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DEPARTMENT OF ENERGY AND MINERAL ENGINEERING

QUANTIFYING THE POTENTIAL LOSSES OF A VANADIUM REDOX FLOW BATTERY

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ABSTRACT

Vanadium redox flow batteries are still in their infancy as a technology, and as such there are still many gaps in the knowledge of their mechanics. An important quality that is still unclear is the limiting electrode, particularly whether it is the negative or the positive electrode which generated more losses and therefore reduced the voltage efficiency of the battery the most. By quantifying these losses the role of those attempting to reduce them in the future is made much simpler as they will not need to identify where they are, just how to improve them (not that this is a simple task by any means). The central hypothesis of this thesis is that the overpotential and losses of the positive electrode due to its unfavorable kinetics are the largest contributor to potential losses at high voltage efficiencies before IR drop dominates the losses. This thesis quantified the loss contributions by source as a function of voltage efficiency and cell current density to confirm this hypothesis. The potential losses at the positive electrode were found to dominate the losses at the negative electrode at low current densities. This was found by a combined linearized Butler-Volmer and Tafel model, which showed that even at its highest points at a current density of $1.6 \times 10^{-4}$ A/cm$^2$, the losses at the negative electrode did not exceed 22% of total losses. The losses of the positive electrode were found to dominate the losses of the negative electrode at all current densities, and this trend continued after Ohmic losses surpassed the combined overpotentials at the positive and negative electrode.
# TABLE OF CONTENTS

LIST OF FIGURES ........................................................................................................... iii

LIST OF TABLES ............................................................................................................... iv

ACKNOWLEDGEMENTS ................................................................................................. v

Chapter 1 Introduction .................................................................................................... 1

Chapter 2 Literature Review .......................................................................................... 3
  Voltage Efficiency of VRFB ......................................................................................... 3
  Relevant Parameters .................................................................................................... 4
  Losses in a VRFB ........................................................................................................ 4
  IR Drop and Ohmic Losses ......................................................................................... 5

Chapter 3 Methodology ................................................................................................. 6
  Redox Kinetics Measurement System .................................................................... 6
  Membrane .................................................................................................................. 6
  Electrolyte Solution ................................................................................................... 6
  Electrochemical Measurements .................................................................................. 7
  Cell Construction ....................................................................................................... 7

Chapter 4 Theory .......................................................................................................... 9
  Nernst Equation .......................................................................................................... 9
  Half-Reactions ............................................................................................................ 9
  Butler-Volmer Equation ............................................................................................ 10
  Tafel Equation ........................................................................................................... 11
  Linearized Butler-Volmer Equation .......................................................................... 11
  Voltage Efficiency ..................................................................................................... 12
  Charge Curve ............................................................................................................. 12
  Hydrogen Evolution .................................................................................................. 14

Chapter 5 Results ....................................................................................................... 15
  Experimental Data ..................................................................................................... 15
  Values Used in Butler-Volmer Equation ................................................................ 16
  Mass Transfer Effects ............................................................................................... 17
  Direct Comparison of Electrodes .............................................................................. 19
  Electrode Kinetics .................................................................................................... 20
  Voltage Efficiency of a Battery ................................................................................ 20
  Accounting for Error ................................................................................................. 25
Chapter 6 Conclusions ........................................................................................................... 26

Potential Losses and Sources ............................................................................................. 26
Voltage Efficiency of VRFB .................................................................................................. 27
Explanation and Discussion ................................................................................................. 27

Chapter 7 Appendix .............................................................................................................. 29

Losses at 75% State of Charge ............................................................................................. 29
Losses at 50% State of Charge ............................................................................................. 30
Losses at 25% State of Charge ............................................................................................. 32
Losses at 0% State of Charge ............................................................................................... 33

BIBLIOGRAPHY .................................................................................................................... 35
### LIST OF FIGURES

<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Diagram of VRFB cell</td>
<td>8</td>
</tr>
<tr>
<td>2</td>
<td>Theoretical charge curve</td>
<td>13</td>
</tr>
<tr>
<td>3</td>
<td>Experimental LSV data</td>
<td>15</td>
</tr>
<tr>
<td>4</td>
<td>Sample LSV data compared to modeled data</td>
<td>16</td>
</tr>
<tr>
<td>10</td>
<td>Impact of Rotation on LSV (V4/V5)</td>
<td>18</td>
</tr>
<tr>
<td>11</td>
<td>Impact of Rotation on LSV (V2/V3)</td>
<td>18</td>
</tr>
<tr>
<td>12</td>
<td>Direct comparison of electrodes</td>
<td>19</td>
</tr>
<tr>
<td>13</td>
<td>Impact of electrode choice on kinetics</td>
<td>20</td>
</tr>
<tr>
<td>5</td>
<td>Modeled charge curve</td>
<td>21</td>
</tr>
<tr>
<td>6</td>
<td>Nyquist plot of cell</td>
<td>22</td>
</tr>
<tr>
<td>7</td>
<td>Voltage Efficiency at 100% SOC</td>
<td>22</td>
</tr>
<tr>
<td>8</td>
<td>Potential losses at 100% SOC</td>
<td>23</td>
</tr>
<tr>
<td>9</td>
<td>Proportion of potential losses at 100% SOC</td>
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<tr>
<td>14</td>
<td>Voltage Efficiency at 75% SOC</td>
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<tr>
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<td>Proportion of potential losses at 50% SOC</td>
<td>31</td>
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<tr>
<td>20</td>
<td>Voltage Efficiency at 25% SOC</td>
<td>32</td>
</tr>
<tr>
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</tr>
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<td>22</td>
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<td>33</td>
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<td>23</td>
<td>Voltage Efficiency at 0% SOC</td>
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<td>Potential losses at 0% SOC</td>
<td>34</td>
</tr>
</tbody>
</table>
Figure 25: Proportion of potential losses at 0% SOC
LIST OF TABLES

Table 1: Transfer coefficient values [7] ................................................................................. 4
Table 2: Values used in Butler-Volmer model ........................................................................ 17
Table 3: Additional values ........................................................................................................ 21
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Chapter 1

Introduction

Recent expansions of renewable energy generation have exacerbated the need for inexpensive, long-lasting, and high capacity energy storage systems due to the intermittent nature of solar and wind power[1]. This need will only expand with time as these intermittent energy sources become more commonplace and begin to displace more conventional sources of energy generation [2]. The addition of these energy sources will place additional stress on the grid and without the implementation of high capacity energy storage may cause it to become unreliable [3], which is not acceptable to the general public and could have disastrous economic implications [4].

It is here that there is potential for a redox flow battery to provide some exceptional improvements to current energy storage and distribution systems in a cost-efficient manner [4]. A redox flow battery can store the excess energy from renewable sources during times of low demand for usage when demand is greater but generation is lacking [1], [2]. The low energy density of the VRFB in comparison to other forms of energy storage is can be solved by the ease at which VRFB systems are scaled up, although this largely limits VRFB usage to larger scale usage [1].

For VRFBs to be studied further and implemented, it is necessary to identify critical properties such as exchange current densities which are often inconsistently reported [5], [6], as well as the magnitude of the potential losses specific to the positive and negative electrodes. This paper intends to prove that it is possible to ascertain accurate values for the exchange current densities and tafel slopes of a VRFB, and that if this is true, it is possible to identify the potential losses at the positive and negative electrode.
Upon review of the existing body of work on the subject, it is clear that many previous papers [5], [6], [7], [8] have inconsistently identified the kinetic parameters used in their calculations, many have used essentially default values. Although there is no clear consensus on these properties yet, there is no reason why it would not be possible to accurately define them.

This research is intended to fill the aforementioned gaps in understanding that were present in previous papers and contribute to a better general understanding of VRFBs. Quantifying losses simplifies the role of those attempting to reduce them in the future, which ultimately will speed up the deployment of these devices in commercial settings. The central hypothesis of this work is that the overpotential of the positive electrode is the largest contributor to energy losses at high voltage efficiencies before IR drop dominates [9] due to its sluggish kinetics. Here, the intent is to quantify the loss contributions by source as a function of voltage efficiency to verify this and provide insights into how this loss changes as a function of cell current. This thesis intends to determine which electrode is responsible and offer some insight into why this is the case.
Chapter 2

Literature Review

Voltage Efficiency of VRFB

At current densities of 80 mA/cm$^2$, using a Nafion 115 membrane, Suc et al [10] found the voltage efficiency of a VRFB to be 87%. This remained constant throughout 30 cycles of use. Zhang et al [11] found the voltage efficiency to be 76.7% when using Nafion 117 81.6% using Nafion 212. Chung et al [12] found the voltage efficiency of a VRFB cell using a Nafion 212 membrane and a bare carbon felt electrode to be 84% at 50 A/cm$^2$ current density. Agar et al [13] found that the voltage efficiency of a VRFB cell comprised of carbon felt electrode and Nafion 117 membrane to be 87.1% at 40 A/cm$^2$. It is difficult to stitch the multitude of points that are presented into a coherent picture of voltage efficiencies across a range of current densities, as they are often measured using slightly different cell compositions and experimental parameters, meaning that even if sufficient data points are constructed to piece together a curve, many may have to be thrown out or modified (and finding the coefficient to multiply the values by would be significant project in its own right) before there would remain a set of coherent, comparable values. Because the voltage efficiency of a VRFB is so directly tied to the IR drop across the cell [9], it is important that similar membranes and electrodes be used to ensure clear comparisons between voltage efficiency values. Relatively few studies report voltage efficiency values relative to a range of current densities as well, most that reference report it at a given current density and then detail how it changes over charge cycles or time, which unfortunately does not fall within the scope of this thesis.
Relevant Parameters

When simulating or modeling overpotentials and Butler-Volmer curves, it is necessary to use accurate values for the transfer coefficients [9]. Most sources are content to leave it at 0.5 [5], [14], essentially the default position, but there is no compelling reasons why this would be the case. Sun et al (2014 Resolving Losses…) [7] notably includes an anodic transfer coefficient of 0.45 in its calculations, displaying that there is at least some reason to believe that the default values may not be ideal. A table detailing other calculated values of transfer coefficient is also provided, as seen below. Because there is little evidence put forth the commonly used default value of 0.5 is actually the correct value when simulating data, an experimentally determined value for transfer coefficient will be used, as it is not difficult to find by simply finding the tafel slope of the results of an LSV test [15]. The effective area of the electrode is significantly larger than the geometric area of the electrode or membrane, and has been found to be 25329 cm² per gram of electrode [16].

<table>
<thead>
<tr>
<th>Electrode Thickness (μm)</th>
<th>400</th>
<th>1200</th>
</tr>
</thead>
<tbody>
<tr>
<td>Geometric j0 (mA/cm²)</td>
<td>4.4</td>
<td>5</td>
</tr>
<tr>
<td></td>
<td>25</td>
<td>21.8</td>
</tr>
<tr>
<td>Tafel Slope (mV/decade)</td>
<td>125</td>
<td>136</td>
</tr>
<tr>
<td></td>
<td>117</td>
<td>134</td>
</tr>
<tr>
<td></td>
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<td>143</td>
</tr>
<tr>
<td></td>
<td>114</td>
<td>125</td>
</tr>
<tr>
<td>Transfer Coefficient</td>
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</tr>
<tr>
<td></td>
<td>0.51</td>
<td>0.45</td>
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<td>0.42</td>
</tr>
<tr>
<td></td>
<td>0.52</td>
<td>0.48</td>
</tr>
</tbody>
</table>

Losses in a VRFB

The two major sources of potential loss taken into account when calculating voltage efficiency, IR drop and overpotential, can be further broken down by examining positive and negative overpotential separately. Derr et al found that the negative electrode can begin to suffer from hydrogen evolution at higher cut-off voltages, and although the positive electrode must
contend with CO\textsubscript{2} evolution, it is generally more favorable than the negative and as such has a lower overpotential [7]. Similarly, Agar et al [13] determined that the negative electrode was the limiting electrode of the cell, implying greater losses would be generated at the negative electrode. Sun et al (2014 Hydrogen Evolution…) [17], Satola et al [18], and Sankar et al [19] identify the phenomenon of hydrogen evolution at the negative electrode as a major contributor to the overpotential, and therefore the voltage efficiency losses of the VRFB cell. Although there is no shortage of discussion in regard to what is happening at the negative and positive electrode, there appears to be no consensus on the exact impact these losses have on the cell, and what their magnitude is proportional to each other and Ohmic losses.

**IR Drop and Ohmic Losses**

IR drop is known to be a major cause of efficiency losses in VRFB cells [20], and is a result of the combined resistance of all components of the cell, including the membrane, electrode, and the electrolyte solution [21]. These losses dominate once the low current density regime has been surpassed, and combined with mass transport losses due to unfavorable electrolyte distribution, will comprise the vast majority of all efficiency losses at mid to high current densities [20]–[23].
Chapter 3
Methodology

Redox Kinetics Measurement System

A rotating disc electrode (RDE) analysis system was used for obtaining experimental data, including LSV, EIS and OCP tests. Three potentiostats were used to monitor open circuit potential (OCP) and conduct linear sweep voltammetry (LSV), as well as Electrochemical Impedance Spectroscopy (EIS), measurements for the full cell and each half-cell. The potentiostats for each half-cell were setup with three electrodes. The electrodes consisted of a Pt counter electrode, an Ag/AgCl reference electrode, and a platinum RDE in the positive half-cell, while a glossy carbon RDE was used in the negative half-cell.

Membrane

An area of 16 cm$^2$ Nafion-117 membrane was used to separate the two solutions and an area of 6.25 cm$^2$ carbon cloth electrode was used in the cell.

Electrolyte Solution

A 375 mL solution, to later be split into two parts, was made of 50 x 10$^{-3}$ mol L$^{-1}$ VO$^{2+}$ and 2 M H$_2$SO$_4$. The solution was examined after mixing to ensure full dissolution of the vanadium species. 250 mL of solution was added to the positive half-cell, while 125 mL was added to the negative half-cell. After the initial pre-charge phase, 125 mL was removed from the positive half-cell so both volumes were equal during discharge. The temperature of the solution was measured during the experiment to be 23°C (296.15 K).
Electrochemical Measurements

OCP was monitored in the positive half-cell during the entirety of the pre-charging. OCP was monitored in the negative half-cell except when LSV and EIS measurements were conducted at different points during the charging phase. The full cell LSV and EIS was also measured at these stages in the charge phase and the total charge applied was measured over time.

The charge entered into the system by the full cell potentiostat at different increments of constant voltage. As the battery was charged and discharged, the open circuit potential and charge data was linked together as the experiment progressed. This allowed us to monitor the OCP as a function of charge over time for the experiment. LSV and EIS measurements were also conducted in order to measure the kinetic response of the system at different points of charge and discharge. EIS tests were taken with an initial frequency of 100 kHz and a final frequency of 1 Hz, as well as an AC Voltage of 10 mV. All LSV tests were performed with a range of 0.3 V to -0.3 V, with a scan rate of 5 mV/s and step sizes of 1 mV.

Potential was measured relative to the Standard Hydrogen Electrode (SHE) as well as a Silver-Silver Chloride Electrode (Ag/AgCl) during the various experiments. The usage of each will be noted so that accurate and direct comparisons can be made between potential measurements.

Cell Construction

Figure 1 below shows the basic construction of the VRFB system as it was constructed for the data collection. The two electrolyte tanks each have three electrodes inserted, working, reference, and counter, to properly perform voltammetry [24]. The working electrode requires a
second electrode, the reference electrode, to measure the potential of the working electrode, which will supply the potential to the electrolyte solution being measured. In RDE systems, a third electrode, the counter electrode, serves as the other end of the half cell made by the working electrode, while the reference electrode just serves as a reference and does not add or remove electrons from the system [24].

![Diagram of VRFB cell](image)

**Figure 1: Diagram of VRFB cell**

The negative electrode tank must have an inert gas bubbled over its surface to avoid oxygen in the air interfering with its contents and potentially rendering the battery inoperable. In the case of these experiments, this was achieved by simply closing off the negative electrolyte tank and attaching it to a source of pressurized argon.
Chapter 4
Theory

Nernst Equation

The Nernst equation is used to determine the potential of the cell as no current flows through it, essentially finding its thermodynamic equilibrium at a given concentration and temperature [25]. This equation is used anytime the OCP or any value that depends on it is solved for. The standard reduction potentials of the positive and negative electrodes of the cell are required to find the final cell potential. \( E^\circ \) is the cell potential at standard conditions and is found using the standard reduction potentials of the redox half-reaction. \( R \) refers to the universal gas constant, \( T \) to the temperature of the solution (in Kelvin), \( a \) to the chemical activity coefficient of the chemical species involved in the reaction. \( F \) refers to the Faraday constant, and \( z \) refers to the electrons active in the stoichiometric reaction [26].

\[
EQ1: \quad E_0 = E_0^\circ - \frac{RT}{zF} \ln \frac{a_{\text{Red}}}{a_{\text{Ox}}}
\]

Half-Reactions

A silver-silver chloride reference electrode of 0.2 V versus SHE (standard hydrogen electrode) was used as a reference electrode. The half-reaction reduction potential of the negative electrode was -0.26 V versus SHE while the reduction potential of the positive electrode was 1.00 V versus SHE [24]. To determine the open circuit potential of the vanadium flow redox battery we began with the Nernst equation and the two half-reactions related to the battery [26]. These reactions are the following:
Positive Electrode:
\[ \text{VO}_2^+_{(aq)} + 2\text{H}^+_{(aq)} + e^- \leftrightarrow \text{VO}^{2+}_{(aq)} + \text{H}_2\text{O}_{(l)} \]

Negative Electrode:
\[ \text{V}^{3+}_{(aq)} + e^- \leftrightarrow \text{V}^{2+}_{(aq)} \]

Pre-Charging Reaction:
\[ \text{VO}^{2+}_{(aq)} + 2\text{H}^+_{(aq)} + e^- \leftrightarrow \text{V}^{3+}_{(aq)} + \text{H}_2\text{O}_{(l)} \]

**Butler-Volmer Equation**

This equation was used to model LSV curves which had been experimentally determined, the comparison of which allowed for the determination of the transfer coefficient by matching the graphs. Additionally, simplified versions of the equation were used in tandem to determine the overpotentials as voltage efficiency of the battery at various current densities and states of charge (SOC). The Butler-Volmer equation describes the relationship between electrical current and electrical overpotential (the difference between the actual potential of the cell and the thermodynamic potential), in which \( j \) represents the electrode current density (A/m\(^2\)), \( j_0 \) represents the exchange current density (A/m\(^2\)), \( \alpha_a \) is the anodic transfer coefficient (Unitless), \( \alpha_c \) is the cathodic transfer coefficient (Unitless), \( z \) is the electrons in the reaction (moles), \( F \) is Faraday’s constant (96485 C/mol), \( R \) is the gas constant (J/Kmol), \( T \) is temperature (K), \( E \) is the electrode potential (V), and \( E_{eq} \) is the equilibrium potential (V).

\[ \text{EQ2: } j = j_0 \left( \exp \left[ \frac{\alpha_a zF}{RT} \left( E - E_{eq} \right) \right] - \exp \left[ -\frac{\alpha_c zF}{RT} \left( E - E_{eq} \right) \right] \right) \]
**Tafel Equation**

The Tafel equation is used when finding the overpotential of the cell, and therefore voltage efficiency, at high current densities. Overpotential is the dominating force on a battery’s performance at low current density levels [5], [20]. It can arise due to the activation energy needed to make a redox reaction proceed on the surface of an electrode or be related to the reaction itself[27]. Regardless of the exact cause, overpotential manifests as the difference between the theoretically calculated and observed potential of the cell [27]. In a battery, the overpotential from each electrode contributes to the energy that is lost when charging or discharging the cell, hence the ties between overpotential and voltage efficiency. Other major sources of energy losses are the ohmic, or IR losses, due to electrolyte and membrane electrical resistances. Overpotential is represented by $\eta$, $R$ represents the universal gas constant, $T$ is temperature in Kelvin, $a$ is the transfer coefficient, $F$ is Faraday’s number, $i$ is cell current, and $i_0$ is the exchange current. Both current values can be replaced by their equivalent exchange current density values in equations in which they are divided by the initial current or current density as the area terms will cancel out.

EQ3: \[ \eta = \frac{RT}{aF} \ln \left( \frac{i}{i_0} \right) \]

**Linearized Butler-Volmer Equation**

The linearized Butler-Volmer equation, also known as the polarization resistance equation, is used in the same contexts as the Tafel equation above, but is applied to the portions of charge or discharge cycle when overpotential and current density are low [25], [27]. Overpotential is represented by $\eta$, $R$ represents the universal gas constant, $T$ is temperature in Kelvin, $a$ is the transfer coefficient, $F$ is Faraday’s number, $i$ is cell current, and $i_0$ is the exchange current.

EQ4: \[ \eta = \frac{RT}{aF} \left( \frac{i}{i_0} \right) \]
Voltage Efficiency

After OCP, overpotential, and $E_{IR}$ have been found, they can be used collectively to find the overpotential of a cell. Voltage efficiency of a battery expresses the losses during the charge and discharge of the battery. $E_{OCP}$ is found using the Nernst equation and represents the open circuit potential of the battery (V), $\eta_+$ is a stand-in for the positive electrode overpotential (V), and conversely $\eta_-$ is the negative electrode overpotential (V). $E_{IR}$ represents the potential losses due to ohmic resistances in the cell (V). $E_{IR}$ is found using the current density of the cell, $j_{cell}$ (A/cm$^2$), $A_{cell}$ or the area over which charge transfer is taking place (cm$^2$), and the resistance of the cell, R (Ω). $E_{discharge}$ is the potential of the cell during discharge, similarly, $E_{charge}$ is the potential of the cell as it charges. The relationship between these two and how much $E_{discharge}$ is lower than $E_{charge}$ is voltage efficiency.

\[
EQ 5: \quad VE = \frac{E_{discharge}}{E_{charge}}
\]
\[
EQ 6: \quad E_{discharge} = E_{OCP} + \eta_+ - \eta_- - E_{IR}
\]
\[
EQ 7: \quad E_{charge} = E_{OCP} - \eta_+ + \eta_- + E_{IR}
\]
\[
EQ 8: \quad E_{OCP} = E_+ - E.
\]
\[
EQ 9: \quad E_{IR} = j_{cell} A_{cell} R \quad [24] \quad [28]
\]

Charge Curve

Figure 2 below (made by adding lines in Microsoft Paint to a graph made in Microsoft Excel) shows an example charge curve of a VRFB. The dominating forces on the chart are in order, thermodynamic and are governed by the Nernst equation, kinetic and governed by the Butler-Volmer equation, Ohmic and
governed by Ohm’s law, and mass transport limitations meaning that they are governed by the Levich equation [29]. Each of these factors dominate certain sections by causing the majority of potential losses at a given current density, and as such precisely identifying where each becomes dominant and to what degree will be useful as it allows for more efficient operation of the battery to become possible. An additional benefit is that if the standard operating current densities are known, it becomes far simpler to choose which modifications will have the most positive impact in its day to day operations. If ohmic losses are problematic for example, the membrane of the battery may be the first place to look for an improvement in the design. In the case that thermodynamic or mass transport losses were a major issue, simply changing the temperature at which the battery operates or introducing a stirring element could mitigate the issue and significantly improve voltage efficiency [30].

Figure 2: Theoretical charge curve
Hydrogen Evolution

The hydrogen evolution reaction is a known issue at the negative electrode [14], [17], [31], [32], and is potentially a major contributor to inefficiencies caused by the negative electrode. The electrolysis of water, \( 2\text{H}_2\text{O}(l) + 2\text{e}^- \rightarrow \text{H}_2(g) + 2\text{OH}^-(\text{aq}) \) is an undesirable reaction that shunts off a portion of the electron flow that was moving across the cell as intended and instead performs an irreversible reaction in the cell’s medium that causes losses. It can be detected by the bubbles it creates, the volume of which can be measured for an even more specific evaluation of the problem [17], [31].
Chapter 5

Results

Experimental Data

LSV tests were performed on the battery during both charge and discharge cycles, and these tests are what will constitute the half and full cell data analyzed in later sections. These results were also simulated using the Butler-Volmer equation using inputs obtained either from previous experimental tests such as Temperature, Electrode Potential, and Equilibrium Potential, as well as the Anodic and Cathodic Transfer Coefficient which were found to differ from previous literature which assumed both of the Transfer Coefficients to be 0.5 [5], [14]. These extracted values were found to lead to better simulations of the real data, and as such were used for all models going forward to better represent the electrochemical state of the battery at various points of charge and discharge. In the figure below, and LSV test was exported to Gamry Echem Analyst, which was then copied into Microsoft Excel. In Excel, the potential was changed to overpotential by subtracting $E_{\text{cell}}$ from $E_{\text{eq}}$.

![Experimental LSV Test](image.png)

Figure 3: Experimental LSV data
Figure 3 shows a representative LSV curve yielded from the tests performed using the methodology outlined above. Tests such as that one were used to create a Butler-Volmer model which could simulate the LSV tests to a high degree of accuracy, and then use the experimentally determined parameters from these simulated tests to calculate overpotential, which then went towards finding the voltage efficiency of the battery across a range of current densities. Figure 4 was found using a similar method to Figure 3, with the addition of a modeled Butler-Volmer curve found using the values in Table 2.

![Figure 4: Sample LSV data compared to modeled data](image)

**Values Used in Butler-Volmer Equation**

The parameters that best matched the experimental data, seen in Figure 4, is reported in Table 2 below. These will be used to determine the overpotential and voltage efficiency of the cell [9]. These values were used to find the positive overpotential specifically, to find the negative overpotential, a different exchange current density of $3.4 \times 10^{-3}$ A/cm$^2$ was used, this being found using the experimentally determined Tafel slope of the negative electrode.
Table 2: Values used in Butler-Volmer model

<table>
<thead>
<tr>
<th>$j_0$ (A/cm$^2$)</th>
<th>$z$</th>
<th>$F$ (C/mol)</th>
<th>$R$ (JK/mol)</th>
<th>$T$ (K)</th>
<th>$\alpha_a$</th>
<th>$\alpha_c$</th>
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<td>96485</td>
<td>8.314</td>
<td>298</td>
<td>0.36 ± 0.01</td>
<td>0.73 ± 0.02</td>
</tr>
</tbody>
</table>

Although the Butler-Volmer model did not perfectly predict the performance of the real battery, its predictions were sufficiently accurate to employ when no experimental test data was available [6], [8]. By applying the experimentally determined transfer coefficient values as determined from the experimental data, it was possible to increase the R-squared value (found using Microsoft Excel’s built in function) from 0.89 to 0.95, a significant improvement [33], [34].

Mass Transfer Effects

The calculations performed above found no evidence of mass transfer playing a major role in the potential losses of a VRFB, but there are ways to corroborate this other than examining the charge and discharge of the cell. An RDE, as indicated by the name, rotates, and this rotation is intended to ensure that mass transport effects are minimized by exposing the electrode to as much fresh solution as possible. If mass transport is a non-negligible source of loss in a VRFB, it would stand to reason that reducing or increasing the rate of rotation would have some impact on the overpotential, presumably lowering it at higher rotation speeds. Potential is relative to an Ag/AgCl electrode.
Figure 5: Impact of Rotation on LSV (V4/V5)

In Figure 10, although there are slight reductions in overpotential required to reach any given exchange current, they are incredibly slight, to the point of being negligible. For an increase of 1000 rpm, this is not indicative of mass transport being a major component in the total overpotential of the cell at 4-5 electrode.

Figure 6: Impact of Rotation on LSV (V2/V3)

Figure 11 shows a similar comparison at the negative electrode. This time however, the 1000 rpm increase is from an initial rate of 0 rpm. There is a slight but noticeable increase when the electrode functions as an anodic electrode, but even this, although certainly distinguishable
from noise, is not large enough to merit inclusion in the general model, particularly considering its occurrence at only one electrode, and not during both charge and discharge. Also of note is this happening at 0 rpm, a relatively extreme case. Potential is relative to an Ag/AgCl electrode.

**Direct Comparison of Electrodes**

![Figure 7: Direct comparison of electrodes](image)

As seen in Figure 12 above, the negative electrode has significantly better kinetics than the positive electrode, yielding much larger increases in current density for each volt of overpotential garnered by the cell. This agrees with the analysis performed earlier in the chapter, which predicted greater losses at the positive electrode dominating those from the negative electrode at low current densities. These tests were run at 1000 rpm and are presented relative to the SHE.
Electrode Kinetics

By directly comparing glossy carbon electrodes to platinum electrodes at 1000 rpm versus SHE, it is possible to see exactly how much of an impact the electrode kinetics have on the overall performance of the cell. The glossy carbon electrodes clearly lag behind the platinum electrodes, generating significantly more overpotential, particularly at the negative electrode at which point the overpotential gained per unit of current density becomes extremely low. This displays the impact of kinetics on the voltage efficiency of the cell, as the significant difference between the two electrode substrates indicates that the kinetics are by no means an insignificant factor.

Voltage Efficiency of a Battery

Voltage efficiency was chosen as the primary metric of study as losses due to overpotential at the electrode are ultimately what will need to be quantified to determine what the losses at the positive and negative electrode actually are [19]. Figure 3 shows the basic charge curve of the
VRFB, based off of the overpotential and Ohmic losses primarily (mass transport losses as predicted by the Levich equation were found to be negligible). The potential shown is relative to SHE.

![Figure 9: Modeled charge curve](image)

Using the values for positive and negative overpotential, as well as the IR drop found using Ohm’s law, the voltage efficiency of the battery was calculated as well. Table 3 shows the additional values required to perform these calculations, the Resistance, R, of the cell, found by analyzing EIS data, and the membrane area of the cell. Figure 6 below shows the full cell Nyquist plot of the impedance of the cell, which was used to help determine the cell resistance. The impedance on this scale is presented in terms of its real and imaginary components [35], which is a factor of the sinusoidal nature of current changes during the EIS test.

<table>
<thead>
<tr>
<th>R (Ω)</th>
<th>Membrane Area (cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.15 ± 0.01</td>
<td>6.25</td>
</tr>
</tbody>
</table>
The voltage efficiency (seen in Figure 6 at 100% SOC, other states of charge are available in the appendix) ranged from 72% at 100% state of charge to 82% at 75% when it peaked. These values are consistent with those presented in the literature review above. The voltage efficiency plummets as higher currents (and accordingly higher current densities) are reached, indicating
greater overpotentials and Ohmic losses in these regions, exactly as predicted. These losses can be further broken down into their constituent components [9], [27].

![Sources of Voltage Loss at 100% SOC](image)

**Figure 12: Potential losses at 100% SOC**

Figure 7 above displays the potential losses that constituted the voltage efficiency curve. The open circuit voltage remains constant as the actual state of charge is not changing, a sweep of varying potential is being applied to the cell to determine what the current yield is. The total potential is a charge curve equivalent to the one shown in Figure 5, and the IR drop as well as the positive and negative overpotentials are the three curves which start at 0 V. These three curves, when subtracted from the open circuit potential, are what create the charge curve seen in Figure 5, and are what will be used to break down the proportion of losses at any given current. For all states of charge, the negative electrode initially dominates the losses immediately after leaving the thermodynamic region, before it is overtaken by the IR drop around 0.02 A. At this point the Ohmic losses take over, as would be expected. Mass transport losses do not make up a major component of the losses at any point. The quick leveling out of the two overpotential values after
initial spikes is what leads to the curved shape of the charge and discharge curves in the kinetic region after the thermodynamic equilibrium point is moved away from. The potential shown is relative to SHE. State of charge was determined using the full cell OCP collated from several tests taken during the charge and discharge of the battery.

![Figure 13: Proportion of potential losses at 100% SOC](image)

Figure 8 directly compares the losses that are subtracted from the open circuit potential by rendering them as percentages of the total loss. As seen in Figure 7 as well, The IR drop becomes the single largest source of potential loss at roughly 0.15 A, and becomes the dominant sources at 0.2 A. Equivalent evaluations made at different states of charge agree with this analysis, and are available in the appendix.
**Accounting for Error**

When possible, all tests that were performed were performed multiple times on the cell, reducing the chance of any one outlier test being taken at face value and polluting the results. Any values that were determined experimentally and fed into a model were compared to the values previously determined in other studies and found in the Literature Review. Due to the nature of the OCP tests and the length of time required for charging and discharging the cell, some tests do not have identical tests to compare against, but still were compared against at least another taken on a different day in similar conditions.
Chapter 6
Conclusions

Potential Losses and Sources

The potential losses at the positive electrode were found to dominate the losses at the negative electrode during the low current density regime. This conclusion is based both upon the combined linearized Butler-Volmer and Tafel model, which showed that even at their greatest extent (at the very lowest current density, 1.6E-4 A/cm²), the potential losses at the negative electrode never exceeded 22% of total losses, even less than the Ohmic losses at that point, which were very small to begin with as Ohmic losses are dependent on current.

The positive electrode always generated at least twice the losses of the negative electrode at equal current densities, and this continued even to the point at which Ohmic losses surpassed the combined overpotentials at the positive and negative electrode, 1.44E-02 A/cm². These proportions held true across all states of charge that

Inspecting the LSV data of the two electrodes operating at identical loads and at the same rpm indicates a similar conclusion, that the positive electrode is less efficient than the negative electrode at all states of charge, and even when using a different electrode composition. This additionally indicates that the difference between the two electrodes can be attributed to the differing kinetics of the two half-reactions taking place, and that there is room for improvement at both. While potentially this improvement could technically be realized by abandoning carbon electrodes in favor of a platinum mesh, this would be prohibitively expensive and other routes must be explored.

Also, of note is the precipitous drop in the voltage efficiency once the charge or discharge of the cell reaches the Tafel region. Before this region the rate of voltage efficiency decreasing
with greater current densities actually decreases, and if this trend continued it would eventually level out. The point at which this change occurs is at 2.88E-03 A/cm², around which the Tafel and linearized Butler-Volmer equations both yield the same overpotential values.

At states of charge lower than 100%, the potency of the positive overpotential plummets compared to Ohmic losses, even at incredibly low current densities. This indicates that in many cases, it would be easier to increase voltage efficiency of the cell by focusing on the membrane, rather than modifying the electrodes. These figures can be seen in the appendix.

Voltage Efficiency of VRFB

The voltage efficiency of the battery is an important metric for determining the losses of a cell, and how to mitigate them. Interestingly, the voltage efficiency did not experience significant changes as the state of charge of the cell shifted. Any marked improvements to the voltage efficiency would have to be made in the either the electrodes, to improve their kinetics, or the membrane, electrolyte and other components, to reduce Ohmic losses. Even though in the majority of situations, when state of charge and current density are taken into account the Ohmic losses are greater, the overpotentials present at both electrodes, particularly the positive electrode, are significant enough to occupy at least 30% of the total losses when taken together, even at high current densities at 0% state of charge.

Explanation and Discussion

Although the precise cause of the greater losses at the positive electrode is beyond the scope of the analysis of this thesis, some initial speculation can be made. One conclusion that is immediately clear is that hydrogen evolution at the negative electrode simply isn’t a major factor in the kinetic losses experienced. Poor reaction kinetics at the positive electrode or a high
activation overpotential at the positive electrode instead dominate this, rendering it relatively unimportant when increasing the efficiency of the battery. Parasitic reactions such as carbon dioxide evolution at the positive electrode [19] may be what is causing it to have a much greater impact, and could well be the reason that the positive electrode appears to be the limiting electrode of the cell. These parasitic reactions have the potential to degrade the electrode surface, reducing functional sites to the detriment of its kinetics.

Further studies to determine the specific causes of these losses could measure the mass of the electrodes before and after usage to ascertain if parasitic reactions are impacting one electrode significantly more than the other and causing it to lose mass and degrade. Additionally, the rates of carbon dioxide and hydrogen evolution at the positive and negative electrodes could be determined by measuring the mass of both gases emitted over a range of states of charge and current densities, providing some insight into the rates at which both occur.
Chapter 7

Appendix

Losses at 75% State of Charge

Figure 14: Voltage Efficiency at 75% SOC

Figure 15: Potential losses at 75% SOC
Figure 16: Proportion of potential losses at 75% SOC

Losses at 50% State of Charge

Figure 17: Voltage Efficiency at 50% SOC
Figure 18: Potential losses at 50% SOC

Figure 19: Proportion of potential losses at 50% SOC
Losses at 25% State of Charge

**Figure 20:** Voltage Efficiency at 25% SOC

**Figure 21:** Potential losses at 25% SOC
Figure 22: Proportion of potential losses at 25% SOC

Losses at 0% State of Charge

Figure 23: Voltage Efficiency at 0% SOC
Figure 24: Potential losses at 0% SOC

Figure 25: Proportion of potential losses at 0% SOC
BIBLIOGRAPHY


with enhanced surface area and catalytic activity for vanadium redox flow batteries,”


ACADEMIC VITA

Forest Edwards

Education:

The Pennsylvania State University, University Park PA

BS in Energy Engineering
Minor in Electrochemical Engineering
Minor in Environmental Engineering
Expected Graduation Date: Spring 2019

Relevant Skills:

Technical Skills
- Strong background in applied electrochemical and corrosion engineering
- Assembly of fuel cells and batteries in airtight conditions
- Preparation of samples using machining tools

Software and Coding
- MatLab
- Python (including the Jupyter and Cantera environments)
- Microsoft Office Suite

Communication and Leadership
- Succeeding on a diverse team with members of many technical backgrounds

Employment:

5/2018-Ongoing    Wage-Roll Researcher
Electric Power Research Institute
- Conducted corrosion experiments on prepared pipe and boiler surfaces to determine the effectiveness of several commercially used corrosion inhibitors
- Designed and conducted experiments using multiple potentiometers to measure kinetic parameters of experimental Vanadium flow batteries
- Completed a paper based on battery findings which is in the final editing and review stage before submission and publication

8/2017-5/2018    Student Researcher
Institute of Energy and the Environment
- Engaged with local farmers to determine whether their properties and financial situations were appropriate for solar installation
- Assembled and coded solar resource measurement devices which could quickly and cheaply ascertain light data that previously would require elaborate, expensive, sensors
- Assisted in the on-site installation of several solar installations for student organizations and the Office of the Physical Plant

6/2014-9/2016    Intern
The LEAF Project
- Designed and constructed irrigation systems that minimized harmful runoff from fertilizers and particulates into nearby streams
- Conducted community and corporate outreach, including presentations at forums, charity events, and town halls
- Wrote and edited grant applications to both state and private organizations