DESIGN, FABRICATION, AND PERFORMANCE EVALUATION OF A REDOX FLOW BATTERY

by

Ethan A. Wise

A thesis submitted to the Faculty of the University of Delaware in partial fulfillment of the requirements for the degree of Bachelor of Mechanical Engineering with Distinction

Spring 2019

© 2019 Ethan A. Wise All Rights Reserved

DESIGN, FABRICATION, AND PERFORMANCE EVALUATION OF A REDOX FLOW BATTERY

by

Ethan A. Wise

Approved:

R. Valery Roy, Ph.D. Professor in charge of thesis on behalf of the Advisory Committee

Approved: _

Ajay K. Prasad, Ph.D. Committee member from the Department of Mechanical Engineering

Approved: _

Matthew DeCamp, Ph.D. Committee member from the Board of Senior Thesis Readers

Approved: _

Michael Chajes, Ph.D. Chair of the University Committee on Student and Faculty Honors

TABLE OF CONTENTS

LI LI A]	LIST OF TABLES v LIST OF FIGURES vi ABSTRACT viii				
C	hapte	er			
1	INT	RODUCTION AND BACKGROUND	L		
	$\begin{array}{c} 1.1 \\ 1.2 \end{array}$	Operating Principles	1 2		
	1.3	Redox Couples	3		
	1.4	Design Considerations	1		
	1.5	Performance Benchmarks	5		
	1.6	Thesis Outline	3		
2	DES	SIGN AND FABRICATION	7		
	2.1	Cell Design	7		
	2.2	Fabrication)		
	2.3	Balance of Plant)		
	2.4	Electrolyte Preparation)		
3	CEI	LL PERFORMANCE	2		
	31	Charging Efficiency	2		
	3.2	OCV Stability	3		
	3.3	Polarization	5		
			_		
		3.3.1 State of Charge)		
		3.3.2 Flow Kate	5		
		3.3.3 Electrode Compression) 1		
		3.3.4 Membrane Thickness	L		

4	CONCLUSION AND PATH FORWARD	23
BI	BLIOGRAPHY	25
Aj	ppendix	
A B	ENGINEERING DRAWINGS OF CELL COMPONENTS PROBLEMS ENCOUNTERED DURING CELL OPERATION .	26 31
	B.1Electrolyte DiscolorationB.2Copper CorrosionB.3Cable Resistance	31 32 32
\mathbf{C}	IDEALIZED CELL PERFORMANCE	33

LIST OF TABLES

1.1	Half cell reactions of the all-vanadium couples	3
1.2	Performance of VRFBs compared to traditional batteries	5
3.1	Default cell configuration.	12
C.1	Idealized Resistance	33

LIST OF FIGURES

1.1	Electrochemical schematic of a redox flow battery	2
1.2	All-vanadium discharge sketch	4
1.3	Oxidation states of vanadium	4
2.1	Electrolyte flow path	8
2.2	Side view of cell	9
2.3	Experimental setup	10
3.1	Electrolyte charging	13
3.2	OCV stability	14
3.3	Polarization transience at constant current	15
3.4	SoC effect on polarization - $5mL/min \dots \dots \dots \dots \dots$	16
3.5	SoC effect on polarization - $15mL/min$	17
3.6	SoC effect on polarization - $25mL/min$	17
3.7	Polarization vs flowrate	18
3.8	Power vs flowrate	19
3.9	Polarization vs compression	20
3.10	Power vs compression	21
3.11	Polarization vs membrane thickness	22
3.12	Power vs membrane thickness	22

A.1	End plate drawing	27
A.2	Current collector drawing	28
A.3	Flow frame drawing	29
A.4	Gasket drawing	30
B.1	Discolored electrolyte	31
B.2	Copper corrosion	32

ABSTRACT

Redox flow batteries are electrochemical devices designed to store and dispense energy. This technology is seen as a promising candidate for grid-scale energy storage. This thesis reviews the operating principles of flow batteries. It also documents the design, fabrication, and performance of a lab-scale, all-vanadium redox flow battery (VRFB). Performance is characterized in terms of cell polarization and maximum power density. The parameters varied were electrolyte flow rate, electrolyte state of charge, membrane thickness, and electrode compression. Electrolyte state of charge and flow rate had a significant performance effect at high current densities and ohmic losses were significant in all configurations. A maximum power density of 0.38 W/cm² was achieved. Improvements to the experimental setup are suggested and topics for further research are discussed.

Chapter 1

INTRODUCTION AND BACKGROUND

Due to the increasing demand for clean energy and improving efficiency of such technologies, the adoption of renewable energy sources is on the rise. Energy sources such as wind and solar are already capable of supplying a large fraction of the required energy in many electrical grids. However, there is a major problem with these sources known as intermittence [1]. The amount of power produced is not constant (e.g. solar) and the variation in supply can be unpredictable (e.g. wind). In either case, supply does not match demand and at times there will either be too much energy or a lack of energy in the grid. If intermittent sources contribute to a small portion of a grid's supply, these variations in supply can be offset by controlling the output of traditional sources. However, if intermittent sources are responsible for more than 10-20% of a grid's total energy output, destabilization can occur [1]. For a renewables-dominated grid to be both reliable and efficient, a grid-scale energy storage solution must be adopted.

1.1 Operating Principles

A redox flow battery is an electrochemical device used to store and dispense energy. These rechargeable batteries convert electrical energy to chemical energy (and vice versa) through the reduction and oxidation of two ionic species which are dissolved in electrolytes. This electrochemical process is visualized in figure 1.1. During discharge, a load is placed across the anode and cathode. The anolyte (negatively charged electrolyte) and catholyte (positively charged electrolyte) are pumped through half cells separated by an ion exchange membrane. The porous anode draws electrons off of the active ions in the anolyte and these electrons travel through the external circuit to the positively charged cathode. At the same time, positively charged ions from the analyte pass through a separating membrane to the catholyte. In this way, potential chemical energy is converted to electrical energy and the electrolytes are discharged. To recharge the electrolytes, a potential greater than the open circuit voltage is applied across the electrodes and the chemical reactions are reversed.



Figure 1.1: Electrochemical schematic of a redox flow battery (from Weber, 2011).

1.2 Flow Battery Characteristics

The voltage of a redox flow cell is determined by the choice of redox couples. The maximum electrical current is determined, in part, by the cell's active area. One of the main advantages of flow batteries over solid-state batteries is the ability to independently design power output and energy capacity [2]. In a flow battery, the energy capacity is determined by the volume of electrolyte which is stored external to the cell. The power output is proportional to the cell's active area. A disadvantage of flow batteries is their low energy density due to solubility limits. Although there are many possible choices of ionic species, most of them suffer from low electrolyte solubility. This leads to low energy density (both per mass and per volume). Therefore, flow batteries are best suited for stationary applications.

1.3 Redox Couples

There are many possible choices for a pair of redox couples. Ideal candidates will be highly soluble, chemically stable, inexpensive, and reversible. In addition, the difference in standard potential between the couples should be substantial to provide a high cell voltage. Based on standard potentials, hydrogen or oxygen gas evolution may also occur in the aqueous solutions.

One possible pair of active species is the all-vanadium pair. This pair is very commonly used due to a high potential and reversibility of the solutions. As an ion, vanadium has four stable oxidation states. The more negatively charged ions V(II) and V(III) are used in the anolyte and the more positively charged states V(IV) and V(V)are used in the catholyte. In order for vanadium to exist in ionic form, a vanadiumbased salt is dissolved in sulfuric acid. During cell operation, protons pass through the membrane to maintain electrostatic equilibrium. The half cell reactions are given in Table 1.1.

 Table 1.1: Half cell reactions of the all-vanadium couples.

	Anolyte	Catholyte
charge	$V^{3+} + e^- \rightarrow V^{2+}$	$VO^{2+} + H_2O - e^- \to VO_2^+ + 2H^+$
discharge	$V^{2+} - e^- \rightarrow V^{3+}$	$VO_2^+ + e^- + 2H^+ \to VO^{2+} + H_2O$

Because vanadium is employed on both sides of the cell, any crossover of active species through the membrane does not permanently degrade the system. Although such crossover does reduce efficiency, it does not lead to the formation of irreversible compounds and the desired chemistry can be restored through subsequent recharging [3]. This property prolongs the usefulness of the electrolytes. Another convenient feature of the vanadium ion is that each of its four oxidation states corresponds to a



Figure 1.2: Electrochemical sketch of discharge with the all-vanadium couples.

distinct color. This allows for easy visual inspection of an electrolyte's approximate state of charge (SoC is the percent of charged ions in a solution). A disadvantage of the vanadium couples is that V(II) ions are susceptible to oxidation from oxygen in the atmosphere [4]. This degradation does change the system's net charge and is irreversible.



Figure 1.3: The four oxidation states of vanadium.

1.4 Design Considerations

Flow battery designs largely resemble those of fuel cells. However, since no gases are present among the reactants, a 3-phase contact is reduced to a 2-phase contact between electrolyte and electrode. Some experimenters have implemented flow fields while others rely on a simpler, flow-through configuration. Both carbon felt electrodes and thinner, carbon paper electrodes have been used. It is also important to mention that, unlike fuel cells, current densities above 0.5 A/cm^2 are readily achievable without any sort of catalysis. This reduces the cost of the electrodes and improves lifetime. Because the electrolytes are highly acidic, it is important that the flow frame in contact with the electrolytes is inert and resists corrosion. At lab-scale, the solutions are usually pumped with syringe pumps or peristaltic pumps.

1.5 Performance Benchmarks

The first fully functional VRFB was developed at the University of New South Wales in 1985. This system provided a power density of up to 85 mW/cm². Since then, commercial systems have been implemented, many of which can store multiple MWh [5]. Energy cost estimates for large scale systems are roughly \$500 per kWh, though cost scales nonlinearly with scale [5]. A comparison of VRFBs to traditional batteries is given in Table 1.2. It can be seen that flow batteries are only competitive based on durability and scalability, not high performance.

Table 1.2: Performance of VRFBs compared to traditional batteries.

	Li-ion battery	Lead-Acid Battery	VRFB
specific energy	150 Wh/kg	35 Wh/kg	25 Wh/kg
voltage	3.5 V	2 V	1.25 V
capacity scale	kWh	kWh	kWh-MWh
lifetime (cycles)	2,000	500	10,000
cost	\$500/kWh	\$150/kWh	\$500/kWh

As flow batteries enter the market, improvement strategies are continuously being developed at the lab scale. Power density is one of the most important metrics to be improved, and there are many possible avenues to improvement. For instance, one group found that simply by thermally pre-treating electrodes, power could be improved by 26% [6]. One of the most recent and significant breakthroughs in performance was achieved by Davies and Tummino who reported a peak power density of 669 mW/cm² [2]. This impressive result was credited primarily to the reduction of ohmic losses through high compression of the carbon felt electrodes.

1.6 Thesis Outline

In chapter 2 of this thesis, the design and fabrication methods for a lab-scale cell will be discussed. In chapter 3, the performance of this cell will be reported. Chapter 4 will conclude the thesis with strategies for future improvement and suggestions for further research.

Chapter 2

DESIGN AND FABRICATION

In the design of a lab-scale, all-vanadium flow battery parameters included the volume of electrolytes, cell active area, and material selection for cell components. Constraints were imposed by available equipment and allowable expenditures.

2.1 Cell Design

A flow battery consists of several material layers and is similar in construction to a fuel cell. The cell fabricated for this project was modeled after the description provided by Davies and Tummino (2018) and consists of 11 layers of material [2]. From the outside of the symmetrical cell to the center, the layers are as follows:

- Aluminum end plate (x2)
- PTFE insulating sheet (x2)
- Copper current collector (x2)
- Graphite flow frame (x2)
- Porous carbon electrode/PTFE-gasket (x2)
- Nafion membrane (x1)

Each graphite flow frame is a block with two elbow channels. The electrolyte enters the graphite flow frame from the side of the cell and flows through the porous electrode (figure 2.1). The porous electrode is compressed between the graphite block and a nafion membrane. A PTFE gasket between the flow frame and membrane surrounds the electrode and prevents leaking. After flowing through the electrode, the electrolyte exits the cell by flowing through an exit channel in the graphite block. Gaskets of various thicknesses can be produced to control compression of a given electrode.



Figure 2.1: Electrolyte flow path.

While the electrolyte is flowing through the porous electrode, it is able to be oxidized or reduced. Released protons will pass through the membrane to the opposing half cell. Released electrons are conducted from the porous electrode, through the graphite block, to the copper current collector before entering the external circuit. Graphite is a suitable material for the flow frame because it has moderate conductivity, resists corrosion from the acidic electrolyte, and is easily machinable. Although graphite is a conductor, it has a higher resistivity than copper. Therefore, the copper current collector is used for effective edge collection and serves as a convenient gripping point. The aluminum end plates provide structural support to the cell. Eight bolt holes around the perimeter allow the cell to be compressed. To prevent conduction through the end plates an insulating, PTFE sheet is placed between the end plate and the current collector. The active area of the fabricated cell is 25.81 cm² while the exterior dimensions of the assembled cell are approximately 9cm x 10cm x 6cm. Fully



Figure 2.2: Side view of cell.

dimensioned engineering drawings are available in Appendix A.

2.2 Fabrication

Fabrication of aluminum, graphite, and copper components was conducted in the Spencer Lab student machine shop. The PTFE gaskets were initially laser cut, but this method left a rough surface on the gasket edge. Due to concerns about excessive electrolyte flow across a poor surface interface, new gaskets were cut using a CNC mill. The nafion membrane was soaked in a 3 M H_2SO_4 aqueous solution for 24 hours before being placed into the cell. To complete assembly, the bolts were firmly tightened.

2.3 Balance of Plant

The anolyte and catholyte were pumped through the cell by two, NE-1000 syringe pumps. Each pump holds a 60 mL syringe and is capable of a maximum flow rate of 28 mL/min. After the electrolytes are pumped through the cell, they are emptied into two separate reservoirs. When discharge is complete, the pumps reverse direction, drawing the electrolyte back through the cell and into the syringe. Both pumps were programmed to automatically repeat this dispense and withdrawal cycle. The anolyte reservoir contains a separate inlet for nitrogen gas which was constantly applied to purge the reservoir of oxygen. The cell was charged and discharged with a VersaSTAT 3 Potentiostat. The potentiostat was paired with a KEPCO power supply to raise the maximum allowable current from 3 A to 20 A.



Figure 2.3: Experimental setup.

2.4 Electrolyte Preparation

The electrolyte was prepared by stirring a $1.5 \text{ M VOSO}_4 3 \text{ M H}_2\text{SO}_4$ aqueous solution. After 48 hours of mixing the vanadium salt had fully dissolved, yielding sulfate anions and vanadium(IV) oxide cations. In this blue solution, all vanadium ions were in the V(IV) state. After placing equal volumes of this solution in both half cells and charging, V(III) and V(V) solutions were obtained. The V(V) solution was removed and replaced with an equal volume of V(IV). The cell was now is the discharged state, and further charging yielded the charged V(II) and V(V) solutions. During initial charging, the applied voltage was kept at 1.7 Volts [7]. The first charging attempt was problematic due to a low current and unexpected electrolyte discoloration. These issues and their solutions are addressed in Appendix B.

Chapter 3 CELL PERFORMANCE

After preparing the electrolytes, the cell was repeatedly discharged under varying configurations to determine the performance impacts of state of charge, flow rate, electrode compression, and membrane thickness. Flow batteries are very similar to fuel cells and experience the same types of losses (activation, ohmic, and mass transport losses). Therefore, performance was characterized in terms of cell polarization and power density. Unless explicitly stated otherwise, each configuration uses the default parameters specified in Table 3.1.

Table 3.1: Default cell configuration.

Flow rate (mL/min)	Electrode compression	membrane & thickness
15	26%	NR 212 (50.8 μ m)

3.1 Charging Efficiency

To prepare the electrolytes, 40 mL of V(IV) was placed into each reservoir. The cell was charged according to the procedure outlined in section 2.4 and initial charging was considered complete when the current plateaued at approximately 100 mA under a terminal voltage of 1.7 V. By integrating current vs time and assuming that all of the vanadium ions in the solutions had undergone a change in charge by the time steady-state was reached, the charging efficiency was determined to be 95%. The charging current vs time is shown in Figure 3.1. The unexpected, initial increase in current may be due to an uneven flow distribution inside the cell. It may have taken several

passes for the center region of the electrode to become saturated with electrolyte. The frequency of the periodic current spikes equals the frequency of pump reversal. This suggests that the electrolytes at either end of the stream were not being charged at the same rate as the rest of the electrolyte.



Figure 3.1: Current vs time for the charging of the V(IV), V(IV) electrolyte pair.

3.2 OCV Stability

To measure the electrolyte stability, the cell was charged to 1.63 Volts and left in open-circuit for one hour while the pumps continued to operate. The voltage decay, shown in figure 3.2, followed an inverse exponential fit and the extrapolated steadystate was approximately 1.56 V. It has been reported elsewhere that after several hours, this gradual decay in voltage is followed by a sudden drop to 0.75 V [8]. No explanation was given, but one reason for this drastic change in behavior may be a slight imbalance of vanadium ions between the reservoirs. Once the less concentrated reservoir is depleted of charged ions, the standard potential will become that of V(III) or V(V) relative to V(IV).



Figure 3.2: Stability of open circuit voltage.

3.3 Polarization

Polarization curves were generated by controlling current and measuring voltage. To ensure that measurements would be reliable and repeatable, the cell was first discharged under a fixed current for one minute. This test was conducted for three different current values. The purpose behind this was to ensure that transient effects on voltage polarization were negated. Although some voltage spikes were detected, these were not time dependent and the settling time was undetectable on the timescale of seconds. In the generation of each of the following polarization curves, a current step time of 2 seconds was used.



Figure 3.3: Voltage vs time at each of three fixed currents.

3.3.1 State of Charge

Although the electrolyte state of charge was not measured quantitatively, it could be qualitatively deduced by variations in open circuit voltage (E_0). A higher open circuit voltage corresponds to a greater state of charge though an accurate empirical relationship has not been developed [9]. Cell polarization vs state of charge is shown at different flow rates in Figures 3.4, 3.5, and 3.6. It was found that a lower state of charge led to significantly higher losses at high current densities. This effect was minimized at higher flow rates.



Figure 3.4: State of charge effect on cell polarization. Flowrate = 5 mL/min.



Figure 3.5: State of charge effect on cell polarization. Flowrate = 15 mL/min.



Figure 3.6: State of charge effect on cell polarization. Flowrate = 25 mL/min.

3.3.2 Flow Rate

The flow rate through each half cell was varied between 5 and 25 mL/min. Polarization curves and corresponding power curves are shown in Figure 3.7 and 3.8 respectively. Greater mass transport greatly reduced losses at high current densities. Between 5 and 15 mL/min, the maximum power density increased by 150%. However, due to sufficient ohmic losses, the maximum power density did not improve at flow rates above 15 mL/min. Because the electrolytes are depleted as they flow through the cell, a state of charge gradient exists across the electrodes. At higher current draws, this gradient is steeper and leads to nonlinearity in the cell's polarization. Increasing the flow rate counteracts this loss by supplying the electrode with more charged ions per unit time. However, a cell without mass transport losses is still limited by ohmic losses. If losses are purely ohmic (linear), the maximum power will occur at half the limiting current (current corresponding to zero voltage). Therefore, there is no benefit to extending linearity beyond half of this limiting current.



Figure 3.7: Flow rate effect on polarization ($E_0 = 1.41$ V).



Figure 3.8: Flow rate effect on power density.

3.3.3 Electrode Compression

In flow batteries, the porous felt electrodes tend to contribute to large ohmic losses. In a recent study, it has been documented that compressing the electrodes can decrease these losses by as much as a factor of three [2]. In order to test this effect, the standard gaskets were replaced with thicker gaskets which provided a compression of only 0.6% instead of the standard 26%. The difference in performance was minimal and is shown in Figures 3.9 and 3.10. Interestingly, the less compressed configuration exhibited less nonlinearity in high discharge losses. These results were verified over several trials but only two compression levels were evaluated. A possible explanation for this behavior is that, in addition to lowering resistance, excessive compression closed many pores in the electrode, thereby decreasing the effective surface area and increasing flow around the edges of the electrode. If true, this would result in a higher mass flow rate per unit area and a decrease in mass transport losses. This response is reflected in the data.



Figure 3.9: Electrode compression effect on polarization ($E_0 = 1.41$ V).



Figure 3.10: Electrode compression effect on power.

3.3.4 Membrane Thickness

The standard nafion NR 212 membrane was compared to a thinner, NR 211 membrane of thickness 25.4 μ m. Polarization and power curves are shown in Figures 3.11 and 3.12. The thinner membrane did not improve power density. If other losses were smaller, a thinner membrane may improve performance [2]. However, as long as the choice of membrane does not boost performance a thicker membrane is preferred so that vanadium crossover and internal current are minimized.



Figure 3.11: Membrane thickness effect on polarization ($E_0 = 1.41$ V).



Figure 3.12: Membrane thickness effect on power.

Chapter 4 CONCLUSION AND PATH FORWARD

A functioning cell and testing setup were assembled and preliminary cell performance has been reported. The impacts of several parameters have been considered. These findings constitute a base-line performance which can be referred to in future flow battery research. The peak power density achieved was 0.38 W/cm². This value is reasonably good, but falls almost 50% below the best result found in the literature [2]. The achieved results are also far inferior to the cell's ideal performance which is estimated in Appendix C. Electrode compression did not improve performance, but this might be remedied in the future by preventing flow around the edges of the electrodes. However, it should be recognized that compression also leads to higher pumping costs. To properly evaluate the net improvement due to compression, parasitic pumping losses ought to be considered.

Suggested topics for further investigation include performance effects of vanadium and acid concentrations. The impact of flow fields should also be considered [7]. The provided results indicate a strong relationship between power density and electrolyte state of charge. In commercial applications the charged electrolytes would make several discharge passes through the cell. Therefore, it would be interesting to study decaying power density under multiple passes. Vanadium is very expensive, and for flow batteries to be commercially competitive a less expensive active species may be necessary. Experimentation with new redox couples would be worthwhile.

Regarding the experimental setup, peristaltic pumps should replace the currently used syringe pumps. The current pumps are not capable of high flow rates and in order to continuously operate they must frequently change the direction of flow. Due to insufficient electrolyte mixing, this back-and-forth flow appears to result in underused electrolyte at either end of the flow network. This is problematic, as it has been demonstrated that state of charge plays a large role in performance. It would also be useful to quantitatively measure the state of charge of the electrolytes. This could be accomplished via spectrophotometry [4].

All future work should be devised in light of the three major cell metrics: cost, power density, and energy density.

BIBLIOGRAPHY

- National Research Council. The National Academies Summit on America's Energy Future: Summary of a Meeting. The National Academies Press, Washington, DC, 2008.
- [2] Trevor J. Davies and Joseph J. Tummino. High-performance vanadium redox flow batteries with graphite felt electrodes. C, 4(1), 2018.
- [3] Adam Z. Weber, Matthew M. Mench, Jeremy P. Meyers, Philip N. Ross, Jeffrey T. Gostick, and Qinghua Liu. Redox flow batteries: a review. *Journal of Applied Electrochemistry*, 41(10):1137, Sep 2011.
- [4] Nak Heon Choi, S.-k Kwon, and Hansung Kim. Analysis of the oxidation of the v(ii) by dissolved oxygen using uv-visible spectrophotometry in a vanadium redox flow battery. *Journal of the Electrochemical Society*, 160:A973–A979, 03 2013.
- [5] Gareth Kear, Akeel A. Shah, and Frank C. Walsh. Development of the all-vanadium redox flow battery for energy storage: a review of technological, financial and policy aspects. *International Journal of Energy Research*, 36(11):1105–1120, 2012.
- [6] Katharine V. Greco, Antoni Forner-Cuenca, Adrian Mularczyk, Jens Eller, and Fikile R. Brushett. Elucidating the nuanced effects of thermal pretreatment on carbon paper electrodes for vanadium redox flow batteries. ACS Applied Materials & Interfaces, 10(51):44430-44442, 2018. PMID: 30335358.
- [7] Mohammed Al-Yasiri and Jonghyun Park. Study on channel geometry of allvanadium redox flow batteries. *Journal of The Electrochemical Society*, 164:A1970– A1982, 01 2017.
- [8] Jingyu Xi, Zenghua Wu, Xinping Qiu, and Liquan Chen. Nafion/sio2 hybrid membrane for vanadium redox flow battery. *Journal of Power Sources*, 166(2):531 – 536, 2007.
- [9] Zhijiang Tang, Douglas S. Aaron, Alexander B. Papandrew, and Thomas A. Zawodzinski. Monitoring the state of charge of operating vanadium redox flow batteries. *ECS Transactions*, 41(23):1–9, 2012.

Appendix A

ENGINEERING DRAWINGS OF CELL COMPONENTS

The aluminum end plates, copper current collectors, graphite flow frames, and teflon gaskets were manufactured on a CNC mill using the following engineering drawings.



Figure A.1: End plate drawing.



Figure A.2: Current collector drawing.



Figure A.3: Flow frame drawing.



Figure A.4: Gasket drawing.

Appendix B

PROBLEMS ENCOUNTERED DURING CELL OPERATION

After assembling the cell but before obtaining performance data, three major problems were encountered. Each problem and its solution is described below.

B.1 Electrolyte Discoloration

To prepare for electrolyte charging, equal volumes of V(IV) are placed on either side of the cell. After charging, the V(III) and V(V) solutions are supposed to be green and yellow respectively. However, after charging for several minutes the solutions became dark and either black or red in shade. This phenomenon was unexpected and could not be found anywhere in the literature. Initially, contamination of the electrolytes was suspected. However, it was discovered that further charging of the solutions eventually yielded distinctly green and yellow solutions. In a partially charged solution, vanadium ions of multiple valences exist. The darkening of the electrolytes was probably due to the fact that a mixed-valence solution will absorb light waves over a greater wavelength spectrum than a single-valence vanadium solution.



Figure B.1: Discolored Electrolyte.

B.2 Copper Corrosion

On each side of the cell, the electrodes make external connections via the copper current collectors. Even while the cell is in the open-circuit configuration, these plates maintain the voltages of their respective electrolytes. Over a period of days, corrosion developed on the current collectors. This corrosion had to be cleaned off during cell disassembly to prevent high surface resistance upon reassembly. A solution was to create a short circuit across the cell terminals during storage. This consumed any remaining charge in the cell and substantially slowed oxidation of the copper.



Figure B.2: Copper Corrosion.

B.3 Cable Resistance

During early charge/discharge testing, the cell was connected to a power supply via standard alligator cables and the terminal voltage was assumed to be equal to the power supply output voltage. However, it was discovered that because the cell's internal resistance was less than one Ohm, a substantial voltage drop was occurring across the cables connecting the cell to the power supply. Thus, the cell's terminal voltage was not equal to the power supply's output voltage. This mistake was corrected by measuring voltage at the cell's terminals via a 4-wire measurement. With this mistake rectified, greater currents through the cell were achieved and charging time was reduced from several hours to about 1 hour.

Appendix C IDEALIZED CELL PERFORMANCE

In the development of any device, it is useful to compare experimental results to those of an idealized scenario. This reveals by how much the system could theoretically be improved. If all mass transport, internal current, and reaction kinetics losses are ignored then power density would be limited purely by cell resistance. By knowledge of cell dimensions (given in Appendix A) and material resistivity, the cell's ideal resistance can be estimated. Contact resistances are ignored. The resulting resistance of 8.4 mOhms (Table C.1), when paired with an open circuit voltage of 1.4 V, yields a peak power density of 3.2 W/cm². The experimentally optimal power density was 16% of this theoretical value. This suggests that surface resistance is significant and that not all of the electrode area is being utilized. The estimate also indicates that the graphite blocks and carbon electrodes are the two largest contributors to resistance.

Material	Resistivity $(\Omega-m)$	Length (m)	$CS-Area (m^2)$	Resistance (Ω)
Copper	2E-8	(3E-2)*2	1E-4	1.2E-5
Graphite	1E-4	(1E-2)*2	5E-3	4.0E-4
Electrode	4E-4	(3E-3)*2	3E-3	8.0E-3
Membrane	2E-7	5E-5	3E-3	3.3E-9
				$\Sigma R = 8.4 E-3$

Table C.1: Idealized Resistance.