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I am submitting herewith a dissertation written by Jacob Russell Houser entitled "An Analysis of the Impact of Design Tradeoffs On System-level Energy and Cost Efficiencies of Redox Flow Batteries." I have examined the final electronic copy of this dissertation for form and content and recommend that it be accepted in partial fulfillment of the requirements for the degree of Doctor of Philosophy, with a major in Mechanical Engineering.

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(Original signatures are on file with official student records.)

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ABSTRACT

Redox flow batteries (RFBs) are a promising grid energy storage technology with the potential to solve numerous problems arising from anticipated increases in renewable energy integration. These systems involve a number of key design tradeoffs, many involving the movement of liquid electrolyte through the system, which impact the overall system efficiency.

This work examines the design of the fluid network throughout RFB systems and how design tradeoffs impact the system efficiency. Insights are gained that inform future research and design decisions. Initially, this work focuses on single cell concerns, primarily flow field design. Two common designs from the literature, serpentine and interdigitated, are analyzed to uncover underlying transport characteristics. These findings are used to develop and evaluate two new flow field designs, the Equal Path Length (EPL) and aspect ratio designs. All four designs are evaluated with regard to a number of metrics including viability to be scaled up to larger sizes.

To assess the viability of these conclusions on a commercial system, a short four cell stack was developed and evaluated for efficiency and mass transport performance. Additional efficiency concerns specific to stack design such as shunt current were explored using a novel in-situ shunt current measurement technique. The relative impact of this self-discharge phenomenon is investigated and its relationship to operating conditions is evaluated.

Finally, a cost model taking into account earlier findings of this dissertation is presented. This model provides context for these findings in terms of real world
applications and financial metrics. This model allows for the exploration of which design factors are key cost drivers and provides a guideline for where future research should focus to reduce cost.

The primary outcome of this dissertation is a new framework for the design of RFBs rooted in the principle that there may not be one panacea solution for every design problem. Unique solutions dependent upon operating conditions and applications are necessary to maximize performance and minimize cost. Using the conclusions presented in this work will guide researchers and system engineers alike, allowing for improved efficiency and minimized costs as RFBs become a viable grid energy storage solution.
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CHAPTER ONE
INTRODUCTION
1.1 Motivation

More than ever before, energy generation and consumption have become defining issues for scientists and the world as a whole. Increasing focus on renewable energy, driven by concerns about carbon emissions and climate change, is driving a dramatic shift in the way energy is produced, both in terms of methods and location. As reliable centralized fossil fuel generation is replaced by a cleaner but more intermittent and decentralized renewable energy portfolio, the energy grid will need to adapt. The primary change that will be required is an increase in grid-scale energy storage ¹.

Large scale energy storage will have the ability to provide stability for the integration of intermittent renewable energy sources such as wind and solar energy. Storage will also allow for peak shaving, resulting in the grid operating more efficiently, in spite of continuously increasing demand. Considering the potential for energy storage to be used for improved grid stability, arbitrage, peak shaving, and renewables integration, grid-scale energy storage is a critical problem for scientists and engineers to solve.

There are numerous technologies at varying states of maturity to address the grid energy storage issue. The most widely implemented is pumped hydroelectric storage, which, while highly effective, carries with it high capital cost as well as location dependence. Compressed air storage suffers from similar geologic dependence as pumped hydroelectric storage, though it requires sealed caverns as opposed to large elevations for reservoirs, in conjunction with lower energy density. Flywheels are another solution that has seen extensive use; however their high rate of self discharge
makes them less ideal for applications where energy needs to be stored for longer periods of time. Supercapacitors have the ability to discharge large amounts of power with millisecond reaction times, but suffer from extremely poor energy density. Chemical energy storage methods, namely hydrogen storage, are promising, although tend to be very energy intensive in terms of their manufacturing cost. Currently, much focus has been devoted to electrochemical energy storage technologies, namely batteries. Lead-acid batteries are the oldest conventionally-used chemistry, offering a low cost, highly efficient storage medium, but suffering from low cycle life, toxicity concerns and poor energy density. Nickel-based batteries have superior durability to their lead acid counterparts, however are more expensive and have lower energy efficiency. Lithium-based batteries are perhaps the most intensely-researched conventional batteries due to their superior energy density, energy efficiency, and self discharge rate. Lithium batteries suffer from serious durability concerns, however, with degradation highly accelerated at high temperature or during deep discharge. Redox flow batteries (RFBs) are another electrochemical storage option that offers numerous advantages over conventional battery systems. RFBs decouple power generation and energy storage capacity, making them highly flexible systems able to be applied to both high power and large energy storage situations. The low energy density and high capital costs of the system are the main obstacles to more widespread commercial integration [2-3].

Research in the field of redox flow batteries has grown substantially in recent years, but generally focuses on two main goals: increasing power density and increasing energy density. Increasing power density is a matter of mitigating the losses, or
overpotential, in the RFB system. This overpotential can generally be broken down into three components. The first is the kinetic overpotential which is the loss associated with the redox reaction itself. The second is the ohmic overpotential which is the loss from the charge conduction inside the battery. The third main source of loss is concentration overpotential, which is the loss stemming from inability to deliver enough reactant to reaction sites to support the redox reaction. These losses result in a discharging voltage lower than the thermodynamic voltage for the cell at a given current, thus leading to lower power density. Most research into increasing energy density is focused on novel electrolytes and increasing the solubility of the electroactive species. Through the use of higher concentrations of electroactive species, more energy is able to be stored in a given volume of solution, thus increasing the energy density of the system.

There is a fundamental gap within the evaluation of these systems, however, which currently hinders progress in the field: lack of understanding key design tradeoffs and how they should be evaluated with regard to system performance. Too often research focuses on attempting to find a unique solution that is capable of functioning as the ideal in every design scenario and operating condition. Such thinking ignores one of the most enticing aspects of the RFB as an energy storage technology: versatility.

Leveraging these design tradeoffs at both the single cell and full stack level will allow for improved energy efficiency and cost competitiveness in current RFB designs and can inform future designs to improve the next generation of RFB systems. This work focuses on demonstrating and characterizing the fundamental tradeoffs between key design parameters related to fluid flow within RFB systems affecting mass transport loss,
parasitic pumping loss, and shunt current loss. This is done under numerous operating conditions in order to test the hypothesis that the desired operational point of the system should be strongly considered when designing the fluid circuit within the system in order to optimize performance of the system. This is done by analyzing the impact of a number of design elements on system losses, overall energy efficiency, and peak power generating capability. These metrics are then be used to conduct an economic analysis of the various design choices made in the study to assess their benefits for implementation in a commercial system. The work is comprised of two major sections: first, a focus on an individual cell in order to demonstrate the viability of such an approach; second, expansion of the approach to a multi-cell stack in order to fully characterize the additional tradeoffs present in a commercial size system.

1.2 Flow Battery Overview

1.2.1 Architecture

Flow batteries date back as far as a 1949 German patent and continued to be developed by NASA through the 1970s. Using an architecture similar to that a fuel cell, but functioning more closely to a traditional enclosed battery, flow batteries are comprised of a stack of individual cells to generate power and rechargeable electroactive species in a liquid electrolyte which stores energy. This electrolyte is typically composed of acid such as sulfuric acid in order to provide the solution with ionic conductivity. This liquid electrolyte circulates through the flow battery stack where a redox reaction takes place. Each stack is composed of a number of cells connected in series electronically. Each of these cells is made up of a positive electrolyte compartment and a negative
electrolyte compartment, both with a porous electrode material for the reaction to occur on. These two compartments are separated by an ion selective membrane which is electronically insulating but ionically conductive. During operation, a typical redox reaction takes place in the cell with an electron oxidized from the electroactive specie on one side of the cell, also generating a proton. The ion exchange membrane conducts the proton across to the other side of the cell, but does not allow the electron to pass, forcing it through an external circuit, generating electricity. The electron then joins the proton on the other side of the cell, reducing the electroactive specie in the electrolyte. When charging the battery, a voltage is applied across the stack and the reverse reactions occur. Each cell is separated from the adjacent cell by an electronically conductive bipolar plate which serves to collect current and evenly distribute the electrolyte across the reaction surface of the electrode. The latter of these goals is typically accomplished using a flow field machined into the surface of the plate. In a full RFB stack, electrolyte would be supplied to each cell using a manifold running through the system. A schematic of a typical RFB stack is shown in Figure 1.1.

1.2.2 Advantages

Redox flow batteries have a number of advantages over alternative energy storage solutions. The primary benefit is that energy storage capacity and power generation capacity are decoupled. The former is strictly a function of the tank size, redox chemistry, and concentration, while the latter is determined by the stack size and
Figure 1.1. Schematic of a flow battery stack and components.
individual cell architecture. This allows RFBs to be extremely flexible in their ability to address various energy storage applications, from high energy to power ratio applications such as supplementing peak demand capacity to low energy to power ratio applications such as frequency regulation. In order to meet the need for large amounts of storage energy to supplement peak demand capacity, a smaller reactor size can be used and a large tank of electrolyte is needed. Conversely, for frequency regulation, a much smaller tank can be used with a larger reactor to account for the additional power requirement and lower overall energy demand. In comparison, a traditional battery system such as a lithium ion battery would require additional battery packs regardless of whether additional power or additional energy was required. This drastically increases cost as either unnecessary electroactive material will be needed, or available power capacity will be wasted.

RFBs have an additional advantage when it comes to the reaction mechanism. In a typical enclosed battery, a solid phase electrode reaction takes place upon each charge and discharge. Through a number of complex processes during these reactions irreversible capacity fade takes place, decreasing the overall charge and discharge capacity of these batteries. For example, in solid intercalation batteries, mechanical stresses from repeated expansion and contraction during cycling can cause fractures in the electrode material, isolating it from the rest of the battery and rendering it useless. Such issues are not present in RFBs due to the far simpler redox reactions that take place on the surface of the carbon electrodes and involve no phase change of the electroactive specie.
Flow batteries due suffer from capacity fade, but the primary source of capacity fade is largely reversible. During operation small amounts of the electroactive specie can cross over the membrane, causing the cell to self-discharge and lowering the coulombic efficiency of the system. Over the course of many cycles this crossover effect can build up and cause capacity fade similar to that seen in traditional enclosed batteries. This lost capacity can be recovered however, by simply removing the electrolyte from the system, mixing it, and redistributing it to each side of the battery. This will require an additional energy penalty during the initial recharge step for the system, but will restore most of the capacity lost due to crossover.

1.2.3 Shunt Current

One efficiency loss that is not unique to flow batteries, but functions uniquely in flow batteries is shunt current. Shunt current is the self-discharge of the battery through the ionically conductive liquid electrolyte. Due to the potential gradient across a stack, even at an open circuit condition electrons can flow through the bipolar plate from the negative side of one cell to the positive side of an adjacent cell. Protons then flow through the ion exchange membrane from the negative side of the cell to the positive side in order to balance the charge. Since the electrolyte manifolding connects all of the cells and stacks in a system, it functions as an ionically conductive bridge for proton transport, thus completing the circuit by allowing the protons now in the positive side of the original cell to flow to the positive side of other cells and completing the discharging reactions. This occurs even during charging and discharging, resulting in less energy being available for discharge and more energy being required for charging. Due to this ionic conductivity in the manifold, its design has a large impact on shunt current in
addition to the pumping requirement for the battery. The operational energy efficiency of an RFB system is a key indicator of financial feasibility, particularly in chemistries such as the all-vanadium redox flow battery where electrolyte costs comprise a substantial portion of the overall system cost.

1.2.4 Flow Battery Performance Metrics

A number of techniques are available in a laboratory setting to analyze the performance of a flow battery or one of its components. Perhaps the most common technique is cycling, in which the battery is repeatedly charged and discharged in order to assess performance. This can be done either galvanostatically until a cutoff voltage is reached, or potentiostatically until a cutoff current is reached. This method does not accurately capture a load profile that would need to be accounted for in commercial use, nevertheless it allows for laboratory scale comparisons of RFB designs. Five typical parameters are derived from these types of tests:

- Coulombic efficiency
- Voltage efficiency
- Electrochemical energy efficiency
- System energy efficiency
- Electrolyte depth of discharge

These metrics can be further defined as

\[
Coulombic\ Efficiency = \frac{\int_{t_{\text{char}}}^{t_{\text{disch}}} I_{\text{disch}} \, dt}{\int_{t_{\text{char}}}^{t_{\text{disch}}} I_{\text{char}} \, dt} \quad (1.1)
\]
\[
Voltage \ Efficiency = \frac{\int_0^{t_{\text{disch}}} V_{\text{disch}} \, dt}{\int_0^{t_{\text{char}}} V_{\text{char}} \, dt}
\] (1.2)

\[
Electrochemical \ Energy \ Efficiency = \frac{E_{\text{disch}}}{E_{\text{char}}}
\] (1.3)

\[
System \ Energy \ Efficiency = \frac{E_{\text{disch}} - E_{\text{ancillary:disch}}}{E_{\text{char}} + E_{\text{ancillary:char}}}
\] (1.4)

\[
Depth \ of \ Discharge = \frac{C_{\text{actual}}}{C_{\text{theoretical}}}
\] (1.5)

Where \( I \) is current, \( V \) is voltage, \( E \) is energy, and \( C \) is capacity. The subscripts refer to charge and discharge.

System energy efficiency is defined as the electrochemical energy removed during discharge minus the energy required to run ancillary systems (i.e. pumps) divided by the electrochemical energy put into the system during charge plus the energy required to run ancillary systems during charging. The primary contributor to these ancillary, also termed parasitic, losses is pumping energy which is a function of flow rate and pressure drop across the system.

Another common technique is the polarization curve. In this method, the system can be controlled potentiostatically or galvanostatically as well. If controlled potentiostatically, the cell is stepped from the open circuit voltage to higher potentials to characterize system charging or to lower and lower potentials to characterize the discharge. If controlled galvanostatically, the system is progressively pushed to higher and higher currents until the system potential reaches a certain point. A polarization
curve is useful in delineating the losses within an electrochemical cell. At low current densities, kinetic losses dominate; ohmic losses dominate at intermediate current density; concentration polarization dominates losses at the highest possible current density for a system. It is this high current density, mass transport-limited region of the polarization curve that will be most important for this work. In this region of the polarization curve, the current drawn from the cell is so high that the cell cannot provide enough reactant, leading to rapidly increasing overpotential. This reactant starvation condition is termed limiting current density for a particular system. Assessment of limiting current density allows for the comparison of cell architectures in terms of mass transport performance. Better mass transport results in higher limiting current density, while worse mass transport results in lower limiting current density.

In addition to the laboratory metrics used to characterize flow battery performance, a number of financial metrics can also be applied to a system in order to determine its feasibility in a real world application. These metrics include:

- Installed Cost
- Payback Period
- Net Present Value (NPV)
- Levelized Cost of Energy Storage (LCOES)
- Rate of Return on Investment

These metrics can be further defined as
\[ C_{\text{installed}} = \frac{C_0}{C_E} \quad (1.6) \]

\[ t_{\text{payback}} = \frac{C_0}{I_{\text{net}}} \quad (1.7) \]

\[ NPV = \sum_{t=0}^{T} \frac{I_{\text{net}}(t)}{(1+r)^t} - C_0 \quad (1.8) \]

\[ LCOES = \frac{C_0 + C_{\text{op, NPV}}}{E_{PV}} \quad (1.9) \]

\[ R_{\text{ret}} = \frac{NPV - C_0}{C_0} \quad (1.10) \]

Where \( I_{\text{net}}(t) \) is the net cash inflow during the period \( t \), \( C_E \) is the total energy capacity of the system, \( T \) is the total number of periods, \( r \) is the discount rate, \( C_0 \) is the total initial investment cost, \( C_{\text{op, NPV}} \) is the net present value of the operating costs over the lifetime of the system, and \( E_{PV} \) is the present value of the energy discharged over the lifetime of the system.

The installed cost is an effective metric for comparing different applications for a storage device by reporting the cost per unit of energy stored. It can essentially be viewed as a cost efficiency to determine which applications a particular system is best suited for. The payback period is the length of time it takes a system to recover the initial investment. This is useful because it gives an idea of how soon an investor can expect to realize profits from an installed system and allows the comparison of different systems.
and applications on a time basis. The net present value is the total value of the investment prorated to account for the time value of money. This allows for a comparison of systems and applications purely on a magnitude of value basis, allowing an investor to know which project will generate the most raw value over its lifetime. The net present value tends to favor larger projects which generate larger incomes, and thus must be considered in conjunction with the other financial metrics presented. The levelized cost of energy storage is a metric similar to the net present value, but it attempts to characterize the value of the energy discharged over the lifetime of the system. This value of energy discharged is also discounted to reflect the time value of money. The final figure for levelized cost of energy storage represents the average price of energy that a system will need to receive during discharge over its lifetime in order to turn a profit. This figure can be more useful than the installed cost due to its ability to factor in all the costs present over the lifetime of the system. The final metric is rate of return on investment. This metric reports the value of the investment realized as a percentage of the initial investment and is useful for comparing projects and systems of different scope and size. A smaller project may bring in less total income, but due to its lower cost, may have a higher rate of return than a much larger project. These metrics are further discussed and analyzed for flow battery systems in chapter 7.

1.3 Method of Approach

In this work a number of electrochemical methods were used to characterize the design choices made and the impacts of various operating conditions on their performance. Discharge curves are one of the simplest ways of analyzing the impact of
the chosen parameters upon mass transport. By discharging the cell at a given constant current density, the available discharge capacity for the given architecture and operating condition can be obtained. This discharge capacity gives an indication of the quality of the mass transport within the cell because the curve will only approach zero voltage once the cell can no longer deliver the required reactant to the reaction site to sustain operation. Cells that more effectively distribute electrolyte will exhibit a greater available discharge capacity in comparison to less effective cells.

Polarization curves are used to more directly assess the mass transport performance of each design and operational parameter. A polarization curve is useful in delineating the losses within an electrochemical cell. At low current densities, kinetic losses dominate; ohmic losses dominate at intermediate current density; concentration polarization dominates losses at the highest possible current density for a system. It is this high current density, mass transport-limited region of the polarization curve that is most important for this work. In this region of the polarization curve, the current drawn from the cell is so high that the cell cannot provide enough reactant, leading to rapidly increasing overpotential. This reactant starvation condition is termed limiting current density for a particular system. Assessment of limiting current density allows for the comparison of cell architectures in terms of mass transport performance. Better mass transport results in higher limiting current density, while worse mass transport results in lower limiting current density.

While these two techniques provide similar information in terms of single cell diagnostics, there are some differences that can provide insight for a more complete
picture of the mass transport within a cell. The primary difference is that polarization curves must be obtained at a constant state of charge (SOC) in order for the results to be compared accurately. The only guaranteed method to accomplish constant SOC in a full cell is for the flow through the cell to be single pass, meaning there is no electrolyte recirculation. Discharge curves inherently require the SOC to constantly change during discharge, and require that the electrolyte be recirculated. Additionally, polarization curves create a mass transport limitation through increasing the demand for reactant, while discharge curves create mass transport limitation through progressively lowering the SOC of the electrolyte. These differences lead to a key operational difference between the two methods. Polarization curves are more effective for low flow rate operation, while discharge curves allow for higher flow rate operation. This is because in order to obtain a polarization curve at high flow rate, a prohibitively large volume of electrolyte would be needed to ensure that the measurement could be single pass. Since the discharge curve utilizes electrolyte recirculation, no such limitation is present. Thus, both techniques were necessary.

The pressure drop across the cell was used to calculate the parasitic pumping loss, which is crucial for the evaluation of the overall energy tradeoff of each design and operational decision. This is because, while various measures can be taken to improve the mass transport performance of the cell, they often come at the expense of higher pressure drop. It is shown in subsequent chapters that this relationship is not the same for each component and operating condition, allowing for various designs to perform better under different operating conditions.
Locally measured current distribution shows where current is generated across the active area of the cell. These measurements are then correlated with fluid flow distributions from CFD simulations or thermal visualization and used to characterize the flow within a cell in order to understand the fundamental physics behind the changes in mass transport seen with different architectures and operating conditions. Local current distribution is a function of concentration and electrolyte velocity, making it an ideal diagnostic for this work.

A CFD simulation is also utilized to further elucidate mass transport within the cell. This simulation provides an in-depth picture of the transport within the cell and gives a more concrete image of why different design choices have particular influences on mass transport performance and pressure drop. This model is validated with the experimental pressure drop values to ensure that it accurately reflects the fluid transport within the cell.

Flow distributions from a thermal visualization setup provide a qualitative confirmation of the flow profiles inferred from the local current distributions and Comsol simulations. This ex-situ method uses color change in a heat sensitive liquid crystal sheet to produce an image of the flow profile within a half cell. This color shift is elicited by switching the flow through a half-cell from cold water to hot water, enabling real time imaging of the transport within the cell. While this method is not able to produce any quantitative data, it is extremely useful for validating computational profiles and other experimental techniques.
The current distributions, CFD simulations, and flow distributions play a critical part in guiding the design of cell architectures that operate more efficiently at a desired operating condition. By examining the impact of various parameters and designs on the tradeoff between mass transport performance and parasitic pumping losses, coupled with understanding the fundamental physics behind these characteristics, engineers can have greater predictive power over future designs. This enables engineers to design systems that can meet the varying operational criteria that exist in industry on a case-by-case basis, as opposed to designing a system which may operate effectively under one condition but inefficiently for others.

Effectiveness of a particular design for a given operating condition is determined based on energy and efficiency analyses. These take into account charging energy, discharging energy, and the parasitic pumping energy required for operation. These values can be converted into electrochemical energy efficiency and overall system energy efficiency for a given set of operating conditions, allowing different designs to be effectively compared based on efficiency, but also based on the metrics from which that efficiency is derived.

1.4 Chapter Preview

In Chapter 2, a thorough review of the existing literature on the subject of redox flow battery design and operating condition based research is presented along with a review of the economic analyses which have been published.
Chapter 3 examines the different mechanisms available within flow field design in order to characterize the strengths of each. This chapter introduces thermal visualization as a novel technique for validating a computational flow distribution and begins to examine the impact of operating conditions, such as electrolyte flow rate and cell current density, on flow field performance. Chapter 4 further delves into the tradeoffs between cell efficiency and system efficiency by introducing two new flow field designs constructed to take advantage of the results presented in Chapter 3. System level energy analysis is used to characterize these tradeoffs and show that each design is best suited for its own set of operating conditions.

Chapter 7 presents a detailed cost analysis which quantifies the results presented in previous chapters in terms of monetary value. These metrics include key system benchmarks including system installed cost, levelized cost of energy storage, net present value, and internal rate of return. The purpose of this chapter is to provide real world context for the findings presented in the previous chapters of this work.
2.1 Flow Field Design

Currently, the majority of work on fluid transport at the single cell level focuses on finding a panacea design which will become the accepted ideal for every case and operating condition. This approach has been used in the search for an ideal electrode and flow field, mostly without consideration of desired operation. Many of these studies within the field have been inspired by or adapted from prior work on flow field or electrode design in fuel cells. The adaptation of many of these designs has been made possible due to advancements in flow battery architecture, most notably those made by Aaron et al. in which a “zero gap” architecture is introduced, leading to improved electrolyte transport within the electrode. A review article detailing the many transport issues within RFBs has been published by Zhou et al. This work identified critical parameters for each component which must be optimized in order to achieve improved concentration overpotential in RFBs including highly permeable porous electrodes, flow fields which balance forced convective transport with pressure drop concerns, and operating conditions such as flow rate and active species concentration. This review still concludes, however, that an optimum flow field and electrode design must be achieved for RFBs to fully realize their potential.

A number of flow field design studies have been conducted on various RFB chemistries. Chen et al. analyzed the velocity distribution within a parallel flow field experimentally and computationally, identifying preferential flow as the cause of poor mass transport. A study by Lisboa et al. attempted to correct the issues present in the parallel flow field through the use of a corrugated fluidic network which introduced
periodic throttling of the flow through the use of tetrahedral channel walls. This approach was able to produce a 400% improvement in the limiting current density when compared to straight parallel channels, as well as identifying several parameters to optimize when utilizing this flow field design. Similar numerical work was conducted by Xu et al. comparing a parallel flow field to a serpentine flow field and a design without a flow field, concluding that serpentine exhibited superior energy efficiency. Further work investigating the serpentine flow field has been conducted by Ke et al. examining flow rate, electrode properties, and channel geometry in an attempt to determine an ideal architecture. Jyothi Latha et al. examined the serpentine flow field as well as electrode compression using computational methods and ex-situ experiments, finding that compression was a key factor as was electrolyte flow over the lands through the electrode. In a separate study, Jyothi Latha et al. investigated the interdigitated design and declared it superior to the serpentine design due to the residence time of the electrolyte in the electrode. Similar results were obtained by Kreutzer when examining the serpentine and interdigitated flow fields at different flow rates. A general model of the interdigitated flow field to evaluate flow distribution and pressure drop for RFBs and fuel cells was introduced by Kee and Zhu focusing on dimensionless properties for the fluid, channel, porous media, and operating conditions. Further modeling work on the interdigitated design was conducted by Yin et al. including an examination of the impact of different inlet configurations and flow rates on electrode potential. A comparison of interdigitated and serpentine flow fields has also been conducted by Knudsen et al. with a specific focus on the scale up and channel geometry of each design. The study makes a
number of conclusions including the importance of channel design, the predictive power
of three dimensional modeling of the fluid flow, and the inability of these proposed
designs to sufficiently reduce pressure drop for large scale industrial implementation.
Additionally, the study found that areas of cell degradation corresponded to regions of
predicted low velocity within the porous electrode, supporting a possible connection
between these phenomena. Darling and Perry compared this interdigitated design to a
flow through design, concluding that due to parasitic losses from high pressure drops, the
flow through design was inferior. Kumar and Jayanti examined the interdigitated,
serpentine, and flow frame designs in a larger active area through the lens of scaling up to
a commercial system. The study found that when scaling these designs, the serpentine
design appeared to gain in performance relative to the other two. Additionally, the
serpentine design was found to have a lower pressure drop than the interdigitated flow
field, although there is a high likelihood that optimization would change these results
significantly.

Reed et al. again compared the flow through design to the standard interdigitated
design as well as an interdigitated design with porous ribs, finding that the porous
interdigitated design prevailed based upon improved cell performance and comparable
cost. Further work by Xu et al. investigating the necessity of a flow field by comparing
a flow through design with a serpentine design claimed that the serpentine design
exhibited superior energy efficiency when each design was operated at its maximum
power point, although the flow through design investigated was far from optimal.
Additionally, the study found support for an ideal flow rate and electrode thickness for
each flow field to increase energy efficiency. Dennison et al. introduced a spiral flow field design which they experimentally compared to serpentine, parallel, and interdigitated designs using a number of different electrode materials. This study is unique in its acknowledgement of the non-uniform interactions between a flow field design and electrode morphology; however, the study still declares the interdigitated flow field as the ideal design, a conclusion that is valid only in certain circumstances. The flow through design has been further studied by Rudolph et al. with the objective of determining optimal inlet and outlet locations, concluding that 89% utilization of the collector surface could be achieved by using a single inlet and outlet.

### 2.2 Electrolyte Flow Rate

A number of studies have considered the impact of other parameters and operating conditions upon the mass transport performance of RFB systems, but fail to satisfactorily account for the interactions between the parameters in question and the other aspects of cell design that affect mass transport in the cell. Ma et al. examined the impact of various electrolyte flow rates on cell performance through the lenses of system efficiency, but fail to acknowledge key parameters contributing to the mass transport such as the flow field and electrode used in the cell. Binyu et al. conducted a study attempting to optimize electrolyte flow rate through the cell using a computational model, concluding that 90 mL/min was the most efficient single flow rate, but that a variable flow rate would be ideal. Xu and Zhao further explored flow rate as a contributor to mass transport performance in conjunction with electrolyte concentration using both numerical and experimental techniques, obtaining correlations for the effective diffusivity
of ions within the porous electrode structure $^{36}$. A similar study by Tang et al. approached the question of flow rate from a system perspective, finding that using a variable flow rate can produce improved efficiency though admitting that many other factors can contribute to the mass transport within the cell $^{37}$. Flow rate has even been a parameter of interest in solid state convection batteries as seen in the work done by Gordon and Suppes. This study concludes that convection can be used to significantly reduce overpotentials in the cell and also elucidates the underlying physics enabling this improved electrochemical performance $^{38}$. Blanc analyzes flow rate as well as several electrolyte properties computationally in his doctoral work, determining that through flow rate optimization, an additional 10% efficiency may be obtained from the RFB system $^{39}$. Another computational work supported by experimental findings has been conducted by Shah et al. examining the impact of electrolyte flow rate as well as electrode porosity on cell efficiency. This model used in this study generates contour plots of electrolyte concentration in the electrode during charge and discharge operations, allowing researchers to conclude that a small increase in electrode porosity can lead to an improvement in cell coulombic efficiency. The study also determines that an optimal flow rate should exist, although mention of this flow rate being highly design dependent is absent $^{40}$. Khazaeli et al. modeled the effect of flow rate on performance in a short six cell RFB stack, finding similar results to previous studies. It was determined that higher flow rate resulted in deeper depth of discharge; however, there appeared to be an inflection point where the gains in depth of discharge for a given increase in flow rate become minimal, suggesting an ideal flow rate for operation. Additionally, the study
finds that increases in flow rate lead to increased pressure drop penalties which resulted in lower energy efficiency for higher flow rates \(^{41}\). Another flow rate study conducted on a stack size system by Konig et al. looked at optimal flow rates based upon SOC and current density. This study found that through optimization, the cell efficiency could be improved by 1.2\%, while discharge capacity could also be improved by 5.4\%. The study also recommends using differing flow rates during charge and discharge due to higher rates of crossover present at higher SOCs \(^{42}\). A somewhat unconventional study has recently been conducted by Nemani and Smith in which not only the volumetric flow rate in relation to the cell stoichiometry is modelled, but also the size of the flow battery tanks in comparison to the actual reactor in order to determine the potential for tank mixing to limit system capacity. This work found that in order to reach 90\% of the theoretical electrolyte utilization, the flow rate must exceed twenty times the stoichiometric flow rate. Furthermore, the study concluded that mixing within the tanks has the potential to be the dominant source of polarization in a system and optimization of this phenomenon could lead to improved performance \(^{43}\).

### 2.3 Velocity Distribution

Similar to these numerous flow rate studies, velocity distribution within the electrode has been studied extensively. Zheng et al. computationally examined mass transport polarization as a function of flow velocity within the electrode as well as electrolyte concentration, finding that at high current densities and states of charge the overpotential was at its greatest. The study concludes that a “plug flow” design will reduce overpotential, although no experimental work is conducted to verify this assertion.
In plane current distribution in flow batteries was introduced by Hsieh et al. to examine the effect of electrolyte flow rate and SOC conditions on the current in the electrode. It was determined that the current near the outlet significantly decreases at extreme states of charge and that depth of discharge is larger at higher flow rates. Further experimental work in this area was conducted by Clement et al. through the use of in plane current distribution to examine the impact of electrode properties such as wettability, surface area, porosity, and thickness on velocity and concentration distributions. This work concludes that charging is not typically a mass transport limited process, but during discharging all of the aforementioned parameters have an effect on performance to some degree. Bhattarai et al. conducted a similar study utilizing in plane voltage distribution to examine flow behavior within the electrode, finding that the open circuit voltage contours obtained could accurately characterize the flow pattern within the electrode.

2.4 Electrode Properties

Electrode properties have also been examined as a contributor to concentration overpotential. Work by You et al. uses computational methods to examine the impact of electrode porosity on the local mass transfer coefficient at two different current densities. The study determined that lower porosity leads to more uniform distribution of overpotential, but increased polarization from a corresponding decrease in the mass transfer coefficient. Liu et al. examined the effect of different electrode materials, layering, and heat treatments on RFB performance in a zero-gap architecture, concluding that layering carbon paper produced superior results when compared with carbon felt.
adding that three layers of paper produced an optimal thickness. The study also produced promising results with heat treatment of electrodes in air, concluding that this may be a viable area for further work\textsuperscript{50}. An investigation by Manahan et al. into the use of a carbon nanoporous layer in addition to a carbon paper electrode was able to produce an 8\% increase in cell power density. It was found that adding this layer nearest to the bipolar plate on the negative side of the cell improved performance due to an increase in active area in a region where the reaction is favored to occur\textsuperscript{51}. Another study focusing on compression of the carbon electrodes in RFBs was conducted by Oh et al. using computational methods. In this study, it was determined that the compression primarily effects the ohmic overpotential of the cell and has negligible impacts upon the kinetics and mass transport within the electrode\textsuperscript{52}. Tucker et al. studied the optimization of electrode characteristics in a hydrogen-bromine cell, including electrode thickness, compression, and architecture. In addition to determining the ideal application site for the catalyst layer to be the membrane, the study asserts that the negative side of the cell is far more sensitive to changes in parameters and should be the focus for future optimization\textsuperscript{53}.

2.5 Electrode Modification

Electrode modification has also been the subject of much research with the goal of improving mass transport performance in RFB systems. Mayrhuber et al. investigated a laser perforating technique to improve mass transport by introducing small holes in the electrode, leading to a claimed 30\% increase in power density with a serpentine flow field\textsuperscript{54}. A similar modification approach by Chen et al. has been reported in which the
electrodes are treated with atmospheric pressure plasma jets, improving the electrode wettability. The study claims to achieve a 22% increase in energy efficiency, attributing this performance improvement to oxygen containing groups and nitrogen doping on the fiber surface increasing electrochemical reactivity.\textsuperscript{55} Heat treatments in a 42% oxygen/58% nitrogen environment were studied by Pezeshki et al., finding performance increases that were attributed to increased electrochemically wetted surface area. This study found that this wetted surface area doubled when treated for 15 hours at 400°C, resulting in a 100-140 mV decrease in activation overpotential. This then correlated to a 13% improvement in electrochemical energy efficiency.\textsuperscript{56} Di Blasi et al. used a nitric acid soak applied to both carbon paper and carbon felt in an attempt to improve battery performance. This technique resulted in much lower charge and discharge capacities for treated carbon felt and slightly lower capacities for treated carbon paper. It is worth noting, however, that the energy efficiency of the cell improved in both treated cases, in spite of the lower capacities obtained.\textsuperscript{57} A different approach was undertaken by Bhattarai et al. in which channel designs similar to those normally present in bipolar plates were machined into the porous electrodes themselves. After investigating four different designs and methods of creating these channels, the work concludes that interdigitated channels present in the electrodes improve electrochemical performance as well as reducing pumping losses.\textsuperscript{58} One study by Fan et al. even went so far as to investigate a suspended electrode and current collector particle within the electrolyte as a means of mitigating the normally diffusion limited transport process in RFBs, observing substantially lower charge transfer resistances using the new “flow electrolyte”\textsuperscript{59}. 

2.6 Thermal Effects

Thermal effects within the cell are another area which has seen substantial work conducted. A transient two dimensional model of such effects has been published by Al-Fetlawi et al. in which the interaction between temperature change, electrolyte flow rate, and cell operating current are examined with respect to cell performance. The study finds that sufficient heat can be generated within the cell to cause damage to the membrane and that cooling is a necessity. The study further asserts that such cooling can be accomplished with a high electrolyte flow rate, which has the added benefit of providing an increase in cell coulombic efficiency. Finally, the study concludes that the heat generation within the system is highly dependent on the operational current density, necessitating a temperature management system for the battery. Tang et al. used a modelling approach to examine the thermal impact of self-discharge reactions due to electroactive species crossover and how such thermal changes might affect cell performance. The study found that such heat generation is important during standby periods where electrolyte is static, but negligible during cell operation. Further computational analysis of such thermal effects has been undertaken by Xiong et al. by examining the combined effect of electrolyte flow rate and temperature on battery efficiency in a full stack. This study concludes by reporting an optimal flow rate and temperature range for optimizing the system and deriving roughly 5% more energy efficiency. Wei et al. continued research into this area with a study that focused on electro-thermal modeling for the VRB with forced cooling, finding that by increasing electrolyte flow rate, coulombic, voltage, and energy efficiency could be increased,
although with higher parasitic pumping losses\textsuperscript{63}. Work by Zhang et al. focused specifically on the performance impact of cell temperature regardless of how the cell achieved a given temperature. Through the use of a circulating water bath at a controlled temperature, they operated a single cell between 15°C and 55°C, finding that increased temperature resulted in higher charge and discharge capacities as well as increased power density. This higher temperature operation also resulted in a slight decline in coulombic efficiency from 96.2\% to 93.7\%\textsuperscript{64}. Recently, Yan et al. conducted additional computational work on full stack thermal behavior, finding that flow rate, environmental conditions, and membrane selection all have an impact upon the thermal behavior of the system\textsuperscript{65}.

### 2.7 RFB Stack Design

RFB stack design has seen far more limited attention when compared to single cell research; however, there are still a number of important contributions to be found in the literature. By far the most prevalent studies concern shunt current within RFB stacks, which is understandable given that shunt losses are one of the major differences between a single cell and multi-cell stack. An equivalent circuit model based on the solution of finite differential equations was proposed by Kaminski and Savinell. This model and solution method served to minimize computational cost and was applicable to a broad range of electrochemical systems, including flow batteries\textsuperscript{66}. One of the earliest investigations of shunt current in flow batteries was conducted by Kanari et al. by applying an equivalent circuit model to enable computer simulation of the self-discharge through the electrolyte in a zinc/bromine battery. The study determined that shunt
current accounted for a 1.8% decrease in coulombic efficiency of the stack, which was roughly one quarter of the total coulombic loss. A similar technique was used in a scale-up study of an iron/chromium RFB conducted by Codina and Aldez. This study examined a setup with three 18 cell stacks hydraulically connected in parallel, using a circuit analog model to determine the shunt effect on each stack and on the three stack system as a whole. The study finds that enhanced shunt current is present in a multi-stack system and is most prevalent in the central stack. Additionally, the study concludes that shunt is most prevalent in the central cell of any given stack in the assembly.

2.8 Shunt Current

Many of the shunt current studies which have been conducted recently focus specifically on the vanadium redox flow battery (VRB). Xing et al. authored a study examining the impact of shunt current in VRBs using an equivalent circuit model and including SOC in their analysis. The study separated the predicted shunt current in the cell channels from that of the manifold, finding that the channel shunt was highest in the earliest cells in the stack, while the manifold shunt current peaked in the middle of the stack and was roughly twice as large. The study concludes that increasing the number of cells in a stack increases the shunt current in the stack, while an increase in current density will result in less efficiency loss due to shunt current. A study using a similar equivalent circuit approach was conducted by Tang et al. focusing on the efficiency and thermal effects of shunt current in a simulated 40 cell VRB stack specifically during standby periods. It was found that during standby, shunt currents and vanadium diffusion across the membrane were significant contributors to rising stack temperatures at 24% of
the total heat generation, allowing the system to rise above 50°C.  

Yin et al. used a different 3-D modelling approach validated through experimental data to examine the shunt current in a small 5 cell stack. The catholyte was found to have higher shunt current loss when compared to the anolyte due to its higher ionic conductivity. An interesting trend was also discovered where shunt current within the channel appeared highest near the outer cells, but was conversely higher in the middle cells in the manifold. Manifold shunt current was also found to be significantly higher than channel shunt current and scaled with an increase in the number of cells in a stack, while channel shunt current magnitude remained relatively stable regardless of an increase in stack size.  

One of the more interesting shunt current studies was conducted by Fink and Remy utilizing external manifolding and external current sensors to directly measure shunt current experimentally. This study found that the measured shunt current values were consistently lower than those predicted by simulation, suggesting that certain imperfections in flow geometry and other parameters could reduce shunt current significantly. The catholyte in the study was again determined to have higher shunt currents due to its increased ionic conductivity. The study found that the coulombic loss due to shunt currents in the stack was 1.8%, but was sure to note that if the number of cells in the stack were increased from five there would be a corresponding increase in coulombic efficiency loss. This work also found an interesting asymmetry between the shunt discharge between cells when the system was not operating, noting that the voltage of inner cells dropped significantly faster than that of the external cells. Finally, the study concludes by determining a correlation between primary channel resistance and
secondary channel resistance and the number of cells in a stack. The results show that with less than 50 cells in a stack the shunt current is most dependent on secondary channel resistance, while with more than 50 cells in a stack the shunt current is most dependent on primary channel resistance.

Studies on shunt current in multi-stack assemblies have also been conducted. One such study examining the impact of different piping designs between stacks was undertaken by Wandschneider et al. in which three stacks connected in series are analyzed, again using an equivalent circuit model. It was found that the introduction of a hydraulic connection between stacks has a significant effect on the total shunt current present in all stacks except for the central stack. Additionally, the distribution of this shunt current within each stack is altered, with the lowest electric potential at the first cell in the first stack and the highest electrical potential at the last cell of the last stack. In this manner, shunt current was found to flow from stack 3 to 1 and from cell 30 to cell 1, with the external currents dominating the inner ones. The study also found that this shunt loss is slightly increased by locating the inlet and outlet of the electrolyte on the same side of the stack. This hydraulic connection effect is further explored by König et al. in addition to various electrical connection techniques using a simulation of an array of six VRB stacks. This study examines the impact of connecting more cells in series, in addition to the effect of different hydraulic connection diameters on efficiency. Predictably, researchers found that as the number of stacks in series is increased, the coulombic and system efficiency both decline. More interestingly, however, was that the effect of differing connection diameters became more pronounced as more stacks were
connected in series, rising from a max coulombic efficiency difference of 0.8% with only two stacks to 5.9% with six stacks. This is largely attributed to severe increases in shunt current with more stacks connected in series. The study concludes that in order to achieve optimum efficiency, either stacks should not be hydraulically connected in series, or pipe diameters must be optimized to limit shunt losses\textsuperscript{74}. Ye \textit{et al}. investigated a three stack system, again using an equivalent circuit model, with a specific focus on the shunt current, pumping loss, and compactness tradeoffs within the system. Higher flow rate deviation between cells in a stack was found as the number of cells in a stack was increased, with deviation being significantly mitigated in assemblies with multiple smaller stacks. Pressure drop trends followed expected geometric trends, as any increase in available cross section for flow through increase in channel or electrode dimensions resulted in a lower pressure drop. The study additionally finds that longer manifolds and branches for electrolyte flow between stacks produces lower shunt currents and can dominate any effect caused by the number of stacks or number of cells in a stack if properly optimized. The study concludes that there is a region for optimal compactness of design, and a region of optimal efficiency of design, but the two do not necessarily overlap\textsuperscript{75}.

\subsection*{2.9 Stack Performance}

Additional stack performance studies have also been conducted aside from shunt current analysis. A study by \textit{Zhao et al}. examined the experimental performance of a 10 kW VRB stack with regard to voltage, coulombic, and energy efficiency. It was found that coulombic and energy efficiency increased with increasing current density, while
voltage efficiency decreased, although the current densities tested were only on the order of tens of mA/cm$^2$. Perhaps the most important finding of this work was that total output power remained relatively stable whether the 8 stacks were connected in series or if two 4 stack series assemblies were connected in parallel $^{76}$. An additional experimental study was conducted by Park et al. using a 31 cell kW class VRB stack. This work demonstrated relatively stable voltage, current, and energy efficiencies of 82.2%, 92.4%, and 76% respectively up to 70 cycles at 60 mA/cm$^2$. Additionally, the study showed that when increasing the current density to 90 mA/cm$^2$, the efficiency values only declined by 2-6% $^{77}$. Work by Kim et al. examined several parameters within the stack both experimentally and computationally using a mixed sulfuric and hydrochloric acid for additional electrolyte stability. The modelling portion of the study showed a flow bias towards earlier cells in a stack, as well as higher modelled shunt current in the middle cells. The experimental data exhibited a significant drop in discharge energy and energy efficiency when increasing the stack current density from 80 to 160 mA/cm$^2$. A 10% energy efficiency drop was also found when increasing the design from a 3 cell stack to a 15 cell stack, although no additional data points were provided to further elucidate the nature of this trend $^{78}$. A study by Turker et al. computationally examined the efficiency of a VRB stack at a range of SOCs and power outputs ranging from 2 kW to 10 kW. The study confirmed that at high SOC, charging efficiency dropped significantly, while at low SOC, discharging efficiency was negatively impacted. The study also concluded that at lower power conditions, pumping losses are more crucial to stack efficiency $^{79}$. Wei et al. examined the impact of non-uniform flow patterns on stack performance through
finite element modeling (FEM) with particular attention paid to the thermal gradients developed within the system. Researchers determined that stack temperatures should rise during the first several cycles, eventually reaching a steady state where temperatures increase and decrease cyclically during discharge and charging respectively. This steady state point is dependent on the overall flow rate of electrolyte as well, with lower flow rates resulting in higher temperatures in the stack. This work additionally examined the impact of three different flow field designs on the uniformity of electrolyte flow in the stack, finding that no flow field, which is similar to a flow through design, produced the highest levels of inhomogeneity, followed by a serpentine parallel design, and then a standard serpentine design providing the most even distribution. It was discovered that introducing these flow field designs caused temperature increases in the electrolyte due to increased pumping power required by a higher pressure drop through the cell. An alternative stack design has also been introduced and modelled by Moro et al. in which the cells are connected in parallel rather than in series through the use of monopolar plates as opposed to bipolar plates. This model incorporated numerous phenomena including electrochemical performance, shunt current losses, and hydraulic concerns within the system. The work shows that for this alternative stack design, shunt current is predicted to be an order of magnitude lower than in the standard series design. Combined with hydraulic pumping losses, this leads to significantly less overall power loss in the stack as a whole. The study concludes that utilization of this alternative stack design can provide an additional 10% energy efficiency, bringing the overall battery efficiency to 85%.

A model proposed by Vynnycky attempts to facilitate modeling of large scale
stacks by approximating much of the transport within the electrode as one dimensional, thus easing the computational burden. The study claims that, coupled with an appropriate numerical scheme, such analysis should yield a reduction in computational resources of 2-3 orders of magnitude and enable the modelling of stack of up to 400 cells. 

2.10 Economic Analysis

A number of economic analyses of RFBs have been published in the literature; however, none of them apply their models extensively to experimental data to quantify the impact of realistic changes to system design. One of the most basic and perhaps most useful economic analyses was developed by Moore et al. in order to examine how cost should drive the design methodology of a VRB system. This design methodology broke the process down into six levels necessary to evaluate the economic feasibility of a system. It includes input information for the VRB, input/output analysis, power capacity considerations, energy capacity considerations, control system and balance of plant, and finally, a total capital investment estimate. While this cost model was developed as a template for undergraduate design projects, it is a useful starting point when examining the complex design problems present in RFB systems. A capital cost sensitivity analysis authored by Zhang et al. further explored the relationship between various VRB parameters and operating conditions and the overall cost of the battery system. The study determines a relative cost sensitivity for a set of fixed power capacity and fixed energy capacity variables, as well as defining an overall capital cost. The work concluded that cycle time, power capacity, and vanadium cost were the primary drivers of overall system costs and are areas that must be focused on for improved economic viability of these
Viswanathan et al. developed a cost model taking into account electrochemical performance at various SOCs and operating conditions in addition to shunt current and pumping losses and applied the model to both VRBs and an iron/vanadium battery chemistry. This study determined that while the iron/vanadium battery provided superior cost efficiency at present for smaller energy storage systems, in the future the all vanadium battery would overtake it, particularly when considering larger storage systems for grid scale storage. Additionally, the work conducts sensitivity analysis on a number of components and even on operational current density, concluding that there is in fact an ideal economic operating current for the system. Another study by Singh and McFarland has done similar analysis, but examined the hydrogen/bromine chemistry instead. The study includes the stack components of the system as well as the balance of plant components necessary to operate the stack in order to estimate levelized cost of three cases, one without complexing agents, one with a complexing agent used on the bromine side and accounting for its effect on current density, and one not accounting for the effect of the complexing agent on current density. Unsurprisingly, the case without the complexing agent proved the most expensive, with the effect of the agent on current density proving even more costly. This is additionally borne out in the sensitivity analysis where it was also determined that system lifetime has a dominant impact on the levelized cost. Work by Hopkins et al. examined the cost differences between RFBs and conventional batteries under the constraint of constant energy efficiency and discharge rate. The study determined that flow batteries have an advantage in terms of cost per kWh, but that this advantage is a strong function of electrolyte energy density.
Crawford et al. conducted a comparative study of various flow battery chemistries, including all vanadium, iron-vanadium, and iron chromium, using a cost performance model which includes shunt analysis, pumping losses, and electrode flow patterns. In this work, researchers found that the all vanadium chemistry was most cost effective for both 0.25 MWh and 4 MWh sizes, while the Fe-V chemistry was more cost effective than the Fe-Cr for smaller energy capacity systems but not for the larger energy capacity. The study also examined the relative impacts of changes in component costs at different energy capacity sizes, determining that at low capacities electrolyte chemical, electrode, and membrane prices all have similar effects on cost per kWh, but at higher storage capacities, the price of electrolyte chemicals is the dominant driver of cost. Finally, the study concludes by finding differing cost trends for two different flow fields. It was discovered that interdigitated flow fields led to lower cost per kWh as the energy to power ratio increased, while a conventional flow system exhibited the opposite trend.

Another chemistry comparison study was conducted by Moore et al. examining the differences in capital costs between an all vanadium RFB and a regenerative hydrogen-vanadium fuel cell (RHVB). The study found that the two technologies had similar capital costs over the span of 20 years, with the VRB costing $70 per kWh per year and the RHVB costing $75 per kWh per year. The majority of the costs for each of these systems is the electrolyte and the cell stacks, with the major difference between the two being the need for a compressor, which is considerably more expensive than a simple pump, to run the RHBV. The study concludes that the VRB also has a lower power
capacity sensitivity index, meaning as power capacity is increased, the RHVB capital cost would increase more than the VRB cost.

A techno-economic model by Dmello et al. examined electrolyte materials selection for cost optimization in redox flow batteries with respect to both aqueous and non-aqueous chemistries. The study used a target viable cost per kWh of $100. For both aqueous and non-aqueous chemistries, as molecular weight in terms of grams per mole of electrons of the active species increases, the cell voltage also must increase to maintain battery price. Similarly, as molality decreases an increase in voltage is necessary to compensate; however, a lower molecular weight can counter this effect. Area specific resistance (ASR) showed a similar trend to the molecular weight trend as well, but lower ASR was shown to only be capable of reducing battery cost to a certain point. The study concludes with a series of recommendations for non-aqueous and aqueous RFB designs in the future. For non-aqueous chemistries, the study recommends decreasing ASR to 2.5 Ω-cm², using cheap or lightweight redox active species, finding a way to lower required salt content, and increase cell voltage. For aqueous systems, the authors find that there are fewer avenues to cost savings, citing only the synthesis of lower cost organic or inorganic redox active species and increasing cell voltage as the only avenues for improvement. Moore et al. further contributed to the economic analysis of RFBs through publication of a study focusing on the impact of current density and voltage efficiency on capital costs of VRBs. This study found that capital cost per kWh was relatively stable with regards to operational current density up until an inflection point, around 2000 mA/cm², at which point cost begins to increase more rapidly. It was also
determined that the membrane cost does not alter the shape of the cost curve, but rather shifts the cost up or down a given offset. The study concluded with the finding that as current density was increased, the amount of vanadium required to store a fixed amount of energy also increased. Work by Minke et al. included another techno-economic evaluation of VRBs, focusing on the use of large cell areas on the order of 2.68 m$^2$ per cell in the system design. The model developed in this study predicts that the manufacture of such large plates will derive a significant economy of scale until reaching production of about 2000 plates per year above which the decrease in production costs becomes substantially smaller. The membrane was determined to be the dominant cost contributor when examining stack construction, but was hypothesized as an area for cost reduction through the use of a SPEEK membrane instead of the more common Nafion. It should be noted that any cost savings predicted from this membrane switch assumes similar cell performance for the two membranes. Due to electrolyte costs comprising roughly half of the total system cost, energy capacity was shown to have a strong impact on the linear power-cost relationship, shifting the slope of this curve upwards with increasing energy capacity. For this reason, electrolyte cost also exhibited the highest cost sensitivity when viewing the system as a whole, making energy and electrolyte savings a prime area for further advancements.

Another economic model of VRBs for medium and large scale energy storage has been published by Li et al. using a novel electrolyte which employs oxalic acid as the reducing agent. The study examines the profitability of VRB systems installed in three different scenarios, replacing lead-acid batteries as uninterrupted power supplies,
providing storage for homeowner distributed solar energy networks, and a large scale wind and solar power installation equipped with a VRB system. For the first of these three, the cost for replacing a 1280 kW/3840 kWh lead-acid battery was between 1.25 and 4.8 million dollars depending on various parameter choices. In the homeowner distributed solar model, profit was considered instead, with the homeowner predicted to realize a profit of $7,536 over the 20 year lifespan of the system while the company owning the system would achieve just over $50,000 in profit over the same 20 year span. For the final scenario of an installation at a large scale intermittent renewable generation plant, payback period was considered and determined to be between 7.4 and 9.5 years depending on the electrolyte levels chosen. Recently, Soberanis et al. published a sensitivity analysis case study on flow batteries as a large scale energy storage system. Three scenarios were examined. First, a mining operation was modeled as both a constant 100 kW of demand and a variable demand peaking at 200 kW and averaging 100 kW throughout the day. Next, a telecommunications constant load demand of 13 kW was modeled. Finally, the third scenario is an off grid community with variable loads and a pre-existing 365 kW diesel generator. This study also compared three types of power installations for supply based on centralized generation. These included a diesel generator coupled with solar and wind generation and an RFB energy storage system, a diesel generator coupled with just an RFB storage system, and a standalone diesel generator. The study identified diesel cost, capital costs, and interest rates as the primary factors impacting feasibility and determined that the high power demand industry sector shows the most promise for implementation with potential savings between 2.5 and 3.5
million dollars. Furthermore, the study found that significant CO$_2$ emissions reduction could be achieved through the implementation of RFB systems$^{94}$. 
CHAPTER THREE

INFLUENCE OF ARCHITECTURE AND MATERIAL PROPERTIES
ON VANADIUM REDOX FLOW BATTERY PERFORMANCE
Abstract
This chapter is revised based on the published paper with permission from Elsevier:


My contributions to this work were collection, reduction, and analysis of data as well as composition of the manuscript. Clement collected current distribution data.

3.1 Introduction

As discussed in chapter 1, mass transport losses limit VRFB performance through increased overpotential at higher current. Crossover is generally a matter of separator engineering, with a typical tradeoff between ohmic losses and crossover. Improving the convective mass transport from the flow field into the porous electrodes has been shown to increase performance, as well as increase utilization of the full SOC window, utilizing a greater fraction of the vanadium in solution available for reaction. Improving this convective mass transport can be accomplished through the modification of the carbon fiber electrodes or introduction of more optimized flow field designs. This improvement reduces the cost of these systems by increasing the practically realized energy density of the charge storage solution. As electrolyte cost is of particular concern in many RFB chemistries, particularly the all-vanadium chemistry which has found the most commercial success, such mass transport gains can prove very lucrative. However, improving convective mass transport usually comes at the cost of increased pumping power requirements; thus, a design tradeoff exists in these systems which must be optimized.
As previously stated, the components with the greatest impact on convective mass transport are the electrodes and flow fields. Flow fields serve to distribute the electrolyte through the electrode, which directly influences cell performance and pressure drop. The extensive research into flow field design that has been conducted in the literature is detailed in chapter 2. The motivation of this chapter is to better understand the fundamental mass transport phenomena present with different flow field designs and to qualify how these are affected by other cell parameters, so that general design guidelines applicable to these systems can be devised and informed decisions can be made in subsequent chapters. In this study, numerical simulations and experimental distributed and overall cell performance data were utilized to compare serpentine and interdigitated designs shown in Figure 3.1(a).

3.2 Method of Approach

Experiments and simulations were conducted at different flow rates, discharge current densities, and with different electrode thicknesses in order to better understand their contributions to transport phenomena and performance in the VRFB. Five types of experimental data were utilized in this work: discharge curves, polarization curves, pressure drop, locally measured current distributions, and flow distributions from a novel thermal analog visualization technique. All tests were performed on a 9 cm$^2$ version of the zero gap architecture cell described by Aaron et al. 16 Two types of flow field design common to flow batteries were investigated for this work: serpentine and interdigitated. All tests were conducted with Nafion™ 117 membranes (E. I. du Pont de Nemours and Company) that were pretreated by soaking for 30 minutes in 1 M sulfuric acid at 80°C,
Figure 3.1. (a) Flow field designs: Interdigitated (left) and Serpentine (right). (b) Computational domains with channels (red) and electrode (purple) for interdigitated design (left) and serpentine design (right).
followed by an identical soak in deionized water. Carbon paper (10AA, SGL Group; 410 μm nominal thickness) was used as received without further treatment for the electrodes in all tests. Flow fields were machined in house from blocks of BMC 940 graphite composite (Bulk Molding Compounds, Inc.).

All tests were conducted with a solution of 1.7 M vanadyl sulfate in 3.3 M sulfuric acid. The tank for the negative side of the cell was filled with 50 mL of electrolyte, while the tank for the positive side was filled with 100 mL of electrolyte. The solution was then charged to 100% state of charge (SOC) and half of the positive side electrolyte was subsequently removed so that equal volumes of V(II) and V(V) remained on their respective sides. Electrolyte reservoirs were purged with nitrogen at all times. Cell temperature was controlled at 30°C for all tests.

### 3.2.1 Discharge and Polarization Curves

The discharge curves were obtained by discharging the electrolyte solution initially at 100% SOC at a constant current until a cutoff voltage of 0.2 V was reached. Two current densities were evaluated: 250 mA cm$^{-2}$ and 500 mA cm$^{-2}$. Tests for both of these current densities were run at 20 mL min$^{-1}$ and 90 mL min$^{-1}$. Additionally, tests were conducted using one, three, and five layers of carbon paper electrodes to investigate the impact that electrode thickness and in-plane permeability has on mass transport. Once discharged, the positive and negative solutions were mixed together to produce 100 mL of half V(III) and half V(IV) solution. This solution was then divided evenly between the two sides of the cell and recharged for the next discharge test. Utilizing remixing minimized the difference in electrolyte solution between discharge tests and allowed
charging capacity to remain stable.

Polarization curves were also recorded at flow rates of 10 mL min\(^{-1}\) and 20 mL min\(^{-1}\) at 50% SOC. To achieve this condition, the electrolyte was charged as described previously and then coulombically discharged to 50% SOC. The low flow rates allowed for the polarization curves to be single pass, ensuring constant SOC at the cell inlet throughout the entire test. Polarization curves were obtained under potentiostatic control from OCV to 0 V in equally spaced increments. The high frequency resistance (HFR) of the cell was measured at 20 kHz at each voltage point and used with the measured current to correct the polarization curves for iR loss, or the voltage loss associated with the ohmic resistance of the membrane in the cell. This correction leaves primarily kinetic and mass transport overpotentials as the losses in the curve, with some remaining ohmic losses in the electrolyte. When operating at high current and mass transport limiting conditions, kinetics are largely consistent, allowing the mass transport loss in the cell to be isolated. A potentiostat (BioLogic Science Instruments, Claix, France) with a 20 A booster was used for the polarization curves and discharge tests.

Pressure drop across each cell was measured for each discharge test using two TemTech PTFE pressure transducers with a pressure range from 0-50 psi (0-344.7 kPa) and a reading accuracy of 0.1 psi (0.7 kPa). One transducer was located at the cell inlet and the other was located at the outlet. Pressure drop data were obtained for a range of flow rates from 10 mL min\(^{-1}\) up to 100 mL min\(^{-1}\).

3.2.2 Current Distribution

In-plane current distribution measurements were carried out via the printed circuit board (PCB) approach outlined in reference 46. However, instead of “partially-
segmented” flow plates, the plates were fully electrically segmented to eliminate any lateral current spread, thus ensuring current generated at the electrode was conducted directly to the corresponding segment on the board. Tests were conducted using a solution of 1.7 M vanadium in 3.3 M sulfuric acid. Electrolyte was circulated at a flow rate of 20 mL min\(^{-1}\) with 50 mL on the negative side and 50 mL on the positive side. The cell was discharged from 50% SOC to the cutoff voltage of 0.2 V at 400 mA cm\(^{-2}\) with a Scribner 857 Redox Cell Test System to obtain charge-discharge curves. Distribution data were collected every second, with the recorded data averaged over 6 second spans.

### 3.2.3 Thermal Visualization of Flow Distribution

A novel ex-situ technique allowed for direct visualization of the electrolyte flow in the electrode using a Reynolds analogy \(^{96}\). This method relates thermal and mass transport, and can give useful insight into the flow distribution and transport mechanisms within the cell. A 120 µm thick, heat sensitive liquid crystal sheet with a temperature sensitivity range of 25-30°C was placed on a half-cell zero gap architecture in place of the ion exchange membrane. A clear PVC plate was then placed on top of this instead of the opposing flow field, gasket, and electrode assembly. A custom end plate with a window machined into it was used for viewing. Water chilled in a bath at 10°C was pumped through the cell for 10 minutes to ensure thermal equilibrium of the electrode was attained. Once the electrode was at thermal equilibrium, water heated in a bath at 35°C was pumped directly through the cell, eliciting a color change response from the liquid crystal sheet in the areas where the convective flow, and hence heat transfer, was the highest. This method allows for a direct visualization of the flow and qualitative
confirmation of the relationship between the observed current distribution measurements and induced electrode convective flow.

### 3.2.4 Computational Fluid Dynamics

Numerical simulations were carried out using Comsol Multiphysics 4.3a. The built-in Free and Porous Media Flow module was employed for this work as it is capable of handling both the free channel flow as well as the flow in the porous carbon paper electrode. This module employs the Navier-Stokes equations for incompressible flow to model the fluid flow in the open channel. In the porous medium, the flow is modeled by the Brinkman equations for fast flow in saturated porous media with a correction term for Forchheimer drag, an inertial term to account for non-linear behavior of the pressure drop in the porous media. These Navier-Stokes and Brinkman equations are shown in Eq. 3.1 and 3.2:

\[
\rho(u \cdot \nabla)u = \nabla \cdot \left[ -p \mathbb{I} + \mu \left( \nabla u + (\nabla u)^{T} \right) \right] + F \\
\rho(u \cdot \nabla)u = \nabla \cdot \left[ -p \mathbb{I} + \frac{\mu}{\varepsilon_p} \left( \nabla u + (\nabla u)^{T} \right) \right] - \left( \frac{\mu}{\kappa_{br}} + \beta_{F} |u| \right) u + F
\]  

(3.1)  

(3.2)

In these equations, \( \rho \) is the fluid density, \( u \) is the superficial velocity, \( p \) is the pressure, \( \mu \) is the dynamic viscosity, \( \varepsilon_p \) is the porosity of the porous media, \( \kappa_{br} \) is the permeability of the porous media (assumed to be isotropic here), \( F \) is the body forces acting upon the fluid, and \( \beta_{F} \) is the Forchheimer coefficient which takes into account density, porosity, permeability, and a non-dimensional friction coefficient based on electrode porosity. The values specified for various simulation parameters are listed in Table 3.1.
The flow field parameters used in the simulations were selected based on the experimental designs used. The electrolyte density was obtained from Rahman et al. The electrode porosity was taken to be 88% by SGL for their 10AA carbon paper material, and was adjusted to a value of 82% to account for electrode compression in the cell. The electrolyte viscosity and electrode permeability were fitted for the model in order to match the experimental data, however are in line with values reported by Darling et al. and Gostick et al., respectively.

The model domains were constructed based on a 9 cm² projected active area electrode. Both designs maintain the same geometric parameters with 1 mm wide by 1 mm deep channels and 1 mm wide lands. These values were chosen based on common flow field dimensions found in the literature. It is possible that optimization of these geometric parameters could improve the performance of the designs; however, such optimization was not the focus of this study. These computational domains are depicted in Figure 3.1b. Mass transport and momentum in the channel is governed by Equation (1), while the transport and momentum in the porous electrode is governed by Equation (2).

The wall boundaries for the channels and porous media were assigned a no-slip condition. The outlet boundary was held at 0 kPa. Two different parametric sweeps were conducted. The first was a flow rate sweep at the inlet boundary from 0-100 mL min⁻¹. The second was a sweep of electrode thickness from 200 µm to 400 µm. The first sweep was performed to verify model consistency through pressure drop correlation with experimental values. The second sweep was conducted to illustrate the difference in mass
Table 3.1. Simulation Parameters

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Simulation Value</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Channel Width/Depth (mm)</td>
<td>1</td>
<td>Chosen</td>
</tr>
<tr>
<td>Land Width (mm)</td>
<td>1</td>
<td>Chosen</td>
</tr>
<tr>
<td>Electrolyte Density (kg m$^3$)</td>
<td>1500</td>
<td>[38]</td>
</tr>
<tr>
<td>Electrolyte Viscosity x 1000 (Pa·s)</td>
<td>3.237</td>
<td>[30]</td>
</tr>
<tr>
<td>Uncompressed Electrode Porosity (%)</td>
<td>88</td>
<td>SGL</td>
</tr>
<tr>
<td>Compressed Electrode Porosity (%)</td>
<td>82</td>
<td>[39]</td>
</tr>
<tr>
<td>Electrode Permeability x 10$^{11}$ (m$^2$)</td>
<td>1.741</td>
<td>[40]</td>
</tr>
</tbody>
</table>
transport response of each design based on a changing parameter (electrode thickness). This illustrates how one flow field is not inherently better than another; but rather, this distinction is dependent upon a more complex combination of electrode, electrolyte, and flow field parameters.

3.3 Results and Discussion

Figure 3.2 shows results for both constant current discharge and polarization curve experiments. In this case the interdigitated design has better overall performance, indicated by higher discharge voltage for a given current density and greater depth of discharge achieved. Superior mass transport performance compared to the serpentine design at a low flow rate of 20 mL min\(^{-1}\) is shown in Figure 3.2(b). As a cell is discharged, the concentration of the active species decreases, directly decreasing the amount delivered to the electrode surface by mass transport mechanisms including diffusion and convection. When this decrease in active species delivery begins to limit the reaction, concentration polarization (also known as mass transport limitation) begins to dominate voltage loss. When this limiting discharge capacity is reached at a given current density, concentration polarization in discharge curves is seen as a sharp non-linear drop in cell voltage. The discharge curve for the interdigitated design reaches the cutoff voltage of 0.2 V after discharging 1.7 Ah out of a theoretically available 2.28 Ah of charge at 250 mA cm\(^{-2}\) and 1.3 Ah at 500 mA cm\(^{-2}\), while the serpentine design only manages 1.4 Ah and 0.6 Ah, respectively. Here, the interdigitated design is able to access
Figure 3.2. (a) Discharge curves of the VRFB with interdigitated and serpentine flow fields at 20 mL min\(^{-1}\) at 250 mA cm\(^{-2}\) and 500 mA cm\(^{-2}\), initial SOC of 100%, theoretical discharge capacity of 2.28 Ah and (b) iR corrected polarization curves at 20 mL min\(^{-1}\), initial SOC of 50%.
15% more of the theoretical discharge capacity when discharged at 250 mA cm$^{-2}$, and 33% more capacity when discharged at 500 mA cm$^{-2}$. The interdigitated design is operable at a lower concentration of reactant than the serpentine design because the interdigitated design more effectively delivers the reactant to the reaction sites within the electrode under these conditions. The polarization curves further support this conclusion, as the interdigitated flow field remains fairly linear throughout, reaching a current density of almost 800 mA cm$^{-2}$, while the serpentine design shows the characteristic voltage drop associated with mass transport limitation at a current density of about 450 mA cm$^{-2}$. The linear interdigitated polarization curve does not show the voltage drop associated with concentration polarization due to mass transport limitation. The lack of a sharp concentration polarization region in the curve indicates that mass transport in the interdigitated design is superior for these conditions with the given materials and architecture. To further explore this mass transport difference, it is necessary to assess the transport mechanisms in each flow field design and determine the flow distributions of the electrolyte in the electrode. This was accomplished with \textit{in-situ} current distribution measurements.

Current distributions were recorded during charge-discharge curves near the voltage cut-off condition under mass transport limited conditions. Since local current directly indicates local rate of reaction, these mass transport limited current distributions can be used to assess the local transport in the electrode generated by each flow field design. Higher current corresponds to increased reaction, which is indicative of better local mass transport under limiting conditions. Figure 3.3 shows a six second average at
Figure 3.3. Experimentally measured current distribution for (a) interdigitated flow field, (b) serpentine flow field at 400 mA cm$^{-2}$. 
the end of a discharge curve, just before the cutoff voltage was reached, for both serpentine and interdigitated flow field designs. The reaction favors regions of higher concentration, i.e. regions of high convective transport into the electrode. This approach enables different mass transport mechanisms present in these two designs to be studied. These distributions indicate a difference in the primary reaction zone; for the serpentine design the edges of the active area are relatively high current regions, whereas the center of the active area is a low current zone. This is most likely due to high pressure drop in the serpentine channels, particularly near the lands on the switchbacks. The high pressure drop associated with multiple switchbacks forces the electrolyte into the electrode and under the lands. This eliminates the flow through the switchbacks to a degree, by providing a parallel flow circuit path with a lower pressure drop for the electrolyte. The interdigitated design shows opposing different trend, with a high current region in the center of the active area. Since the digits are not connected, all of the electrolyte is forced to flow through the electrode in a linear flow circuit, and follows the path of least resistance to the exit in order to minimize pressure drop. This results in transport being focused in the center of the flow field, where the path length through the porous media will be the shortest.

The computational model provides further insight to these current distributions. The practical average electrode velocity magnitude distributions for each flow field design are shown in Figure 3.4. These distributions are for a cut plane midway through the thickness of the electrode domain in the model. The serpentine design has elevated velocity along the edges of the flow field, particularly over the lands where the high
Figure 3.4. Computed velocity profiles in m s\(^{-1}\) at a cut plane through the center of the electrode domain for (a) interdigitated and (b) serpentine designs.
pressure drop of the switchbacks forces the electrolyte to jump over the lands and through the electrode material to reach the outlet. The interdigitated design conversely has higher velocities in the center of the electrodes. The higher velocities tend to be towards the last few digits closer to the outlet, indicating that the electrolyte does not deviate from its path along the inlet channel until it is past the first few digits in this design. This tendency can also be seen in the current distributions in Figure 3.3, as the region near the inlet indicates lower local current than the region near the outlet in the interdigitated design. When the cell is operated in the mass transport limited region at a low SOC and the current localizes near the inlet channel and last digit, the computational and current distribution results agree well. Preferential flow towards the later digits is therefore an opportunity for further optimization.

The predicted distribution of convective velocity in the electrode was qualitatively verified using the thermal visualization method. Video files showing the evolution of these distributions prior to reaching steady state have been included as supplementary material in Appendix A. The black regions are lower temperature regions, representing more restricted transport, while the blue regions result from higher temperature and more effective convective transport into the electrodes. The interdigitated design in Video 3.1 exhibits the same preferential flow towards the last digit as is seen in the computational model, as this region sees the greatest color change in the liquid crystal sheet. For the serpentine design in Video 3.2 there is a heightened color change along the edges over the lands, creating the same striping pattern generated in the simulation. These
distributions also qualitatively agree with the current distribution results presented in Figure 3.3.

At higher flow rates the mass transport differences largely vanish, as shown in the discharge curves for serpentine and interdigitated designs at 90 mL min\(^{-1}\) in Figure 3.5. At both current densities the discharge curves for the designs nearly overlay, with the serpentine design even slightly outperforming the interdigitated design at 250 mA cm\(^{-2}\). Each set reaches the cutoff voltage at a similar discharge capacity, indicating that the effective mass transport in each design at these conditions is similar.

At higher flow rates where the differences in flow field architectures are minimized, it is important to examine parasitic losses in the cell resulting from pumping power requirements. The pumping power equation for liquid electrolyte is:

\[
P = \frac{\Delta p \cdot Q}{\eta}
\]

(3.3)

Here, \(Q\) represents the flow rate of electrolyte through the cell, while \(\eta\) is the pump efficiency. If both of these variables are held constant as they are in the 90 mL min\(^{-1}\) cases above, then the pumping power, \(P\), becomes solely a function of pressure drop, \(\Delta p\).

Figure 3.6 shows experimental and computational pressure drop measurements and calculations taken over a sweep of flow rates from 10 mL min\(^{-1}\) up to 100 mL min\(^{-1}\). The experimental measurements and simulation values qualitatively agree with some discrepancy in absolute value (primarily for the interdigitated). This disagreement could be a result of non-isotropic electrode properties which can be expected due to the preferential fiber orientation of the paper electrode structure, as well as uneven flow between pairs of digits, and electrode penetration into the flow field domain when
Figure 3.5. Discharge curves of the VRFB with interdigitated and serpentine flow fields at 90 mL min$^{-1}$ at 250 mA cm$^{-2}$ and 500 mA cm$^{-2}$, initially at 100% SOC, theoretical discharge capacity of 2.28 Ah.
**Figure 3.6.** Experimentally measured and computationally predicted pressure drop data for serpentine and interdigitated flow field designs.
compressed, none of which is accounted for in the model. Figure 3.6 also illustrates the additional pressure drop resulting from increasing the flow rate in each flow field in order to reduce the mass transport differences. While the pressure drop ratio between serpentine and interdigitated remains roughly constant, slightly increasing from a factor of 2.05 at 20 mL min\(^{-1}\) to 2.47 at 90 mL min\(^{-1}\), the magnitude of the pressure drop difference increases. At 20 mL min\(^{-1}\), the pressure drop for the serpentine design is only 8.96 kPa greater than that of the interdigitated design. At 90 mL min\(^{-1}\), this difference is nearly tripled at 64.60 kPa. This increase has a direct impact on the pumping loss through the relationship in Eq. 3. The additional pumping power requirement of a high flow rate cell makes the interdigitated flow field advantageous for these architectures and discharge conditions. It should be noted however that pressure drop in a serpentine architecture can be reduced with a multiple serpentine channel design. However, this reduces the unintentional bypass flow under the lands which is responsible for much of the performance enhancement. The degree of parallelization as well as the channel dimensions can therefore be viewed as an engineering design feature which can be optimized to balance the improved convective electrode velocity with increased pressure drop for greatest overall system efficiency.

Due to the different architectures used to induce convective transport in different regions of the electrode, these two flow field designs respond differently to changes in conditions such as flow rate, as shown previously, and electrode thickness. Figure 3.7 shows the initial discharge performance of the two flow fields for the three different electrode thicknesses tested at 20 mL min\(^{-1}\) with an available total capacity of 2.28 Ah.
Figure 3.7. Discharge curves of the VRFB with interdigitated and serpentine flow fields at 20 mL min\(^{-1}\) initially at 100% SOC, theoretical discharge capacity of 2.28 Ah with (a) one electrode layer; (b) three electrode layers; and (c) five electrode layers; and (d) iR corrected voltage difference between the two designs \(V_{\text{interdigitated}} - V_{\text{serpentine}}\); positive values indicate comparatively superior interdigitated voltage efficiency at the given current.
The interdigitated design is preferable for thinner electrode structures, as seen in Figure 3.7(a), discharging 1.68 Ah (74% depth of discharge) at 250 mA cm\(^{-2}\) and 1.28 Ah (56% depth of discharge) at 500 mA cm\(^{-2}\) while the serpentine design manages only 1.39 Ah (61% depth of discharge) and 0.62 Ah (27% depth of discharge) respectively. With increased electrode thickness, seen in Figure 3.7(b), the interdigitated design still outperforms the serpentine design; however, the distinction is not as significant. Under these conditions the interdigitated design is only able to discharge an additional 0.18 Ah (8% additional depth of discharge) at 250 mA cm\(^{-2}\) and 0.28 Ah (12% additional depth of discharge) at 500 mA cm\(^{-2}\) while the serpentine design increases by 0.30 Ah (13% additional depth of discharge) and 0.57 Ah (25% additional depth of discharge) respectively. The serpentine design gains almost twice as much discharge capacity as the interdigitated design by increasing the number of electrode layers from one to three. This demonstrates that increased electrode thickness has a different effect on the performance of these two flow field designs. When increasing the number of electrode layers to 5, shown in Figure 3.7(c), the serpentine and interdigitated designs reach roughly the same amount of discharge at 1.72 Ah (75% depth of discharge) at 250 mA cm\(^{-2}\). When discharging at 500 mA cm\(^{-2}\) the interdigitated design is only capable of discharging 1.34 Ah (59% depth of discharge), a drop of 10% from the three layer cell, while the serpentine design only sees a 3% drop to 1.12 Ah (49% depth of discharge). This trend clearly shows that the mass transport mechanisms in these two flow fields respond differently to increased electrode thickness. As the thickness of the electrode increases, the cross sectional area for flow in the electrode region increases as well. In the
serpentine design, the fraction of flow into the electrode is a function of the relative values of pressure drop in the channels versus the electrode. The decrease in pressure drop through the electrode associated with increased thickness will increase convection into the electrode. The result is a greater volume of electrolyte being forced into the electrode as the electrode thickness is increased, while allowing the average electrolyte velocity in the electrode to remain unchanged. As the electrode thickness is increased, the amount of flow available to be drawn into the electrode will diminish, leading to a decrease in performance with increased electrode thickness evidenced by the performance decrease seen in 5 layer cells. In the interdigitated design, the entire volume of electrolyte is already being forced through the electrode domain, thus no increase in volumetric flow rate through the electrode can occur. However, with the increased cross sectional area for flow, the average electrolyte velocity in the electrode will decrease, resulting in decreased mass transport into the electrode. The increase in electrode surface area with additional electrode thickness initially counterbalances this effect, resulting in improved performance when increasing electrode thickness from one layer to three layers, but decreased performance as mass transport limitations become dominant in thicker electrodes. Thus, the two flow field designs respond to increased electrode thickness in different fashion, a feature that can be useful in design optimization.

Polarization curves under these conditions further support the findings from the discharge curves and pressure drop measurements. Figure 3.7(d) shows the voltage difference between the two flow field designs for polarization curves with 1, 3, and 5 electrode layers, calculated as the serpentine voltage at a given current density subtracted
from the interdigitated voltage at that same current density. As the number of electrode layers is increased, the difference in voltage at a given current decreases. Additionally, cell architectures with 3 layers performed best for both flow field designs in terms of limiting current density, which is consistent with literature. The interdigitated design with three layers is capable of reaching a limiting current density of just over 800 mA cm$^{-2}$, while the serpentine design achieves a limiting current density of 609 mA cm$^{-2}$. This allows the architectures with 3 layers to be compared at higher current densities than the other two electrode thicknesses. When increasing the number of electrode layers to 5 the difference becomes negative at lower current densities. This indicates that with 5 electrode layers at lower current densities the serpentine design actually has a slightly higher voltage at a given discharge current density than the interdigitated design. While the interdigitated design does overtake the serpentine design for the 5 electrode architecture, the difference in voltage remains below that of the 3 electrode cells, indicating that the performance for the serpentine cell is less affected by the additional layers as described above and shown in Figure 3.7(c).

This trend is also supported by the computational simulation. Figure 3.8 shows the simulated average electrolyte velocity in the electrode domain which takes into account the non-uniformity of the distribution in both the in-plane and through-plane directions. Simulations were conducted at an inlet electrolyte flow rate of 20 mL min$^{-1}$ for each flow field with electrode thicknesses of 200 µm, 300 µm, and 400 µm. As the electrode thickness increases, the average velocity of the electrolyte in the electrode for each of the flow field designs decreases. The electrolyte velocity in the interdigitated
Figure 3.8. Simulated average velocity of the electrolyte inside the electrode domain for serpentine and interdigitated flow field designs at 20 mL min$^{-1}$ total flow rate into VRB with different electrode thicknesses.
The average velocity of the electrolyte in the electrode domain for the interdigitated design decreases from 2.3 mm s\(^{-1}\) at 200 µm, to 1.61 mm s\(^{-1}\) at 300 µm, and 1.27 mm s\(^{-1}\) at 400 µm. The serpentine velocities at these electrode thicknesses are 2.36 mm s\(^{-1}\), 2.32 mm s\(^{-1}\), and 2.26 mm s\(^{-1}\), respectively. While the predicted serpentine velocities are higher than the interdigitated velocities for all three cases, the interdigitated design shows generally better mass transport performance in both the polarization curves and the discharge curves. This is due to a residence time effect created by the different transport mechanisms described above between the two flow field designs and is further explained by Jyothi Latha et al.\(^{23}\). The electrolyte velocity in the electrode still has a significant impact on mass transport, however, as seen in the experimental results in Figure 3.7. The computational results further support the experimental finding that increasing the electrode thickness will decrease cell performance in an interdigitated design, while improving cell performance in a serpentine design based on a balance between mass transport and active area for reaction.

The trend of decreasing average electrolyte velocity seen in Figure 3.8 suggests that the performance should become worse for each design as electrode thickness is increased, only more so for the interdigitated design. This was not observed experimentally. The apparent improvement in mass transport in the experimental data is likely also a result of the increased surface area available for reaction due to the added electrode layers. This allows the kinetics to appear better by providing more surface area to support the same rate of reaction. By alleviating mass transport limitations in a larger portion of the electrode, the effective current density decreases, leading to a lower
effective kinetic overpotential. The inherent kinetics of the system remains unchanged, however. The interdigitated design suffers additional mass transport loss with the additional electrode thickness, and is not able to take advantage of this additional surface area as much as the serpentine design, which sees improved performance with the additional electrode layers. Thus, one flow field design is not inherently better than another. The architecture of the cell, porous electrode transport properties, as well as the operating parameters must be taken into account when trying to optimize flow field architecture.

3.4 Conclusions

Convective mass transport in the electrodes of VRBs is critical to overall cell performance and operation. Flow field architecture is a key component affecting this mass transport and cell performance, as well as the overall pressure drop and pumping requirement of the cell. However, as the results of this study demonstrate, no optimal architecture can be defined independently of operating conditions, electrode properties, and electrolyte properties. For a given set of operating conditions, one flow field may show better performance than another in terms of limiting current density and available discharge capacity. At different operating conditions, however, it is possible for this performance advantage to be mitigated, eliminated, or reversed. At low flow rates and with thin electrodes, there is a significant performance gain when using an interdigitated flow field versus a serpentine one. At higher flow rates, or with thicker electrodes, this performance gap was erased altogether. Different transport mechanisms in each architecture can be engineered in concert with electrolyte flow rate and physical
properties such as viscosity, and electrode thickness and morphology to achieve system optimization including higher efficiency, deeper depth of discharge, and acceptable pressure drop.

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CHAPTER FOUR
ARCHITECTURE FOR IMPROVED MASS TRANSPORT IN REDOX FLOW BATTERIES
Abstract

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My contributions to this work were collection, reduction, and analysis of data as well as composition of the manuscript. Pezeshki and Aaron assisted in design of experiment.

4.1 Introduction

At high current, mass transport limits the achieved discharge capacity and current density of VRFBs. While a cell would likely not operate at the limiting current density, a high limiting current density is a useful indicator of good mass transport and tolerance of response to dynamic load variation. In chapter 3, it was established that high limiting current densities have been realized by improving the convective mass transport into the porous electrode \[29\]. Additionally, improved mass transport allows for better utilization of the full state of charge (SOC) window by accessing a greater fraction of the vanadium in solution available for reaction. This greater utilization results in increased effective energy stored per unit of vanadium in solution, reducing system capital investment cost per kWh. Species crossover is also a matter of concern for discharge capacity, but is primarily a function of separator engineering involving a tradeoff between ohmic losses and crossover. Other approaches to increasing system energy density, such as increasing vanadium solubility, generally do not reap the same cost benefit because they require more of the electroactive specie to be added to solution. However, most mass transport
improvements designed to enhance performance are a design tradeoff between improved convective transport and increased pumping power requirements, necessitating further study and optimization of mass transport and flow field design.

In chapter 3, it was shown that the comparison of flow field designs is dependent upon other design parameters and operating conditions such as electrode thickness and flow rate. Thus, absolute comparisons of flow field designs should not be made. In fact, it should be noted that the results of the previously mentioned comparison studies can be completely altered by changing other geometric features of a particular design, so that no such absolute comparison of one design as universally better or worse can be made without additional constraints. Therefore, a deeper fundamental understanding of the complex interrelated phenomena which affect overall performance is needed to enable design of next generation architecture without relying on trial and error testing. Thus, the motivation of this chapter is to continue to expand the fundamental knowledge of RFB flow field design and implement the design guidelines established in chapter 3. This is accomplished by demonstrating a modified energy efficiency metric that accurately compares the impacts, both positive and negative, of multiple flow field designs. Based upon the determined design guidelines, two new flow field designs are presented and evaluated with this metric to determine their performance characteristics in comparison with the designs most commonly studied in the literature. First, an Equal Path Length (EPL) flow through design was developed, seen in Figure 4.1(a). Subsequently, an Aspect Ratio (AR) flow through design, shown in Figure 4.1(b), was developed to further improve upon the EPL design. To evaluate these designs, this study uses a number of
**Figure 4.1.** Flow field designs with outline of active area: (a) Equal Path Length Flow Through (EPL), (b) Serpentine, (c) Interdigitated, and (d) Aspect Ratio (AR). Corresponding simulated flow patterns at a cut plane through the center of the electrode: (e) Equal Path Length Flow Through (EPL), (f) Serpentine, (g) Interdigitated and (h) Aspect Ratio (AR). Note: Cells tested have same active area; scale for flow patterns in m/s.
different experimental methods, computational simulations, and performance metrics to make a comprehensive comparison, including polarization curves, discharge curves, charge-discharge cycles, pressure drop measurements, pump energy analyses, power density analyses, and computational fluid dynamics simulations.

4.2 Method of Approach

Tests were conducted at varying operating conditions in order to explore the differing responses in limiting current density and discharge capacity for various flow field designs. All tests were conducted with a 9 cm$^2$ cell design based upon the zero gap architecture described by Aaron et al. 16. Four types of flow field designs were investigated in this work. The first two, serpentine and interdigitated, are common within flow battery and fuel cell literature, while the last two are the EPL and AR designs, all of which are seen in Figure 4.1. All tests were conducted with Nafion® 117 membranes (E. I. du Pont de Nemours and Company). The membranes were pretreated by soaking for 30 minutes in 1 M sulfuric acid at 80 °C, followed by an identical soak in deionized water. Carbon paper electrodes (10AA, SGL Group; 410 μm nominal thickness) were used as received, without further treatment, for all tests. Flow fields were machined in-house from BMC 940 graphite composite (Bulk Molding Compounds, Inc.).

A solution of 1.7 M vanadyl sulfate in 3.3 M sulfuric acid (Alfa Aesar) was used to conduct all tests. Experiments began with 50 mL of electrolyte in the tank for the negative side of the cell, while 100 mL of electrolyte was placed in the tank for the positive side. The electrolyte was potentiostatically charged at 1.8 V in a separate charging cell until a cutoff current density of 10 mA cm$^{-2}$ was reached; at this point, the
electrolyte was assumed to be at 100% SOC. Then, 50 mL of solution was drained from the positive side of the cell so that equal volumes of V(II) and V(V) remained on the negative and positive sides, respectively. A nitrogen purge was maintained in the electrolyte reservoirs at all times. Cell temperature was controlled at 30 °C for all tests to prevent vanadium precipitation within the cell. Additional temperature conditions were not considered due to the negligible effect on electrolyte viscosity (and, by extension, flow field performance), rendering such a study outside the scope of this work.

4.2.1 Discharge, Polarization, and Power Density Curves

The discharge curves were acquired via constant current discharge with the solution originally at 100% SOC until a cutoff voltage of 0.2 V was reached. Current densities of 50 mA cm\(^{-2}\), 250 mA cm\(^{-2}\), and 500 mA cm\(^{-2}\) were evaluated. Tests for these current densities were conducted at a flow rate of 20 mL min\(^{-1}\). After discharging, the electrolyte from the positive and negative tanks were mixed together to produce 100 mL of half V(III) and half V(IV) solution. Half of this solution was then placed on the positive side, with the other half on the negative side. The solution was recharged for the next discharge test. Through this remixing approach, imbalances in vanadium concentration that occur as a result of crossover are ameliorated.

Polarization curves were taken at 50% SOC with a flow rate of 10 mL min\(^{-1}\) to ensure a mass transport limiting condition was achieved. Additionally, this SOC represents a functional operating condition of a commercial flow battery system. Near the center of the SOC range, the polarization curve will not change appreciably, and will only exhibit significant changes at extreme SOCs which are atypical operating conditions for a realistic flow battery system. For these tests, the electrolyte was fully charged (to
ensure consistent charge capacity) and then coulombically discharged in a separate cell to achieve a 50% SOC condition. During polarization curve measurement, the electrolyte was passed through the cell only once without recirculation ("single-pass") so that a constant SOC was maintained at the cell inlet during the entire experiment and later data points were not affected by a lower SOC due to recirculation. The polarization curves were taken under potentiostatic control from open circuit voltage (OCV) of 1.43 V to 0 V in 14 equally-spaced potential steps lasting 8 seconds each. The high frequency resistance (HFR) of the cell was also measured at 20 kHz at each voltage step and was used with the measured current to correct the polarization curves for iR loss. This correction eliminates the ohmic losses in the membrane. Through such iR correction, mass transport and kinetic overpotentials are left as the primary losses in the curves. Because the same electrode material is used in all tests, kinetic overpotentials are assumed to be consistent; therefore, any difference in the iR corrected polarization curves can be largely attributed to differences in transport. A VSP potentiostat (BioLogic Science Instruments, Claix, France) with a 20 A booster was used for the polarization curves and discharge tests.

Two PTFE pressure transducers (TEMC Inc.) with a pressure range from 0-50 psi (0-344.7 kPa) and a reading accuracy of +/- 1% were used to measure pressure drop across each cell. Pressure drop data were also obtained for a range of flow rates from 10 mL min\(^{-1}\) up to 100 mL min\(^{-1}\) in 10 mL min\(^{-1}\) increments for the serpentine and interdigitated designs. For the EPL and AR designs, pressure drop was measured in a similar fashion, until the upper pressure range of the transducers was reached.
Power density curves were calculated from polarization curves as the product of the voltage and current density at a given point on the curve. Power density curves were obtained at flow rates between 10 and 50 mL min\(^{-1}\) in 10 mL min\(^{-1}\) increments. Here, *peak power density* is defined as the maximum power density obtained by a flow field design at a given flow rate, while the *adjusted peak power density* is defined as the peak power density minus the pumping power required at the given flow rate. Pumping power, \(P_{pump}\), is calculated using Eq (4.1), where \(Q\) represents the flow rate of electrolyte through the cell, \(\eta\) is the pump efficiency, and \(\Delta p\) is the pressure drop across the cell.

\[
P_{pump} = \frac{\Delta p \cdot Q}{\eta} \quad (4.1)
\]

### 4.2.2 Energy Analysis and Cycling Efficiencies

Energy analyses were derived from the aforementioned discharge curves, as well as data from charge-discharge cycling with the EPL and AR flow field designs. These charge-discharge data were obtained by charging the electrolyte at a constant current until reaching a cutoff voltage of 1.8 V. The electrolyte was then discharged until reaching a cutoff voltage of 0.2 V. This process was repeated until the charging and discharging capacities for four consecutive cycles were within 1% of each other. The remixing protocol described in the previous section was utilized between tests to allow for the same electrolyte to be used and the maximum capacity to remain constant.

Two types of efficiency were analyzed for this study: cell-based energy efficiency and system-based energy efficiency defined in Eqs (4.2) and (4.3), respectively.

\[
\eta_{cell} = \frac{E_{\text{disch}}}{E_{\text{ch}}} \quad (4.2)
\]
\[ \eta_{\text{system}} = \frac{E_{\text{disch}} - E_{\text{pump,disch}}}{E_{\text{ch}} + E_{\text{pump,ch}}} \] (4.3)

Where \( \eta_{\text{cell}} \) is the cell-based energy efficiency, \( E_{\text{disch}} \) is the total energy discharged, \( E_{\text{ch}} \) is the total energy charged, \( E_{\text{pump,disch}} \) is the energy required for pumping the electrolyte during the discharge portion of a cycle, and \( E_{\text{pump,ch}} \) is the energy required for pumping the electrolyte during the charge portion of a cycle. The total discharged and charged energies are defined in Eq (4.4).

\[ E_{\text{ch(\text{disch})}} = I \cdot \int V_{\text{ch(\text{disch})}} \cdot dt \] (4.4)

\( E_{\text{ch(\text{disch})}} \) represents the charge or discharge energy from the cell, \( V \) represents the charge or discharge voltage, \( I \) represents the charge or discharge current, and \( t \) represents the charge or discharge time.

The pumping energy values were calculated based on the measured pressure drop across the cell as well as the flow rate of the electrolyte and the total pumping time during charge or discharge.

\[ E_{\text{pump}} = \frac{\Delta p \cdot Q}{\eta_{\text{pump}}} \cdot t \] (4.5)

\( Q \) represents the flow rate of electrolyte through the cell, while \( \eta_{\text{pump}} \) is the pump efficiency. If both of these variables are held constant (as they are in the 20 mL min\(^{-1}\) cases above), then the pumping energy, \( E_{\text{pump}} \), becomes solely a function of pressure drop, \( \Delta p \), and discharge or charge time, \( t \). The system efficiency in Eq (4.3), then, accurately reflects the true gains of a system improvement while incorporating effects on parasitic losses.
4.2.3 Computational Fluid Dynamics

Comsol Multiphysics 4.3a was used to carry out numerical simulations of the four flow fields in question. The Free and Porous Media Flow module was used due to its ability to handle both the electrolyte flow in the open channel as well as the flow through the porous carbon paper electrode. Details of the methods used for these simulations are provided in Chapter 3.

4.3 Results and Discussion

Figure 4.2(a) and (b) show energy analyses carried out for constant current discharge experiments conducted with serpentine, interdigitated, and EPL flow fields at 250 mA cm\(^{-2}\) and 500 mA cm\(^{-2}\) respectively, at the relatively low flow rate of 20 mL min\(^{-1}\). Figure 4.2(c) shows a third experiment conducted on only serpentine and interdigitated flow fields at 250 mA cm\(^{-2}\) with a high flow rate of 90 mL min\(^{-1}\). This higher flow rate test was not able to be performed for the EPL design due to high pressure drop.

Examining the serpentine and interdigitated designs first, it is clear in all three discharges that the interdigitated design outperforms the serpentine design, as evidenced by the larger amount of both gross electrochemical energy and net energy discharged. The former is defined as the total energy discharged from the cell, while the latter is the gross electrochemical energy minus pumping losses. An important conclusion can be drawn by examining these results more closely, however; it can be seen that the parasitic energy consumption of the pump is minor, accounting for less than 1% of the total energy discharged from the cell. This trend becomes more apparent as a cell is discharged at higher current densities, as seen in Figure 4.2(b) where the energy consumed by the pump
Figure 4.2. Calculated energy analysis of the high performance VRFB with serpentine, interdigitated, and EPL flow fields at 20 mL min$^{-1}$, initial SOC of 100%, constant current discharges of (a) 250 mA cm$^{-2}$ and (b) 500 mA cm$^{-2}$ and (c) serpentine and interdigitated designs at 250 mA cm$^{-2}$ and 90 mL min$^{-1}$. 
is almost non-existent when compared to the total energy discharged. As the operating current density of the cell is increased, energy is discharged more rapidly; however, the energy per unit time consumed by the pump does not change because the flow rate and pressure drop are unchanged. Due to this growing disparity, it can be concluded that pressure drop, and the associated parasitic pumping losses, are much less critical for high performance cells. This conclusion is only valid for low flow rates, however, as is evidenced in Figure 4.2(c) which shows substantially increased parasitic losses on the order of 4-7% of the total energy discharged when increasing the electrolyte flow rate from 20 mL min\(^{-1}\) to 90 mL min\(^{-1}\). This increased loss is due to the additional energy required to support the higher flow rate. When increasing the flow rate, however, a corresponding increase in pressure drop also occurs. This compounding effect drastically increases the pumping energy required per unit time and results in non-negligible pumping losses for the system at high flow rate, which will be further exacerbated for larger active area cells.

The conclusion that pressure drop can be less important at certain operating conditions is an important one for flow field design as it allows for greater design flexibility. Eliminating pressure drop as a major design driver simplifies the task of creating an optimized flow field and helps provide a shorter list of criteria needed for future designs. Additional conclusions drawn from previous work can further help to inform flow field design\(^{95}\). Any effective flow field design will need to maximize the fraction of electrolyte flowing through the electrode, while also distributing this electrolyte evenly to maximize electrode utilization. Neither the serpentine nor
interdigitated design fully accomplishes this task, as the former concentrates flow towards the edges of the electrode, while the latter concentrates flow in the center of the cell as seen in the computational simulations in Figure 4.1. The flow field must be able to maintain high current density operation and deep discharges at a low flow rate in order to ensure that parasitic pumping losses remain minimal relative to the electrochemical power for this design. From these conclusions, the EPL design and subsequently the AR design, seen in Figure 4.1, were proposed to best achieve the necessary requirements.

The EPL design utilizes two long parallel channels that span the width of the cell active area with one across the top (inlet) of the active area and one across the bottom (outlet). The remainder of the active area consists of the flow field plate in direct contact with the compressed electrode between the two channels, similar to the area over the lands in an interdigitated design, to improve mass transport properties. The use of two equal length parallel channels guarantees that the path length and, thus, the hydraulic resistance are constant across the entire width of the active area, preventing the uneven flow paths present in other flow frame and flow through designs. The electrolyte is forced to flow through the electrode perpendicular to the channels in order to reach the outlet, which ensures two main design criteria are met. The first is that the entire volume of the electrolyte is forced through the electrode, eliminating the bypass flow characteristic of serpentine designs. The second is a uniform distribution of electrolyte flow across the entire electrode area, avoiding potential dead zones which are present in both the serpentine and interdigitated designs. This uniform flow is evident in the thermal visualization test seen in Video 4.1, included as supplementary material in Appendix A,
as well as the computational simulations seen in Figure 4.1 depicting a uniform velocity profile in the electrode. The video clearly demonstrates a uniform flow of electrolyte across the entire active area of the cell, in stark contrast to the distributions seen from serpentine and interdigitated designs in previous work [41]. Meeting these two criteria ensures improved mass transport performance through reduction of concentration overpotential while operating at a low flow rate to reduce the pumping requirement to a negligible level.

The energy analysis of the discharge curves for these three flow fields supports the observation that energy lost due to pressure drop becomes negligible at high current densities. While the higher pressure drop associated with the EPL design does result in a higher parasitic pumping loss, it is clear from Figure 4.2(a) that, even at a lower current density of 250 mA cm\(^{-2}\), the net energy discharged under these conditions is higher than that of the other two standard flow field designs. Under these conditions, the EPL design discharges an additional 0.08 Wh of net energy compared to the interdigitated design and a full 0.3 Wh more net energy than the serpentine design, or increases of 3.5% and 25% respectively. As the discharge current density increases, this disparity grows, as seen in Figure 4.2(b). When discharging the cells at 500 mA cm\(^{-2}\), the EPL design is able to attain 0.3 Wh more net energy discharged than the interdigitated and 0.88 Wh more net energy discharged than the serpentine design, increases of 25% and 73%, respectively. Since the cell built with the EPL design uses the same type of membrane and electrodes as the serpentine and interdigitated cells in order to maintain consistent ohmic and kinetic losses, it can be concluded that this improvement is entirely attributed to increased mass
transport performance of the EPL design. This analysis also demonstrates the EPL design’s improved tolerance to dynamic loading. While the interdigitated and serpentine designs lose 40.9% and 75.3% of their net discharge capacity when increasing the discharge current from 250 mA cm$^{-2}$ to 500 mA cm$^{-2}$, the EPL design only loses 20.7% of its net discharge capacity over the same current density increase. Referencing Figure 4.3, it is evident that, when discharging at a given current density, the EPL design exhibits a much higher discharge voltage, indicative of better mass transport. This increase in discharge voltage is responsible for the increased discharge energy of the cell as shown in Eq (4). Since the current during discharge is held constant between tests, the difference in energy discharged between tests with different flow fields is solely a function of voltage and discharge time. The EPL design exhibits higher discharge voltage due to improved mass transport, meaning that more energy is transferred per vanadium ion charged or discharged. Improved mass transport also allows the cell to utilize a larger percentage of the total vanadium in solution for charging and discharging, meaning the usable SOC window is larger. When discharging at a constant current, the accessible capacity is directly proportional to the discharge time of the cell, thus resulting in additional energy discharged in the EPL design which is a key factor for industrial applications and results in better ability to adapt to dynamic loads.

As the EPL design is scaled up to a larger active area for commercial applications, the pressure drop will increase with the increased path length, leading to higher parasitic losses that may not be as negligible as those in the 9 cm$^2$ design. In order to further minimize pressure drop in the cell to account for this, as well as improve the scalability
Figure 4.3. (a) Discharge curves of the VRFB with serpentine, interdigitated, and EPL flow fields at 20 mL min\(^{-1}\) at 250 mA cm\(^{-2}\), initial SOC of 100\%, theoretical discharge capacity (dashed line) of 2.28 Ah and (b) single pass iR corrected polarization curves of the VRFB with interdigitated, serpentine, EPL, and Aspect Ratio flow fields at 10 mL min\(^{-1}\), initial SOC of 50\%. 
of the EPL design, an improved flow field design was developed. The Aspect Ratio
design is intended to function in much the same way as the EPL design. By keeping the
same channel design, uniform electrolyte distribution is achieved, maximizing electrode
utilization. This design elongates the 9 cm$^2$ active area so that it is 4.5 cm wide and only
2 cm long, creating a shorter path length for the electrolyte through the electrode domain,
while maintaining the same active area as the square EPL design. This shorter path
length results in a lower pressure drop than the EPL design. The shift in active area
dimensions allows for the cell to maintain the same active area and transport behavior
with comparable performance to the EPL design, but offer reduced pressure drop.

Figure 4.3a shows discharge curves for the serpentine, interdigitated, and EPL,
flow field designs. It is clear that the EPL design outperforms both the serpentine and
interdigitated designs in this test. The EPL design is able to discharge 1.8 Ah, or 79% of
the 2.28 Ah of theoretical electrolyte capacity, which compares favorably to the 74% and
61% values attained by the interdigitated and serpentine designs, respectively. Figure
4.3b shows polarization curves for all four flow field designs. These curves demonstrate
that the EPL and AR designs achieve a much higher limiting current density under mass
transport limited conditions than either of the other two flow fields. Taking a
polarization curve at 10 mL min$^{-1}$, it can be seen that the EPL and AR designs both reach
a similar limiting current density of over 600 mA cm$^{-2}$, compared to 300 mA cm$^{-2}$ for the
interdigitated design and 200 mA cm$^{-2}$ for the serpentine design. This figure
demonstrates that the Aspect Ratio design achieves a similar limiting current density at a
similar iR corrected voltage to the impressive gains seen in the EPL design. The two
curves have roughly the same voltage across the entire current density range, demonstrating the superior mass transport which the EPL and AR designs offer over the two standard designs tested. Additionally, the EPL and AR design exhibit a much more stable voltage over a wider range of currents when compared to the serpentine and interdigitated designs. This further supports the conclusion that these novel flow field designs have a better tolerance to dynamic loading than previous architectures.

Figure 4.4 shows the pressure drop of all four flow fields tested, as well as simulated pressure drop values from the computational model. In this figure it is clearly shown that the EPL and AR designs carry a much higher pressure drop across the cell compared to either the serpentine or interdigitated design. While this may present a problem for high flow rate or low current density operation, as previously discussed, such concerns are less critical when considering the superior performance of these flow fields at low flow rates. The simplicity of these designs will also reduce production costs and time, a concern which must be addressed for the purposes of scaling up such a system. This simplicity of design also results in a highly predictable linear pressure drop in relation to flow rate, path length, and electrode thickness, making design for system scale up easier to predict. Additionally, the true benefit of the Aspect Ratio design can be seen in a significantly lower pressure drop across the cell compared to the EPL design. At the 20 mL min\(^{-1}\) operating condition, the Aspect Ratio design has a pressure drop of 165.47 kPa (1.633 atm) compared to the 227.53 kPa (2.245 atm) of pressure drop seen in the EPL design. This 27% reduction in the pressure drop of the cell leads to significant reduction of parasitic pumping loss for conditions where such losses remain a factor,
Figure 4.4. Experimentally measured pressure drop data for serpentine, interdigitated, EPL, and Aspect Ratio flow field designs as well as simulated pressure drop data for EPL and Aspect Ratio designs.
leading to further improved efficiency above the improvement already realized with the
EPL design. This reduction in pressure drop also allows the cell to be operated at a wider
range of flow rates, as pressure drop becomes less of a limiting factor for the system
components at a wider range of operating conditions. The computational model allows
for further insight into the usefulness of these flow fields as commercial designs by
allowing for simulations of 100 cm$^2$ versions of both the EPL and AR flow fields. These
simulations maintained all of the same relative geometries for each design in addition to
using the same volumetric flow rate per unit active area as in the 9 cm$^2$ simulations. With
only one layer of carbon paper electrode, the simulation predicts a pressure drop of 4,767
kPa (47.05 atm) for the 100 cm$^2$ EPL design. This is likely too large to allow for viable
commercial implementation, making the pressure reduction in the AR design a necessity.
The simulation predicts a pressure drop of 985.9 kPa (9.730 atm) for the AR design with
one layer of carbon paper electrode. Previous studies have found that three layers of
carbon paper provides improved performance in a zero gap architecture, which will
further mitigate pressure drop [47, 48]. For a 100 cm$^2$ AR design with three layers of
carbon paper, the simulation predicts a pressure drop of only 494.3 kPa (4.878 atm),
showing an order of magnitude improvement over the single layer EPL design and
substantiating the prospects of similar flow field designs for commercial implementation.
This pressure drop could be further improved through the use of a felt electrode in which
transport is facile, however this would come at the expense of the kinetic performance of
the cell.

The improved performance of the Aspect Ratio design is further supported by
energy analyses calculated for system cycling tests and subsequent efficiency values seen in Figure 4.5. In terms of gross charging energy, the two flow fields are relatively similar, with a slightly higher energy input for the EPL design. The two flow fields are equally similar in terms of electrochemical discharge performance as well, with the EPL design holding a near imperceptible advantage in terms of electrochemical energy discharged. When accounting for the pumping requirement of each cell build, however, the Aspect Ratio design clearly demonstrates it is the superior option. The Aspect Ratio design requires less net energy into the cell during charging, but gets a substantial amount of net energy above that of the EPL design out of the cell. The conclusion drawn from this disparity can be more clearly seen in Figure 4.5(b). The efficiencies calculated from these cycling tests show that the EPL design and the Aspect Ratio design have similar coulombic and cell-level energy efficiencies. The major difference occurs in the system-level energy efficiency of the two designs, however. This metric shows a system efficiency of 54% for the Aspect Ratio design compared to 47% for the EPL design, a significant 7% improvement for these particular cells tested. Because of the relatively similar cell-level energy efficiency in both designs, this improvement in system energy efficiency is entirely attributable to the improved pressure drop for the Aspect Ratio design seen in Figure 4.4.

The AR design is inherently more scalable than all types of square flow field designs. In a square flow field design, such as the serpentine, interdigitated, or EPL designs, a larger active area increases pressure drop across the cell at a given flow rate as
Figure 4.5. (a) Energy analysis of the high performance VRFB with EPL and Aspect Ratio flow field designs at 20 mL min\(^{-1}\), 200 mA cm\(^2\) constant current averaged over 5 cycles and (b) corresponding cell and system efficiencies.
the path lengths for the electrolyte to travel through the electrode are increased. Additionally, a higher flow rate will be required to maintain the same level of cell performance across a larger active area and increased cross-sectional area for electrolyte flow. This two-fold effect will result in a substantially increased pumping cost as cells are scaled up to a commercially-relevant size. Because of the transport mechanism utilized, the Aspect Ratio design is capable of increasing active area without increasing the electrolyte path length through the electrode, simply by elongating the electrode and channels. By maintaining the same path length, no appreciable increase in pressure drop should be seen in the flow field. When scaling up this design, an increase in electrolyte flow rate will still be necessary to account for the larger active area and increased cross-sectional area for flow, however.

It should be emphasized that these findings are applicable for a specific set of operating conditions, namely a high current density cell operating at a low flow rate. As concluded in previous work, flow field design is largely dependent upon desired operating conditions and properties of the materials used in the cell. This is supported by the energy analysis seen in Figure 4.6, showing the impact of parasitic pumping loss on cells built with the EPL design and Aspect Ratio design when discharged at 50 mA cm$^{-2}$. While both designs are able to discharge a large fraction of the energy capacity, the pumping energy required to do so is substantially higher when viewed as a percentage of the energy discharged. The Aspect Ratio design loses 19.6% of the energy discharged to pumping requirements under these conditions, while the EPL design loses 30.6% of electrochemical energy to pumping losses. This increase in parasitic loss is due to the larger overall
Figure 4.6. Energy analysis of the high performance VRFB with EPL and Aspect Ratio flow fields at 20 mL min$^{-1}$, initial SOC of 100%, constant current discharge of 50 mA cm$^{-2}$. 
discharge time for the cell. When discharging a cell at a high current density, the energy is discharged at a high rate and the pump is operating for a reduced period of time. If the current density is reduced, the total discharge time increases and the pump will be operating for a long period of time. This will result in the total energy required by the pump to increase, leading to a larger percentage of the energy needed to be allocated toward pumping requirements.

Design based upon operating conditions is further supported when examining the power density curves for each of these flow field designs. Figure 4.7 shows that, at high current densities and low flow rates, the pumping power requirement is negligible in comparison to the overall cell power, accounting for less than a 1% loss in power for all cases. Further examining this data, it can be seen that as flow rate is increased, the associated cell power density increase is diminishing until there is essentially no benefit to increasing the flow rate in the cell. This indicates that the cell is no longer limited by advective mass transport in the electrode, but instead is limited by other factors such as diffusive mass transport in the boundary layers around individual electrode fibers. From an operational perspective, this limitation implies that there is an optimal flow rate at which to operate in order to obtain maximum system power. This is because, as the additional power gained per unit increase in flow rate becomes smaller, the pumping power required to provide that additional flow rate increases at a constant rate. Eventually, this pumping requirement overtakes the improvement in cell power density, resulting in a net loss of power for increased flow rate.

Figure 4.8 compares the peak power density obtained for the EPL and AR flow
Figure 4.7. Power density curves for the high performance VRFB with (a) EPL and (b) AR flow fields at flow rates of 10 mL min\(^{-1}\), 30 mL min\(^{-1}\), and 50 mL min\(^{-1}\), calculated from single pass polarization curves at 50% SOC.
Figure 4.8. Peak power density of the high performance VRFB with EPL and AR flow fields at flow rates from 10 to 50 mL min$^{-1}$, calculated from single pass polarization curves at 50% SOC.
fields at different flow rates, allowing a further conclusion to be drawn about the mass transport characteristics of these two flow fields. This figure shows that the two designs achieve a similar peak power density at lower flow rates. When the flow rate is increased, however, the EPL design demonstrates a higher peak power density compared to the AR design. This is due to the larger inlet and outlet regions that are necessary in the AR design. As the aspect ratio of the design is increased, the channels for the inlet and outlet of the cell must be longer in order to continue to ensure equal path length and uniform flow. These channels create a section of the electrode that sees little to no electrolyte flow compared to what the rest of the active area receives. Furthermore, the electrode overlaps the channel at both the inlet and the outlet in order to prevent the electrode from being compressed into the channel. This creates another portion of the electrode that does not see appreciable electrolyte flow and does not contribute to the cell performance. Additional testing was performed to verify this, with the results included in an Appendix as section 4.6. The lack of such advective transport in these regions hinders the overall performance of the cell, particularly in the AR design where the ratio of these regions to those with fully developed flow is much higher. This implies that development of flow field designs should take precautions to limit the necessary size of such regions of the electrode to best utilize the electrode material. While this result means that the EPL design is slightly preferable for a maximum power application, it should be noted that the AR design is still preferable when operating a cell with the goal of maximizing energy efficiency and the choice of flow field should be based upon the intended operational use of the system.
4.4 Conclusions

For high performance RFBs, parasitic pumping losses are not as significant a factor in system net power. By operating a cell at a higher current density, the relative pumping energy requirements are reduced due to the high ratio of cell power to pumping power. Calculating energy efficiency with the inclusion of pumping loss enables the combined effects of improved electrochemical performance and greater parasitic loss to be quantified. This enables flow field designs with enhanced mass transport to be developed, such as the Equal Path Length flow through design. These designs outperformed other flow field designs common in the literature in terms of lower concentration overpotential, leading to more available capacity and net energy discharged, in spite of a substantially larger pressure drop. Furthermore, these designs exhibit a better tolerance to dynamic load variation, a key factor for such systems to be implemented commercially. By introducing an Aspect Ratio design, the pressure drop penalty of the Equal Path Length flow through design was mitigated without sacrificing overall cell performance under most operating conditions. This leads to higher system efficiency and a wider flow rate operational window, as well as improved design flexibility which should benefit commercially-sized systems. The EPL design achieves a higher maximum power density, though such conditions are much less energy efficient, making them less favorable for many applications. In this manner, the Aspect Ratio design further improves upon the substantial benefits seen in the EPL design for high energy efficiency operation, while the EPL design is superior in terms of maximum power density operation. While scale-up to a conventionally larger plate with these designs would likely not be optimal, the higher
performance enables thinking about new optimization pathways not possible before. These could include higher pressure operation, smaller plate sizes, or continuation along the path shown with improved overall performance but continued innovation toward reduced pressure drop with the enhanced mass transport. These overarching conclusions about the parasitic loss and overall cell efficiency are not limited to the specific designs tested, but can be applied as design guidelines for future flow field development, regardless of system scale.

4.5 Acknowledgments

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4.6 Appendix

To examine the impact of the inlet and outlet regions of the flow field designs on performance the electrodes were trimmed at the top and bottom to reduce the active area to 7.2 cm$^2$ in each design and shorten the path length of the electrolyte through the electrode. The EPL path length was shortened by 0.3 cm while the AR path length was only shortened by 0.2 cm due to its greater width. The electrodes were then positioned in the cell so as not to cover the inlet and outlet channels, thus creating a “gap” between the edge of the electrode and the edge of the gasket. A cell with the AR flow field design with the same type of shortened electrode was also tested, but with the 7.2 cm$^2$ electrode
covering the inlet channel so there was no gap at the inlet and a larger gap at the outlet. These design changes are illustrated in Figure 4.9. Peak power density curves were obtained for these conditions in the same manner as previously described. The results of these additional tests are shown in Figure 4.10.

From Figure 4.10, we can clearly see that removing the sections of the electrode over the inlet and outlet channels helped to improve the power density of the system in the AR design, while having a slight negative effect on the EPL design. It is important to remember that these power densities are evaluated based upon the 7.2 cm² electrode, and not the 9 cm² electrode used in previous tests. In the AR design, the majority of the electrode volume that was removed is believed to be a recirculation “dead zone” based on CFD simulation that saw little electrolyte flow and reduced the apparent power density of the cell by contributing little to the electrochemical reaction. In the EPL design, more of the removed electrode volume was useful electrode that received adequate electrolyte flow. This is due to the narrower geometry and desire to keep the active area constant between the two designs. The result of the removal of a larger portion of active electrode was a slight decrease in the power density, somewhat offset by the removal of some “dead zone” electrode as well. When the smaller electrode was repositioned in the AR design to cover the inlet channel and leave no gap between the electrode and gasket, a large decline in power density was observed due to the reintroduction of the “dead zone” over the inlet.

The conclusion that a portion of the electrode over these channels is within a recirculation zone is supported by the total current generated in each design at 50 mL min⁻¹. Figure 4.11 depicts the geometry of the “dead zone” at the inlet and outlet of the EPL.
Figure 4.9. Flow field designs with 7.2 cm² “gapped” electrodes: (a) EPL, (b) AR, and (c) AR with the inlet channel covered. Dotted lines indicate the region for the normal 9 cm² electrode, while shaded regions designate the 7.2 cm² electrode.
Figure 4.10. Peak power density of the high performance VRFB with EPL and AR flow fields with 9 cm$^2$ and 7.2 cm$^2$ electrode configurations at flow rates from 10 to 50 mL min$^{-1}$, calculated from single pass polarization curves at 50% SOC.
**Figure 4.11.** A COMSOL model of the through plane view of “dead zone” geometry in EPL and AR flow field designs. Darker gray areas depict regions where no flow is present, lighter gray areas show higher electrolyte flow, and arrows designate electrolyte flow direction.
and AR flow field designs. This inactive volume of electrode is defined as the narrow region between the channel and the gasket that is not in the direct hydraulic path between channels. Additionally, a section directly above the channel beginning at the top edge of the channel and extending upwards to the membrane at a 45 degree angle is also considered to be inactive. Using this geometry, it is possible to predict the resulting change in total current generated by removing the sections of electrode described above.

When removing the sections of electrode described previously in the AR design, the total current generated in this 7.2 cm$^2$ electrode was nearly the same as in the 9 cm$^2$ electrode. This compares favorably to the predicted value of 94.2% based on the design geometry.

In the EPL design, the total current generated with the smaller 7.2 cm$^2$ electrode was only 84.2% of the total generated in the 9 cm$^2$ electrode, in very good agreement with the predicted value of 82.8%. When moving the smaller electrode to cover the inlet channel in the AR design, the total current drops to 87% of the total achieved by the other two AR tests, slightly lower than the predicted value of 90%.
CHAPTER FIVE
INVESTIGATION OF THE IMPACT OF FLOW FIELD ACTIVE AREA SIZE ON RFB PERFORMANCE
Abstract

This article hasn’t been published anywhere, nor will it be prior to submission of the final version of my ETD, so a publication statement was not included. A manuscript will be submitted for publication. This work was authored by Jacob R. Houser, Yasser Ashraf Gandomi, Douglas S. Aaron, and Matthew M. Mench.

My contributions to this work were collection, reduction, and analysis of data as well as composition of the manuscript. Gandomi assisted in collection and analysis of crossover data and manuscript preparation. Aaron assisted in analysis of data and manuscript preparation.

5.1 Introduction

The flow field is one of the most essential components in a redox flow battery, providing even distribution of electrolyte throughout the electrode. As shown in Chapters 3 and 4, there are a number of different flow field designs available for use in RFB systems. Many of these flow fields utilize different transport mechanisms to deliver the electroactive species to the reaction site. Serpentine flow fields, for example utilize the pressure drop in the channel to induce the electrolyte to “jump” over the lands and into the electrode, whereas designs like the interdigitated flow field separate the inlet and outlet channels from each other and force the electrolyte to flow through the electrode. As demonstrated in the previous chapters, each of these approaches has advantages and disadvantages and the insight that can be gained from these differences can inform future flow field designs and lead to innovations as seen in the equal path length (EPL) and aspect ratio flow through designs.

One aspect of flow field design that is critically important to the improvement of commercial systems however has been severely neglected in the literature. The scale up
of flow field designs from laboratory size to commercial size active areas is seldom
examined, but can play a crucial part in the viability of a given design in a real world
system. Because each of the four flow field designs introduced in the previous chapters
functions slightly differently, they will respond differently to a uniform increase in the
active area of the cell. Because each of these flow fields will respond differently to the
larger scale, it is likely that performance differences between the flow fields will also
change based on the size of the active area.

The objective of this chapter is to demonstrate the ways in which each of these
flow field designs differ when increasing the active area. To that end, each of the four
flow fields will be examined at three different active area sizes, 5 cm$^2$, 9 cm$^2$, and 25 cm$^2$,
with the exception of the aspect ratio design which will not be tested at 25 cm$^2$. By
utilizing similar techniques used in the previous two chapters, it will be possible to fully
characterize the change in the mass transport seen by each of these flow fields as the
active areas are increased in size. Polarization curves at 50% state of charge will allow
for examination of the limiting current density, showing the true mass transport
performance of each design and how it scales with active area. Cycling of the battery
with each of these designs will allow for energy based analysis similar to that seen in
Chapter 4 in order to fully determine how each flow field performs on a system level.
This is a crucial component of any scale up analysis, as the purpose of the study is to
examine how the designs would function in a commercial system where parasitic losses
and pressure concerns are even greater. Finally, computational fluid dynamics will be
utilized in order to examine the flow distributions throughout each of the scaled up
designs as well as the magnitude of the electrolyte velocity throughout the electrode domain. This CFD data will then be correlated to the performance data in order to make a definitive conclusion on the impact of increased active area size on the performance of each flow field design.

5.2 Method of Approach

Similarly to the previous two chapters, a number of operating conditions were tested in this chapter in order to adequately characterize the mass transport performance of each flow field design as the active area is increased. Each of the four flow fields discussed previously is examined, with the serpentine, interdigitated, and EPL designs studied at active areas of 5 cm$^2$, 9 cm$^2$, and 25 cm$^2$. The aspect ratio design was also investigated with active areas of 5 and 9 cm$^2$. A 25 cm$^2$ aspect ratio design was not tested because the geometry of such a cell would require custom hardware which would call into question whether such data would truly be comparable to the other 11 results gathered using the same cell hardware.

All membranes used in these studies were Nafion 117, just as in the previous two chapters. The membranes underwent the same pretreatment as described in chapter 4, and were kept consistent between tests so as not to alter the internal cell resistance for each different active area size. Sigracet GFD3 carbon felt was used for this study as opposed to the 10AA carbon paper examined in the previous two chapters. This change was necessitated by the increased active area examined. As the active area of the electrode is increased, the pressure drop through the cell also increases, particularly for the serpentine design as will be described in detail throughout this chapter. The
additional thickness of the carbon felt allows for the use of the same zero gap architecture used in chapters 3 and 4 without incurring catastrophic pressure drop through the cell. Electrodes were used as received without any further treatment. Flow plates were machined in house out of BMC.

For these tests a solution of 1.5 M vanadyl sulfate in 3.3 M sulfuric acid (Alfa Aesar) was used as opposed to the higher concentrations used in chapters 4 and 5 in order to mitigate precipitation concerns in the cells. Similarly to the prior tests, experiments began with 50 mL of V(IV) on the negative side of the cell and 100 mL of V(IV) on the positive side. The same potentiostatic charging procedure was applied, and half of the positive electrolyte was drained as before, resulting in the volume of electrolyte being equal on each side of the cell. A continuous nitrogen purge was maintained in the electrolyte containers throughout the testing to prevent the charged electrolyte discharging when in contact with oxygen. The electrolyte reservoir temperature as well as the cell temperature were controlled at 30 °C for all tests to further mitigate precipitation concerns in the system.

5.2.1 Polarization Curves and Discharge Data

The polarization curves presented in this chapter were gathered in a different manner than those in the previous chapters. Due to the need for additional flow through larger active area cells in order to maintain the same overall cell stoichiometry, conducting single pass polarization curves would require a prohibitively large volume of electrolyte. An area specific volumetric flow rate of 4 mL/min/cm² was chosen for all tests, resulting in an overall flow rate of 20 mL/min for 5 cm² cells, 36 mL/min for 9 cm² cells, and 100 mL/min for 25 cm² cells. For this reason, galvanostatic polarization curves
were used, with the discharge current of the cell being slowly stepped up until reaching a final cutoff voltage of 0.3 V. For the 5 cm² cells, steps of 50 mA/cm² were used until reaching 300 mA/cm² after which steps of 100 mA/cm² were used. Steps of 55 mA/cm² were used for 9 cm² cells, and steps of 20 mA/cm² were used for 25 cm² cells until reaching a current density of 400 mA/cm² after which steps of 40 mA/cm² were used. In between each of these discharge steps, the cell was recharged sufficiently so that there was no net change in SOC. This was accomplished by counting the number of coulombs discharged during each step during the polarization curve and subsequently charging the cell at a constant current density of 100 mA/cm² for a length of time which would replenish the coulombs removed during the previous charging step. Average voltage values for each 30 second discharge step were used to determine the individual polarization values. After the cutoff voltage of 0.3 V was reached, one final polarization curve step was taken potentiostatically at 0.2 V for 30 seconds to obtain a true limiting current density for each flow field design and size. The average current value over this 30 second discharge was used to determine the limiting current density.

Discharge tests were conducted at two different conditions for each flow field design. The two conditions were constant current discharges with current densities of 500 mA/cm² and 750 mA/cm². Such high current densities were chosen in order to examine the systems at mass transport limited conditions. These currents are too high to support charging steps, so the cells were charged potentiostatically in an external charging cell at 1.8V. From these results the similar metrics to those discussed in the previous chapters could be calculated and comparisons of the scalability of each distinct
flow field design can be evaluated.

5.2.2 Computational Fluid Dynamics

Comsol Multiphysics 4.3a was used to carry out numerical simulations of the four flow fields in question for each of the three active area sizes examined. The Free and Porous Media Flow module was used due to its ability to handle both the electrolyte flow in the open channel as well as the flow through the porous carbon paper electrode. Details of the methods used for these simulations are provided in Chapter 395. The only notable change in these simulations are those regarding the electrode properties. The porosity, permeability, and thickness of the GFD3 carbon felt electrodes differs from that of the 10AA carbon paper and the new values are 0.94, $6.90 \times 10^{-11}$ m², and 1.7 mm respectively.

5.2.3 Crossover Studies

During the operation of all-vanadium redox flow batteries, crossover of vanadium ions cannot be stopped. As a result of crossover, the available capacity of the battery decreases during cycling. In this work, a unique setup has been designed and fabricated to measure the rate of crossover in VRFBs. The setup includes custom built electrochemical and flow cells and is equipped with UV/Vis spectroscopy setup that empowers real time measuring of the crossover. Here, the focus is on the concentration gradient as the driving force for crossover. Further details regarding the setup is available in recent publications from our lab.101–103

Three different flow field designs were considered in this work including serpentine, interdigitated, and flow-through. The active area for the flow fields were 5, 9, and 25 cm². Therefore, overall, 9 different cells were assembled. Nafion® 117 membrane
was used in all the cells. As-received carbon felt electrodes (GFD3, SGL group) were utilized. The nominal thickness of the electrodes was 3 mm. To conduct the crossover experiments, two electrolytes were prepared; vanadium-rich and vanadium-deficient electrolytes. Vanadium-rich electrolyte was 1.5M VOSO₄·xH₂O (20.87 wt% vanadium, 99.9% purity, Alfa Aesar) dissolved in 3.3M sulfuric acid (H₂SO₄). The vanadium-deficient electrolyte was aqueous 4.8M sulfuric acid. The electrolytes were pumped using peristaltic pumps at volumetric flow rates of 50, 30, and 22 mL·min⁻¹ for cell configurations of 25, 9, and 5 cm² respectively. The vanadium-deficient electrolyte was investigated using UV/Vis spectroscopy in real-time. Using the scripts written in-house, the concentration of vanadium ions within the vanadium-deficient electrolyte was determined. The total time of the experiment was ~24 hours for each configuration.

5.3 Results and Discussion

Figure 5.1 (a) shows polarization curves for the serpentine flow field design at 5 cm², 9 cm², and 25 cm² at flow rates of 20 mL/min, 36 mL/min, and 100 mL/min respectively. It is evident from these curves that the serpentine design scales well by maintaining a consistent area specific volumetric flow rate of 4 mL/min/cm² between cells of different sizes, with the limiting current density increasing by 84.6% from 408 mA/cm² to 753 mA/cm² when increasing the active area to 9 cm² and by an additional 46.9% to 1106 mA.cm² when scaled to 25 cm². While this may seem to suggest that the serpentine design is a promising design for scale up, examining the results for the
Figure 5.1. Polarization curves of 5 cm$^2$, 9 cm$^2$, and 25 cm$^2$ flow fields taken at 40 mL/min, 72 mL/min, and 200 mL/min respectively. Flow field designs analyzed are (a) serpentine, (b) interdigitated, (c) equal path length, and (d) aspect ratio.
remaining designs suggests the situation is more complex. Figure 5.1 (b) depicts similar data for the interdigitated design with the same active area sizes at the same flow rates. This data shows that the interdigitated design achieves a significantly higher limiting current density compared to the serpentine design at 5 cm$^2$, reaching 682 mA/cm$^2$. As the interdigitated design is scaled up however, it does not improve nearly as dramatically, and while it reaches a similar limiting current density as the serpentine design at 9 cm$^2$, 712 mA/cm$^2$ compared to 753 mA/cm$^2$, the limiting current density at 25 cm$^2$ is significantly lower, only jumping to 719 mA/cm$^2$. This is only an increase of 1% compared to the 46.9% increase seen with the serpentine design. This is further complicated when examining the results for the EPL and aspect ratio designs shown in Figure 5.1 (c) and (d) respectively. The EPL design shows a higher limiting current density of 1225 mA/cm$^2$ at 5 cm$^2$, and when scaled to 25 cm$^2$ the limiting current density reaches the highest value of any flow field design tested at 1511 mA/cm$^2$, an increase of 9.7% over the limiting current density of 1378 mA/cm$^2$ measured with the 9 cm$^2$ EPL cell. The aspect ratio design, due to employing a similar principle to the EPL design shows a similar effect. The 5 cm$^2$ cell reaches a lower limiting current density than the EPL design at 1038 mA/cm$^2$ however, this is still significantly higher than either the serpentine or interdigitated design. When scaled up to 9 cm$^2$ the aspect ratio design sees an increase in limiting current density similar to that of the EPL design, reaching 1176 mA/cm$^2$ for an increase of 13.3% compared to 12.5% for the EPL design.

Figure 5.2 (a) through (c) shows the simulated average velocity magnitude of the electrolyte within the electrode domain for each of the flow field designs studied at each
Figure 5.2. Simulated velocity magnitude of the electrolyte through the electrode domain for all flow field designs studied at (a) 5 cm$^2$, (b) 9 cm$^2$, and (c) 25 cm$^2$. 
active area size and a range of area specific volumetric flow rates. It is unsurprising that the EPL design exhibits the highest electrolyte velocities of any flow field design under every condition, with the aspect ratio design not far behind. Interestingly, however, the serpentine design exhibits the third best average electrolyte velocity magnitude of the flow fields with the interdigitated design showing the lowest velocities of the four. This is due partially to a phenomenon that was explored in Chapter 3 when it was determined that as electrode thickness increased, serpentine designs would see little change in electrolyte velocity in the electrode while interdigitated designs would see a significant decrease due to more cross sectional flow area for the same volumetric flow of electrolyte.

In the case of scaling the flow fields however, there is an additional factor at play. If the area specific volumetric flow rate is kept the same for each flow field active area size so that the reactant supply per unit active area is maintained, each flow field will scale differently. Figure 5.3 (a) shows the simulated electrolyte velocity magnitude in the electrode for each flow field design with active areas of 5, 9, 25, 50, and 100 cm² at 8 mL/min/cm². In terms of the magnitude of the velocities themselves this reveals little new information, but the slope of each of these lines has a key implication for the scale up of the particular flow field. The slope of each data set in this figure can be seen as the rate of increase in electrode velocity per increase in active area size. A steep positive slope would therefore indicate the desirable instance of a flow field that is able to gain more velocity as the active area is increased, while a shallower positive slope indicates a flow field that does not scale as well. When evaluating each flow field design through
Figure 5.3: Rate of change of simulated (a) velocity magnitude and (b) pressure drop at 8 mL/min/cm² for each flow field and active area investigated.
this lens, it can clearly be seen that the EPL design exhibits the best velocity scalability, followed by the serpentine design, then the aspect ratio design, with the interdigitated design showing the worst scalability. This is due to the rate at which the cross sectional area for flow increases with respect to the increase in total volumetric flow through the cell for each flow field. In order to increase the active area, the electrode size is increased in both the x and y directions, however, only the increase in the x direction dimension manifests as an increase in cross sectional area for flow as this cross section is in the x-z plane. Because the volumetric flow rate is scaled proportionally with the electrode active area, this means that it increases at a faster rate than the cross sectional area for flow, resulting in a higher velocity per unit cross sectional area as a given design is scaled up. For example, when increasing the EPL flow field design from 5 cm² to 9 cm² to 25 cm², the volumetric flow rate increases by factors of 1.8 and 5 respectively to account for the larger amount of electrode. The x dimension for this electrode only increases by factors of 1.34 and 2.236, from 2.236 cm to 3 cm to 5 cm. Since the electrode thickness has not changed, it is easy to see that the total volumetric flow rate through this cross section is increasing at a higher rate than the cross section itself.

The magnitude of the change in cross sectional area for flow differs greatly for the aspect ratio design due to its larger electrode x dimension, resulting in the lower velocity increase per unit active area increase. When scaling the EPL design from 5 cm² to 9 cm², the x dimension only increases by 0.764 cm. The same change in active area for the aspect ratio design results in an x dimensional increase of a full 1.27 cm, resulting in 66.2% more additional cross sectional area for flow in the aspect ratio design compared
to the similarly constructed flow through flow field. This trend will only become more exacerbated as the designs are scaled further, with a theoretical 50 cm$^2$ aspect ratio design realizing a further increase of 6.785 cm compared to the much smaller additional 2.071 cm that would be needed for a 50 cm$^2$ EPL design.

The phenomenon discussed above is even more pronounced for the interdigitated flow field. Since this design essentially operates as many aspect ratio flow fields in parallel, the cross sectional area for flow can be seen as effectively increased based on the number of pairs of digits. As the x dimension is increased as the flow field is scaled up, the cross sectional area for each pair of digits will scale in a manner similar to the flow through design. The cumulative effect of adding this small amount of cross sectional area for flow over every pair of digits results in a much more rapid increase in effective cross sectional area for flow, contributing to the poor performance of this design based on this metric. An additional concern for this flow field is that more pairs of digits must be added as the design is scaled up if the channel to land ratio is to be preserved. This addition of more pairs of digits further serves to increase the effective cross sectional area for flow and compounds the problem stated before, resulting in very poor scale up performance and predictions for the interdigitated flow field design.

Perhaps the most interesting of these four designs when evaluated with this metric is the serpentine design. Due to its nature as a more passive flow by design which utilizes the pressure drop in the channel to force convection into the electrode, this design has a much more complex relationship with the increase in cell active area when scaled up to commercially viable sizes. Since the electrode domain in this design is still square
just as in the case of the flow through and interdigitated designs, the cross sectional area for flow will increase in the same manner. As shown in chapter 3, however, an increase in the cross sectional area for flow does not necessarily mean a decrease in the electrolyte velocity in this flow field design due to lower electrode pressure drop inciting more electrolyte to flow through the electrode. Similarly to the interdigitated design, the serpentine design requires more channels to be added as the design is scaled up in order to maintain the same channel to land ratio. This both increases the pressure drop in the channel domain and increases the cross sectional area for flow over each of the lands where it has been shown the electrolyte jumps into the electrode. Additionally, this jumping phenomenon makes it nearly impossible to fully account for the electrolyte fraction that flows through the electrode as electrolyte is capable of entering and exiting the electrode domain multiple times. These complex tradeoffs make it difficult to predict how individual changes to the serpentine design could affect the scalability of the design. Such exploration is outside the scope of this work, however these results demonstrate that perhaps the serpentine design more than any other design evaluated here shows the most opportunity for continued optimization to take advantage of the tradeoffs present when increasing the cross sectional area for flow.

These observations demonstrate the limitations of the interdigitated flow field and the promise of an EPL type design for commercial scale up. As the active area of the cell becomes larger, the flow rate for the interdigitated flow field will have to be scaled significantly to keep pace and maintain the same electrochemical performance. An EPL
type design, however will not have to scale the flow rate as aggressively, thus alleviating the concerns associated with the pumping power required for this type of flow field.

An even more interesting deduction can be made when examining the slopes of the aspect ratio and serpentine designs in Figure 5.3 (a) together. While the aspect ratio design exhibits higher velocity magnitudes with smaller active areas, the slope for this flow field at the tested length to width ratio is actually slightly shallower than that of the serpentine design. This leads to a point at an active area of 50 cm$^2$ where the serpentine design actually overtakes the aspect ratio design in terms of electrolyte velocity magnitude. Since the aspect ratio design is essentially a modified version of the EPL flow field design, this indicates that there is an optimal ratio between the length and width of the flow field below which the serpentine design will become a more viable candidate for scale up.

An additional concern when scaling up any flow field design is the pressure drop associated with the additional active area. Figure 5.4 shows the pressure drops for all 4 flow fields examined at each of the three active areas and flow rates investigated. From this figure it is clear that the EPL design exhibits by far the most severe pressure drop across the cell at every active area investigated. This is unsurprising due to the forced convective nature of the design and the long path length through the electrode which the electrolyte is forced to take. Examining Figure 5.4 (a) and (b) demonstrates a key finding about the pressure drop results for the serpentine and aspect ratio designs. From these results it is evident that the serpentine design exhibits lower pressure drop for both the 5 cm$^2$ and 9 cm$^2$ designs, however the difference between these two pressure drops at 9 cm$^2$
Figure 5.4: Simulated pressure drop of the electrolyte through the electrode domain for all flow field designs studied at (a) 5 cm$^2$, (b) 9 cm$^2$, and (c) 25 cm$^2$. 
is minimal, amounting to only 804 Pa at the highest flow rate condition. When investigating the 25 cm$^2$ serpentine and aspect ratio designs shown in Figure 5.4 (c) the aspect ratio design exhibits a significantly lower pressure drop than the serpentine design. This result demonstrates how, by limiting the path length the electrolyte is required to take through the electrode, the aspect ratio design mitigates the pressure drop concerns present within the cell. The serpentine design, on the other hand, requires additional channel switchbacks to be added in addition to increased path length through the electrode, resulting in substantially higher pressure drop upon scale-up. Because the aspect ratio design is able to effectively limit the increase in electrolyte path length, it can actually realize a significantly lower pressure drop than a serpentine flow field when considering larger active areas.

The advantage of the aspect ratio design becomes even more evident when examining Figure 5.3 (b) which shows the rate of change of the pressure drop at 8 mL/min/cm$^2$ for each flow field and active area size. Here it is evident that the pressure drops for all flow field designs are relatively bunched at smaller active area sizes. When increasing the active area size to 25 cm$^2$ however, the pressure drops diverge significantly. While the serpentine design increases by a factor of 32.7 when scaled from 9 cm$^2$ to 25 cm$^2$, from 54,595 Pa to 1,840,000 Pa, the aspect ratio design shows a more modest jump by a factor of 12.8 from 58,755 Pa to 811,000 Pa. This difference in the rate of increase of the pressure drop is more than enough to counteract the slightly slower rate of velocity magnitude increase exhibited by the aspect ratio design. Furthermore, the vast gap in pressure drop scalability between the two designs means that the aspect ratio
dimensions can easily be optimized to eliminate the velocity scalability deficiency without compromising its superior pressure drop scalability.

These conclusions are further supported by analyzing experimental discharging data. Figure 5.5 shows the discharge capacity of each flow field design at all three active area sizes and current densities of 500 mA/cm² and 750 mA/cm². Examining Figure 5.5 (a), it becomes immediately evident that the predicted rapid increase in serpentine electrolyte velocity upon scale up is supported by the available capacity. While the 5 cm² serpentine flow field is barely able to discharge at all due to the poor mass transport performance, a steady increase in capacity discharged is seen as the design is scaled to 9 and 25 cm² active areas. At 500 mA/cm², the serpentine flow field gains an additional 0.947 Ah of available capacity when scaling from 5 cm² to 9 cm² and a further increase of 0.571 Ah when increasing to 25 cm². Additionally, the gap between the available capacity at these two different current densities shrinks from 15.2% to 3.6% as the active area increases from 9 to 25 cm². These trends are due to the improved mass transport in the larger active area design supplying more electroactive specie to the reaction site and enabling operation at lower states of charge, even at high current densities.

The capacity results for the interdigitated design, seen in Figure 5.5 (b), also concur with the simulated velocity magnitude values. As the interdigitated active area is increased, the available discharge capacity for the flow field design remains relatively constant for the 500 mA/cm² case and actually decreases for the 750 mA/cm² case. This is likely due to the larger active area providing more opportunity for mass transport gradients such as the ones explored in Chapter 3 to arise within the cell. Because flow in
Figure 5.5. Available discharge capacity at current densities of 500 mA/cm² and 750 mA/cm² for all 3 active area sizes for (a) serpentine, (b) interdigitated, (c) EPL, and (d) aspect ratio flow field designs. (Theoretical capacity: 2.01 Ah)
an interdigitated flow field design tends to concentrate towards the later digits, the larger overall number of digits in a larger cell will lead to more area where the cell does not have adequate transport. Since the velocity magnitude in this design increases at a very modest rate as the active area is increased, it cannot counteract the development of these area of poor transport and suffers a decrease in performance because of it. While the results in Chapter 3 suggest that the serpentine design would also exhibit a tendency towards higher gradients with an increase in active area, because of the concurrent large increase in the velocity magnitude through the electrode it is able to overcome this issue and actually improve its performance upon scale up.

Figure 5.5 (c) and (d) shows these same discharge results for the EPL and aspect ratio designs respectively. The EPL design appears to show little change in the available discharge capacity upon scale up, in spite of the predicted increase in electrolyte velocity magnitude. This agrees well with previous results seen in Figure 5.1 (c). From the polarization curves seen in this figure it is clear that the 500 mA/cm$^2$ condition is not mass transport limiting for the EPL design, while the 750 mA/cm$^2$ condition would only be slightly so. Because these conditions are dominated by other losses, increased velocity as the flow field scales up has almost no impact on the available capacity at 500 mA/cm$^2$, and provides a modest increase of 3.5% when scaling from 5 cm$^2$ to 25 cm$^2$ at 750 mA/cm$^2$. While the aspect ratio design is similar to the EPL design in terms of the mass transport mechanism used, the geometry of the flow field results in lower electrolyte velocities through the electrode as has been acknowledged in previous chapters. When examining smaller active area flow fields on the order of 5 cm$^2$ which
have lower velocity magnitudes, this difference shows up in the form of lower available capacity as seen in Figure 5.5 (d). When scaled up to 9 cm$^2$, however, the aspect ratio design becomes comparable to the EPL design in terms of available discharge capacity. This is because the velocity magnitude increase predicted in Figure 5.3 (a) results in this larger design no longer being mass transport limited under these conditions, as supported by the polarization curve in Figure 5.1 (d).

Further insights can be gained from analyzing the discharge energy results for each of these flow field designs presented in Figure 5.6. The same trends present in the discharge capacity results are also seen in this figure, with the serpentine design discharging substantially more gross energy as the active area increases, the interdigitated flow field discharging slightly less, the EPL design remaining relatively stable, and the aspect ratio design approaching the EPL design as it reaches the same non-mass transport limited state. When taking the parasitic pumping losses into account, however, it becomes clear that the EPL design may not be the most promising choice for scale up after all. At small active area sizes, the pumping losses experienced by all four designs are negligible, ranging from fractions of a percent for the interdigitated design to 1% for the 9 cm$^2$ EPL design at 750 mA/cm$^2$. When increasing the active area size to 25 cm$^2$ these pumping losses become significant for both the serpentine and EPL designs. Due to its high pressure drop, even though the EPL design discharges more energy than any other flow field at this active area size the net energy discharged is actually lower than that of the serpentine design. The EPL design manages to discharge 1.528 Wh at 500 mA/cm$^2$ and 1.137 Wh at 750 mA/cm$^2$, but when factoring in the pumping losses the net
Figure 5.6. Available gross and net discharge energy at current densities of 500 mA/cm² and 750 mA/cm² for (a) serpentine, (b) interdigitated, (c) EPL, and (d) aspect ratio flow field designs.
energy discharged is only 1.112 Wh and 0.867 Wh respectively. When compared to the net discharge energies of 1.248 Wh and 0.874 Wh for the serpentine design, it becomes clear that a pure EPL design is not necessarily the most suitable for scale up. While a 25 cm² aspect ratio design was not experimentally tested for this work, the simulated values for pressure drop and velocity seen in Figure 5.3 (d) suggest that it would be able to compete with and surpass the serpentine design in this regard due to its significantly lower rate of pressure drop increase upon scale up combined with its similar velocity magnitude increase.

The manner in which these flow field designs behave in terms of other system level losses is also important to assess. One such loss that scale-up may have an impact upon is vanadium crossover causing capacity decay. Figure 5.7 shows the concentration of vanadium ions diffused to the vanadium-deficient side of the crossover setup during the crossover experiment. In Figure 5.7, the data corresponding to flow-through flow field designs have been shown with circles, the interdigitated design with triangles, and the serpentine design with diamonds. As illustrated in Figure 5.7, the concentration of diffused vanadium ions from the vanadium-rich electrolyte to vanadium-deficient electrolyte increases with increased active area regardless of the flow field design. It is also important to note that, based on Figure 5.7, for 5 and 9 cm² designs, the influence of flow field design on the rate of vanadium crossover is not significant. However, increasing the size of active area to 25 cm² results in higher crossover with interdigitated flow field designs. Also, it is important to note that the linearity of the trendlines depicted in Figure 5.7 is of great importance. The serpentine flow field design at 25 cm² does not
Figure 5.7. Concentration of diffused vanadium ions in the vanadium-deficient electrolyte during crossover testing.
show a linear trend for the rate of crossover during the time of experiment. The major reason for such a behavior was leakage of the cell during the conducting of the experiment. Based on the trends observed, it is hypothesized that the serpentine design in addition to the interdigitated design will demonstrate higher rate of crossover for increased active area cells (i.e. 25 cm$^2$ and higher). It is important to note that the observations made here are specific for the cell components and operating conditions used in this work. Altering any of these parameters, will have influence on the trend demonstrate in Figure 5.7.

5.4 Conclusions

When increasing the size of the active area in a redox flow battery, the flow field chosen is of critical importance to the final design. This is true not just in the sense of mass transport performance, but also in regards to the parasitic pumping loss, the internal cell pressure that will need to be contained, and the operational flow rate that the pumping system will need to deliver. In this chapter it has been demonstrated that results achieved through testing a flow field on a smaller scale may differ when attempted on a larger active area cell. While the pressure drop and parasitic pumping concerns for the aspect ratio design are more significant than that of the serpentine design at both 5 cm$^2$ and 9 cm$^2$, when examining a 25 cm$^2$ design it is clear that the aspect ratio design is far superior, making it the more scalable of the two flow field designs. Additionally, it is evident that the interdigitated design, while performing substantially better than the serpentine design at smaller scales, does not maintain this advantage when active area size is increased to more commercially feasible sizes. The severe increase in the cross
sectional area for flow results in a lack of sustained electrolyte velocity through the electrode and fading mass transport performance when compared to the three other designs examined. These conclusions are further supported by the available discharge capacity and discharge energy for each of these designs. The discharge energy result in particular highlights the complex tradeoff that is present between transport and pressure drop, showing the importance of optimizing designs for both of these concerns.

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CHAPTER SIX
MULTI-CELL STACK ARCHITECTURE, NOVEL SHUNT CURRENT MEASUREMENT, AND EFFICIENCY CONCERNS IN REDOX FLOW BATTERIES
Abstract

This article hasn’t been published anywhere, nor will it be prior to submission of the final version of my ETD, so a publication statement was not included. A manuscript will be submitted for publication. This work was authored by Jacob R. Houser, Douglas S. Aaron, and Matthew M. Mench.

My contributions to this work were system design and fabrication, collection, reduction, and analysis of data as well as composition of the manuscript. Aaron assisted in analysis of data and manuscript preparation.

6.1 Introduction

Redox flow batteries are typically installed not as single cell units, but as a collection of cells connected in series called a stack. This allows for increased power capacity, shared ancillary resources, and even greater overall flexibility for these systems. The process of scaling up from an individual cell to a stack is not without its challenges however. As most cells in a stack are hydraulically connected in parallel, the manifolding and pumping concerns become more complex. A new phenomenon specific to stacks, shunt current, becomes present as an additional loss within the system. While the higher power and pumping requirement make studies done on RFB stacks unique from single cell studies, the same approach can be applied when examining the system efficiency and performance.

One of the most unique and interesting concerns when investigating a flow battery stack is shunt current. While Chapter 5 examined how the results and conclusions made in Chapters 3 and 4 could be applied as a single cell is scaled up for use in a redox flow battery stack, shunt current is a system loss that is only present in a stack configuration and has to be studied on these larger system configurations. Due to the additional
complexities of building and operating a full flow battery stack, limited work has been done on this type of system loss, leaving a large gap in the literature.

In Chapters 3 and 4 it was demonstrated that operating conditions and system design can play a large part in the overall performance of a redox flow battery, particularly concerning energy efficiency. While these findings are valuable, the lack of such work done on a full RFB stack represents a further gap in the literature of the field. In this chapter, the construction, operation, and performance of a small 4 cell RFB stack is examined. This work shows that the approach taken in Chapters 3 and 4 to understanding the fluid transport and efficiency concerns in these systems is applicable to a larger multi cell system as well. Of specific concern is how performance and efficiency scales with flow rate when feeding multiple cells and distributing flow evenly among multiple cells hydraulically in parallel. This issue is mainly a function of the stack manifolding. A number of different approaches have been taken to studying manifolding in RFB stacks. *Kim et al.* examined flow bias in a stack both experimentally and computationally, finding a bias towards the earlier cells in the stack for their manifolding design 78. Work by *Wei et al.* examined the impact of non-uniform flow within the individual cells of a stack, including the impact of higher flow rate. While this study does not explicitly examine manifold design, a number of its findings can be extrapolated to obtain a sense of how non-uniform flow distributions among the cells in a stack could impact the performance of the system overall 80. Another study by *Moro et al.* examined an alternative design where the cells in a stack are connected in parallel to reduce shunt
current and hydraulic pumping losses. The authors found that this approach yields significantly less parasitic loss and improves system efficiency\textsuperscript{81}.

Conversely, shunt current is a system level loss that is not present in single cell designs and must be studied in the context of a full RFB stack. This self discharge mechanism arises due to the potential gradient across the stack and the available ionic pathway between cells connected electronically in series. The potential gradient across the stack causes an electron to disassociate from a V(II) ion and be conducted across the bipolar plate to the positive side of the adjacent cell. In order to maintain charge neutrality, a proton from the same negative electrolyte travels across the membrane. This positive charge can then be carried through the ionically conductive fluid pathway to the adjacent cell where the freed electron was drawn by the potential gradient across the stack. A schematic of this phenomenon along with an equivalent circuit diagram are shown in Figure 6.1.

Limited work has been done on this phenomenon in spite of its importance for the eventual commercial viability of larger RFB systems. Numerous shunt current models have been published in the literature, with varying degrees of complexity, focusing primarily on an equivalent circuit model based on solid phase potential.\textsuperscript{69,70} Some experimental work has been done to validate such models. Yin et al. experimentally measured the solid phase potential distribution in a short 5 cell stack in order to compare these values with the shunt current model developed in their work, but did not directly measure the current in the liquid phase.\textsuperscript{71} Fink and Remy were able to directly measure shunt current in an operating stack using external manifolding equipped with current
Figure 6.1. (a) Schematic of the shunt mechanism within the vanadium redox flow battery and (b) the representative equivalent resistor network to describe shunt current.
sensors. This work provides the best experimental findings on the topic within the current literature, showing the distribution of shunt across numerous cells, but does so using an external manifold instead of an internal one which is more likely to be used in a commercial system.\textsuperscript{72} Other studies have been done examining multi-stack systems as well, reporting findings on the most efficient means of connecting multiple discrete stacks hydraulically, but not examining the shunt current with a direct experimental measurement.\textsuperscript{73–75}

While these studies are valuable, insufficient work has been done on overall manifold design and experimental shunt current measurement in redox flow batteries. In this work, the impact of pumping losses and operating conditions presented in previous chapters are examined in a short RFB stack. Similar techniques to those used in the previous two chapters will be employed here, namely polarization curves, discharge tests, and cycling tests. Each of these techniques will be carried out on the stack as a whole, in addition to the individual cells in the stack in order to fully characterize the performance of the system as well as its constituent parts. Furthermore, this work will demonstrate how the findings in the previous chapters are applicable to an RFB stack and are not limited to laboratory scale systems. A novel in-situ shunt current measurement technique will also be presented, allowing for the capability to experimentally measure the shunt current in the internal manifold of an operating redox flow battery.
6.2 Method of Approach

6.2.1 Stack Design

In order to investigate the concerns discussed in the introduction to this work, a short RFB stack was built as seen in Figure 6.2. The stack is composed of 4 redox flow cells connected electronically in series through the use of three bipolar plates. On the external ends of cells one and four are two monopolar plates which contact the copper current collectors and connect the stack to the external load. Two different sets of bipolar and monopolar plates were manufactured for this study, one set with internal stack manifolding and another set with external stack manifolding. The bipolar and monopolar plates with internal manifolding are made out of BMC 940 graphite composite (Bulk Molding Compounds, Inc.) and are 1/8” and 1/4” thick respectively. A 50 cm² aspect ratio flow field was machined into each side of the bipolar plates, while the same size aspect ratio flow field was machined into only the active side of each monopolar plate. All membranes used were Nafion 117 (E. I. du Pont de Nemours and Company) pretreated by soaking in 3.3 molar sulfuric acid for 24 hours. All electrodes used were untreated SGL GFD3 carbon felt. In order to minimize pressure drop through the larger cell active area, two layers of GFD 3.3 were used on each side of each cell.

The design for the internal manifolding of the stack utilizes a single inlet into a PVC manifolding plate where the inlet flow is split into three separate manifold paths. Each path is designed to feed every third cell in a stack assembly. In the case of this study, since the stack is only comprised of four total cells, the first manifold branch is the only one that feeds multiple cells, supplying electrolyte to both cells one and four. Once
Figure 6.2. RFB stack design including (1) compression plate, (2) manifolding plate, (3) current collector isolation plate, (4) current collector, (5) monopolar flow plate, (6) gaskets, (7) porous carbon electrode, (8) ion exchange membrane, and (9) bipolar plate.
the electrolyte has passed through the cells, all three separate manifold flows rejoin and exit the stack through an identical PVC manifolding plate on the opposite end of the stack. Details of this design can be seen in Figure 6.2.

6.2.2 Stack Performance Tests

Three types of performance tests were used in this work to evaluate the stack design mass transport performance as well as the energy efficiency, individual cell polarization curves, pressure drop measurements, and full stack cycling. Stack cycling was performed at current densities of 20 mA/cm$^2$, 40 mA/cm$^2$, and 80 mA/cm$^2$ and at flow rates of 200 mL/min, 300 mL/min, and 400 mL/min. This cycling data will then be used similarly to the data obtained in Chapter 4 and in conjunction with pressure drop data in order to attain gross and net energy efficiency values for each set of operating conditions and demonstrate that the findings from these previous chapters are applicable to a full stack design. Pressure drop data for the stack was obtained in the same manner and with the same equipment as in Chapters 3 and 4.

Individual cell polarization curves were attained using the same protocol described in Chapter 5 to accommodate for the large volumetric flow rate requirement of the stack. Small ports for potential probes were drilled into the exposed side of each bipolar plate to allow for measurement and control of each individual cell potential. The potentiostat was connected to the solid phase potential leads as opposed to the full stack current collectors, allowing for polarization of just the bipolar plates for an individual cell.

The electrolyte used for all tests was 1.5 M vanadium in 3.3 M sulfuric acid with 125 mL of electrolyte on each side of the stack. A nitrogen purge was maintained over
the electrolyte at all times during system operation. Electrolyte was temperature controlled at 30 C for all tests conducted.

**6.2.3 In-situ Shunt Current Measurement**

For measurement of the shunt current present in the ionically conductive liquid phase electrolyte in the manifold, a technique similar to that used by Gandomi et al. to measure potential distribution in a solid phase electrode was adapted.\textsuperscript{104} Potential probes made from 127 µm platinum wire coated with PTFE were inserted into the stack between two compressible viton gaskets. The exposed platinum tips of these probes were positioned in the flowing electrolyte just prior to the start of the active area of each cell, as well as in the corresponding location at the outlet of each cell.

A small cell for measuring the OCV was constructed and can be seen in Figure 6.3. Two platinum probes identical to those inserted into the stack were inserted into two compartments through which the electrolyte flows prior to entering the stack, separated by a Nafion 117 membrane. A mercury-mercurous sulfate reference electrode was inserted through the top channel of the cell into a sulfuric acid reservoir in contact with the membrane. All probe voltage values are measured against this reference electrode.

The conductivity of the electrolyte was measured in an ex-situ conductivity cell and determined to be 0.2932 S/cm for the 1.5 M vanadium and 3.3 M H\textsubscript{2}SO\textsubscript{4} solution used in this study. This conductivity value, in conjunction with the geometry of the channels and manifolds within the system was used in order to determine the resistances for all of the ionically conductive fluid pathways within the system. Using these resistances and the experimentally measured electrolyte potentials, the shunt current between each cell in the stack as well as the total shunt current for each cell is able to be
Figure 6.3. External reference cell design including (1) electrolyte flow compartment, (2) electrolyte inlet, (3) sulfuric acid filling port, (4) reference electrode port, and (5) sulfuric acid reservoir.
determined. An example of an equivalent circuit diagram for such analysis can be seen in Figure 6.1 (b).

6.3 Results and Discussion

One of the primary concerns when designing a stack is the even supply of electrolyte to all cells within the stack. If this condition is not met, a scenario where one cell is starved of electrolyte will occur. This cell will suffer severe mass transport overpotential and the cell voltage will decrease severely, limiting the efficiency of the battery at best and causing a potentially hazardous amount of corrosion of the bipolar plate at worst. Figure 6.4 shows the individual cell potentials of each cell in the stack when cycling at 20 mA cm\(^{-2}\), 40 mA cm\(^{-2}\), and 80 mA cm\(^{-2}\) and a volumetric flow rate of 200 mL min\(^{-1}\). Figure 6.4 (d) also shows the average voltage spread for each of these cells, as well as the maximum voltage spread between cells during cycling. From these results it is evident that the four cells operate at very similar voltages under all conditions which is indicative of similar mass transport conditions. The average voltage spread for each operating condition never rises above 8 mV, with the maximum voltage spread never rising above 200 mV. This maximum voltage spread occurs for all cases near the end of the discharging portion of the cycle where electrolyte state of charge is lowest and, thus, any mass transport discrepancies become magnified. It is worth noting that even as the most mass transport limited cell in the stack is experiencing a sharp decrease in operating voltage, all other cells have also begun a sharp decrease due to mass transport limitations at similar times. Because of this similar behavior, the slight uptick in voltage spread towards the end of the cycle can be ignored and the mass transport performance of
Figure 6.4. Individual cell potentials of the RFB stack during cycling with a flow rate of 200 mL min⁻¹ at (a) 20 mA cm⁻², (b) 40 mA cm⁻², and (c) 80 mA cm⁻² as well as (d) the average and maximum voltage difference between cells at these three conditions.
all cells can be considered similar.

Figure 6.5 shows the pressure drop across the cell for flow rates up to 400 mL/min which is the highest flow rate tested. From this data it can be seen that the pressure drop increases somewhat linearly as expected for an aspect ratio flow field design. Of further note, is the relative magnitude of the pressure drop. Even though this flow field design uses a forced convection mass transport mechanism as described in prior chapters, the pressure drop across the stack remains manageable, reaching only 403.3 kPa at 400 mL/min. This low pressure drop further demonstrates why the aspect ratio design is viable for scaled up RFB design. Even though a total flow rate of 400 mL/min is entering the stack, the dominant source of pressure drop within the stack is still through the electrode domain. Due to the cells being fed in parallel, each one only experiences 100 mL/min of electrolyte flow. Because these pressure drops are in parallel, they are not additive, resulting in a pressure drop similar to that of a single aspect ratio flow field operating with a flow rate of 100 mL/min. The additional use of two layers of carbon felt electrodes also reduces the pressure drop by increasing the cross sectional area for flow, as discussed in previous chapters.

The importance of the ability to reduce pressure drop within a stack is further emphasized when examining the cycling efficiency and net charge and discharge energy at various operating conditions. In the same way that pumping requirements serve as a parasitic loss in single cell operation, so too do they hurt the overall efficiency of a stack. While the parallel construction of the stack manifolding is able to keep the pressure drop under control, this is not the case for the volumetric flow rate. Because this operational
Figure 6.5. Pressure drop across the stack for volumetric flow rates up to 400 mL/min.
contributor to parasitic loss cannot be mitigated upon scale up, it becomes even more crucial to keep pressure drop lower across the system. Figure 6.6 shows the gross and net energy efficiencies for the stack when cycling at current densities of 20 mA cm$^{-2}$, 40 mA cm$^{-2}$, and 80 mA cm$^{-2}$ at a flow rate of 200 mL min$^{-1}$. The gross energy efficiency follows an expected trend with the 20 mA cm$^{-2}$ current density producing an efficiency of 71.8%, the 40 mA cm$^{-2}$ case producing an energy efficiency of 68.7%, and the 80 mA cm$^{-2}$ condition producing the lowest energy efficiency at 64.1%. This decrease in energy efficiency at such low current densities is due to the low area specific volumetric flow rate. When operating at 200 mL min$^{-1}$, each cell only receives 50 mL min$^{-1}$ which is equivalent to 1 mL min$^{-1}$ cm$^{-2}$. From this gross energy result the lowest current density appears to be the ideal operating point, but when taking pumping losses into account, the net energy efficiencies for these three current densities are 60.0%, 62.6%, and 61.2% respectively. Similarly to the single cell cases examined in previous chapters, while the lower current density operating point has a much higher raw energy efficiency, it requires a much longer time to discharge and charge that energy. Because the flow rate and pressure drop remain the same across all cases, the rate of energy lost to pumping power is the same for all current densities. This means that the ratio of rate of energy charged or discharge to rate of pumping energy is lower for low current density operation, leading to a worse net energy efficiency.

Notably, the highest current density tested, the 80 mA cm$^{-2}$ case, does not exhibit the highest net energy efficiency. While it is higher than the 20 mA cm$^{-2}$ case, it is 1.4% lower than the 40 mA cm$^{-2}$ case. This is due to the additional mass transport
Figure 6.6. Gross and Net energy efficiencies for the 4 cell RFB stack with a flow rate of 200 mL min$^{-1}$ at current densities of 20 mA cm$^{-2}$, 40 mA cm$^{-2}$, and 80 mA cm$^{-2}$.
overpotential present for this higher current density at this low flow rate. Because the increased overpotential lowers the discharge voltage and raises the charge voltage, even though the current density is higher the overall rate of energy flow is lower than that of the 40 mA cm\(^{-2}\) case. This further demonstrates the need for in depth optimization analysis when designing any RFB system, as the net energy efficiency for this highest current density is still greater than that of the lowest current density.

While eliminating mass transport overpotential should be a clear objective when discussing how to improve RFB systems, achieving this goal may not be as easy as simply increasing the volumetric flow rate. Figure 6.7 shows the gross and net energy efficiencies for the stack when cycling at 80 mA cm\(^{-2}\) for 200 mL min\(^{-1}\), 300 mL min\(^{-1}\), and 400 mL min\(^{-1}\). While increasing the flow rate improves the gross energy efficiency by as much as 1.5%, when taking the additional pumping losses into account it becomes immediately obvious that this small gain is insufficient. This again is a result of the manner in which flow rate must be scaled when operating a stack as opposed to a single cell. For a single cell, to increase the flow rate through the active area by 25 mL min\(^{-1}\) all that is needed is that same amount of additional flow. When examining a stack, however, if the flow rate through each cell is to be increased by 25 mL min\(^{-1}\), this amount of additional flow is required for each cell in the stack. In the case of the four cell stack in question this results in an additional 100 mL min\(^{-1}\) of flow required of the pump, but still only provides the efficiency gains of an additional 25 mL min\(^{-1}\) through each cell. Due to the cells being hydraulically fed in parallel, the pressure drop requirement is not exacerbated any more than in a single cell, however this additional flow rate requirement
Figure 6.7. Gross and Net energy efficiencies for the stack when cycling at 80 mA cm$^{-2}$ for flow rates of 200 mL min$^{-1}$, 300 mL min$^{-1}$, and 400 mL min$^{-1}$.
is sufficient to overcome the efficiency gained through improved mass transport, resulting in a decrease in net energy efficiency of 2.7% when increasing the flow rate to 300 mL min\(^{-1}\) and an additional 6.5% when increasing the flow rate to 400 mL min\(^{-1}\).

One of the most unique and least explored areas of stack design is the examination of shunt current through the ionically conductive electrolyte pathway. This current is driven by the potential gradient across the stack which grows larger and larger as more cells are stacked in parallel. This mechanism is described previously and can be seen in Figure 6.1 (a). Figure 6.8 shows the total stack potential during cycling at 20 mA cm\(^{-2}\), 40 mA cm\(^{-2}\), and 80 mA cm\(^{-2}\) with a volumetric flow rate of 200 mL min\(^{-1}\). This full stack voltage is the sum of the individual cell voltages similar to those shown in Figure 6.4. It is this potential difference that drives the shunt current phenomenon. This is true not only of the outermost cells in the stack, but also the interior cells. The potential gradient between any two cells in a stack will be the sum of the potential of those two cells as well as all of the cells between them. From this simple result it becomes easy to see how as a stack grows larger, this potential difference can become quite extreme, even as individual cell potentials remain at their normal magnitude.

This increasingly powerful potential gradient can be more directly demonstrated using the novel shunt current measurement method described in section 6.2.3. Figure 6.9 shows the potential of each of the four platinum manifold potential probes positioned at each cell inlet during the same cycling conditions seen in Figure 6.8. The first notable difference seen in these results is the magnitude of the potentials. Examining the potential at the inlet of cell 4 under the 20 mA cm\(^{-2}\) cycling condition it is seen to rise as
Figure 6.8. Full stack potentials for cycling tests with a flow rate of 200 mL min$^{-1}$ at (a) 20 mA cm$^{-2}$, (b) 40 mA cm$^{-2}$, and (c) 80 mA cm$^{-2}$.
**Figure 6.9.** Stack manifold potentials for cycling tests with a flow rate of 200 mL min⁻¹ at (a) 20 mA cm⁻², (b) 40 mA cm⁻², and (c) 80 mA cm⁻².
high as 4.637 V. When compared with the individual cell potentials seen previously, this may seem impossible, but when accounting for the additive nature of the individual cell potentials connected in series this result makes sense. Comparing this potential with the relatively low potential at the inlet of cell 1 results in a maximum potential difference of 4.41 V between these two locations in the system. This driving force is sufficient to produce a non-negligible amount of shunt current within the manifold. Such potential gradients are present between all cells in a stack, however, as the potential gradients between cell 4 and cells 2 and 3 are also significant at 3.198 V and 1.585 V respectively. These potential differences will drive a shunt current between each of these cells as well, resulting in a larger total shunt loss for the system. Another interesting conclusion that can be drawn from this data is how the potential difference increases as the individual cells in question are further apart in the stack. This means that as a stack grows larger, this driving force will also become larger and likely lead to higher shunt currents.

Because the shunt current is also a function of the conductivity of the path between these driving potentials, however, it is necessary to examine these results more in depth to draw a more concrete conclusion about such a trend.

Using the electrolyte conductivity reported in section 6.2.3 along with the dimensions of the channels and manifolds within the system, it is possible to calculate the total resistance between each of the platinum probes inserted into the stack. These resistance values are shown in Table 6.1. All of these values are similar, ranging from 614.35 Ω to 669.65 Ω. Through a simple application of Ohm’s Law, it is then possible to use the resistance values to calculate the induced shunt current between each pair of cells.
Table 6.1. Resistances between electrolyte potential probes.

<table>
<thead>
<tr>
<th>Probes</th>
<th>Resistance (Ω)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 to 2</td>
<td>658.61</td>
</tr>
<tr>
<td>1 to 3</td>
<td>661.37</td>
</tr>
<tr>
<td>1 to 4</td>
<td>614.35</td>
</tr>
<tr>
<td>2 to 3</td>
<td>664.13</td>
</tr>
<tr>
<td>2 to 4</td>
<td>666.89</td>
</tr>
<tr>
<td>3 to 4</td>
<td>669.65</td>
</tr>
</tbody>
</table>
in the stack based upon the measured potentials at each of the probes. Because all of the resistances between probes are similar, the shunt will be almost exclusively a function of this potential difference between probes. Figure 6.10 shows the shunt current values for the 20 mA cm⁻² cycling experiment at a flow rate of 200 mL min⁻¹. Each graph depicts the individual shunt currents present between each cell based upon the potentials measured by the platinum probes at the cell inlets as well as the total shunt current into or out of the cell. For the purposes of this study, positive shunt values will be considered current leaving the cell while negative shunt values will be considered current entering the cell. As is expected, the highest shunt current between any two cells is that between the first and fourth cell, peaking at a value of 7.247 mA. This is due to the large potential gradient between these two outermost cells. Additionally, due to the three chimney design of the manifold, these two cells are fed through the same manifold chimney, resulting in the lowest overall resistance between any two cells in the assembly. The interior cells exhibit much lower shunt currents due to their lower potentials compared to the outermost cells in the stack. The peak shunt current for any one cell is seen flowing out of cell 4, reaching a maximum value of 14.273 mA. This amounts to 1.43% of the total stack current when cycling under these conditions. When combined with the maximum shunt current from the other cells, the resulting total shunt current of 19.082 mA amounts to 1.91% of the total cycling current for the system. While this may not seem like a substantial portion of the overall system current, it must be noted that this system is still a relatively small laboratory scale stack and is only comprised of 4 cells. As seen in both Figure 6.9 and 6.10, the potential gradients and thus the shunt currents at
Figure 6.10. Shunt current values for the four cell stack during cycling at 20 mA cm$^{-2}$ and a flow rate of 200 mL min$^{-1}$ for (a) cell 1, (b) cell 2, (c) cell 3, and (d) cell 4.
the outermost cells are highest. When adding additional cells, these gradients will continue to increase, driving progressively larger shunt currents as they do so.

Figure 6.11 shows the expected average shunt currents between cell 1 and all other cells when increasing the size of the stack to 10 cells based upon the data obtained from the four cell stack tested in this chapter. All resistances between cells were calculated based upon the same three chimney manifolding geometry used in the 4 cell stack. As expected, the current between cell 1 and cell 10 in this theoretical stack is the highest, reaching a value of 18.924 mA. This value alone exceeds the total shunt for cell 1 in the smaller 4 cell stack analyzed in this study and is a full 1.9% of the total operating current of the system under these conditions. When examining the total shunt current for cell 1 in this theoretical 10 cell stack, a value of 90.99 mA is attained. This value is significantly larger than that of the 4 cell stack and is a full 9.1% of the overall system operating current. This increase in shunt by a factor of 5 after simply adding six cells to the stack demonstrates how severe shunt concerns can become when expanding a design to a commercial size, particularly when considering that most commercial systems are composed of many more cells in series. In order to mitigate these types of concerns, manifolding designed to increase the resistance for transmission of this shunt current is necessary.

Another conclusion that can be attained from this novel setup is the impact of the mode of operation upon the shunt current within the system. When operating an RFB stack galvanostatically, the potentials of the solid phase material are constantly changing, and thus so is the overall potential gradient across the stack. As this potential gradient
Figure 6.11. Predicted shunt current between cell 1 and all other cells in a theoretical 10 cell stack utilizing a similar manifolding design to the experimental 4 cell stack.
changes, so too will the shunt current driven by it. Conversely, when the system is operated potentiostatically, the solid phase potentials are immediately driven to whatever potential is specified, essentially determining the shunt current seen in the system by specifying what potential gradient will be present to drive it. This becomes particularly important when examining the charging method for the system where the potential gradients across the stack are the highest. Figure 6.12 (a) shows the average potential of each of the electrolyte probes during charging steps controlled potentiostatically and galvanostatically. The potentiostatic charging step held the stack at a constant voltage of 6.8 V until a cutoff current density of 20 mA cm\(^{-2}\) was reached. The galvanostatic charging step held the system at a constant current density of 20 mA cm\(^{-2}\) until a cutoff voltage of 6.8 V was reached. From this figure it is clear that the electrolyte potentials for the potentiostatic charge are slightly higher than those of the galvanostatic charge. This is particularly evident when examining probe 4 where the two values deviate by a full 246 mV. This is because when charging potentiostatically, the individual cell potentials are immediately forced to 1.7 V, creating the maximum potential gradient across the stack immediately and maintaining this gradient for the duration of the charge. When charging galvanostatically, the initial cell potentials are significantly lower and allowed to gradually rise as the state of charge increases, only reaching the 1.7 V maximum at the end of the charging step.

While a difference of only 246 mV may seem small in comparison to the overall stack voltage, even at this scale the impact upon the shunt current is noticeable. Figure 6.12 (b-e) shows the shunt current for each individual cell in the stack under both
Figure 6.12. (a) Electrolyte potential probe voltages for potentiostatic and galvanostatic charges as well as the induced shunt currents for (b) cell 1, (c) cell 2, (d) cell 3, and (e) cell 4.
charging conditions. For the outermost cells in the stack, cells 1 and 4, the shunt current is noticeably smaller when charging galvanostatically. When employing a constant current charge, cell 1 experiences 1.104 mA less shunt current while cell 4 experiences 0.778 mA less shunt. While the interior cells experience slightly more total shunt under the galvanostatic charging condition, this increase is not significant enough to overcome the shunt savings present in the outer cells when using a constant current charge. The difference in total shunt current for the two types of charges is only 0.69 mA overall, however, this discrepancy will only grow if more cells are added to the stack and the driving potentials present in the outermost cells are increased further.

6.4 Conclusions

When examining RFB systems in the context of a multi-cell stack, a number of additional concerns arise. Manifold design, shifts in efficiency tradeoffs, and shunt current losses all become factors that must be considered. While these concerns must be kept in mind, however, conclusions made in previous chapters about the need to examine operating conditions and desired applications hold true. In this work pumping losses have been shown to play an even more pivotal role as the total flow rate necessary for operating a stack must scale proportionally with the number of cells in the stack. This fact demonstrates how, even though mitigating mass transport losses is a paramount concern in RFB systems, simply increasing the flow rate in order to do so is not a feasible solution when designing a large scale system and other methods must be explored. This work also demonstrated the use of a novel in-situ shunt current measurement technique that is minimally invasive and can produce direct measurements of this stack specific
loss. As more cells are added to an RFB stack, the potential gradients that drive shunt increase, allowing this self-discharge phenomenon to become a substantial drain on overall system efficiency. When this occurs, not only do standard stack design concerns such as manifold geometry need to be taken into account, but the method in which the system is operated must be thoroughly examined as well in order to mitigate the driving potential for shunt current.

6.5 Acknowledgements

The authors would like to acknowledge the University of Tennessee Chancellor’s Fellowship, the Bredesen Center for Interdisciplinary Research and Graduate Education, and the James A. Euler Memorial scholarship for support.
CHAPTER SEVEN
ECONOMIC ANALYSIS OF CELL AND STACK LEVEL REDOX
FLOW BATTERY DESIGN CONCERNS
Abstract
This article hasn’t been published anywhere, nor will it be prior to submission of the final version of my ETD, so a publication statement was not included. A manuscript will be submitted for publication. This work was authored by Jacob R. Houser, Douglas S. Aaron, and Matthew M. Mench.

My contributions to this work were collection, reduction, and analysis of data as well as composition of the manuscript. Aaron assisted in analysis of data and manuscript preparation.

7.1 Introduction

While the electrochemical performance of a redox flow battery is of utmost importance, a greater context is needed in order to truly characterize the impact of any advance in the design of these systems. Without putting these discoveries into the context of real world applications and financial metrics, it is impossible to know what impact they might have upon the feasibility of the redox flow battery system to meet the needs of real world energy storage. In Chapters 3 and 4 a number of advances in terms of flow field design and single cell operation were made, leading to improved efficiencies at both the electrochemical and system levels. In Chapter 6, it was demonstrated that redox flow battery stacks suffer from all of the same design tradeoffs as the individual cells in addition to concerns unique to these larger scale systems. This further demonstrates the necessity of analyzing these design choices from a financial viewpoint as the cost of installation, operation, and potential revenue are the key metrics that will ultimately determine the success of the systems. The purpose of this Chapter will be to address the impact of these advances on a number of different financial metrics for a variety of different energy storage applications.
In these previous chapters, 4 flow field designs were examined in order to demonstrate how their properties were uniquely suited to very different applications. This is further borne out when examined through a financial lens as a given flow field may be advantageous for one application, while failing to be as cost effective as the alternatives for other applications. This will be demonstrated through the use of a cost model taking into account a number of design metrics, but most importantly the depth of discharge (DoD) and energy efficiency of a given flow field at different discharge current densities and flow rates. Stack data from Chapters 5 and 6 will be utilized as well in order to provide estimates for the scalability of single cell performance as well as pressure drop through the system and shunt current losses. The primary metrics which will be utilized to characterize system cost performance include payback period, installed cost per kWh, Levelized Cost of Energy Storage, Net Present Value, and Internal Rate of Return. The storage applications analyzed include Transmission System, Peaker Replacement, Frequency Regulation, Distribution Substation, Distribution Feeder, Microgrid, Island Grid, Commercial/Industrial, Commercial Appliance, and Residential\textsuperscript{105}. Transmission Systems integrate intermittent energy sources, provide grid stability, and reduce transmission losses and congestion. Peaker Replacement systems provide arbitrage, spinning and non-spinning reserve, and quick response times. Frequency Regulation involves maintaining frequencies within a tolerance zone by raising or lowering output to follow instantaneous load changes. Distribution Substations provide flexible peaking capacity and help with stability. Distribution Feeders are smaller in scale, placed along the feeder, and also help with stability and reliability.
Microgrid systems support sub-grids that can disconnect from the main grid, providing ramping support for stability and short term power outputs. Island Grid systems support physically isolated electricity networks and focus on discharge time as opposed to short term power output. Commercial/Industrial storage applications are behind the meter peak shaving and demand charge reduction systems capable of multiple operating modes. Commercial Appliance systems are smaller such systems sized more for one specific appliance. Residential systems are behind the meter systems for home use and aid in distributed generation.

This chapter will show that the key metrics determining the viability of various designs prove to be the power to energy ratio in addition to the overall capacity requirements of the application. The impact of electricity pricing during periods of peak demand and off peak demand will be analyzed as well in order to demonstrate that the magnitude of the pricing difference has a substantial impact upon the viability of a system. System lifetime is also included in the study in order to demonstrate the value of redox flow battery systems beyond their installation.

7.2 Method of Approach

7.2.1 Cycling Experiments

Depth of discharge and energy efficiency data for the cost model was collected for each of the four flow field designs discussed in Chapters 3 and 4. Starting with 50 mL of 1.5 molar vanadium electrolyte on the positive and negative sides of the cell, each cell construction underwent charge-discharge cycling at various flow rates and current densities. Three discharge current densities were tested, 250 mA/cm$^2$, 500 mA/cm$^2$, and
750 mA/cm² in order to highlight mass transport behavior as well as high efficiency
operation, with the charging current being held constant at 100 mA/cm² for all tests.
Each discharge current density was tested at multiple flow rates, with the serpentine and
interdigitated flow fields being tested at 10 mL/min, 40 mL/min, 70 mL/min, and 100
mL/min while the flow through and aspect ratio flow fields were only tested at 10
mL/min, 40 mL/min, and 70 mL/min due to pressure drop concerns with the pump tubing
used.

Depth of discharge data was obtained from each of these cycling experiments by
dividing the initial discharge capacity for the first discharge by the theoretical capacity
(2.01 Ah) of the electrolyte solution, thus yielding a maximum possible experimental
depth of discharge for each design case. The energy efficiency for each design case was
obtained by dividing the total energy discharged from the battery during cycling by the
total energy required to charge the battery during cycling. Linear interpolation was then
used to define values for each of these metrics for flow rates in increments of 10 mL/min
between the flow rates tested.

7.2.2 Cost Model

The impact of flow field design choices, operational choices, and application
parameters on cost were modeled in order to assess the impact of each on the viability of
RFB systems for commercial implementation. This model uses the experimental results
for depth of discharge, energy efficiency, and cell pressure drop at each of the operational
points described in section 7.2.1. The application parameters used include project
lifetime, total power capacity, total energy capacity, 100% depth of discharge equivalent
cycles per day, operational days per year, annual energy capacity, and total project energy capacity. Key model parameters are shown in Table 7.1.

The ranges for off-peak and on-peak electricity prices are due to the variation in energy rates based on location and utility provider. The references cited provide evidence of the large distribution of rate schedules that currently exist, allowing for the extremes of these time-of-use based rates to be analyzed in this work.

The total number of stacks needed to meet the application requirements is defined as

\[ N_S = \frac{C_p}{N_c I_c \eta V_{OCV}} \]  

(7.1)

Where \( N_S \) is the number of stacks, \( C_p \) is the system power capacity in Watts, \( N_c \) is the number of cells in a stack, \( I_c \) is the current per cell in Amps, \( \eta \) is energy efficiency, and \( V_{OCV} \) is nominal open circuit voltage at 50% SOC in Volts. The current per cell is defined as the current density multiplied by the active area of a single cell. The total electrode area required is defined as

\[ A_{elec} = \frac{N_S N_c A_{cell}}{10000} \]  

(7.2)

Where \( A_{elec} \) is the total electrode area in m² for the system and \( A_{cell} \) is the active area for a single cell in cm². The system cycle time in hours is simply defined as the total energy capacity divided by the total power capacity. The moles of vanadium required for the system is defined as

\[ M_V = \frac{t_{cycle} C_p}{F \eta V_{OCV} C_{DoD}} \]  

(7.3)
Table 7.1. Model Parameters

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Simulation Value</th>
<th>Reference</th>
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<tr>
<td>Vanadium Concentration (mol)</td>
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</tr>
<tr>
<td>H$_2$SO$_4$ Concentration (mol)</td>
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<td>Chosen</td>
</tr>
<tr>
<td>Discount Rate</td>
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<td>Off-Peak Electricity Price ($/kWh)</td>
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<td>PG&amp;E, PSEG</td>
</tr>
<tr>
<td>On-Peak Electricity Price ($/kWh)</td>
<td>0.0801 - 0.288</td>
<td>PG&amp;E, PSEG</td>
</tr>
<tr>
<td>Vanadium Cost ($/kg)</td>
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<td>[83]</td>
</tr>
<tr>
<td>Membrane Cost ($/m$^2$)</td>
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<td>[83]</td>
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<tr>
<td>Graphite Plate Cost ($/m$^2$)</td>
<td>51</td>
<td>[83]</td>
</tr>
<tr>
<td>Electrode Cost ($/m$^2$)</td>
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<td>[83]</td>
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<tr>
<td>Pump Efficiency</td>
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<tr>
<td>Cell Active Area (cm$^2$)</td>
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<td>Chosen</td>
</tr>
<tr>
<td>Cells per Stack</td>
<td>100</td>
<td>Chosen</td>
</tr>
</tbody>
</table>
Where $M_v$ is the moles of vanadium required in one side of the battery, $t_{cycle}$ is the cycle time in hours, $F$ is Faraday’s constant in Amp-hours/mole, and $C_{DoD}$ is the maximum depth of discharge attainable for the system as a percentage of the theoretical capacity. This is then multiplied by the molar mass of vanadium oxide, doubled, and divided by 1000 in order to obtain the total mass of vanadium oxide that is required for the system in kg.

Pumping requirements were also included in the model and designated as an operational cost as opposed to an efficiency loss in the system. This determination is largely a matter of preference as such costs can be considered either during installation as an efficiency loss in the system, thus raising the installed cost per kWh of the system but keeping operating costs lower, or after installation as an operating expense, thus keeping capital costs lower while incurring a higher variable cost. The pumping power is defined as

$$P_{pump} = \frac{\Delta p \cdot Q_{total}}{\eta_{pump} \cdot 1000} \quad (7.4)$$

Where $P_{pump}$ is the pumping power in kW, $\Delta p$ is the pressure drop across the system in Pascals, $Q_{total}$ is the total system flow rate in m$^3$/s, and $\eta_{pump}$ is the pump efficiency.

The pumping energy cost per year is then calculated as

$$C_{pump} = P_{pump} t_{charge} n_{cycles} d_{op} C_{off} + P_{pump} t_{discharge} n_{cycles} d_{op} C_{on} \quad (7.5)$$

Where $C_{pump}$ is the pumping cost in $/year, t_{charge}$ is the time it takes to charge the system one full capacity, $n_{cycles}$ is the number of cycles the system undergoes per day, $d_{op}$
is the total days per year the system is in operation, and \( C_{off} \) and \( C_{on} \) are the off-peak and on peak costs of energy in $/kWh respectively.

The capital cost of vanadium required for the system is calculated as

\[
C_v = m_v c_v
\]

(7.6)

Where \( C_v \) is the total cost of vanadium in $, \( m_v \) is the mass of vanadium in kg, and \( c_v \) is the rate cost of vanadium in $/kg.

Membranes for this model were assumed to be Nafion 117. The capital cost of membranes required for the system is calculated as

\[
C_{mem} = c_{mem} A_{elec}
\]

(7.7)

Where \( C_{mem} \) is the total cost of membrane material for the system in $ and \( c_{mem} \) is the rate cost of membrane material in $/m\(^2\).

The cost of the graphite plates for the system is defined as

\[
C_{GP} = c_{GP} N_S (N_c + 1) \left( \frac{A_{cel}}{10000} \right)
\]

(7.8)

Where \( C_{GP} \) is the total cost of the graphite plates in $ and \( c_{GP} \) is the rate cost of graphite plates in $/m\(^2\).

The cost of the electrode material for the system is defined as

\[
C_{elec} = 2 \cdot c_{elec} A_{elec}
\]

(7.9)

Where \( C_{elec} \) is the total cost of the electrode material in $ and \( c_{elec} \) is the rate cost of electrode material in $/m\(^2\).

The total installed cost of the flow battery system including the balance of plant is defined as
The factor of 1.3 in equation 7.10 is included to account for balance of plant concerns including pumps, piping, temperature control systems, and power electronics. This factor is a conservative estimate based upon values reported in the literature.\textsuperscript{89} This total cost can then be divided by the energy capacity in kWh to obtain the first of four key metrics to be discussed in this chapter, installed cost per kWh.

In this cost model it is assumed that the entirety of the system is financed through debt. The yearly cost associated with financing the flow battery project can be derived from the equation

\[
C_{\text{debt}} = C_{\text{total}} \frac{r(1 + r)^n}{(1 + r)^n - 1} \tag{7.11}
\]

Where \( C_{\text{debt}} \) is the loan payment per year in $, \( r \) is the interest rate of the debt, and \( n \) is the length of the loan repayment period in years.

The gross income from the flow battery system is defined as

\[
I_{\text{gross}} = C_{\text{on}} C_E n_{\text{cycles}} d_{\text{op}} \tag{7.12}
\]

Where \( I_{\text{gross}} \) is the gross income per year in $ and \( C_E \) is the energy capacity of the system in kWh. The charging cost of the system can be calculated with a similar formula shown below in equation 7.13, with the only difference being the shift from on-peak electricity price to off-peak electricity price.

\[
C_{\text{charge}} = C_{\text{off}} C_E n_{\text{cycles}} d_{\text{op}} \tag{7.13}
\]

The pumping energy cost, loan payment cost, and charging cost can all then be subtracted from the gross income to obtain a value for the net income per year brought in
by the system, shown below in equation 7.14.

\[ I_{net} = I_{gross} - (C_{charge} + C_{debt} + C_{pump}) \]  

(7.14)

This net income allows for the calculation of the second key financial metric for flow battery systems, the net present value. This can be calculated using the equation introduced in chapter 1 as equation 1.8 and shown again below as equation 7.15.

\[ NPV = \sum_{t=1}^{t} \frac{I_{net}(t)}{(1 + r)^t} - C_0 \]  

(7.15)

Here, t is the total system lifetime in years, while r is the discount rate to account for the time value of money. The net present value is useful in this instance because it allows for the characterization of the overall value of the flow battery project in terms of present day dollars. If the NPV for the project is positive, then it indicates that the system is a worthwhile investment, while if the NPV is negative, it indicates that the capital that would be used to undertake the project would be better allocated in another investment.

The next key metric that can be calculated from this model is the levelized cost of energy storage. This metric is similar to the net present value in that it attempts to characterize future assets in terms of current ones. In this case, the asset in question is stored energy capacity. This metric can be calculated using equation 1.9, reprinted here as equation 7.16.

\[ LCOES = \frac{C_0 + C_{op.NPV}}{E_{PV}} \]  

(7.16)
In this equation, $C_{op.NPV}$ is the net present value of the operating costs in $, while $E_{PV}$ is the present value of the energy discharged over the lifetime of the system in kWh. The NPV of the operating costs can be calculated using equation 7.15, while the present value of the energy discharged can be calculated using equation 7.17, shown below.

$$E_{NPV} = \sum_{t=1}^{T} \frac{C_E}{(1+r)^t} \quad (7.17)$$

This metric is useful in order to determine the average price that a storage installation will need to receive from discharge over the span of its lifetime in order to produce a profit. Because it incorporates all the costs over the system lifetime, it allows for a better comparison of design choices than a simple calculation of installed cost per kWh.

Another useful cost metric for evaluating these myriad designs is the payback period. This is defined as the time, in years, that the system will need to operate in order to repay the initial investment in the system. It is useful because it also incorporates operating costs as well as the initial investment and gross revenue. The shorter the payback period, the better. It is defined as shown below in equation 7.18.

$$t_{payback} = \frac{C_0}{I_{net}} \quad (7.18)$$

In the case of a negative net revenue, it is possible for the payback period to be negative. Cases where this is true should be ignored, however, as they represent cases where the system is operating at a net loss and would therefore never be implemented.
The final cost metric utilized in this work is the rate of return on initial investment for the system as a percentage. This can be defined as the gain or loss realized from the project based on the total cost of the system over the lifetime of the system. It can be defined as

\[
R_{ret} = \frac{NPV - C_0}{C_0}
\] (7.19)

This metric is useful because it allows a comparison of projects of different size and scope by reporting the benefit of the project as a percentage of the funds invested. The higher the rate of return, the more beneficial the investment is in terms of income generated per dollar invested. In this way, a smaller project with a lower net present value due to its size can be compared favorably to a larger project with a high net present value. While the larger project may bring in more income, it is also significantly more expensive to undertake, and may have a much lower rate of return than a smaller project that generates income on a smaller initial investment.

**7.3 Results and Discussion**

Examining first the installed cost of an RFB system which is independent of the cost of electricity, it is possible to see to which applications flow battery systems are most suitable. Table 7.2 shows the lowest installed cost of a system for each of the ten use cases mentioned earlier as well as the architecture and operational parameters which produce them. From this result it is clear that applications with high energy to power ratios provide the most economically sensible options to deploy these systems.
The foremost of these high energy use cases is the Transmission System, with an installed cost of only 160.72 $/kWh. This is notably the largest case studied in terms of the total energy storage requirement as the 800 MWh of required storage doubles that of the next largest case. The raw magnitude of the energy storage requirement is not the main driver behind the promising cost efficiency of the system, however. When examining the remaining nine cases, the next lowest installed cost actually belongs to the much smaller Island Grid scenario which only requires 8 MWh of energy storage. This is merely 1% of the energy storage requirement for the Transmission System case, yet the Island Grid case shows very similar installed cost of 165.29 $/kWh which is only 4.57 $/kWh more than that of the Transmission System. Furthermore, much larger systems such as the Peaker Replacement and Distribution Substation cases show higher installed cost at 173.28 and 175.28 $/kWh respectively. This is due to the energy to power ratio mentioned beforehand. While these two larger systems require more energy to be stored, they only boast 4 to 1 energy to power ratios. The Transmission System and Island Grid cases have the same 8 to 1 energy to power ratio, the highest ratio of any case examined in this work.

One of the major issues with installed cost as a comparator for different architectures and use scenarios is the lack of accounting for operational concerns. By simply examining how much the components and installation of a system cost without examining the lifetime of the project or the way the system will be operated, essential information is omitted and key insights are lost. This is particularly evident in the approach used in this work which chooses to frame parasitic losses such as pumping...
<table>
<thead>
<tr>
<th>Application</th>
<th>$/kWh</th>
<th>Current Density (mA/cm^2)</th>
<th>Flow Field Design</th>
</tr>
</thead>
<tbody>
<tr>
<td>Transmission System</td>
<td>160.72</td>
<td>500</td>
<td>EPL</td>
</tr>
<tr>
<td>Peaker Replacement</td>
<td>173.28</td>
<td>500</td>
<td>EPL</td>
</tr>
<tr>
<td>Frequency Regulation</td>
<td>301.39</td>
<td>750</td>
<td>EPL</td>
</tr>
<tr>
<td>Distribution Substation</td>
<td>175.28</td>
<td>500</td>
<td>EPL</td>
</tr>
<tr>
<td>Distribution Feeder</td>
<td>186.53</td>
<td>750</td>
<td>EPL</td>
</tr>
<tr>
<td>Microgrid</td>
<td>232.47</td>
<td>750</td>
<td>EPL</td>
</tr>
<tr>
<td>Island Grid</td>
<td>165.29</td>
<td>500</td>
<td>EPL</td>
</tr>
<tr>
<td>Commercial/Industrial</td>
<td>178.21</td>
<td>500</td>
<td>EPL</td>
</tr>
<tr>
<td>Commercial Appliance</td>
<td>198.01</td>
<td>750</td>
<td>EPL</td>
</tr>
<tr>
<td>Residential</td>
<td>204.06</td>
<td>750</td>
<td>EPL</td>
</tr>
</tbody>
</table>
concerns as operational costs instead of efficiency losses. For this reason, all of these minimum installed costs are attained through architectures which utilize the EPL flow field design operating at a flow rate of 7.78 mL/min/cm² due to the large SOC window which it is able to access and its high energy efficiency. Figures 7.1 and 7.2 show the available depth of discharge and energy efficiency, respectively, for all of the conditions considered in the model and all four flow field designs. One interesting trend that can be observed is that half of the applications achieve this minimum installed cost by operating at a current density of 500 mA/cm², while the other half prove more cost efficient when operating at 750 mA/cm². When examining the application parameters for the cases which can be optimized using the higher current density, it is noticeable that they are the applications with the lowest energy to power ratios. As this ratio shifts further toward high power operation, being able to discharge at a high current to achieve this high power becomes more efficient than maximizing the depth of discharge the battery is able to achieve. The lone exception is the Residential application which has the same 4 to 1 energy to power ratio as the Peaker Replacement and Distribution Substation applications. The major difference here is the magnitude of the energy stored. While the difference in total energy storage required was not enough of a factor to allow the Peaker Replacement application to overtake the Island Grid application in terms of cost efficiency, the energy storage requirement of the Residential application at 0.01 MWh is two orders of magnitude below that of the Island Grid. This is simply not enough storage needed to allow for the additional depth of discharge of the 500 mA/cm² operating point to overcome the savings the 750 mA/cm² operating point offers on cell components.
Figure 7.1. Depth of discharge under all model operating conditions for (a) serpentine, (b) interdigitated, (c) EPL, and (d) aspect ratio flow field designs.
Figure 7.2. Energy efficiency under all model operating conditions for (a) serpentine, (b) interdigitated, (c) EPL, and (d) aspect ratio flow field designs.
A better metric for examination of these use cases is rather the Levelized Cost of Energy Storage (LCOES). This metric accounts for the total fixed cost of the system, but also takes into account the costs associated with operating the system as well as the manner in which the system is used over its installed lifetime. Notably, this means that the on-peak and off-peak cost of electricity will become a factor due to the manner in which this work treats the pumping cost associated with each system. Table 7.3 shows the lowest LCOES of a system for each of the ten use cases mentioned earlier as well as the architecture and operational parameters which produce them. For these results, the smallest total values of the on-peak and off-peak electricity rate, 0.0801 and 0.0296 $/kWh respectively, were used. Because LCOES does not take into account revenue, only the cost and operation of a system, minimizing both of these values generates the lowest operational cost for the system and thus, the lowest possible LCOES.

The most notable change from the installed cost to the levelized cost is that the minimum LCOES for all applications now occurs when using the aspect ratio flow field design at 1.11 mL/min/cm². The two changes show how crucially important it is to manage the pumping requirement for a system. As seen in Figure 7.1 and explored in Chapter 4, the aspect ratio design is best able to balance the high performance at low flow rate of a flow through design with the low pressure drop exhibited by an interdigitated design. This balance allows for improved levelized cost when compared with either more extreme option. This minimum also occurs at different current densities than the minimum installed cost, providing further insight into the factors that truly determine the suitability of a design to a given application. The Transmission System and Island Grid
Table 7.3. RFB system LCOES

<table>
<thead>
<tr>
<th>Application</th>
<th>$/MWh</th>
<th>Current Density (mA/cm²)</th>
<th>Flow Field Design</th>
</tr>
</thead>
<tbody>
<tr>
<td>Transmission System</td>
<td>154.9</td>
<td>500</td>
<td>Aspect Ratio</td>
</tr>
<tr>
<td>Peaker Replacement</td>
<td>162.2</td>
<td>500</td>
<td>Aspect Ratio</td>
</tr>
<tr>
<td>Frequency Regulation</td>
<td>92.3</td>
<td>750</td>
<td>Aspect Ratio</td>
</tr>
<tr>
<td>Distribution Substation</td>
<td>188.2</td>
<td>500</td>
<td>Aspect Ratio</td>
</tr>
<tr>
<td>Distribution Feeder</td>
<td>286.6</td>
<td>500</td>
<td>Aspect Ratio</td>
</tr>
<tr>
<td>Microgrid</td>
<td>114.5</td>
<td>500</td>
<td>Aspect Ratio</td>
</tr>
<tr>
<td>Island Grid</td>
<td>158.8</td>
<td>500</td>
<td>Aspect Ratio</td>
</tr>
<tr>
<td>Commercial/Industrial</td>
<td>322.2</td>
<td>500</td>
<td>Aspect Ratio</td>
</tr>
<tr>
<td>Commercial Appliance</td>
<td>353.0</td>
<td>500</td>
<td>Aspect Ratio</td>
</tr>
<tr>
<td>Residential</td>
<td>358.0</td>
<td>500</td>
<td>Aspect Ratio</td>
</tr>
</tbody>
</table>
applications still have two of the five lowest levelized costs at 154.9 and 158.8 $/MWh respectively, however the Frequency Regulation and Microgrid applications exhibit the two lowest levelized cost figures. While this may seem surprising due to the fact that these two applications showed the worst installed cost, when further examining the ways each of these systems operates it becomes evident why LCOES favors them. The Frequency Regulation and Microgrid applications have the two lowest energy to power ratios at 1 to 2 and 1 to 1 respectively. This means that each battery cycle will take less time to complete compared to systems with much larger ratios. These faster cycles result in less overall operational time for the battery, thus reducing the total operating cost that is accrued over the lifetime of the system. Furthermore, the Frequency Regulation application is the only case where a current density other than 500 mA/cm$^2$ provides the best result. Because this application has such a low energy to power ratio at 1:2, it achieves its lowest LCOES when using a current density of 750 mA/cm$^2$. This result is a perfect example of how LCOES is better able to capture the cost of a system when compared to installed cost. It demonstrates how cost savings can come in the form of lower fixed costs by pursuing applications with high energy to power ratios as in the case of Transmission Systems, or that savings can occur by reducing variable costs as in the Frequency Regulation application. LCOES also demonstrates how RFB systems are poorly suited for smaller scale implementation, as the four highest levelized costs belong to the four smallest systems analyzed.

Comparing the LCOES results for different flow field designs can also provide insight into the ability of each design to provide different advantages when building a
system. Figure 7.3 (a) shows the LCOES for the Transmission System when designed using each flow field at 1.11 mL/min/cm$^2$, where the minimum LCOES values for all 4 designs are found, and all 3 current densities studied. From this figure as well as Figures 7.1 (b) and 7.2 (b) it is clear that the interdigitated flow field operates best when at low flow rates and low current densities in order to take advantage of its low pressure drop at a high efficiency and depth of discharge operating point. Conversely, the EPL design demonstrates the highest LCOES at this low current density and is optimized when operating at 500 mA/cm$^2$, with the 750 mA/cm$^2$ condition showing similar results at 3.1 $$/MWh. This is due to the large pumping costs incurred when operating at such a low current density and the ability of the flow field to achieve high depth of discharge and energy efficiency at high current density and low flow rate as seen in Figures 7.1 (c) and 7.2 (c). The aspect ratio design, as discussed before, occupies a nice middle ground between the interdigitated and EPL designs, showing high enough transport performance with only moderate pumping costs to operate effectively at the increased current density of 500 mA/cm$^2$ with the lowest LCOES of any design. The serpentine design also achieves its best LCOES under these low flow conditions due to its severe pressure drop accrued upon scale up as discussed in Chapter 5. Under such low flow, however, the depth of discharge and energy efficiency are relatively poor as seen in Figures 7.1 (a) and 7.2 (a), leading to an optimal current density of 250 mA/cm$^2$ and making the flow field inoperable at 750 mA/cm$^2$.

While it may seem that cost is always minimized at an extreme with regard to area specific flow rate, with installed cost being minimized at the highest flow rate and
Figure 7.3. Levelized cost of energy storage for the Transmission System application for (a) all four flow field designs at 1.11 mL/min/cm² and three different current densities, and (b) the interdigitated design at all flow rates and current densities analyzed.
LCOES being minimized at the lowest flow rate, this is not always the case. Figure 7.3 (b) provides an interesting insight by examining the LCOES for the Peaker Replacement application at all three current densities when using an interdigitated flow field design. While the minimum overall LCOES occurs at the 1.11 mL/min/cm² and 250 mA/cm² condition, for higher current densities the minimum levelized cost occurs at intermediate flow rates of 3.33 mL/min/cm² and 4.44 mL/min/cm² for the 500 mA/cm² and 750 mA/cm² cases respectively. This is due to the sharp increase in both depth of discharge and energy efficiency at these low flow rates and high current densities as seen in Figures 7.1 (b) and 7.2 (b). Additionally, the cycle times at these higher current densities is shorter, further muting the effect of pumping costs as the flow rate is increased. Past these minimums, the increase in depth of discharge and energy efficiency declines as the pressure drop increases at a faster rate, and the cost begins to increase.

While these cost based metrics are very useful for evaluating different architectures for various applications, it is also necessary to take into account the operational profit that can be derived from a system built with a given architecture. To this end, three additional metrics are examined, Net Present Value (NPV), Payback Period, and Rate of Return. Table 7.4 shows the NPV, Payback Period, and Rate of Return for all ten applications. In order to ascertain the best case scenario for these metrics, the results were obtained using the greatest difference between on-peak and off-peak electricity rate, $0.288 and $0.0455 respectively. This will allow for the largest gross income possible. When examining these results, it becomes immediately obvious that redox flow batteries are not suitable for the four smallest applications, Distribution
### Table 7.4. RFB system NPV, Payback Period, and Rate of Return

<table>
<thead>
<tr>
<th>Application</th>
<th>NPV ($MM)</th>
<th>Payback Period (years)</th>
<th>Rate of Return</th>
<th>Flow Field Design</th>
<th>Flow Rate (mL/min/cm$^2$)</th>
<th>Current Density (mA/cm$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Transmission System</td>
<td>160.000</td>
<td>5.519</td>
<td>3.624</td>
<td>Interdigitated</td>
<td>1.11</td>
<td>250</td>
</tr>
<tr>
<td>Peaker Replacement</td>
<td>60.900</td>
<td>6.087</td>
<td>3.285</td>
<td>Aspect Ratio</td>
<td>1.11</td>
<td>500</td>
</tr>
<tr>
<td>Frequency Regulation</td>
<td>7.110</td>
<td>1.623</td>
<td>6.161</td>
<td>Aspect Ratio</td>
<td>1.11</td>
<td>750</td>
</tr>
<tr>
<td>Distribution Substation</td>
<td>0.860</td>
<td>8.087</td>
<td>2.473</td>
<td>Aspect Ratio</td>
<td>1.11</td>
<td>500</td>
</tr>
<tr>
<td>Distribution Feeder</td>
<td>-0.236</td>
<td>24.000</td>
<td>0.824</td>
<td>Aspect Ratio</td>
<td>1.11</td>
<td>500</td>
</tr>
<tr>
<td>Microgrid</td>
<td>1.302</td>
<td>3.388*</td>
<td>5.903</td>
<td>Aspect Ratio</td>
<td>1.11</td>
<td>750</td>
</tr>
<tr>
<td>Island Grid</td>
<td>1.480</td>
<td>5.768</td>
<td>3.467</td>
<td>Interdigitated</td>
<td>1.11</td>
<td>250</td>
</tr>
<tr>
<td>Commercial / Industrial</td>
<td>-0.388</td>
<td>27.935</td>
<td>0.358</td>
<td>Aspect Ratio</td>
<td>1.11</td>
<td>500</td>
</tr>
<tr>
<td>Commercial Appliance</td>
<td>-0.049</td>
<td>53.149</td>
<td>0.1881</td>
<td>Aspect Ratio</td>
<td>1.11</td>
<td>500</td>
</tr>
<tr>
<td>Residential</td>
<td>-0.0025</td>
<td>55.378</td>
<td>0.1861</td>
<td>Aspect Ratio</td>
<td>1.11</td>
<td>500</td>
</tr>
</tbody>
</table>
Feeder, Commercial/Industrial use, Commercial Appliance, and Residential. Since all four of these cases exhibit negative NPV, they do not offer value as an investment and should not be pursued. This is due to the low total amount of energy discharged over the lifetime of the project. Since only a small amount of total energy is discharged, there is not enough revenue to make up for the capital costs of the system, and the projects are considered poor investments. This suggests that there is a minimum lifetime energy storage requirement for a system to be profitable.

Another notable result is that the aspect ratio design is no longer the predominant flow field design as it was when examining LCOES. The interdigitated design achieves the highest NPV for both the Transmission System and Island Grid applications. As noted previously, these two application have the highest energy to power ratio of all systems at 8:1. This will result in longer cycle times compared to other applications, regardless of current density, and thus places a greater importance upon operational costs, specifically pumping costs. As seen previously, the interdigitated design is best employed under conditions where it can use its low pressure drop, high efficiency, and high depth of discharge at low flow rate and low current density conditions to minimize pumping costs. These high energy, low power scenarios provide the perfect opportunity for such a flow field design to thrive.

It comes as no surprise that the larger systems examined also allow for the highest NPV, with the Transmission System and Peaker Replacement applications at 160.00 and 90.60 $MM respectively. More interestingly, however, is that the shortest payback periods belong to the low energy to power ratio applications. The Frequency Regulation
case has the shortest payback period at 1.623 years, with the Microgrid application next shortest at 3.388 years. This result arises due to two main factors, the size of the systems, and their ability to keep operating costs low. Because these systems are on the smaller side in terms of both power and energy capacity, the total cost for installation is also small, in spite of the cost per kWh figure exceeding that of their larger counterparts. Additionally, because these systems have a low energy to power ratio, they boast fast cycles and minimal operating costs and charging costs. This is further evidenced by both systems operating optimally when using a 750 mA/cm² current density which further lowers cycle times. By keeping these costs down, the net income for the systems remains high in spite of the smaller amount of energy they discharge in a cycle. This low cost operation resulting in relatively high net income, combined with a low total installation cost, allows for a much quicker repayment of the initial investment, although the overall values of the projects are much lower as evidenced by their NPV results.

Another useful aspect of cost analysis is to help guide the future of research by identifying the parameters that are most important in reducing the installed and levelized cost of redox flow battery systems. Figure 7.4 shows the minimum installed and levelized cost for the Transmission System and Frequency Regulation applications when altering the cost of various components including vanadium, membranes, bipolar plates, and electrodes by 10%, 25% and 50% in either direction. This allows for a comparison of the benefit of reducing these various component costs for high energy to power ratio applications and low energy to power applications. From this figure it is clear that both the LCOES and installed cost are most sensitive to changes in the vanadium price, as
Figure 7.4. Change in minimum system LCOES and installed cost when increasing and decreasing (a) vanadium cost, (b) membrane cost, and (c) bipolar plate and electrode cost.
these curves have a steeper slope when compared to those for the membrane and bipolar plate/electrode curves. The larger, higher energy to power ratio Transmission System application is more sensitive to such changes in active specie cost than the smaller Frequency Regulation system, as the larger amount of vanadium required to store such an amount of energy dominates the cost metrics for this system. Indeed, when reducing the vanadium cost by 50%, the LCOES for this large system reduces to 63.4% of its initial value and the installed cost reduces to 53.9% of the initial value.

When examining the smaller, low energy to power ratio Frequency Regulation system, it becomes evident that the vanadium cost still has the highest sensitivity for both LCOES and installed cost, however the membrane cost is not far behind when considering installed cost. When reducing the vanadium cost for this system by 50%, the LCOES and installed cost decrease to 75.9% and 72.8% of their initial values. If this same 50% reduction in cost is instead applied to the membrane, the levelized cost does not change appreciably, resulting in a slightly lower 91.1% of the initial value. The installed cost changes much more dramatically, however, resulting in an installed cost of 80.6% of the initial value, over twice the decrease seen in the LCOES. Both of these values are significantly higher than those for the Transmission system, which only sees reductions to 96.7% of initial cost for both the LCOES and installed cost. This makes sense as the energy to power ratio dictates where the main costs of the system should lie. A high energy to power ratio means that costs associated with increased storage will display more sensitivity, whereas a low energy to power ratio application will have higher sensitivity to costs associated with the cell hardware. Observing Figure 7.4 (c), it
can be deduced that the membrane is the cell hardware component that dominates this portion of the cost, as even halving the bipolar plate and electrode costs produces minimal cost reduction to 96.5% of initial installed cost, even for the Frequency Regulation application.

While examining the sensitivity of the system cost to changes in component costs is useful, such analysis can also be undertaken on cell performance metrics. Figure 7.5 (a) shows the change in system costs for the Transmission System and Frequency Regulation applications with improved depth of discharge. The difference in the response of these two applications serve to prove an important point. The high energy to power ratio Transmission system sees significant cost savings when increasing the depth of discharge, decreasing to 80.1% of the original LCOES and 87.4% of the installed cost when the depth of discharge is increased by 20%. Conversely, the Frequency Regulation scenario with its lower ratio only decreases LCOES to 84.7% and installed cost to 90.8% of the original cost. This highlights how research focus should shift based upon the intended application. Whereas a high energy application should focus efforts on the storage medium, mass transport, and depth of discharge, a high power application can still focus on these areas, but can additionally seek to improve the membrane as a pathway to lower costs as exemplified in Figure 7.4 (b).

One final observation can be made from Figure 7.5 (a). The installed cost curves for both the Transmission System and the Frequency Regulation applications show inflection points at 10% and 15% additional depth of discharge. This is due to the fact that depth of discharge inherently carries an upper limit. While these two scenarios
Figure 7.5. Change in system cost for at 5%, 10%, 15%, and 20% increases in (a) depth of discharge for the Transmission System and Frequency Regulation applications and (b) change in cell voltage for all systems.
initially had optimal installed costs when using an EPL flow field design at 7.77 mL/min/cm² and 500 mA/cm², when this condition reaches a maximum allowable depth of discharge of 100%, other conditions begin to approach and even overtake the cost per kWh of this architecture. In both of these cases, the inflection point marks the point beyond which it becomes more advantageous to increase the current density from 500 mA/cm² to 750 mA/cm². Even though these higher current density conditions still lag behind in terms of depth of discharge, the cap that is placed on the 500 mA/cm² condition allows them to narrow it enough that the savings with respect to the power provided and cell components needed overcomes this gap.

Figure 7.5 (b) shows the change in system cost for increases in cell voltage of up to 20%. Only one curve is shown as this rate of change is nearly identical for the LCOES and installed cost, as well as for both the Transmission System and Frequency Regulation applications. When the cell voltage is increased by 20%, the system cost is decreased to 83.3% of its initial value. While this cost sensitivity still does not manage to overtake that of the vanadium cost and depth of discharge for the Transmission System, it makes the cell voltage the highest sensitivity parameter for a low energy to power ratio application such as Frequency Regulation.

As mentioned previously, changes in current density can also have a substantial impact upon the cost of an RFB system. Figure 7.6 shows the change in LCOES and installed cost under various conditions. Figure 7.6 (a) shows the change in LCOES for the Frequency Regulation application when using the optimal aspect ratio flow field as well as the Transmission System when using both an EPL and an interdigitated flow
Figure 7.6. Change in (a) LCOES for the Transmission System application when using EPL and interdigitated designs and Frequency Regulation when using aspect ratio design and (b) installed cost when using EPL design for all three current densities.
field. The trends in this figure show how each flow field can exhibit unique responses to a change in current density depending on the application. While the EPL design clearly benefits from higher current densities, the inverse is true for the interdigitated design in spite of the fact that the application is the same. Furthermore, even when changing the application, the aspect ratio design shows a trend similar to that of the EPL design, with the optimal current density occurring at 750 mA/cm$^2$. This is again due to the unique advantages each design possesses. The interdigitated design benefits from a low pressure drop, and therefore can operate at such a low current density without accruing excessive pumping losses. The poorer mass transport of this design, however, makes it unsuitable for high current operation. The inverse is true of the other two flow fields. Their high pressure drop precludes them from operating at low current densities, but their superior mass transport allows them to operate at high current and discharge quickly to mitigate losses.

Figure 7.6 (b) shows the installed cost difference when altering the current density for the Transmission System and Frequency Regulation cases when using the EPL flow field. This plot clearly demonstrates that unique optimization points exist based upon the application, even when using the same flow field design. While the Transmission System installed cost is relatively constant and has a minimum at 500 mA/cm$^2$, the Frequency Regulation scenario shows a clear improvement as it trends to higher current densities. This shows that increasing current density during operation should be a research focus only when concerned with low energy to power ratio applications.
7.4 Conclusions

The economic analysis of redox flow battery design concerns is a highly complex field dealing with numerous tradeoffs and optimizations to be made. One of the most important parameters to consider when examining what operating conditions and design choices must be made when designing a system is the energy to power ratio of the application. This ratio dictates the relative sizes of the various costs associated with the systems, most notably the operating costs and the fixed costs of installation. Additionally, the energy to power ratio has a strong influence upon the cost sensitivity of the system to changes in component costs and changes of operational parameters. The model shows that regardless of application or cost metric, the cost of vanadium and the voltage of the cells are key factors in the system cost, while changes in the cost of electrodes and bipolar plates can be considered negligible. Increased depth of discharge is most beneficial for high energy to power applications, while membrane cost is a substantial factor in the cost of low energy to power cases. Finally, optimization of different economic metrics leads to different optimal operating conditions and architectures, even for the same application. For example, the Transmission System application attains its minimum installed cost using an EPL flow field at 500 mA/cm$^2$, its minimum LCOES using an aspect ratio flow field at the same current density, and its maximum NPV using an interdigitated flow field at 250 mA/cm$^2$. This goes to further prove the assertion that a single, optimal design for all cases is unlikely and that design decisions should be made on a case by case basis taking into account the application and knowledge of the tradeoffs within the RFB system.
7.5 Acknowledgments

The authors would like to acknowledge the University of Tennessee Chancellor’s Fellowship, the Bredesen Center for Interdisciplinary Research and Graduate Education, and the James A. Euler Memorial scholarship for support.
8.1 Summary of State of the Art

As intermittent renewables become more cost competitive and increase their share of the energy mix, grid energy storage will become an increasing necessity as well. One promising technology for this application is the redox flow battery due to its scalability and decoupled power and energy capacities. For this technology to become cost competitive, however, improved energy efficiency at high current density through reduced mass transport polarization is required. A state of the art architecture that accomplishes this goal has been pioneered by Aaron et al. using a zero gap architecture.\textsuperscript{16} Mench, Zawodzinski, and their colleagues have managed to reach current densities in excess of 400 mA/cm\textsuperscript{2} with efficiencies of 80\% by using treated 10AA carbon paper as well.\textsuperscript{106}

Due to the shift to this more condensed zero game architecture as opposed to a flow by gapped design, the mass transport concerns present in these systems, specifically the design and implementation of a flow field intrinsic upon the bipolar plate, has become an area of much interest. Many studies approach this concern with the goal of specifying an optimal flow field design or comparing two or more designs to determine which is superior.\textsuperscript{18,20,22,23,107,108} While these types of studies can be instructive in certain scenarios, they fail to characterize flow field design in the context of a larger system and take into account the application intended. Furthermore, many studies examine individual parameters which have an impact upon the mass transport polarization in these systems such as electrolyte flow rate and electrode properties, but fail to take into account how these parameters interact with different flow field designs and the impact these
interactions have upon the system level efficiency of the system.\textsuperscript{34–37,42,50–53} Scale-up of flow field designs is also sparsely examined in the literature and is limited to work on PEM fuel cell flow fields as well as a study by You et al. examining an interdigitated flow field design upon scale up.\textsuperscript{109,110}

Stack design has been examined in the literature, but similar to the analysis of flow field design focuses too much on identifying a panacea solution to a complex series of tradeoffs. Studies conducted by Zhao et al. and Park et al. examined the experimental performance of kW class VRB stacks, reporting voltage, coulombic, and energy efficiencies. The values reported were 82.2\%, 92.4\%, and 76\% respectively when cycling at 60 mA/cm\textsuperscript{2}.\textsuperscript{76,77} Kim et al. used a combination of experimental and modeling approaches, finding a large drop in energy efficiency when increasing the number of cells in the stack.\textsuperscript{78} A number of computational approaches to stack analysis have also been undertaken.\textsuperscript{79,81,82} The most notable of these works in regards to this study is that published by Wei et al. This work used FEM in order to examine stack temperature, as well as the impact of three different flow field designs on the uniformity of electrolyte flow in the stack. The study concluded that no flow field produced the worst results, followed by a serpentine parallel design, and a standard serpentine design as the best. While many of these studies are quite robust, they fail to take into account the system level efficiencies, pumping concerns, and application based design necessary to fully characterize stack design.

Numerous shunt current modelling studies have been conducted, all utilizing a resistor network in conjunction with modelled solid phase potentials to determine the
shunt through the manifold. Work done by Fink and Remy takes a more direct experimental approach to this phenomenon by directly measuring the shunt current in an external manifold with hall effect sensors, reporting a coulombic loss of 1.8% in the system. Networks of multiple stacks have also been examined for shunt current concerns including systems connected hydraulically in series and in parallel. None of these studies is capable of a direct experimental measurement of shunt current in an operating battery with an internal manifold, however.

There have been numerous economic analyses which have attempted to quantify the present state of cost competitiveness for these systems as well. Some of the most useful work in this arena was done by Moore et al. examining how cost should drive the design of RFB systems as well as the differences in cost between a VRB and a regenerative hydrogen fuel cell. Another study by Viswanathan et al. further developed the cost model for VRBs to take into account shunt current and pumping losses, while Singh and McFarland did similar work on the hydrogen/bromine chemistry. Work by Dmello et al. examined electrolyte material cost with respect to both aqueous and non-aqueous chemistries determining that there are limited opportunities for cost reduction in aqueous systems. Most recently, Soberanis et al. published a study examining three scenarios for RFBs to be used as a large scale energy storage system. The study concludes that high power demand applications are most favorable to these systems and have opportunities for significant cost savings. These models are a solid foundation upon which to build a newer analysis which takes into account flow field design, experimental data, and operating conditions to assess cost.
8.2 Summary of Work

Chapters 3 and 4 of this work are concerned with examining the role flow field design plays in RFB mass transport overpotential as well as overall cell energy efficiency. Chapter 2 explored the different transport mechanisms employed by two of the most common flow fields found in the literature, interdigitated and serpentine. It was discovered through the use of Comsol CFD simulation as well as a novel ex-situ flow visualization diagnostic that the interdigitated design uses forced convection with a flow preference towards the later digits while the serpentine design allowed the pressure drop in the channel to force the electrolyte to “jump” into the electrode domain over the lands. These conclusions were further supported by current distribution data showing the current for the interdigitated design highest in the center of the electrode towards the outlet and the serpentine design highest along the edges of the electrodes over the lands at the switchbacks.

Discharge and polarization curves taken for these two flow field designs revealed that the interdigitated design performed best when using one layer of SGL 10AA carbon paper as an electrode. At 20 mL min\(^{-1}\) the interdigitated design was able to discharge 15% more capacity at 250 mA cm\(^{-2}\) and 33% more capacity at 500 mA cm\(^{-2}\). Additionally, the interdigitated design reached a current density of 800 mA cm\(^{-2}\) compared to only 450 mA cm\(^{-2}\) for the serpentine design while also boasting a lower pressure drop. While these findings are supported by the Comsol results showing higher average velocity magnitude through the electrode for the interdigitated design, when increasing either the electrode thickness or flow rate of electrolyte, mass transport
differences between these two designs decreased and became negligible. This was determined to be due to a lower pressure drop through the electrode domain inciting increased flow into the electrode when using a serpentine design. This does not occur in the interdigitated design as all of the electrolyte is already forced through the electrode domain, thus resulting in lower velocity as the cross sectional area for flow is increased.

Chapter 4 uses the findings from Chapter 3 to inform two new flow field designs, Equal Path Length and aspect ratio, to take advantage of the transport mechanism used in the interdigitated design. Using an energy analysis of discharge curves for each design, the conclusion can be made that for high current density, low flow rate operation parasitic pumping losses are negligible, on the order of 1%. This allows flow field designs like the EPL design to dominate by forcing all of the electrolyte to flow through the electrode domain between just two supply channels. The work also concludes that at low current density and high flow rate, these pumping losses become meaningful, up to 7% of total energy discharged. When discharging at 500 mA cm$^{-2}$, the EPL design is able to discharge 25% and 73% more energy than the interdigitated and serpentine designs respectively. Due to high pressure drop, however, the EPL design was found to be incapable of operating at high flow rates.

To ameliorate this issue, the aspect ratio design was proposed and attained similar mass transport performance to the EPL design as seen by the similar limiting current densities of their polarization curves at 600 mA cm$^{-2}$. This design uses a wider active area to produce a shorter path length for the electrolyte flow in the electrode. This allows for greatly reduced pressure drop over an order of magnitude lower than that of the EPL.
design when simulated at 100 cm$^2$. Energy analysis of these two designs when cycling at 200 mA cm$^2$ shows the impact of this reduced pressure drop as the aspect ratio achieves an energy efficiency of 54% compared to the EPL design energy efficiency of only 47% due to parasitic pumping losses. This study also concludes that operating conditions are extremely important to consider when designing a flow field, as when discharging at 50 mA cm$^2$ the aspect ratio and EPL flow fields lose 19.6% and 30.6% respectively of the total energy discharged to pumping concerns. Furthermore, there exists an ideal flow rate for each flow field at each operating condition. As flow rate is increased, it is shown that the increase in power density grows smaller even as the pumping power continues to increase steadily. Eventually the increase in pumping power overtakes that of the cell discharge power and the optimal flow rate is reached. The final conclusion of the chapter demonstrates how the larger inlet and outlet region of the aspect ratio design causes a loss of power compared to the EPL design and should be considered when using this flow field.

In Chapter 5 the scale-up of the active area of the cell is considered for all 4 flow field designs introduced in Chapters 3 and 4. From polarization curves taken with 5 cm$^2$, 9 cm$^2$, and 25 cm$^2$ flow fields while keeping a constant area specific volumetric flow rate it was determined that the interdigitated design sees almost no increase in limiting current density while the serpentine, EPL, and aspect ratio designs see increases of 84.6%, 12.5%, and 13.3% respectively when active area was increased from 5 to 9 cm$^2$. This was determined to be due to the rate of increase of the cross sectional area for flow compared to the increase in flow rate. It was concluded that each flow field would have a
different rate of velocity magnitude change as flow field active area was increased. Based on Comsol simulations of larger flow field designs, this led to the prediction that the serpentine design would have a higher velocity than the aspect ratio design once reaching an active area of 50 cm$^2$, but a significantly higher pressure drop beginning at 25 cm$^2$. These simulated results are supported by discharge data obtained at mass transport limited high current density conditions. As the serpentine design is scaled up and gains velocity, the available capacity increases dramatically. The interdigitated design sees no such increase upon scale up due to it’s negligible velocity gains, while the EPL design sees no increase as its velocity magnitude was already past the saturation point where advective transport is not the limiting factor. The aspect ratio design still sees an increase upon scale up as it reaches this saturation point.

When examining the gross discharge energy of these designs upon scale up an identical trend is seen. The net energy discharged tells a different story, however. At smaller active areas the pumping loss is around 1% of energy discharged. For serpentine and EPL designs at 25 cm$^2$, however, the pumping concerns become important. The EPL design discharges 1.528 Wh at 500 mA/cm$^2$ and 1.137 Wh at 750 mA/cm$^2$ of gross energy, but only 1.112 Wh and 0.867 Wh when taking pumping losses into account. The serpentine design has a similar issue, with net discharge energies of 1.248 Wh and 0.874 Wh. While the aspect ratio design was not tested at this larger active area, these net energy results suggest that it may be the more promising design for scale-up under these conditions.

Chapter 6 applies the principles explored in chapters 3 through 5 to a short 4 cell
RFB stack and investigates stack specific design concerns. A 4 cell RFB stack was designed and fabricated to allow for analysis of cycling efficiencies and pumping concerns, as well as the implementation of a novel in-situ shunt current measurement technique. The analysis in this portion of the work revealed that increased current density and rapid discharging is not always sufficient to overcome the large pumping losses associated with stack operation. Additionally, it was discovered that improving mass transport performance through increased flow rate is far less plausible when operating a stack due to the necessity of the flow rate to scale with the number of cell in the stack.

Shunt currents in the 4 cell stack were found to reach up to 19.082 mA amounting to a self discharge current equal to 1.91% of the operating current of the system when cycling at 20 mA cm$^{-2}$. While these losses may seem miniscule at this scale, it is predicted that they could reach upwards of 9% of the total system cycling current through the addition of just six more cells to bring the stack up to a total of 10 cells. Furthermore, it was demonstrated that the mode of system operation can be an additional factor to consider when evaluating shunt current. A potentiostatic charge compared with a galvanostatic charge was found to produce an additional 0.69 mA of shunt current for just the small four cell stack evaluated in this study. When these findings are applied to a larger system, such differences are likely to increase further.

In Chapter 7, the design tradeoffs evaluated in previous chapters were examined through an economic lens to put these conclusions in the context of ten real world applications. This initial analysis concluded that the most cost efficient applications in
terms of installed cost are those with high energy to power ratios such as the Transmission System case at 160.72 $/kWh and the Island Grid case at 165.29 $/kWh.

When taking operating costs into account by evaluating the levelized cost, however, the two applications with the lowest energy to power ratio, Frequency Regulation and Microgrid, become the most economically feasible. This is due to their low operational costs arising from their shorter operational cycles, although it should also be noted that the Transmission System and Island Grid remain in the lowest five LCOES figures.

When examining how these metrics are impacted by flow field design, the ideal operating conditions for each flow field are uncovered. The interdigitated design operates best at a low current density and low flow rate to take advantage of its low pressure drop at a high efficiency operating point. The EPL design is more cost effective at high current densities due to its excellent mass transport characteristics providing good energy efficiency under such conditions and higher power operation mitigating pumping losses. The aspect ratio design occupies a middle ground between these two designs as it combines a lower pressure drop with a high power operating condition.

When examining the Net Present Value and Payback Period for these applications and operating conditions, it can also be concluded that RFBs are more suitable for larger scale storage projects. The three smallest cases examined, Commercial/Industrial, Commercial Appliance, and Residential, all have negative NPVs to go along with lengthy Payback Periods. The large, high energy to power ratio projects were found to have the highest NPVs and were best designed using the interdigitated flow field operating at a low current density. The shortest Payback Periods were found to belong to the low
energy to power ratio systems which tend to be of medium overall size and are best operated using an aspect ratio design at higher current density.

Examining the cost sensitivity of these systems to various inputs provided more insight. Vanadium cost was determined to be the single greatest driver of cost for any application, while membrane cost becomes a close second when examining low energy to power ratio applications. Bipolar plate and electrode costs were found to be negligible under all conditions. Depth of discharge has a significant effect on all systems, similar to the cost impact of vanadium cost, but due to the inherent upper limit of this variable the cost savings for the installed cost have diminishing returns as the EPL flow field reaches 100% DoD. Changes in current density were found to have varied effects depending on the application, flow field design, and evaluation metric in question. For example, the EPL design provides reduced LCOES when increasing current density and exhibits the same trend for most applications when examining installed cost. The design does exhibit an inflection point for installed cost for high energy to power ratio applications at an intermediate current density however. The interdigitated design has the opposite trend when examining LCOES, resulting in increased costs when increasing current density. Due to its similarity to the EPL design, the aspect ratio design shows similar trends, however the relative magnitudes of the cost and locations of any inflection points will differ.

8.3 Recommendations

While this dissertation provides numerous new results and insights into redox flow battery design, it is also clear that there are numerous opportunities to expand upon
the findings presented here. It was therefore the objective of the author to ensure that all hardware and models used were capable of allowing for the continuation of this work by future generations of researchers.

8.3.1 Flow Field Design Study

The results in Chapters 3 and 4 provide the framework for a new approach to thinking about how flow field designs are evaluated. By shifting the approach to an understanding of the transport mechanism used by each design and the unique tradeoffs that they offer, it is possible to determine that each flow field has an ideal application for which it should be utilized. In this work, the focus of the modeling efforts is based entirely in analysis of the fluid dynamics within each flow field design to determine flow patterns, electrolyte velocities, and pressure drops. The addition of an electrochemical simulation in conjunction with this CFD simulation would provide additional insights into reaction locations and local concentration polarizations that develop within the cell for each flow field design. Such an approach would be easily validated with the use of current distribution experiments as seen in Chapter 3. This would provide another level of predictive power with regard to flow field mass transport performance and could result in the development of empirical equations relating the various simulation parameters to the experimental performance of a design.

An additional avenue that could be explored with regard to this study is an optimization approach to flow field design. Having identified the type of transport mechanism that is ideal for a given application, the flow field design in question could be optimized to ideally balance the numerous tradeoffs discussed throughout this work. Examples of parameters that should be examined include the channel to land ratio in both
serpentine and interdigitated designs, the length to width ratio in the aspect ratio design, as well as channel depth and width in all designs. The impact of all of these parameters on the mass transport overpotential, pressure drop, and system energy efficiency provides a complex optimization problem that can provide fodder for a wealth of future studies.

8.3.2 Flow Field Scale-Up Study

The interaction between a given flow field design, mass transport performance, and the size of the active area of a cell is notable enough to warrant its own consideration separate from the flow field design study mentioned previously. This work can be seen as a bridge between the single cell laboratory scale work done in Chapters 3 and 4 and the full stack and cost model work of Chapters 6 and 7. As seen in the results of this chapter, the flow field design and mass transport mechanism chosen can have a great impact upon the performance of a cell when the active area is increased to more commercially viable sizes. This work only experimentally examines these phenomena up to active areas of 25 cm² and only simulates these flow field designs up to 100 cm².

Similarly to the recommendation for the flow field design study, an optimization approach to flow field scale up is an area that has not been explored, but could have a tremendous impact upon the field. As noted with both the serpentine and interdigitated flow field designs, the addition of extra channels and lengths of channels upon scale up creates additional complexity when examining these types of designs at larger active areas. This would likely mean that optimal channel to land ratios, numbers of switchbacks and digits, and other geometric factors will differ depending on the size of the active area investigated. While in this work, none of these parameters were modified so as to generate a true comparison, a study which examines how these factors can be
scaled with the active area size would provide even more insight into the scalability of these designs.

8.3.3 RFB Stack Performance Study

As seen in Chapter 6, the concerns present in a full RFB stack are similar in many ways to those present in a single cell. The mass transport and parasitic losses are of utmost importance to overall system performance. For this work, the system was examined under relatively stable operating conditions to demonstrate these facts. Subsequent work on this system should look to expand the range of operating conditions examined and the variety of parameters measured. While the system is equipped to measure temperature distribution throughout the stack, this metric was not employed in this study. Additionally, stacks of different sizes, with different manifold configurations, and with different flow field designs could also be studied.

8.3.3 RFB Stack Shunt Current Study

Also introduced in Chapter 6 is a novel method of measuring the shunt current present in an RFB stack. This method provides a means to directly measure the shunt within the manifold and examines how this self discharge is effected by the operating conditions of the system. While this proof of concept study presented here is ground breaking, it focuses mainly on the very carefully controlled operating conditions mentioned in the previous section and examining the impact they have on the shunt current. Future work would be able to examine this shunt current as a function of a number of other critical stack parameters, namely the size of the stack, the manifold architecture and orientation, and the concentration and composition of the electrolyte.
An examination of the relative benefits and comparability of internal and external manifolding would also provide useful insights and allow for a testbed which could be more readily modified in order to study manifolding concerns within the stack. The novel shunt current measurement technique could still be employed in this case, and would provide useful data to validate assumptions made about stack manifolding design.

8.3.4 RFB Cost Analysis

This chapter, in spite of the tremendous amount of insight and analysis it provides, is perhaps the one with the most opportunity for continued exploration. The major focus of Chapter 7 is the impact that flow field design choice and mass transport considerations have on the cost efficiency and economic feasibility of an RFB system in various real world applications. Such analysis is novel and allows for a number of interesting conclusions to be made about what is really important when designing an RFB system, however, there are numerous other concerns present within these systems which could benefit from the same treatment.

The addition of a similar study taking into account crossover, ohmic losses, and other membrane concerns would be a logical next step in this approach. This aspect of the RFB system involves another unique tradeoff between ohmic losses and crossover similar to those discussed when examining the mass transport in this work. Additionally, as is concluded in chapter 7, the membrane is one of the most crucial components when examining the system cost of RFBs, particularly when dealing with low energy to power ratio applications. The inclusion of crossover into this analysis would also be very impactful, as the electrolyte cost is the most important driver for system cost under all applications.
8.4 Overall Conclusions and Outlook

The fundamental goal of this dissertation was to examine the design tradeoffs present in redox flow batteries with respect to the mass transport and fluid dynamics within the system. Two commonly used flow field designs, serpentine and interdigitated, were analyzed in order to determine the different mass transport mechanisms they employ and under what conditions each of these mechanisms would be most advantageous. A novel flow visualization technique was developed in order to validate the velocity distributions obtained from a Comsol CFD simulation. From these findings, two new flow field designs were developed and tested, and Equal Path Length design and an aspect ratio design, in order to take advantage of the forced convection used to great success by the interdigitated flow field design. All four of these designs were evaluated based on their electrochemical performance as well as the energy efficiency they were able to provide. From this analysis it could be concluded that increased parasitic pumping losses from increased pressure drop can be considered negligible at high power conditions, but are a serious concern requiring a different design approach at low power, high energy conditions.

These same four flow field designs were also examined with regard to scaling up their active area sizes to reflect more commercially realistic systems. This analysis confirmed many of the previous findings regarding the role that pressure drop and parasitic pumping losses play at different operating conditions. Additional insights were also drawn regarding the rapid rate of pressure drop increase upon scaling up the
serpentine design, causing it to be less favorable in that regard then the aspect ratio design.

Many of the findings and evaluation methods presented previously were applied to a small four cell RFB stack in order to show their applicability to larger scale systems. Similar conclusions were reached and it was also determined that pumping concerns play an even greater role in stack design as the flow rate must scale with the number of cells in the stack. A novel in-situ shunt current measurement technique was also demonstrated, allowing for the direct measurement of this self-discharge in an internal manifold for the first time. The difference between the shunt current during different methods of charging was also explored and it was concluded that once again, operating conditions must be accounted for during RFB design.

A cost model was developed in order to examine how these experimental findings and different design choices would impact system cost. This provided a context for the work of the previous chapters in terms of real world applications. It was further demonstrated that each design choice has a unique impact on different cost metrics and that more than just the optimal design for electrochemical performance is dependent on application. Cost sensitivities for various model parameters were also investigated, identifying the areas for research that are most promising for reducing the overall system costs to the targets identified to make them commercially viable.

This thesis demonstrates a new approach to examining the design aspect inherent to redox flow batteries. These methods along with the tools developed will allow for greater predictive power and more informed design decisions when creating the next
generation of these systems. All of the components and tradeoffs analyzed in this work have large impacts not only on the system performance, but equally important, the system cost. With the proper application of these tools and analysis, future designs can be optimized and costs reduced as these systems move towards becoming the solution to the problem of grid energy storage.
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APPENDIX
Appendix A: Flow Field Thermal Visualization Videos

File 1 Video 3.1. Thermal visualization video of the interdigitated design…………………………………………………Interdigitated_Flow.mp4
File 2 Video 3.2. Thermal visualization video of the serpentine design………………………………………………………Serpentine_Flow.mp4
File 3 Video 4.1. Thermal visualization video of the flow through design………………………………………………………Flow_Through_Flow.mp4
VITA

Jacob R. Houser was born in Cincinnati, OH and grew up in Buffalo, NY. From a young age he showed a fascination and aptitude for mathematics and science. He graduated from Rensselaer Polytechnic Institute in 2012 with a dual degree in Mechanical Engineering and Management. He continued his academic pursuits at the University of Tennessee, receiving a PhD in Mechanical Engineering under the guidance of Matthew Mench. Jacob is a fellow in the Bredesen Center for Interdisciplinary Research and Graduate Education in addition to a Chancellor’s Fellow in the Mechanical, Aerospace, and Biomedical Engineering Department. He is passionate about mechanical design and is pursuing Design Engineering work in industry.