Engineering Consulting Firm

Proposal: Case AKT

Verde Energy: RFB Malfunction

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1. INTRODUCTION

1.1. Scenario

The following investigation aims to diagnose any inefficiencies with the Redox Flow Battery (RFB) used by the start-up Verde Energy on the behest of our clients, Cambridge Consumables. Based on the testimony and data collected by Cambridge Consumables, the RFB was working properly for a few months after its installment, but a brief look into the battery function later revealed that the parameters have changed over time and over cycles. Inspection of the battery structure revealed degradation of the piping but its replacement to a more chemically compatible material did not yield satisfactory results in terms of battery function. Therefore, leaks to the external environment from the RFB tanks have been eliminated as a potential source of inefficiency. The report will analyze battery metrics compared to the standard and expected performance levels and will provide the diagnosis of the malfunction along with recommendations to get the system back to its normal state.

1.2. Background on RFBs

Before diving into the data analysis, a brief overview of the technical components of an RFB are provided as reference for the discussion on the parts of the battery that might be malfunctioning. RFBs consist of tanks of electrolytes and active species along with a cell stack. The active species go through a porous electrode in the cell stack where redox reactions occur and electrons are transferred through a circuit. The charged active species are then separated through an ion exchange membrane (IEM) and returned to their respective tanks via a series of pumps and pipes. There are two tanks in the RFB system: a catholyte and an anolyte. These two tanks correspond to cathodes (positive-reductive species) and anodes (negative-oxidative species), respectively, of a typical battery system (Weber, 2011). **Figure 1.** below depicts the RFB system. The main difference between a conventional battery and an RFB is that the active species for redox reactions are all aqueous and change in concentration during the charge and discharge cycles without any physical change in the system (i.e., deposition on a metal electrode).

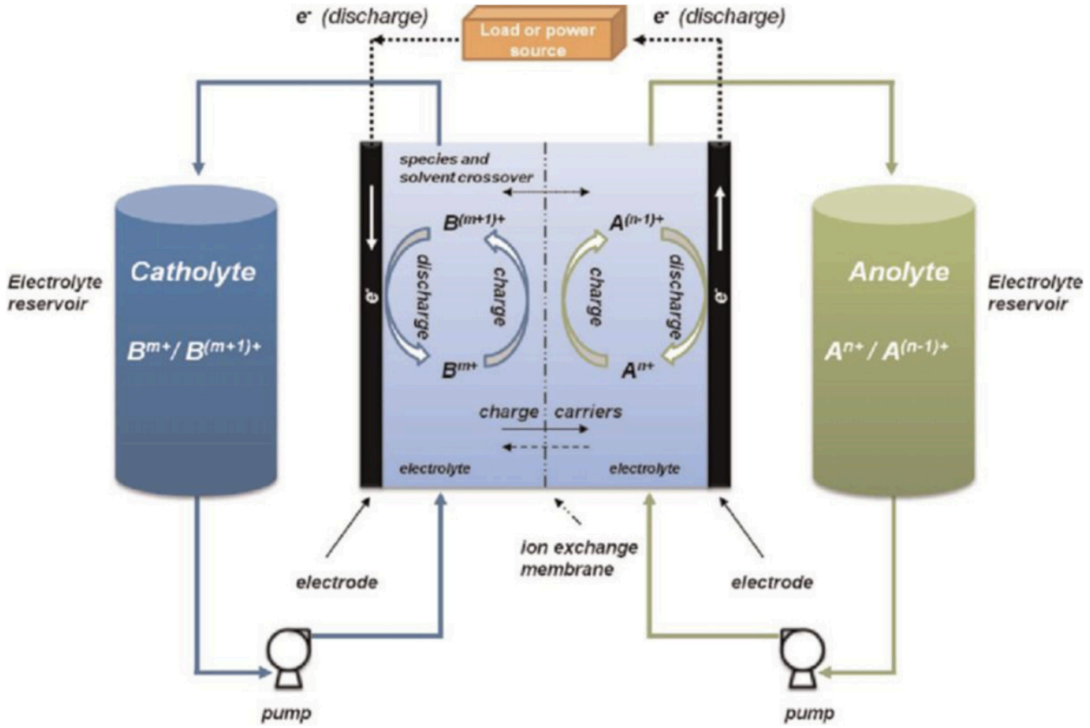

Figure 1. Redox Flow Battery (RFB) schematic (Dassisti, 2022)

It is important to define the term “cycle” for this report. A battery “cycle” refers to the period during which a battery is charged and discharged. A battery is charged when energy is stored in the tanks and discharged when energy is released and electrons are moved through the external circuit.

In addition to the system components, it is important to introduce the key frameworks behind the efficiency of an RFB. Overpotentials are affected by kinetics, ohmic resistances, and mass transport between the electrolytes and through the separator (Weber, 2011). Kinetics refers to the speed of redox reactions and the relationship between the overpotential of the electrolytes and the current density generated. At high enough reaction speeds, current densities and kinetics- ohmic resistance (ionic conduction resistances) become dominant in the overpotential and current density relationship. At high enough current densities, mass transport, or the speed of transport of electrolytes to reaction sites at the IEM, drops the overpotential due to fewer electrolytes reaching the cell stack.

2. METHODS

To understand the inefficiency issues that might be causing the RFB system to malfunction, data sets on the battery charge and discharge potential were analyzed at different time steps, throughout several cycles, and compared to the normal battery function. Normal battery metrics were taken from data gathered during the early cycles of the battery immediately after installment. The following values were calculated based on the system parameters and data collected to understand how the battery performs over different cycles: charge capacity, discharge capacity, coulombic efficiency, voltaic efficiency, energy efficiency, and overpotential and current density relationships (polarization data) throughout normal and malfunctioning cycles. All of the data was provided by Cambridge Consumables and the analysis completed by the consulting firm.

The discharge and charge capacity were calculated to compare how much current the RFB can produce and store (charge) and how much it can release (discharge). The discharge and charge capacity are dependent on the cycling current of the battery and the time of each cycle. Coulombic efficiency is the quotient of discharge capacity over the charge capacity and indicates what percentage of the energy produced can be released by the battery. The equations for discharge capacity, charge capacity, and Coulombic efficiency can be found below in equations (1), (2), and (3) respectively (Arenas, 2017). These parameters were determined and compared for the normal functioning cycle and 9 of the malfunctioning cycles.

$$Q_{discharge} = It \tag{1}$$

$$Q_{charge} = It \tag{2}$$

$$\eta_C = Q_{discharge}/Q_{charge} * 100\% \tag{3}$$

Voltaic efficiency was another metric determined for all 10 cycles of data. Voltaic efficiency refers to the quotient of the average discharge and charge potentials, see equation (4) (Arenas, 2017). Voltaic efficiency compares the potential required to release current in the battery and the potential required to induce the reverse reaction to charge the battery.

$$\eta_V = V_{discharge}/V_{charge} * 100\% \tag{4}$$

The energy efficiency is essentially the product of voltaic and coulombic efficiencies. It refers to the ratio of energy (Joules) required to discharge versus charging the battery. The general equation for energy efficiency is shown below in equation (5). Equation (5) defines energy efficiency in relationship to Coulombic and voltaic efficiency (Arenas, 2017).

$$\eta_E = \eta_V \eta_C \tag{5}$$

Finally, the polarization data for the normal and malfunctioning cycle was compared to see how the overpotential affects the current density of the RFB under each condition. This allows us to observe the resistance regimes at which the battery operates at various overpotentials and determine whether kinetics, ohmics, or mass transport dominate the battery's function in the normal and malfunctioning states to determine how to improve the inefficiencies.

3. RESULTS

The following section summarizes the results of the data analysis done on the data provided by Cambridge Consumables. It is important to note that the plots referenced in this section refer to a normal RFB cycle as cycle 0 while the data from multiple malfunctioning cycles were collected and referred to as cycles 36, 40, 44, 48, 52, 56, 60, 64, and 68. Tables for all calculated and plotted values for the parameters below can be found in the Appendix.

3.1. Discharge and Charge Capacities

The discharge and charge capacities both remained constant throughout all 10 cycles compared at a value of 172.97 MA-s. The discharge and charge capacities can be seen below in **Figure 2.** and **Figure 3.** respectively.

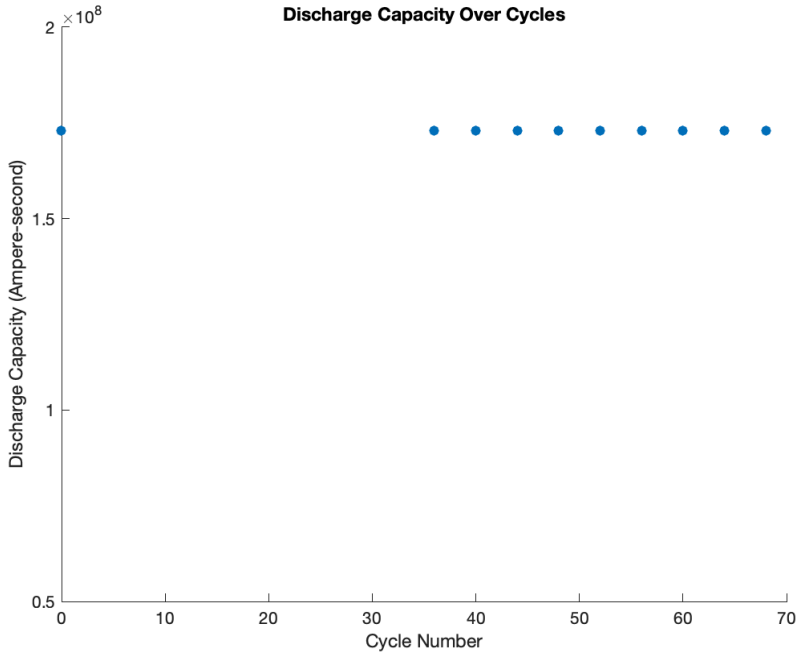

Figure 2. Discharge capacity of the RFB over several cycles

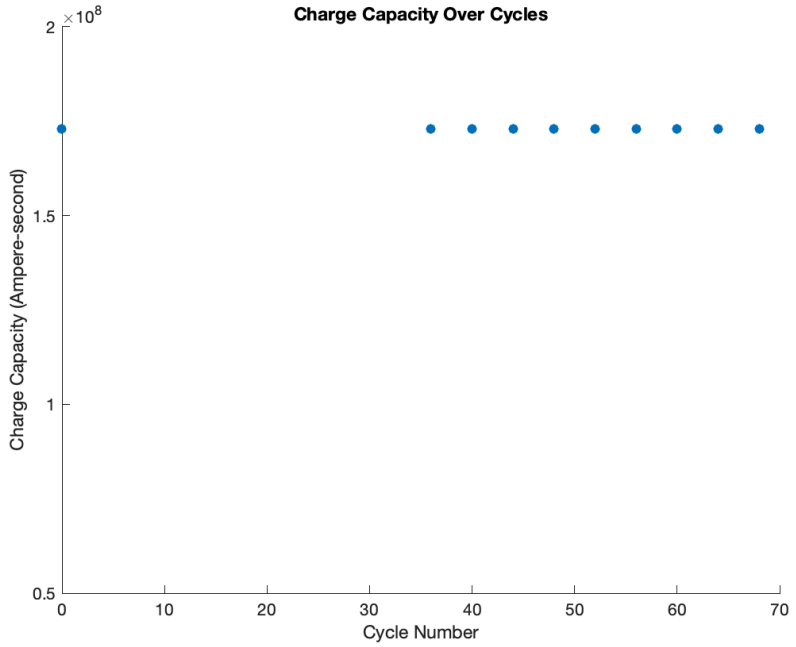

Figure 3. Charge capacity of the RFB over several cycles

3.2. Coulombic Efficiency

Since the discharge and charge capacities were at the same value throughout cycles, the Coulombic efficiency remained at 100% for all the cycles evaluated (**Figure 4.**).

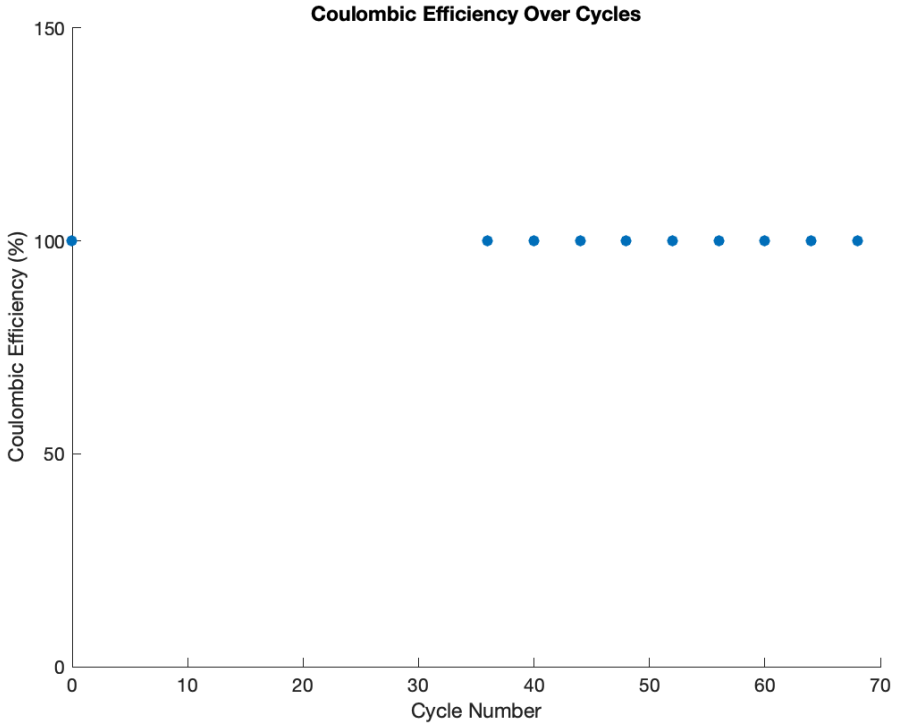

Figure 4. Coulombic efficiency of the RFB over several cycles

3.3. Voltaic Efficiency

The voltaic efficiency appears to be decaying logarithmically at increasing discharge/charge cycles (**Figure 5.**). Overall, from the normal cycle 0 to the last cycle of data collection, cycle 68, the voltaic efficiency decreases by over 55%—a large reduction.

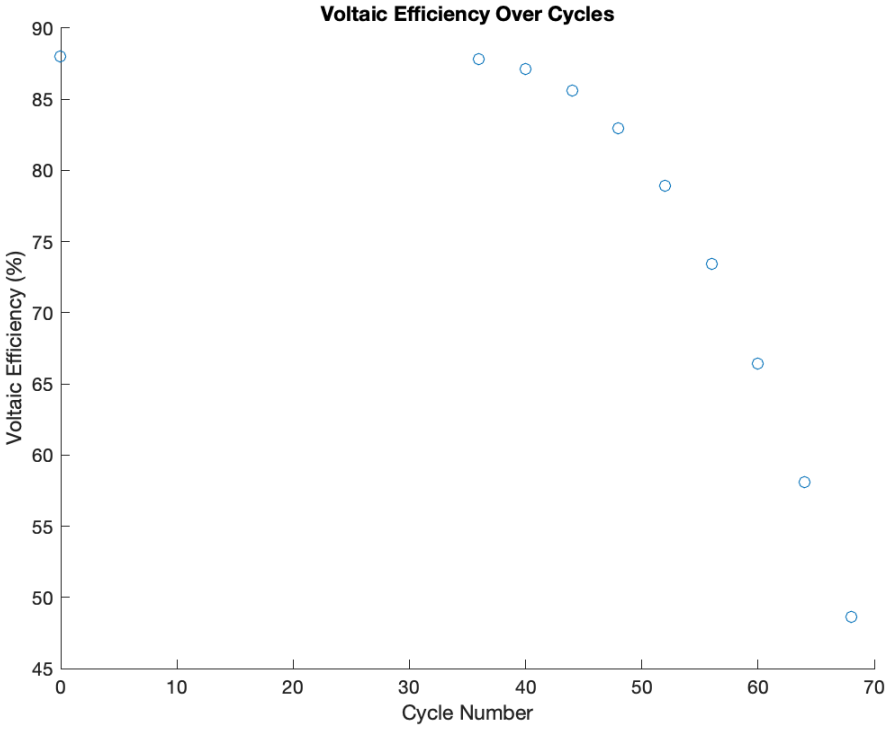

Figure 5. Voltaic efficiency of the RFB over several cycles

3.4. Energy Efficiency

Since the voltaic efficiency decreases and the Coulombic efficiency remains at a constant 100%, the energy efficiency as a product of these two metrics yields another logarithmic decay over the cycles from the normal measured cycle (**Figure 6.**). Thus the efficiency values are exactly the same when compared to the voltaic efficiency for each cycle meaning there is also a 55% reduction in efficiency across the cycles evaluated.

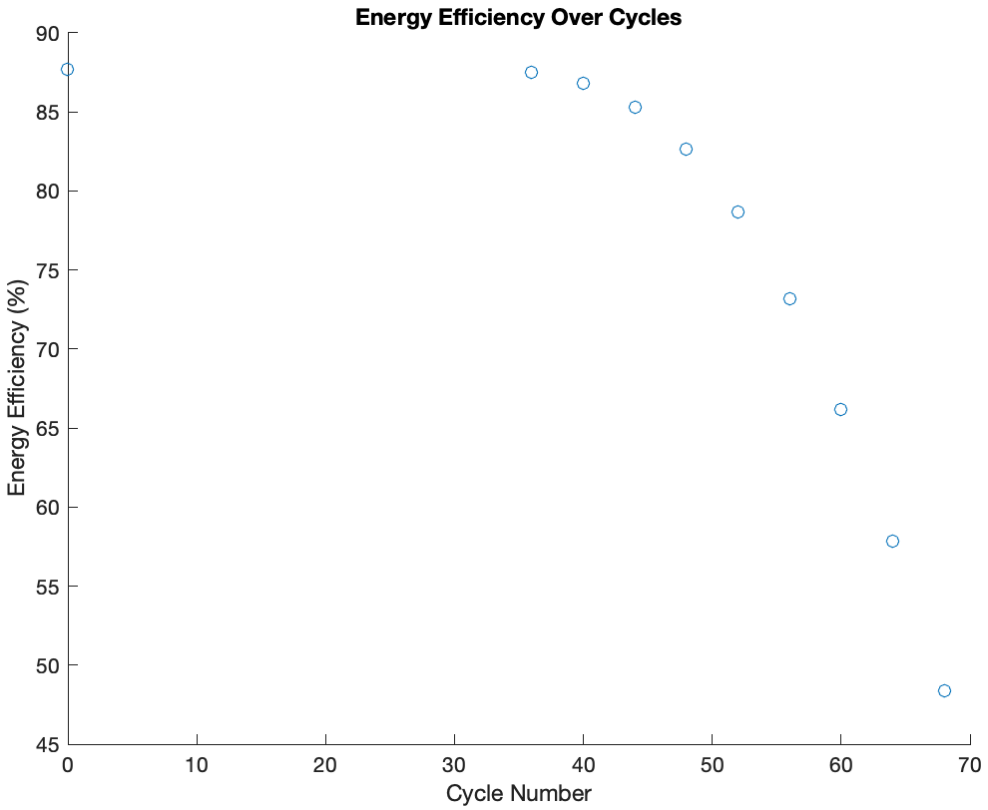

Figure 6. Energy efficiency of the RFB over several cycles

3.5. Battery Polarization

The battery polarization graph in **Figure 7.** provides an overview of the resistances (i.e., kinetics, ohmic resistances, or mass transport) that are dominant or limiting in the RFB under normal and malfunctioning conditions to understand what is fundamentally working differently in the system. As can be seen below, under normal cycle conditions, The overpotential (the difference between applied potential and equilibrium potential) changes inversely and linearly until around 3500 A/m^2 current density at which point it drops off- when mass transport limitations begin to dominate. However, in the malfunctioning state, the overpotential only changes inversely and linearly with current density without a drop and at a steeper slope than the normal state. The change in the linear regime (the ohmic regime) and the disappearance of the drop (mass transport limitations) imply that ohmic resistance is dominating in the malfunctioning RFB.

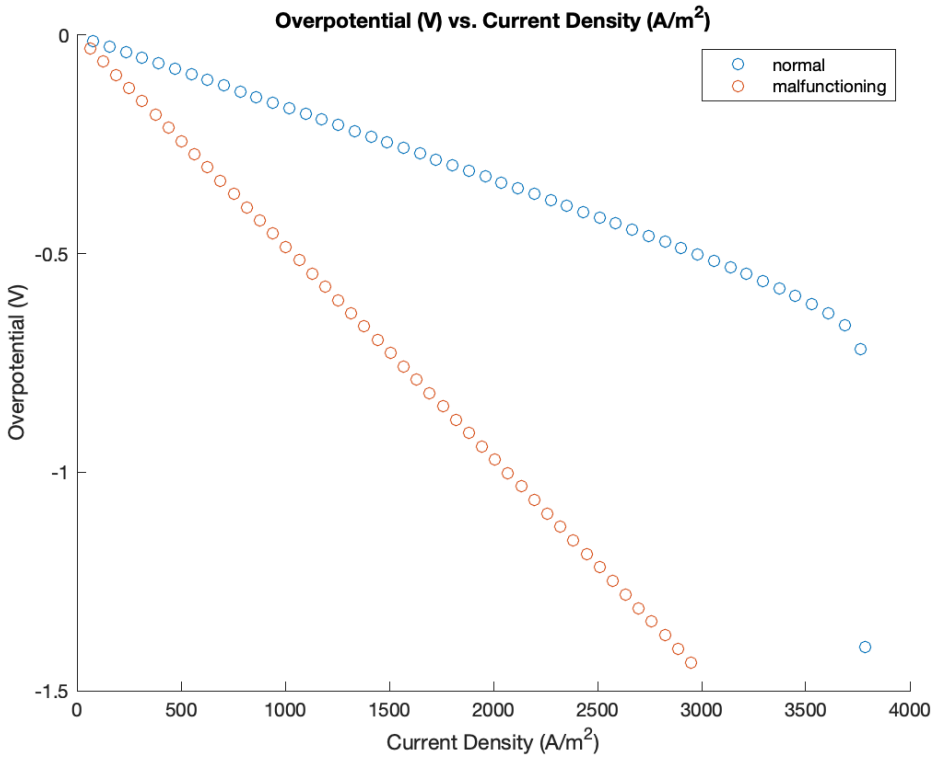

Figure 7. Graph comparing the relationship of overpotential and current density for a normal and malfunctioning RFB

4. DISCUSSION

Since the charge and discharge capacities remain the same and the Coulombic efficiency is constant at 100%, no capacity losses are indicating a crossover of active species across the IEM and separator. Capacity is proportional to the concentration and volume of active species and electrolytes in the storage tanks; therefore, constant capacity means a constant system concentration and volume (Yao, 2021). Thus, a crossover of active species to the opposing tank is eliminated as a possible malfunction in the RFB. It also indicates that the IEM and separators in the inert electrode layers are performing their jobs adequately for electrolyte redox reactions. Another problem that can be eliminated is the self-decomposition of the active species. Again, because the relative concentrations of the active materials remain the same and capacity is unchanged, the active materials are not self-decomposing via nucleophilic addition or substitution, disproportionation, dimerization, polymerization, or any other side reactions (Yao, 2021). Electrolyte side reactions or dendrite formation and electrode passivation can also be ruled out due to this reason (Yao, 2021).

Based on the results, the main areas of inefficiency are related to the voltaic and energy efficiencies in addition to the changes in polarization profiles in the RFB. The rapid decline in both efficiency metrics at the same scale and rate suggests issues with the potential charged and discharged at each cycle. Since the efficiencies decrease, the discharged potential is much lower than the charged potential signifying the battery's inability to move electrolytes and ions effectively in the piping and increasing resistance in the RFB. As discussed in section 3.5, the battery polarization data reveals an increase in ohmic resistance in the system. Because the slope of ohmic resistance is increasing, there are only three factors that could be causing this result based on the definition of ohmic resistance in equation (6) below.

$$R_{\boldsymbol{\Omega}} = L/(kA) \quad \text{(F. Brushett, personal communication, October 2, 2024)} \tag{6}$$

The cross-sectional area of the cell stack (A), is not decreasing as there were no visible indications of clogging and no changes in capacity to indicate any clogging of materials. The pathway length (L) of the cell stack is also not changing since it is a closed system and there is no way to increase the path length of the cell stack to increase ohmic resistance. Finally, the conductivity (k) must be the culprit in the increase of ohmic resistance due to the definition of conductivity in equation (7). While the concentration of a species (C_i), the charge number of ions of the redox species (z_i), and Faraday's constant (F) are not changing, the mobility factor (u_i) is the only term that could impact the speed of ion movement. Ion mobility refers to the speed of ions through a material under a specific potential gradient (Jablonský, 2023). Decreases in ion mobility lead to decreased conductivity and subsequently increased ohmic resistance without impacting capacity since the concentrations and volume of catholyte and anolyte remain the same but the speed of ions is changing.

$$k = F^2 \sum_i z_i^2 u_i C_i \quad \text{(F. Brushett, personal communication, October 2, 2024)} \tag{7}$$

As mentioned in the Cambridge Consumables report, the sealant was found degraded and replaced with a more chemically compatible material to avoid external leakage. However, there were no comments on the quality of the replacement, and communication with the representative from Cambridge Consumables indicates there was no inspection regarding the quality. Additionally, there was no check if the sealant penetrated the electrolyte solution. Therefore, the consultants concur that a possible source of inefficiency is likely to be a direct

cause of piping sealant infiltrating the electrolyte solutions. In general, the sealant in the solution could physically slow down the movement of ions as a physical barrier. It could also increase the viscosity of the electrolyte solution, increasing the ion mobility factor due to higher resistance to transport. Improper sealing of the pipes could also lower the pressure differential in the pipes and decrease the driving force for electrolyte and ion movement.

5. RECOMMENDATIONS

Based on the results and discussion presented in the report, the following recommendations are made to improve the efficiency of the RFB and should be implemented in the indicated order:

(1) Check the pressure differential across piping/pumps: If the pressure differential is not as expected under normal function and as dictated by the manufacturer's manual, then reseal the pipes properly while ensuring none of the material contaminates the inside.

(2) Take samples from the anolyte and catholyte solutions, the walls of pipes, and check for sealant contamination through spectrometry and viscosity tests: If there is contamination of the electrolytes or piping, then all pipes must be cleaned and resealed and the contaminated electrolytes must be either completely filtered or replaced. Replacement or filtration decisions can be made by chemical feasibility and relative costs. Also, check the walls of the pipes for any obstructions in the electrolyte path for the sealant that could reduce electrolyte and ion mobility.

(3) If none of the above: review the spectrometry and viscosity tests for any other sources of contamination and compare them to the electrolyte properties of a 'clean' or 'normal' cycle to determine if there are any other sources for an ionic conductivity drop and ohmic resistance increase.

6. References

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7. Appendix

It is important to note that the tables referenced in this section refer to a normal functioning RFB cycle as cycle 0 whereas the data from multiple malfunctioning cycles were collected and referred to as cycles 36, 40, 44, 48, 52, 56, 60, 64, and 68.

Table 1. Discharge capacity over cycles in Ampere-seconds

Cycle Number	Discharge Capacity (Ampere-seconds)
0	172970000
36	172970000
40	172970000
44	172970000
48	172970000
52	172970000
56	172970000
60	172970000
64	172970000
68	172970000

Table 2. Charge capacity over cycles in Ampere-seconds

Cycle Number	Charge Capacity (Ampere-seconds)
0	172970000
36	172970000
40	172970000
44	172970000
48	172970000
52	172970000
56	172970000
60	172970000
64	172970000
68	172970000

Table 3. Coulombic efficiency over cycles

Cycle Number	Coulombic Efficiency (%)
0	100
36	100
40	100
44	100
48	100
52	100
56	100
60	100
64	100
68	100

Table 4. Voltaic efficiency over cycles

Cycle Number	Voltaic Efficiency (%)
0	87.99
36	87.81
40	87.14
44	85.62
48	82.96
52	78.94
56	73.44
60	66.44
64	58.09
68	48.61

Table 5. Energy efficiency over cycles

Cycle Number	Energy Efficiency (%)
0	87.99
36	87.81
40	87.14
44	85.62
48	82.96
52	78.94
56	73.44
60	66.44
64	58.09
68	48.61