the bromine gas evolved at the positive electrode traverse though the separator membrane causing loss of energy. To address the cross over problem, the concept of ‘single active species’ was initiated by Pelligri and Spaziante. Skyllas-Kazacos et al practically realized this concept, by assembling an all liquid symmetric RFB based on vanadium. The aqueous all- vanadium chemistry patented in 1986, is the most studied and established RFB system so far. The redox reactions occurring in the all-vanadium RFB are as follows;

At the positive electrode;

\[ VO_2^+ + 2H^+ + e^- \leftrightarrow VO^{2+} + H_2O \quad E^0 = 1.0 \text{ V vs. SHE} \quad (5) \]

At the negative electrode;

\[ V^{3+} + e^- \leftrightarrow V^{2+} \quad E^0 = 0.2 \text{ V vs. SHE} \quad (6) \]

These predict an overall cell voltage is 1.2 V vs. the SHE. A proto-type all-vanadium RFB revealed high coulombic efficiencies of ~70% suggesting, a large portion of the charge input can be taken
out in discharge. Systematic investigations has resulted in significant improvements in all-vanadium RFB system via advanced electrode materials, electrode designs, and compatible membranes. All-vanadium RFB system has been commercialized by many companies including Sumitomo Electric, Prudent Energy (www.pdenergy.com), American Vanadium (http://www.americanvanadium.com), Cellenium (www.vanadiumbattery.com), REDT (http://www.redtenergy.com), and Ashlawn Energy (http://www.ashlawnenergy.com). Despite the technological advancements, the capital cost of all-vanadium RFBs are too high to enable widespread market penetration. In addition, there are efficiency losses that hinders the long-term stability. It was demonstrated, water electrolysis is a major reason for the efficiency loss that occurs at close proximity to the potential of V (II)/V (III) redox couple. As a result, it was unfeasible to achieve long term cycling without loss of some water to hydrogen evolution. Figure 1.4 shows the chemistry of some of the first-generation aqRFBs.

The first naRFB system was reported by Matsuda et al using tris(2,2’-bipyridine)ruthenium(II) tetrafluoroborate as the active species, which had an open circuit potential of 2.6 V. All-uranium and all-neptunium based RFBs based organometallic complexes with β-diketonate and polyketonate ligands were proposed by Yamamura et al. Chakrabarthi et al reported a non-aqueous RFB having ruthenium acetylacetonate as the active material with an open circuit potential of 1.8 V. The library of coordination complexes

![Figure 1.4. Schematic of charge transport in some first-generation aqRFB systems](image-url)
evaluated for naRFBs has grown since these initial studies to include vanadium acetylacetonate,\textsuperscript{36} chromium acetylacetonate,\textsuperscript{37} manganese acetylacetonate,\textsuperscript{38} 1,10-phenanthrolinecobalt(II) hexafluorophosphate,\textsuperscript{39} tris(2,2'-bipyridine)nickel(II) tetrafluoroborate,\textsuperscript{40} tris(2,2'-bipyridine)iron(II) tetrafluoroborate,\textsuperscript{40} and bis(acetylacetone)ethylenediamine cobalt.\textsuperscript{41} Use of phosphate ligands such as trimethyl phosphate (TMPO) has improved the solubility up to 1.5 – 1.9 M in propylene carbonate solvent. Trimethyl phosphate complexes of nickel and iron have been evaluated as naRFB active species.\textsuperscript{42} Anderson et. al. at Sandia National Lab explored redox active complexes of ethanolamine, diethanolamine, ethylhexanoate or triflate anions together with copper, iron, and other metals, which were all liquids at room temperature.\textsuperscript{43, 44} These ionic-liquids demonstrated reversible redox behaviors, but were highly viscous leading to poor floe-cell performance.\textsuperscript{10} A few examples of redox active coordination complexes used in naRFB systems are shown in Figure 1.5.

Another strategy for redox active species in RFBs is to employ organic molecules rather than metal-based species. Using organic redox couples is a promising approach to reduce the overall cost towards the overarching goal of improving market penetration of RFB systems. There is high tunability of redox potential and solubility through structural modifications of organic molecules.\textsuperscript{45, 46} In addition, most of the organic materials can be obtained from earth abundant

Figure 1.5. Schematic of charge transport in some coordination complexes used as naRFB active species

\begin{figure} 
\centering
\includegraphics[width=\textwidth]{figure1.5.png}
\caption{Schematic of charge transport in some coordination complexes used as naRFB active species}
\end{figure}
natural sources (Ex: Food) and plants. A broad range of organic molecules have been identified as aqueous and non-aqueous RFB active species. TEMPO, PTIO, DBBB, quinoxalines, modified quinones, alloxazine, viologen derivatives, 2,1,3-benzothiadiazole (BzNSN), 9-fluorenone, and flavin are among the scaffolds that have been studied towards this end. In addition, redox active polymers have also been identified as suitable charge-carriers in RFBs.

1.4. Motivation to Further Explore Redox Active Molecules as Charge-Carriers for RFBs

RFB development is still in its early stages compared to other secondary battery systems such as the Li+ ion technology. There are critical challenges that need to be addressed in order to achieve broad commercialization. To be competitive in the energy storage space, RFBs should have improved volumetric capacities, lower capital and operational costs, enhanced round trip efficiencies, and longer cycling times. The lack of suitable charge-carriers has been identified as a root cause for these challenges.

The volumetric capacity of the state-of-art all-vanadium RFB is ~90 kJ/L. Most of the existing RFB systems have limited energy capacities in the range of 30-40 kJ/L, which can be attributed to the low active species concentrations and narrow cell voltages. Accordingly, a key enabling development is identifying redox active molecules with wider potentials, higher solubility with kinetically fast and chemically reversible redox reactions. Darling et. al. reported that a molar solubility of ~4-5 mol/L and ~1-2 mol/L is required for aqueous and non-aqueous RFB charge-carriers respectively, to achieve the energy capacity targets. Employing redox active compounds that exhibits multi-electron transfer can be an alternative strategy to enhance energy density without increasing solubility.

The high capital costs of current state-of-the-art RFBs are critically linked to the expensive active materials used. Therefore, it might be useful to discover novel electroactive species based
on inexpensive components.\textsuperscript{10} The Department of Energy’s (DOE’s) Advanced Research Projects Agency-Energy (ARPA-E) recently set a capital cost target of $100 per kW h for 1 hour of storage for widespread adoption.\textsuperscript{5}

In addition to the above-mentioned challenges, the RFB active compounds and complexes underscored some important parameters such as long-term stability.\textsuperscript{10} This stability must be maintained across all charge states, as decomposition upon oxidization or reduction has a direct impact on energy storage (charge/discharge efficiency) as well as device lifetime. A molecular level knowledge of redox behavior and stability is a guide to designing next-generation active species.

Another critical area that requires immediate attention, is development of ion-selective and cost-effective membranes that are compatible with the redox pairs. Identifying membranes with high conductivity and less crossover can refine the efficiency and lifetime of the whole battery system.\textsuperscript{10} Any of the above discussed challenges would warrant the exploration of novel redox active molecules as charge-carriers of RFBs. The “ideal” RFB active material is a redox active compound that (1) undergoes kinetically fast and chemically reversible redox reactions; (2) exhibits multiple reversible redox events over a large electrochemical window; (3) has high chemical, electrochemical, and cell-component stability over multiple oxidation states; (4) exhibits high solubility; and (5) is accessible from inexpensive, earth abundant starting materials.

1.5. **Scope and Outline of Thesis**

The primary goal of this thesis research was to develop new charge carriers for RFBs using molecular-level design principles guided by electrochemical analysis to address stability, solubility, and energy density. Towards this end, two new classes of redox active molecules were discovered and evaluated as active species for RFBs. In chapter 02, the redox behavior of an emissive organic dye molecule (BODIPY-PM567) was explored as a charge carrier for naRFBs. The electrochemical properties of PM567 predicted it can be used as both positive and negative
active material. A theoretical cell voltage of 2.32 V was predicted for a RFB that uses PM567 as both positive and negative electrolyte material and charge-discharge cycling experiments demonstrated coulombic efficiencies around 73% over 100 cycles. Upon charging, the PM567 molecule was stable for short amounts of time, but eventually decomposed to a mixture of redox active compounds. This new mixture of compounds did not change further over the course of my measurements (~1 week), a good indication of long-term stability. This study emphasized the importance of evaluating the stability of active species at longer time scales, as RFBs are for long term energy storage.

Chapter 03 explores the fundamental electrochemical behavior of methylene blue, a common organic dye used in textile industry. The overarching goal of this particular project was to understand the feasibility of using dye-containing wastewater as electrolyte solution for aqueous RFBs. Electrochemical characterization of methylene blue revealed a pH tunable, two-electron transfer redox reaction with high electron transfer rate constants. Galvanostatic charge-discharge experiments demonstrated ~100% coulombic efficiency up to 100 cycles. Chronoamperometry and spectroelectrochemistry studies further demonstrated that methylene blue was stable to deep cycling enabling its use as a novel charge-carrier for flow batteries. The proposed method constitutes an interdisciplinary approach towards the cultivation of a novel green energy technology through wastewater management.

Chapter 04 transitions from electrolyte development to a broader viewpoint, investigating the effect of concentration on charge-discharge characteristics of RFB systems. Most evaluations of charge carriers are performed at dilute conditions and these concentrations are orders of magnitude lower than what is practical for an RFB. We noted that the lithium ion battery community has for some time recognized that charge discharge characteristics are affected by concentration, yet the RFB community has not fully investigated analogous relationships. Accordingly, we hypothesized that the electrochemical behavior of non-aqueous electrolytes may
differ at high concentrations due to changes in solvation structure, aggregation, solution resistance, and mass transport, which in turn affect the overall cell performance. Accordingly, the changes in charge-discharge profiles with concentration were evaluated, using four redox active molecules: ferrocene (Fc), cobaltocenium hexafluorophosphate ([Co(Cp)₂PF₆]) N-methylphthalimide (N-meth), and TEMPO, that were previously identified as RFB active species. Four different combinations were studied across a range of concentrations including the maximum possible concentration for a given system. Through charge-discharge and impedance spectroscopy, it was found that membrane fouling and species crossover were major culprits of behavioral changes in charge-discharge profiles at elevated concentrations.

Chapter 05 builds on the knowledge of solubility limitations of non-aqueous electrolyte species to develop a novel method to increase the energy density of RFBs. naRFBs are promising candidates as high-capacity energy storage devices and their energy density is directly related to the active species concentration, cell voltage, and the number of electrons transferred per redox process. Although the wide redox windows associated with the organic solvents used in naRFBs are useful to realize high open circuit voltages, the low solubilities of electrolytes often minimize the energy densities. In particular, this chapter describes a method of mixing multiple active components as an alternative route to increase energy density, which has the effect of increasing overall concentration and/or electrons transferred. Fc/TEMPO and [Co(Cp)₂PF₆]/N-meth, were studied as positive and negative active species mixtures, respectively in a proof-of-concept study. The resulting system showed two, one electron redox processes that establish a cell voltage of 1.8 V with no apparent deleterious interactions between the active species. Charge-discharge experiments further established the use of active species mixtures in RFBs to achieve higher energy densities.

Finally, chapter 06 summarizes the key findings of each research project. The future research directions are also discussed in this chapter based on the results throughout the thesis. The
importance of deriving approaches focusing on the structure-function relationships of redox active molecules is emphasized towards the end goal of creating a synthetically optimized charge-carrier for RFB applications. Particular attention is given to nanoscopic polynuclear architectures of relevance to EES. We believe that these nanoparticles are excellent candidates as a suite of first-row transition metals may be used to systematically tune redox properties while simultaneously addressing long-term stability, membrane crossover, and solubility, factors that impact the overall efficiency of RFBs.
Chapter 02-Characterization of a BODIPY Dye as an Active Species for Redox Flow Batteries

The following work has appeared previously: A. M. Kosswattaarachchi, A. E. Friedman and T. R. Cook, ChemSusChem, 9, 3317 (2016).

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2.1. Introduction

The existing compounds and complexes underscore some important parameters regarding active species in RFBs, including solubility and long-term stability. Decomposition of the charge carriers has a direct impact on energy storage (coulombic efficiency) as well as device lifetime. In some cases, the initial redox-active species may act as a precursor that forms an electrolyte mixture once charged. In other cases, irreversible degradation may occur, requiring electrolyte regeneration. A knowledge of redox behavior and stability serves as a guide to understand the performance of an RFB and aids in the design of next-generation electrolytes. Generally, CV studies are employed to evaluate the reversibility and kinetic behavior of active species, along with charge–discharge studies that show long-term cycling stability. A caveat associated with CV is that the timescale of a typical experiment is only seconds to minutes. Therefore, a molecule that appears reversible by CV may exhibit significant redox changes when it remains charged even for relatively short amounts of time (minutes to hours). Herein, we have evaluated a boron-dipyrromethene (BODIPY) dye, PM 567, as a precursor for the active species in both positive and negative electrolyte solutions of an RFB. BODIPY dyes are extensively studied for their interesting electrochemical, photochemical and electrogenerated chemiluminescence properties. It was reported that PM 567, a variant in which all core C-H sites are substituted, shows two well-separated and reversible redox couples even at slow scan rates (~50 mV/s) indicating that the
radical ions formed upon oxidation and reduction are stable at the CV timescale.\(^{63, 64}\) The occurrence of two reversible redox events makes PM 567 a potential candidate as an active species in an all-organic RFB. Bulk electrolysis, UV-Vis, and mass spectrometry experiments have been used to interrogate the stability of oxidized and reduced PM 567 stored over the course of one week. Related studies were performed using ferrocene and cobaltocenium hexafluorophosphate that serve as models for oxidation and reduction stability, respectively. A model cell was used as the basis for charge-discharge experiments indicating that despite the lack of long-term stability of PM 567, the decomposition products exhibit redox stability, giving rise to a plateauing coulombic efficiency over the course of 100 cycles.

### 2.2. Results and Discussion

#### 2.2.1 Voltammetric behavior of PM 567 in CH\(_3\)CN with a Pt working electrode

The CV of 6 mM PM 567 dissolved in 0.1 M TBAPF\(_6\) in anhydrous CH\(_3\)CN at a scan rate of 0.5 V/s is shown in Figure 2.1.

![Cyclic voltammograms recorded with a scan rate of 0.5 V/s\(^{-1}\) at a platinum working electrode in 6 mm PM567 and 100 mm TBAPF\(_6\) in acetonitrile at room temperature](image)

*Figure 2.1. Cyclic voltammograms recorded with a scan rate of 0.5 V/s\(^{-1}\) at a platinum working electrode in 6 mm PM567 and 100 mm TBAPF\(_6\) in acetonitrile at room temperature*

For comparison, a CV of 0.1 M TBAPF\(_6\) in anhydrous CH\(_3\)CN is also shown with no significant current response in the region of interest (−2 V to 1 V vs. Ag/Ag\(^+\)). The CV profile shows two redox events as expected,\(^{63}\) with \(E_{1/2}\) values of 0.73 V (Pa1/Pc1) and −1.59 V (Pa2/Pc2) vs. Ag/Ag\(^+\).
corresponding to oxidation and reduction of PM 567, respectively. As shown in Figure 2.1 after twenty-five cycles the CV is largely unchanged save for a small response near 0 V vs. Ag/Ag⁺. The lack of significant changes indicates that across the time scale of a CV experiment PM 567 shows good reversibility and electrochemical stability.

### 2.2.2 Bulk electrolysis followed by cyclic voltammetry

The stability and electrochemical behavior of the oxidized/reduced states of a molecule are key determinants of efficiency as an active species in an energy storage device. The charged states of the active species must be stable with respect to chemical decomposition, membrane crossover, and self-discharge, all pathways that potentially reduce the efficiency of a device. A practical battery must remain charged for times far exceeding that of a typical CV experiment. With this in mind, chronoamperometry studies were carried out to obtain bulk quantities of charged species for stability studies. Both CV and UV-Vis spectroscopy were performed on the resulting oxidized and reduced materials.

#### 2.2.2.a Bulk electrolysis of ferrocenium and cobaltocene

To validate these methods of assessing long term stability, analogous studies were performed on ferrocene and cobaltocene, selected due to the celebrated reversible redox chemistry. Ferrocene and cobaltocene are electrochemically stable organometallic compounds and are often used as internal standards in redox reactions owing to their inherent inertness. Hwang et al. have exploited the promising electrochemistry of ferrocene and cobaltocene in redox flow cells. They achieved a coulombic efficiency of ~ 78.6% across three cycles and a discharge potential of 1.1-1.4 V was obtained. During these pioneering studies, the ferrocene and cobaltocene were not stored in their charged states for any significant duration, prompting our study of the cyclic voltammetry and UV-Vis absorbance of ferrocenium and cobaltocene course of one month to parallel our experiments on PM 567.
Ferrocene was bulk oxidized to obtain ferrocenium in an H-cell (Figure 2.S1). CVs were obtained before and immediately following bulk oxidation. As shown in Figure 2.2 the CV profiles of the ferrocene and ferrocenium do not significantly differ, with the only change being the value of the open circuit potential. No additional peaks appear, indicating that ferrocenium is stable far beyond the timescale of a typical CV experiment. UV-Vis spectroscopy data (Figure 2.3) showed no change over the course of one month, which further shows that ferrocenium is stable when stored under inert conditions.\(^{66}\) Accordingly, RFBs using ferrocene as an active species will maintain charge provided that oxygen is excluded from the electrolyte solution. Similar experiments were carried out with cobaltocene. As expected, the CV profile of cobaltocene similarly remains stable upon reduction. UV-Vis studies show that the metallocene is stable for at least one month when stored under inert conditions (Figure 2.S2 and Figure 2.S3).

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**Figure 2.2.** Cyclic voltammograms recorded with a scan rate of 0.5 \(\text{Vs}^{-1}\) at a platinum working electrode before and after the bulk oxidation of a solution of ferrocene and \(\text{TBAPF}_6\) in acetonitrile at room temperature
2.2.2.b **Bulk oxidation of PM 567**

The CV of PM 567 in CH$_3$CN indicates an $E_{1/2}$ of 0.73 V vs. Ag/Ag$^+$. Accordingly, a potential of 1.3 V vs. Ag/Ag$^+$ was applied to a Pt working electrode until the dye was fully oxidized. CVs of the resulting solution were taken at time points ranging from hours to days. Electronic absorption spectra were also obtained at each time point to provide further insight regarding any changes in composition. Figure 2.3 shows the current vs. time curve for the bulk oxidation of PM 567. The observation that the anodic current never reaches zero is consistent with previous experiments using PM 567 reported by Sartin et al.$^6^4$ The persistent current was rationalized by diffusion of material from the counter electrode compartment through the separator that reduces a small amount of oxidized dye. The ongoing crossover of this reducing contaminant provides continuous substrate for oxidation and thus a non-zero current.

The CVs of the oxidized species taken at various time points are shown in Figure 2.4. Immediately after the bulk oxidation, the cyclic voltammetry profile of PM 567 has changed. Two

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**Figure 2.3. UV/Vis absorbance spectra of the bulk oxidized solution of ferrocene and TBAPF6 in acetonitrile at room temperature**
quasi-reversible redox couples occur at the same peak potentials as with neutral PM 567. In addition, three anodic and two cathodic peaks appear, which are irreversible. This suggests that the radical ion species formed upon oxidation of PM 567 is not stable over the ~30 minutes required for bulk oxidation and setup of the CV experiment. Furthermore, the CVs continue to change over the course of six hours, with the peak current density of the Pa2/Pc2 couple decreasing over time.

Despite the initial evolution of the voltammograms away from the idealized redox waves observed for the neutral dye, after 1 day a remarkable stability occurs, with no further change through a week of monitoring the CV responses. This lack of further change suggests that although PM 567 may initially degrade, the resulting solution still maintains a redox fidelity that allows for its use as an active species and motivated charge-discharge studies (vide infra). UV-Vis absorbance data further confirms that initial changes in composition stabilize after 24 hours (Figure 2.4). A comparison between the UV-Vis of PM 567 and its oxidized counterpart show striking changes immediately after electrolysis. Most notably a new band is observed at 770 nm and the intensity of the characteristic 514 nm band of BODIPY decreases by roughly half. This

Figure 2.4. Cyclic voltammograms recorded at a platinum working electrode (0.5 Vs⁻¹ scan rate) and UV/Vis spectra of in the bulk oxidized solution PM567 and TBAPF₆ in acetonitrile at room temperature
decrease in intensity is consistent with the loss of an electron that can no longer participate in the \( \pi \rightarrow \pi^* \) transition. Although a small decrease in the band at 770 nm does occur over the course of one week, this minor change does not appreciably affect the redox response.

**2.2.2.c Bulk reduction of PM 567**

Bulk reduction was carried out with a working electrode potential of \(-2 \) V vs. Ag/Ag\(^+\). Similar to the bulk oxidation experiment, the change in CV profile was studied for a week with complementary monitoring by UV-vis. Figure 2.S5 shows the current vs. time curve for the bulk reduction of PM 567. Unlike the bulk oxidation curve, the current vs. time curve describing the bulk reduction fully decays to the background.

![Cyclic voltammograms recorded at a platinum working electrode (0.5 Vs\(^{-1}\) scan rate) and UV/Vis spectra of in the bulk reduced solution PM567 and TBAPF\(_6\) in acetonitrile at room temperature](image)

**Figure 2.5.** Cyclic voltammograms recorded at a platinum working electrode (0.5 Vs\(^{-1}\) scan rate) and UV/Vis spectra of in the bulk reduced solution PM567 and TBAPF\(_6\) in acetonitrile at room temperature

As seen in Figure 2.5 the CV of the bulk reduced species introduces three irreversible oxidation peaks. Unlike with the oxidation where some changes were observed over the course of hours, the reduced dye is even more stable after the initial induction period, persisting from hours to one week. The UV-Vis spectra of the bulk reduced species are shown in Figure 2.5. A similar attenuation in intensity of the 514 nm band occurs, however no new low energy bands are
introduced. As with the oxidation, slight changes occur over the course of days, but these small spectral differences do not have an impact on redox response.

2.2.3 Analyzing the products of bulk electrolysis

Initial investigations of chronoamperometry performed on BODIPY dyes invoke decomposition and potential polymerization of the radical species formed based on mass spectrometry results wherein peaks were observed at twice the m/z value of the parent BODIPY dyes.\textsuperscript{64}

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{figure26.png}
\caption{Experimental FT-ICR-MS of PM567, oxidized PM567, and reduced PM567}
\end{figure}

The changes observed via CV prompted further mass spectroscopy analysis of the effects of oxidation and reduction products to determine the fate of the dye molecule (Figure 2.6). As shown
in Figure 2.S6, the mass spectrum of PM 567 includes four main peaks, including one that corresponds to a dimer at an m/z value of 659. The isotopic distribution of these peaks is diagnostic of the presence of boron where a central peak dominates a given cluster.

In the oxidized PM 567 spectrogram, three main peaks are observed. These are assigned to the species shown in Figure 2.7. The peak at an m/z of 571 corresponds to a dimeric species where one methyl group and one fluorine atom have fragmented from the dye. It should be noted that the peaks at m/z = 242 and 629 do not display characteristic isotopic distributions consistent with the presence of boron. The peak at 629 coincidentally matches the m/z value expected for a simple BODIPY dimer, a potential decomposition product that was suggested in a previous report. However, the isotopic resolution illustrated in Figure 2.7 provides strong evidence that no boron remains in the species giving rise to this signal. A second entity also consistent with this m/z value and lacking BF$_2$ fragments is a dimer of the parent dipyrromethene with an associated PF$_6^-$ from the supporting electrolyte.

**Figure 2.7.** Calculated(red) and experimental(black) FT-ICR-MS peaks of oxidized and reduced PM567

In the FT-ICR-mass spectrum of reduced PM 567 (Figure 2.6), there are three main peaks. This mass spectrogram includes the peaks at 242 and 629 that were observed in the oxidation and result from the loss of the BF$_2$ moiety. As shown in Figure 2.7 the unique new peak that appears at 803 agrees well with a dimeric species that has lost two methyl groups and one fluorine from the PM 567 core and includes one PF$_6^-$.
2.2.4 **PM 567 as a precursor for active species in an all-organic RFB**

As observed from the CVs of the bulk electrolyzed PM 567, the neutral PM 567 is no longer the active species in the RFB. The new solution formed upon charging is a mixture of compounds partially identified by mass spectrometry. The final species responsible for redox activity show current response at similar potentials as neutral PM 567 (Figure 2.4 and Figure 2.5). Because the bulk species do not exhibit significant potential shifts, the theoretical cell voltage remains ~2.32 V once the system has stabilized.

2.2.5 **Diffusion coefficients and heterogeneous electron transfer rate constants**

An established method to determine the diffusion coefficients associated with a redox species uses a plot of peak current vs. the square root of scan rate associated with a given redox event.\(^39, 41, 47\) The Randles-Sevcik equation has been used to determine the diffusion coefficients from CV data obtained at platinum and glassy carbon working electrodes (~10\(^{-5}\) cm\(^2\) s\(^{-1}\); Figure 2.S7–Figure 2.S18). The Nicholson method was used to determine the heterogeneous electron transfer rate constants ~10\(^{-2}\) cm s\(^{-1}\).\(^67-69\) These values are summarized in Table S1. As discussed above, PM 567 acts a precursor to a mixture of active species that form the oxidized and reduced dye. Because these are not isolable species, similar experiments to determine their diffusion coefficients and electron transfer rate constants cannot be performed.

2.2.6 **Solubility**

The solubility of PM 567 in CH\(_3\)CN was determined using electronic absorption spectroscopy of saturated solutions of the dye. Filtered stock solutions were diluted to absorbances of less than 1.0. The molar absorptivity coefficient for PM 567 was determined to be 7.9 \(\times\) 10\(^4\) M\(^{-1}\) cm\(^{-1}\), in agreement with an earlier report.\(^70\) Using the Beer-Lambert relationship, the maximum solubility of PM 567 was 0.2 M in CH\(_3\)CN, taken as the average of three solutions. The least soluble component of an electrolyte couple in an RFB determines the upper limit of energy density. When
the oxidized and reduced electrolyte materials are equally or more soluble than the neutral species, they will remain in solution upon redox cycling. We observe no precipitation in our PM 567 system, indicating that the solubility of the neutral dye may be used to define an expected energy density. Using the calculated solubility of 0.2 M and a theoretical open circuit voltage of 2.32 V, energy density of the RFB can be estimated using the Equation (4). According to the equation 1, an energy density of 22 kJ/L is estimated for a PM 567 RFB. The energy density of all-vanadium RFBs reaches 90-126 kJ/L in some systems owing to the higher solubility of the active species. These calculations use theoretical energy densities and will be affected when discharge voltages are reduced due to cell design (high internal resistance, membrane crossover, etc.).

2.2.7 Charge-discharge experiments

A static cell was fabricated for initial performance evaluations of PM 567 as an active species. This Teflon cell mimics the working compartments of an RFB system without any flow, enabling the use of small volumes. Initially, both compartments of the cell contained PM 567 in a neutral state. Galvanostatic conditions were used with potential cut offs for both charge and discharge. A charging current of 0.12 mA and discharging current of 0.04 mA was used to ensure complete redox cycling (initial state-of-charge of 30%). A charge cut off voltage of 2.4 V was selected so as to slightly exceed the ideal 2.32 V cell potential predicted by CV experiments. The discharge cut off was set to 0.2 V. Figure 2.8 shows cycles 17-19 as representative curves of the cycling study. A charging plateau occurred around ~2.2 V, falling to ~1.6 V upon discharge. Potential losses during discharge have been previously attributed mass transport limitations and high internal resistances associated with cell designs. The resistance of the cell used here was measured across the two working electrodes prior to the first charge and after every five cycles. The
resistance grew from 15 to 807 kΩ over the course of charge discharge experiment (Figure 2.8). The low conductivity of the electrolyte and the presence of a separator were two factors contributing to the ohmic drop. As a result of these losses, the discharge voltages are lower than the cell voltages predicted by CV.

**Figure 2.8.** Representative constant current cycling curves for 1 mm PM567 and 100 mm TBAPF₆ in acetonitrile; charging current 0.12 mA and discharging current 0.04 mA; at room temperature

A long term cycling study was performed using 100 charge/discharge cycles. As shown in Figure 2.9 the charging capacity decreases throughout the first 40 cycles, consistent with dynamic

**Figure 2.9.** Charge capacity, discharge capacity, and coulombic efficiency of the PM567 cell
capacities previously observed for a polymeric BODIPY study. After an induction phase of 40 cycles, stable battery cycling was observed. The coulombic efficiency stabilized around 73%. Unknown side reactions, crossover of active species through the separator and mass transport limitations have all been invoked as factors governing the loss of coulombic efficiency in RFBs. Although PM 567 undergoes initial side reactions as evidenced by mass spectrometry and UV-Vis analyses of bulk electrolysis samples, both the oxidized and reduced solutions clearly stabilize, consistent with the plateau in coulombic efficiency observed during charge-discharge experiments.

2.3. Conclusions

A non-aqueous, all-organic RFB model system using a BODIPY dye, PM 567, in TBAPF$_6$/CH$_3$CN was demonstrated using a laboratory scale static cell set up. The stability during storage of the oxidized/reduced species were studied using bulk electrolysis and UV-Vis spectroscopy. The radical cations/anions of PM 567 were stable at the short timescale of cyclic voltammetry but this stability did not extend to longer time scales. Both UV-Vis and CV experiments showed significant changes over the course of hours that were in stark contrast to parallel experiments using ferrocene and cobaltocene, which remained quite stable in all charged states during storage. Despite the loss of well-defined oxidation and reduction waves for PM 567, solutions of the dye did show reproducible redox behavior over the course of days to a week, indicating a promising stability for the purposes of charge-discharge cycles. The CV of these redox stabilized species predict an open circuit voltage of 2.32 V for a RFB with PM 567 as precursors for active species. Mass spectrometry provided evidence for the loss of BF$_2$ fragments in both the oxidized and reduced states of the dye as a major decomposition product. The cycling performance of the cell with PM 567 initially achieved a coulombic efficiency of 73% after a short induction period, making the dye an interesting example of a precursor that proves unstable upon charging yet provides access to a redox stable mixture at longer timescales. These results
suggest that stability and redox studies at short, medium, and long time-scales are all critical to fully assess potential active species. Molecules with promising redox couples based on CV may decompose, but this decomposition does not rule out use in RFB designs since the resulting mixtures may show stable charge/discharge cycles.

2.4. Supporting Information

Experimental

Electrolytes

Electrolyte solutions were prepared by dissolving the active species and tetrabutylammonium hexafluorophosphate (TBAPF$_6$ Alfa Aesar, USA) in anhydrous acetonitrile obtained from Grubbs-type solvent purification system (Pure Process Technology, USA). TBAPF$_6$ was recrystallized thrice using hot methanol and dried under vacuum. The active species PM 567 (Sigma Aldrich, USA), ferrocene (Sigma Aldrich, USA) and cobaltocene (BTC, UK) were used as received.

Cyclic voltammetry experiments

Concentrations of PM 567 and TBAPF$_6$ used were 6 mM and 100 mM, respectively. Cyclic voltammetry measurements were carried out using a Bio-Logic SP 300 potentiostat/galvanostat and the EC-Lab software suite. Both 3 mm diameter glassy carbon discs and 2 mm diameter platinum discs (CH Instruments, USA) were used as working electrodes. The working electrodes were polished with a micro cloth pad using 0.05 μM alumina powder (CH Instruments, USA). After polishing, the electrodes were ultrasonically cleaned and rinsed thoroughly with acetone and deionized water and allowed to dry before use. Potentials during the cyclic voltammetry were measured relative to a non-aqueous Ag/Ag+ reference electrode with 10 mM AgNO$_3$ and 100 mM TBAPF$_6$ in CH$_3$CN solvent (BASi, USA). A Pt wire (CH Instruments) served as the counter electrode. All experiments were carried out at room temperature inside a nitrogen filled glove box.
(Vigor Tech, USA). All cyclic voltammetry measurements were iR compensated at 85% with impedance taken at 100 kHz using the ZIR tool included within the EC-Lab software.

**Bulk electrolysis experiments**

Bulk electrolysis experiments were performed in a two compartment H-cell (Adams and Chittenden, USA) inside a nitrogen filled glove box. The compartments of the H-cell were separated by a glass frit (porosity 10-16 μm). The potential at the working electrode was controlled with reference to an Ag/Ag⁺ non aqueous reference electrode. A platinum mesh was employed as the working electrode and a Pt wire served as the counter electrode. The reference electrode and the working electrode occupied the same compartment containing 20 mL of the solution of 6 mM PM 567 and 100 mM supporting electrolyte in CH₃CN. The counter electrode compartment contained 20 mL of 100 mM TBAPF₆ in CH₃CN solution. After bulk electrolysis, the solution in the working electrode compartment was transferred to a three electrode cell for cyclic voltammetry measurements.

**Solubility determination**

A saturated solution was prepared by the sequential addition of solid PM 567 into CH₃CN (5 mL) with stirring until a suspension was formed. The solution was allowed to settle for a two hours and subsequently filtered through glass wool to remove any undissolved material. An aliquot of this solution was diluted in CH₃CN and the UV-Vis spectrum was recorded on a Cary 8454 UV-Vis diode array system. The absorbance recorded at 514 nm for three independent trials was used to determine the maximum solubility of PM 567 in CH₃CN. The molar absorption coefficient of PM 567 was determined using three stock solutions serially diluted to absorbances between 1.0 and 0.1 using the Beer-Lambert relationship.
**UV-Vis spectroscopy**

UV-Vis absorbance of the electrolyte solutions before and after bulk electrolysis were measured using a Cary 8454 UV-Vis spectrometer and a 1 cm path length airtight cuvette (Starna, USA).

**Mass spectrometry**

Mass spectra were collected using a Bruker Daltonics SolariX 12 tesla Fourier Transform Ion Cyclotron Resonance Mass Spectrometer.

**Charge-discharge experiments**

A custom-made Teflon cell was used for charge-discharge experiments. (Figure 2.S19) Each compartment contained 1 mL of the 1 mM of the active species in 100 mM TBAPF₆. The electrolytes were separated by an AMI-7001 anion exchange membrane (2 cm × 1 cm, Membrane International Inc., USA). Prior to each experiment, the membrane was pre-conditioned by soaking in a solution containing 100 mM TBAPF₆ in CH₃CN for 24 hours. Two graphite felt electrodes (0.9 cm × 0.6 cm × 1 cm, Fuel Cell Store, USA) were used. The electrode was submerged (~0.7 cm in the solution) leaving a small volume at the top to connect Pt-wire current collectors at which leads were attached. The electrodes were placed with a small gap from the membrane. Galvanostatic conditions were employed with charge and discharge currents of 0.12 mA and 0.04 mA for the PM 567 system and 0.05 mA and 0.01 mA for the ferrocene/cobaltacenium hexafluorophosphate system, respectively. The cells were charged up to overall cell potentials of 2.4 V (PM 567) and 1.38 V (ferrocene/cobaltacenium hexafluorophosphate) and discharged to 0.2 V. All charge-discharge experiments were performed in a nitrogen filled glove box.
**Figure 2.S1.** Plot of current versus time for the bulk oxidation at a platinum mesh electrode in 3 mM Ferrocene and 100 mM TBAPF$_6$ in CH$_3$CN at room temperature

**Figure 2.S2.** Cyclic voltammogram recorded with a scan rate of 0.5 V/s at a platinum working electrode in a solution of 3 mM cobaltacene and 100 mM TBAPF$_6$ in CH$_3$CN at room temperature

**Figure 2.S3.** UV-Vis absorbance spectra of a solution with 3 mM cobaltaceneium and 100 mM TBAPF$_6$ in CH$_3$CN at room temperature
Figure 2.S4. Plot of current versus time for the bulk oxidation at a platinum mesh electrode in 6 mM PM 567 and 0.1 M TBAPF$_6$ in CH$_3$CN at room temperature

Figure 2.S5. Plot of current versus time for the bulk reduction at a platinum mesh working electrode in 6 mM PM 567 and 100 mM TBAPF$_6$ in CH$_3$CN at room temperature

Figure 2.S6. Calculated (red) and experimental (black) FT-ICR mass spectra peaks of PM 567
**Figure 2.S7.** Cyclic voltammograms of the PM 567 oxidation redox couple, recorded at a platinum working electrode in 6 mM PM 567 and 100 mM TBAPF$_6$ in CH$_3$CN at room temperature with different scan rates

**Figure 2.S8.** Cyclic voltammograms of the PM 567 reduction redox couple, recorded at a platinum working electrode in 6 mM PM 567 and 100 mM TBAPF$_6$ in CH$_3$CN at room temperature with different scan rates

**Figure 2.S9.** Quasi reversible $\Delta E$ variation with the scan rate, for the Pa1/Pc1 redox couple recorded at a platinum working electrode
Figure 2. S10. Quasi reversible $\Delta E$ variation with the scan rate, for the Pa2/Pc2 redox couple recorded at a platinum working electrode.

Figure 2. S11. Plot of the peak current of Pa1 recorded at a platinum working electrode, versus the square root of scan rate.
Figure 2.S12. Plot of the peak current of Pc2 recorded at a platinum working electrode, versus the square root of scan rate

Figure 2.S13. Cyclic voltammograms of the PM 567 oxidation redox couple, recorded at a glassy carbon working electrode in 6 mM PM 567 and 100 mM TBAPF$_6$ in CH$_3$CN at room temperature with different scan rates
Figure 2.5. Cyclic voltammograms of the PM 567 reduction redox couple, recorded at a glassy carbon working electrode in 6 mM PM 567 and 100 mM TBAPF$_6$ in CH$_3$CN at room temperature with different scan rates

Figure 2.5. Quasi reversible $\Delta E$ variation with the scan rate, for the Pa1/Pc1 redox couple recorded at a glassy carbon working electrode
**Figure 2.S16.** Quasi reversible $\Delta E$ variation with the scan rate, for the Pa2/Pc2 redox couple recorded at a glassy carbon working electrode

**Figure 2.S17.** Plot of the peak current of Pa1 recorded at a glassy carbon working electrode, versus the square root of scan rate
**Figure 2.S18.** Plot of the peak current of Pc2 recorded at a glassy carbon working electrode, versus the square root of scan rate.

**Table 1.S1.** Calculated diffusion coefficients and heterogeneous electron transfer rate constants

<table>
<thead>
<tr>
<th>Electrode Type</th>
<th>Redox Couple</th>
<th>Diffusion Coefficient ($\times 10^{-5} \text{ cm}^2 \text{s}^{-1}$)</th>
<th>Heterogeneous electron transfer rate constant ($\times 10^{-2} \text{ cm s}^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>GC</td>
<td>Pa1/Pc1</td>
<td>2.6</td>
<td>2.4</td>
</tr>
<tr>
<td></td>
<td>Pa2/Pc2</td>
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<td>Pa1/Pc1</td>
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<td>2.8</td>
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<tr>
<td></td>
<td>Pa2/Pc2</td>
<td>3.0</td>
<td>2.8</td>
</tr>
</tbody>
</table>
Figure 2.S19. Teflon cell for the charge-discharge experiments. Measurements are in inches. Alum = aluminum.

Figure 2.S20. Change in resistance of the cell during charge/discharge cycles
Figure 2.S21. Charge-discharge cycles 2-3 of the PM 567 system

Figure 2.S22. Charge-discharge cycles 40-42 of the PM 567 system

Figure 2.S23. Representative constant current cycling curves for 0.1 M ferrocene as positive electrolyte material and 0.1 M cobaltocenium hexafluorophosphate as the negative electrolyte material with 1.0 M TBAPF$_6$ in CH$_3$CN; charging current 0.05 mA and discharging current of 0.01 mA; at room temperature
Figure 2.S24. Charge capacity, discharge capacity and coulombic efficiency per cycle in a ferrocene/cobaltocenium cell
Chapter 03-Repurposing an Industrial Dye, Methylene Blue, as an Active Component for Redox Flow Batteries


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3.1. Introduction

Methylene blue (MB) is among the most commonly used organic dyes in the textiles, printing, and pesticides industries. When used as a textile dye, only ~5% of MB generally adheres and the surplus is eluted with water. Large amounts of MB-containing wastewater (>10^3 L) are released from textile mills on a daily basis. Water effluents containing the dye are highly colored even at low concentrations, owing to its high molar absorption coefficient (~8.4×10^4 L mol^-1 cm^-1 at 664 nm). As a result, the penetration of sunlight is hindered in MB-contaminated water bodies, challenging the photosynthetic capacity of aquatic plants. At amounts >7.0 mg/kg, MB is reported to cause high blood pressure, mental disorders, nausea and abdominal pain in humans. Long term accumulation of the dye leads to allergic dermatitis, skin irritations, cancer and mutations. Any one of these effects warrants removal of the dye prior to wastewater discharge and strategies for dye uptake remain an active area of research. A wide range of strategies reported for MB removal include photocatalytic/electrochemical degradation, ozonation, coagulation-flocculation, membrane filtration, chemical precipitation, ion-exchange, microbiological treatments, absorption, and adsorption. Even though these methods offer routes for removal, none are currently scalable to treat large amounts of wastewater at low cost and high efficiency. An alternative to treating MB-containing wastewater is to identify a secondary use. MB is a well-established redox indicator and demonstrates a two-proton two-electron redox reaction to form leuco methylene blue (LMB). Multi-electron transfer
half-reactions are interesting for EES devices with high energy densities. The reversible multi-electron transfer redox couple of MB makes it an attractive candidate as a charge-carrier in EES devices such as RFBs.

Phenothiazine dyes have been evaluated as active species for non-aqueous RFBs. To date, there are no systematic studies of MB as a charge-carrier in aqueous RFBs. By establishing the potential of the dye to serve as an active charge carrier, MB-containing waste water becomes an attractive feedstock for energy storage in aqueous flow batteries. Accordingly, we carried out electrochemical characterizations along with membrane compatibility and cross-over experiments on simulated MB wastewater. These studies underscore an environmentally sustainable repurposing of MB-containing wastewater that aligns with the growing interest in establishing industrial micro-grids based on EES.

3.2. Results and Discussion

3.2.1 Cyclic voltammetry of methylene blue

The CV of 0.1 mM MB in 0.5 M H$_2$SO$_4$ obtained using a Pt working electrode is shown in Figure 3.1. The $E_{1/2}$ is 0.24 V versus the Ag/AgCl (saturated KCl) aqueous reference electrode. There were no significant changes observed in the CV profile after 50 repeated scans indicating that MB does not undergo any chemical changes that would manifest in an altered redox behavior.

![Figure 3.1. Repeated 50 cycles of CVs using a 0.1 mM MB in 0.5 M H2SO4 solution obtained at Pt working electrode at a scan rate of 300 mV/s; room temperature](image)
over the timescale of the CV experiment. CVs were also obtained at various pH values (Figure 3.S1). MB demonstrates a potential shift of \(~270\) mV when the pH is changed from 4 to 10. This pH-dependence is due to the proton-coupled electron-transfer (PCET) involved in the redox chemistry of MB. Active species that invoke PCET redox chemistry have been previously observed in a handful of other molecules, the most notable being quinones.\(^{98-101}\) This pH tunability can serve as the basis for enhancing cell voltages by shifting the \(E_{1/2}\) values.\(^{102}\) In this work, we focus on the redox behaviors of MB under acidic conditions. Scan-rate-dependent CV data are shown in Figure 3.S2. The peak separations were \(~30\) mV and did not increase with scan rate suggesting a completely reversible two-electron transfer redox reaction.\(^{103}\)

### 3.2.2 Rotating Disk Voltammetry of methylene blue

RDE experiments were carried out over a range of rotation rates from 500 rpm to 3300 rpm (Figure 3.4(a)) to determine kinetic information about the MB/LMB redox couple. The limiting currents determined at 0.20 V Vs. Ag/AgCl were plotted against the square root of the rotation rate to obtain the Levich plot (Figure 3.4(b)). Slope of the Levich plot was used to estimate the diffusion coefficient for MB using the Levich equation.\(^{58}\) A diffusion coefficient of \(2.73 \times 10^{-6}\) cm\(^2\)/s is in the same order as the literature reported values for similar aqueous RFB active species. Figure 3.4(c) shows the Koutecky–Levich plots, which were used to determine the mass-transfer-independent kinetic current \(i_k\) for the MB redox reaction. These \(i_k\) values were subsequently fit by the Butler-Volmer equation via a Tafel plot. Using the Tafel equation the rate constant was calculated to be \(4.34 \times 10^{-2}\) cm/s, indicating a high electron transfer rate for the 2e\(^-\) transfer reduction.\(^{104}\) MB has an electron transfer rate constant greater than that of a water soluble ferrocene derivative (3.6\(\times10^{-5}\) cm/s),\(^{105}\) methyl viologen (2.8\(\times10^{-4}\) cm/s),\(^{106}\) 4-HO-TEMPO (2.6\(\times10^{-4}\) cm/s),\(^{106}\) flavin mononucleotide (5.3\(\times10^{-3}\) cm/s),\(^{58}\) and alloxazine (1.2\(\times10^{-5}\) cm/s).\(^{55}\) The
contributions to iR drop from low rates of surface electrochemical reactions should be minimal with MB, owing to its high electron transfer rate constant.\textsuperscript{101.}

3.2.3 Bulk cycling of methylene blue using chronoamperometry

Cyclic voltammetry established that as MB is reduced to LMB, no significant decomposition occurs during the experiment. To assess if a molecule is capable of longer-term energy storage, it is necessary to establish the stability of the redox partners involved beyond the short duration of typical CV experiments, which may obscure decomposition for two reasons: first, a CV experiment is short, typically lasting from seconds to minutes; second, a CV experiment only oxidizes or reduces a small percentage of the active species and thus subsequent chemical decomposition may be slow.\textsuperscript{107} As such, a bulk electrolysis experiment wherein the sample was cycled fully between MB and LMB, simulating a 100% state-of-charge cycling, was performed for

\textbf{Figure 3.3.} Rotating disk data (a), Levich plot (b), Koutecky-Levich plot (c), and Tafel plot (d)
50 cycles over seven hours (Figure 3.S3). CVs were obtained before and after bulk cycling. The CV profiles remained largely unchanged, indicating that both MB and LMB were stable at higher concentrations and longer time scales (Figure 3.S3(c)). The cell used for these experiments contained an AMI-7001 membrane that became discolored during use. We also observed a significant fade in both charge and discharge capacity over the 50 cycles (Figure 3.S3(b)).

3.2.4 Investigations on the observed capacity decay

Capacity fades may occur due to one of three mechanisms; i) decomposition of the active species; ii) active species cross-over iii) active species interaction with the membrane (i.e. adsorption or chemical reaction). The fact that no new features were observed in the CVs before and after cycling indicate that chemical decomposition is unlikely. To study membrane cross-over versus membrane adsorption, we assembled an H-cell where only one side contained MB, separated by the AMI-7001 membrane. Over the course of one month, both sides of the H-cell were monitored by UV-Vis absorbance to track the migration of MB. After 30 days there was no evidence of MB crossover to the blank side of the H-cell (Figure 3.S4); however, the absorbance of MB on the active side of the H-cell decreased to ~55% of the initial concentration. The blue appearance of the membrane (see Figure 3.S5) indicates that MB was removed from solution. SEM images of the membrane after the experiment showed a surface-layer of material. The lack of any blue color on the reverse-side indicates that MB precipitated on the solution-exposed areas, forming a film. This film formation has two ramifications on charge capacity: first, it lowers the concentration of MB in solution, directly lowering the number of electrons that may be stored; second, it could increase the impedance of the membrane resulting in a higher overpotential for charging and discharging. As discussed below, the galvanostatic cycling demonstrated high voltaic efficiencies. Since the cut-off voltage was constant during cycling, an increase in overpotential would lower the total charge stored. Since it is clear that MB is being removed from solution, yet the voltage efficiency remained high, the loss in charge and discharge
capacity is attributed entirely to precipitation of the MB on membrane surface and not an increase in internal resistance due to film formation.

In order to investigate if adsorption of the dye depends on the chemical composition of the separator, absorbance measurements of MB solutions were obtained after immersing three different membranes of equal size for 24 hours. Figure 3.6 shows that the CMI 7000 cation-exchange membrane adsorbs the highest amount of MB. Nafion NE1035 proton-exchange membrane adsorbed an insignificant amount of MB over 24 hours (Figure 3.S6). It should be noted that these deposited films did not show any noticeable changes upon exposure to air.

![Figure 3.5. Digital photograph of the MB solutions after immersing different membranes for 24 hours and the images of membranes before and after dipping in MB solutions](image)

**Figure 3.5. Digital photograph of the MB solutions after immersing different membranes for 24 hours and the images of membranes before and after dipping in MB solutions**

### 3.2.5 Symmetric charge-discharge cycling

The suitability of MB for RFBs was further evaluated by galvanostatic cycling. These experiments compliment potentiostatic charging to characterize the stability of redox species over multiple charge-discharge cycles.\(^{107, 109}\) Prior to the experiment, MB was reduced using ascorbic acid to obtain LMB. Complete conversion of MB to LMB can be observed from the color change of solution from blue to colourless. In the beginning of the galvanostatic cycling experiment, MB was reduced at the negative electrode and LMB was oxidized at the positive electrode. With this
In symmetric configuration, potential side effects of additional components are eliminated. With Nafion NE1035 as the membrane separator, an electrolyte solution comprising 2.5 mL of 0.5 mM MB in 50 mM H$_2$SO$_4$ was charged and discharged at 0.05 mA for twelve cycles. Initially, MB was reduced at the negative electrode and LMB was oxidized at the positive electrode. The theoretical state of charge (SOC) of 2.5 mL of 0.5 mM of MB is 0.24 C. The achieved SOC was ~75% in the first cycle, growing to ~90% by the fourth cycle. The Figure 3.8 shows the cycling profiles obtained for the galvanostatic charge-discharge experiment. From cycles 4 to 12 the SOC remained stable at ~90% with constant capacity retention (Figure 3.9) and coulombic efficiencies of ~95% were obtained for all twelve cycles. These results are consistent with previous observations that MB does not adsorb or crossover through the Nafion NE1035 proton-exchange membrane.

In contrast, similar experiments using AMI-7001 as the separator show the effects of adsorption, wherein the achieved SOCs drops from ~90% to ~56% (Figure 3.9). Figure 3.S7 shows the cycling profiles obtained for this experiment. The observed capacity decay could be mitigated by pre-soaking the membrane in electrolyte solution containing MB for 24 hours. Despite adsorption, the voltage efficiencies remained high (~99%) for AMI-7001. Figure 3.9 shows the

**Figure 3.7.** Galvanostatic cycling profiles of methylene blue with Nafion NE1305 proton-exchange membrane: 1st cycle to 3rd cycle (a) and 10th cycle to 12th cycle (b)
charge-discharge capacities and corresponding coulombic efficiencies for this experiment. High coulombic efficiencies of ~100% were retained in all 50 cycles.

### 3.2.6 Spectroelectrochemistry experiments

![Graph showing percent state-of-charge and coulombic efficiencies for 12 cycles with Nafion NE1035 proton-exchange membrane over 30 hrs (top) and 50 cycles with AMI 7001 anion-exchange membrane over 7 days (bottom).](image)

**Figure 3.9.** Percent state-of-charge and coulombic efficiencies for 12 cycles with Nafion NE1035 proton-exchange membrane over 30 hrs (top) and 50 cycles with AMI 7001 anion-exchange membrane over 7 days (bottom)

We further studied the stability of LMB through spectroelectrochemistry. The MB solution was bulk reduced in a spec-echem cell and the absorbance was monitored over time. The data are shown in Figure 3.S8. The peaks in the visible region associated with MB decrease over time as bulk reduction proceeds and the color changes from blue (MB) to colorless (LMB). After the bulk reduction, the sample was exposed to air and the peak intensity increased back to the original
height confirming that LMB is stable under anaerobic conditions and is suitable for long term energy storage.\textsuperscript{111} Furthermore, it is notable that the reaction of LMB with O\textsubscript{2} simply regenerates MB rather than decomposition to species beyond the MB/LMB dyad, an important feature since oxidation in air will only affect charge capacity and not the longer-term stability of the system.

3.2.7 Expected energy densities from a methylene blue RFB system

Using the reported solubility of 0.1 M for MB\textsuperscript{112} and a theoretical open circuit voltage of 1 V for a RFB system paired with a well-established redox couple such as Mn\textsuperscript{3+/2+},\textsuperscript{113} an energy density of 9.6 kJ/L is estimated. This is on the low end but on par with other emerging systems of interest. The energy densities of some other aqueous RFB systems with organic molecules are 45.5 kJ/L (Br\textsubscript{2}/AQDS),\textsuperscript{53,114} 14.7 kJ/L (AQDS/BQDS),\textsuperscript{114} 72.3 kJ/L (FeCN\textsubscript{6}\textsuperscript{3-}/2-/FMN),\textsuperscript{58} and 24.4 kJ/L (FeCN\textsubscript{6}\textsuperscript{3-}/2-/DHQA).\textsuperscript{52} Since the redox couple of MB is sensitive to pH, the cell voltage of MB RFBs may be further tuned to increase energy density.\textsuperscript{102}

3.3. Conclusions

In summary, we have studied the electrochemical behavior of the MB/LMB couple to establish the feasibility of the dye as a charge carrier in RFBs. Methylene blue demonstrated a two-proton two-electron redox reaction with a high electron transfer rate constant under acidic conditions. Bulk electrolysis experiments revealed exceptional stability of methylene blue at all relevant oxidation states. High coulombic efficiencies of ~100\% were obtained for 50 cycles over seven days in galvanostatic charge-discharge experiments. In addition, we have studied the interaction of MB with membrane separators. Nafion NE1035 is a suitable separator for MB RFBs as we observed no adsorption or crossover during charge/discharge experiments. In contrast, although voltage efficiencies were high when AMI-7001 was used, a significant capacity decay was observed in the cycling experiment, owing to the adsorption of methylene blue. These results demonstrate that methylene blue is a viable active species in RFBs and given the significant
amount of MB-containing wastewater generated by industry, these results motivate strategies to repurpose such eluents for energy storage. Further experiments to identify compatible charge-carriers to build prototype flow battery systems together with methylene blue are ongoing. The proposed method will be an alternative route towards wastewater management giving rise to a green-energy storage technology.

3.4. Supporting Information

Experimental Section

Materials

Methylene blue (MB, Acros Organics, USA) and Sulfuric acid (Fisher Chemical, USA) were used as received without additional purification. AMI 7001 anion-exchange and CMI 7000 cation-exchange membranes were purchased from Membrane International Inc., USA. Nafion NE1035 proton-exchange membrane was purchased from Fuel Cell Store, USA.

Electrolyte solution preparation

Electrolyte solutions were prepared by dissolving a 0.1 mM or 2.5 mM concentration of MB in 0.5 M H₂SO₄.

Cyclic voltammetry (CV)

CVs were performed at room temperature using a Bio-Logic SP 200 potentiostat/galvanostat and the EC-Lab software suite. Cyclic voltammograms were recorded at a scan rates ranging from 50 mV/s to 2000 mV/s using a 2 mm diameter Platinum working electrode (CH Instruments, USA), a Pt wire auxiliary electrode (CH Instruments, USA), and a Ag/AgCl aqueous reference electrode (CH Instruments, USA). Cyclic voltammograms were iR
compensated at 85% with impedance taken at 100 kHz using the ZIR tool included within the EC-Lab software.

**Rotating Disk Electrode (RDE) experiments**

A Pine MSR rotator (PINE Research, Durham, NC) was used for RDE experiments. Same electrode configuration as the CV experiments was used, except that the working electrode was a platinum fixed-disk PEEK shroud working electrode (PINE Research, Durham, NC). The working electrode was rotated at values spanning from 500 RPM to 3300 RPM, while the voltage was linearly swept from 0 V vs. OCV to 0.1 V vs. Ag/AgCl, at 5 mV/s. All RDE experiments were repeated three times.

**Chronoamperometry**

Two compartments of the H-cell were separated by an AMI-7001 anion exchange membrane (Membrane International Inc., USA). Both compartments of the H-cell were purged with nitrogen throughout the experiment. Potential at the working electrode was at −0.004 V and 0.4 V vs. Ag/AgCl aqueous reference electrode for reduction and oxidation, respectively. A platinum mesh was employed as the working electrode, and a Pt wire served as the counter electrode. Reference electrode, and working electrode occupied the same compartment containing 3 mL of the solution of redox active species. Counter electrode compartment contained 3 mL of 0.5 M H₂SO₄. Upto 50 cycles of bulk reduction, and oxidation were performed, and the solution in working electrode compartment was transferred to a three electrode cell for cyclic voltammetry measurements.

**Membrane cross-over studies**

The amount of MB cross-over through AMI-7001 anion exchange membrane was monitored using a H-cell set up (Adams and Chittenden, USA). A volume of 10 mL of 0.1 mM MB
in 0.5 M H₂SO₄ was in one compartment of the H-cell. The other half of the H-cell was filled with 10 mL of 0.5 M H₂SO₄. Both compartments contained stir bars and the solutions were stirred continuously throughout the experiment. A 1 mL aliquot from each side of the H-cell was used to measure the UV-Vis absorbance for a month. The membrane was studied using scanning electron microscopy (Hitachi S4000, USA) before and after the cross-over study.

**Membrane interaction studies**

The amount of methylene blue adsorbed by different types of membranes were evaluated using UV-Vis spectroscopy. AMI 7001, CMI 7000, and Nafion NE1035 membranes (1 cm×2 cm) were each immersed in a volume of 3 mL of 0.1 mM MB in 0.5 M H₂SO₄ in scintillation vials. After 24 hours, the absorbance measurements of the MB solutions were recorded using a Cary 8454 UV-Vis diode array system.

**Galvanostatic cycling**

Charge-discharge testing was done in a glass H-cell (Adams and Chittenden, USA) and a Bio-Logic SP 200 potentiostat/galvanostat. Negative electrode compartment contained 2.5 mL of 2.5 mM or 0.5 mM MB in 0.5 M H₂SO₄. Positive electrode compartment was filled with MB, chemically reduced using ascorbic acid as a reducing agent. The compartments of the H-cell were separated by an AMI-7001 anion exchange or Nafion NE1035 membrane (~0.05 cm², Membrane International Inc., USA). Two platinum mesh electrodes were placed in the posolyte and negolyte chambers. Electrodes attached to Pt wire current collectors were submerged in the electrolyte solutions (~0.5 cm). Membranes were soaked in the electrolyte solutions for 24 hours before each experiment. Galvanostatic conditions of 0.15 mA charging current and 0.15 mA discharge current was used with AMI 7001 anion-exchange membrane. Charging and discharging currents of 0.05 mA was used in the cycling experiment with the Nafion NE1035 proton-exchange membrane.
**Spectroelectrochemistry experiments**

A spectroelectrochemical cell kit from BASi, USA was used to monitor the spectral changes as MB was getting reduced. The potential at the Pt minigrid working electrode was controlled at −0.1 V vs. Ag/AgCl. UV-Vis absorbance spectra were recorded at various time points of bulk reduction using a Cary 8454 UV-Vis diode array system.

![Fig 3.1](image1.png)

**Figure 3.S1.** CV profiles of MB at different pH values

![Fig 3.2](image2.png)

**Figure 3.S2.** Scan rate-dependent CVs of a 0.1 mM MB in 0.5 M H₂SO₄ solution obtained using a Pt working electrode at room temperature
Figure 3.S3. Controlled potential electrolysis data for 0.1 mM MB in 0.5 M H2SO4; Capacity versus time plot (a), Capacity and coulombic efficiency of each cycle (b), and CV profiles before and after bulk electrolysis (c)
Figure 3.S4. UV-Vis absorbance data for the cross-over study
Figure 3.S5. Digital photographs and SEM images of the membrane before and after the cross-over study.
Figure 3.S6. UV-Vis absorbance of methylene blue solutions after soaking different membranes for 24 hours

Figure 3.S7. Galvanostatic cycling profiles of methylene blue with AMI 7001 anion-exchange membrane: 1st cycle to 5th cycle (a) and 45th cycle to 50th cycle (b)
Figure 3.S8. Current vs time curve for bulk reduction of MB (a), UV-Vis spectra obtained in the bulk reduction (b), and UV-Vis spectra of the bulk reduced solution exposed to air (c).
Chapter 04-Concentration-dependent charge-discharge characteristics of non-aqueous redox flow battery electrolyte combinations


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4.1. Introduction

Non-aqueous redox flow batteries (naRFBs) use redox active species and supporting electrolyte materials dissolved in organic solvents and are promising high-capacity energy storage devices 5, 115. A large collection of coordination complexes 35-37, 41, 116, 117, organic compounds 13, 50, 118-122, and redox active polymers 59, 115, 123 have been explored as charge-carriers in naRFBs. The popularity of naRFBs is primarily attributed to the wider potential windows that are enabled in organic solvents versus aqueous redox flow batteries 14, 25. These non-aqueous systems provide access to higher cell voltages that would otherwise exceed the breakdown voltage of water. Since energy capacity is directly related to cell potential and concentration, the open circuit voltage is one of the most important parameters of any flow battery. Although some coordination complexes are quite soluble 124, typical naRFB electrolytes are plagued by solubilities that are much lower than aqueous electrolyte species such that cell potential gains to energy density are negated 15, 125. Current and energy densities are thus largely limited by the low solubilities of electrolyte solutions 13, 125.

Recent efforts have sought to increase energy densities by addressing solubility using one of three methods: The first method is the design and synthesis of redox active molecules with improved solubilities in organic solvents. Previously, the low solubility of redox active components was identified as a major cause of low current densities and low energy densities of naRFBs 116, 125-127. Cabrera et al. 124, 128 developed a series of chromium-based coordination complexes with
a maximum solubility of 1 M in acetonitrile. Charge-discharge experiments were performed at a concentration of 0.01 M of the active species. Sevov et al. \cite{sevov2010} published bis(pyridylimino)isoindolato-based (BPI) coordination complexes as negolyte material for naRFBs. It was reported that a nickel BPI complex possessed a solubility of 0.7 M in acetonitrile. H-cell cycling studies were carried out at 0.002 M of the active species. Another recent report showed that acetyl substitution on ferrocene enhanced solubility (0.81 M in propylene carbonate) as well as open circuit voltage \cite{wang2018}. Galvanostatic charge-discharge studies were carried out in a coin cell using 0.5 M acetyl ferrocene (AcFc) as the posolyte in a Li/AcFc battery system. Thompson, Sanford, and co-workers \cite{thompson2019} reported a suite of chromium and vanadium acetylacetonate complexes and assessed their solubilities and electrochemical behaviors as a function of the ligand structure. The ester functionalization of acetylacetonate ligands resulted in solubilities of 1.8 M in acetonitrile. Cycling studies were done in a static H-cell and a flow cell using 0.05 M and 0.1 M concentrations, respectively. In addition to neutral organic moieties, charged functional groups may also enhance solubility, as demonstrated with ferrocene derivatives evaluated by Wang and co-workers \cite{wang2018}. Functionalized ferrocenes served as catholytes in a Li metal-organic hybrid redox flow battery. As with the coin cell system described above, flow studies were performed at high concentrations, in this case 0.8 M. The second method to increase active species concentration was developed by Takechi et al. \cite{takechi2019}. This method requires the careful selection of electrolyte and supporting electrolyte such that the charge carrier and supporting electrolyte form a molten salt that remains soluble at high concentrations relative to just the charge carrier on its own. Flow cell studies were done at 1 M concentration. The third method combines the role of organic solvent and charge carrier into a single molecule. Cong at al. \cite{cong2019} replaced organic solvent with low melting point redox active molecules to achieve a highly concentrated negolyte.
With a few exceptions \cite{127, 129, 133, 134}, even when higher concentrations were possible, subsequent studies were often performed at millimolar concentrations. Recent literature regarding Li-ion batteries has demonstrated that at high concentrations, major changes in the electrochemical behavior of non-aqueous electrolytes take place \cite{135}. These changes were attributed to the changes in solvation structure of the ions. Studies establishing the role of concentration on electrochemical behavior of naRFBs are rare despite the influence that such effects may have on cell performance \cite{125}. To the best of our knowledge, there are not many reports in the naRFB literature that contrast the performance of active species at both low and high concentrations to establish charge-discharge profiles at analytically relevant and device relevant conditions \cite{14, 136}.

Herein, we report a study of the role of concentration on charge-discharge characteristics for four different naRFB electrolyte combinations using well-established electroactive compounds: ferrocene (Fc), cobaltocenium hexafluorophosphate ([Co(Cp)_2]PF_6), N-methylphthalimide (N-meth), and 2,2,6,6-Tetramethylpiperidine 1-oxyl (TEMPO). All four of these compounds have emerged as candidates for naRFBs \cite{65, 116, 120, 129, 133, 134, 137}. Kim and co-workers \cite{65} studied ferrocene and cobaltocenium hexafluorophosphate as positive and negative electrolyte materials, respectively. Up to three charge-discharge cycles were reported using 0.01 M active species in acetonitrile. Ding et al. \cite{133} reported the use of metallocenes as redox active electrolyte compounds in a lithium-based redox flow battery. They analyzed a battery utilizing ferrocene and ferrocenium hexafluorophosphate in dimethyl sulfoxide (DMSO) as a posolyte and cobaltocene in dioxolane (DOL) as a negolyte. It was demonstrated that a change in concentration of the active species from 0.1 M to 1 M did not affect the coulombic, voltage, nor energy efficiency in this system. Li et al. reported an all-organic redox flow battery using 0.1 M TEMPO/1.0 M NaClO_4/acetonitrile and 0.1 M N-methylphthalimide/1.0 M NaClO_4/acetonitrile as positive and negative electrolyte solutions, respectively \cite{47}. Here, we evaluate four combinations (Fc/[Co(Cp)_2]PF_6, Fc/N-meth, TEMPO/N-meth, and TEMPO/[Co(Cp)_2]PF_6). Fc/N-meth and TEMPO/[Co(Cp)_2]PF_6 have not yet
been reported as active species combinations. Cycling experiments were performed at a variety of concentrations. Changes in charge-discharge profiles at different concentrations are reported. In addition, we discuss the effect of different catholyte/anolyte combinations on charge-discharge cycling. determined for each species at both dilute and saturated concentrations.

4.2. Results and Discussion

4.2.1 Effect of active species concentration on charge-discharge performance

Theoretical energy densities are usually calculated for flow battery systems using the maximum solubility of redox active species and theoretical open circuit voltages predicted from cyclic voltammetry (Equation 04). Although maximizing concentrations is attractive from the standpoint of energy densities, there are practical ramifications to using saturated electrolyte solutions. These include the changes to internal resistance, membrane cross-over, and potential fouling of the membrane, which in turn affect the discharge voltages and energy capacities of any given RFB system. As previously mentioned, cycling studies done at high concentrations are scarce in the naRFB literature. Thus, there is a need to compare and contrast the charge-discharge characteristics under saturated conditions against the dilute concentrations commonly used.

4.2.2 Determination of Solubilities

In this study, we first determined the solubility limits of each species in 0.05 M TBAPF$_6$/CH$_3$CN using electronic absorption spectroscopy. Yan and co-workers recently published a perspective article on the selection of solvents and supporting electrolyte for naRFBs. In this perspective, CH$_3$CN is identified as a good solvent for naRFB applications due to its low viscosity and high ionic conductivity. In addition, CH$_3$CN has been the most often used organic solvent in non-aqueous electrochemistry experiments as well as naRFB studies. All four compounds selected in this study were readily soluble in CH$_3$CN. Molar absorptivity coefficients of Fc, [Co(Cp)$_2$]PF$_6$, 

63
TEMPO, and N-meth were 86 M$^{-1}$ cm$^{-1}$, 200 M$^{-1}$ cm$^{-1}$, 9.5 M$^{-1}$ cm$^{-1}$, and 2,320 M$^{-1}$ cm$^{-1}$, respectively. The presence of TBAPF$_6$ did not have a significant effect on these values compared to literature values determined in the absence of supporting electrolyte $^{141-144}$. Maximum solubilities were determined to be 0.14 M, 1.0 M, 22 M, and 0.70 M for Fc, [Co(Cp)$_2$]PF$_6$, TEMPO, and N-meth respectively. Solutions of each active species were made at the highest possible concentrations as determined by UV-Vis absorbance studies. Saturation was confirmed by adding additional material to the saturated solutions, resulting in no additional dissolution. Since each of these species is either oxidized or reduced during the operation of a flow battery, it is equally important to ensure that the redox products are also soluble. In our cycling studies at high concentrations, we did not observe any precipitation for any combination of electrolytes. Therefore, the initial concentrations of charge carriers provide an accurate upper limit of concentration from which to determine the theoretical energy densities for these battery systems.

4.2.3 Voltammetric behavior

CV experiments are informative to understand redox behavior at dilute conditions but are typically not run under saturated conditions. We performed saturation CV experiments in 0.05 M TBAPF$_6$ in anhydrous CH$_3$CN at scan rates of 300 mV/s (Figure 4.1). The CV profiles at dilute concentrations enable calculation of E$_{1/2}$ values. These values were 0.08 V, −1.23 V, 0.35 V, and −1.86 V for Fc, [Co(Cp)$_2$]PF$_6$, TEMPO, and N-meth, respectively. As shown in Figure 4.1, at saturated concentrations, Fc, and [Co(Cp)$_2$]PF$_6$ have discernible oxidation/reduction peaks with well-defined $i_{pa}$ and $i_{pc}$ values. In contrast, TEMPO and N-meth show ever-increasing current response as the potential sweeps more positive and negative, respectively, a behavior that has been observed in aqueous quinone systems $^{100}$. In addition, with [Co(Cp)$_2$]PF$_6$, it was apparent that the reversibility of the redox couple was influenced by concentration. At 0.01 M, the cathodic to anodic peak current ratio was 1:1 and at 1 M, it became 1.5. This phenomenon was also observed in a recent aqueous RFB publication, which used MnO$_4$−/MnO$_4^{2−}$ as a redox couple $^{145}$. 

64
The reduction of anodic peak current was due to the lower diffusion coefficient of cobaltocene relative to cobaltocenium at high concentrations. As expected, following the Randles-Sevcik equation, the current densities at saturated conditions were correlated with solubility in the following order: TEMPO > \([\text{Co(Cp)}_2\text{PF}_6]\) > N-Meth > Fc.

4.2.4 Change in solution conductivities with concentration

The conductivity of electrolyte solutions has a large impact on the voltage losses observed in the discharge of RFBs. Concentration is one key factor which affects a solutions’ conductivity. The conductivity of each solution was calculated as the reciprocal of resistivity obtained following the Equation (16) below.

\[
R = \frac{\rho l}{A} \tag{7}
\]

In Equation (7), \(R\) is the resistance, \(\rho\) is the resistivity, \(l\) is the length and \(A\) is the cross sectional area. The Figure 4.2 shows the change in solution conductivities as the concentration...
was varied. All the conductivity values were in par with those reported for similar naRFB electrolyte solutions[^146]–[^147]. For [Co(Cp)$_2$]PF$_6$, conductivity increased (~37 mS cm$^{-1}$ to ~196 mS cm$^{-1}$), when concentration was increased from 0.01 M to 1 M (Figure 4.2) consistent with the addition of a complex salt. As the concentration increased for the neutral species, the conductivities of Fc, TEMPO, and N-meth all decreased. This phenomena has been previously observed in other naRFB electrolyte solutions and was attributed to increased molecular interactions, aggregations and solvent volume fraction at higher concentrations[^137]–[^146]. In addition to solution conductivity changes, there can be differences in solvation structure as shown by Hu and co-workers, which also affects the charge-discharge profiles. They showed how the solvation structure of ferrocenylmethyl dimethyl ethyl ammonium bis(trifluoromethanesulfonyl)imide

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(Fc1N112-TFSI) active species changed at higher concentrations through computational methods.

4.2.5 Charge-discharge experiments

All charge-discharge experiments were performed in a nitrogen filled glove box to ensure that the active species remain stable across the experiments as ferrocenium is known to interact with oxygen and decompose. Figure 4.3 shows the four combinations employed in this study. Flow batteries using Fc/[Co(Cp)2]PF6 and TEMPO/N-meth systems have been previously studied. In addition to following up on those reports, we introduce the combinations of FC/N-meth and TEMPO/[Co(Cp)2]PF6. The theoretical state of charges (SOCs) at elevated concentrations are large values and it takes a longer time to achieve a certain percentage state of charge compared to diluted conditions. In our charge-discharge experiments at high concentrations, inconsistencies were observed from cycle to cycle with some of the systems. We attribute these inconsistencies to active species cross-over and membrane fouling. Since we were interested in

![Figure 4.3. Combinations of organic electrolytes employed in this study for charge-discharge experiments.](image-url)
the ramifications of concentration on electrochemical behavior, we sought to minimize effects from membrane fouling by using a lower SOC (5% or 1%) scheme that limited the overall time of the charging cycles. Furthermore, it should be noted that the molar concentrations used in these experiments result in charge capacities that meet or exceed 100% SOC capacities for many systems studied in the literature at millimolar concentrations. Therefore, even with the low SOC threshold, a significant amount of total charge was stored in each cycle.

4.2.6 Effect of active species combinations on charge-discharge experiments

Although the sides of a flow battery are ideally isolated, in practice, crossover and electron transfer kinetics may play a role in the charge-discharge behavior when different combinations of posolyte/negolyte materials are used. These studies were carried out at dilute conditions where redox cycling was well defined based on the peaks observed in CV experiments. Representative charge-discharge curves for first five cycles and respective coulombic, voltage, and energy efficiencies for the first fifteen cycles of each system obtained at dilute conditions are shown in Figure 4.4. Coulombic, voltage, and energy efficiencies for each charge-discharge cycle were determined following Equations (13), (14), and (15), respectively. The theoretical SOC for the cells at 0.01 M concentration of active species with a half-cell volume of 3 mL is 0.8 mAh. Charging was performed until a capacity of 0.04 mAh (5% theoretical SOC) was achieved. All four systems show clear discharge plateaus. Fc/[Co(Cp)2]PF6 and Fc/N-meth entities showed the most consistent charge-discharge curves as evidenced by coulombic efficiency calculations. Coulombic efficiencies for the first 15 cycles were as high as ~90% for both these systems. For TEMPO/N-meth coulombic efficiencies were scattered between 60-90%. A previous report on these two active components showed stable coulombic efficiencies around 90% for the first 20 cycles. A flow cell was used in those experiments under galvanostatic control using a different supporting electrolyte (Sodium hypochlorite, NaClO), which could contribute to more stable efficiencies. In TEMPO/[Co(Cp)2]PF6 combination, coulombic efficiencies gradually decreased.
from ~80% to ~60%. Similar decreases observed in the literature were attributed to species cross-over with time. Voltage efficiencies of all four systems were stable over 15 cycles. For Fc/[Co(Cp)₂]PF₆ and TEMPO/N-meth combinations voltage efficiency was around 60%. It was around 50% for Fc/N-meth and TEMPO/[Co(Cp)₂]PF₆ systems. The theoretical energy densities calculated for the four systems using Equation (4) were 646 J/L, 1,157 J/L, 1,206 J/L, and 1,013 J/L for Fc/[Co(Cp)₂]PF₆, Fc/N-meth, TEMPO/N-meth, and TEMPO/[Co(Cp)₂]PF₆ systems, respectively. The energy densities for all four systems at 0.01 M concentration were also calculated using the average discharge potentials as the cell voltage in Equation (4). These values were 362 J/L, 603 J/L, 729 J/L, 507 J/L for Fc/[Co(Cp)₂]PF₆, Fc/N-meth, TEMPO/N-meth, and TEMPO/[Co(Cp)₂]PF₆ systems, respectively. The mismatch between theoretical and experimental energy densities reflects voltage losses during discharge due with cell design and over potentials. It has been reported that the discharge performance of a battery depends on the concentration of the redox active species. This phenomenon was studied on a number of aqueous RFBs but has not been extended to non-aqueous systems. Hence, we investigated the role of concentration on cycling performance in selected naRFB systems.

![Figure 4.4](image)

**Figure 4.4.** Representative charge-discharge curves using 0.01 M active species in 0.05 M TBAPF₆/CH₃CN, and respective coulombic, voltage, and energy efficiencies for the first 15 cycles of each system.
least soluble redox active species in a given catholyte/anolyte combination determines the highest concentration that can be used in an RFB.

4.2.6.a \( \text{Fc/}[\text{Co(Cp)}_2]\text{PF}_6 \) system

Figure 4.5 shows cycling profiles at three different concentrations using Fc as the catholyte and \([\text{Co(Cp)}_2]\text{PF}_6\) as the anolyte. The maximum concentration for this system was 0.14 M, restricted by the solubility of ferrocene. Charge capacity cutoffs were 0.04 mAh (5% of the theoretical state of charge of 0.8 mAh), 0.28 mAh (5% of the theoretical state of charge of 5.6 mAh), and 0.56 mAh (5% of the theoretical state of charge of 11.2 mAh) for 0.01 M, 0.07 M, and 0.14 M concentrations, respectively. Voltage efficiencies increased from ~60% to ~80% with increasing concentration. A voltage efficiency of less than 100% may arise from the following three phenomena: Ohmic losses, activation polarization, and concentration polarization.

![Figure 4.5](image_url)  
Figure 4.5. Charge-discharge curves for Fc/[Co(Cp)] PF₆ in 0.05 M TBAPF₆/CH₃CN at different concentrations (A); coulombic, voltage, and energy efficiencies for the first 5 cycles (B); Nyquist plots for impedance before, and after cycling at different concentration.
inherent resistance of the electrolyte solution and membrane contribute to ohmic losses. Concentration polarization introduces resistance from changes in electrolyte concentration across the cell resulting in regions of poor conduction. Activation polarization reflects the overpotential associated with the redox reaction occurring between the active species and the electrode. As discussed above, solution resistance increased for Fc and decreased for \([\text{Co(Cp)}_2]\text{PF}_6\), as the concentration was higher. We attribute the observed voltage efficiency improvements in the Fc/[\text{Co(Cp)}_2]\text{PF}_6 system, to the increased conductivity of [\text{Co(Cp)}_2]\text{PF}_6, which has ultimately lead to lesser ohmic losses.

In a Nyquist plot, the high frequency intercept provides information about the resistance of the membrane and electrolyte solution, i.e. the ohmic losses. The low frequency intercept of a Nyquist plot combines the solution resistance with the charge-transfer resistance that contains contributions from activation polarization and concentration polarization. As shown in Figure 4.5(b), voltage efficiencies increased with cycling for 0.07 M and 0.14 M concentrations. For the 0.01 M solution, voltage efficiency did not significantly change during cycling. This result matches well with the EIS data obtained Figure 4.5(c)). The low frequency intercept values were \(~2,900 \, \Omega\) (0.01 M), \(~3,600 \, \Omega\) (0.07 M), and \(~2,400 \, \Omega\) (0.14 M) before cycling and \(~3,100 \, \Omega\) (0.01 M), \(~2,300 \, \Omega\) (0.07 M), and \(~1,500 \, \Omega\) (0.14 M) after cycling. The increase in voltage efficiencies with cycling has been observed in previous flow battery studies.

Coulombic efficiencies decreased from \(~90\%\) to \(~50\%\) with increasing concentration, giving rise to lower energy efficiencies. We attribute this drop to increased membrane cross-over at the elevated concentrations as observed with the UV-Vis experiments described below. In addition, for 0.07 M and 0.14 M solutions, coulombic efficiencies increased with cycling (\(~60\%\)~\(~70\%\) for 0.07 M and \(~50\%\) to \(~60\%\) for 0.14 M). Using Equation (4), the theoretical energy density values for the 0.01 M, 0.07 M, and 0.14 M concentrations were calculated to be 646 J/L, 4,530 J/L, and
9,050 J/L, respectively. The experimental energy densities were 362 J/L for 0.01 M, 2,700 J/L for 0.07 M, and 6,750 J/L for 0.14 M concentrations.

4.2.6.b  

**Fc/N-meth system**

Charge-discharge studies performed with Fc as the posolyte and N-meth as the negolyte are shown in Figure 4.6.

![Graphs showing charge-discharge studies](image)

**Figure 4.6.** Charge-discharge curves for Fc/N-meth in 0.05 M TBAPF₆/CH₃CN at different concentrations (A); coulombic, voltage, and energy efficiencies for the first 5 cycles (B); Nyquist plots for impedance before, and after cycling at different concentrations.

As with the Fc/[Co(Cp)₂]PF₆ system, ferrocene limits the maximum concentration to 0.14 M. In contrast to Fc/[Co(Cp)₂]PF₆, voltage efficiencies of this system did not increase with concentration and were stable around 50% in all experiments (Figure 4.6(b)). In addition, discharge voltages did not increase with time, as was seen with the 0.07 M and 0.14 M solutions of Fc/[Co(Cp)₂]PF₆. EIS data before and after cycling did not substantially change, consistent with
the invariance of voltage efficiency (Figure 4.6(c)). Theoretical energy density values of 1,157 J/L, 8,104 J/L, and 16,209 J/L were calculated for the 0.01 M, 0.07 M, and 0.14 M concentrations, respectively. The energy densities were also calculated using the average discharge voltages as the cell voltage in Equation (4). They were 603 J/L for 0.01 M, 4,390 J/L for 0.07 M, and 7,430 J/L for 0.14 M concentrations. The coulombic efficiencies decreased significantly from ~90% - ~10% when concentration was increased from 0.01 M to 0.14 M. For both 0.07 M and 0.14 M solutions, coulombic efficiencies decreased with cycling, which was attributed to species cross-over. Accordingly, the overall cell performance was largely degraded in Fc/N-meth system when high concentrations of active species were utilized.

4.2.6.c TEMPO/N-meth system

The maximum solubility of N-meth was determined to be 0.70 M in a 0.05 M TBAPF$_6$/CH$_3$CN solution. Accordingly, for the TEMPO/N-meth combination, the highest concentration used in charge-discharge experiments were 0.70 M. The theoretical state of charge for a cell with 0.70 M concentration and 3 mL half-cell volume is 56.2 mAh. Unlike the other combinations, the 0.70 M system was charged to 1% of the theoretical state-of-charge owing to the significantly longer charge/discharge time at such a high concentration. Charge-discharge cycles are shown in Figure 4.7(a). Voltage, coulombic, and energy efficiencies were ~10% to ~20% in the first four cycles and were erratic from cycle to cycle. At the 5th cycle, coulombic efficiency increased to ~90% and then dropped to ~30% by the 7th cycle. Furthermore, we performed cycling experiments at 0.01 M, 0.07 M and 0.14 M concentrations to a 5% theoretical state-of-charge. Coulombic efficiencies spanned ~60%~90% in all solutions. The voltage efficiencies decreased drastically with increasing concentration (~60%~10%). One major reason for this behavior could be the decrease in solution conductivity of TEMPO as the concentration was increased (Figure 4.7). Using Equation (4), the theoretical energy density values obtained for 0.01 M, 0.07 M, 0.14 M, and 0.7 M concentrations were 1,210 J/L, 8,440 J/L, 16,900 J/L, and 84,400 J/L, respectively. Energy
densities were also calculated and they were 729 J/L for 0.01 M, 1,690 J/L for 0.07 M, 3,380 J/L for 0.14 M, and 3,370 J/L for 0.7 M concentrations. Increasing the concentration of the active species downgraded the overall cell performance in the TEMPO/N-meth system.

\[\text{Figure 4.7. Charge-discharge curves for TEMPO/N-meth in 0.05 M TBAPF}_6/\text{CH}_3\text{CN at different concentrations (A); coulombic, voltage, and energy efficiencies for the first 5/7 cycles (B).}\]

4.2.6.d TEMPO/[Co(Cp)₂]PF₆

Figure 4.8 shows charge-discharge profiles for TEMPO/[Co(Cp)₂]PF₆ at different concentrations. For cycling studies performed at 0.01 M, 0.07 M, and 0.14 M concentrations, voltage efficiencies were stable around ~50%. EIS data before and after cycling didn’t change significantly for the 0.01 M and 0.07 M concentrations as shown from Figure 4.8(c). At 0.14 M, voltage efficiency gradually increased with cycling. Coulombic efficiencies were scattered around ~70%~90% at all concentrations except for 1.0 M solution. Upon cycling, coulombic efficiencies decreased for the 0.14 M, 0.01 M, and 1.0 M solutions. The highest concentration utilized for this system was 1.0 M. As seen in Figure 4.8(b), at 1.0 M concentration, the coulombic efficiency was ~40% for the first cycle. In the 4\textsuperscript{th} cycle this value decreased to ~20%. Species cross-over and membrane fouling are suspected to be the dominant contributors to these losses \cite{127}, as evidenced by significant color changes to the membrane. Voltage efficiencies were between 60-80%.
Theoretical energy densities calculated using Equation (4) were 646 J/L, 7,090 J/L, 14,200 J/L, and 101,300 J/L for 0.01 M, 0.07 M, 0.14 M, and 1.0 M concentrations, respectively. The experimental energy densities calculated for each concentration were 507 J/L for 0.01 M, 3,550 J/L for 0.07 M, and 7,090 J/L for 0.14 M. Using the first and second cycles in the 1.0 M concentration system, the calculated energy density was 77,200 J/L and after the fourth cycle the discharge voltage drops to ~0.5 V resulting in an energy density of ~24,100 J/L.

4.2.7 Active species cross-over

Elevated active species cross-over at high concentrations was hypothesized to be a major culprit for the coulombic efficiency losses observed in the charge-discharge experiments. In order
to test this hypothesis, UV-Vis absorbance measurements of the supporting electrolyte compartment in an H-cell were recorded before and after 24 hours (Figure 4.9). For Fc, [Co(Cp)_2]PF_6, TEMPO, and N-meth the UV-Vis absorbance values at 440 nm, 405 nm, 460 nm, and 292 nm, respectively, were used to estimate the active species cross-over concentrations using the Beer Lambert relationship \(^{153}\). The values obtained are shown in Table (1).

### 4.3. Conclusions

A series of non-aqueous redox flow battery systems utilizing ferrocene or TEMPO as catholyte and cobaltocenium hexafluorophosphate or N-methylphthalimide as anolyte were studied to investigate the effect of concentration and posolyte/negolyte combination on the charge-discharge characteristics. UV-Vis spectroscopy was used to determine the maximum solubilities of the selected redox active species. For Fc, [Co(Cp)_2]PF_6, TEMPO, and N-meth
maximum solubilities were 0.14 M, 1.0 M, 22 M, and 0.70 M, respectively in 0.05 M TBAPF$_6$/CH$_3$CN.

Table 1. Cross-over concentrations of electrolyte solutions at varied concentrations

<table>
<thead>
<tr>
<th>Active Species</th>
<th>Initial Concentration</th>
<th>Crossover concentration after 24 hours (mM)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fc</td>
<td>10 mM</td>
<td>0.88</td>
</tr>
<tr>
<td></td>
<td>140 mM</td>
<td>2.0</td>
</tr>
<tr>
<td>[Co(Cp)$_2$]PF$_6$</td>
<td>10 mM</td>
<td>0.37</td>
</tr>
<tr>
<td></td>
<td>1 M</td>
<td>10</td>
</tr>
<tr>
<td>TEMPO</td>
<td>10 mM</td>
<td>4.5</td>
</tr>
<tr>
<td></td>
<td>22 M</td>
<td>100</td>
</tr>
<tr>
<td>N-meth</td>
<td>10 mM</td>
<td>0.07</td>
</tr>
<tr>
<td></td>
<td>700 mM</td>
<td>0.62</td>
</tr>
</tbody>
</table>

The effects of concentration on coulombic efficiencies are largely obscured due to species crossover at high concentrations. Although this crossover occurs even at low concentrations, decreases in coulombic efficiencies at elevated concentrations that occurred in all four systems strongly suggest that the discovery of appropriate membranes for naRFBs remain an outstanding challenge that must be solved before these systems can realize their theoretical energy densities. That said, crossover was minimal for the Fc/[Co(Cp)$_2$]PF$_6$ and high efficiencies were maintained even at high concentrations. Another reason for the observed consistency in coulombic efficiencies is the well-established electrochemical stability of Fc/Fc$^+$ and [Co(Cp)$_2$]/[Co(Cp)$_2$]$^-$. In comparison to N-meth, for example, which also has a low crossover, the inherent instability of the organic radical anion results in inconsistent charge-discharge curves.
With respect to voltage efficiencies, the Fc/[Co(Cp)₂]PF₆ system showed an increase with increasing concentrations. This increase was attributed to an enhancement of solution conductivity when more complex salt was dissolved. In other systems the overall impedance increased at higher concentrations giving rise to low voltage efficiencies, validating the need to measure electrolyte combinations separately.

This study shows that different combinations of posolyte/negolyte materials behave differently under uniform charge-discharge conditions. In addition, increasing the concentration dramatically changed the static cycling profiles due to differences in solution resistance, membrane fouling and species crossover, but these effects were not universal for each. The experiments establish the necessity for static-cell measurement of new electrolyte combinations not only at millimolar concentrations but also at concentrations more relevant to theoretical energy densities. Once validated by static-cell measurements, such systems can be optimized for charge/discharge parameters, flow rates, flow types etc. ultimately to address device-level design.

### 4.4. Supporting Information

**Experimental**

**Chemicals**

Anhydrous acetonitrile (CH₃CN) was obtained from a Grubbs-type solvent purification system (Pure Process Technology, USA). Tetrabutylammonium hexafluorophosphate (TBAPF₆, Alfa Aesar, USA) was used as received as the supporting electrolyte in all experiments unless blank voltammograms revealed undesired current response in which case crystallization from methanol was carried out. Ferrocene (Sigma Aldrich, USA), cobaltocenium hexafluorophosphate (Strem Chemicals Inc., USA), 2,2,6,6-tetramethylpiperidine 1-oxyl (TEMPO, Acros Organics, USA), and N-methylphthalimide (Alfa Aesar, USA) were used as received.
**Solution preparation**

Electrolyte solutions were prepared by dissolving the active species in 0.05 M TBAPF$_6$/CH$_3$CN.

**Solubility measurements**

Four stock solutions were prepared by dissolving the active species in 0.05 M TBAPF$_6$/CH$_3$CN. UV-Vis absorbances of solutions were recorded using a 1 cm path length cuvette (Starna, USA) on a Cary 8454 UV-Vis diode array system. For Fc, [Co(Cp)$_2$]PF$_6$, TEMPO, and N-meth the peak wavelengths used for calculations were 440 nm, 405 nm, 460 nm, and 292 nm respectively. Five concentrations were used to determine the molar absorptivity coefficients of each compound using the Beer-Lambert relationship. Then, saturated solutions were prepared by adding the desired active species to 100 µL of 0.05 M TBAPF$_6$ in CH$_3$CN until subsequent additions resulted in the persistence of solids. These solutions were allowed to settle for one hour and filtered through glass wool. Three aliquots of each solution were diluted in 0.05 M TBAPF$_6$/CH$_3$CN to obtain absorbance measurements between 0.1-1.0. Absorbances recorded at the respective wavelengths selected for each species were used to extrapolate the maximum solubility in 0.05 M TBAPF$_6$/CH$_3$CN.

**Cyclic voltammetry (CV)**

CVs were performed at room temperature inside a nitrogen filled glove box (Vigor Tech, USA) using a Bio-Logic SP 200 potentiostat/galvanostat and the EC-Lab software suite. Experiments were run with 0.01 M and saturated solutions of each compound in 0.05 M TBAPF$_6$ in CH$_3$CN. Cyclic voltammograms were recorded at a scan rate of 300 mV/s using a 3 mm diameter glassy carbon working electrode (CH Instruments, USA), a Pt wire auxiliary electrode (CH Instruments, USA), and a Ag/Ag$^+$ non-aqueous reference electrode with 0.01 M AgNO$_3$ in
0.05 M TBAPF$_6$/CH$_3$CN (BASi, USA). Cyclic voltammograms were iR compensated at 85% with impedance taken at 100 kHz using the ZIR tool included within the EC-Lab software.

**Charge-discharge experiments**

Charge-discharge testing was done in a nitrogen filled glove box using a glass H-cell (Adams and Chittenden, USA) and a Bio-Logic SP 200 potentiostat/galvanostat. The four different combinations of Fc/TEMPO as posolyte and [Co(Cp)$_2$]PF$_6$/N-meth as negolyte were investigated using 3 mL volumes of electrolyte solutions. The compartments of the H-cell were separated by an AMI-7001 anion exchange membrane (~0.05 cm$^2$, Membrane International Inc., USA). Two graphite felt electrodes (2 cm × 1 cm × 0.5 cm, Fuel Cell Store, USA) were placed in the posolyte and negolyte chambers. Electrodes attached to Pt wire current collectors were submerged in the electrolyte solutions (~0.5 cm). Membranes and graphite felt electrodes were soaked in 0.05 M TBAPF$_6$/CH$_3$CN solution for one hour before each experiment. A custom charge-discharge profile was created using the Modulo Bat technique found in the EC-Lab software. Three conditions were defined: 1) Galvanostatic conditions with 0.5 mA current. 2) potentiostatic conditions using cut-off voltages of 1.34 V, 2.4 V, 2.5 V, and 2.1 V for Fc/[Co(Cp)$_2$]PF$_6$, Fc/N-meth, TEMPO/N-meth, and TEMPO/[Co(Cp)$_2$]PF$_6$, respectively. These cut-off voltages were determined from the CVs at dilute concentrations based on the separation of the oxidation and reduction events. 3) Discharge at a constant current of 0.1 mA. Charging was initiated under galvanostatic conditions (condition 1). If the cut-off voltage was reached, the system switched to condition 2, maintaining an upper voltage as defined for each system. Switching between conditions 1 and 2 enables a charging of the battery to a desired state-of-charge without exposing the electrolyte to high voltages. Under both conditions, if a pre-set state-of-charge was achieved, in this case 5% or 1%, the system switched to condition 3, the constant-current discharge. Charging was reinitiated when a cell potential of 0.2 V was reached.
Electrochemical impedance spectroscopy (EIS)

The resistance of each electrolyte solution was determined using EIS. Two Pt working electrodes (Surface area of 0.0314 cm$^2$, CH Instruments, USA) separated by a distance of 0.75 cm were immersed in electrolyte solutions for all the readings. The low frequency intercepts of the Nyquist plots were used to determine the resistances of each solution. Impedance measurements were also recorded before and after cycling, in the H-cell described above. An amplitude of 10 mV from the open circuit voltage was scanned through a frequency range of 1 MHz to 100 mHz using a Bio-Logic SP 200 potentiostat/galvanostat.

Membrane cross-over studies

Active species cross-over at dilute and saturated conditions were determined using UV-Vis spectroscopy in the H-cell described above. Both compartments of the H-cell were filled with 3 mL volume of 0.05 M TBAPF$_6$/CH$_3$CN (supporting electrolyte solution) and to only one compartment, the redox species was added. The two sides of the H-cell were separated by an AMI-7001 anion exchange membrane. The solutions were stirred for a time period of 24 hours and UV-Vis absorbances of aliquots of the supporting electrolyte solution were measured. Using the Beer-Lambert relationship, the active species cross-over occurring over 24 hours was determined for each species at both dilute and saturated concentrations.
Chapter 05-Mixed-Component Catholyte and Anolyte Solutions for High-Energy Density Non-Aqueous Redox Flow Batteries


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5.1. Introduction

The energy density of a flow battery is critically linked to the active species concentration, number of electrons transferred in the redox reactions, and the cell voltage as expressed by Equation (4). Low active species concentration ($C_{\text{active}}$) is identified as a major culprit for the poor energy densities reported for naRFBs.13, 15, 125, 132 Accordingly, there have been different approaches reported in terms of increasing the concentration of redox active species in naRFBs to achieve high-energy densities. Three methods have been reported so far, to address the issue of low concentration of redox active species in naRFBs. The design and synthesis of redox active molecules having improved solubilities in organic solvents, is the first method. A series of chromium based coordination complexes were studied by Cabrera et al.124, 128 These complexes were reported to have a maximum concentration of 1 M in acetonitrile. Sevov et al.121, 126 reported bis(pyridylimino)isoindolato-based (BPI) based coordination compounds as negative electrolyte materials for naRFBs. A nickel BPI complex demonstrated a solubility of 0.7 M in acetonitrile. In another recent report, it was shown that acetyl substitution on ferrocene enhances solubility upto 0.81 M in propylene carbonate.129 A series of chromium and vanadium acetylacetonate complexes were reported by Thompson, Sanford, and co-workers.130 They studied the solubility and electrochemical behavior as a function of ligand structure. The ester functionalization of acetylacetonate ligands were identified as a method to increase the solubility of these complexes. (1.8 M in acetonitrile) Wang and co-workers154 demonstrated that utilization of charged functional
groups instead of neutral organic moieties lead to improved solubilities. They studied a series of ferrocene derivatives and observed the solubilities as high as 0.8 M in propylene carbonate. Takechi et al.\textsuperscript{131} developed a second method to increase active species concentration, by minimizing the dissolving solvents. In the third approach, redox inactive supporting electrolyte and solvents were replaced by low melting point redox active molecules to achieve concentrated catholyte species.\textsuperscript{132} In addition to increasing the energy density by addressing \( C_{\text{active}} \), several literature reports have focused on enhancing the number of electrons transferred \((n)\) per molecule.\textsuperscript{128} In a recent report, Laramie et al proposed mixing of positive and negative electrolyte materials in terms of achieving a common ion exchange naRFB with multi electron transfer.\textsuperscript{108} They studied two low potential redox couples of iron(II) tris(2,2′-bipyridine) tetrafluoroborate as negative electrode reactions and one redox couple of ferrocenylmethyl dimethyl ethyl ammonium tetrafluoroborate together with the high potential redox couple of iron(II) tris(2,2′-bipyridine) tetrafluoroborate as positive electrode reactions.

The above mentioned methods for increasing \( C_{\text{active}} \) are attractive with the caveat of being limited to special molecules. Especially, the method two and three requires careful selection of molecules with suitable redox behaviors that form/are molten salts at room temperature and were focused on designing catholyte materials with increased concentrations.\textsuperscript{131, 132} In this paper, we propose mixing of redox active components as a method to increase the overall concentration and the number of electrons transferred for both catholyte and anolyte materials. A modified Equation (4) is proposed for volumetric energy density of a RFB when mixtures of active species are used.

\[
U = \frac{1}{2} F V_{\text{cell}} \sum_{i=1}^{N} (n_i C_{\text{active}}^i)
\]

Where \( n \) is the number of electrons transferred in the individual redox reactions, \( C_{\text{active}} \) is the concentration of each redox active species in the mixture. The \( V_{\text{cell}} \) and \( F \) has the same meanings.
as Equation (4). The theoretical cell voltage ($V'_{cell}$) for a mixed component RFB is determined by Equation (9).

$$V'_{cell} = \left[ \sum_{i=1}^{N} \frac{E^0_i}{N} \right]_{\text{cathode}} - \left[ \sum_{i=1}^{N} \frac{E^0_i}{N} \right]_{\text{anode}}$$  \hspace{1cm} (9)

Where, $E^0_i$ represents the standard potential of each redox active species. The Equation (9) determines the cell voltage at the 50% of the state of charge for a mixed component flow battery.

Mixing of redox active components will have a number of advantages compared to the methods reported so far. Firstly, mixing components is less exhaustive. Secondly, a wide range of molecules with desired electrochemical behaviors can be tested for this method. Molecules can be selected from a suite of naRFB active species reported so far and be tested with this method. In addition, this procedure will allow to study multielectron transfer systems, which are scarce in literature and are attractive for high-energy density naRFBs.\textsuperscript{108, 128} We evaluated a naRFB system, where ferrocene (Fc) together with 2,2,6,6-tetramethylpiperidine 1-oxyl (TEMPO) was the catholyte and cobaltocenium hexafluorophosphate ([Co(Cp)\textsubscript{2}]PF\textsubscript{6}) with N-methylphthalimide (N-meth) was the anolyte. These compounds were selected due to their well-established electrochemical properties, their stabilities at their relevant oxidation states, and their low-cost commercial availability. All four active species are readily soluble in a common solvent, acetonitrile.\textsuperscript{47, 65} In addition, all of these molecules have been previously explored as naRFB active species.\textsuperscript{65, 116, 133, 134, 137, 155} The compatibility of the Fc with TEMPO as a posolyte mixture and [Co(Cp)\textsubscript{2}]PF\textsubscript{6} with M-meth as a negolyte mixture were analyzed using cyclic voltammetry (CV), chronoamperometry, and UV-vis spectroscopy. In addition, charge-discharge experiments were also performed to see the suitability of these mixtures for energy storage.
5.2. Results and Discussion

The naRFBs are expected to have higher energy densities compared to aqueous RFBs. Hence, improving the energy densities is an important area of research which has obtained a lot of attention in the naRFB community. There are three methods to enhance the energy density of a naRFB; increasing the number of electrons transferred in the redox processes, the cell voltage, and the concentration of active components. In this work, we have focused on increasing the total concentration and the number of electrons transferred by mixing redox active components. We choose Fc with TEMPO as the posolyte and, ([Co(Cp)₂]PF₆) with N-meth as the negolyte in our study. All four species have well-established one electron transfer redox couples.

5.2.1 Electrochemical compatibility and stability at a short time scale

Cyclic voltammetry (CV) provides an initial insight into the electrochemical reversibility and stability of redox couples.

![Figure 5.1. Cyclic voltammograms of individual species (...) and mixtures (-) obtained at a scan rate of 500 mV/s using a glassy carbon working electrode; (+) = posolyte side, (-) = negolyte side](image)
The Figure 5.1 shows the cyclic voltammograms of individual species and the mixtures. CVs of the mixtures are a combination of the CV profiles of those of individual species. Cycling of the posolyte and negolyte mixtures were performed upto 50 cycles. There were no changes observed in the CV profiles throughout cycling. No undesirable peaks appeared throughout cycling. These observations suggest that at least at the time scale of this CV experiment, active species mixtures were electrochemically and chemically compatible and stable. The standard potential values ($E^0$) were also determined from the cyclic voltammograms. They were; 0.35 V, 0.11 V, −1.28 V, and −1.93 V vs. Ag/Ag⁺ for TEMPO, Fc, ([Co(Cp)₂]PF₆, and N-meth, respectively. Following the Equation (4), the theoretical cell voltage of the proposed RFB system is ~1.84 V, using the standard potential ($E^0$) values obtained from CV profiles. This theoretical cell voltage is larger compared to a RFB with Fc as posolyte and ([Co(Cp)₂]PF₆) as negolyte RFB.

5.2.2 Diffusion controlled mass transport

![Figure 5.2. Peak current vs. square root of scan rate plots as individual and mixtures of species](image-url)
In a RFB, electrolyte solutions are circulating from external reservoirs to the cell components and back to the tanks. The electron transfer from/to the electrodes has to take place while the electrolyte solutions are flowing over the surface of the electrodes. In order for the electron transfer to take place in the limited amount of time, the redox reactions should have fast heterogeneous electron transfer kinetics.

A way to demonstrate fast electron transfer, is to see if the redox reactions are diffusion controlled. We hypothesized that mixing of electrolyte species could affect the mass transport processes of each species due to interactions of active components with each other. To test this hypothesis, a scan rate dependent CV study was performed with individual and mixtures of species in 0.05 M TBAPF$_6$ in CH$_3$CN. Randles-Sevcik plots were made for each species as individual and mixtures of components (Figure 5.2). The linear plots suggest diffusion controlled redox reactions. Hence, all redox reactions showed diffusion controlled processes meaning diffusion is the limiting factor and the heterogeneous electron transfer is fast. Since the redox couples showed quasi-reversible behavior (peak separations increased with increasing scan rate), an average value for the diffusion coefficients were obtained using Randles-Sevcik equations for reversible and irreversible redox reactions.

The diffusion coefficients from individual CV studies are; 2.4×10$^{-5}$ cm$^2$s$^{-1}$ for Fc, 2.4×10$^{-5}$ cm$^2$s$^{-1}$ for TEMPO, 2.3×10$^{-5}$ cm$^2$s$^{-1}$ for [Co(Cp)$_2$]PF$_6$, and 1.7×10$^{-5}$ cm$^2$s$^{-1}$ for N-meth. The diffusion coefficients for each species in mixtures are; 2.1×10$^{-5}$ cm$^2$s$^{-1}$ for Fc, 2.8×10$^{-5}$ cm$^2$s$^{-1}$ for TEMPO, 2.6×10$^{-5}$ cm$^2$s$^{-1}$ for [Co(Cp)$_2$]PF$_6$, and 2.3×10$^{-5}$ cm$^2$s$^{-1}$ for N-meth. The diffusion coefficients of all four species aren’t changed significantly when mixed with another active species. Hence, it can be concluded that mixing did not significantly affect the mass transport processes of individual species and all the redox processes have fast electron transfer kinetics which is essential for a RFB application.
5.2.3  Electrochemical compatibility and stability at long time scale

5.2.3.a  Bulk cycling

CV data provides information about the electrochemical stability and compatibility of a mixture of redox active species for a short time scale. Bulk cycling can be used to determine the stabilities at a longer time scale. Changes in charge capacity throughout cycling is useful in identifying interactions between components in a mixture. Accordingly, bulk cycling of each species were first performed, followed by that of mixtures. Bulk cycling of individual species sets a baseline stability expected to see from each species. As shown in Figure 5.3, individual cycling of Fc and TEMPO showed only a small capacity fade during the experiment time of ~7.5 hours. Charge capacity retention of the mixture in the long cycling time (~15 hours) was lesser than that for the individual species. This is attributed to high species cross-over at high-concentration at a longer time length through the membrane separator. Coulombic efficiencies of individual species cycling

![Figure 5.3. Charge retention (a, b) and coulombic efficiency (c, d) plots for individual and mixture bulk cycling](image)
and that of the mixture were stable around ~100%. This suggests minimal interaction between Fc and TEMPO. In addition, no precipitation was observed, suggesting the oxidized species are not interacting with each other to make solids. It also shows that oxidized species possess the same solubilities as the neutral species, and the concentration of neutral species can be added to get the overall active species concentration following Equation (8).

![Cyclic voltammograms obtained before and after charge-discharge experiments using cation and anion exchange membranes; (+) = posolyte side, (-) = negolyte side](image)

**Figure 5.4.** Cyclic voltammograms obtained before and after charge-discharge experiments using cation and anion exchange membranes; (+) = posolyte side, (-) = negolyte side

Individual cycling of [Co(Cp)2]PF6 and N-meth also showed a capacity fade. Capacity decay of N-meth cycling was larger compared to other three species. Capacity decay of the mixture was largely similar to that of N-meth. Coulombic efficiencies of the mixture were similar to that observed with cycling of individual species and were stable around ~90%. This suggest that the [Co(Cp)2]PF6 and N-meth does not interact chemically or electrochemically with each other. No precipitation of species was observed either.

The decrease in capacities with long term cycling was attributed to species cross-over. In order to test this hypothesis, and to ensure the observed capacity decay is not owing to electrochemically inactive products, CVs of the positive and negative electrode compartment
solutions were obtained after charge-discharge experiments using both cation and anion exchange membranes as separators. Figure 5.4 shows that after ~20 hours of charge-discharge positive and negative compartments contain some amounts of negolyte and catholyte species, respectively. Accordingly, we conclude that the observed capacity decay is largely a result of species cross-over through the membranes.

5.2.3.b **UV-vis absorbance spectroscopy**

RFBs are long term EES devices. It’s important that the electrolyte solutions are stable at the charged state for a long time. UV-vis spectroscopy is a valuable method in determining the stability of mixtures of active species. Accordingly, Fc/TEMPO and [Co(Cp)2]PF6/N-meth...
solutions were bulk oxidized and reduced, respectively and UV-vis absorbance measurements were obtained for a time period of four days. As seen from Figure 5.5, the oxidized Fc/TEMPO mixture remained largely stable across the study. It can be claimed that there aren’t any significant interactions between the two species at the oxidized state. A similar observation was made with the bulk reduced [Co(Cp)$_2$]PF$_6$/N-meth solution. The absorbance peak characteristic of N-meth at ~200 nm was decreased initially and remained stable after 3 hours across the experiment. However, cobaltocene absorbance peak around ~400 nm didn’t change significantly with time suggesting minimal interactions between cobaltocene and reduced N-meth. Overall, the UV-vis experiments have demonstrated that the active components remain stable as a mixture at the charged states, which is attractive for long term energy storage.

5.2.4 Charge-discharge experiments

![Charge-discharge experiment results using an anion exchange membrane at a diluted concentration and cyclic voltammograms obtained before after cycling; (+) = posolyte side, (−) = negolyte side](image-url)

**Figure 5.6.** Charge-discharge experiment results using an anion exchange membrane at a diluted concentration and cyclic voltammograms obtained before after cycling; (+) = posolyte side, (−) = negolyte side
Figure 5.7. Charge-discharge experiment results using a cation exchange membrane at a diluted concentration and cyclic voltammograms obtained before after cycling; (+) = posolyte side, (−) = negolyte side

Figure 5.6 shows the charge-discharge cycling experiment performed upto ~18 hours, using 5 mM concentration of each species and half-cell volumes of 5 mL with an anion exchange membrane as the separator. Theoretical capacity of the cell is 1.3 mAh. Charging was performed upto 0.25 mAh, which is ~25% of the theoretical state of charge (SOC). Coulombic efficiencies of ~97% was observed for all the charge-discharge cycles. An energy density of ~530 J/L was calculated for this system using Equation (8). Multiple plateaus in galvanostatic charge-discharge curves indicate that multiple electron transfers occur at unique half-cell potentials. The CVs obtained before and after cycling are also shown in Figure 5.6. No new peaks appeared after cycling. Peak currents have not significantly changed after cycling. For [Co(Cp)_2]PF_6 and N-meth, peak positions have shifted after cycling. A small amount of species cross-over was observed after ~18 hours. Despite the cross-over through the membrane, the peak intensities of posolyte
material did not decrease significantly, possibly due to solvent evaporation over the extended time period of the experiment. Furthermore, the extent of posolyte crossover was rather low as compared to negolyte cross-over. Figure 5.7 shows the charge-discharge cycling experiment performed using a cation exchange membrane. Coulombic efficiencies were stable around ~94% for all cycles. The energy density calculated using Equation (8) was ~627 J/L. The CVs obtained at different time points of the experiment is also shown in Figure 5.7. Compared to the anion exchange membrane, the species cross-over seems higher when the cation exchange membrane was used as observed from the CV profiles.

In order to determine the electrochemical behaviors at higher concentrations, CV data were collected at 0.05 M active species concentrations (Figure 5.8). At a scan rate of 50 mV/s, all four species demonstrated distinct oxidation/reduction peaks with anodic to cathodic peak ratios of unity, suggesting reversibility.36 At much higher scan rates, the peak currents continue to increase, as was observed with aqueous quinone systems.100

![Figure 5.8. CVs obtained at 0.05 M concentration at a scan rate of 50 mV/s using a glassy carbon working electrode](image)

Figure 5.9 shows a representative charge-discharge cycle performed with 25 mM concentration of each species. Half-cell volumes were 4 mL. Theoretical capacity of this cell is 5.3 mAh. Charging was performed up to 1.25 mAh (25% SOC). A coulombic efficiency of ~ 85% was obtained for the long charge-discharge cycle. An energy density of ~2653 J/L was calculated
Species cross-over is larger than that was observed with the previous charge-discharge experiment, possibly owing to high concentration used in this experiment. No additional peaks appear and the peak currents remain significantly unchanged. Charge-discharge experiments were also performed at elevated concentrations of 0.1 M (50 mM of each active species) and 0.2 M (100 mM of each active species; Figure 5.10). In both experiments, half-cell volumes of 0.5 mL were used with an anion exchange membrane as the separator. The theoretical capacities for the two systems were 1.3 mAh and 2.6 mAh. Charging was performed up to 50% and 25% of the theoretical state of charges for the 0.1 M and 0.2 M concentrations, respectively. The coulombic efficiencies were ~90% for the 0.1 M concentration. For 0.2 M concentration, the coulombic efficiency was ~85%. In these cycling studies at high concentrations, no precipitation was
observed. Therefore, the initial concentrations of charge carriers can be used as an accurate upper limit of concentration to calculate the theoretical energy densities using Equation (8). The energy density calculated for the 0.1 M concentration using the average $V_{\text{cell}}$ of the first discharge plateau was 3,714 J/L. An energy capacity of 7,718 J/L was obtained for the 0.2 M concentration.

The non-linear relationship between experimental energy density and concentration reflects that overpotential losses are lessened when higher concentrations were used. The high coulombic efficiencies observed throughout cycling demonstrates the electrolyte mixtures show minimal interactions even at high concentrations. These experiments establish the ability of the mixed component electrolytes to be used as high-energy density RFB materials.

### 5.3. Conclusions

The energy density of a RFB is critically linked to the active species concentration, number of electrons transferred in the redox reaction, and the cell voltage. In this work, mixing of redox active species is proposed as a method of increasing concentration or the number of electrons...
transferred in the redox processes for naRFBs. CV, chronoamperometry, UV-vis spectroscopy, and charge-discharge experiments were used to show the feasibility of using a mixture of ferrocene and TEMPO as posolyte and [Co(Cp)₂PF₆] and N-meth as negolyte in an naRFB. CV experiments demonstrated the short term stability and compatibility of the active species across 50 cycles. In addition, a theoretical cell voltage of ~1.84 V was determined for a naRFB system consisting Fc/TEMPO as catholyte and [Co(Cp)₂PF₆]/N-meth as anolyte. Scan rate dependent CV experiments were performed and peak current versus square root of scan rate plots were made to show that mixing of components did not significantly affect the mass transport processes of individual species. The diffusion coefficients of each species as a mixture was determined using the Randles-Sevcik equations and they were compatible to the values obtained from individual CV studies. Chronoamperometry experiments were carried out to determine the long term compatibility and stability of active species mixtures. The high coulombic efficiencies (~100% for Fc/TEMPO and ~90% for [Co(Cp)₂PF₆]/N-meth) obtained for the bulk cycling experiments suggested minimal interactions between active species. The charge capacity retention plots showed decays over longer time scales, which was attributed to active species cross-over. In order to show the active component mixtures are stable at the charged state UV-vis absorbance experiments were performed. Fc/TEMPO and [Co(Cp)₂PF₆]/N-meth mixtures demonstrated good electrochemical and chemical stabilities upto 4 days. Charge-discharge experiments were performed at a dilute concentration of 10 mM of active species using both cation and anion exchange membranes. Coulombic efficiencies around ~97% and ~94% were obtained when anion and cation exchange membranes were used, respectively. CVs obtained after cycling showed no additional peaks or significant peak current changes suggesting the stability of mixtures in charge-discharge processes. Higher active species concentrations of 50 mM, 100 mM, and 200 mM were also used in a charge-discharge experiments. Coulombic efficiencies of ~84%, ~90%, and ~85% were obtained for 0.05 M, 0.10 M, and 0.20 M total concentrations of
active species, respectively. Species cross-over at elevated concentration was larger compared to the dilute conditions.

Overall, it was demonstrated that Fc/TEMPO and [Co(Cp)$_2$PF$_6$]/N-meth mixtures are suitable as electrolyte mixtures for an naRFB. Further experiments are being done to identify more suitable electrolyte species to extend this method to more than just two components in terms of increasing the number of electrons involved or the concentration of active species.

5.4. Supporting Information

Experimental

Chemicals

The supporting electrolyte tetrabutylammonium hexafluorophosphate (TBAPF$_6$, Alfa Aesar, USA) was crystallized from methanol before using. Anhydrous acetonitrile (CH$_3$CN) was obtained from a Grubbs-type solvent purification system (Pure Process Technology, USA). Ferrocene (Sigma Aldrich, USA), cobaltocenium hexafluorophosphosphate (Strem Chemicals Inc., USA), 2,2,6,6-tetramethylpiperidine 1-oxyl (TEMPO, Acros Organics, USA), and N-methylphthalimide (Alfa Aesar, USA) were used as received.

Solution preparation

Electrolyte solutions were prepared by dissolving the active species in 0.05 M TBAPF$_6$ in CH$_3$CN.

Cyclic voltammetry (CV)

CVs were collected using a Bio-Logic SP 200 potentiostat/galvanostat and the EC-Lab software suite. Active species with a supporting electrolyte concentration of 0.05 M in CH$_3$CN were used in all experiments. Cyclic voltammograms were recorded using a 3 mm diameter glassy carbon working electrode (CH Instruments, USA), a Pt wire auxiliary electrode (CH Instruments, USA), and a Ag/Ag$^+$ non-aqueous reference electrode with 0.01 M AgNO$_3$ in 0.05 M TBAPF$_6$ in
CH\textsubscript{3}CN (BASi, USA). All measurements were obtained at room temperature inside a nitrogen filled glove box (Vigor Tech, USA). Cyclic voltammograms were iR compensated at 85% with impedance taken at 100 kHz using the ZIR tool included within the EC-Lab software.

**Chronoamperometry/bulk electrolysis**

Bulk cycling experiments were performed in a nitrogen filled glove box using a glass H-cell (Adams and Chittenden, USA) with a Bio-Logic SP 200 potentiostat/galvanostat. An active species concentration of 5 mM was used for individual bulk electrolysis experiments and for mixture cycling experiments equal concentrations of active species were used such that the overall concentration of active species is 10 mM. Working electrode compartment contained 4 mL of the active species with 0.05 M TBAPF\textsubscript{6} in CH\textsubscript{3}CN and counter electrode compartment had 4 mL of 0.05 M TBAPF\textsubscript{6} in CH\textsubscript{3}CN. Pt mesh working electrode and a Pt wire counter electrode were used in the bulk cycling experiments. The compartments of the H-cell were separated by an AMI-7001 anion exchange membrane or a CMI 7000 cation exchange membrane (~0.05 cm\textsuperscript{2} Membrane International Inc., USA). Membranes were soaked in 0.05 M TBAPF\textsubscript{6} in CH\textsubscript{3}CN solution for 24 hours before each experiment. Bulk cycling was performed using the chronoamperometry techniques available in EC lab software suite at constant potentials, selected from the CV data (For Fc/TEMPO individual and mixture cycling potential cut offs were 1 V and -0.5 V vs. Ag/Ag\textsuperscript{+} and for and [Co(Cp)\textsubscript{2}]PF\textsubscript{6}/N-meth cycling studies they were -2 V and 0.5 V vs. Ag/Ag\textsuperscript{+}). The time cut offs were 15 mins and 30 mins for individual species and mixtures, respectively to ensure complete bulk electrolysis.

**UV-vis absorbance**

Fc/TEMPO and [Co(Cp)\textsubscript{2}]PF\textsubscript{6}/N-meth electrolyte mixtures were bulk oxidized and reduced, respectively and UV-vis absorbance measurements were made for a time period of four days to determine the stability of the mixtures in charged state. UV-vis absorbances of solutions
were recorded using a 1 cm path length cuvette (Starna, USA) on a Cary 8454 UV-vis diode array system.

**Charge-discharge experiments**

Charge-discharge testing was done in a glass H-cell (Adams and Chittenden, USA) using a Bio-Logic SP 200 potentiostat/galvanostat in a nitrogen filled glove box. Charge- discharge experiments used active species dissolved in 0.05 M TBAPF$_6$ in CH$_3$CN. The compartments of the H-cell were separated by an AMI-7001 anion or a CMI 7000 cation exchange membrane (~0.05 cm$^2$ Membrane International Inc., USA). Two graphite felt electrodes (2 × 1 × 0.5 cm, Fuel Cell Store, USA) were placed in the posolyte and negolyte chambers. Electrodes attached to Pt wire current collectors submerged in the electrolyte solutions (~0.5 cm). Membranes and graphite felt electrodes were soaked in 0.05 M TBAPF$_6$ in CH$_3$CN solution for one hour before each experiment. A custom charge-discharge profile was created using the Modulo Bat technique found in the EC-Lab software. Three conditions were defined: 1) Galvanostatic conditions with 0.6 mA current. 2) Potentiostatic conditions using cut-off voltage of 2.3 V. The cut-off voltage was determined from the CVs based on the separation of the oxidation and reduction events. 3) Discharge at a constant current of 0.1 mA. Charging initiated under galvanostatic conditions (condition 1). If the cut-off voltage was reached, the system switched to condition 2, maintaining an upper voltage as defined for each system. Under both conditions, if a preset state-of-charge was achieved, in this case 25%, the system switched to condition 3, the constant-current discharge. Charging was reinitiated when a cell potential of 0.1 V was reached.
Chapter 06-Conclusions and Future Work

6.1. Future of BODIPY molecules as charge-carriers in all organic symmetric naRFBs

Chapter 02 centered on a PM 567, a member of the BODIPY family that is has been previously noted for its well-defined reversible oxidation and reduction chemistry. These features made it attractive as an active species for RFBs. Our work served as a cautionary tale of sorts, as the growing interest in RFBs had led to an ever-increasing library of potential charge carriers that are oftentimes initial screened by simple CV experiments. As we showed, well-defined redox features from CV are insufficient to fully assess a molecule’s suitability as an active species. Herein, it is found that the stability suggested from CV does not persist at longer timescales. We studied the evolution of the electrolyte solution using mass spectrometry, UV-vis, and electroanalytical techniques. Our investigations concluded that although PM 567 undergoes chemical changes when stored both in an oxidized and reduced state, these changes ultimately result in highly stable redox-active solutions that provide the basis for charge storage in RFBs. A static cell was used for charge-discharge studies that establish that PM 567 may be an attractive precursor for electrolyte solutions. Because the dye can be used as both the positive and negative electrolyte active species, a symmetric RFB design is enabled that lessens the impact of membrane crossover. To the best of our knowledge, only one other study of BODIPY-based materials had been published prior to this work and we expected our research provided an important foundation for the use of such dyes as redox charge carriers in the context of RFBs, an area of significant interest given the ramifications for energy storage and global energy concerns. However, possible side reactions and low solubility are two challenges that need to be addressed for BODIPY molecules to be successfully employed in naRFB devices. It is established that the substituents affect the properties such as stability and solubility of a given BODIPY molecule. A wide variety of molecules are attainable via the BODIPY core modification. Hence, a logical next
step would be to systematically evaluate the effect of varied substituents around the BODIPY core on the electrochemical and physicochemical properties of relevance to RFB performance. Following our work, Heiland et al. assessed all the positions of the BODIPY core on the basis of literature CV data together with computational modeling and designed a fully substituted molecule to provide solubility, aggregation, radical cation and anion stabilities, a large potential window, and synthetic accessibility. However, this particular BODIPY dye still exhibited an unexpected reactivity. Accordingly, it is necessary that rational design is used in conjunction with bulk electrolysis experiments and the workup of the resulting products towards developing BODIPY electrophores as ideal charge-carriers for long-term energy storage.

6.2. Methylene Blue-containing waste water for energy storage

In recognizing growing efforts to remove harmful organic substances from wastewater, we became interested in methylene blue, one of the most commonly used hazardous organic dyes, owing to its propensity to undergo two-electron two-proton reductions. We hypothesized that this redox couple may serve as the basis for energy storage in flow batteries. In chapter 03, we describe a series of experiments carried out on simulated wastewater solutions containing methylene blue, spanning a range of electroanalytical methods including cyclic voltammetry, chronoamperometry, spectroelectrochemistry, UV-vis, and galvanostatic cycling techniques. Our work revealed that methylene blue is stable at short and long time scales at all relevant oxidation states, enabling its use as active species in energy storage devices. This stability manifested in ~100% coulombic efficiencies across all charge-discharge cycles. In addition, we characterized the interactions of methylene blue with common ion-exchange membranes and identified Nafion NE1035 to be a compatible membrane, with no dye adsorption and crossover that warrants high capacity retention across cycling. The next step forward is to evaluate the effluents from industrial mills to determine the feasibility of using actual waste water solutions as electrolytes in RFBs. It is hypothesized that the large amounts of salts present in such waste
water samples would enhance the conductivity, an added advantage towards minimizing potential losses in device level.

6.3. **Nanoscopic polynuclear architectures as next-generation charge-carriers for naRFBs**

naRFBs are attractive solutions for EES due to their wider breakdown voltage windows and capability to operate at a range of different temperatures. However, there remains a need to decrease materials costs and increase cell performance by identifying systems that are both inexpensive and have high-energy capacities. The concentrations used for initial evaluations of non-aqueous charge carriers in the literature rarely align with concentrations used for calculations of theoretical energy densities. Although, there have been great improvements in the identification of new active species with high solubilities, charge-discharge experiments are typically performed at dilute concentrations. In light of this, we have selected a suite of archetypical charge carriers and conducted charge-discharge profiles at dilute to saturated concentrations to reveal the ramifications on coulombic, voltage, and energy efficiencies.\textsuperscript{158, 159} Through galvanostatic cycling experiments and impedance spectroscopy, it was found that membrane fouling and species crossover were major culprits of behavioral changes in charge-discharge profiles at elevated concentrations.

To design and develop the next generation naRFB charge-carriers, there are two main issues that need to be addressed as evidenced from our studies: 1) solubility is not in the expected regimes suitable for practical applications and 2) the membrane cross-over is a major culprit for capacity fade, especially at elevated concentrations. One strategy to address these issues would be to exploit nano-sized redox active charge-carriers. Nanoscopic polynuclear architectures are excellent candidates as a suite of first-row transition metals may be used to systematically tune redox properties while simultaneously addressing long-term stability, membrane crossover, and solubility, factors that impact the overall efficiency of RFBs. The factors that govern these
properties are rooted in molecular chemistry, yet there is a critical gap in knowledge in how to synthesize new redox active compounds that meet necessary performance targets. Filling this gap requires an understanding of the structure-function relationships that inform how size, nuclearity, ligand design, and metal composition control the redox activity of relevance to EES. Whereas pioneering work on small organic molecules, coordination complexes, redox active polymers reveals the power of a leveraging molecular-level knowledge,\textsuperscript{124, 126, 128} to date such a systematic approach is underdeveloped for nanoscopic clusters, despite their ability to address long-term stability, membrane crossover, and solubility, factors that impact the overall efficiency of RFBs. Towards this end, Polyoxometalates (POMs) and other metal oxide nanoparticles are identified as emerging classes of polynuclear assemblies for charge carriers. We have already embarked upon investigations of self-assembled, polyoxovanadate-alkoxide (POV-alkoxide) clusters as electrolytes for naRFBs.\textsuperscript{160, 161} The future work of this project entails identifying the structural components of POV-alkoxide clusters and other metal oxide nanoparticles that contribute most strongly to its energy storage capabilities through a structure-function feedback loop, and using the knowledge resulting from our electrochemical experiments to design a superior electroactive material. The fundamental knowledge obtained through identification of these structure-function relationships will enable informed electrolyte design, transforming the landscape of energy storage with naRFBs.
Appendix A

Overview of General Analytical Strategy

The general strategy for evaluating redox active charge-carriers encompasses a series of electroanalytical techniques and logically ramp in complexity from single-cell to H-cell studies. Appendix A Fig.1 shows the basic electrochemical cell setups used for single and H-cell experiments.

![Diagram of electrochemical cell setups](image)

**Appendix A Fig.1.** Strategies for molecular redox characterization; Single cell and H-cell setups (WE-working electrode, CE-counter electrode, and RE-reference electrode)

I. Single Cell Studies

Three-electrode single-cell studies are ideal to perform initial electrochemical screening of the redox active molecules that avoid complications associated with the presence of membrane separators and other complexities arising from flow cell design.

a. Cyclic voltammetry

Cyclic voltammetry (CV) experiments is the primary voltammetric technique used to determine short-time-scale electrochemical reversibility.\(^{103, 118, 162}\) The CV profiles will elucidate the kinetics and reversibility of all redox events, and will indicate a preliminary \(V_{cell}\) for each
species. Since this technique provides information about the stability of an electrolyte across all of its charge states, it serves as a gatekeeper to determine if advanced testing is warranted.\textsuperscript{124, 130}

The kinetics of an electron transfer reaction can be described using diffusion coefficient \( (D_0) \) and heterogeneous electron transfer rate constant \( (k_0) \). \( D_0 \) and \( k_0 \) parameterize the mass transport and electron transfer properties of an electrochemical reaction that have ramifications on charge transfer resistance and are therefore critically important for establishing the viability of a charge carrier.\textsuperscript{163, 164} CV data are commonly used to extract \( D_0 \) values using the Randles-Sevcik method,\textsuperscript{165} and \( k_0 \) values using the Nicholson\textsuperscript{67} and Kochi-Klinger methods.\textsuperscript{166}

In Randles-Sevcik method, a scan-rate-dependent CV study is performed. A linear relationship between peak currents and the square root of scan rate indicates diffusion controlled redox reactions.\textsuperscript{36, 41, 103} For a reversible redox couple, peak current, \( i_p \) is given by the following Equation;

\[
i_p = 2.69 \times 10^5 n^{3/2} A c D_0^{1/2} v^{1/2}
\]

(A1)

For an irreversible redox couple, the peak current, \( i_p \) is given by the following Equation;

\[
i_p = 2.99 \times 10^5 n^{3/2} \alpha^{1/2} A c D_0^{1/2} v^{1/2}
\]

(A2)

In Equations (A1) and (A2), \( n \) is the number of electrons transferred, \( \alpha \) is the charge transfer coefficient \( (\alpha \sim 0.5) \), \( A \) is the electrode area of the working electrode, \( c \) is the bulk concentration of the active species, \( D_0 \) is the diffusion coefficient of the active species and \( v \) is the scan rate. Since there is no equation to explicitly calculate the diffusion coefficients for a quasi-reversible reaction, the values obtained from the reversible and irreversible treatments are used as the upper and lower limits of \( D_0 \).
The Nicholson and Kochi-Klinger methods all use steady-state models for the calculation of electrode reaction rates using CV data obtained at different scan rates and are based on peak-to-peak separation ($\Delta E_p$). The Nicholson method is frequently used to estimate $k_0$ by relating $\Delta E_p$ with a dimensionless kinetic parameter ($\psi$). The dimensionless parameter ($\psi$) is obtained by introducing the $\Delta E_p$ values to the working curve described by Nicholson and Shain, and the heterogeneous electron transfer rate constant ($k_0$) for the redox reaction is calculated using the following Equation:\(^{167}\)

$$k_0 = \psi \left[ \frac{\pi n F D_0 \nu}{RT} \right]^{1/2}$$ \hspace{1cm} (A3)

In Equation (A3), the symbols $n$, $D_0$ and $\nu$, has the same meaning as in Equation (A1) and (A2). $F$ the Faraday constant, $\psi$ is the Nicholson dimensionless parameter, $R$ is the gas constant, and $T$ is the temperature. The Kochi-Klinger method also depends on $\Delta E_p$ for estimating $k_0$. The following Equation is used to calculate the $k_0$: \(^{166}\)

$$k_0 = 2.18 \left[ \frac{\alpha n F D_0 \nu}{RT} \right]^{1/2} \exp \left[ \frac{-\alpha^2 n F (E_{pa} - E_{pc})}{RT} \right]$$ \hspace{1cm} (A4)

Wherein $\alpha$ is the charge-transfer coefficient (~0.5) and $E_{pa}$ and $E_{pc}$ are the anodic and cathodic peak current potentials.

\textit{b. Rotating Disk Voltammetry}

Rotating Disk Electrode Voltammetry (RDE) is a hydrodynamic electrochemical technique, which uses a general three electrode cell. However, the working electrode is rotated at various rates to obtain a steady state current response. By running linear sweep voltammetry (LSV) at various rotation rates, different electrochemical phenomena can be evaluated. RDE data can also be used to extract $D_0$ values using the Levich method, \(^{168}\) and $k_0$ values using the Koutecky-Levich method. \(^{169}\)
The Levich method uses the plateau currents of LSV profiles at different rotation rates in RDE experiments. These limiting currents are plotted against the square root of the rotation rate to obtain the Levich plots for each redox couple. The slopes of these Levich plots are used to calculate values for $D_0$ using the Levich equation. The limiting current in a RDE experiment is given by the following Equation:

$$i = 0.620 \ nFAcD^{2/3} \nu^{-1/6} \omega^{1/2} \quad (A5)$$

In Equation (A5), $n$ is the number of electrons involved in the reaction, $F$ is the Faraday constant, $A$ is the surface area of the working electrode, $c$ is molar concentration in mol cm$^{-3}$, $\nu$ is the kinetic viscosity in cm$^2$ s$^{-1}$, and $\omega$ is the routing angular velocity in rad s$^{-1}$.

By employing the current responses at varied overpotentials, Koutecky–Levich plots are constructed, to determine the mass-transfer-independent kinetic currents $i_k$ for redox reactions. These $i_k$ values are subsequently fit to the Butler-Volmer equation via Tafel plots. Using the Tafel equation shown below, the rate constants were calculated.

$$\log i_k = \log (nFaC \ k_0) + \frac{nF \alpha \eta}{2.303 \ RT} \quad (A6)$$

In Equation (A6), $n$ is the number of electrons, $\alpha$ is the transfer coefficient, $R$ is the gas constant, $T$ is temperature, $k_0$ is the standard kinetic rate constant, and $\eta$ is the over potential.

c. Impedance Spectroscopy

Impedance is a measure of the ability of a circuit to resist the flow of electrical current. Impedance measurements are carried out in a three electrode single-cell configuration to obtain information about solution resistance. Electrochemical Impedance Spectroscopy (EIS) measurements are made by applying a small sinusoidal potential of fixed frequency. The responses at a wide range of frequencies are plotted and analyzed to extract impedance values.
One common type of graphical representation used in EIS is called the Nyquist plot. The low frequency intercepts of the Nyquist plots are used to determine the resistances of each solution. The resistance associated with supporting electrolyte and solvent largely contributes to overall flow cell impedance. Thompson, Monroe and co-workers have shown that the solution resistance can be as large as $2.0 \times 10^7 \ \Omega \cdot \text{cm}$ and as small as $9.7 \times 10^{-2} \ \Omega \cdot \text{cm}$ depending on the solvent/supporting electrolyte combination.$^{147}$ Although the solution resistance is easily compensated for and obviated in a CV experiment, it has an unavoidable deleterious effect on voltaic efficiency during charge/discharge experiments. The value of single-cell impedance spectroscopy is that it will enable identifying optimal solvent and supporting electrolyte conditions prior to the introduction of a membrane electrode assembly. As these components are introduced in static test H-cells, we will be able to systematically evaluate their subsequent contributions to impedance.

II. Static H-Cell Studies

Static H-cell experiments provide access to bulk electrolysis techniques. Such methods to determine longer-term stability of all redox active molecules, along with coulombic efficiencies. The most commonly used static H-cell experiments in RFB studies include chronoamperometry, chronopotentiometry (glavanostatic charge-discharge) and membrane compatibility studies. A library of H-cells for electrolyte volumes ranging from ~1 mL to ~50 mL per one half-cell were used in work discussed in this thesis. These H-cells include a homebuilt Teflon cell (Appendix A Fig.2)$^{59, 118}$ as well air-tight glass H-cells (Adams and Chittenden, USA). All cells are modular with respect to the membrane separator, with cross sectional areas of 2 cm$^2$ to 5 cm$^2$, allowing us to isolate contributions from membrane impedance. In addition, control experiments may be performed with standard H-cells with glass frit separators (10-16 µm porosity).
a. **Chronoamperometry**

Given the short amount of time that an electrolyte candidate exists in its charged state during a standard CV experiment, multiple cycles that suggest long-term stability may be misleading. In fact, many promising electrolyte materials such as Fe(bpy)$_3$(BF$_4$)$_2$,$^{35,108}$ V(acac)$_3$,$^{170}$ TEMPO$^{171}$, 9-fluorenone$^{13}$, 23DDB$^{109}$, DBMMB$^{13}$ that show invariant CV traces undergo decomposition over hours or days when stored in their charged states. Chronoamperometry or controlled potential electrolysis can be used to bulk electrolyze redox active molecules of interest and subsequently evaluated using CV and UV-vis spectroscopy to see any changes in the electrochemical behaviors over a long-time period.$^{118,127,172}$ We have custom made teflon capped UV-vis cells that enables us to monitor the stability or instability of molecules without the interference from oxygen or water. Controlled potential bulk-cycling experiments$^{108,173}$ are commonly used to determine the coulombic efficiencies of each redox event. Bulk cycling will also be complementary to the previously discussed bulk electrolysis experiments to get an insight into the stability of oxidized/reduced states of a redox active molecule at long time scales.

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**Appendix A Fig.2.** A H-cell configuration that approximates the conditions of a flow system but allow for characterization with small volumes of electrolyte
b. Chronopotentiometry

Redox active molecules that possess good long-term stability are further studied in prototype static liquid battery configurations using H-cells. Such experiments use constant currents for charging and discharging and voltage cut-off values are set to avoid any damage to the system. Charge-discharge profiles are used to learn about coulombic efficiencies, capacity retention, and active species cross-over.\textsuperscript{36, 38, 41, 59, 108, 126, 174} Static H-cell charge-discharge experiments will also give an idea about the voltage efficiencies and overall energy efficiencies that can be expected from the system.\textsuperscript{37, 118, 130} Coulombic, voltage, and energy efficiencies for each charge-discharge cycle were determined following Equations (A7), (A8), and (A9), respectively.

\[
Coulombic \; efficiency \; (CE) = \frac{\text{Charge output}}{\text{Charge input}} \tag{A7}
\]

\[
Voltage \; efficiency \; (VE) = \frac{\text{Discharge voltage}}{\text{Charge voltage}} \tag{A8}
\]

The discharge voltage is taken as the average voltage in the discharge plateau of a charge-discharge cycle. The energy efficiency of any charge-discharge cycle is obtained by multiplying the coulombic efficiency by the voltage efficiency.

\[
Energy \; efficiency = CE \times VE \tag{A9}
\]

c. Membrane compatibility studies

Membrane fouling and active species cross-over are identified as two major culprits of low coulombic efficiencies and self-discharge of RFBs\textsuperscript{10}. The active species cross-over can be determined using a method similar to that developed by Brushett and co-workers\textsuperscript{153}. A given active species with supporting electrolyte is stored on one side of an H-cell and aliquots from the
blank control side will be subjected to UV-vis spectroscopy and CV over the course of longer time lengths (days-months) to determine the rate of cross-over.

In addition to the above stated experiments, UV-vis spectroscopy, spectroelectrochemistry and mass-spectrometry is also employed to further analyze the redox active materials.
References


